Products from Reactions of Trityl Halides with Lithium Dialkylamides. The following procedure is representative. To a 40-mL centrifuge tube fitted with a septum was added 0.5 mL of a 0.55 M LDA (1.1 mmol) solution in THF and 9.5 mL of THF. The solution was cooled to -78 °C, and 0.63 mL of a THF solution containing 0.21 mmol of Ph_3CCl and 55.4 mg of pentadecane was added. After 1 h, the reaction was quenched with 1 mL of methanol and warmed to room temperature. Hexane (5 mL) was added, and the solution was washed with water and brine and dried with $MgSO_4$. A GC yield of triphenylmethane was obtained with pentadecane as an internal standard. The solvent was removed, and the relative yields of triphenylmethane, (4-benzhydrylphenyl)triphenylmethane (**2**), and trityl "trimer" were determined by ^1H NMR spectroscopy by comparison of the methine signals at δ 5.55, 5.50, and 5.46, respectively. Dimer **2** was isolated by preparative silica gel TLC (1:2, CH_2Cl_2-hexane elution): mp 221-224 °C (lit.[9a] mp 226-227 °C); ^1H NMR δ 5.50 (s, 1 H), 6.89 (d, 2 H), 7.1-7.4 (m, 27 H); ^{13}C NMR δ 56.4, 64.7, 125.9, 126.3, 127.4, 128.3, 128.4, 129.4, 131.6, 131.2, 141.3, 143.9, 144.7, 146.8.

Reaction of Triphenylcarbenium Tetrafluoroborate with LDA. Ph_3CBF_4 (0.0326 g, 0.099 mmol) was weighed into a flask that was then flushed with nitrogen and cooled to -78 °C. Following the addition of 3 mL of THF, 1.5 mL of 0.5 M LDA solution (0.75 mmol) was added. The reaction was quenched after 1 h by addition of methanol. Ether (5 mL) was added, and the resulting solution was washed with water and brine and dried over $MgSO_4$. The product was analyzed by GC (pentadecane standard) and by ^1H NMR as described above.

(4-Methoxyphenyl)diphenylmethane (4-H). (4-Methoxyphenyl)diphenylchloromethane (**4-Cl**) (0.23 g, 0.94 mmol) was dissolved in 5 mL of THF. After the solution was cooled to -78 °C, 2.2 mL of a 0.75 M LDA solution in THF (1.65 mmol) was added, and the mixture was stirred for 3 h. The reaction was quenched with 2 mL of methanol, and 5 mL of ether was added. The solution was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield 0.20 g (78%) of **4-H**: ^1H NMR δ 3.07 (s, 3 H), 5.50 (s, 1 H), 7.0-7.5 (m, 14 H).

Bis(4-methoxyphenyl)phenylmethane (5-H) was prepared in 75% yield from bis(4-methoxyphenyl)phenylchloromethane (**5-Cl**) following the procedure given above: ^1H NMR δ 3.07 (s, 3 H), 5.46 (s, 1 H), 7.0-7.5 (m, 14 H).

Kinetic Studies of Reductions of Trityl Chloride by Lithium Dialkylamides. The reactions were similar to the product studies. The solutions contained a 10-fold excess of lithium dialkylamide. Several similar solutions were prepared, and the reactions were commenced simultaneously. Periodically, a reaction mixture was quenched with methanol. Following a workup, the yield of triphenylmethane was determined by GC (pentadecane standard). Each pseudo-first-order rate constant was calculated from the results of 4 or 5 reactions run for varying amounts of time.

Kinetic Study of Reactions of Trityl Chloride with Lithium Azide. The following is representative. Lithium azide (5.7 mg, 0.12 mmol) was weighed into a dried flask, 10 mL of THF was added, and the solution was cooled to -78 °C. To this solution was added 0.125 mL of a 0.048 M TCl solution in THF. At the appropriate time, 1 mL of a 1 M LDA solution was added to trap unreacted TCl. After the mixture was stirred for 0.5 h at room temperature, 1 mL of methanol was added followed by 5 mL of ether. The reaction mixture was washed with water and brine and dried over $MgSO_4$. The yield of triphenylmethane was determined by GC with a pentadecane internal standard. Triphenylmethyl azide was calculated as the difference between the theoretical and actual yield of triphenylmethane. Each pseudo-first-order rate constant was calculated from the results of 4 reactions run for varying amounts of time.

Kinetic Study of Reactions of Trityl Chloride with Methanol. The following procedure is representative. Methanol (3 mL) was added to a solution of 0.21 g (0.75 mol) of TCl and 22 mL of THF at -78 °C. At the appropriate time, the reaction mixture was saturated with anhydrous K_2CO_3, and lithium azide was added to quench the unreacted halide. Yields of triphenylmethyl methyl ether were determined by GC with an internal standard.

Competition Studies. Chloride **4-Cl** (0.3368 g, 0.99 mmol) and TCl (0.2837 g, 1.02 mmol) was dissolved in 4.5 mL of THF, and the solution was cooled to -78 °C. The mixture was stirred, and 0.68 mL of a 0.75 M solution of LDA in THF (0.51 mmol) was added. The solution turned from an orange to a brown color. The reaction was treated with 2 mL of methanol after 3 h. The reaction mixture was warmed to room temperature and stirred for 2 h, and the products were isolated as in the product studies. The relative amounts of the products were determined by ^1H NMR spectroscopy by comparing the areas of the methine signals from **4-H** and **2**. The competition between chloride **5-Cl** and TCl was also performed by this procedure.

Isotope-Labeling Studies. The reductions of trityl halides were performed with dideuterated lithium dialkylamides by the procedure given above for the product studies. The reaction mixtures contained at least a 6-fold excess of the base. The triphenylmethane product was isolated from the reaction mixture by radial chromatography (silica gel, 1:2 CH_2Cl_2-hexane elution). The purified product was analyzed by deuterium content by ^1H NMR and ^2H NMR spectroscopy and mass spectrometry.

Kinetic Isotope Effect Studies. Base solutions containing either $LiNR_2$-d_1 or equimolar amounts of $LiNR_2$-d_0 and $LiNR_2$-d_2 were prepared. TCl or TBr reductions were conducted by the procedure used in the product studies. A 6-fold excess of base was employed. The product triphenylmethane was isolated and analyzed as described above.

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Steric and Electronic Effects on the Conformations and Singlet Oxygen Ene Regiochemistries of Substituted Tetramethylethylenes. The Origin of the Geminal Effect[1]

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Abstract: The reactions of singlet oxygen with 22 allylically substituted tetramethylethylenes have been studied. Steric and electronic effects on the regiochemistries of the ene reactions have been discovered. Large groups and electron-rich groups increase geminal hydrogen abstraction. Molecular mechanics calculations have been conducted and reveal that the site of hydrogen abstraction is correctly predicted by the rotational barriers of the methyl groups.

