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On the Regioselectivity of Coupling of Substituted Allyl Radicals. Steric Versus FMO Control

Daniel J. Pasto* and Gaël L'Hermine
Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, IN 46556

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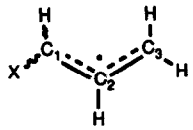
Abstract: *The photo-induced decomposition of substituted-homoallylic 4-nitrobenzenesulfenates produces substituted allyl radicals which undergo dimerization and coupling with the 4-nitrobenzenethiyl radical. The regioselectivity of the dimerization of the allyl radicals is controlled by both steric and FMO properties depending on the nature of the substituent.*

Introduction

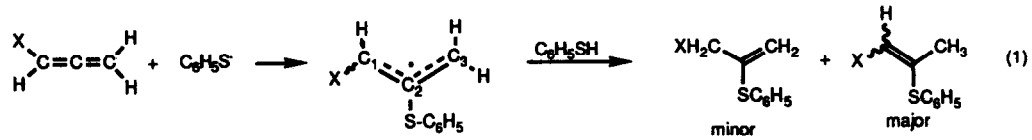
One area of research in the author's laboratories has focused on the study of the factors affecting the regioselectivity of reactions of substituted allyl radicals. The results of *ab initio* MO calculations carried out on a wide variety of both electron-donating and electron-withdrawing heterofunctionally-substituted allyl radicals indicate that the largest coefficient of the singly-occupied MO (SOMO) is at the substituted carbon atom (C_1) of the allyl radical.[1] The results of the theoretical calculations have also indicated that the introduction of such substituents onto the allyl radical greatly alters the C-C bond lengths of the allyl radical; the length of the C-C bond bearing the substituent being considerably longer than that of the nonsubstituted C-C bond;[1,2] thus, such heterofunctionally substituted allyl radicals might be more appropriately referred to as vinyl-substituted methyl radicals.[2] (In alkyl-substituted allyl radicals the effect of the alkyl group on the relative magnitudes of the coefficients at C_1 and C_3, and on the C_1-C_2 and C_2-C_3 bond lengths is much less pronounced.) The appearance of the largest coefficient of the SOMO at the heterofunctionally-substituted carbon atom of the allyl radical would suggest that in kinetically controlled reactions, i.e. reactions occurring via very early transition states controlled by frontier molecular orbital (FMO) interactions, such reactions should preferentially occur at the substituted carbon atom of the allyl radical.

The results of earlier studies on the regioselectivity of the combination reactions of alkyl-substituted allyl radicals with the methyl radical showed that the dominant mode of combination occurred at the least substituted end of the allyl radical.[3] It was suggested that steric effects controlled the regioselectivity of the combination process. As was pointed out above, however, alkyl groups attached to the terminus of the allyl radical do not cause a significant effect on the

relative magnitudes of the coefficients at C_1 and C_3 of the SOMO and, thus, steric effects might well dominate over FMO control in the radical coupling of alkyl-substituted allyl and methyl radicals. In heterofunctionalized allyl radicals, however, the coefficients at C_1 and C_3 of the SOMO differ to a much greater extent than in the alkyl-substituted allyl radicals[1] and, thus, FMO effects might be expected to exert a greater effect on the regioselectivity of the reactions of such hetero-substituted allyl radicals.



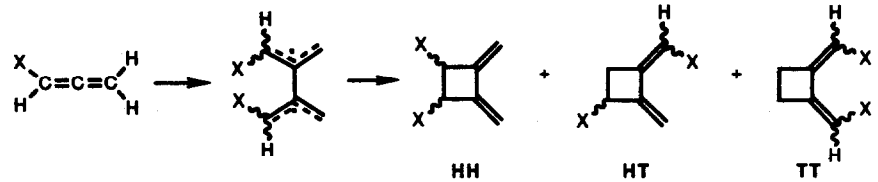
Our initial attempt to study the regioselectivity of the reaction of heterofunctionalized allyl radicals involved the free-radical, chain-addition of benzenethiol to a number of heterofunctionalized allenes [Eq (1)].[1] The results of these studies showed that hydrogen atom abstraction by the heterofunctionalized allyl radicals occurred preferentially at C_3.[1] These results were interpreted in terms of thermodynamic control, and not FMO kinetic control, dictating the regioselectivity of the hydrogen atom abstraction process despite the fact that the hydrogen atom abstraction reaction is significantly exothermic.[1]



(1)

