3.54 (s, 1 H, OH), 2.00 (s, 3 H, 7a-CH_3), 1.83 (s, 3 H, 8b-CH_3), 1.34 (s, 3 H, 6a-CH_3), 1.27 ppm (s, 3 H, 2a-CH_3); ^{13}C NMR in Table II. Anal. Calcd for $C_{29}H_{50}O_3$, C, 77.97; H, 11.28. Found: C, 77.68; H, 11.50. **2b** [(2*R*,6*R*,4′*R*,8′*R*)-6-hydroxy-2,6,7,8-tetramethyl-2-(4′,8′,12′-trimethyltridecyl)chroman-5(6*H*)-one]: yield 410 mg, 19.8%; colorless oil; UV (THF) λ 318 (ϵ 2990), 245 nm (5030); CD (*n*-hexane) λ 349 ($\Delta\epsilon$ −10.7), 327 (0.0), 304 (+15.6), 262 (0.0), 240 nm (−5.6); IR (neat) ν 3420, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.51 (s, 1 H, OH), 2.00 (s, 3 H, 7a-CH_3), 1.83 (s, 3 H, 8b-CH_3), 1.33 (s, 3 H, 6a-CH_3), 1.28 ppm (s, 3 H, 2a-CH_3); ^{13}C NMR in Table II. Anal. Calcd for $C_{29}H_{50}O_3$: C, 77.97; H, 11.28. Found: C, 77.68; H, 11.49.

Oxygenation of 2,2,5,7,8-Pentamethylchroman-6-ol (4) in the Presence of Potassium Hydroxide. A solution of **4** (220 mg, 1 mmol) in dry THF (20 mL) was added to a stirred suspension of KOH (179 mg, 3 mmol) in dry THF (50 mL) at 0 °C under an oxygen atmosphere. After being stirred for 3 h at 0 °C, the reaction mixture was treated as described above. In 16% yield, **5** (38 mg) was isolated.

Acyloin Rearrangement. A solution of **6** (236 mg, 1 mmol) in dry THF (20 mL) was added to a stirred suspension of KO_2 (70 mg, 1 mmol) in dry THF (50 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. On its thin-layer chromatogram [silica gel G-200/*n*-hexane–ethyl ether (1:1) v/v)] only **5** was found. In 95% yield, **5** (224 mg) was obtained.

With silica gel (1.5 g) suspended in a mixture of *n*-hexane and ethyl ether (1:1 v/v, 10 mL), **6** (15 mg) was stirred for 1.5 h at room temperature. The reaction mixture was filtered and concentrated under reduced pressure. The thin-layer chromatogram and ^1H NMR spectrum revealed that the residue was **6** without **5**. This indicates that silica gel does not act as a catalyst of the conversion from **6** to **5**.

A solution of **3a** (40 mg, 0.09 mmol) in [D_8]THF (0.5 mL) was added to the suspension of KO_2 (40 mg, 0.56 mmol) in [D_8]THF (0.5 mL) at 0 °C. The reaction mixture was stirred for 5 min. In the ^1H NMR spectrum of its supernatant, all the signals due to **2a** and no signals due to **3a** were observed. On the thin-layer chromatogram [silica gel G-200/*n*-hexane–ethyl ether (1:1 v/v)], only **2a** was found. By silica gel column chromatography, **2a** (32 mg) was isolated in 80% yield.

Labeling Experiments. (A) Labeling of Methyl Groups in 5 and 6. [5a-CD_3, 7a-CD_3, or 8b-CD_3]**4** was synthesized from 2,2,7,8-, 2,2,5,8-, or 2,2,5,7-tetramethylchroman-6-ol, respectively, and [D_2]formaldehyde in the presence of [D]hydrochloric acid and $SnCl_2$ in isopropyl ether.[17] Using equimolar KO_2, [5a-CD_3, 7a-CD_3, or 8b-CD_3]**4** was oxygenated. Labeled **5** and **6** were obtained after the same work up as described above. [6a-CD_3]**5** from [5a-CD_3]**4**: MS, *m*/*e* 239 (M^+); ^1H NMR the intensity of a peak at 1.34 ppm is reduced from 9 H to 6 H; ^{13}C NMR no peak at 30.1 ppm. [7a-CD_3]**5** from [7a-CD_3]**4**: MS, *m*/*e* 239 (M^+); ^1H NMR no peak at 1.99 ppm. [8b-CD_3]**5** from [8b-CD_3]**4**: MS, *m*/*e* 239 (M^+); ^1H NMR no peak at 1.82 ppm. [5a-CD_3]**6** from [5a-CD_3]**4**: MS, *m*/*e* 239 (M^+); ^1H NMR no peak at 1.33 ppm. [7a-CD_3]**6** from [7a-CD_3]**4**: MS, *m*/*e* 239 (M^+); ^1H NMR no peak at 1.90 ppm. [8b-CD_3]**6** from [8b-CD_3]**4**: MS, *m*/*e* 239 (M^+); ^1H NMR no peak at 1.99 ppm.

(B) Labeling with $^{18}O_2$. For the oxygenation of **4**, a high-vacuum manifold equipped with a reaction flask, a mercury manometer, and an ampule containing $^{18}O_2$ (300 mL, ^{18}O 90 atom %, The British Oxygen Company Ltd., London, UK) was used. In the reaction flask, **4** (1.32 g, 6 mmol), KO_2 (430 mg, 6 mmol) and dry THF (50 mL) were placed. The mixture was frozen with liquid nitrogen. Dissolved air was removed by a freeze–thaw procedure, which was repeated five times in vacuo. A sealed end of the ampule in the degassed manifold was broken and $^{18}O_2$ was introduced into the flask. The reaction mixture was stirred for 1 h at 0 °C. After purification by silica gel column chromatography, [^{18}O]**5** (170 mg, 18.3 %) and [^{18}O]**6** (125 mg, 13.4 %) were obtained. [^{18}O]**5**: MS, *m*/*e* 238 (M^+), ^{18}O incorporation 85%; IR (KBr) ν 3420, 1655, 1613 cm^{-1}; ^{13}C NMR ($CDCl_3$, a 1:1 mixture of **5** and [^{18}O]**5**) δ 202.925 ([^{18}O]**5**, $C{=}^{18}O$), 202.963 ppm (**5**, $C{=}^{16}O$). [^{18}O]**6**: MS, *m*/*e* 238 (M^+), ^{18}O incorporation 85%; IR (KBr) ν 3450, 1641 cm^{-1}; ^{13}C NMR ($CDCl_3$, a 1:1 mixture of **6** and [^{18}O]**6**) δ 75.955 ([^{18}O]**6**, $C{-}^{18}OH$), 75.979 ppm (**6**, $C{-}^{16}OH$).

