A Study of the Regioselectivity of the Radical Addition of "RSAr" Derived from the Photolysis of *tert*-Homoallyl and *tert*-Alkyl 4-Nitrobenzenesulfenates to Substituted Allenes and Alkenes

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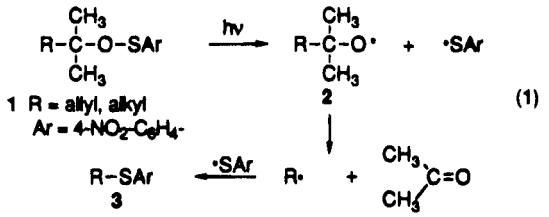
Received January 14, 1994®

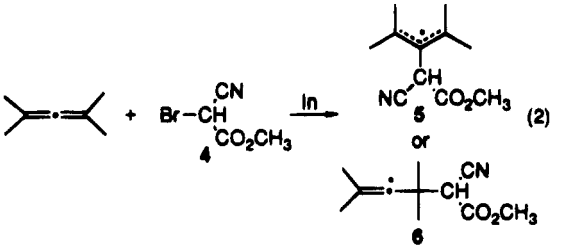
The regioselectivity of the free radical addition of "RSAr" derived from the photolysis of *tert*-homoallyl and *tert*-alkyl 4-nitrobenzenesulfenates, followed by β-scission of the alkoxy radicals to produce the allyl or alkyl radicals R•, to 1,1- and 1,3-dimethylallene and acrylonitrile and methyl acrylate has been determined. The regioselectivity of addition of "RSAr" to 1,1- and 1,3-dimethylallene occurs by the addition of the arylthiyl radical to the center carbon atom of the allene chromophore, whereas the regioselectivity of the addition to acrylonitrile and methyl acrylate varies with the nature of the R•. The results are interpreted in terms of the relative reactivities of the π systems toward radical addition and the relative rates of β-scission of the intermediate alkoxy radicals versus the rates of addition of the 4-nitrobenzenethiyl radical and R• to the π systems.

The recent discovery in our laboratories that the photolysis of *tert*-homoallyl and *tert*-alkyl 4-nitrobenzenesulfenates **1** results in the ultimate formation of substituted allyl and alkyl radicals by the β-scission of the initially formed alkoxy radicals **2** has provided a new and efficient nonchain method for the generation of alkoxy, alkyl, and allyl free radicals which allows for a detailed study of the chemical properties of these radical systems.[1] In the absence of other acceptor species the dominant mode of reaction is coupling of the alkyl and allyl radicals with the 4-nitrobenzenethiyl radical to form the allyl or alkyl 4-nitrophenyl sulfides **3** (eq 1). In the presence of



an unsaturated system the arylthiyl, alkyl, and allyl radicals can undergo addition to the π system. In the present article the results of a study on the regioselectivity of the radical addition of "RSAr", generated as shown in eq 1, to 1,1- and 1,3-dimethylallene (11DMA and 13DMA) and to acrylonitrile (ACN) and methyl acrylate (MAC) are reported. The results of these studies show some very interesting contrasts in the regioselectivity of addition of "RSAr" to the different π systems.

A number of studies on free radical addition reactions to substituted allenes have been reported. It appears that, in general, attack by carbon-centered radicals occurs at a terminal carbon atom of the allene chromophore,[2] whereas attack by heteroatom-centered radicals occurs at the central carbon atom of the allene chromophore.[3] However, it has been reported that the radical chain addition of bromomalononitrile (**4**) undergoes addition of the carbon-centered radical to both the terminal and the central carbon atoms, the extent of attack at the central carbon atom to form **5** increasing with increasing alkyl substitution on the allene chromophore (eq 2).[4] The addition of free radicals to ACN and MAC occurs only at the β-carbon to produce the more stable radical **7** (eq 3).[5]



Results

Addition of "RSAr" to 1,1-Dimethylallene (11DMA). The photolysis of **8a–c** in the presence of 11DMA has been carried out in freeze-degassed solutions of the reactants in benzene-d_6 in sealed NMR tubes. The ^{1}H NMR spectra of the reaction mixtures taken after the complete disappearance of **8a–c** indicated the clean formation of only the products shown in eq 4. The relative amounts of the products formed were determined by the direct integration of the ^{1}H NMR spectra of the reaction mixtures. When carried out on a larger scale in regular benzene the product mixtures could be separated by MPLC on silica gel giving fractions containing a mixture of the regioisomers of **9** and **10**, a mixture of the regioisomeric dimers **11** and **12**, and sulfides **3** (the latter being identified by comparison of their ^{1}H NMR spectra with those of authentic materials).

The regioselectivity shown in the simple adducts **9**, rather than that shown in structure **13**, is assigned on the basis of the chemical shifts of the methylene protons

® Abstract published in *Advance ACS Abstracts*, July 1, 1994.

