Analysis of the Diastereoselectivity of Sulfinate Formation in the Oxidation of *sec*-Alkyl 4-Nitrobenzenesulfenates with Singlet Oxygen and *m*-Chloroperbenzoic Acid and Sulfinate versus Sulfonate Formation in the Singlet Oxygen Oxidation of the Alkyl 4-Nitrobenzenesulfenates

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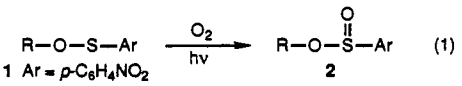
Abstract: The diastereoselectivities in the self-photoinduced single oxygen and *m*-chloroperbenzoic acid oxidations of two series of *sec*-alkyl 4-nitrobenzenesulfenates to the corresponding 4-nitrobenzenesulfinates have been measured. The diastereoselectivities are only moderate but show some interesting trends with the nature and size of the functions in the alkyl group. Sulfonate formation also occurs, the extent of which increases with increasing size of the substituents in the alkyl group. The sulfonates are not formed by the further oxidation of the sulfinates. A mechanism for the formation of the sulfinates and sulfonates is proposed that involves the initial formation of a peroxysulfoxide intermediate which, when sterically unencumbered, can react with the starting sulfenate to generate two molecules of sulfinate but, when sterically encumbered, undergoes ring closure to form an alkoxythiadioxirane intermediate which can react with the starting sulfenate or undergo ring opening to produce the sulfonate. The effect of the incursion of other reactions on the relative yields of the sulfinates and sulfonates is also discussed.

Introduction

Recent studies in the author's laboratories have focused on the photoinduced homolytic dissociation of alkyl and homoallylic 4-nitrobenzenesulfenates **1** which leads to the ultimate formation of alkyl and allyl 4-nitrophenyl sulfides.[1] However, in the presence of oxygen, a unique, self-photoinduced oxidation of the alkyl sulfenates **1** by singlet oxygen ($^1O_2$) occurs to form the corresponding sulfinates **2** (eq 1)[2] The alkyl 4-nitrobenzenesulfenates



(1)

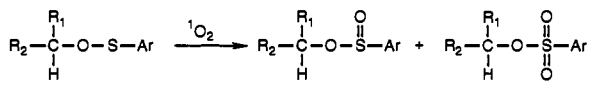
possess an intense absorption band at $\lambda_{max} \sim 347$ nm. The results of *ab initio* MO calculations on 4-nitrobenzenesulfenic acid indicated that the lowest-energy electronic transition involved the excitation of a highly localized, π-type nonbonded electron on the sulfur atom to a highly delocalized π^* MO, suggesting that the long wavelength absorption arises from an n $\rightarrow \pi^*$ transition. The self-induced oxidation was quenched in the presence of *trans*-piperylene, suggesting that the triplet state of the sulfenates was involved. The oxidation reaction was also quenched by the presence of 1,3-cyclohexadiene, resulting in the formation of the endo peroxide, suggesting that $^1O_2$ is the active oxidizing agent. *pri*- and *sec*-alkyl 4-nitrobenzenesulfenates undergo oxidation to sulfinates by $^1O_2$; however, *tert*-alkyl 4-nitrobenzenesulfenates do not undergo oxidation by $^1O_2$ to the corresponding sulfinates.[3]

The oxidation of a sulfenate to a sulfinate results in the generation of a stereogenic center at the sulfur atom. If there is a stereogenic center in the alkyl group, the result is the formation of a pair of diastereoisomers which can be easily observed by NMR spectroscopy. In the present article, the diastereoselectivities of the $^1O_2$ and *m*-chloroperbenzoic acid (*m*CPBA) oxidations of two series of *sec*-alkyl 4-nitrobenzenesulfenates are reported, along with a comparison of sulfinate versus sulfonate formation and the effect of the incursion of other $^1O_2$ oxidation reactions of sulfides derived from the previously described photoinduced decompositions of allyl and alkyl 4-nitrobenzenesulfenates on the relative yields of sulfinate and sulfonate formation.[1]

Results

A series of *sec*-alkyl 4-nitrobenzenesulfenates **3** have been prepared and subjected to self-photoinduced oxidation by $^1O_2$ in $CDCl_3$ and by *m*CPBA in CH_2Cl_2. The ^1H NMR spectra of the reaction solutions were periodically monitored until the complete disappearance of the sulfenate. In general, the ^1H NMR spectra of the final reaction solutions were very clean and allowed for the unambiguous identification of all of the products formed during the oxidation reactions as well as the determination of relative yields.

The oxidation of the sulfenates **3** with 1 mol equiv of *m*CPBA produces predominantly a mixture of the diastereomeric sulfinates **4** (eq 2). Small quantities of the corresponding sulfonates **5** are also formed.



3a R_1 = -CH_3, R_2 = -CH_2CH_3
3b R_1 = -CH_3, R_2 = -$CH(CH_3)_2$
3c R_1 = -CH_3, R_2 = -$C(CH_3)_3$
3d R_1 = -C_6H_5, R_2 = -CH_3
3e R_1 = -C_6H_5, R_2 = -CH_2CH_3
3f R_1 = -C_6H_5, R_2 = -$CH(CH_3)_2$
3g R_1 = -C_6H_5, R_2 = -$C(CH_3)_3$

4 **5**

(2)

The oxidation of the sulfenates **3** with $^1O_2$, however, produces complex mixtures of products, the structures of which could be readily assigned by comparison of the NMR spectral charac-

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(1) Pasto, D. J.; L'Hermine, G. *J. Org. Chem.* **1990**, *55*, 5815–5816.