Registry No. *RRR*-1, 59-02-9; **2a**, 101226-09-9; **2b**, 101313-10-4; **3a**, 101226-08-8; **3b**, 101313-09-1; **4b**, 950-99-2; **5**, 80311-41-7; **6**, 65223-11-2.

Supplementary Material Available: A listing of bond lengths, bond angles, atomic coordinates, and thermal parameters and the profiles of Eu(fod)$_3$-induced shifts of **2a**, **2b**, **3a**, **3b**, **5** and **6** (7 pages). Ordering information is given on any current masthead page.

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[17] Weisler, L. U.S. Patent **1949**, 2464539.

Additions of Singlet Oxygen to Alkoxy-Substituted Butadienes. An Unexpectedly Large s-Cis/s-Trans Ratio in an (*E*,*Z*)-Diene or a Kinetic Anomeric Effect?

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A study of the rates of reaction of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-1,4-di-*tert*-butoxy-1,3-butadiene with singlet oxygen demonstrated that rapid physical quenching and/or dioxetane formation do not competitively inhibit endoperoxide formation in the (*E*,*E*)-diene. Instead we suggest that an abnormally large s-cis/s-trans equilibrium constant for the (*E*,*Z*)-diene is the reason for the larger observed rate constant ($k_{\text{obsd}} = K_{\text{eq}}k$) for endoperoxide formation in the (*E*,*Z*)-diene in comparison to its *E*,*E* isomer. The possibility that anomeric interactions in the transition state for the reaction of the (*E*,*Z*)-diene contribute to the large rate of endoperoxide formation cannot be unequivocally ruled out.

Fritzsche[1] described in 1867 the photooxidation of napthacene. Although unrecognized at the time it was one of the first reported 4 + 2 cycloadditions preceeding by more than 60 years the monumental report of Diels and Alder.[2] Ascaridole, the first structurally established transannular epidioxide, was not reported by Wallach until 1912.[3] Since these early reports the 4 + 2 cycloaddition

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[1] Fritzsche, J. *Compt. Rend.* **1867**, *64*, 1035. Schaap, A. P. "Singlet Molecular Oxygen" "Benchmark Papers in Organic Chemistry"; Dowden, Hutchinson, and Ross: Stroudsburg, PA, 1976; Volume 5.

[2] Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1928**, *460*, 98.

[3] (a) Wallach, O. *Nachr. K. Ges. Wiss. Gottingen* 1912, 422. (b) Wallach, O. *Annalen* **1912**, *392*, 59. (c) Arbuzov, A. *Russ. Chem. Rev.* **1965**, *34*, 558.

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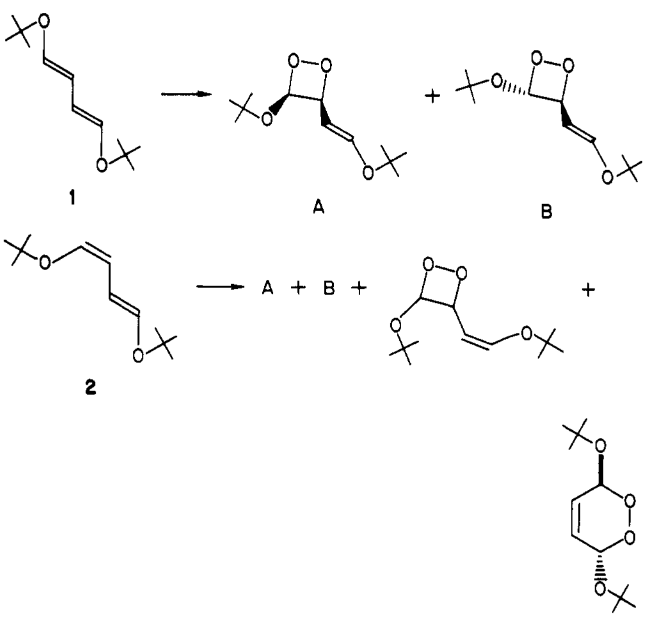
Scheme I

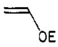
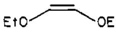
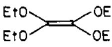
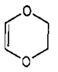


of singlet oxygen has proven to be a ubiquitous mode of reaction of singlet oxygen with organic substrates. However, despite the proven synthetic utility of this reaction, mechanistic investigations have lagged behind those reported for the ene[4] and 2 + 2[5] cycloaddition reactions of singlet oxygen. Only recently has the 4 + 2 cycloaddition enjoyed the same mechanistic attention that has been devoted to the other modes of singlet oxygen addition.[6]

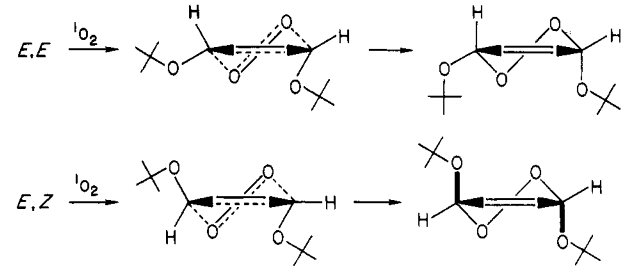
We have recently reported the reactions[7] of singlet oxygen with (*E,E*)- and (*E,Z*)-1,4-Di-*tert*-butoxy-1,3-butadienes (**1** and **2**). These reactions generate the unprecedented observation of a successful 4 + 2 cycloaddition with an (*E,Z*)-diene but unsuccessful cycloaddition with its *E,E* isomer (Scheme I). This observation appears to be unique to singlet oxygen[8] since Miller[9] has reported the successful cycloaddition of maleic anhydride to both **1** and **2**.

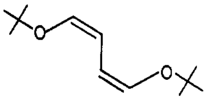
Five possible explanations for this novel behavior are the following: (1) The endoperoxide formed from the (*E,E*)-diene **1** rearranges under the experimental conditions to the dioxetanes. This appears to be an unlikely explanation since the rearrangement of the endoperoxide would have to be rapid even at −78 °C to go undetected. Rearrangements of endoperoxides to dioxetanes have previously been observed[10] but usually result in the formation of more highly conjugated systems and require acid catalysis. In addition, rearrangement in the other direction, of a dioxetane to an endoperoxide, cannot be utilized to explain the formation of an endoperoxide in the reaction of the (*E,Z*)-diene **2**. This reverse reaction has not been previously observed and can be discounted in this case by the observation that all four dioxetanes are formed[7] in the reactions of **1** and its (*Z,Z*) isomer **3** and no endoperoxides are found in these reactions under identical photooxidation conditions.