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(4) Bartels, H. M.; Boldt, P. *Liebigs Ann. Chem.* **1981**, 40–46.

(5) For a review see: Giese, R. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: New York, 1986.

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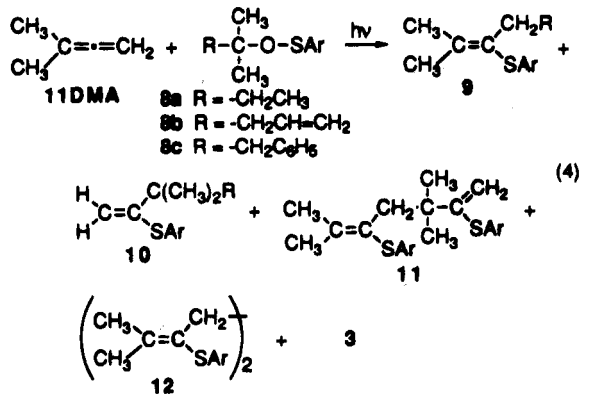
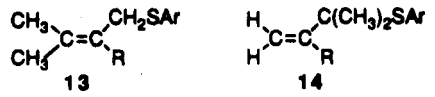


in the adducts. The chemical shifts of the methylene



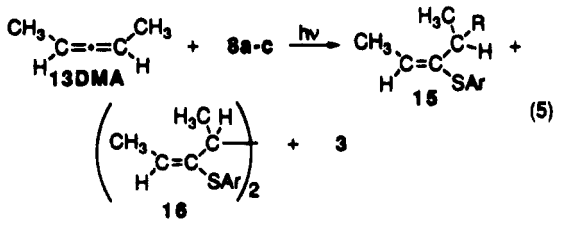
groups in the adducts **9** appear in the δ 2.50–2.90 region. In the adducts having the regioselectivity shown in **13** the chemical shift of the methylene protons between the C=C and the sulfur atom is expected to appear near δ 3.90.[1] In addition, in adducts of structure **13** long-range homoallylic coupling between the methylene protons of the R group and the vinylmethyl protons should be observable. There is no observable long-range coupling to the vinyl-methyl groups in the adducts assigned structure **9**. The assignment of the regioselectivity in adducts **10** is based on the chemical shifts of the two vinylic protons which appear in the δ 5.30–5.60 region. This is at lower field than would be expected for a 1,1-dialkyl-substituted alkene having the structure **14**.[6]

The formation of the allyl-radical dimers **11** and **12** was indicated by their ^{1}H NMR spectra and by high-resolution MS. The assignment of the structure of **11** is based on the presence of a singlet at δ 1.30 for the geminal methyl groups, singlets at δ 2.01 and 2.03 for the vinylic methyl groups, a singlet at δ 2.68 for the CH_2 group, and multiplets at δ 5.60 and 5.80 for the two vinyl protons. The structure of **12** is assigned on the basis of resonances at δ 1.96 and 1.99 for the two sets of equivalent vinyl methyl groups and at δ 2.50 for the protons of the two chemically identical methylene groups. The third possible coupling product of the intermediate allyl radical involving bond formation at the more highly substituted end of both of the allyl radicals was not detected. The relative yields of **9**–**12** are given in Table 1.

Table 1. Relative Yields of the Products Formed in the Photoinduced Decomposition of 8a–c in the Presence of 1,1-Dimethylallene

sulfenate	9	10	11	12	3
8a	40.5	8.1	35.1	2.7	13.6
8b	50.0	14.1	23.1	2.6	10.2
8c	70.8	5.5	14.6	4.1	5.3

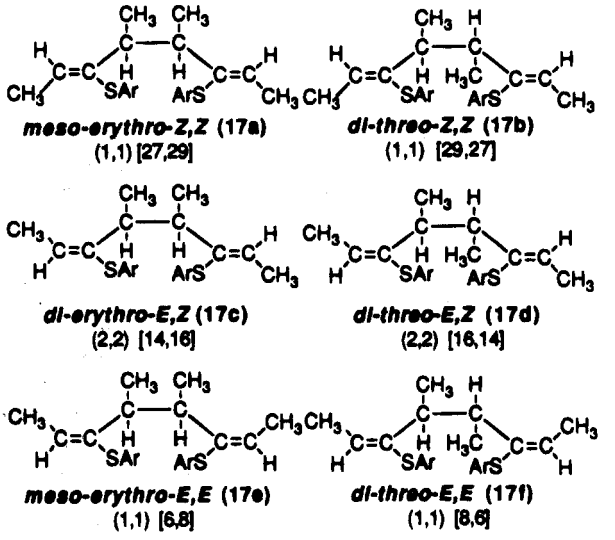
Addition of "RSAr" to 1,3-Dimethylallene (13DMA). In a similar manner the photolysis of the sulfenates **8a–c** in the presence of 13DMA produces mixtures of the diastereisomers of the simple adducts **15** and allyl dimers **16** (eq 5) and varying amounts of the sulfides **3**. The diastereoisomeric mixtures of **15** and **16** were cleanly