(2) Pasto, D. J.; Cottard, F.; Horgan, S. *J. Org. Chem.* **1993**, *58*, 4110–4114.

(3) The *tert*-alkyl sulfenates undergo photoinduced homolytic dissociation with the ultimate formation of alkyl 4-nitrophenyl sulfides (eq 3, which undergo further oxidation with $^1O_2$ as described in the accompanying article.[4]

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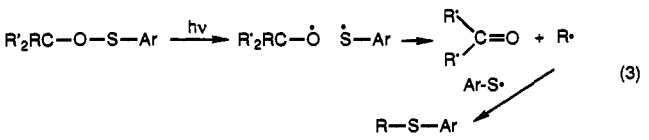
Table 1. Chemical Shifts of the Methine Protons and the $\Delta\delta$ in the Sulfinates 4 and Sulfonates 5

sulfenate	R_1	R_2	δ sulfinate	δ sulfonate	$\Delta\delta$
3a	Me	Et	4.47, 4.45	4.75	0.29
3b	Me	*i*-Pr	4.36, 4.35	4.62	0.26
3c	Me	*t*-Bu	4.25, 4.15	4.52	0.29
3d	Ph	Me	5.50, 5.40	5.72[a]	0.25
3e	Ph	Et	5.20, 5.15	5.42[a]	0.24
3f	Ph	*i*-Pr	4.95, 4.90	5.15[a]	0.23
3g	Ph	*t*-Bu	5.00, 4.88	5.25[b]	0.30

[a] Observed in the ^{1}H NMR spectrum of the crude reaction mixture but could not be isolated by chromatographic techniques. [b] Prepared in $CDCl_3$ solution but could not be isolated and fully characterized.

teristics of the products with those of authentic substances, except for the three sulfonates **5d–f**. The 4-nitrobenzenesulfonates **5d–f** could not be prepared by conventional methods because of apparent elimination occuring under the reaction conditions. Sulfonate **5g** could be prepared in $CDCl_3$ and its ^{1}H NMR spectrum recorded, which allowed for the assignment of the structure of the sulfonate in the photooxidation mixture. (However, **5g** could not be isolated pure for further characterization.) A comparison of the ^{1}H chemical shifts of the methine protons of the sulfinates and sulfonates, given in Table 1, shows a reasonably consistent $\Delta\delta$, which allowed for the assignment of the structures of the sulfonates **5d–f**. The other products formed in the oxidation process are identical with those formed in the $^1O_2$ oxidation of alkyl 4-nitrophenyl sulfides and sulfoxides, which is described in the accompanying article.[4]

Control experiments showed that the sulfinates **4** ($\lambda_{max} \sim 255$ nm) do not undergo further oxidation to the sulfonates **5** by $^1O_2$, and they do not undergo diastereoisomerization. In addition to the sulfinates and sulfonates formed by the direct oxidation of the sulfenates, the mixtures obtained from the $^1O_2$ oxidation reactions contained varying amounts of $^1O_2$ oxidation products derived from the alkyl 4-nitrophenyl sulfides (sulfoxides, sulfones, and carbonyl compounds) formed in the reaction shown in eq 3,which occurs competitively with the $^1O_2$ oxidation of the



(3)

sulfenates. The identification of these oxidation products and the mechanism proposed for their formation are described in the accompanying article.[4]

The diastereoisomeric ratios of the sulfinates, determined by the integration of the methine proton region and methyl region for **3a–c**, in the ^{1}H NMR spectra of the oxidation reaction mixtures derived in the $^1O_2$ and *m*CPBA oxidation reactions of **3a–g**, the sulfinate:sulfonate ratios, and the relative yields for the formation of the sulfinates are given in Table 2. In the case of the oxidation of the sulfenates **3** with *m*CPBA, the methine proton resonance of the major diastereoisomer formed always appears at higher field, indicating the presence of the same relative stereochemistry between the two stereogenic centers in the major diastereoisomer.

Discussion

The oxidation of **3a** with either $^1O_2$ or *m*CPBA shows only a very low degree of diastereoselectivity. In addition to the formation of sulfinate **4a** with $^1O_2$, a small amount of sulfonate **5a** is also formed. In the addition of **3b**, slightly higher degrees of diastereoselectivity are observed with both oxidizing agents, with the major diastereoisomer being the same in both oxidation reactions. Again, some sulfonate formation is observed in the reaction of **3b** with $^1O_2$, and the relative yield of sulfinate plus sulfonate has decreased at the expense of formation of sulfide oxidation products.[4] A higher degree of diastereoselectivity is observed in the oxidation of **3c**, again with the same diastereoisomer predominating with both oxidizing reagents. In the oxidation of **3c** with $^1O_2$, the relative yield of sulfonate has increased significantly and the relative yield of sulfinate plus sulfonate has again decreased. There is an obvious trend in this alkyl,methyl series of substituted alkyl 4-nitrobenzenesulfenates for increased diastereoselectivity, increased sulfonate formation, and overall decreased formation of sulfinate plus sulfonate as the size of the alkyl group R_2 increases.

