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The C_3H_5O Radical System. Formation and Reactions of the Allyloxy and Oxiranylmethyl Radicals Generated by the Photolysis of the Allyl and 4,5-Epoxy-2-methyl-2-pentyl 4-Nitrobenzenesulfenates

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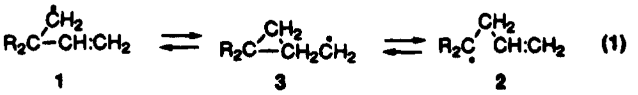
Introduction

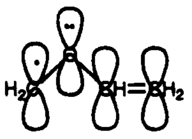
The 3-buten-1-ylcyclopropyl carbinyl radical system has been extensively studied, both experimentally and theoretically.[1] The 3-buten-1-yl radical is heavily favored in the equilibrium shown, and substituted 3-buten-1-yl radicals are known to undergo rapid equilibration via the cyclopropylmethyl radical intermediate **3** (eq 1).



$$\underset{\mathbf{1}}{R_2\overset{\dot{C}H_2}{C}-CH{:}CH_2} \rightleftarrows \underset{\mathbf{3}}{R_2\overset{CH_2}{C}\!-\!CH_2\dot{C}H_2} \rightleftarrows \underset{\mathbf{2}}{R_2\overset{CH_2}{\dot{C}}\;CH{:}CH_2} \qquad (1)$$

Oxiranylmethyl radical intermediates **4** (Scheme 1) have been generated in radical chain reactions from halo epoxides **5**,[2] from β,γ-epoxy *O*-thiocarbonylimidazole derivatives **6**,[3] by the addition of a free radical to butadiene oxide derivatives **7**,[4] and in the photoinduced reactions of β,γ-epoxy ketones.[5] The resulting oxiranylmethyl radicals undergo ring opening to form the allyloxy radical **8**, except when π stabilizing groups are attached to the ring carbon atom which leads to the formation of the (vinyloxy)methyl radical **9**.[6]

The mode of ring opening of the non-π-substituted systems is somewhat surprising in that the radical center in the allyloxy radical **8** is a localized radical center, whereas in the (vinyloxy)methyl radical **9** the radical center is stabilized by interaction with the nonbonded pair of electrons on the oxygen atom,[7] as well as by further delocalization within the butadiene-type π system represented in **10**.



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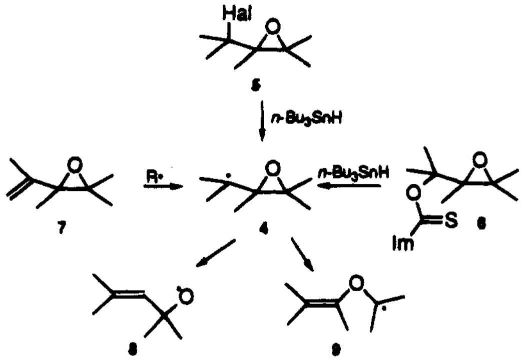
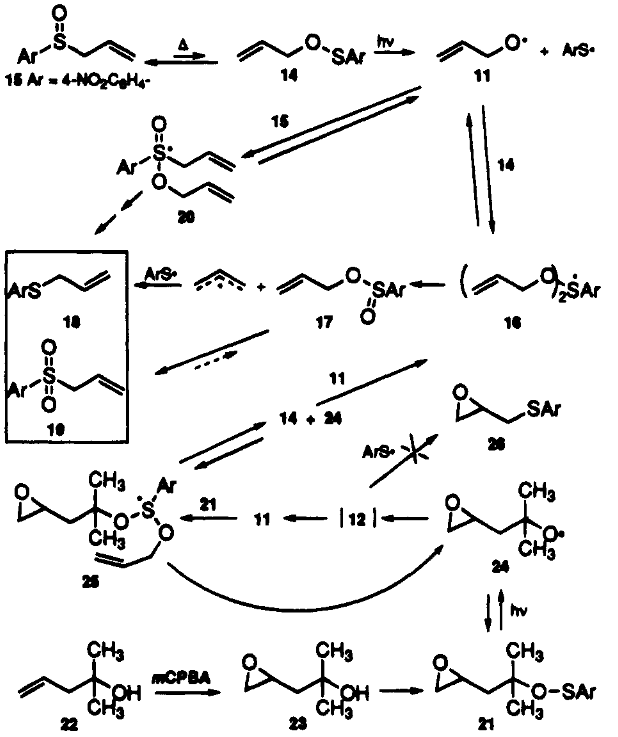
Scheme 1



Scheme 2



The recent discovery in the author's laboratories of the facile generation of substituted alkoxy and alkyl radicals, the latter by the β-scission of the initially formed alkoxy radicals, by the photolysis of alkyl 4-nitrobenzenesulfenates[8] has provided the opportunity to generate and study the chemical properties of the parent allyloxy (**11**) and oxiranylmethyl (**12**) radicals shown in eq 2, as well as what is believed to be reactions of hypervalent sulfuranyl radicals formed by the addition of the allyloxy radical to the starting sulfenates.

$$\underset{\mathbf{13}}{R_2\overset{CH_2}{\dot{C}}\;CH{:}CH_2} \rightleftarrows \underset{\mathbf{12}}{H_2\overset{O}{C}\!-\!CH_2\dot{C}H_2} \rightleftarrows \underset{\mathbf{11}}{H_2\overset{O\bullet}{C}\!-\!CH{:}CH_2} \qquad (2)$$