separated by column chromatography on silica gel. The two diastereoisomers of **15a** (there are two *dl*-pairs of diastereoisomers possible) were isolated in an approximate 1:1 ratio. The regioselectivity in **15a** has been assigned on the basis of the ^{1}H NMR spectral characteristics of the *E*- and *Z*-adducts. For example, the allylic proton resonances in **15a** appear at δ 1.80 and 1.90, being at much higher field than that expected for the adduct of opposite regioselectivity as shown in structure **13**. The regioselectivity of addition to form the adducts **15b** and **15c** has been assigned on a similar basis.

The ^{1}H NMR spectrum of the mixture of the diastereoisomers of **16** derived from the photolysis of **8a–c** contained eight clearly resolved doublets in the vinylmethyl region, eight less-well resolved doublets in the saturated-methyl region, and eight quartets in the vinyl-proton region indicating the formation of the six diastereoisomers shown as **17a–f**. (The number of the

Chart 1



vinyl-methyl and vinyl-proton resonances expected for each of the diastereoisomers are given in parentheses after the structure number. The relative ratios of the diastereoisomers are given in brackets; two numbers being given due to the inability to distinguish between the related *erythro* and *threo* diastereoisomers.) The vinyl-methyl and vinyl-proton regions of the ^{1}H NMR spectrum of a mixture of the diasteroisomers is shown in Figure 1. It is important to notice that the doublets in the higher-field, vinyl-methyl region are of greater intensity than those in the lower-field region. Conversely, the lower-field resonances in the vinyl-proton region are of greater intensity than those in the higher-field, vinyl-proton region. The *E*-, and *Z*-stereochemical assignments have been made on the basis that a vinyl proton *trans* to a –SR group is expected to appear at lower field than when *cis* to a –SR group.[6] The extension of this trend to the relative chemical shifts of the vinyl-methyl groups leads to the expectation that a vinyl-methyl *trans* to the –SR group will also appear at lower

(6) Pasto, D. J.; Johnson C. R. *Organic Structure Determination*; Prentice Hall, Inc.: New York, 1969; p 174.

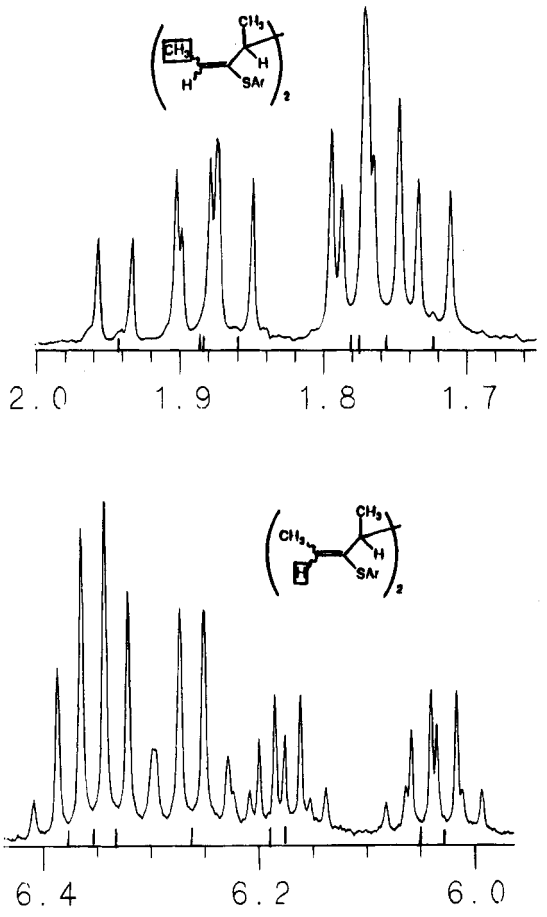
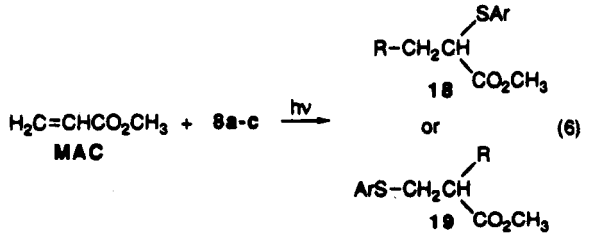


Figure 1. The vinyl-methyl and vinyl-proton regions of the ^{1}H NMR spectrum of the mixture of diastereoisomers of **16a–f**. The upward-pointing hatch marks indicate the chemical shifts of the doublets and quartets in the two regions.

field than a *cis*-vinyl-methyl group. The relative intensities of the high- and low-field vinyl-methyl and vinyl-proton regions are in accord with these expectations.