The ene reaction first explored in detail by Alder[2] 45 years ago involves the reaction of an olefin containing an allylic hydrogen with an unsaturated electron-deficient enophile to give a 1:1 adduct (eq 1). Interest in the ene reaction has been sustained since this

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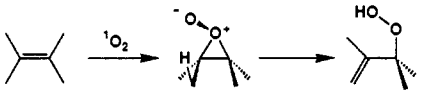
(1)

early report because of its synthetic[3] and biochemical[4] importance and because of the fascinating mechanistic diversity exhibited by this deceptively simple reaction.

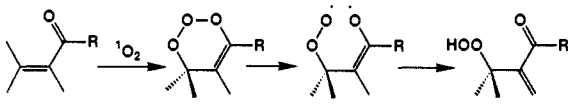
Nickon and Bagli[5] recognized many years ago during a study of the ene reactivity of steroids that the allylic hydrogen which is oriented approximately orthogonal to the olefinic plane was preferentially abstracted. This phenomenon is a result of the electronic requirement for overlap between the p-orbitals of the developing double bond in the transition state of the ene reaction.[6] As a result, only those olefins with properly aligned allylic hydrogens or those flexible enough to adopt this required geometry in the transition state are suitable ene substrates.

The mechanism of the ene reaction has been exhaustively debated, and both concerted and stepwise reactions[7] have been recognized. The singlet oxygen ene reaction[8] in particular has been extensively studied, and a consensus for a stepwise mechanism has developed. The fascinating characteristics of the singlet oxygen reaction which support this conclusion include the following: (1) a very low activation barrier for reaction, which has been used by Gorman and co-workers[9] to argue for a reversibly formed exciplex, and (2) high intramolecular (product) and low intermolecular (kinetic) isotope effects.[10] Furthermore, the stereochemical dependence of the product isotope effects observed with *cis*- and *trans*-tetramethylethylenes-d_6 by Stephenson and co-workers[11] has been used to argue for an intermediate with perepoxide symmetry (eq 2).



(2)

In 1980[12] a new mechanism for the singlet oxygen ene reaction was suggested in order to rationalize the high geminal selectivity observed during photooxidations of α,β-unsaturated ketones and the more rapid reactions of s-cis in comparison to s-trans enones. This mechanism depicted in eq 3 invokes a 4 + 2 cycloaddition



(3)

of singlet oxygen to the α,β-unsaturated ketone followed by cleavage of the weak allylic O–O bond in the trioxene intermediate and hydrogen abstraction. Geminal selectivity has also been

Table I. Photooxidation Products Formed in the Reactions of **2**

R	% relative yields 3[a]	4[a]
SO_2Ph	83	17
SO_2(*p*-MePh)	83	17
SO(*p*-NO_2Ph)	79	21
SOPh	76	24
SO(*p*-MePh)	75	25
SO(*p*-MeOPh)	74	26
S(*p*-NO_2Ph)	52 (50.3)[c]	48 (49.6)[c]
SPh	58	42
S(*p*-MePh)[b]	63 (63.6)[c]	37 (36.4)[c]
S(*p*-MeOPh)[b]	67	33
Br	51	44[d]
OMe	39	52[e]
OEt	39	52[e]
CN	30	64[d]

[a] Determined by cutting and weighing of NMR peaks, unless otherwise noted. [b] This reaction was not carried to 100% completion in order to prevent overoxidation at sulfur. The relative yields were determined at <15% conversion. [c] Capillary GC yield. [d] A product formed in 5% yield has not been identified. [e] The remainder is due to abstraction of hydrogen from the allylic methylene.

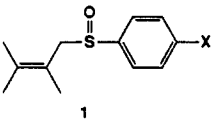
Table II. Photooxidation Products[a] in the Reactions of Alkyl-Substituted **2**[b]

R	% relative yields 3[c]	4[c]
Me	37	63
Et	40	60
*i*Pr	55	45
*t*Bu	78	22

[a] Average of three independent determinations. [b] Measured after 100% conversion to products. No other products were observed. [c] Determined by cutting and weighing appropriate NMR peaks.

observed in the reactions of α,β-unsaturated aldehydes,[13] acids,[14] esters,[15] and aldimines[16] and the 4 + 2 mechanism invoked to explain the regiochemistry in the latter two cases.

Consequently, we were somewhat surprised when we discovered in 1988[1] that allylic sulfoxides **1**, which are incapable of 4 + 2



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cycloaddition, showed a marked preference for abstraction of hydrogen geminal to the carbon bearing the sulfoxide group. After our initial report Foote and co-workers[17] pointed out that contrary to what was previously believed, some s-trans enones are reasonably reactive and suggested an alternative to the 4 + 2 mechanism.

We present here the results of a more detailed study of sulfoxides **1** and other allylically substituted substrates.

Results and Discussion

Photooxidation of oxygen saturated acetone-d_6 solutions of the substituted tetramethylethylenes, depicted in Table I, demonstrates that the preference for geminal hydrogen abstraction is a general phenomenon. No ene product formed by abstraction of hydrogen from the allylic methylene carbon was observed except in the reactions of the methyl and ethyl allylic ethers. The reactive vinyl ether product was not directly observed but was converted rapidly to a bis(hydroperoxide). Reduction of the bis(hydroperoxides)

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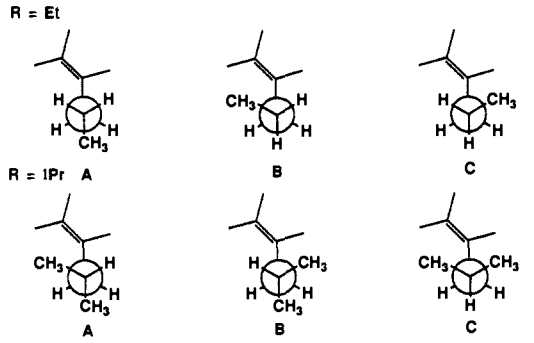
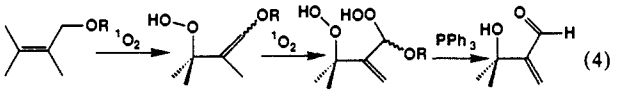
Chart I. Newman Projections of MM2 Energy Minima for **2**



with PPh_3 resulted in isolation of the same aldehyde in the two reactions (eq 4). All the relative yields reported in Table I were

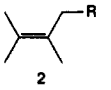


(4)

determined by cutting and weighing appropriate peaks from expanded portions of the NMR spectra and are reproducible to within ±4%. In addition, the relative product yields for the *p*-nitro- and *p*-methylphenyl sulfides were also determined by reduction of the hydroperoxides with PPh_3 and analysis by capillary GC.

Examination of Table I reveals that geminal selectivity decreases in the sulfur series, sulfone > sulfoxide > sulfide, and in the sulfide series, *p*-MeO > *p*-Me > H > *p*-NO_2, suggesting that both steric and electronic effects play important roles in determining ene regiochemistry.