Results and Discussion

The parent allyloxy (**11**) and oxiranylmethyl (**12**) radicals have been generated from the sulfenates **14** and **21** shown in Scheme 2. Allyl 4-nitrobenzenesulfenate (**14**) is prepared by the reaction of allyl alcohol with 4-nitrobenzenesulfenyl choride and can be isolated if extreme care is exercised during workup and isolation. (Small amounts of sulfinate **17** are also formed by the self-induced, photo-induced singlet oxygen oxidation of

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[1] For a review, see: Beckwith, A. L. J.; Ingold, K. U. *Free Radical Rearrangements*, Vol. 1; de Mayo, Ed.; Academic Press: New York, 1980; pp 161-310.

[2] Krosley, K. W.; Gleicher, G. J.; Clapp, G. E. *J. Org. Chem.* **1992**, *57*, 840.

[3] Rawal, V. H.; Newton, R. C.; Krishnamurthy, V. *J. Org. Chem.* **1990**, *55*, 5181-5183. Johns, A.; Murphy, J. A. *Tetrahedron Lett.* **1988**, *29*, 837-840. Barton, D. H. R.; Motherwell, R. S. Hay; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. I* **1981**, 2363-2367.

[4] Russell, G. A.; Shi, B. Z. Talk no. 98, Division of Organic Chemistry, National American Chemical Society meeting, Denver, CO. Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *J. Chem. Soc., Chem. Commun.* **1988**, 294-296.

[5] Carlson, R. G.; Huber, J. H.-A.; Henton, D. E. *J. Chem. Soc., Chem. Commun.* **1973**, 223-224.

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the sulfenate **14**).[9] Sulfenate **14** undergoes a [2.3]-sigmatropic rearrangement to produce the allyl sulfoxide **15**.[10] However, at above 60 °C a sufficient concentration of **14** is present which undergoes the desired photolysis to form the allyloxy and (4-nitrophenyl)thiyl radicals. The photolysis experiments descibed in this article have been initiated with the sulfoxide **15**.

The formation of **11** as an intermediate in the reaction is not immediately apparent from the structures of the products formed in the reaction which are allyl 4-nitrophenyl sulfide (**18**) and allyl 4-nitrophenyl sulfone (**19**) (shown in the boxed-in area in Scheme 2). Also formed are varying amounts of allyl alcohol, the amount of which decreases with decreasing concentration of the starting sulfoxide **15** (~25% at 1.4 M down to ~3% at 0.1 M) and disulfide. This observation indicates that the allyloxy radical abstracts a hydrogen atom from either the starting sulfenate or the products formed in the reaction (benzene-d_6 is used as a solvent in order to avoid the possibility of the solvent acting as a hydrogen atom donor[8]). Under the conditions of minimal formation of allyl alcohol the sulfide–sulfone ratio approaches 1:1.

The formation of **18** and **19** can occur by two possible pathways. One pathway involves the addition of the allyloxy radical to the sulfenate **14** to form an intermediate hypervalent sulfuranyl radical **16**[11] which undergoes fragmentation to produce the allyl radical and sulfinate **17**,[12] the latter then undergoing a [2.3]sigmatropic rearrangement to form the sulfone **19**.[13] The allyl radical combines with the arylthiyl radical to form the sulfide **18**.[14] Alternatively, the allyloxy radical can add to the sulfoxide **15** to produce the hypervalent sulfuranyl radical intermediate **20** which can undergo fragmentation directly to form the sulfone **19** and the allyl radical. (The addition of alkoxy radicals to sulfoxides has been observed and has been shown to be a reversible process.[15]) Monitoring the course of the reaction by removing aliquots of the reaction mixture and recording the ^{1}H NMR spectra showed an increase in the concentration of the sulfinate **17** (a small amount of **17** was present in the starting sulfoxide **15**) which disappeared as the reaction progressed with the ultimate formation of the sulfone **19**. No other intermediates or products were detected during the course of the reaction which could arise from the allyloxy radical. The results of the present study allow for the identification of the pathway via **17** as a mode for the formation of the sulfide **18** and sulfone **19**. The available results do not provide any indication as to the possible intermediacy of **20** in the formation of **18** and **19**.

The other entry into the C_3H_5O radical system is achieved by the photolysis of the sulfenate **21** followed by β-scission of **24** to form the oxiranylmethyl radical (**12**) and acetone. [The sulfenate **21** is easily prepared by the epoxidation of the homoallylic alcohol **22** to produce the epoxy alcohol **23** which on reaction with 4-nitrobenzenesulfenyl chloride produces the required sulfenate **21** (bottom of Scheme 2)]. The irradiation of sulfenate **21** produces a complex mixture of products which were separated into volative and nonvolatile fractions. The ^{1}H NMR spectrum of the volatile fraction showed the presence of allyl alcohol and 4,5-epoxy-2-methyl-2-pentanol. The components of the nonvolatile fraction were separated by chromatography and were identified by comparison of the NMR spectra of the fractions with the NMR spectra of authentic materials. The nonvolatile fraction was shown to contain sulfide **18**, sulfone **19**, disulfide, and what is believed to be Ar–SO–S–Ar (see Experimental Section). No other products are indicated to be formed as intermediates or final products on the basis of the NMR spectra recorded at intermediate times during the photolysis. The relative yields of the products was determined by integration of the vaious regions or the ^{1}H NMR spectrum of the crude reaction mixture. The sulfide **17**, sulfone **18**, 4,5-epoxy-2-methyl-2-pentanol, allyl alcohol, and disulfide were formed in a ratio of 47:17:27:9:37 (acetone is also formed). It is interesting to note that the ratio of sulfide to sulfone of 2.76:1.00 observed in the photolysis of **21** is quite different from that observed in the photolysis of **14** of ~1:1.