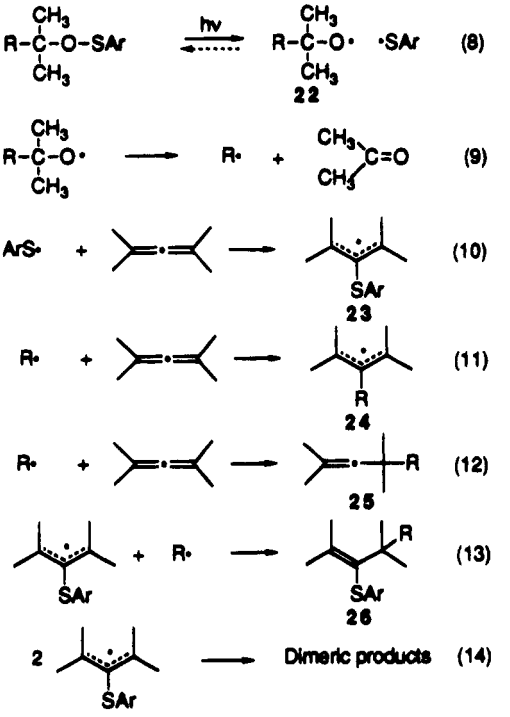
Addition of "RSAr" to Methyl Acrylate (MAC). The photolysis of **8a** (R = $-CH_2CH_3$) in the presence of MAC resulted in the formation of **18a** in low yields (~13%), with extensive formation of sulfide **3** and polymerization of the MAC (eq 6). The adduct **18a** was



isolated by column chromatography, and its structure has been assigned on the basis of its ^{1}H NMR spectrum which contained a double doublet at δ 3.88 for the proton α to the ester function and double doublets at δ 1.80 and 2.00 for the diastereotopic protons α to the stereogenic center. In an adduct of the type of structure shown as **19a** the proton α to the ester function would appear at much higher field than that observed for the product.

The photolysis of **8b** (R = $-CH_2CH{=}CH_2$) in the presence of MAC results in the formation of **19b** in fairly good yield, along with some polymerization of the MAC. In the case of structure **19b** the assignment of the

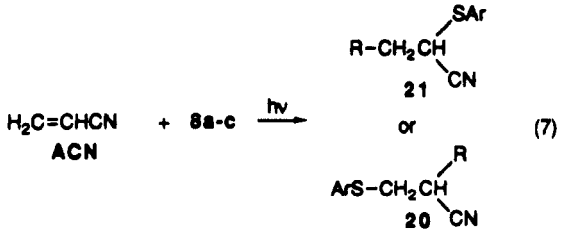
Scheme 1



regioselectivity of addition was not as obvious. The non-4-nitro derivative of **19b** was prepared, and then its ^{1}H NMR spectral characteristics were compared with that of the product formed in the reaction. The similarity in the ^{1}H NMR spectra of the two compounds allowed for the unambiguous assignment of the structure of the adduct as **19b**.

The photolysis of **8c** (R = $-CH_2C_6H_5$) in the presence of MAC did not produce an isolable product corresponding to either structures **18c** or **19c**. The ^{1}H NMR spectrum of the crude reaction mixture indicated the formation of only a polymer of MAC.

Addition of "RSAr" to Acrylonitrile (ACN). The photolysis of **8a** and **8c** in the presence of ACN did not result in the formation of any detectable amounts of the simple adducts **20** or **21** (eq 7), but produced only apparent polymeric material. The irradiation of **8b** in the presence of ACN led to the formation **20b** in fairly good yield.



Discussion

The results described above can be rationalized on the basis of the relative rates of the various competing reactions shown in Scheme 1. It was originally hoped that the rate of β-scission of the *tert*-alkoxy radicals **22** (eq 9) *and* the rate of the addition of the resulting C-centered radical R· to the substituted allene (eq 11) would be faster than the reaction of the highly resonance delocalized and stabilized 4-nitrobenzenethiyl radical with an allene to form the substituted allyl radical **23** (eq 10) thus resulting only in the addition of the R· to

the substituted allene (eq 11 or 12).[7,8] The rate of β-scission of alkoxy radicals increases as the degree of substitution increases at the carbinol carbon atom and as the stability of the radical being formed increases,[1,9] thus favoring the formation of the allyl and benzyl radicals from **8b** and **8c** (R = allyl and benzyl in **22**) and disfavoring the formation of the ethyl radical from **8a** (R = ethyl in **22**). Yet in all cases addition of the 4-nitrobenzenethiyl radical occurs first to produce the intermediate radical **23** (eq 10). However, it might be argued that the addition of R• occurs first to produce the intermediate radical **25** (eq 12) which then couples with the arylthiyl radical to form the observed product **26** (eq 13). If this were the case, it would not then be possible to rationalize the formation of **26** and the dimeric products **11**, **12**, and **16** (eq 14) via a single common intermediate or pathway. It is most reasonable to conclude that both the 4-nitrobenzenethiyl radical and 11DMA and 13DMA are sufficiently reactive together to result in only the formation of **23** before β-scission of the alkoxy radical and addition of the resulting R• can occur to form either **24** or **25**.