Steric Effects. Oxygen saturated acetone-d_6 solutions 5×10^{-2} M in tetramethylethylenes **2** (R = Me, Et, *i*Pr, and *t*Bu[18]) con-



2

taining 1×10^{-5} M Rose Bengal were irradiated at −80 °C through a 0.5% $K_2Cr_2O_7$ filter solution. The progress of the reactions were monitored by ^1H NMR. The allylic hydroperoxides **3** and **4** were the only products detected at any point during the reaction. The relative yields of **3** and **4** (Table II) were determined by the same method used for the compounds appearing in Table I. Reduction of the reaction mixtures with Ph_3P produced the corresponding alcohols in the same ratio as their precursor hydroperoxides. Examination of Table II reveals that increasing the size of the substituent R from CH_3 to *t*Bu is accompanied by a dramatic increase in the amount of geminal product **3**, from 37% to 78% of the reaction mixture. No abstraction of hydrogen from the methylene carbon was observed despite the fact that it would lead to the thermodynamically favored product, the trisubstituted olefin, in the reaction of **2** (R = CH_3).

3 **4**

Houk and co-workers[19] attributed the propensity of the ene reaction to occur on the more substituted side of trisubstituted olefins (the "cis effect") to lower rotational barriers in the more highly conjested environment. They pointed out that since the activation barriers for ene reactions are very small (0–5 kcal/mol) that even small differences in rotational barriers can dictate regiochemistry.

In order to determine if methyl rotational barriers also play a role in these more highly substituted olefins we have examined

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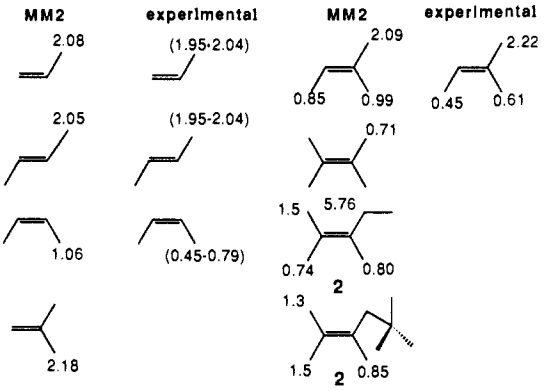
Table III. MM2 Structural Parameters

R	$\Delta H_f^{a,b}$ (kcal/mol)	θ^c c	t	g	$\theta_R{}^d$
H	−16.35	106			
Me	−21.55	111	107	106	90
Et					
A	−27.41 (81.25)	110	107	107	90
B	−26.70 (13.01)	113	106	105	102
C	−26.38 (5.74)	118	109	98	81
*i*Pr					
A	−34.11 (68.17)	113	107	105	102
B	−33.80 (30.65)	118	109	96	81
C	−32.54 (1.18)	120	119	65	96
*t*Bu	−40.69	119	120	64	95

[a] Heat of formation in kcal/mol. [b] % population in parentheses. [c] Dihedral angle, θ, of hydrogen at cis (c), trans (t), and geminal (g) methyls nearest to perpendicular to the olefinic plane. [d] θ_R = dihedral angle of homoallylic carbon of substituent R relative to olefinic plane.

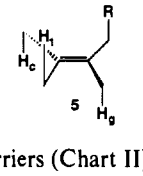
Chart II. Comparison of Calculated and Experimental Rotational Barriers[a]



[a] In kcal/mol.

the structures of **2** (R = H, Me, Et, *i*Pr, and *t*Bu) by molecular mechanics.[20] MM2 local minima located on the energy surfaces of **2** (R = Et and *i*Pr) are depicted in Chart I. The calculated heats of formation and the dihedral angles of the hydrogens nearest to perpendicular at the cis(c), trans(t), and geminal(g) positions for these six conformations and for **2** (R = H, Me, and *t*Bu), for which only one conformation could be located, are listed in Table III.

The calculations predict that tetramethylethylene (TME), **2** (R = H), exists in an alternating up and down conformation with one hydrogen on each methyl close to orthogonal to the olefinic plane consistent with previous force field[21] and quantum mechanical studies.[19] The lowest energy conformations of the substituted TME's maintain the basic structure of TME (except for R = *t*Bu) with the hydrogens best aligned with the π system on each methyl and the R group arranged in the alternating up–down conformation **5**. The substituents R only deviate from perpendicular (θ in Table III) to the olefinic plane to compensate for destabilizing methyl olefin gauche interactions (e.g., conformation B in **5**, R = Et, and A in **5**, R = *i*Pr).



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The methyl rotation barriers (Chart II) in **2** (R = Me and *t*Bu) were calculated from the steric energies at the maximum and minimum on the MM2 rotation surface. The rotation surface was generated by fixing the allylic hydrogen olefin dihedral angle at 5° increments and allowing the rest of the structure to minimize.

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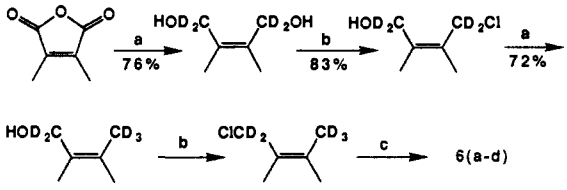
Table IV. Product Yields in the Photooxidations of Allylic Sulfides **6**[a-c]

compd	% relative yields 7	8	9
6a	66	28	7
6b	63	27	10
6c	61	27	12
6d	56[d]	29	15

[a] In acetone-d_6 at −80 °C. [b] Average of three independent NMR determinations. [c] Measured at <15% conversion in order to prevent overoxidation at sulfur unless otherwise noted. [d] Measured at 100% conversion. No reaction at sulfur.

Scheme I. Synthesis of **6a–d**[a]



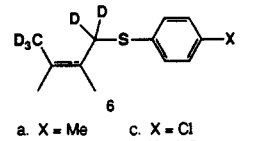
[a] a. $LiAlD_4$, ether, 0 °C; b. 1 equiv of NCS, $(CH_3)_2S$, CH_2Cl_2, −20 °C; c. sodium thiolates.

In **2** (R = *t*Bu) which exhibits a large geminal selectivity, the geminal methyl has a substantially smaller rotational barrier than either the cis or trans methyls. In **2**, R = Me, which exhibits a much reduced geminal selectivity in comparison to **2**, R = *t*Bu, the trans and geminal methyl groups have very similar rotational barriers. Also reported in Chart II are comparisons of experimental[22] and MM2 rotational barriers for several mono-, di-, tri-, and tetrasubstituted olefins. The excellent agreement in the trend of the rotational barriers between the calculated and experimental values lends support to the validity of the MM2 method. The MM2 calculations, however, do appear to overestimate the rotational barriers of cis methyl groups by 0.3–0.4 kcal/mol. The much larger methylene (5.76 kcal/mol) in comparison to methyl rotational barrier in **2** (R = CH_3) provides a convenient explanation for the lack of methylene hydrogen abstraction in the majority of olefins that have been examined.

A reasonable linear correlation of %**3** versus the Taft steric parameter[23] E_s (%**3** = −0.18Es + 0.039; r = 0.983) corroborates our suggestion that it is the steric character of these substituents which influences the rotational barriers and consequently the ene regiochemistries.