In an attempt to observe FMO control in reactions of heterofunctionalized allyl radicals it was decided that it would be necessary to consider more exothermic reactions that should occur much earlier along the reaction coordinate in which, according to Hammond's postulate,[4] the transition state for reaction should reflect the ground state structure and electronic properties of the substituted allyl radical. One such reaction would be the ring-closure of bisallyl radicals formed in the [2 + 2], diradical-intermediate cyclodimerization of heterofunctionalized allenes [Eq (2)]. A detailed analysis of the results derived from a study of the [2 + 2] cycloaddition of heterofunctionalized allenes with 1,1-dichloro-2,2-difluoroethene,[5] in which extensive competitive [2 + 2] head-to-head (**HH**), head-to-tail (**HT**) and tail-to-tail (**TT**) cyclodimerization of the substituted allenes occurs, did not lead to a reasonable understanding of the factors controlling the regioselectivity of ring closure of the intermediate bisallyl diradical intermediates.[5] In a very recent study, however, evidence for a FMO, kinetically-controlled ring-closure of the diradical intermediates formed in the [2 + 2] cycloaddition reactions of heterofunctionalized allenes with *t*-butylthioacrylonitrile has been observed.[6] The initially formed cycloadducts **1** slowly undergo

reversible ring opening to the diradical intermediates and reclosure to ultimately form the more thermodynamically stable cycloadducts **2** [Eq (3)].[6]



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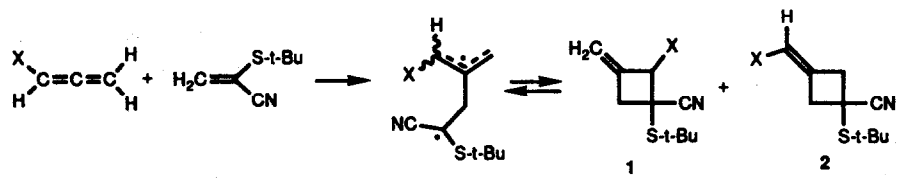
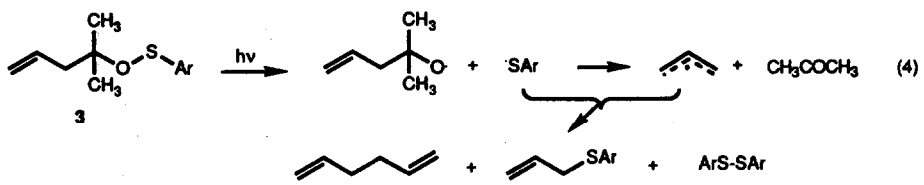


(3)

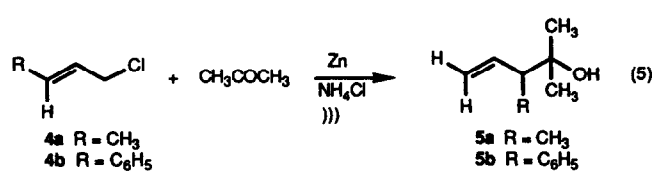
In this article is presented the results of a study on the regioselectivity of the coupling of substituted allyl radicals formed in the photo-induced decomposition of substituted homoallylic 4-nitrobenzenesulfenates illustrated in Eq (4) for the parent system.[7]



(4)

Results

Synthesis of the Substituted Homoallylic 4-Nitrobenzenesulfenates. The synthesis of the substituted homoallylic alcohols **5a** and **5b** has been accomplished in excellent yield by the zinc-induced condensation of **4a** and **4b** with acetone in saturated aqueous ammonium chloride at 25 °C with sonication [Eq (5)].[8] The chloro-substituted homoallylic alcohol **7** was similarly prepared as shown in Eq (6). The substituted homoallylic alcohols **8a** and **8b** were prepared as illustrated in Eq (7). Mixtures of *E*- and *Z*-isomers were produced in each case, with the *E*- and *Z*-isomers of **8a** being separable by column chromatography on silica gel. The substituted homoallylic alcohols were converted to the corresponding 4-nitrobenzenesulfenates by treatment with 4-nitrobenzenesulfenyl chloride in methylene chloride in the presence of triethylamine.



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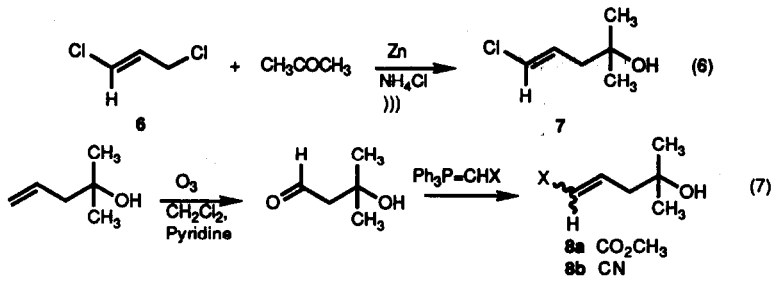
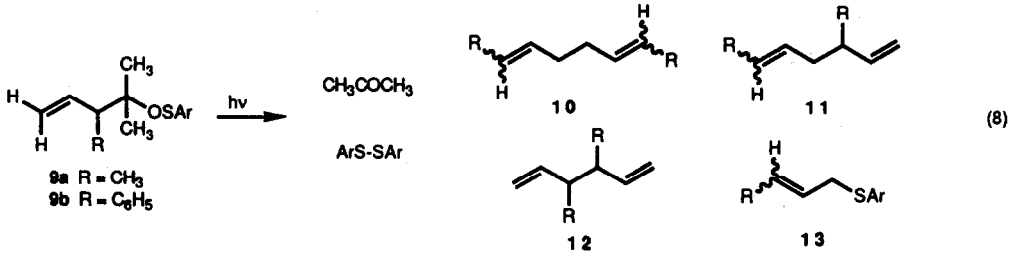
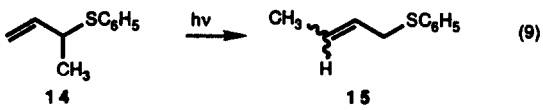