The situation changes dramatically in the addition of "RSAr" to MAC and ACN as the structure and reactivity of the R• is varied. Alkenes are well known to be less reactive toward free radical addition compared to allenes and alkynes. Thus, in the reactions with MAC and ACN both ArS• and R• species can be present at the same time and compete for reaction with the alkene as well as undergoing coupling to form sulfide. This is undoubtedly the reason for the larger amounts of the sulfide coupling products formed in the reactions with ACN and MAC. When the R• is the nonstabilized, highly reactive ethyl radical, the ethyl radical wins out over the 4-nitrobenzenethiyl radical for addition to the alkene. However, when the competition is between the allyl and the 4-nitrobenzenethiyl radical, the latter appears to be more reactive and adds to the alkene resulting in a "reversal" of the regioselectivity of the addition of the "RSAr" to the alkene π system.

On the *E,Z*-Product Distributions. In prior studies on the free radical addition of benzenethiol to substituted allenes[3b,c] and on the coupling reactions of substituted allyl radicals with the 4-nitrobenzenethiyl radical in the photolysis reactions of substituted *tert*-homoallylic 4-nitrobenzenesulfenates,[1] *E,Z*-equilibration of the product alkenes is observed. This equilibration process involves the reversible addition of the arylthiyl radical to the product alkene which, after C—C bond rotation and expulsion of the arylthiyl radical, results in *E,Z*-equilibration. Therefore, the relative yields of the stereoisomers of the simple adducts and the dimeric products repesent the thermodynamically controlled product distributions and not the kinetically controlled product distributions.

Experimental Section

General Methods. The synthesis of 1,1- and 1,3-dimethylallene has been carried out as reported in the literature.[10a,b]

Preparation of Alkyl 4-Nitrobenzenesulfenates 8a–c. To a 50-mL three-neck flask containing 5 mmol of the 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 and was stirred 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 the alkyl 4-nitrobenzenesulfinate which was further purified by column or rotating-disk, thin-layer chromatography on silica gel in a darkened hood using 3:1 Skellysolve B:CH_2Cl_2 as eluent.

8a: dark red liquid; UV ($CHCl_3$) λ_{max} = 345 nm; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.50 Hz, 3 H), 1.28 (s, 6 H), 1.70 (q, J = 7.5 Hz, 2 H) 7.30 (d, J = 9.00 Hz, 2 H), 8.15 (d, J = 9.00 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.6, 24.5, 35.5, 86.9, 119.9, 123.7, 144.5, 154.2; HREIMS calcd for $C_{11}H_{15}NO_3S$ m/z 241.077, found m/z 241.079.

8b: dark red liquid; ^{1}H NMR (C_6D_6) δ 0.99 (s, 6 H), 2.17 (d, J = 7.32 Hz, 2 H), 4.97 (ddt, J = 17.04, 1.82, 1.41 Hz, 1 H), 5.02 (ddt, J = 10.11, 1.82, 1.05 Hz, 1 H), 5.66 (ddt, J = 17.04, 10.11, 7.32 Hz, 1 H), 6.73 (d, J = 8.96 Hz, 2 H), 7.74 (d, J = 8.96 Hz, 2 H); ^{13}CNMR (C_6D_6) δ 24.97, 45.65, 85.82, 118.79, 120.09, 123.96, 133.51, 145.21, 153.61; HREIMS calcd for $C_{12}H_{16}NO_3S$ m/z 254.085, found m/z 254.085.

8c: dark red liquid; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6 H), 3.00 (s, 2 H), 7.05 (d, J = 8.76 Hz, 2 H), 7.25 (m, 5 H), 8.00 (d, J = 8.76 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 48.0, 86.3, 119.8, 123,7, 126.6, 127.9, 130.6, 136.6, 144.5, 153.9; HRFAB calculated for MH^+ m/z 304.100, found m/z 304.100.

Preparation of Alkyl 4-Nitrophenyl Sulfides. To a solution of 5 mmol of 4-nitrobenzenethiol and 0.2 g (5 mmol) of sodium hydroxide in 15 mL of ethanol in a 50-mL flask was added 5 mmol of the alkyl halide. The reaction mixture was stirred at room temperature for 12 h. Water (15 mL) was added, and the resulting mixture was transferred to a separatory funnel and extracted with 30 mL of ether. The organic layer was separated and washed with saturated aqueous K_2CO_3 (3 × 20 mL) and then saturated aqueous NH_4Cl (3 × 20 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed under reduced pressure to give the sulfide which was purified by column chromatography on silica gel using an eluent system composed of Skellysolve B and CH_2Cl_2.