The results indicate that the alkoxy radical **24** undergoes both intermolecular hydrogen atom abstraction to form the epoxy alcohol and β-scission to produce the oxiranylmethyl radical (**12**) which then undergoes ring opening to form only the allyloxy radical (**11**). That intermolecular hydrogen atom abstraction is competitive with β-scission must be due to the fact that the β-scission process involves the formation of a nonstabilized, primary alkyl radical center in **12** which disfavors β-scission.

The ring opening of the oxiranylmethyl radical must occur faster than coupling with the arylthiyl radical to form sulfide **26**, the rate of which should be very fast and diffusion controlled. It has been reported that, in the radical-chain reduction of β,γ-epoxy-1-chloropropane with triphenyltin hydride, allyl alcohol is the only product formed.[17] The intermediate oxiranylmethyl radical is not trapped by hydrogen-atom transfer from the triphenyltin hydride which is in contrast with that observed in the reduction of cyclopropylmethyl chloride in which cyclopropylmethane is formed as a product.[18] In the competi-

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[6] Cook, M.; Hares, O.; Johns, A.; Murphy, J. A.; Patterson, C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1419. Strogryn, E. L.; Gianni, M. H. *Tetrahedron Lett.* **1970**, *34*, 3025.

[7] Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062–3072.

[8] Pasto, D. J.; L'Hermine, G. *J. Org. Chem.* **1990**, *55*, 5815–5816.

[9] Pasto, D. J.; Cottard, F.; Horgan, S. *J. Org. Chem.* **1993**, *58*, 4110–4114.

[10] Braverman, S.; Stabinsky, Y. *J. Chem. Soc., Chem. Commun.* **1967**, 270.

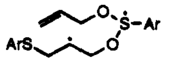
[11] Chatgilialogu, C. Free Radical Chemistry of Sulfenic Acids and Their Derivatives in *The Chemistry of Sulphenic Acids and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, **1988**; pp 550–554.

[12] The β-scission proposed to occur with **16**, **20**, and **25** is essentially identical with the well-known β-scission of alkoxy radicals which occur to split out the most stable radical (Walling, C.; Clark, R. T. *J. Am. Chem. Soc.* **1974**, *96*, 4530. Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593).

[13] Braverman, S. *Int. J. Sulfur. Chem. C* **1971**, *6*, 149. Braverman, S. Rearrangements Involving Sulfones in *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Ed.; John Wiley & Sons, New York, 1988; pp 670–676.

[14] Although the allyl and (4-nitrophenyl)thiyl radicals are present in solution at the same time, the dominant mode of coupling is to form allyl 4-nitrophenyl sulfide (see ref 8). 1,5-Hexadiene is formed in rather low yield and is difficult to detect in the presence of the other allyl derivatives **14**, **17**, **18**, and **19**. An alternative for the formation of allyl 4-nitrophenyl sulfide would be the addition of the (4-nitrophenyl)thiyl radical to the allyl group of **14** (producing structure i) or **16** followed by fragmentation to the allyl 4-nitrophenyl sulfide.

[15] Gara, W. B.; Roberts, B. P. *J. Chem. Soc. Perkin Trans. II* **1977**, 1715.



i

[16] See footnote 12.

[17] Krosley, K. W.; Gleicher, G. J.; Clapp, G. E. *J. Org. Chem.* **1992**, *57*, 840.

[18] Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275.

Table 1. Total Energies (au) and $\langle S^2 \rangle$ Values (in Parentheses)

	structure				
method/basis set	**27**	**28s**	**28a**	**29s**	**29ac**
UHF/6-31G* [a]	−191.27916 (0.7676)	−191.28583 (0.7708)	−191.28480 (0.7804)	−191.30192 (0.7611)	−191.30210 (0.7822)
UHF/6-31+G* [a]	−191.28499 (0.7676)	−191.29299 (0.7685)	−191.29213 (0.7755)	−191.30846 (0.7604)	−191.30912 (0.7739)
UHF/6-31++G** [a]	−191.29389 (0.7673)	−191.30247 (0.7687)	−191.30173 (0.7757)	−191.31723 (0.7603)	−191.31778 (0.7732)
UHF/6-311G(2d,p)[a]	−191.33408 (0.7679)	−191.34398 (0.7678)	−191.34370 (0.7737)	−191.35876 (0.7595)	−191.35880 (0.7684)
UMP2/6-31G* [a]					
E_{SCF}	−191.28250	−191.29146	−191.29211	−191.84575	−191.84558
E_{UMP2}	−191.85136	−191.85236	−191.85079	−191.84575	−191.84558
QCISD(T)/6-31G* [b]					
E_{SCF}	−191.27916	−191.28583	−191.28480	−191.30192	−191.30210
E_{UMP2}	−191.81754	−191.81899	−191.81667	−191.81449	−191.81315
E_{UMP3}	−191.84279	−191.84546	−191.84366	−191.85020	−191.84894
$E_{UMP4(SD)}$	−191.84685	−191.84951	−191.84778	−191.85367	−191.85243
$E_{UMP(SDQ)}$	−191.85235	−191.85631	−191.85443	−191.85936	−191.85824
$E_{QCISD(T)}$	−191.87078	−191.87631	−191.87488	−191.87933	−191.87876

[a] Full geometry optimization. [b] On the UHF/6-31G* optimized structures.