Photo-Induced Decomposition of the Substituted Homoallylic 4-Nitrobenzenesulfenates. The irradiation of **9a** in benzene-d_6 solution with 350 nm wavelength light cleanly produces a mixture of acetone, bis-(4-nitrophenyl) disulfide, methylallyl dimers **10a - 12a**, and the *E*- and *Z*-isomers of **13** [Eq (8)]. The identification of the structures of the products was accomplished by the comparison of the NMR spectrum of the product mixture with those of authentic samples of the products. The ratio of the products was readily determined by the integration of the NMR spectrum of the product mixture. An authentic sample of a mixture of the *E*- and *Z*-isomers of **13** was prepared by the reaction of crotyl chloride with 4-nitrobenzenethiolate, the stereochemistry of the *E*- and *Z*-isomers of **13** being assigned on the basis of the relative magnitudes of the vinyl proton coupling constants. An authentic sample of the methylallyl dimers **10a - 12a** was prepared by the treatment of crotyl chloride with magnesium in refluxing ether.[9] The isomeric **10a - 12a** were separated by preparative GC and their structures assigned on the basis of their NMR spectral characteristics. The ratio of the allyl sulfides **13a** to the methylallyl dimers **10a - 12a** was 59: 41, while the *E*:*Z* ratio of **13a** was 77:23. The ratio of **10a:11a:12a** was 39:47:14, with **12a** being a 1:1 mixture of the *dl*- and *meso*-isomers.



The possibility of regio- and stereoisomerization of the allyl aryl sulfides was investigated. 3-Buten-2-yl phenyl sulfide (**14**) was prepared by the methylation of the anion of allyl phenyl sulfide[10] and subjected to irradiation under conditions identical to those of the photolysis reaction. The irradiation of **14** resulted in the clean isomerization to a 77:23 mixture of the *E*- and *Z*-isomers of 2-buten-1-yl phenyl sulfide **15** [Eq (9)].

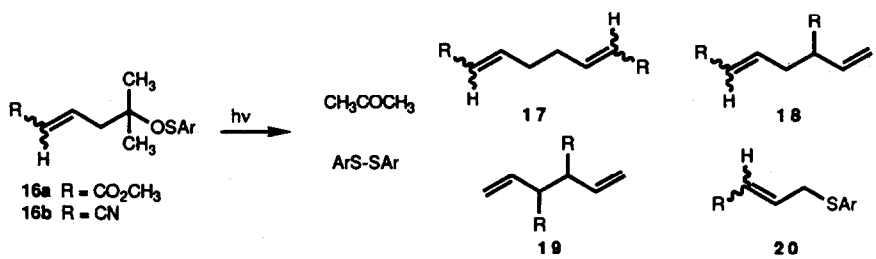


14 15 (9)

In a second control experiment a 3:1 mixture of **9a** and allyl phenyl sulfide was subjected to the photolysis conditions resulting in the formation of allyl 4-nitrophenyl sulfide in addition to the expected products derived only from **9a**.

Photo-Induced Decomposition of 9b. The photolysis of **9b** cleanly produces acetone, bis-(4-nitrophenyl) disulfide, a small amount of **5b**, the phenylallyl dimers *E*-**11b** and **12b**, and *E*-3-phenyl-2-propen-1-yl 4-nitrophenyl sulfide (*E*-**13b**). Fractions of a mixture of *E*-**11b** and **12b** and pure *E*-**13b** were isolated by preparative TLC. An authentic sample of *E*-**13b** was prepared by the reaction of *E*-cinnamyl chloride with 4-nitrophenylthiolate. An authentic sample of *E*-**11b** and **12b** was obtained as a mixture of side reaction products formed in the zinc-induced condensation of **4b** with acetone. The *E*-stereochemistry about the phenyl-substituted double bonds in **11b** and **13b** was assigned on the basis of the magnitude of the vinyl proton coupling constants. **12b** consisted of a 1:1 mixture of the *dl*- and *meso*-isomers. The integration of the NMR spectrum of the crude reaction mixture indicated a ratio of **5b**:**13b**:**11b** plus **12b** of 7:65:28, with the ratio of **11b**:**12b** of 1:1.

Photo-Induced Decomposition of E- and Z-16a. The photolysis of *E*- and *Z*-**16a** produces identical mixtures of products including acetone, bis-(4-nitrophenyl) disulfide, the substituted allyl dimers *E,E*-**17a**, *E*-**18a** and **19a**, and *E*-**20a** [Eq (10)]. The *E*-stereochemistry in the products has been assigned on the basis of the magnitude of the vinyl proton coupling constants and the expectation that the *E*-isomer is the more thermodynamically stable stereoisomer formed under the radical-induced isomerizing conditions. The integration of the NMR spectrum of the crude reaction mixture indicated the formation of *E*-**20a** to **17a** - **19a** in a ratio of 63:37, with the **17a**:**18a**:**19a** ratio being 19:65:16. **19a** is formed as an ~1:1 ratio of the *dl*- and *meso*-isomers.