3a: low melting yellow-orange solid; UV ($CDCl_3$) λ_{max} = 345 nm; ^{1}H NMR ($CDCL_3$) δ 1.40 (t, J = 7.39 Hz, 3 H), 3.00 (q, J = 7.39, 2 H), 7.35 (d, J = 9.03 Hz, 2 H), 8.10 (d, J = 9.03 Hz, 2 H); ^{13}C NMR ($CDCL_3$) δ 13.5, 25.8, 123.7, 125.8, 144.6, 147.8; HREIMS calcd for $C_8H_9NO_2S$ m/z 183.035; found m/z 183.035.

3b: yellow-orange liquid; ^{1}H NMR ($CDCl_3$) δ 3.62 (ddd, J = 6.50, 1.41, 1.01 Hz, 2 H), 5.15 (ddd, J = 10.07, 1.41, 1.15 Hz, 1 H), 5.25 (ddd, J = 16.90, 1.15, 1.01 Hz, 1 H), 5.83 (ddd, J = 16.90, 10.07, 6.50 Hz, 1 H), 7.28 (d, J = 9.05 Hz, 2 H), 8.12 (d, J = 9.05 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.9, 118.8, 123.6, 126.4, 131.7, 144.9, 146.8; HREIMS calcd for $C_9H_9NO_2S$ m/z 195.035, found 195.033.

3c: yellow-orange liquid; ^{1}H NMR ($CDCl_3$) δ 4.23 (s, 2 H), 7.30 (d, J = 8.86 Hz, 2 H), 7.20–7.40 (m, 5 H), 8.05 (d, J = 8.86 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 36.8, 123.8, 126.4, 127.7, 128.6, 128.7, 135.3, 145.0, 147.2; HREIMS calcd for $C_{13}H_{11}NO_2S$ m/z 245.051, found m/z 245.052.

Procedure for the Photolysis of 8a–c in the Presence of 11DMA, 13DMA, ACN and MAC. *Analytical Scale.* A degassed, sealed pyrex NMR tube containing a C_6D_6 solution of the sulfenate (c = 10^{-2}–10^{-3} M) and the allene or the alkene in a 1:1.5 ratio was irradiated in a Rayonet photochemical chamber reactor, Model RPR-100, equipped with 350.0-nm lamps until the complete disappearance of the sulfenate as

(7) Very few rate constants have been measured for the addition of radicals to substituted allenes.

(8) It is interesting to note that no products are observed to be formed that would have arisen by the addition of the initially formed alkoxy radical to either 11DMA or 13DMA.

(9) Walling, C.; Clark, R. T. *J. Am. Chem. Soc.* **1974**, *96*, 4530. Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

(10) (a) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; 1981; Chapter VI, p 190. (b) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; 1981; Chapter VI, p 160.

determined by ^1H NMR analysis. The relative ratios of the products were determined by integration of the NMR spectrum.

Preparative Scale. Preparative scale reactions were carried out in benzene ($c = \sim 10^{-2}$ M) in sealed 100-mL Pyrex tubes. The solvent was removed under reduced pressure, and the products were separated by MPLC on silica gel using an eluent system composed of Skellysolve F and CH_2Cl_2 and were characterized by ^1H and ^{13}C NMR spectroscopy and HRMS measurements.

9a: ^1H NMR ($CDCl_3$, on mixture of **9a−10a**, characterizable resonances only) δ 0.88 (t, J = 7.31 Hz, 3 H), 1.98 (s, 3 H), 1.99 (s, 3 H), 2.24 (t, J = 7.44 Hz, 2 H), 7.20 (d, J = 9.00 Hz, 2 H), 8.10 (d, J = 9.00 Hz, 2 H).

10a: 1H NMR ($CDCl_3$, on mixture of **9a−10a**, characterizable resonances only) δ 0.82 (t, J = 7.48 Hz, 3 H), 1.16 (s, 6 H), 5.28 (s, 1 H), 5.66 (s, 1 H), 7.50 (d, J = 9.00 Hz, 2 H), 8.15 (d, J = 9.00 Hz, 2 H); ^{13}C NMR (on mixture, $CDCl_3$) δ 8.9, 13.7, 21.2, 21.9, 23.5, 26.6, 33.5, 36.6, 42.0, 120.4, 123.6, 123.9, 125.7, 128.7, 129.4, 144.6, 144.8, 145.7, 146.9, 148.5, 151.2; NH_3 HRCIMS (on mixture) calcd for ($M + NH_4^+$) m/z 269.133, found m/z 269.133.

9b: ^1H NMR ($CDCl_3$, on mixture of **9b−10b**, characterizable resonances only) δ 1.98 (s, 3 H), 1.99 (s, 3 H), 7.20 (d, J = 9.05 Hz, 2 H).