Table 2. Relative Energies (kcal mol^{-1})

basis set	**27**	**28s**	**28a**	**29s**	**29ac**
UHF/6-31G* [a]	14.39	10.20	10.85	0.11	0.00
UHF/6-31+G* [a]	15.14	10.12	10.66	0.41	0.00
UHF/6-31++G** [a]	14.99	10.61	10.07	0.35	0.00
UHF/6-311G(2d,p)[a]	15.49	9.29	9.45	0.02	0.00
UMP2/6-31+G* [a]					
E_{SCF}	16.33	10.71	10.30	0.47	0.00
E_{UMP2}	0.63	0.00	0.99	4.15	4.26
QCISD(T)/6-31G* [b]					
E_{SCF}	14.39	10.21	10.86	0.11	0.00
E_{UMP2}	0.91	0.00	1.45	2.82	0.79
E_{UMP3}	4.65	2.97	4.10	0.00	0.79
$E_{UMP4(SD)}$	4.28	2.61	3.70	0.00	0.78
$E_{UMP4(SDQ)}$	4.40	1.99	3.09	0.00	0.70
$E_{QCISD(T)}$	5.36	1.89	2.79	0.00	0.39

[a] Fully geometry optimized. [b] Total energies calculated at the geometry optimized 6-31G* level during the QCISD(T) run.

tive ring opening of the cyclopropyloxiranylmethyl radical, only the oxirane ring undergoes ring opening,[19] again suggesting the great propensity for ring opening of the oxiranylmethyl radical.

The formation of sulfide **18** and sulfone **19** is suggested to occur by the addition of the allyloxy radical to the starting sulfenate **21** to produce an intermediate hypervalent sulfuranyl radical (**25**) which undergoes the rapid expulsion of the alkoxy radical **24** (the reversal of sulfuranyl radical formation) which continues the cycle for product formation. There is no evidence that the sulfinate corresponding to the sulfenate **21** is formed by β-scission resulting in the formation of the allyl radical. The more rapid decomposition of the proposed sulfuranyl radical **25** to produce sulfenate **14** and alkoxy radical **24** relative to the formation of the allyl radical and sulfinate corresponding to **21** or the sulfinate **17** and a *tert*-alkyl radical can be attributed to a greater decrease in internal steric congestion in the proposed mode of fragmentation relative to that in the other possible processes. The resulting sulfenate **14** then undergoes further reaction as shown in the top portion of Scheme 2. However, the difference in the sulfide:sulfone ratios observed from **14** (**15**) and **21** suggests that the overall processes may not be quite as simple as suggested and that more that single process, or other processes, may be involved in leading to product formation.

Theoretical Calculations. In order to gain a better understanding of the observed results, *ab initio* molecular orbital calculations have been carried out on the ground-state structures of the radicals **11**−**13**[18] shown in eq 2 at the UHF 6-31G*, 6-31+G*, 6-31++G**, 6-311G(2d,p), and the UMP2/6-31+G* levels of theory with complete geometry optimization using the GAUSSIAN90 package of programs.[19,20] The total energies of the minimum-energy radical species located in this study and the $\langle S^2 \rangle$ values are given in Table 1. The relative energies are given in Table 2, and the optimized structural parameters are given in Table 3.

Calculations on the oxiranylmethyl radical indicate the existence of a single minimum-energy conformation shown in structure **27**. The SOMO in **27** is alligned for interaction with the in-plane Walsh-type orbitals of the three-membered ring. Calculations on the (vinyloxy)methyl radical located two minimum-energy conformations shown in structures **28s** and **28a**.[20] The SOMOs of **28s** and **28a** correspond to that illustrated in representation **10**. Calculations on the allyloxy radical[21] also located two minimum-energy conformations shown in structures **29s** and **29ac**. The SOMOs in **29s** and **29ac** are highly localized on the oxygen atom.

An inspection of the relative energies given in Table 2 shows that the relative energies of the five radical species are very similar at the four UHF levels.[22] That the allyloxy radical is lower in energy than the (vinyloxy)methyl radical is not consistent with our initial intuition. The results of the calculations derived by the UHF method are consistent with the experimental results obtained in this study *if* thermodynamics controls product formation. The similarity in the relative energies suggests that the incorporation of diffuse and additional polarization functions beyond the 6-31G* level has little effect on the relative energies of the C_3H_5O radicals.

The relative energies calculated at the optimized UMP2/6-31+G* level, however, are very different, being in the sequence (vinyloxy)methyl ∼ oxiranylmethyl <

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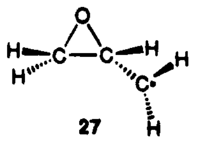
[19] Krosley, K. W.; Gleicher, G. J. *J. Phys. Org. Chem.* **1993**, *6*, 228.