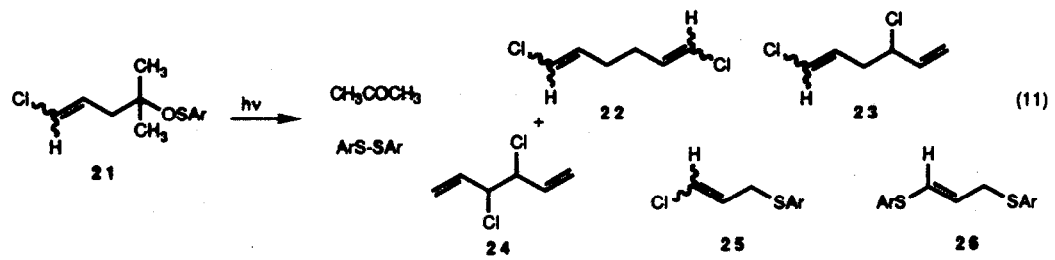
16a R = CO_2CH_3
16b R = CN

(10)

Photo-Induced Decomposition of 16b. The photolysis of a 55:45 mixture of *E*- and *Z*-**16b** produces predominantly a 55:45 mixture of *E*- and *Z*-**20b**. The NMR spectrum of the crude reaction mixture did not contain any resonances characteristic of the vinyl groups of **18b** or **19b**. Weak resonances appeared in the δ 5.4 - 5.6 and 6.6 - 6.8 regions similar to those for the vinyl

protons of NCCH=CH- of **8a** and **16b**; however, attempts to isolate the material(s) responsible for these weak resonances was not successful. It appears that very little, or no, coupling of the cyanoallyl radical occurred to produce the cyano-substituted allyl dimers **17b** - **19b**.

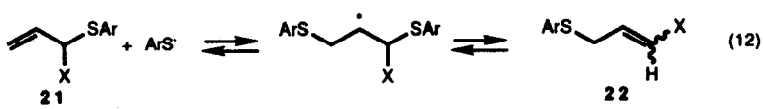
Photo-Induced Decomposition of 21. The photolysis of *E*-**21** produces a mixture of the *E*- and *Z*-isomers of **25**, along with small amounts of bis-(4-nitrophenyl) disulfide, the chloroallyl dimers **22** - **24** (~5%) and the bis-sulfide **26** [Eq (11)]. The NMR spectrum of the volatile fraction showed the presence of **22**, **23** and **24** in a 11:55:34 ratio. Attempted separation and isolation of the individual isomers **22** - **24** from the benzene-d_6 solvent could not be accomplished. Column chromatography of the nonvolatile residue on silica gel led to the isolation of pure fractions of *E*- and *Z*-**25** and *E*-**26**.



(11)

Discussion

Formation of Substituted-Allyl 4-Nitrophenyl Sulfides. In all cases the most thermodynamically stable substituted-allyl 4-nitrophenyl sulfides are observed as the coupling products. The results of the two control experiments indicate that regio- and stereoisomerization occur under the reaction conditions. The isomeriza-tion reactions involve the reversible addition of an arylthiyl radical to the substituted-allyl aryl sulfide as illustrated in Eq (12). Prior *ab initio* MO calculations on substituted propenes indicate that the 1-substituted-1-propenes are lower in energy than the 3-substituted-1-propenes[1], and *E*-,*Z* equilibration resulting in the formation of the lower energy *E*-stereoisomer. Unfortunately, the regio- and stereoisomerization of the coupling products wipes out the desired information concerning the regio- and stereoselectivity of the combination reactions of the substituted-allyl radicals with the 4-nitrophenylthiyl radicals.



(12)

Analysis of the Regioselectivity of the Coupling of the Substituted Allyl Radicals. The regioisomerization of the substituted-allyl aryl sulfides induced by the reversible addition of the

arylthiyl radical to the allyl aryl sulfides does not occur with the substituted-allyl dimers, although stereoisomerization of the substituted double bonds does occur as indicated by the results derived with *E*- and *Z*-**16a**. The relative percentages of C_3-C_3, C_3-C_1 and C_1-C_1 coupling are summarized in Table 1, along with the total preferences for C_3- and C_1-coupling. The self-coupling of the methylallyl radical shows a preference for C_3-C_3 coupling by an ~2:1 ratio, and suggests that steric effects dominate over FMO SOMO effects. The regioselectivity preference for the coupling of the chloroallyl radical is very similar. The methoxycarbonyl-substituted allyl radical shows little preference for C_3 versus C_1 coupling. This must be due a trade-off between steric effects that would favor C_3-C_3 coupling and FMO SOMO effects that would favor C_1-C_1 coupling. However, the phenyl-substituted allyl radical displays a distinct preference (3:1) for C_1-C_1 coupling. In this case the FMO SOMO controlled coupling dominates over the steric effects that would favor C_3-C_3 coupling. The fact that C_1-C_1 coupling of the methyl-, methoxycarbonyl- and phenyl-substituted allyl radicals produces *dl*- to *meso*-isomer ratios of ~1:1 suggests that the transition structures for substituted-allyl radical coupling occurs rather early along the reaction coordinate with a rather long C---C interaction distance in which steric and FMO interactions are not highly developed resulting in low degrees of regioselectivity of coupling.