Electronic Effects. Allylic sulfides **2** (R = *p*-NO_2PhS–, PhS–, pMePhS–, and *p*-MeOPhS–) were photooxidized at −80 °C in acetone-d_6 through a 0.5% $K_2Cr_2O_7$ filter solution. Despite the identical steric demands of the substituents in these sulfides, the extent of geminal hydrogen abstraction (%**3**) decreases in the order *p*-MeOPhS– > *p*-MePhS– > PhS– > *p*-NO_2PhS– (Table I).

In order to develop further insight into the origin of this substituent-induced regioselectivity the photooxidations of the deuterated sulfides **6a–d** were examined. These sulfides were synthesized as outlined in Scheme I. Photooxidations of these deuterated allylic sulfides at −80 °C resulted in formation of three rather than two allylic hydroperoxides (**7**, **8**, and **9**) in the yields reported in Table IV.[6] Geminal selectivity (%**7**) increased with increasing electron density at sulfur as depicted graphically in Figure 1. In addition, hydrogen abstractions to give **7** and **9**, but not **8**, were sensitive to the changing electronic character of the substituent.



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a. X = Me c. X = Cl
b. X = H d. X = NO_2

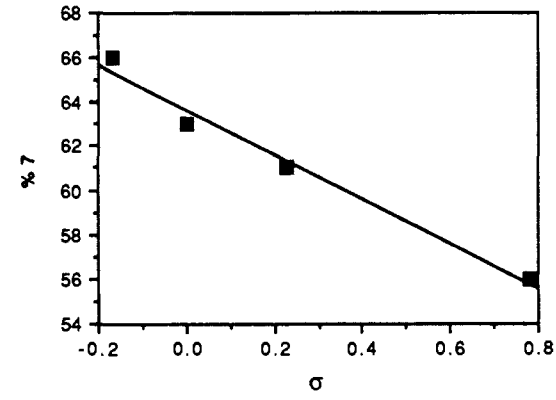
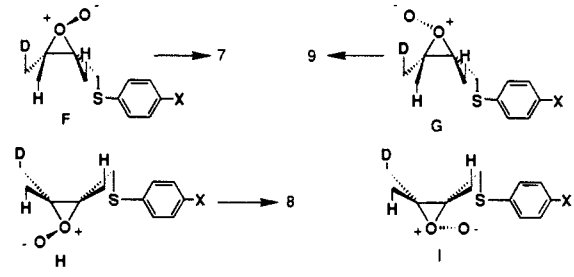
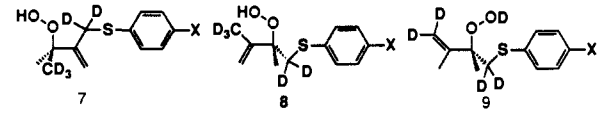


Figure 1. Yield of **7** versus the Hammett substituent parameter.

Scheme II. Perpepoxides Formed in the Reaction of **6**

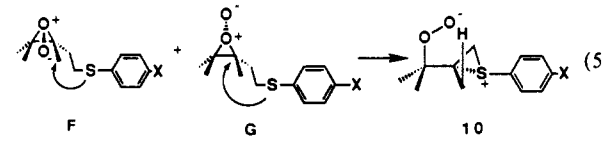




These allylic sulfides most likely exist in alternating up–down conformations which were previously established to be quite general for tetramethylethylene and substituted derivatives, **2**.[1] The alternating up–down conformation is further stabilized in these sulfides by electron donation from the electron-rich π-bond to the σ^* carbon sulfur bond. Eclipsed conformations, preferred by many heteroatoms,[24] but less so by sulfur,[25] are sterically destabilized in these congested molecules. The four possible starting materials like perepoxides, formed by addition of singlet oxygen to the two faces of the stable up–down conformation of **6**, and the ene products formed by their collapse are depicted in Scheme II.

An electronic interaction[26] between the diffuse electron pairs on sulfur and the nascent perepoxide leading to an increased population of perepoxides F and G at the expense of perepoxides H and I (Scheme II) cannot be responsible for the geminal selectivity, since the yield of **8** is insensitive to the electronic character at sulfur.

The absence of methanol addition products during photooxidation of **2** (R = *p*-MePhS–) in methanol argues against, but does not rigorously exclude, the anchimerically assisted pathway depicted in eq 5. Episulfonium ion[27] **10** can only collapse to **7**



(5)

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and its formation would occur solely at the expense of **9**. The observed trend of increasing geminal regioselectivity (%**7**) with increasing electron density at sulfur is also consistent with this anchimerically assisted route.

As an alternative we suggest that regioselectivity [**7**/(**8** + **9**)], is determined by the rotational barriers of the three methyl groups, which can be influenced by the electronic character of the substituents. Increasing the electron-withdrawing ability of the substituents in **6** will lead to an increased contribution of the hyperconjugative[28] resonance form **11**, and consequently a

11

lengthening of the carbon–sulfur bond and a decrease in the effective size of the thiol substituent. The results with the alkyl-substituted TME's **2** (R = Me, Et, *i*Pr, and *t*Bu) has demonstrated that a decrease in the size of the substituent will induce rotational barrier changes which result in decreased geminal regioselectivity. This explanation is consistent with the experimental observation of a decreasing yield of **7** in the order *p*-MePhS– > PhS– > *p*-ClPhS– > *p*-NO_2PhS–.

A definitive choice between the anchimerically assisted and hyperconjugative explanations is difficult, however, because of the small magnitude of the electronic effect.[29]

Conclusion

A rotational barrier argument, which has only been previously utilized to explain the singlet oxygen ene regiochemistry in trisubstituted olefins, has been shown to correctly predict singlet oxygen ene regiochemistry in tetrasubstituted olefins.

Experimental Section

Preparative gas chromatographic separations were carried out on a GOW-MAC Series 550 gas chromatograph equipped with a thermal conductivity detector and a 0.25 in. by 10 or 20 ft column packed with 20% Carbowax 20M on NAW Chromosorb W 80/100. Analytical gas chromatographic measurements were carried out on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector and a HP 10 m by 0.53 mm cross-linked FFAP capillary column. Chromatographic separations were also carried out on a Harrison Research Model 7624T Chromatotron using plates coated with EM Science 7749 silica gel 60PF254. Proton and carbon NMR were obtained on a JEOL FX270 at 269.7 and 67.8 MHz, respectively, and proton and deuterium on a JEOL GX 400 at 399.78 and 61.37 MHz, respectively. The proton and carbon spectra are referenced to TMS and the deuterium to internal $CDCl_3$. Infrared spectra were obtained on a Mattson Cygnus 100 FT-IR spectrometer. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectrometry.

Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was freshly distilled from CaH_2. Carbon tetrachloride was purified by distillation from P_2O_5 and hexane and ethyl acetate by simple distillation. The sodium thiolates were prepared according to a literature procedure.[30] 1-Bromo-2,3-dimethyl-2-butene,[31] 2,3-dimethyl-2-butenyl *p*-methylphenyl sulfide,[31] 1-[(4-methylphenyl)sulfinyl]-2,3-dimethyl-2-butene,[31] 1-[(4-methylphenyl)sulfonyl]-2,3-dimethyl-2-butene,[31] 2,3-dimethyl-2-butenyl *p*-methoxyphenyl sulfide,[32] 2,3-dimethyl-2-butenyl phenyl sulfide,[32] and 2,3-dimethyl-2-butenyl *p*-nitrophenyl sulfide,[32] were synthesized as previously reported. The alcohols 2,3-dimethyl-3-pentanol, 2,3-dimethyl-3-hexanol, and 2,3,5-trimethyl-3-hexanol were synthesized by the method of Ejchart.[33]

General Photolysis Conditions. The singlet-oxygen reactions were performed in 5-mm NMR tubes containing 0.5 mL of acetone-d_6. The temperature was maintained by submersion in a methanol bath held at −78 °C by the use of a refrigerator probe (FTS Systems Inc. Flexicool). Prior to photolysis, the samples were saturated with oxygen for 20 min. The concentrations of the starting materials and dye were approximately 5×10^{-2} M and 2×10^{-5} M, respectively. The irradiation was conducted under continuous oxygen bubbling by using a 750-W, 120-V tungsten halogen lamp and by filtering out the high-energy light with a 1-cm 0.5% $K_2Cr_2O_7$ filter solution. The spectral data for the products of the reactions reported in Table I appear in refs 1, 31, and 32.

2-Ethyl-3-hydroperoxy-3-methyl-1-butene. ^{1}H NMR (acetone-d_6) δ 1.04 (t, J = 8 Hz, 3 H), 1.30 (s, 6 H), 2.15 (q, J = 8 Hz, 2 H), 4.85 (s, 1 H), 5.03 (s, 1 H), 10.01 (s, 1 H).

3-Hydroperoxy-2,3-dimethyl-1-pentene. ^{1}H NMR (acetone-d_6) δ 0.80 (t, J = 8 Hz, 3 H), 1.30 (s, 3 H), 1.57 (m, 2 H), 1.75 (s, 3 H), 4.86 (s, 1 H), 4.89 (s, 1 H), 9.96 (s, 1 H).

2-(1-Hydroperoxy-1-methylethyl)-1-pentene. ^{1}H NMR (acetone-d_6) δ 0.94 (t, J = 8 Hz, 3 H), 1.31 (s, 6 H), 1.52 (m, 2 H), 2.10 (t, J = 8 Hz, 2 H), 4.84 (s, 1 H), 5.04 (s, 1 H), 9.94 (s, 1 H).

3-Hydroperoxy-2,3-dimethyl-1-hexene. ^{1}H NMR (acetone-d_6) δ 0.88 (t, J = 7 Hz, 3 H), 1.26 (m, 2 H), 1.32 (s, 3 H), 1.48 (m, 2 H), 1.75 (s, 3 H), 4.84 (s, 1 H), 4.85 (s, 1 H), 9.89 (s, 1 H).

2-(1-Hydroperoxy-1-methylethyl)-4-methyl-1-pentene. ^{1}H NMR (acetone-d_6) δ 0.91 (d, J = 6 Hz, 6 H), 1.30 (s, 6 H), 1.47 (m, 1 H), 2.01 (d, J = 6 Hz, 2 H), 4.85 (s, 1 H), 5.11 (s, 1 H), 9.98 (s, 1 H).

3-Hydroperoxy-2,3,5-trimethyl-1-hexene. ^{1}H NMR (acetone-d_6) δ 0.90 (d, J = 7 Hz, 6 H), 1.38 (s, 3 H), 1.49 (q, 2 H), 1.68 (m, 1 H), 1.77 (s, 3 H), 4.88 (s, 1 H), 4.91 (s, 1 H), 9.91 (s, 1 H).

2-(1-Hydroperoxy-1-methylethyl)-4,4-dimethyl-1-pentene. ^{1}H NMR (acetone-d_6) δ 0.98 (s, 9 H), 1.30 (s, 6 H), 2.11 (s, 2 H), 5.03 (s, 1 H), 5.22 (s, 1 H), 9.44 (s, 1 H).

3-Hydroperoxy-2,3,5,5-tetramethyl-1-hexene. ^{1}H NMR (acetone-d_6) δ 0.98 (s, 9 H), 1.30 (s, 3 H), 1.47 (s, 2 H), 1.80 (s, 3 H), 4.86 (s, 1 H), 4.96 (s, 1 H), 9.80 (s, 1 H).

1-Cyano-2,3-dimethyl-2-butene. To a solution of 570 mg (3.5 mmol) of 1-bromo-2,3-dimethyl-2-butene in 6 mL of dry acetonitrile was added 590 mg (6.6 mmol) of cuprous cyanide, which was dried in a vacuum oven at 100 °C overnight. The solution was stirred and refluxed under a nitrogen atmosphere for 4 h. The reaction mixture was then poured into 30 mL of saturated NaCl and extracted with three 8-mL portions of ethyl ether. The combined organic layer was washed with two 5-mL portions of saturated NaCl and dried with $MgSO_4$. The solvent was removed under reduced pressure to give 110 mg (28%) of crude product. The cyanide was purified by preparative gas chromatography, and the retention time was 17 min when using a 20-ft column at 100 °C: ^{1}H NMR (acetone-d_6) δ 1.70 (s, 3 H), 1.73 (s, 3 H), 1.77 (s, 3 H), 3.23 (s 2 H).

1-Methoxy-2,3-dimethyl-2-butene. A solution of 170 mg (1.04 mmol) of 1-bromo-2,3-dimethyl-2-butene and 60 mg (1.11 mmol) of sodium methoxide in 10 mL of anhydrous methanol was stirred at room temperature for 2 h. The reaction mixture was then poured into 30 mL of saturated NaCl and extracted with three 8-mL portions of petroleum ether. The combined organic layer was washed with three 5-mL portions of saturated NaCl and dried with $MgSO_4$. The solvent was removed under reduced pressure to give 28 mg (24%) of crude product. The ether was purified by preparative gas chromatography, and the retention time was 12 min when using a 20 ft column at 90 °C: ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 6 H), 1.74 (s, 3 H), 3.29 (s, 3 H), 3.91 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.7 (q, J = 125 Hz), 20.1 (q, J = 125 Hz), 20.8 (q, J = 125 Hz), 57.6 (q, J = 140 Hz), 73.2 (t, J = 141 Hz), 124.9 (s), 130.1 (s).