10b: 1H NMR ($CDCl_3$, on mixture of **9b−10b**, characterizable resonances only) δ 1.20 (s, 6 H), 5.30 (s, 1 H), 5.70 (s, 1H), 7.50 (d, J = 9.05 Hz, 2H); ^{13}C NMR (on mixture, $CDCl_3$) δ 21.3, 23.6, 26.8, 32.7, 34.0, 41.8, 45.4, 115.2, 117.7, 120.8, 122.9, 123.9, 125.7, 128.3, 129.3, 134.4, 137.5, 144.8, 145.4, 145.8, 146.9, 148.2, 150.9; HREIMS (on mixture) calcd for $C_{14}H_{17}NO_2S$ m/z 263.098, found m/z 263.097.

9c: ^1H NMR ($CDCl_3$, on mixture of **9c−10c**, characterizable resonances only) δ 1.80 (s, 3 H), 2.00 (s, 3 H), 2.60 (m, 2 H), 2.80 (m, 2 H), 7.25 (d, J = 9.02 Hz, 2 H), 8.10 (d, J = 9.02 Hz, 2 H).

10c: 1H NMR ($CDCl_3$, on mixture of **9c−10c**, characterizable resonances only) δ 1.20 (s, 6H), 2.82 (s, 2 H), 5.30 (s, 1 H), 5.57 (s, 1 H), 7.60 (d, J = 9.02 Hz, 2 H), 8.15 (d, J = 9.02 Hz, 2 H); ^{13}C NMR (on mixture, $CDCl_3$) δ 21.1, 23.5, 26.7, 34.8, 36.6, 43.0, 47.1, 122.1, 122.7, 124.0, 125.9, 126.0, 126.3, 127.7, 128.3, 128.4,128.9, 129.0, 130.5, 137.9, 141.2, 144.8, 145.7, 145.8, 146.9, 148.0, 150.3; NH_3 HRCIMS (on mixture) calcd for ($M + NH_4^+$) m/z 331.148 found m/z 331.149.

11: ^1H NMR (on mixture of **11** and **12**, $CDCl_3$, characterizable resonances only) δ 1.30 (s, 6 H), 2.01 (s, 3 H), 2.03 (s, 3 H), 2.70 (s, 2 H), 5.60 (s, 1 H), 5.80 (s, 1 H), 7.40 (d, J = 8.98 Hz, 2 H).

12: ^1H NMR (on mixture of **11** and **12**, $CDCl_3$, characterizable resonances only) δ 1.96 (s, 6 H), 1.99 (s, 6 H), 2.50 (s, 4 H), 7.20 (d, J = 8.87 Hz, 4 H), 8.10 (d, J = 8.87 Hz, 4 H); ^{13}C NMR (on mixture, $CDCl_3$) δ 21.1, 22.7, 23.5, 23.8, 27.1, 33.4, 44.2, 44.8, 120.5, 122.6, 123.8, 123.9, 124.3, 125.3, 126.0, 126.4, 127.9, 144.7, 144.9, 145.3, 145.7, 147.7, 148.2, 148.2, 149.4, 149.4, 149.9, 154.0; HREIMS (on mixture) calcd for $C_{22}H_{24}N_2O_4S_2$ m/z 444.117, found m/z 444.119.

15a: (one diastereoisomer) ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.39 Hz, 3 H), 1.10 (d, J = 6.82 Hz, 3 H), 1.40 (m, 1 H), 1.60 (m, 1 H), 1.60 (m, 1 H), 1.80 (dd, J = 6.68, 0.41 Hz, 3 H), 2.30 (m, 1 H), 6.30 (dq, J = 6.68, 0.41 Hz, 1 H), 7.25 (d, J = 9.03 Hz, 2 H), 8.10 (d, J = 9.03 Hz, 2 H).

15a: (second diastereoisomer) ^1H NMR ($CDCl_3$, characterizable resonances only) δ 0.85 (t, J = 7.40 Hz, 3 H), 1.00 (d, J = 6.74 Hz, 3 H), 1.90 (d, J = 7.03 Hz, 3 H), 2.80 (m, 1 H), 6.20 (q, J = 7.03 Hz, 1 H), 7.40 (d, J = 9.02 Hz, 2 H); ^{13}C NMR (of mixture, $CDCl_3$) δ 11.8, 12.1, 15.0,15.9, 18.9,19.2, 23.4,28.2, 37.9, 44.7, 123.8, 123.9, 125.9, 126.7, 130.2, 135.0, 136.5, 139.3, 144.8, 145.0, 147.7, 149.9; NH_3 HRCIMS (on mixture) calcd for ($M + NH_4^+$) m/z 269.132, found m/z 269.135.