Table 1. Regioselectivities of Coupling of Substituted Allyl Radicals

Substituent	C_1-C_1	C_1-C_3	C_3-C_3	C_1(total)	C_3(total)
-CH_3	14	47	39	38	62
-CO_2CH_3	16	65	19	48	52
-Cl	34	55	11	62	38
-C6H5	50	50	---	75	25

C_1 and C_3 "totals" are based on percentages of $[(C_1\text{-}C_1) + 1/2(C_1\text{-}C_3)]$ and $[1/2(C_1\text{-}C_3) + (C_3\text{-}C_3)]$.

Summary

Overall, these results of this study suggest that the transition structures for substituted-allyl radical coupling occur very early along the reaction coordinate involving rather long C---C distances in which both electronic and steric effects can competitively contribute to the regioselectivity of the coupling process.

Experimental

General Procedure for the Preparation of Homoallylic Alcohols. To an open flask containing 20 mL of saturated aqueous ammonium chloride 2.6 g (40 mmol) of zinc dust and 200

mmol of acetone at 25 °C was added 40 mmol of the allyl halides **4a**, **4b** or **6**. Ultrasonic and magnetic stirring were alternately applied for periods of 25 and 5 min for a minimum of 3 hr, or until the total disappearance of the zinc. The aqueous solution was filtered and extracted with 25 mL of ether. The organic extract was washed with three 10-mL portions of water and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was purified by column chromatography.

2,3-Dimethyl-4-penten-2-ol (**5a**) (76%) was prepared as described above and has been characterized previously.[11]

2-Methyl-3-phenyl-4-penten-2-ol (**4a**) (88%). ^1H NMR: ($CDCl_3$) δ 1.16 (s, 3H), 1.19 (s, 3 H), 1.66 (s, 1 H), 3.27 (d, J = 9.27 Hz, 2 H) 5.25 (ddd, J = 10.14, 1,10, 0.6 Hz, 1 H), 5.34 (ddd, J = 16.96, 1.10, 0.8 Hz, 1 H), 5.95 (ddd, J = 16.96, 10.14, 9.27 Hz, 1 H), 7.2 - 7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.6, 27.7, 30.7, 61.7, 72.1, 117.6, 126.5, 128.1, 129.0, 137.7, 141.1. EIMS gives no parent ion. Isobutane CIMS gives an intense peak at m/z 233 corresponding to $(M + C_4H_9)^+$.

5-Chloro-2-methyl-4-penten-2-ol (**7**) (60%). ^1H NMR: ($CDCl_3$) δ 1.26 (s, 3 H), 1.30 (s, 3 H), 2.40 (s, 1 H), 4.31 (d, J = 9.20 Hz, 2 H), 5.15 (ddd, J = 16.87, 1.93, 0.62 Hz, 1 H), 5.19 (dd, J = 9.95, 1.92 Hz, 1 H), 6.30 (ddd, J = 16.87, 9.95, 9.65 Hz, 1 H), 7.2 - 7.4 (m, 5 H). ^{13}C NMR ($CDCl_3$) δ 25.1, 26.5, 72.1, 73.2, 119.1, 134.9. EIMS gives no parent ion. Isobutane CIMS gives a base peak at 117 and 119 (1 Cl atom) corresponding to 1-chloro-4-methyl-1,3-pentadiene.

Preparation of *E*- and *Z*-5-Carbomethoxy-2-methyl-4-penten-2-ol (*E*-**8a** and *Z*-**8a**). Ozone was passed through a solution of 4 mmol of 2-methyl-4-penten-2-ol dissolved in 40 mL of CH_2Cl_2 containing 6 mmol of pyridine at -78 °C until a bluish color persisted. The reaction mixture was allowed to warm to 25 °C and was then washed with two 10-mL portions of aqueous hydrochloric and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was dissolved in 40 mL of CCl_4 and 1.67 g (4 mmol) of carbomethoxymethylene triphenylphosphorane was added. The solution was refluxed for 24 hr under an argon atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using 1:4 hexane-ether as eluent giving pure fractions of *E*- and *Z*-**8a**.

E-**8a**. ^1H NMR: ($CDCl_3$) δ 1.27 (s, 6 H), 1.40 (s, 1 H), 2.39 (dd, J = 7.76, 1.35 Hz, 2 H), 3.74, (s, 3 H), 5.91 (dt, J = 15.62, 1.35 Hz, 1 H), 7.03 (dt, J = 15.62, 7.76 Hz, 1 H). ^{13}C NMR: ($CDCl_3$) δ 29.4, 46.42, 51.4, 70.6, 124.0, 145.0, 166.7. EIMS gives no parent ion. Isobutane CIMS give MH^+ at m/z 159.