[20] GAUSSIAN90, Revision I. 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. Gaussian, Inc., Pittsburgh, PA, 1990.

[21] The results of theoretical calculations on the C_3H_5O radical systems have been presented at the Denver National American Chemical Society meeting before the Division of Organic Chemistry (Le, M.-S.; Jackson, E.; presentation no. 104 before the Division of Organic Chemistry, National American Chemical Society meeting, Denver, CO, March 29, 1993). Further calculations by Professor Jackson (personnal communication) has led him to the conclusion that the ring-opening of the epoxymethyl radical to the allyloxy radical is thermodynamically disfavored but kinetically favored.

[22] The postscript letters **s**, **a**, and **ac** imply syn, anti, and anticlinal conformations.



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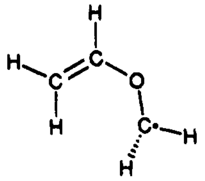
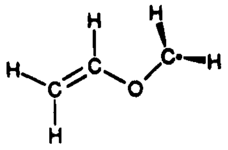
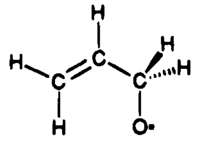


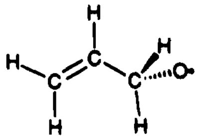
28s



28a



29s



29ac

allyloxy. (However, the relative SCF energies obtained at the optimized UMP2/6-31+G* level parallel those derived at the UHF levels.) The suggestion that the oxiranylmethyl radical is essentially the same in energy as the (vinyloxy)methyl radical, however, does not seem reasonable.

An inspection of the calculated structural parameters for **28s**, **28a**, **29s**, and **29ac** at the UHF and UMP2/6-31G* levels shows a very high degree of consistency, particularly in the comparison of the calculated bond lengths. Such is not true for the oxiranylmethyl radical **27**. The O−C bond lengths calculated at the UMP2/6-31G* level are considerably longer (0.05 and 0.04 Å) than those calculated at the UHF levels which all very similar. It is not obvious why this is so, but it has a substantial effect on the relative energy of the oxiranylmethyl radical.

In view of the fact that the addition of diffuse and polarization functions beyond the 6-31G* level had little effect on the relative energies of the C_3H_5O radical species calculations were carried out the radical species at the QCISD(T)/6-31G* level on the 6-31G* optimized structures. The relative energies produced at the various levels of correlation and CI are given in Table 2. At the UMP2 level the results are somewhat similar to those derived from the geometry optimization calculations. At the higher levels of correlation and at the QCISD(T) level the allyloxyl radical **29s** is predicted to be lowest in energy, with the oxiranylmethyl radical being only 4−5 kcal mol^{-1} higher in energy. The results obtained at the QCISD(T) level are somewhat similar to those derived for the 3-buten-1-yl−cyclopropylcarbinyl system in which calculations carried out at the CI level with a SVP basis gave an energy difference favoring the 3-buten-1-yl radical by 3.7 kcal mol^{-1} compared to the experimental values of 3.2 and 5.2 kcal mol^{-1}.[23] Thus it would appear that CI calculations are required to achieve a reasonable estimate of the energy differences in such cyclic−acyclic systems.

Continuing experimental and theoretical studies are being carried out on substituted derivatives of **14** and **21** and on other heteroatom-containing analogs.

Experimental Section

The synthesis and characterization of allyl 4-nitrophenyl sulfide (**18**) has been reported in the literature.[8]

Reaction of Allyl Alcohol with 4-Nitrobenzenesulfenyl Chloride. To a 50 mL three-neck flask containing 5 mmol of allyl alcohol and freshly distilled triethylamine (1.6 mL, 11.5 mmol) in 15 mL of anhydrous CH_2Cl_2 under an argon atmosphere immersed in a dry ice/acetone bath in a darkened hood was added with stirring a solution of 4-nitrobenzenesulfenyl chloride (0.95 g, 5 mmol) in 10 mL of CH_2Cl_2. 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 organic phase was washed with cold 3% hydrochloric acid (2 × 10 mL) and cold water (3 × 10 mL) and was dried ($MgSO_4$). The solvent was removed under reduced pressure in an aluminum-foil wrapped flask giving allyl 4-nitrobenzenesulfenate (**14**) along with small amounts of allyl 4-nitrobenzenesulfinate (**17**). In some preparations the sulfenate **14** was not observed, instead allyl 4-nitrophenyl sulfoxide was isolated along with small amounts of the sulfinate **17**. The sulfoxide **15** and the sulfinate **17** were separated by column chromatography on silica gel.

Allyl 4-Nitrobenzenesulfenate (14). ^1H NMR ($CDCl_3$) δ 4.67 (ddd, J = 6.00, 1.2, 1.2 Hz, 2 H), 5.33 (dm, J = 11.1, 1 H), 5.38 (dm, J = 17.4 Hz, 1 H), 5.82 (m, 1 H), 7.62 (apparent d, J = 9.00 Hz, 2 H), 8.20 (apparent d, J = 9.00 Hz, 2 H).