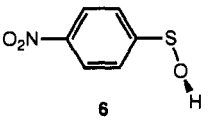
Table 2. Diastereoselectivities in the *m*CPBA and $^1O_2$ Oxidations of Sulfenates 3, Sulfinate:Sulfonate Ratios, and Relative Yields of Sulfinates 4

sulfenate	R_1	R_2	*m*CPBA DE	$^1O_2$DE	4:5 ratio	yield of 4
3a	Me	Et	51.49	51:49	93:7	45
3b	Me	*i*-Pr	53:47	57:43	93:7	32
3c	Me	*t*-Bu	56:44	60:40	80:20	28
3d	Ph	Me	**54:46**	**44:56**	75:25	30
3e	Ph	Et	**59:41**	**48:52**	75:25	19
3f	Ph	*i*-Pr	61:39	55:45	66:34	~12[a]
3g	Ph	*t*-Bu	64:36	58:42	65:35	29

[a] The ^{1}H NMR spectrum of the crude reaction mixture contained many overlapping multilpets and an accurate integral was not possible to obtain.

In contrast to the alkyl,methyl series **3a–c**, in which the same major diastereoisomer is formed in both the $^1O_2$ and *m*CPBA oxidation reactions, such is not the case in the alkyl,phenyl series. In the oxidation of the sulfenates **3d–g** with *m*CPBA, the same diastereoisomer is preferentially formed, as judged by the relative chemical shifts of the methine protons in the two diastereoisomers, and the diastereoselectivity increases as the size of the alkyl group R_2 increases. In the alkyl,phenyl series, however, the major diastereoisomer formed in the oxidation of **3d,e** with $^1O_2$ corresponds to the minor diastereoisomer formed with *m*CPBA, while with **3f,g**, the major diastereoisomer formed with $^1O_2$ corresponds to the major diastereoisomer formed with *m*CPBA. This is an unusual crossover in diastereoselectivity in the $^1O_2$ oxidation reaction. In common with the alkyl,methyl series, however, increased sulfonate formation is observed as the size of the alkyl group R_2 increases and the relative yields of sulfinate plus sulfonate decrease.

Extensive molecular modeling and *ab initio* calculations have been carried out on model systems in an attempt to gain an understanding of the trend in the diastereoselectivities. *Ab initio* calculations carried out at the 3-21G level with partial optimization using the GAUSSIAN92 suite of programs[5] on 4-nitrobenzenesulfenic acid indicated that the conformation represented in structure **6** is the lowest in energy and that the predominantly 3pπ nonbonded-pair orbital on the sulfur atom is the HOMO.[2]



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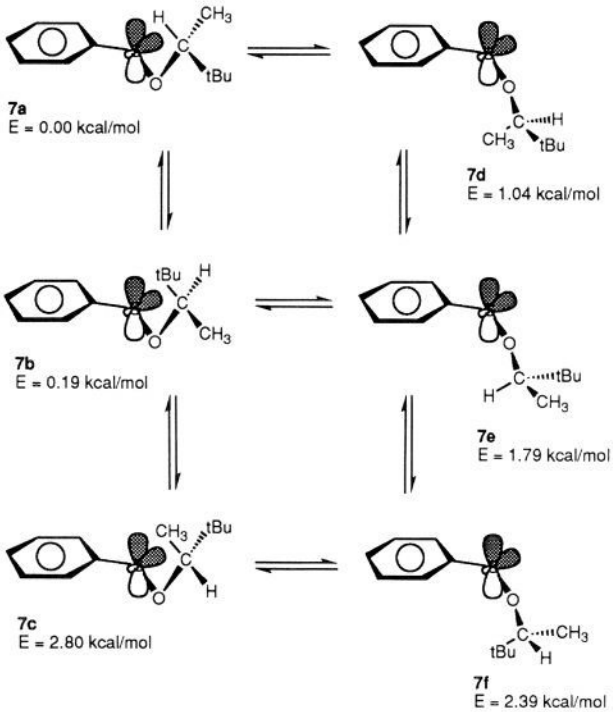
MM2 molecular mechanics[6,7] and *ab initio* calculations (3-21G level with partial optimization)[8] on **7** possessing the *R*-configuration at the stereogenic center in the alkyl group indicated that the conformation shown in **7a** is lowest in energy (the relative energies derived from the MM2 calculations are given in Scheme 1). The lowest-energy conformation has the

(4) Pasto, D. J.; Cottard, F. *J. Am. Chem. Soc.* **1994**, *114*, following article in this issue.

(5) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN90, Revision I; Gaussian, Inc.: Pittsburgh, PA, 1990.

(6) Chem 3D Plus, The Molecular Modeling System, Version 3.0, Cambridge Scientific Computing, Suite 61, Cambridge, MA 02139.