1-[(4-Nitrophenyl)sulfinyl]-2,3-dimethyl-2-butene. To a solution of 190 mg (0.80 mmol) of *p*-(nitrothio)phenyl sulfide in 7 mL of CH_2Cl_2 was added 170 mg (0.79 mmol) of MCPBA in 5 mL of CH_2Cl_2 dropwise at 0 °C. The reaction mixture was stirred at room temperature for 30 min and then poured into 5 mL of aqueous 10% $NaHCO_3$. The organic layer was separated, washed with two 5-mL portions of saturated NaCl, and dried with $MgSO_4$. The solvent was removed at low pressure, and 158 mg (79% yield) of the product was obtained after chromatographic purification: ^{1}H ($CDCl_3$) δ 1.46 (s, 3 H), 1.71 (s, 6 H), 3.53 (d, J = 9 Hz, 1 H), 3.83 (d, J = 9 Hz, 1 H), 7.79 (d, J = 6 Hz, 2 H), 8.39 (d, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.7 (q, J = 127 Hz), 20.8 (q, J = 126 Hz), 21.0 (q, J = 127 Hz), 64.4 (t, J = 140 Hz), 116.7 (s), 123.8 (d, J = 170 Hz), 125.3 (d, J = 168 Hz), 135.6 (s), 149.4 (s), 151.8 (s).

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(29) As pointed out by a referee, the ratio of cis to geminal rotational barriers does not change as one goes from **2** (R = CH_3) to **2** (R = *t*Bu) as seen in Chart II. This would lead one to predict that the ratio **7**/**9** should remain constant contrary to what is observed (Table IV). It should be pointed out, however, that unlike olefins **2**, only the effective size, not the size of the substituents relative to an external reagent is changing in **6**. The approach geometry relative to the face occupied by the substituent may well play a minor role in these reactions.

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1-(Phenylsulfinyl)-2,3-dimethyl-2-butene was prepared by the method described for the synthesis of 1-[(4-nitrophenyl)sulfinyl]-2,3-dimethyl-2-butene and 150 mg of the product was obtained as a colorless oil by using 260 mg of the sulfide and 164 mg of MCPBA: yield 84%; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3 H), 1.67 (s, 6 H), 3.46 (d, J = 12 Hz, 1 H), 3.78 (d, J = 12 Hz, 1 H), 7.45–7.70 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.7 (q, J = 126 Hz), 20.8 (q, J = 125 Hz), 21.0 (q, J = 126 Hz), 64.5 (t, J = 140 Hz), 117.3 (s), 124.3 (d, J = 164 Hz), 128.9 (d, J = 166 Hz), 131.0 (d, J = 162 Hz), 134.5 (s), 144.1 (s).

1-[4-(Methoxyphenyl)sulfinyl]-2,3-dimethyl-2-butene was prepared by the method described for the synthesis of 1-[4-(nitrophenyl)sulfinyl]-2,3-dimethyl-2-butene, and 88 mg of the sulfoxide was obtained as a colorless oil by using 102 mg of sulfide and 97 mg of MCPBA: yield 81%; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.63 (s, 3 H), 1.66 (s, 3 H), 3.42 (d, J = 12 Hz, 1 H), 3.79 (d, J = 12 Hz, 1 H), 3.86 (s, 3 H), 7.00 (d, 8 Hz, 2 H), 7.54 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (q, J = 126 Hz), 20.5 (q, J = 125 Hz), 20.8 (q, J = 126 Hz), 55.4 (q, J = 144 Hz), 64.3 (t, J = 140 Hz), 114.3 (d, J = 162 Hz), 117.2 (s), 125.9 (d, J = 162 Hz), 134.0 (s), 134.8 (s), 161.8 (s).

1-(Phenylsulfonyl)-2,3-dimethyl-2-butene. To a solution of 46 mg (0.24 mmol) of 2,3-dimethyl-2-butenyl phenyl sulfide was added 103 mg (0.5 mmol) of MCPBA in 5 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 1 h and then poured into 10 mL of 10% aqueous $NaHCO_3$. The organic layer was separated, washed with two 5-mL portions of saturated NaCl, and dried with $MgSO_4$. The solvent was removed at low pressure, the residue was chromatographed, and 34 mg (63% yield) of a white solid was obtained: mp 99–100 °C; IR (neat) 3058, 3005, 2926, 2863, 1448, 1375, 1277, 1245, 1139, 1070, 1023, 869, 781, and 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 3 H), 1.63 (s, 3 H), 1.79 (s, 3 H), 3.87 (s, 2 H), 7.5–7.9 (m, 5 H); ^{13}C ($CDCl_3$) δ 19.4 (q, J = 127 Hz), 20.5 (q, J = 126 Hz), 20.9 (q, J = 126 Hz), 61.8 (t, J = 135 Hz), 115.8 (s), 128.3 (d, J = 162 Hz), 128.9 (d, J = 162 Hz), 133.4 (s), 135.9 (d, J = 162 Hz), 139.1 (s).

2,3,5,5-Tetramethyl-3-hexanol was synthesized by the Ejchart[33] method in 62% yield: bp 110 °C/20 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 7 Hz, 3 H), 0.91 (d, J = 7 Hz, 3 H), 1.05 (s, 9 H), 1.20 (s, 3 H), 1.44 (s, 2 H), 1.67 (m, 1 H); ^{13}C NMR δ 17.1 (q, J = 125 Hz), 17.7 (q, J = 124 Hz), 24.5 (q, J = 124 Hz), 29.7 (s), 31.8 (q, J = 125 Hz), 40.2 (d, J = 126 Hz), 50.2 (t, J = 123 Hz), 76.2 (s).

2,3-Dimethyl-2-pentene.[18] A solution of 490 mg (4.22 mmol) of 2,3-dimethyl-3-pentanol and 3 mL of polyphosphoric acid was heated to 130 °C under a nitrogen atmosphere. The volatile product was trapped with a liquid nitrogen cold-finger to give 337 mg of crude product: (30% pure) yield 24%. The olefin was purified by preparative gas chromatography with a retention time of 13 min using a 20 ft column at 40 °C: ^{1}H NMR δ 0.93 (t, J = 7 Hz, 3 H), 1.63 (s, 9 H), 2.05 (q, J = 7 Hz, 2 H).

2,3-Dimethyl-2-hexene[18] was made by the method described for 2,3-dimethyl-2-pentene in 33% yield. The final purification was carried out by gas chromatography: ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 7 Hz, 3 H), 1.37 (m, 2 H), 1.64 (br s, 9 H), 1.99 (t, J = 8 Hz, 2 H).

2,3,5-Trimethyl-2-hexene[18] was made by the method described for 2,3-dimethyl-2-pentene in 31% yield and purified by gas chromatography: ^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 7 Hz, 6 H), 1.61 (s, 3 H), 1.65 (s, 6 H), 1.71 (m, 1 H), 1.91 (d, J = 7 Hz, 2 H).

2,3,5,5-Tetramethyl-2-hexene[18] was made by the method described for 2,3-dimethyl-2-pentene in 35% yield and purified by gas chromatography: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.65 (s, 6 H), 1.68 (s, 3 H), 2.01 (s, 2 H).