Allyl 4-Nitrophenyl Sulfoxide (15). ^1H NMR ($CDCl_3$) δ 3.55 (dd, J = 12.98, 7.51 Hz, 1 H), 3.70 (dd, J = 12.98, 7.39 Hz, 1 H), 5.25 (dd, J = 16.97, 0.92 Hz, 1 H), 5.40 (broadened d, J = 9.92, 1 H), 5.70 (m, 1 H), 7.90 (apparent d, J = 8.77 Hz, 2 H), 8.40 (apparent d, J = 8.77 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 60.1, 123.8, 123.9, 124.6, 125.3, 149.2, 150.2; HR EIMS calcd for $C_9H_9NO_3S$ 211.030, found 211.030.

Photo-induced Oxidation of Allyl 4-Nitrobenzenesulfenate (14) to Allyl 4-Nitrobenzenesulfinate (17). A 0.33 M solution of **14** in $CDCl_3$ maintained under an O_2 atmosphere was irradiated at 350 nm for several hours. The ^1H NMR ($CDCl_3$) spectrum of the product showed δ 4.23 (dddd, J = 12.37, 6.08, 1.17, 1.28 Hz, 1 H), 4.59 (dddd, J = 12.37, 5.94, 1.30, 1.30 Hz, 1 H), 5.30 (dm, J = 10.31 Hz, 1 H), 5.35 (dm, J = 17.21 Hz, 1 H), 5.89 (dddd, J = 17.21, 10.31, 6.08, 5.94 Hz, 1 H), 7.94 (app d, J = 8.86 Hz, 2 H), 8.41 (app d, J = 8.86 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 66.5, 120.1, 124.2, 126.7, 131.6, 150.1, 150.9; HR FAB MS calcd for $(M + H)^+$ 228.033, found 228.033.

Preparation of Allyl 4-Nitrophenyl Sulfone. To a solution of 5 mmol of allyl 4-nitrophenyl sulfide in 50 mL of CH_2Cl_2 at 0 °C was slowly added 10 mmol of *m*-chloroperbenzoic acid dissolved in 30 mL of CH_2Cl_2. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was transferred to a separatory funnel, and any remaining peracid was destroyed by washing the organic phase with 10% aqueous sodium sulfite. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel using a 4:1 mixture of CH_2Cl_2:Skellysolve F as eluent: colorless solid, mp 140−142 °C; ^1H NMR ($CDCl_3$) δ 3.90 (br d, J = 7.41 Hz, 2 H), 5.15 (br d, J = 17.04 Hz, 1 H), 5.80 (ddt, J = 17.14, 10.14, 7.41 Hz, 1 H), 8.10 (d, J = 8.96 Hz, 2 H), 8.40 (d, J = 8.96 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 60.7, 123.9, 124.2, 125.6, 130.1, 143.6, 150.8; HR FAB MS calcd for $C_9H_9NO_4S$ $(M + H^+)$ 228.033, found 228.032.

Isomerization of Sulfinate 17 to Sulfone 19. A solution of sulfinate **17** in C_6D_6 in a sealed NMR tube was irradiated at 350 nm at ~60 °C. The ^1H NMR spectrum periodically recorded indicating the conversion of the sulfinate **17** to the sulfone **19**.

Preparation of 4,5-Epoxy-2-methyl-2-pentyl 4-Nitrobenzenesulfenate. To a stirred solution of 0.55 mL (5 mmol) of 2-methyl-4-penten-2-ol (**22**)[8] in 50 mL of CH_2Cl_2 at 0 °C was slowly added a solution of 5 mmol of *m*-chloroperoxybenzoic acid dissolved in 30 mL of CH_2Cl_2. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was transferred to a separatory funnel, and the organic phase was washed with 10% aqueous sodium sulfite until a starch−iodine test was negative.

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[23] Care must be exercised in generating the initial guess orbitals to obtain the correct configuration of the allyloxy radical.

[24] The direct comparison of the energies of the five radical species at the UHF level should not be impaired in view of the very similar ⟨S^2⟩ values, indicating that all of the calculated wave functions suffer very similar extents of spin contamination.

[25] Quenemoen, K.; Borden, W. T.; Davidson, E. R. Feller, D. *J. Am. Chem. Soc.* **1985**, *107*, 5054.