Z-**8a**. ^1H NMR: ($CDCl_3$) δ 1.27 (s, 6 H), 2.30 (br s, 1 H), 2.85 (dd, J = 7.89, 1.52 Hz, 2 H), 3.72 (3, 3 H), 5.96 (dt, J = 11.61, 1.52 Hz, 1 H), 6.44 (dt, J = 11.61, 7.89 Hz, 1 H). ^{13}C NMR: ($CDCl_3$) δ 29.5, 42.2, 51.1, 70.9, 121.5, 146.0, 167.2. EIMS gives no parent ion. Isobutane CIMS give MH+ at m/z 159.

Preparation of *E*- and *Z*-5-Cyano-2-methyl-4-penten-2-ol (*E*-**8b** and *Z*-**8b**). A solution of 4.0 mmol of *t*-butyl lithium in pentane was added to 4.0 mmol of diethyl

cyanomethylphosphonate in 20 mL of CH_2Cl_2 at -78 °C under an argon atmosphere. To the solution was added 4.0 mmol of the hydroxyaldehyde prepared as outlined in the foregoing section. The reaction mixture was allowed to warm to 25 °C and was stirred at 25 °C for 2 hr. The reaction mixture was washed with two 10-mL portions of 10% hydrochloric acid and with two 10-mL portions of cold water and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane-ether as eluent giving a 1:6 ratio of a mixture of *E*-**8b** and *Z*-**8b**.

E-**8b**: ^{1}H NMR: ($CDCl_3$) δ 1.23 (s, 6 H), 1.90 (s, 1 H), 2.37 (dd, *J* = 7.60, 1.43 Hz, 2 H), 5.38 (dt, *J* = 16.35, 1.43 Hz, 1 H), 6.80 (dt, *J* = 16.35, 7.60 Hz, 1 H). ^{13}C NMR: ($CDCl_3$) δ 29.4, 47.2, 70.4, 102.2, 117.2, 152.1. EIMS (on mixture) gives no parent ion. Isobutane CIMS: MH+ m/z 126.

Z-**8b**: ^{1}H NMR: ($CDCl_3$) δ 1.26 (s, 6 H), 1.90 (s, 1 H), 2.57 (dd, *J* = 7.70, 1.25 Hz, 2 H), 5.44 (dt, *J* = 11.05, 1.25 Hz, 1 H), 6.66 (dt, *J* = 11.05, 7.70 Hz, 1 H). ^{13}C NMR: ($CDCl_3$) δ 29.4, 45.5, 70.7, 101.5, 116.0, 151.3.

General Procedure for the Synthesis of the Substituted Homoallylic Sulfenates. All operations are carried out in an unlighted hood and in aluminum-wrapped flasks. To a 50 mL three-neck flask containing the homoallylic alcohol (4 mmol) and freshly distilled triethylamine (11.5 mmol) in 15 mL of anhydrous CH_2Cl_2 at -78 °C was added a solution of 4-nitrobenzenesulfenyl chloride (5 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at -78 °C for 15 min and then allowed to warm to 25 °C for 30 min. The organic phase was extracted with two 10-mL portions of cold 3% hydrochloric acid and then with three 10-mL portions of ice water and then dried (MgSO4). The solvent was removed under reduced pressure producing essentially quantitative yields of the light-sensitive sulfenates. Most sulfenates proved to be stable enough to purify by rotating disk chromatography on silica gel under reduced light conditions.

2,3-Dimethyl-4-penten-2-yl 4-Nitrobenzenesulfenate (**9a**). **9a** was isolated by chromatographic purification as a dark red liquid. ^{1}H NMR: (C_6D_6) δ 0.94 (d, *J* = 6.90 Hz, 3 H), 0.96 (s, 3 H), 0.98 (s, 3 H), 2.32 (dqdd, *J* = 8.20, 6.80, 1.10, 0.6 Hz, 1 H), 4.97 (ddd, *J* = 16.56, 1.85, 1.10 Hz, 1 H), 4.99 (ddd, *J* = 10.85, 1.85, 0.6 Hz, 1 H), 5.67, (ddd, *J* = 16.56, 10.85, 8.20 Hz, 1 H), 6.75 (d, *J* = 9.04 Hz, 2 H), 7.75 (d, *J* = 9.04 Hz, 2 H). ^{13}C NMR: (C_6D_6) δ 15.0, 22.4, 23.0, 47.7, 87.9, 116.1, 120.1, 124.0, 139.8, 145.3, 153.6. EIMS produces no parent ion. Isobutane CIMS shows MH+ m/z 268.