15b: (one diastereoisomer) ^1H NMR ($CDCl_3$) δ 1.10 (d, J = 6.78 Hz, 3 H), 1.80 (dd, J = 6.69 Hz, J = 0.5 Hz, 3 H), 2.10 (m, 1 H), 2.30 (m, 1 H), 2.50 (m, 1 H), 4.90 (m, 2 H), 5.70 (m, 1 H), 6.30 (dq, J = 6.69 Hz, J = 0.5 Hz, 1 H), 7.25 (d, J = 9.05 Hz, 2 H), 8.10 (d, J = 9.05 Hz, 2 H).

15b: (second diastereoisomer) ^1H NMR ($CDCl_3$, characteristic resonances only) δ 1.00 (d, J = 6.76 Hz, 3 H), 1.90 (d, J = 7.04Hz, 3 H), 2.20 (m, 2 H), 3.05 (m, 1 H), 6.15 (q, J = 7.04 Hz, 1 H), 7.40 (d, J = 9.00 Hz, 2 H), 8.10 (d, J = 9.00 Hz, 2 H); ^{13}C NMR (of mixture, $CDCl_3$) δ 15.9, 19.2, 39.8, 42.8, 116.6, 123.9, 125.8, 135.4, 135.9, 136.4, 144.8, 147.3; NH_3 HRCIMS (on mixture) calcd for ($M + NH_4^+$) m/z 281.131, found m/z 281.131.

15c: (one diastereoisomer) ^1H NMR ($CDCl_3$, characteristic resonances only) δ 1.00 (d, J = 6.72 Hz, 3 H), 1.67 (d, J = 7.03 Hz, 3 H), 6.05 (q, J = 7.03 Hz, 1 H), 7.35 (d, J = 9.00 Hz, 2 H).

15c: (second diastereoisomer) ^1H NMR ($CDCl_3$, characteristic resonances only) δ 1.10 (d, J = 6.59 Hz, 3H), 1.72 (d, J = 6.65 Hz, 3 H), 6.25 (q, J = 6.65 Hz, 1 H), 7.25 (d, J = 9.05 Hz, 2 H); ^{13}C NMR (of mixture, $CDCl_3$) δ 14.7, 15.9, 18.8, 19.3, 38.2, 41.6, 41.9, 44.9, 123.7, 123.9, 125.9, 126.0, 126.02, 126.5, 128.1, 129.0, 129.1, 135.2, 135.6, 135.7, 139.9, 140.0, 140.1, 144.8, 145.0, 147.2, 149.4; NH_3 HRCIMS (on mixture) calcd for ($M + NH_4^+$) m/z 331.148, found m/z 331.146.

16: (mixture of six diastereoisomers) ^1H NMR (CDCl3), see Figure 1; HREIMS (on mixture) calcd for $C_{22}H_{24}N_2O_4S_2$ m/z 444.118, found m/z 444.118.

18a. ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7.31 Hz, 3 H), 1.50 (m, 2 H), 1.58 (m, 1 H), 2.00 (m, 1 H), 3.75 (s, 3 H), 3.80 (dd, J = 7.95, 7.06 Hz, 1 H), 7.50 (d, J = 9.00 Hz, 2 H), 8.15 (d, J = 9.00 Hz, 2 H); HREIMS calcd for $C_{12}H_{15}NO_4S$ m/z 269.072, found 269.072.

19b: ^1H NMR ($CDCl_3$) δ 2.50 (m, 2 H), 2,80 (m, 1 H), 3.15 (dd, J = 13.32, 5.78 Hz, 1 H), 3.30 (dd, J = 13.32, 8.29 Hz, 1 H), 5.20 (m, 2 H), 5.40 (ddt, J = 17.45, 10.45, 7.06 Hz, 1 H), 7.40 (d, J = 9.00 Hz, 2 H), 8.10 (d, J = 9.00 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.0, 35.7, 44.6, 52.0, 118.4, 124.0, 126.9, 133.7, 145.4, 146.4, 173.6; HREIMS calcd for $C_{13}H_{15}NO_4S$ m/z 281.072, found m/z 281.074.

20b: ^1H NMR ($CDCl_3$) δ 2.50 (m, 2 H), 2.90 (m, 1 H), 3.22 (dd, J = 7.74, 3.87 Hz, 2 H), 3.30 (dd, J = 7.74, 3.87 Hz, 2 H), 5.30 (m, 2 H), 5.80 (m, 1 H), 7.40 (d, J = 9.00 Hz, 2 H), 8.15 (d, J = 9.00 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.6, 33.7, 35.3, 119.6, 120.5, 124.3, 127.8, 137.5, 146.0, 147.0; HREIMS calcd for $C_{12}H_{12}N_2O_2S$ m/z 248.062, found m/z 248.059.

Supplementary Material Available: Copies of ^1H and ^{13}C NMR spectra of the "RSAr" adducts and products derived from the reactions with 11DMA, 13DM, MAC, and ACN (24 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.