Table 3. Calculated Structural Parameters for 27, 28a, 28s, 29s, and 29ac

parameter	basis set				
	6-31G*	6-31+G*	UMP2/6-31+G*	6-31++G**	6-311G(2d,p)
27					
C_1-O_2	1.412	1.414	**1.462**	1.414	1.410
O_2-C_3	1.398	1.399	**1.437**	1.399	1.396
C_1-C_4	1.470	1.470	1.457	1.469	1.466
C_1-C_3	1.465	1.465	1.477	1.465	1.462
C_3-H_5	1.077	1.077	1.088	1.078	1.077
C_3-H_6	1.078	1.077	1.088	1.078	1.077
C_1-H_7	1.078	1.076	1.089	1.078	1.077
C_4-H_8	1.073	1.073	1.082	1.074	1.073
C_4-H_9	1.074	1.074	1.083	1.074	1.073
$C_1-O_2-C_3$	62.83	62.77	61.24	62.81	62.82
$C_4-C_1-O_2$	116.79	116.82	116.17	116.83	116.89
$H_5-C_3-O_2$	115.35	115.18	114.89	115.26	115.37
$H_6-C_3-O_2$	115.45	115.30	115.18	115.38	115.47
$H_7-C_1-O_2$	113.57	113.32	112.68	113.51	113.63
$H_8-C_4-C_1$	120.72	120.64	120.92	120.58	120.57
$H_9-C_4-C_1$	119.84	119.98	119.75	119.88	119.80
$C_4-C_1-O_2-C_3$	113.24	113.26	112.74	113.19	113.12
$H_5-C_3-O_2-C_1$	−110.62	−110.64	−110.37	−110.56	−110.45
$H_6-C_3-O_2-C_1$	110.96	111.03	110.88	110.88	110.70
$H_7-C_1-O_2-C_3$	−108.15	−108.36	−108.48	−108.27	−108.05
$H_8-C_4-C_1-H_7$	16.43	12.85	6.82	14.79	16.94
$H_9-C_4-C_1-H_7$	192.59	191.47	189.37	192.41	192.46
28s					
C_1-C_2	1.319	1.322	1.329	1.322	1.315
C_2-O_3	1.350	1.350	1.377	1.350	1.347
O_3-C_4	1.357	1.357	1.373	1.357	1.353
C_1-H_5	1.073	1.073	1.082	1.073	1.072
C_1-H_6	1.073	1.073	1.083	1.073	1.072
C_2-H_7	1.073	1.073	1.085	1.073	1.073
C_4-H_8	1.076	1.076	1.086	1.076	1.075
C_4-H_9	1.072	1.072	1.080	1.072	1.072
$C_1-C_2-O_3$	127.85	127.74	127.23	127.71	127.97
$C_2-O_3-C_4$	119.64	120.08	117.15	120.12	119.60
$H_5-C_1-C_2$	123.43	123.52	123.61	123.46	123.36
$H_6-C_1-C_2$	118.96	118.79	118.41	118.65	118.63
$H_7-C_2-C_1$	122.17	122.22	123.30	122.15	121.88
$H_8-C_4-O_3$	116.83	116.92	116.69	117.11	117.13
$H_9-C_4-O_3$	112.17	112.24	111.83	112.40	112.42
$C_4-O_3-C_2-C_1$	12.56	12.14	14.31	12.19	12.69
$H_8-C_4-O_3-C_2$	41.86	41.31	38.78	40.51	40.23
$H_9-C_4-O_3-C_2$	185.72	186.10	184.71	186.36	185.69
28a					
C_1-C_2	1.317	1.319	1.324	1.319	1.312
C_2-O_3	1.352	1.352	1.381	1.352	1.348
O_3-C_4	1.352	1.355	1.375	1.355	1.352
C_1-H_5	1.074	1.074	1.083	1.074	1.074
C_1-H_6	1.073	1.073	1.082	1.073	1.072
C_2-H_7	1.076	1.076	1.089	1.077	1.076
C_4-H_8	1.077	1.077	1.086	1.077	1.076
C_4-H_9	1.072	1.071	1.080	1.072	1.071
$C_1-C_2-O_3$	122.09	122.10	121.27	122.05	122.23
$C_2-O_3-C_4$	118.55	118.62	114.98	118.63	118.25
$H_5-C_1-C_2$	121.48	121.60	121.48	121.51	121.43
$H_6-C_1-C_2$	119.96	119.77	119.55	119.65	119.66
$H_7-C_2-C_1$	122.67	122.70	123.83	122.63	122.37
$H_8-C_4-O_3$	117.26	117.27	117.19	117.44	117.49
$H_9-C_4-O_3$	112.56	112.64	112.19	112.81	112.91
$C_4-O_3-C_2-C_1$	179.71	181.08	161.84	180.48	179.29
$H_8-C_4-O_3-C_2$	30.71	31.14	32.11	29.79	27.80
$H_9-C_4-O_3-C_2$	175.34	176.81	178.65	176.52	174.33
29s					
C_1-C_2	1.317	1.320	1.327	1.302	1.312
C_2-C_3	1.506	1.506	1.504	1.506	1.503
C_1-H_4	1.075	1.075	1.085	1.075	1.075
C_1-H_5	1.074	1.075	1.085	1.075	1.074
C_2-H_6	1.079	1.079	1.090	1.080	1.079
C_3-H_7	1.090	1.089	1.103	1.090	1.090
C_3-H_8	1.090	1.089	1.102	1.090	1.090
C_3-C_9	1.383	1.382	1.386	1.382	1.378
$C_1-C_2-C_3$	125.01	125.26	124.20	125.22	124.94
$C_2-C_5-O_9$	114.91	115.07	116.28	115.05	115.10
$H_4-C_1-C_2$	121.15	121.02	121.17	120.96	121.10
$H_5-C_1-C_2$	121.61	121.69	121.21	121.53	121.40
$H_6-C_2-C_1$	120.10	119.99	120.51	119.99	120.09