Table I. Rates of Dioxetane Formations

	solvent	k_r, M^{-1} s^{-1}	ref
	Me_2CO	2.9×10^4	20
	Me_2CO	4.7×10^7	20
	Me_2CO	4.5×10^7	20
	Me_2CO	2.2×10^5	20

Scheme II





3

(2) Physical quenching of singlet oxygen competitively inhibits chemical reaction in the planar s-cis conformation adopted by the (*E,E*)-diene **1** but not in the twisted s-cis conformation adopted by the (*E,Z*)-diene **2**. Irie[11] has examined the requirement for a specific geometry during the charge transfer quenching process using diastereotopic systems. Significant differences in the quenching rates were observed for the quenching of (*R*)-(−)-1,1′-binaphthyl fluorescence by (*S*)-(−)- and (*R*)-(+)-*N*,*N*-dimethyl-1-phenylethylamines, giving credence to the suggestion that the diene geometry may be playing an important role in endoperoxide formation.

(3) Rapid dioxetane formation in the (*E,E*)-diene **1** competitively inhibits endoperoxide formation. This suggestion is difficult to evaluate since the rates of singlet oxygen 2 + 2 additions are available in only a few cases. (See Table I for examples.) We anticipate, however, that the electron-rich alkoxy substituents in dienes **1** and **2** will enhance the rates of both the 4 + 2[6c] and 2 + 2[12] reactions. We are not aware of an (*E,E*)-diene in which both 2 + 2 and 4 + 2 reactions compete and for which kinetic data are available to make a quantitative comparison. Gollnick,[13] however, has reported the surprising observation that 4 + 2 addition of singlet oxygen to 2,5-dimethyl-2,4-hexadiene is faster than 2 + 2 addition in CCl_4 but slower in methanol.

(4) Anomeric interactions stabilize the transition state for addition of singlet oxygen to a greater extent in the (*E,Z*)-diene than the (*E,E*)-diene. Two anomeric interactions are possible in the reaction of **2** while only one is possible in the reaction of **1** (Scheme II). Experimental evidence for a peroxide anomeric-like interaction has been

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[4] Gollnick, K.; Kuhn, H. J. *Singlet Oxygen* Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; p 287.

[5] Schaap, A. P.; Zaklika, K. A. *Singlet Oxygen* Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; p 173.

[6] (a) Clennan, E. L.; L'Esperance, R. P. *Tetrahedron Lett.* **1983**, 4291. (b) Clennan, E. L.; Mehrsheikh-Mohammadi, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 5932. (c) Clennan, E. L.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1984**, *49*, 1321. (d) Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1983**, 3303.

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

[8] Other oxygen-containing dienophiles have not yet been explored.

[9] Hiranuma, H.; Miller, S. I. *J. Org. Chem.* **1983**, *48*, 3096.

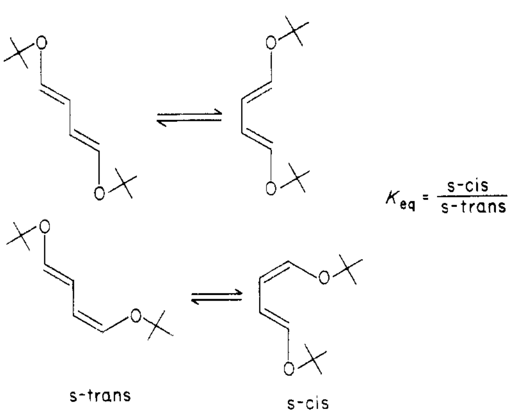
[10] (a) Wilson, T. *Photochem. Photobiol.* **1969**, *10*, 441. (b) LeRoux, J. P.; Goasdoue, C. *Tetrahedron* **1975**, *31*, 2761. (c) Schaap, A. P.; Burns, P. A.; Zaklika, K. A. *J. Am. Chem. Soc.* **1977**, *99*, 1270.

[11] Yorozu, T.; Huyashi, K.; Irie, M. *J. Am. Chem. Soc.* **1981**, *103*, 5480.

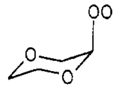
[12] Schaap, A. P.; Zaklika, K. A. *Singlet Oxygen* Wasserman, H. H., Murray, R. W., Ed.; Academic: New York, 1979; p 236.

[13] Gollnick, K.; Griesbeck, A. *Tetrahedron* **1984**, *40*, 3235.

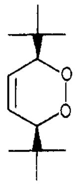
Scheme III



obtained by examination of the crystal structure[14] of *p*-dioxane hydroperoxide 4. In 4 the dioxane ring is a perfect chair with an axial hydroperoxy group. Ab initio calculations[15] have also detected a general tendency of the n orbital of a peroxy linkage to become coplanar with an adjacent polar bond. Despite this convincing evidence that the peroxy group can be stabilized by anomeric interactions it could be argued that a substantial kinetic anomeric effect in a very exothermic reaction is a violation of the Hammond postulate and is not likely to occur. We point out, however, that the exothermicity of the product-forming step, collapse of the exciplex,[16] in singlet oxygen reactions is unknown, therefore demanding careful consideration of this possibility. This suggestion is ostensibly supported by the observation that return to normal behavior is observed when the oxygens isolating the *tert*-butyl groups from the (*E*,*E*)-butadiene are removed. Endoperoxide 5 is the only product of addition of singlet oxygen to (*E*,*E*)-2,2,7,7-tetramethyl-3,5-octadiene.[17]



4



5

(5) The s-trans/s-cis equilibrium constant is larger for the (*E*,*Z*)-diene 2 than for the (*E*,*E*)-diene 1 (Scheme III). Despite the fact that chemical intuition would indicate that K_{eq} (s-cis/s-trans) should be larger for an *E* than a *Z* substituted diene, Allinger[18] has reported molecular mechanics results which indicate that is in fact not the case for (*E*) and (*Z*)-1,3-pentadienes. ($\Delta\Delta G°_{E-Z}$ = 0.13 kcal/mol).[19]

We report here a study of the reactions of dienes 1–3 and discuss their propensity to undergo 4 + 2 cycloadditions with singlet oxygen in light of the preceeding discussion.

Table II. Young Second-Order Rate Constants for the Reactions of Singlet Oxygen with Dienes 1-3 as a Function of Solvent[a]

compd	solvent	$10^{-7}k$, M^{-1} s^{-1}
1	acetonitrile	20.3[b]
	acetone	9.1
	CH_2Cl_2	8.5
	THF[c]	11.0
2	acetonitrile	10.9
	acetone	5.7
	CH_2Cl_2	5.3
	THF	5.5
3	acetonitrile	3.8
	acetone	1.5
	CH_2Cl_2	2.0
	THF	1.9

[a] Rates are the average of three to five independent determinations and are only accurate to ±15%. [b] Rates were measured by using mesoporphyrin IX dimethyl ester as the sensitizer and 1,3-diphenylisobenzofuran as the fluorescent probe. [c] Tetrahydrofuran.