Scheme 1



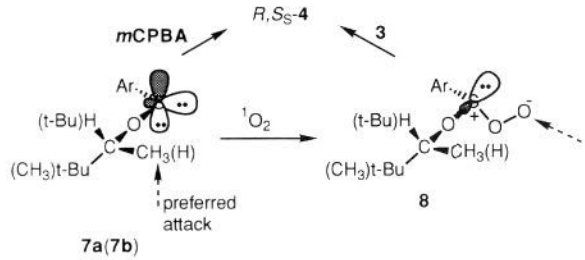
largest alkyl group (*tert*-butyl) attached to the stereogenic center oriented essentially antiperiplanar to the sulfur atom with the aryl–C–S–O–C dihedral angle close to that calculated for **6**[2] of ~97°. Conformation **7b**, having the methyl group oriented antiperiplanar to the sulfur atom, is only slightly higher in energy. The relative preference for **7a** over **7b**, and **7a** and **7b** relative to the other conformations, should decrease as the size of the alkyl group R_2 decreases from *tert*-butyl to isopropyl to ethyl. In conformations **7a,b**, the methyl and *tert*-butyl groups shield the top lobe of the 3pπ AO on the sulfur atom (the HOMO), thus sterically favoring attack by an oxidizing agent at the bottom lobe of the 3pπ AO of the sulfur atom as shown in Scheme 2. This model predicts that the absolute configuration produced at the sulfur atom should be *S* in the sulfinate directly formed with *m*CPBA and in the peroxysulfinate intermediate **8** when the absolute configuration at the stereogenic center in the alkyl group is *R*.

The oxidation of **3a** by either $^1O_2$ or *m*CPBA shows very little diastereoselectivity. An inspection of a molecular model of **3a** having a conformation similar to that shown in **7a**, in which the larger ethyl group is antiperiplanar to the sulfur atom, indicates that the methyl group is sufficiently far from the top lobe of the 3p AO on the sulfur atom that little diastereoselection should be expected. In the conformation corresponding to **7b**, the methyl group of the ethyl group can be oriented away from the sulfur atom, effectively making the ethyl group the same in size as the methyl group. In the case of **3b**, however, a conformation of **7b** must be populated that projects one of the methyl groups of the

(7) Bond stretching parameters for S–O: 5.000 (KS), 1.693 (length), 0.000 (bond dipole). Angle bending parameters for S–O–C: 0.500 (KS), 109.471 (–XR_2–) dv (–XRH–), dv (–XH_2). Angle bending parameters for C–S–O: 0.500 (KS), 109.471 (–XR_2–), dv (–XRH–), dv (–XH_3). Torsional parameters for C–S–O–C: dv's (V_1, V_2, and V_3). Torsional parameters for C–C–O–S: dv's (V_1, V_2, and V_3). Torsional parameters for C–C–S–O dv's (V_1, V_2, and V_3). All default values (dv) for the parameters provided by the program were accepted.

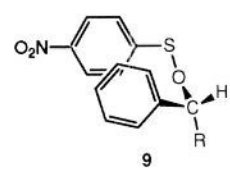
(8) The parameters optimized include the aryl–C–S, S–O, O–C, C–H, and C–C (at the stereogenic center) bond lengths, the aryl–C–S–O, S–O–C, O–C–H, and O–C–C bond angles and the aryl–C–S–O–C, S–O–C–H, and S–O–C–C torsional angles. The C–C and C–H bond lengths of the aromatic ring were assigned values of 1.396 and 1.078 Å with all good angles 120°. The C–H bond lengths in the methyl groups were assigned as 1.09 Å, bond angles of 109.44°.

Scheme 2



isopropyl group over the top lobe of the 3p AO of the sulfur atom, thus encouraging attack at the bottom lobe of the 3pπ AO. In the case of **3c**, there is no conformation of **7b** which does not project a methyl group of the *tert*-butyl group toward the top lobe of the 3pπ AO on the sulfur atom. It must be admitted that the stereo shieldings described in the foregoing are long range in nature which results in the rather low diastereoselectivities observed in the oxidation reactions.

The unusual diastereoselectivity results obtained in the $^1O_2$ oxidation of the alkyl,phenyl series cannot be rationalized on the basis of the simplicity illustrated in Scheme 2. Molecular modeling calculations have been carried out on substituted-benzyl benzenesulfenates 9(R = methyl and *tert*-butyl) having the



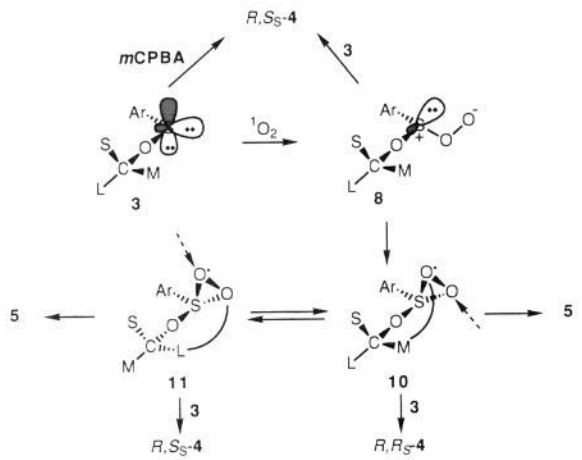
9

R-configuration at the stereogenic center in the alkyl group. Very interestingly, the lowest-energy conformations of **9** have the aromatic ring of the benzyl moiety oriented over the aromatic ring of the sulfenate. The preference for this conformation must be due to a long-range attractive interaction between the aromatic rings which results in the π stacking of the two aromatic systems. In the conformation shown as **9**, the aromatic ring of the benzyl moiety projects toward the top lobe of the 3pπ AO on the sulfur atom, again suggesting that the preferred mode of attack by an oxidizing agent is at the bottom lobe of the 3pπ AO with the formation of the S-configuration at the sulfur atom. This appears to be the case with **3f,g** but not with **3d,e**.