Table 3 (Continued)

	basis set				
parameter	6-31G*	6-31+G*	UMP2/6-31+G*	6-31++G**	6-311G(2d,p)
29s					
$H_7-C_3-C_2$	110.81	110.75	111.14	110.67	110.62
$H_8-C_3-C_2$	110.82	110.72	111.07	110.67	110.63
$H_7-C_3-C_2-H_6$	58.71	58.58	58.36	58.61	58.48
$H_8-C_3-C_2-H_6$	−58.42	−58.65	−58.14	−58.55	−58.32
$O_9-C_3-C_2-H_6$	179.92	179.98	180.02	180.02	180.05
29ac					
C_1-C_2	1.320	1.322	1.319	1.322	1.314
C_2-C_3	1.502	1.503	1.502	1.502	1.500
C_1-H_4	1.075	1.075	1.085	1.075	1.075
C_1-H_5	1.077	1.077	1.087	1.077	1.077
C_2-H_6	1.078	1.078	1.089	1.078	1.077
C_3-H_7	1.091	1.091	1.105	1.092	1.091
C_3-H_8	1.087	1.086	1.100	1.087	1.086
C_3-O_9	1.387	1.387	1.392	1.387	1.382
$C_1-C_2-C_3$	124.00	123.93	123.07	123.92	123.97
$C_2-C_3-O_9$	112.51	112.52	113.36	112.53	121.58
$H_4-C_1-C_2$	121.71	121.58	121.82	121.49	121.65
$H_5-C_1-C_2$	121.83	121.83	121.59	121.74	120.47
$H_6-C_2-C_1$	120.53	120.42	121.04	120.39	110.40
$H_7-C_3-C_2$	110.62	110.63	110.96	110.53	111.50
$H_8-C_3-C_2$	111.63	111.69	111.76	111.65	112.58
$H_7-C_3-C_2-H_6$	64.90	63.73	62.91	63.96	64.11
$H_8-C_3-C_2-H_6$	184.17	183.33	182.40	183.45	183.28
$O_9-C_3-C_2-H_6$	−50.97	−52.06	−52.58	−51.84	51.75

The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure giving a 50% yield of the epoxy alcohol **23**: ^1H NMR ($CDCl_3$) δ 1.32 (s, 3 H), 1.33 (s, 3 H), 1.57, (dd, $J = 14.25$, 7.49 Hz, 1 H), 1.81 (dd, $J = 14.25$, 4.24 Hz, 1 H), 2.47 (dd, $J = 4.89$, 2.70 Hz, 1 H), 2.80 (dd, $J = 4.55$, 4.48 Hz, 1 H), 3.13 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.5, 29.6, 45.7, 46.6, 49.3, 70.5; HR MS no parent ion observed, CIMS (ammonia) indicated a parent ion at m/z 117 ($M + H^+$).

To a 50 mL three-neck flask containing 5 mmol of the alcohol **23** and freshly distilled triethylamine (1.6 mL, 11.5 mmol) in 15 mL of anhydrous CH_2Cl_2 under an argon atmosphere immersed in a dry ice/acetone bath in a darkened hood was added with stirring a solution of 4-nitrobenzenesulfenyl chloride (0.95 g, 5 mmol) in 10 mL of CH_2Cl_2. After the addition of the sulfenyl chloride was completed the reaction mixture was stirred for 15 min and was then allow to warm to room temperature for 30 min. The organic phase was washed with cold 3% hydrochloric acid (2 × 10 mL) and cold water (3 × 10 mL) and was dried ($MgSO_4$). The solvent was removed under reduced pressure in an aluminum-foil wrapped flask giving a dark red, viscous liquid: ^1H NMR (C_6D_6) δ 1.05 (s, 3 H), 1.10 (s, 3 H), 1.37 (dd, $J = 14.40$, 7.45 Hz, 1 H), 1.62 (dd, $J = 14.40$, 3.99 Hz, 1 H), 2.02 (dd, $J = 5.12$, 2.56 Hz, 1 H), 2.31 (dd, $J = 5.12$, 3.99 Hz, 1 H), 2.70 (m, 1 H), 6.75 (apparent d, $J = 9.11$ Hz, 2 H), 7.80 (apparent d, $J = 9.11$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.2, 25.8, 43.9, 46.3, 48.4, 85.5, 120.1, 123.9, 144.8, 153.5; HR FAB MS calcd for $C_{12}H_{16}NO_4S$ ($M + H^+$) 270.080, found 270.079.

Procedure for the Photolysis of 14 and 21. Solutions of **14** (**15**) or **21** in $CDCl_3$ in NMR tubes were triply freeze-degassed and sealed under reduced pressure. The tubes were irradiated with a GE-275W sunlamp at ~60 °C. The progress of the reactions was monitored by periodic recording of the ^1H NMR spectra of the reactant solutions.

The components of the reaction mixtures derived from **15** (**14**) were directly identified by comparison of the chemical shifts appearing in the ^{1}NMR spectrum of the product mixture with those of authentic materials.

The reaction mixture derived from the photolysis of **21** was separated into volatile and nonvolative fractions on a vacuum line. The C_6D_6 solution of the volatile fraction showed the presence of only allyl alcohol and 4,5-epoxy-2-methyl-2-pentanol. The nonvolatile residue was subjected to chromatography on silica gel giving fractions of allyl 4-nitrophenyl sulfide, 4-nitrophenyl disulfide, and allyl 4-nitrophenyl sulfone as identified by the comparison of the ^{1}NMR spectra of the fractions with those of authentic materials. A fourth fraction was isolated which possessed an ^1H NMR spectrum showing *only* four, equal intensity apparent doublets at δ 7.63, 7.81, 8.27, and 8.34 suggesting the structure Ar−SO−S−Ar. A HRMS of this product could not be obtained.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for **15**, **17**, **19**, **21**, and **23** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.