Table III. Chemical Quenching Rates for (*E*,*E*)-Diene 1 and (*Z*,*Z*)-Diene 3

compd	$10^{-7}k_r$, M^{-1} s^{-1}
1[a]	9.6
3[b]	1.4

[a] Measured in acetone in competition with 3. [b] Measured in acetone in competition with tetramethylethylene (β = 1.17 × 10^{-3})[15] and k_d[16] = 2.17 × 10^4 s^{-1}.

Results and Discussion

Synthesis. The dienes 1–3 were synthesized by the method of Hiranuma and Miller[9] as a mixture of isomers in a ratio of 45:45:10 (*E*,*Z*–*Z*,*Z*–*E*,*E*) and were separated by preparative gas chromatography. An attempt to enrich the mixture in the *E*,*E* isomer in order to reduce the GC collection time by irradiation of a neat sample with a 450-W medium-pressure Hanovia lamp for 30 min failed. The *Z*,*Z* isomer, however, precipitated out of a mixture of the isomers in the freezer and could be conveniently isolated by filtration and purified by low-temperature recrystallization from pentane. The *E*,*E* 1 and *Z*,*Z* 3 isomers are stable solids in contrast to the *E*,*Z* 2 isomer, which is a liquid that discolors rapidly at room temperature. All three dienes were purified immediately before use. Their structures are consistent with the spectral data presented in the Experimental Section.

Kinetics. The rates of reaction of these dienes (Table II) were measured in acetone, acetonitrile, methylene chloride, and tetrahydrofuran by utilizing the Young kinetic method.[21] The rates determined by this method reflect the sum of all chemical and physical interactions by which the dienes can remove singlet oxygen from solution. Low concentrations and conversions of the dienes were necessary in order to circumvent quenching of the fluorescence of the 1,3-diphenylisobenzofuran probe during the rate determinations.[22] The partial rate factor[23] for the formation of the endoperoxide from diene 2 was cal-

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[14] Nord, A. G.; Lindberg, B. *Acta Chem. Scand.* **1973**, *27*, 1175.

[15] Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

[16] Gorman, A. A.; Gould, I. R.; Hamblett. I. *J. Am. Chem. Soc.* **1982**, *104*, 7098.

[17] Clennan, E. L.; L'Esperance, R. P., unpublished results.

[18] Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 7928.

[19] Ths s-cis form of (*Z*)-1,3-pentadiene has a twist angle (<1234) of 46°.

[20] Faler, G. R. Ph.D. Dissertation, Wayne State University, Detroit Michigan, 1977.

[21] Young, R. H.; Wehry, R. H.; Martin, R. I. *J. Am. Chem. Soc.* **1971**, *93*, 5774.

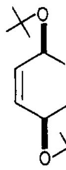
[22] (a) Thomas, M. J.; Foote, C. S. *Photochem. Photobiol.* **1978**, *27*, 683. (b) Clennan, E. L.; Mehrsheikh-Mohammadi, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7112.

[23] Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35. Partial rate factors for formation of all of the dioxetanes in each reaction cannot be calculated by this method since several of the dioxetanes arise from a common intermediate.

culated ($k_{\text{endoperoxide}}$ = % yield endoperoxide × 5.7×10^7 M^{-1} s^{-1}) by using the rate of formation and the yield of endoperoxide formed in acetone[7] and is 1.03×10^7 M^{-1} s^{-1}.

The separation of the Young rates of reaction of dienes **1** and **3** into chemical and physical components was accomplished by the method of Higgins, Foote, and Cheng[24] (Table III). The relative rate of reaction of the (*E*,*E*)-diene **1** and (*Z*,*Z*)-diene **3** ($k_{E,E}/k_{Z,Z}$) was determined by measuring the disappearance of the dienes.[24] Twelve sets of data were collected in which the % conversions of the (*Z*,*Z*)-diene were always greater than 5% and of the (*E*,*E*)-diene always less than 98% (see Experimental Section for complete details). The absolute chemical rate of reaction of singlet oxygen with the (*E*,*E*)- and (*Z*,*Z*)-diene was then determined from this relative rate by measuring the chemical rate of reaction of the (*Z*,*Z*)-diene relative to tetramethylethylene ($k_{Z,Z}/k_{\text{TME}}$). Tetramethylethylene is known to react only chemically (not physically) with singlet oxygen and its β-value has been accurately determined in acetone.[25] At the beginning of this work we had anticipated that the easily oxidized and planar[26] s-cis conformation of the (*E*,*E*)-diene might contribute a physical component to the competitive inhibition. The near identical rate of chemical quenching (Table III) and the Young rates (Table II), however, demonstrate the lack of a physical component to this reaction and rules out physical quenching as a contributing competing reaction (possibility 2).

In the presence of all competitive processes that remove singlet oxygen from solution ($k = 9.1 \times 10^7$ M^{-1} s^{-1} in acetone) a conservative estimate[26] that the rate of endoperoxide formation in the reaction of **1** is equal to that measured for the reaction of diene **2** (1.03×10^7 M^{-1} s^{-1}) requires that approximately 9.5% of *cis*-3,6-di-*tert*-butoxy endoperoxide **6** is formed. Examination of a ^{1}H NMR spectrum with excellent signal to noise, however, demonstrated that less than 1% of **6** was formed. The observation of less than 1% of an endoperoxide in the reaction of the (*E*,*E*)-diene **1** corresponds to approximately 90% additional inhibition of endoperoxide formation which cannot be attributed to competitive processes including dioxetane formation (possibility 3).



6

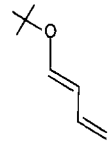
The absence of a detectable amount of an endoperoxide in the reaction of the (*E*,*E*)-diene **1** allows an estimation of 1×10^6 M^{-1} s^{-1} as the upper limit for the rate of formation of **6**. This rate corresponds to a $\Delta\Delta G^{\ddagger}$ for endoperoxide formation of 1.3 kcal/mol where $\Delta\Delta G^{\ddagger} = DG^{\ddagger}(E,E) - \Delta G^{\ddagger}(E,Z)$. This stabilization of the *E*,*Z* endoperoxide transition state is 0.6–0.9 kcal/mol larger than the reported[27] free energy preference for axial *tert*-butoxytetrahydropyran. It should be noted however that the endoperoxide has two less 1,3-diaxial interactions than the tetrahydropyran. On the other hand, this stabilization is also larger than that expected based on the anticipated slightly more favorable s-cis/s-trans ratio in this (*E*,*Z*)-diene ($\Delta\Delta G°_{E\text{-}Z}$ = 0.13 kcal/mol)[18] in comparison to its *E*,*E* isomer.

Table IV. Product Ratios in the Reactions of Dienes 7 and 8 with Singlet Oxygen

compd	9/(10 + 11)[a]
7	0.89
8	2.85

[a] Determined by integration of the ^{1}H NMR spectrum.