One aspect of the results of the $^1O_2$ oxidation studies thus far ignored is the formation of the sulfonates **5**. Sulfonate formation increases as the size of the alkyl group R_2 increases in both the alkyl,methyl and the alkyl,phenyl series. Control experiments have shown that the sulfonates are *not* formed by the further oxidation of the sulfinates **4** by $^1O_2$. These data suggest the intervention of another intermediate in addition to the peroxysulfinate intermediate **8**, which leads to the direct formation of the sulfonates and affects the diastereoselectivity in the $^1O_2$ oxidation in the alkyl,phenyl series.

The overall results can be rationalized in terms of Scheme 3, in which M an L represent medium and large groups. As described for Scheme 2, attack by either oxidizing agent should occur at the bottom lobe of the sulfur atom in both the alkyl,methyl and alkyl,phenyl series. In the reactions of (*R*)-alkyl sulfenates with *m*CPBA, this will lead to the preferred formation of the *R*,S_S-diastereoisomer of the sulfinates **4**. (The S subscript indicates the absolute configuration at the sulfur atom.) Attack by $^1O_2$ should also preferrably occur at the bottom lobe, producing the peroxysulfenate intermediate **8** having the absolute configuration shown. (Approach of either oxidizing agent to the more sterically hindered top lobe of the 3pπ AO on the sulfur atom will result in the *R*-configuration at sulfur.) Reaction of **8** with another molecule of sulfenate **3**, again with preferred attack at the bottom

Scheme 3



lobe of the $3p\pi$ AO, will produce two molecules of the R,S_S-diastereoisomer of **4**. As the size of the M and L groups in **8** increases, the approach of the sulfenate **3** to **8** will experience increasing steric interference providing time for **8** to undergo ring closure *anti* to the alkoxy group to produce the alkoxythiadioxirane intermediate shown as the two conformations **10** and **11**. (The one oxygen atom is labeled by * in order to trace the stereochemistry of the overall process.) In conformation **10**, the M group is closer to *O than to O and will thus shield the *O from attack by a molecule of the sulfenate. Attack should occur at the unstarred O, producing the R,R_S-diastereoisomer with net inversion at the sulfur atom. Such would be the case with **3d,e**, in which the methyl and ethyl groups are smaller than the phenyl group. In the case of **3f,g**, in which the alkyl group may present a larger "size" than that of the phenyl group (i.e., the exchange of M for L and L for M in **10** and **11**), conformation **11** should be dominant, in which the L group is closer to the O than *O, inducing attack at *O and producing the R,S_S-diastereoisomer with net retention at the sulfur atom. Thus the crossover from **3d,e** to **3f,g** would appear to be possible. Finally, as the size of the M and L groups in the alkoxythiadioxirane intermediate increases, increased steric hindrance to approach by a molecule of the sulfenate **3** to form two molecules of sulfinate **4** will occur with the ring opening of the alkoxythiadioxirane intermediate to the sulfonates **5** becoming more probable.

The decrease in the relative yields of sulfinate plus sulfonate as the size of R_1 and R_2 increase is due to the competitive formation of alkyl 4-nitrophenyl sulfides illustrated in eq 3.[1] It appears that the homolytic fragmentation of the O–S bond in the excited state of the sulfenates is facilitated by an increase in the size of the R_1 and R_2 groups (i.e., relief of internal steric strain). The alkoxy radicals thus formed undergo β-scission to produce a carbon-centered radical which then combines with the 4-nitrophenylthiyl radical to form the corresponding alkyl 4-nitrophenyl sulfide. The side reaction products produced during the photooxidation of the sulfenates **3** correspond to those observed from the $^1O_2$ oxidation of the sulfides and corresponding sulfoxides.[4]

Summary

The diastereoselectivities for the *m*-chloroperbenzoic acid and the self-photoinduced singlet oxygen oxidation of a series of alkyl 4-nitrobenzenesulfenates to the corresponding sulfinates containing a stereogenic center in the alkyl group have been determined. On the basis of molecular mechanics modeling studies and the results of *ab initio* MO calculations, a model has been proposed for predicting the absolute configuration generated at the sulfur atom based on the absolute configuration at the stereogenic center in the alkyl group. Further studies will be carried out in an attempt to improve the diastereoselectivity of the oxidation processes and to determine the absolute configuration generated at the sulfur atom by the use of optically active alkyl arenesulfenates.

Experimental Section

General Procedure for the Synthesis of the Alkyl 4-Nitrobenzenesulfenates. A 50 mL three-neck flask containing 5 mmol of the alcohol, freshly distilled triethylamine (1.6 mL, 11.5 mmol), and 15 mL of anhydrous methylene chloride under an argon atmosphere was placed in dry ice in a darkened hood. A solution of 4-nitrobenzenesulfenyl chloride (0.95 g, 5 mmol) in anhydrous methylene chloride (10 mL) was added with stirring. After the addition of the sulfenyl chloride was completed, the reaction mixture was stirred for 15 min and was then allowed to warm to room temperature for 30 min. The reaction mixture was washed with cold 3% hydrochloric acid (2 × 10 mL) and cold water (3 × 10 mL), and the organic phase was dried ($MgSO_4$). The solvent was removed under reduced pressure in an aluminum-wrapped flask, giving the sulfenates in essentially quantitative yields as dark-red viscous liquids. When sufficiently thermally and photochemically stable, the sulfenate was purified by rotating-disk, thin-layer chromatography using an eluent system composed of Skellysolve B and methylene chloride in a 3:1 ratio.