2-Methyl-3-phenyl-4-penten-2-yl 4-Nitrobenzenesulfenate (**9b**). **9b** was purified by chromatography giving a dark red liquid. ^{1}H NMR: (C_6H_6) δ 1.05 (s, 6 H), 3.34 (d, *J* = 9.40 Hz, 1 H), 5.03 (ddd, *J* = 16.91, 1.80, 0.96 Hz, 1 H), 5.09 (ddd, *J* = 10.16, 1.80, 0.29, 1 H), 6.20 (ddd, *J* = 16.91, 10.16, 9.40 Hz, 1 H), 6.66 (d, *J* = 9.10 Hz, 2 H), 7.15 - 7.20 (m, 5 H), 7.72, (d, *J* = 9.10 Hz, 2 H). No parent ion could be observed by either EIMS or CIMS.

E-5-Carbomethoxy-2-methyl-4-penten-2-yl 4-Nitrobenzenesulfenate (*E*-**16a**). *E*-**16a**, a dark red liquid, underwent partial decomposition during attempted chromatographic purification, but a sufficiently pure fraction was isolated for characterization of its structure and its photo-induced

decomposition products. ^{1}H NMR: (C_6D_6) δ 0.91 (s, 6 H), 2.09 (d, J = 7.65 Hz, 2 H), 3.43 (s, 3 H), 5.83 (d, J = 15.60 Hz, 1 H), 6.75 (d, J = 8.73 Hz, 2 H), 6.97 (dt, J = 15.60, 7.65 Hz, 1 H), 7.79 (d, J = 8.73 Hz, 2 H). ^{13}C NMR: ($CDCl_3$) δ 25.0, 43.6, 51.1, 85.3, 120.3, 124.0, 125.0, 143.2, 145.5, 152.8, 166.0. EIMS showed no parent ion. Isobutane CIMS showed MH^+ at m/z 312.

Z-5-Carbomethoxy-2-methyl-4-penten-2-yl 4-Nitrobenzenesulfenate (*Z*-**16a**). *Z*-**16a** was obtained as a dark red liquid. ^{1}H NMR: (C_6D_6) δ 1.01 (s, 6 H), 3.08 (dd, J = 7.38, 1.50 Hz, 2 H), 3.34 (s, 3H), 5.84 (dt, J = 11.55, 1.50 Hz, 1 H), 6.00 (dt, J = 11.55, 7.32 Hz, 2 H), 6.72 (d, J = 9.09 Hz, 2 H), 7.74 (d, J = 9.09 Hz, 2 H). ^{13}C NMR: ($CDCl_3$) δ 25.1, 39.8, 50.7, 85.8, 120.3, 122.1, 124.0, 144.2, 145.4, 152.9, 166.2. EIMS showed no parent ion. Isobutane CIMS showed MH^+ at m/z 312.

E- and Z-5-Cyano-2-methyl-4-penten-2-yl 4-Nitrobenzenesulfenates (*E*-**16b** and *Z*-**16b**). An inseparable mixture of *E*-**16b** and *Z*-**16b** was isolated by rotating-disk chromatography as a dark liquid. The ^{1}H NMR resonances of the *E*- and *Z*-isomers have been assigned on the basis of the relative intensities and magnitudes of the coupling constants. ^{1}H NMR: (C_6D_6) *Z*-**16b**; δ 0.76, (s, 6 H), 1.78 (dd, J = 7.70, ~0.4 Hz, 2 H), 4.70, (dt, J = 10.98, ~0.4 Hz, 1 H), 5.79, (dt, J = 10.98, 7.70 Hz, 1 H), 6.72 (d, J = 9.00 Hz, 2 H), 7.78 (d, J = 9.00 Hz, 2 H). ^{13}C NMR: (C_6D_6) δ 24.9, 42.8, 85.0, 102.7, 115.7, 125.2, 134.2, 143.6, 148.3, 152.5. *E*-**16b**: ^{1}H NMR: (C_6D_6) δ 0.86 (s, 6 H), 2.33 (dd, J = 7.62, 0.70 Hz, 2 H), 4.63 (dt, J = 16.17, 0.70 Hz, 1 H), 6.09 (dt, J = 16.17, 7.62 Hz, 1 H), 6.72 (d, J = 6.09 Hz, 2 H), 7.82 (d, J = 9.00 Hz, 2 H). ^{13}C NMR: (C_6D_6) δ 24.8, 44.4, 84.8, 103.5, 117.0, 126.2, 135.0, 145.5, 149.2, 152.5. No parent ion could be observed by either EIMS or CIMS.

3-Chloro-2-methyl-4-penten-2-yl 4-Nitrobenzenesulfenate (**21**). **21** was purified by chromatography giving a dark red oil. ^{1}H NMR: (C_6D_6) δ 1.03 (s, 3 H), 1.08 (s, 3 H), 4.18 (ddd, J = 8.90, 1.10, 0.57 Hz, 2 H), 4.92 (ddd, J = 10.14, 1.13, 0.57 Hz, 1 H), 5.05 (ddd, J = 16.87, 1.13, 1.10 Hz, 1 H), 5.71 (ddd, J = 16.87, 10.14, 8.90 Hz, 1 H), 6.83 (d, J = 8.92 Hz, 2 H), 7.76 (d, J = 8.92 Hz, 2 H). ^{13}C NMR: (C_6D_6) δ 22.2, 22.7, 69.1, 86.6, 119.5, 120.4, 124.0, 134.5, 145.5, 152.6. No parent ion could be observed by EIMS or CIMS.