(*E*)- and (*Z*)-1,4-Di-*tert*-butoxy-1,3-butadienes (7 and 8). In order to further distinguish between possibility 4, anomeric stabilization, and possibility 5, an abnormally favorable s-cis/s-trans equilibrium constant, the isomeric dienes **7** and **8** were investigated.[28] Dienes **7** and **8** were obtained as a 40:60 mixture of isomers, respectively, by the procedure of Everhardus et al.[29] and were purified by preparative gas chromatography (see Experimental Section for details). Irradiation of oxygen saturated acetone-d_6 solutions of these dienes containing rose bengal as a sensitizer resulted in their complete disappearance in 45 min. The singlet oxygen nature of these reactions were verified by the additions of 1,4-diazabicyclo[2.2.2]octane (DABCO) which totally inhibited the formation of the oxidized products. Only the unreacted diene was observed in the reaction mixtures after 45 min of irradiation in the presence of this singlet oxygen quencher. The stereochemical integrities of these dienes under the reaction conditions were also verified by irradiation of argon saturated reaction mixtures. In addition, examination of the reaction mixtures after partial photooxidation revealed no isomerized diene.



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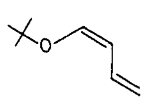
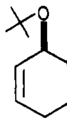


8

In the reactions of both the *E* and *Z* isomers 2 + 2 as well as 4 + 2 oxidations products were formed. The endoperoxide **9** dioxetane ratio in both reactions was determined by integration of the NMR reaction mixtures after decomposition of the dioxetanes. Dioxetanes and endoperoxides were the only products of these reactions as verified by low-temperature NMR;[28] however, determination of the endoperoxide dioxetane ratio was most conveniently measured as **9**/(**10** + **11**) (Table IV) due to integration problems. The large ratio found in the singlet oxidation of the (*Z*)-diene **8** appears to mitigate against anomeric interactions as the sole reason for the observed selective endoperoxide formation (Possibility 4). The same number of anomeric interactions (one) are developing in the transition states of both the *E* and *Z* isomers.



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[24] Competitive kinetics accomplished by following the appearance of the products rather than the disappearance of the starting materials is inherently more accurate but impossible in this study due to the instability of the products. Higgins, R.; Foote, C. S.; Cheng, H. *Adv. Chem. Ser.* **1968**, *77*, 102.

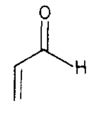
[25] Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1984**, 725.

[26] (a) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657 and references therein. (b) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *Ibid.* **1985**, *107*, 6842.

[27] (a) deHoog, A. J.; Buys, H. R.; Altona, C.; Havinga, E. *Tetrahedron* **1969**, *25*, 3365. (b) Eliel, E. L.; Giza, C. A. *J. Org. Chem.* **1968**, *33*, 3754.

[28] Clennan, E. L.; Lewis, K. K., unpublished results.

[29] Everhardus, R. H.; Peterse, A.; Vermeer, D.; Brandsma, L.; Arens, J. F.; Recl.: *J. R. Neth. Chem. Soc.* 1974, *93*, 90.



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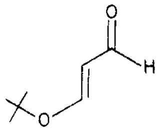
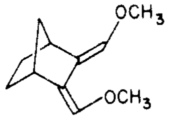


11

In an attempt to detect an unexpected large population of the s-cis conformer the absorption spectra of dienes 1–3 were taken in *n*-heptane. The extinction coefficients (ϵ) and absorption maximum are reported in Table V. The smaller extinction coefficient for the (*E*,*Z*)-diene 2 in comparison to its *E*,*E* and *Z*,*Z* isomers is consistent with an increased population of the s-cis conformation in the (*E*,*Z*)-diene. s-Trans conformations usually have ϵ values in the range of 14 000–30 000 and s-cis conformations in the range of 3000–12 000.[30] Chapman and co-worker's[26] ultraviolet spectra of matrix isolated 1,3-butadiene is in accord with this suggestion. They report that the magnitude of the extinction coefficient for the s-cis conformer is only 45% of that reported for the s-trans conformer. Using the approximations that $\epsilon_{\text{s-trans}} = \epsilon_{Z,Z}$ and $\epsilon_{\text{s-cis}} = 10\,000$, eq 1 allows us to estimate that the mole fraction

$$N_{\text{s-cis}} = \frac{\epsilon_{E,Z} - \epsilon_{\text{s-trans}}}{\epsilon_{\text{s-cis}} - \epsilon_{\text{s-trans}}} \qquad (1)$$

of the s-cis conformation present at 25 °C is approximately 0.30. This abnormally large equilibrium constant is more than large enough to account for the estimated 1.3 kcal/mol energy difference between the transition states for endoperoxide formation in the (*E*,*E*)- and (*E*,*Z*)-dienes.[31] We suggest that a favorable dipole–dipole alignment (Scheme IV) is responsible for the unexpected stability of the *E*,*Z*-s-cis conformation. Sustmann and co-workers[32] reported that diene 12 is the only product of bis elimination of methanol from the bis(dimethyl acetal) of *trans*-2,3-norbornanedicarbaldehyde, demonstrating than the (*E*,*Z*)-diene can attain the s-cis conformation necessary for 4 + 2 cycloaddition.



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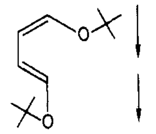
Miller[9] reports that the cycloadditions of tetracyanoethylene (TCNE) with dienes 1 and 2 have similar rates. The increased selectivity of the more reactive dienophile, singlet oxygen, for the (*E*,*Z*)-diene is therefore in violation of the reactivity selectivity principle.[33] Similar observations[34] have been made in other cycloadditions including those of TCNE,[35] maleic anhydride,[36] and *N*-arylmaleimide.[37] This apparent violation of the reactivity selectivity principle, however, is in accord with frontier molecular orbital theory.[38] The smaller HOMO–LUMO separation in the singlet oxygen reaction results in an increased sensitivity to structural changes which effect changes in this separation.[39] Reactivity–selectivity phenomena in singlet oxygen reactions is currently undergoing closer scrutiny.

Table V. Extinction Coefficients and Wavelength Maximum for Dienes 1–3

compd	run	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}	r
1	1	245	28 776	0.9999
	2		31 662	0.9995
	average		30 219 ± 1443	
2	1	251	24 250	0.9999
	2		24 521	0.9993
	3		24 944	0.9998
	average		24 572 ± 371	
3	1	254	31 339	0.9999
	2		30 559	0.9993
	3		31 376	0.9997
	average		31 092 ± 533	

Scheme IV



Conclusion

The chemical rate (Table III) of reaction of dienes 1–3 and the lack of a physical quenching component allows dismissal of the possibilities that rapid physical quenching (possibility 2) or dioxetane formation (possibility 3) preclude (competitively inhibit) endoperoxide formation. Instead we suggest that an abnormally large s-cis/s-trans equilibrium constant for the (*E*,*Z*)-diene 2 (possibility 5) is the reason for the larger observed rate constant ($k_{\text{obsd}} = K_{\text{eq}}k$) for endoperoxide formation in the (*E*,*Z*)-diene in comparison to its (*E*,*E*) isomer. Despite the fact that the larger equilibrium constant can account for most if not all the difference in the activation barriers for the two reactions we cannot unequivocally rule out a contribution to the larger rate of cycloaddition (k_{obsd}) by anomeric interactions (larger k) in the transition state for the reaction of the *E*,*Z* isomer (possibility 4).