2-Butyl 4-Nitrobenzenesulfenate (3a): dark red liquid; UV ($CHCl_3$) λ_{max} = 345 nm; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.46 Hz, 3 H), 1.35 (d, J = 6.21 Hz, 3 H), 1.65 (m, 1 H), 1.80 (m, 1 H), 3.75 (m, 1 H), 7.25 (d, J = 8.99 Hz, 2 H), 8.15 (d, J = 8.99 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.5, 19.6, 29.4, 86.4, 120.0, 123.0, 145.0, 152.2; HR CIMS (isobutane) calculated for (MH^+) 228.070, found 228.067.

3-Methyl-2-butyl 4-Nitrobenzenesulfenate (3b): ^{1}H NMR ($CDCl_3$) δ 0.96 (d, J = 6.81 Hz, 3 H), 0.96 (d, J = 6.89 Hz, 3 H), 1.26 (d, J = 6.36 Hz, 3 H), 2.05 (m, 1 H), 3.60 (m, 1 H), 7.30 (d, J = 9.07 Hz, 2 H), 8.40 (d, J = 9.07 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.9, 16.7, 18.5, 33.2, 89.8, 120.1, 124.1, 145.0, 152.6; HR CIMS (isobutane) calculated for (MH^+) 242.085, found 242.084.

3,3-Dimethyl-2-butyl 4-Nitrobenzenesulfenate (3c): ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.25 (d, J = 6.60 Hz, 3 H), 3.55 (q, J = 6.60 Hz, 1 H), 7.30 (d, J = 9.08 Hz, 2 H), 8.20 (d, J = 9.08 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.7, 25.9, 35.7, 93.7, 120.4, 124.0, 144.9, 152.9; HR CIMS (isobutane) calculated for ($M + H^+$) 256.101, found 256.098.

1-Phenylethyl 4-Nitrobenzenesulfenate (3d): ^{1}H NMR ($CDCl_3$) δ 1.70 (d, J = 6.30 Hz, 3 H), 4.75 (q, J = 6.30 Hz, 1 H), 7.20 (d, J = 9.00 Hz, 2 H), 7.35 (m, 5 H), 8.15 (d, J = 9.00 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 23.4, 86.7, 120.0, 124.6, 126.5, 128.3, 128.7, 137.0, 141.3, 151.8; HR CIMS (isobutane) calculated for (MH^+) 276.069, found 276.069.

1-Phenylpropyl 4-Nitrobenzenesulfenate (3e): ^{1}H NMR ($CDCl_3$) δ 0.90 (dd, apparent triplet, J = 7.20 Hz, 3 H), 1.90 (m, 1 H), 2.15 (m, 1 H), 4.45 (d, J = 6.80, 6.80 Hz, 1 H), 7.20 (d, J = 9.15 Hz, 2 H), 7.35 (m, 5 H), 8.15 (dd, J = 9.15 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.9, 30.1, 92.0, 120.0, 123.9, 126.9, 128.1, 128.4, 139.9, 144.8, 151.7; HR CIMS (isobutane) calculated for (MH^+) 290.085, found 290.085.

2-Methyl-1-phenylpropyl 4-Nitrobenzenesulfenate (3f): ^{1}H NMR ($CDCl_3$) δ 0.80 (d, J = 6.81 Hz, 3 H), 1.15 (d, J = 6.64 Hz, 3 H), 2.25 (m, 1 H), 4.30 (d, J = 7.54 Hz, 1 H), 7.20 (d, J = 8.9 Hz, 2 H), 7.27 (m, 2 H), 7.33 (m, 3 H), 8.10 (d, J = 8.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.5, 19.2, 34.8, 97.0, 120.2, 113.9, 127.5, 128.2, 139.2, 144.9, 151.7; HR CIMS (isobutane) calcd for (MH^+) 304.101, found 304.102.

2,2-Dimethyl-1-phenylpropyl 4-Nitrobenzenesulfenate (3g): ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 4.37 (s, 1 H), 7.20 (d, J = 9.04 Hz, 2 H), 7.30 (m, 5 H), 8.15 (d, J = 9.04 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.3, 36.7, 98.4, 120.8, 124.0, 127.8, 128.2, 128.3, 138.3, 145.1, 151.7; HR CIMS (isobutane) calcd for ($M + H^+$) 318.116, found 318.115.

General Procedure for the Synthesis of the Alkyl 4-Nitrobenzenesulfinates. To a magnetically stirred solution of 5 mmol of the 4-nitrobenzenesulfenate in 50 mL of methylene chloride was added dropwise at 0 °C a solution of 5 mmol (1.6 g) of 55% *m*-chloroperbenzoic acid in 30 mL of methylene chloride. After addition, the reaction was stirred at 0 °C for another 1 h. The reaction mixture was transferred to a separatory funnel. Excess peracid was destroyed with 10% sodium sulfite solution until a starch–iodide test was negative. The layers were separated. The organic layer was washed with saturated aqueous sodium chloride solution (2 × 30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residues were subjected to chromatographic purification by column chromatography on silica gel. The mixtures of the diastereomeric sulfinates were eluted with ethyl acetate, while the corresponding sulfonates, formed by overoxidation, were eluted with a 4:1 mixture of CH_2Cl_2/Skelly Solve F.