(*Z*)-2,3-Dimethyl-2-butene-1,4-diol-1,1,4,4-d_4. A solution of 583 mg (4.6 mmol) of 2,3-dimethylmaleic anhydride, 259 mg (6.2 mmol) of $LiAlD_4$, and 25 mL of anhydrous ether was stirred under a nitrogen atmosphere at 0 °C for 3 h. Water (235 μL) was added dropwise with continuous stirring, followed by 235 μL of 10% aqueous NaOH and three 235 μL portions of water. The resulting slurry was stirred for an additional 1 h at room temperature. The mixture was then filtered through Celite, and the precipitate was washed with ether. After drying with $MgSO_4$ the ether was removed under reduced pressure, and 420 mg (76% yield) of the diol was obtained by Kugelrohr distillation: ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 17.4 (q, J = 126 Hz), 62.2 (m), 132.5 (s).

(*Z*)-4-Chloro-2,3-dimethyl-2-butenol-1,1,4,4-d_4 was made from the diol in 83% yield by the Corey method.[34] The monochloride was unstable and was used immediately: ^{1}H NMR ($CDCl_3$) δ 1.81 (s, 6 H).

(*Z*)-2,3-Dimethyl-2-butenol-1,1,4,4,4-d_5. A solution of 308 mg (2.2 mmol) of (*Z*)-1-chloro-2,3-dimethyl-2-butenol-1,1,4,4-d_4, 106 mg (2.5 mmol) of $LiAlD_4$, and 15 mL of anhydrous THF was refluxed for 6 h under a nitrogen atmosphere. Water, 74 μL was added with continuous stirring, followed by 73 μL of 10% aqueous NaOH, and three 73 μL portions of water. The resulting slurry was stirred for 1 h. The mixture was filtered through Celite, and the precipitate was washed with ether. After drying with $MgSO_4$, the solvents were removed under reduced pressure, and 170 mg (76% yield) of the alcohol was obtained by Kugelrohr distillation: ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 1.75 (s, 3 H).

(*Z*)-1-Chloro-2,3-dimethyl-2-butene-1,1,4,4,4-d_5. The above alcohol was converted to the chloride by Corey's method.[34] To a solution containing 214 mg (1.6 mmol) of *N*-chlorosuccinimide in 10 mL of anhydrous CH_2Cl_2 was added 100 mg (1.6 mmol) of methyl sulfide at 0 °C. The reaction mixture was stirred for 0.5 h and then cooled to −20 °C, and 160 mg (1.5 mmol) of the alcohol in 1 mL of CH_2Cl_2 was added dropwise over a 1-min period. The resulting solution was stirred for 1 h at 0 °C and poured into 10 mL of ice-cold brine. After shaking and separating the mixture, the aqueous phase was extracted with two 5-mL portions of ether. The combined organic phase was washed with two 5-mL portions of cold brine and dried with $MgSO_4$. Evaporation of the solvents gave the crude chloride which was unstable and used immediately without further purification: ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3 H), 1.78 (s, 3 H).

(*Z*)-2,3-Dimethyl-2-butenyl *p*-Methylphenyl Sulfide-1,1,4,4,4-d_5 (6a). A solution of 220 mg (1.5 mmol) of sodium 4-(methylthio)phenoxide and the above d_5 crude monochloride in 10 mL of absolute ethanol was stirred for 30 min. The solvent was removed under reduced pressure, and the residue was dissolved in 20 mL of ether. This ether solution was washed with two 10-mL portions of saturated NaCl and dried with $MgSO_4$. Ether was removed under reduced pressure, and the product was purified by chromatotron using hexane elution. The yield for two steps was 24%. Only a trace of the d_4 and greater than 95% of the d_5 isomers were detected by mass spectrometry, consistent with the NMR analysis: ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 3 H), 1.77 (s, 3 H), 2.31 (s, 3 H), 7.07 (d, J = 8 Hz, 2 H), 7.25 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.1 (q, J = 125 Hz), 19.5 (m), 20.7 (q, J = 125 Hz), 21.0 (q, J = 125 Hz), 39.4 (m), 123.0 (s), 129.4 (d, J = 162 Hz), 129.5 (s), 131.2 (d, J = 160 Hz), 133.5 (s), 136.3 (s); exact mass calcd for $C_{13}H_{13}D_5S$ 211.1444, found 211.1442.

(*Z*)-2,3-Dimethyl-2-butenyl *p*-nitrophenyl sulfide-1,1,4,4,4-d_5 (6d) was synthesized by the method used for **6a**: ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H), 1.79 (s, 3 H), 7.32 (d, J = 9 Hz, 2 H), 8.11 (d, J = 9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.2 (q, J = 125 Hz), 19.8 (m), 20.9 (q, J = 125 Hz), 36.9 (m), 120.9 (s), 123.7 (d, J = 165 Hz), 126.5 (d, J = 169 Hz), 131.4 (s), 144.8 (s), 149.0 (s).

(*Z*)-2,3-Dimethyl-2-butenyl *p*-chlorophenyl sulfide-1,1,4,4,4-d_5 (6c) was synthesized by the method used for **6a**: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3 H), 1.78 (s, 3 H), 7.14–7.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.4 (q, J = 125 Hz), 19.6 (m), 20.7 (q, J = 127 Hz), 38.8 (m), 122.4 (s), 128.5 (d, J = 166 Hz), 130.6 (s), 131.4 (d, J = 164 Hz), 132.2 (s), 135.6 (s).

(*Z*)-2,3-Dimethyl-2-butenyl phenyl sulfide-1,1,4,4,4-d_5 (6b) was synthesized by the method used for **6a**: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3 H), 1.78 (s, 3 H), 7.14–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.1 (q, J = 125 Hz), 19.6 (m), 20.8 (q, J = 125 Hz), 38.7 (m), 122.6 (s), 126.1 (d, J = 161 Hz), 128.6 (d, J = 160 Hz), 129.8 (s), 130.3 (d, J = 162 Hz), 137.2 (s).