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX270 at 270 and 63.8 MHz, respectively, and all the chemical shifts referenced to Me_4Si. Mass spectral data were obtained on a VG-ZAB-1F mass spectrometer by electron impact or ammonia chemical ionization. Infrared spectra were obtained on a Beckman-Microlab 600 spectrometer. Preparative gas chromatographic separations were carried out on a Varian Aerograph 90-P utilizing a 0.25 in. by 20 ft column packed with 20% Carbowax 20M on Chromosorb W. Analytical gas chromatographic studies were carried out on a Perkin-Elmer Sigma 3B utilizing a 0.125 in. by 6 ft column packed with 10% Carbowax 20M on Chromosorb W. Peak areas were recorded with a Hewlett-Packard 3390A integrator. All melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Acetone-d_6 (Aldrich) and bulk acetone were distilled from $CaSO_4$ under a N_2 atmosphere and stored over 4A molecular sieves. Methylene chloride-d_2 (Aldrich) was filtered through activity 1 basic alumina prior to use. Bulk methylene chloride for preparative reactions and kinetic studies was stirred over sulfuric acid, washed with water and saturated sodium bi-

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(30) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structure Analysis*; Macmillan: New York, 1976; p 346.

(31) This represents a $\Delta G°$ of 0.71 kcal/mol for the s-trans to s-cis equilibrium at 25 °C. Reference 18 suggests that $\Delta G°$ for an (*E*,*E*)-diene is approximately 2.7 kcal/mol. ($\Delta\Delta G° = 2.7–0.7 = 2.0$ kcal/mol).

(32) Dern, M.; Korth, H.-G.; Kopp, G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 337.

(33) Johnson, D. C. *Tetrahedron* **1980**, *36*, 3461.

(34) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(35) Kiselev, V. D.; Konovalov, A. I.; Veisman, E. A.; Ustyugov, A. N. *J. Org. Chem. USSR* (*Engl. Transl.*) **1978**, *14*, 118.

(36) Mielert, A.; Braig, Ch.; Sauer, J.; Martelli, J.; Sustmann, R. *Justus Liebigs Ann. Chem.* **1980**, 954.

(37) Samuilov, Ya. D.; Uryadova, L. F.; Solomonov, B. N.; Konovalov, A. I. *J. Org. Chem. USSR* (*Engl. Transl.*) **1978**, *11*, 1931.

(38) Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569.

(39) Sustmann, R.; Schubert, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 840.

carbonate, dried over $MgSO_4$, and distilled from P_2O_5 prior to the basic alumina treatment. Crotonaldehyde, cyclohexenone, 2,3-dimethyl-2-butene, and triglyme were all obtained from Aldrich and distilled before use. The 1,4-dihydroxy-2-butyne (Aldrich) was recrystallized from ethyl acetate. Isobutylene (Pfaltz and Bauer), *tert*-butylacetylene (Aldrich), rose bengal (Aldrich), tetraphenylporphine (Aldrich), mesoporphyrin IX dimethyl ester (Sigma), THF-d_8 (Aldrich), and CD_3CN (Aldrich) were used as purchased.

1,4-Di-*tert*-butoxy-2-butyne was synthesized by the method of Hiranuma and Miller[9] and purified by vacuum distillation: bp 80–85 °C (1.5 mmHg) [lit. bp 77–78 °C (1 mmHg)]; yield 51% (lit. yield 68%); ^{1}H NMR ($CDCl_3$) δ 4.04 (s, 4 H), 1.20 (s, 18 H).

(1*E*,4*E*)-, (1*E*,4*Z*)-, and (1*Z*,4*Z*)-di-*tert*-butoxy-1,3-butadienes were synthesized by the method of Hiranuma and Miller[9] and purified by gas chromatography. The preparative GC oven was set to 125 °C, the injector to 190 °C, the detector to 190 °C, and the collector to 170 °C. The retention times under these conditions are 118, 108, and 89 min for **1**, **2**, and **3**, respectively. 1*E*,4*E* isomer **1**: ^{1}H NMR(acetone-d_6) δ 6.39 (dd, J = 8.1, 2.9 Hz, 2 H), 5.45 (dd, J = 8.1, 2.9 Hz, 2 H), 1.18 (s, 18 H); ^{13}C NMR (acetone-d_6) δ 141.4, 107.6, 76.4, 28.4. 1*E*,4*Z* isomer **2**: ^{1}H NMR (acetone-d_6) δ 6.54 (d, J = 12.4 Hz, 1 H), 6.02 (d, J = 6.6 Hz, 1 H), 5.79 (dd, J = 12.4, 11.0 Hz, 1 H), 4.94 (dd, J = 11.0, 6.6 Hz, 1 H), 1.21 (s, 9 H), 1.20 (s, 9 H); ^{13}C NMR (acetone-d_6) δ 142.4, 137.0, 104.9, 104.6, 76.3, 76.1, 28.1. 1*Z*,4*Z* isomer, **3**: ^{1}H NMR (acetone-d_6) δ 6.09 (dd, J = 3.2, 1.5 Hz, 2 H), 5.33 (dd, J = 3.2, 1.5 Hz, 2 H), 1.22 (s, 18 H); ^{13}C NMR (acetone-d_6) 138.0, 101.9, 76.2, 28.1.

***trans*-1,4-Di-*tert*-butoxy-2-butene** was prepared by the method of Brandsma[29] with the following adaptations. Liquid ammonia (7.5 mL) was condensed into a three-neck round-bottom flask equipped with a dry ice condensor, stopper, and rubber septum containing a solution of 3.00 g (0.015 mol) of 1,4-di-*tert*-butoxy-2-butyne, 2.22 g (0.03 mol) of *tert*-butyl alcohol, and 2.25 mL of tetrahydrofuran. To this mixture 0.12 g (0.034 mol) of lithium metal which was etched in methanol was added over a 10-min period. After this addition was complete, stirring was continued at room temperature for 30 min. The mixture was then poured over ice, extracted twice with ether, dried over anhydrous $MgSO_4$, filtered, and rotary evaporated to give 2.97 g of a material which was a 50:50 mixture of starting material and product as indicated by NMR. This material was recycled under the same conditions to finally give 1.83 g of material with less than 8% starting material. This material was utilized in the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 5.80 (m, 2 H), 3.90 (d, 4 H), 1.20 (s, 18 H).