2-Butyl 4-Nitrobenzenesulfinate (4a): pale yellow liquid; UV ($CHCl_3$) λ_{max} = 255 nm; ^1H NMR of minor diastereoisomer ($CDCl_3$) δ 0.90 (t, J = 6.80 Hz, 3 H), 1.42 (d, J = 6.25 Hz, 3 H), 1.60 (m, 2 H), 4.47 (m, 1 H), 7.90 (d, J = 8.71 Hz, 2 H); ^1H NMR of major diastereoisomer δ 1.00 (t, J = 6.80 Hz, 3 H), 1.30 (d, J = 6.30 Hz, 3 H), 1.57 (m, 2 H), 4.45 (m, 1 H), 7.91 (d, J = 8.71 Hz, 2 H); ^{13}C NMR of the mixture of the two diastereomers ($CDCl_3$) δ 9.5, 9.6, 21.3, 21.4, 30.2, 30.4, 79.5, 79.8, 124.2, 126.3, 126.4, 149.9, 152.0; HR CIMS (isobutane) calcd for ($M + H^+$) 244.064, found 244.064.

3-Methyl-2-butyl 4-Nitrobenzenesulfinate (4b): ^1H NMR of minor diastereoisimer ($CDCl_3$) δ 0.85 (t, J = 7.90 Hz, 3 H), 1.40 (d, J = 8.84 Hz, 3 H), 1.78 (m, 2 H), 4.34 (m, 1 H), 7.80 (d, J = 9.0 Hz, 2 H), 8.40 (d, J = 9.0 Hz, 2 H); ^1H NMR of major diastereoisomer 0.95 (t, J = 6.47 Hz, 3 H), 1.25 (d, J = 8.84 Hz, 3 H), 1.90 (m, 2 H), 4.37 (m, 1 H), 7.88 (d, J = 8.84 Hz, 2 H), 8.37 (d, J = 8.84 Hz, 2 H); ^{13}C NMR of the mixture of the two diastereomers ($CDCl_3$) δ 17.6, 17.7, 17.9, 18.1, 18.5, 33.7, 34.0, 36.8, 82.6, 83.1, 124.2, 126.3, 126.4, 150.0, 152.2; HR CIMS (isobutane) calcd for ($M + H^+$) 258.080, found 258.080.

3,3-Dimethyl-2-butyl 4-Nitrobenzenesulfinate (4c): ^1H NMR of major diastereoisomer ($CDCl_3$) δ 0.90 (s, 9 H), 1.40 (d, J = 6.40 Hz, 3 H), 4.15 (q, J = 6.40 Hz, 1 H), 7.90 (d, J = 8.68 Hz, 2 H), 8.37 (d, J = 6.40 Hz, 2 H); ^1H NMR of minor diasteroisomer δ 0.95 (s, 9 H), 1.26, (d, J = 6.41 Hz, 3 H), 4.25 (q, J = 6.41 Hz 1 H), 7.95 (d, J = 6.40 Hz, 2 H), 8.37 (d, J = 6.40 Hz, 2 H); ^{13}C NMR of the mixture of the two diastereomers ($CDCl_3$) δ 16.6, 17.3, 25.6, 25.7, 34.7, 35.3, 85.3, 86.5, 124.1, 124.15, 126.0, 126.4, 149.8, 149.9, 152.2; HR CIMS (isobutane) calcd for ($M + H^+$) 272.101, found 272.098.

1-Phenylethyl 4-Nitrobenzenesulfinate (4d): ^1H NMR of minor diastereoisomer ($CDCl_3$)δ 1.63 (d, J = 6.58 Hz, 3 H), 5.50 (q, J = 6.58 Hz, 1 H), 7.80 (d, J = 8.90 Hz, 2 H), 8.30 (d, J = 8.90 Hz, 2 H); ^1H NMR of major diastereomer δ 1.67 (d, J = 6.56 Hz, 3 H), 5.40 (q, J = 6.56 Hz, 1 H), 7.75 (d, J = 8.80 Hz, 2 H), 8.20 (d, J = 8.80 Hz, 2 H); ^{13} NMR of the mixture of the two diastereomers ($CDCl_3$) δ 23.8, 24.1, 77.4, 78.9, 123.7, 124.1, 126.1, 126.2, 126.4, 126.6, 128.2, 128.4, 128.7, 128.8, 140.6, 140.7, 149.8, 149.9, 151.4, 152.1; HR CIMS (isobutane) calcd for ($M + H^+$) 292.064, found 292.063.

1-Phenylpropyl 4-Nitrobenzenesulfinate (4e): ^1H NMR of major diastereoisomer ($CDCl_3$) δ 0.90 (t, J = 7.40 Hz, 3 H), 2.02 (m, 2 H), 5.15 (dd, J = 6.90, 6.90 Hz, 1 H), 7.70 (d, J = 8.75 Hz, 2 H), 8.15 (d, J = 8.75 Hz, 2 H) (protons of the unsubstituted phenyl ring cannot be assigned); ^1H NMR of minor diastereoisomer δ 0.92 (t, J = 7.40 Hz, 3 H), 1.90 (m, 2 H), 5.20 (dd, J = 6.90, 6.90 Hz, 1 H), 7.80 (d, J = 8.87 Hz, 2 H), 8.35 (d, J = 8.87 Hz, 2 H) (protons on the unsubstituted ring cannot be assigned); ^{13}C NMR of the mixture of the two diastereomers ($CDCl_3$) δ 9.8, 30.5, 30.9, 80.7, 84.5, 123.5, 124.0, 126.1, 126.2, 126.4, 126.6, 126.9, 128.0, 128.2, 128.7, 137.0, 139.6, 149.7, 149.9, 150.9, 152.0; HR CIMS (isobutane) calcd for ($M + H^+$) 306.080, found 306.083.