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Registry No. **2** (R = SO_2Ph), 84602-85-7; **2** (R = SO_2(*p*-MePh)), 86925-63-5; **2** (R = SO(*p*-NO_2Ph)), 114597-46-5; **2** (R = SOPh), 101384-22-9; **2** (R = SO(*p*-MePh)), 51954-48-4; **2** (R = SO(*p*-MeOPh)), 114597-52-3; **2** (R = S(*p*-NO_2Ph)), 114597-58-9; **2** (R = SPh), 79597-54-9; **2** (R = S(*p*-MePh)), 119561-09-0; **2** (R = S(*p*-MeOPh)), 123358-92-9; **2** (R = Br), 5072-70-8; **2** (R = OMe), 20518-48-3; **2** (R = OEt), 20174-79-2; **2** (R = CN), 4786-36-1; **2** (R = Me), 10574-37-5; **2** (R = Et), 7145-20-2; **2** (R = *i*-Pr), 32540-07-1; **2** (R = *t*-Bu), 33175-59-6; **2** (R = H), 563-79-1; **3** (R = SO_2Ph), 123358-87-2; **3** (R = SO_2(*p*-MePh)), 114597-44-3; **3** (R = SO(*p*-NO_2Ph)), 114614-33-4; **3** (R = SOPh), 114597-48-7; **3** (R = SO(*p*-MePh)), 114597-50-1; **3** (R = SO(*p*-MeOPh)), 114597-53-4; **3** (R = S(*p*-NO_2Ph)), 114597-59-0; **3** (R = SPh), 114597-56-7; **3** (R = S(*p*-MePh)), 122145-08-8; **3** (R = S(*p*-MeOPh)), 123358-93-0; **3** (R = Br), 67228-75-5; **3** (R = OMe), 114597-61-4; **3** (R = OEt), 114597-63-6; **3** (R = CN), 114597-65-8; **3** (R = Me), 127130-14-7; **3** (R = Et), 127130-15-8; **3** (R = *i*-Pr), 127130-16-9; **3** (R = *t*-Bu), 127130-17-0; **4** (R = SO_2Ph), 123358-88-3; **4** (R = SO_2(*p*-MePh)), 114597-45-4; **4** (R = SO(*p*-NO_2Ph)), 114597-47-6; **4** (R = SOPh), 114597-49-8; **4** (R = SO(*p*-MePh)), 114597-51-2; **4** (R = SO(*p*-MeOPh)), 114597-54-5; **4** (R = S(*p*-NO_2Ph)), 114597-60-3; **4** (R = SPh), 114597-57-8; **4** (R = S(*p*-MePh)), 123358-95-2; **4**

(R = S(*p*-MeOPh)), 123358-94-1; **4** (R = Br), 114597-55-6; **4** (R = OMe), 114597-62-5; **4** (R = OEt), 114597-64-7; **4** (R = CN), 114597-66-9; **4** (R = Me), 127130-18-1; **4** (R = Et), 127130-19-2; **4** (R = *i*-Pr), 127130-20-5; **4** (R = *t*-Bu), 127130-21-6; **6a**, 127130-10-3; **6b**, 127130-11-4; **6c**, 127130-12-5; **6d**, 127130-13-6; **7a**, 127130-22-7; **7b**, 127130-23-8; **7c**, 127130-24-9; **7d**, 127130-25-0; **8a**, 127130-26-1; **8b**, 127130-27-2; **8c**, 127130-28-3; **8d**, 127130-29-4; **9a**, 127130-30-7; **9b**, 127130-31-8; **9c**, 127130-32-9; **9d**, 127130-33-0; $H_3CCH(CH_3)C(OH)(CH_3)C-H_2C(CH_3)_2CH_3$, 5396-09-8; (*Z*)-$HOCD_2C(CH_3)$=$C(CH_3)CD_2OH$, 70576-51-1; (*Z*)-$ClCD_2C(CH_3)$=$C(CH_3)CD_2OH$, 127130-34-1; (*Z*)-$D_3CC(CH_3)$=$C(CH_3)CD_2OH$, 127130-35-2; (*Z*)-$D_3CC(CH_3)$=$C-(CH_3)CD_2Cl$, 127130-36-3.

The Photocyclization of *o*-Alkoxy Phenyl Ketones

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Abstract: Several *o*-alkoxybenzophenones and *o*-(benzyloxy)benzophenones and -acetophenones photocyclize to 3-hydroxy-2,3-dihydrobenzofurans. Quantum yields generally are quite high, except for *o*-(benzyloxy)acetophenone. The *o*-ethoxy and *o*-benzyloxy ketones form two diastereomeric products, the *Z* isomer being highly preferred in hydrocarbon solvents, the *E* isomer being formed in comparable yield in methanol or with added pyridine. The reaction involves δ-hydrogen abstraction by the ketone triplets followed by cyclization of the 1,5-biradical intermediates. The biradicals have such short lifetimes that they usually cannot be detected by flash spectroscopy or trapped by thiols. Triplet state lifetimes, determined both by steady-state quenching studies and by flash kinetics, reveal that hydrogen abstraction rate constants are quite low. Arrhenius plots for triplet decay indicate activation energies of 3–5 kcal/mol and *A* values of 10^9 for the δ-hydrogen abstraction. MMX calculations and spectroscopic data all indicate that the ketones exist primarily in conformations with the carbon α to the ether oxygen twisted well away from the carbonyl. The low observed rate constants are ascribed to even lower equilibrium populations of conformers in the geometry required for reaction in the triplet state than in the ground state. 2,6-Diacylphenyl ethers show ten times the triplet reactivity of their monoacyl equivalents. In these cases, the ether function is twisted 90° such that the target C–H bond is much closer to a carbonyl. The large solvent effects on the stereochemistry of cyclization despite short biradical lifetimes suggest that bond rotations may induce intersystem crossing of the triplet biradicals. The low cyclization quantum yield from *o*-(benzyloxy)acetophenone and the formation of *o*-benzoylacetophenone as a major side product suggest that the 1,5-biradicals partially cyclize into the benzene ring to generate spiroenol intermediates. Rate constants for quenching of the triplet ketones by 2,5-dimethyl-2,4-hexadiene were measured. The k_q values are $\geq 5 \times 10^9$ M^{-1} s^{-1} for the *o*-methoxy ketones but only $1–3 \times 10^9$ for the *o*-benzyloxy ketones. This rare steric effect on triplet energy transfer is attributed to twisting of the benzoyl chromophores caused by steric congestion.

Over the past decade there has been a growing interest in two questions that, although not generally related, are both involved in intramolecular hydrogen abstraction by triplet ketones: how conformational factors affect intramolecular bifunctional photoreactions;[1-5] and what determines the lifetimes of photogenerated biradicals.[6] Much of the early experimental evidence related to both questions was provided by studies of the Norrish type II reaction of ketones,[7,8] in which γ-hydrogen atom abstraction by n,π* excited states[9] produces 1,4-biradicals.[10]

Since Scaiano first successfully observed type II biradicals by flash spectroscopy,[11] there has developed a realization that intersystem crossing (isc) of triplet-generated biradicals usually determines their lifetimes.[6,11-13] Unfortunately, how (or why) isc varies with structure in 1-hydroxy-1,4-biradicals has not been answered satisfactorily.[13] The early recognition that the type II reaction varies with ketone structure from exclusive cleavage to exclusive cyclization revealed that product formation from biradicals can be subject to strong conformational and stereoelectronic control.[14-19]

As regards conformational effects, there are three extreme boundary conditions that can determine the kinetics of intramolecular excited-state reactions and decay: (1) conformational interconversion being much slower than decay; (2) conformational interconversion being much faster than decay; and (3) reaction of a "reactive" conformation being much faster than rotations to nonreactive geometries, such that the bond rotations that form the "reactive" conformation become rate determining.[1-3] The earliest quantitative examples all involve γ-hydrogen abstraction: Lewis provided the most dramatic example of ground-state conformational control,[20] Alexander and Lewis both considered the ramifications of conformational equilibrium;[20,21] and we provided

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