(*E*)- and (*Z*)-*tert*-butoxy-1,3-butadiene (7 and 8) were synthesized by a modified procedure of Brandsma.[29] To a flame-dried 25-mL round-bottom flask, equipped with a reflux condensor and septum containing 1.00 g (5 mmol) of *trans*-1,4-di-*tert*-butoxy-2-butene was added 6.25 mL of 1.6 M *n*-BuLi under a N_2 atmosphere at 0 °C. This reaction mixture was allowed to stir at room temperature for 4.5 h. The reaction was quenched with methanol, extracted with diethyl ether, and dried with $MgSO_4$. Removal of the solvent at atmospheric pressure resulted in 0.684 g of crude material, which was purified by gas chromatography. (Retention times: 7, 35 min; 8, 28 min. The column was 125 °C, collector 200 °C, detector 225 °C, injector 200 °C, and flow rate He 100 mL/min.) ^{1}H NMR [7] δ 6.79 (d, J = 12.5 Hz, 1 H), 6.25 (ddd, J = 16.9, 11.0, 10.3 Hz, 1 H), 5.56 (dd, J = 12.5, 11.0 Hz, 1 H), 4.86 (dd, J = 16.9, 2.2 Hz, 1 H), 4.68 (dd, J = 10.3, 2.2 Hz, 1 H), 1.27 (s, 9 H), [8] 6.67 (dddd, J = 17.4, 10.9, 10.4, 0.9 Hz, 1 H), 6.35 (dddd, J = 6.2, 1.5, 0.9, 0.7, 1 H), 5.09 (dddd, J = 10.9, 6.2, 0.7, 0.7 Hz, 1 H), 4.97 (dddd, J = 17.4, 2.4, 0.7, 0.7 Hz, 1 H), 4.79 (dddd, J = 10.4, 2.4, 1.5, 0.7 Hz, 1 H), 1.27 (s, 9 H).

3,6-Dihydro-3,6-di-*tert*-butoxy-1,2-dioxin was synthesized by adding 2 g of an isomeric mixture of 1,4-di-*tert*-butoxy-1,3-butadiene **1**–**3** and 12 mg tetraphenylphorphine to 40 mL of CH_2Cl_2. This solution was saturated with oxygen and irradiated with a 750-W Sylvania BRP lamp at −76 °C through a sodium nitrite filter solution for 3 h. The reaction mixture was allowed to sit at room temperature for a week. The solvent was rotatory evaporated, and the endoperoxide was obtained by flash chromatography (CH_2Cl_2): ^{1}H NMR (acetone-d_6) δ 5.89 (d, J = 1.5 Hz, 2 H), 5.38 (d, J = 1.5 Hz, 2 H), 1.12 (s, 18 H); ^{13}C NMR (acetone-d_6) δ 125.1, 89.3, 73.9, 27.0; IR (neat) 1697 (w), 1085 (s), 883 (m), 843 (m) cm^{-1}.

Table VI

run	time, min	% conversion *Z*,*Z*	% conversion *E*,*E*	ln ($Z,Z_f/Z,Z_0$)[a]	ln ($E,E_f/E,E_0$)[b]
1	15	9	42	0.0914	0.546
	25	15	67	0.163	1.11
2	15	16	81	0.177	0.168
	20	42	97	0.539	3.53
	25	44	98	0.571	4.22
3	15	6	47	0.067	0.66
	20	12	67	0.129	1.12
	25	26	89	0.298	2.20
4	13	7	54	0.074	0.787
	15	13	69	0.137	1.17
	17	15	75	0.159	1.38
	20	26	89	0.302	2.27

[a] Z,Z_f, **3** final concentration; Z,Z_0, **3** initial concentration. [b] E,E_f, **1** final concentration; E,E_0, **1** initial concentration.

Table VII

run	time, min	% conversion *Z*,*Z*	% conversion TME	ln ($Z,Z_f/Z,Z_0$)	ln (1 − TMEO-H/ TME_0)
1	5	30	24	0.352	0.278
	10	42	40	0.541	0.509
	15	59	53	0.881	0.748
2	5	16	14	0.172	0.155
	10	33	35	0.395	0.427
	15	55	65	0.796	1.06
3	4	22	19	0.251	0.211
	8	45	48	0.595	0.656
	10	60	64	0.921	1.02
	12	60	64	0.904	1.02

3,6-Dihydro-3-*tert*-butoxy-1,2-dioxin was synthesized by irradiation through 0.5% $K_2Cr_2O_7$ or 75% w/v $NaNO_2$ filter solutions 0.2–0.7 M oxygen saturated acetone-d_6 solutions of **7** and **8** in the presence of rose bengal at −78 °C. The reactions were monitored at −65 °C by low-temperature NMR: ^{1}H NMR (acetone-d_6) δ 6.13 (dddd, J = 10.2, 4.4, 1.5, 1.5 Hz, 1 H), 5.78 (dddd, J = 10.2, 4.0, 2.2, 1.8 Hz, 1 H), 5.39 (brd, J = 2.2 Hz, 1 H), 4.59 (ddd, J = 16.8, 4.0, 1.5 Hz, 1 H), 4.25 (dddd, J = 16.8, 4.4, 1.8, 1.1, 1 H), 1.24 (s, 9 H).

General Photolysis Conditions for NMR Experiments. A mixture of 2–4 mg (0.01–0.02 mol) of the diene and 10 μL of 10^{-3} M rose bengal solution (1.1 mg/mL) was added to a 1-mL volumetric flask, and this mixture was diluted to volume with acetone-d_6. A portion of this solution (0.5–0.7 mL) was pipeted into a 5-mm NMR tube and saturated with oxygen for 25 min at −76 °C while being protected from the room lights. The reaction was irradiated through a 0.5% $K_2Cr_2O_7$ filter solution. The progress of the reaction was monitored by low-temperature NMR at −80 °C. In THF-d_8 the reaction times were 2, 1, and 1.5 h for the *E*,*E* **1**, *E*,*Z* **2**, and *Z*,*Z* **3** dienes, respectively. In THF and CD_2Cl_2 solutions, tetraphenylporphine was used as sensitizer and the reaction mixtures were irradiated through a sodium nitrite filter solution.

Young Kinetic Method. See ref 6 for details.

Ultraviolet spectra of dienes **1**–**3** were obtained in HPLC grade *n*-heptane. A minimum of six points were collected for each Beer's law plot, and at least three different stock solutions were utilized.