2-Methyl-1-phenylpropyl 4-Nitrobenzenesulfinate (4f): ^1H NMR of the minor diastereoisomer ($CDCl_3$) δ 0.80 (d, J = 6.81 Hz, 3 H), 1.05 (d, J = 6.38 Hz, 3 H), ~2.05 (m), 4.95 (d, J = 7.86 Hz, 1 H), 7.80 (d, J = 8.90 Hz, 2 H), 8.35 (d, J = 8.90 Hz, 2 H) (protons of the unsubstituted phenyl group cannot be assigned); ^1H NMR of the major diastereomer δ 0.75 (d, J = 6.81 Hz, 3 H), 1.04 (d, J = 6.64 Hz, 3 H), ~2.05 (m), 4.90 (d, J = 7.70 Hz, 1 H), 7.65 (d, J = 8.90 Hz, 2 H), 8.10 (d, J = 8.90 Hz, 2 H) (protons of the unsubstituted phenyl group cannot be assigned); ^{13}C NMR of the mixture of the two diastereomers ($CDCl_3$) δ 18.4, 18.6, 18.8, 18.9, 34.4, 34.6, 83.6, 88.4, 123.4, 124.0, 126.1, 126.5, 127.1, 127.3, 127.8, 127.9, 128.5, 128.6, 138.8, 138.9, 149.8, 150.5, 151.9; HR CIMS (isobutane) calcd for ($M + H^+$) 320.096, found 320.094.

2,2-Dimethyl-1-phenylpropyl 4-Nitrobenzenesulfinate (4g): ^1H NMR of the minor diastereoisomer ($CDCl_3$) δ 0.95 (s, 9 H), 5.00 (s, 1 H), 7.80 (d, J = 8.70 Hz, 2 H), 8.40 (d, J = 8.70 Hz, 2 H) (protons of the unsubstituted aromatic ring cannot be assigned); ^1H NMR of the major diasteromer δ 0.92 (s, 9 H), 4.88 (s, 1 H), 7.60 (d, J = 8.70 Hz 2 H), 8.00 (d, J = 8.7 Hz, 2 H) (protons of the unsubstituted aromatic ring cannot be assigned); ^{13}C NMR of the mixture of the two diastereomers ($CDCl_3$) δ 26.0, 26.1, 35.6, 35.8, 84.8, 90.1, 123.2, 124.2, 124.4, 126.1, 126.4, 127.3, 127.5, 128.0, 128.1, 128.3, 128.4, 137.7, 149.5, 150.1, 152.0; HR CIMS (isobutane) calcd for ($M + H^+$) 334.117, found 334.109.

General Procedure for the Preparation of the Alkyl 4-Nitrobenzenesulfonates. The procedure described above for the prepration of the alkyl 4-nitrobenzenesulfinates was employed using 2 mol equiv of *m*CPBA.

2-Butyl 4-Nitrobenzenesulfonate (5a): ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.44 Hz, 3 H), 1.30 (d, J = 6.24 Hz, 3 H), 1.65 (m, 2 H), 4.75 (m, 1 H), 8.10 (d, J = 8.70 Hz, 2 H), 8.40 (d, J = 8.70 Hz, 2 H); ^{13}C NNR ($CDCl_3$) δ 9.2, 20.4, 29.5, 83.8, 124.3, 128.9, 143.4, 150.5; HR CIMS calcd for ($M + H^+$) 260.059, found 260.060.

3-Methyl-2-butyl 4-Nitrobenzenesulfonate (5b). ^1H NMR ($CDCl_3$) δ 0.86 (d, J = 6.80 Hz, 3 H), 0.88 (d, J = 6.82 Hz, 3 H), 1.30 (d, J = 6.39 Hz, 3 H), 1.85 (m, 1 H), 4.62 (m, 1 H), 8.10 (d, J = 8.77 Hz, 2 H), 8.40 (d, J = 8.77 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.5, 33.2, 86.9, 124.3, 128.9, 143.3, 150.4; HR FAB calcd for the fragment $C_8H_8NO_5S$ 230.012, found 230.011.

3,3-Dimethyl-2-butyl 4-Nitrobenzenesulfonate (5c). (Attempts to purify by column chromatography on silica gel led to decomposition.) ^1H NMR ($CDCl_3$, on oxidation reaction mixture): δ 0.85 (s, 9 H), 1.30 (d, J = 6.40 Hz, 3 H), 4.52 (q, J = 6.40 Hz, 1 H), 8.15 (d, J = 8.66 Hz, 2 H), 8.40 (d, J = 8.66 Hz, 2 H). MS: no parent ion could be observed by either EIMS or CIMS (isobutane).

Supplementary Material Available: ^1H and ^{13}C NMR spectra of all alkyl 4-nitrobenzenesulfenates, -sulfinates, and -sulfonates reported in this article (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.