Competitive Kinetics[24] **($k_{E,E}/k_{Z,Z}$).** A mixture consisting of 5 mg of *E*,*E* **1** (2×10^{-5} mol), 4.5 mg of triglyme (2×10^{-5} mol, internal standard), and 20 μL of 10^{-3} M rose bengal solution were placed in a 2-mL volumetric flask and diluted to volume with acetone-d_6. This solution was divided into four parts by pipeting 0.5 mL into 5-mm NMR tubes. These tubes were protected from stray light and were stored in a dry ice/acetone bath. These solutions were saturated with oxygen for 5 min at −76 °C and then irradiated through a 0.5% $K_2Cr_2O_7$ filter solution with a Sylvania

BRP lamp under continuous oxygen agitation. The disappearance of the dienes were monitored by using a Sigma 3B analytical gas chromatograph. (Conditions: injector, 180 °C; detector, 180 °C; oven programming 93 °C, 30 min; ramp rate, 5 °C/min, final temperature, 110 °C, 10 min, He flow rate 35 cm^3/min.) The peak areas were determined using a Hewlett-packard integrator and are the average of two to four injections. The irradiation times were adjusted for a minimum conversion of 5% for 1 and a maximum conversion of 98% for 3 (Table VI).

($k_{TME}/k_{Z,Z}$). This ratio was determined as described above. In this case the appearance of the allylic hydroperoxide from the ene reaction of 2,3-dimethyl-2-butene (TME) was monitored rather than the disappearance of starting material. The allylic hydroperoxide was monitored by gas chromatography after conversion to the allylic alcohol (TMEOH) with triphenylphosphine.[40] Its concentration was determined by reference to a calibration curve (Table VII).

Acknowledgment. We thank the National Science Foundation (CHE-8418603) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

Registry No. **1**, 86528-14-5; **2**, 86528-15-6; **3**, 79989-51-8; **6**, 101347-18-6; **7**, 52752-58-6; **8**, 52752-57-5; **9**, 101314-72-1; t-$BuOCH_2C{\equiv}CCH_2OBu$-t, 79989-39-2; (E)-t-$BuOCH_2CH{=}CHCH_2OBu$-t, 52752-63-3; O_2, 7782-44-7.

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

Reactions of the 2-Allylbenzyl Radical: Relative and Absolute Rate Constants for Abstraction of Hydrogen Atom from Thiophenol, Dicyclohexylphosphine, Phenols, and Arylalkyl Donors[1]

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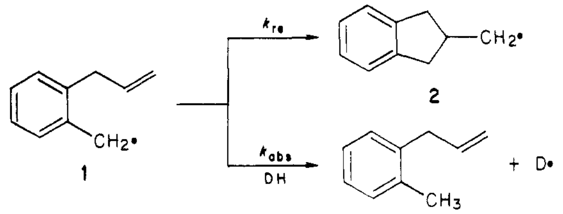
Relative and absolute rate expressions for hydrogen atom abstraction (k_{abs}) by the 2-allylbenzyl radical from thiophenol, dicyclohexylphosphine, and a series of alkyl-substituted aromatic hydrogen donors relative to exo cyclization to the 2-indanylmethyl radical (k_{re}) are presented. The Arrhenius parameters for the competition of the rearrangement of 2-allylbenzyl with abstraction from arylalkyl and heteroatom donors were as follows (donor, log $((A_{re}/A_{abs})/M)$, $E_{abs} - E_{re}$, kcal/mol): p-xylene, 4.007, −2.881; p-xylene-d_6, 3.470, +0.0792; m-xylene, 4.038, −2.881; diphenylmethane, 3.977, −5.267; diphenylmethane-d_2, 3.501, −2.694; fluorene, 3.059, −5.644; fluorene-d_2, 3.101, −4.227; dicyclohexylphosphine, 3.197, −9.895; thiophenol, 2.983, −12.832. From the expression for k_{re} for the 2-allylbenzyl to 2-indanylmethyl cyclization, $\log (k_{re}/s^{-1}) = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$, rate expressions for abstraction (A_{abs}, E_{abs}) are derived. Individual rate constants at 160 and 170 °C for other arylalkyl and phenolic donors are also presented. Evidence for a contribution of hydrogen atom tunneling to the rate of abstraction from diphenylmethane and xylene is presented.

Relative rates of hydrogen atom abstraction by the benzyl and 2-allylbenzyl radicals from a wide variety of aromatic hydrocarbon and heteroatom hydrogen donors have recently been reported by Bockrath[2] and by this laboratory.[3] By contrast, absolute rate expressions for most donors of interest are lacking. Although Jackson and O'Neill have reported rate expressions for hydrogen abstraction by benzyl radical from substituted toluenes and have reported evidence of tunneling in the reaction of benzyl with toluene,[4] the unusually high Arrhenius parameters reported have been questioned.[5] Chain transfer constants for the abstraction of hydrogen atom by polystyryl radical have been reported for a variety of donors,[6] but in general, reliable rate expressions for hydrogen atom transfer to benzylic radicals are not available. A number of mechanistic studies[7,8] of thermal decomposition mechanisms of hydrocarbons related to coal chemistry would benefit from absolute rate expressions for hydrogen atom transfer. Up to the present, rate expressions for hydrogen atom transfer steps in such studies depended on estimates.[7] Our recent development[9,10] of an absolute rate expression for the cyclization of the 2-allylbenzyl radical (**1**) to the 2-indanylmethyl radical (**2**) (eq 1) ($\log (k_{re}/s^{-1}) = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$, $\theta = 2.3RT$/kcal/mol), using some of the data presented in this paper, allows the competition of this radical "clock"[11] reaction, k_{re}, with abstraction (k_{abs}) by **1** from donors to provide relative and absolute rates of atom abstraction. We now report relative and absolute rate expressions and isotope effects for the abstraction of hydrogen from a series of hydrocarbon, thiol, and phosphine donors and provide evidence suggesting the



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[2] Bockrath, B. B.; Bittner, E.; McGrew, J. J. Am. Chem. Soc. 1984, 106, 135–138.

[3] Franz, J. A.; Barrows, R. D.; Camaioni, D. M. Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem. 1983, 28, 77–80.

[4] Jackson, R. A.; O'Neill, D. W. J. Chem. Soc. D. 1969, 1210–1211. Jackson, R. A. J. Chem. Soc. 1963, 5281.

[5] Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, pp 74–75.

[6] Ingold, K. U. Pure Appl. Chem. 1967, 15, 49.

[7] Poutsma, M. L.; Dyer, C. W. J. Org. Chem. 1982, 47, 4903–4907.

[8] Gilbert, K. W.; Gajewski, J. J. J. Org. Chem. 1982, 47, 4899–4902.

[9] Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. J. Org. Chem. 1986, 51, 19–25.

[10] Franz, J. A.; Barrows, R. D.; Camaioni, D. M. J. Am. Chem. Soc. 1984, 106, 3964.

[11] Griller, D.; Ingold, K. U. Acc. Chem. Res. 1980, 13, 317–328.

0022-3263/86/1951-1446$01.50/0