Preparation of a Mixture of E- and Z-2-Buten-1-yl 4-Nitrophenyl Sulfide (*E*-**13a** and *Z*-**13a**). To 15 mL of ethanol was added 0.2 g (5 mmol) of sodium hydroxide, 0.78 g (5 mmol) of 4-nitrobenzenethiol and 0.49 mL (5 mmol) of crotyl chloride. The mixture was stirred at 25 °C for 12 hr. Water (15 mL) was added to the reaction mixture was extracted with 30 mL of ether. The extract was washed with water and dried ($MgSO_4$), and the solvent was removed under reduced pressure giving an 83:17 mixture of *E*- and *Z*-**13a** as a colorless liquid.

E-**13a**. ^{1}H NMR: ($CDCl_3$) δ 1.70 (ddt, J = 6.45, 1.60, 1.20 Hz, 3 H), 3.64 (dqd, J = 6.80, 1.21, 1.20 Hz, 2 H), 5.52 (dtq, J = 15.12, 6.80, 1.60 Hz, 1 H), 5.77 (dtq, J = 15.12, 6.45, 1.21 Hz, 1 H), 7.53 (d, J = 9.04 Hz, 2 H), 8.12 (d, J = 9.04 Hz, 2 H). ^{13}C NMR: (C_6D_6) δ 17.7, 34.4, 123.8, 124.90, 126.4, 129.1, 145.3, 147.6.

Z-**13a**. ^{1}H NMR: ($CDCl_3$) δ 1.74 (*J* = 6.91 Hz), 3.70 (*J* = 7.43 Hz), 5.55, 5.73, 7.53 (d, *J* = 9.04 Hz), 8.12 (d, J = 9.04 Hz). (All of the coupling constants and relative integrals could not be assigned due to the overlapping with the resonances of *E*-**13a**). ^{13}C NMR: ($CDCl_3$) δ 12.8, 29.0, 123.8, 124.2, 126.5, 129.1, 145.3, 147.5. HR EIMS (on mixture): exact mass calcd for $C_{10}H_{11}NO_2S$, 209.0510; found, 209.0515.

E-1-Phenyl-1-propen-3-yl 4-Nitrobenzenesulfenate (E-13b). *E*-**13b** was prepared in 72% yield from 0.78 g (5 mmol) of 4-nitrobenzenethiol and 0.76 g (5 mmol) of cinnamyl chloride following the procedure described above. The crude reaction mixture was treated with 25 mL of cold hexane to induce the precipitation of the product. ^{1}H NMR: ($CDCl_3$) δ 3.84 (d, *J* = 6.93 Hz, 2 H), 6.24 (dt, *J* = 15.68, 6.93 Hz, 1 H), 6.63 (d, *J* = 15.68 Hz, 1 H), 7.20 - 7.36 (m 5 H), 7.36 (d, *J* = 8.88 Hz, 2 H), 8.11 (d, *J* = 8.88 Hz, 2 H). ^{13}C NMR: ($CDCl_3$) δ 35.0, 123.1, 123.8, 126.3, 126.8, 128.0, 128.6, 134.0, 136.1, 145.2, 146.8. HR EIMS: exact mass calcd for $C_{15}H_{13}NO_2S$, 271.0667; found, 271.0665.

Preparation of a Mixture of E- and Z-1-Chloro-1-propen-3-yl 4-Nitrophenyl Sulfides (E-25 and Z-25). A mixture of *E*- and *Z*-**25** was prepared in 67% yield from 0.78 g (5 mmol) of 4-nitrobenzenethiol and 0.47 mL (5 mmol) of 1,3-dichloropropene following the procedure described above. The mixture was purified by column chromatography on silica gel using a 95:5 mixture of hexanes-ether as eluent giving a viscous oil of a 1:1 mixture of *E*- and *Z*-**25**.

Z-**25**. ^{1}H NMR: ($CDCl_3$) δ 3.85 (dd, *J* = 7.20, 1.40 Hz, 2 H), 5.89 (dt, *J* = 7.20, 7.16 Hz, 1 H), 6.24 (dt, *J* = 7.16, 1.40 Hz, 1 H), 7.37 (d, *J* = 9.01 Hz, 2 H), 8.14 (d, *J* = 9.01 Hz, 2 H). ^{13}C NMR: ($CDCl_3$) δ 28.7, 122.0, 123.9, 126.4, 126.9, 145.4, 146.0.

E-**25**. ^{1}H NMR: ($CDCl_3$) δ 3.68 (dd, *J* = 7.17, 1.28 Hz, 2 H), 6.00 (dt, *J* = 13.25, 7.17 Hz, 1 H), 6.25 (dt, *J* = 13.25, 1.28 Hz, 1 H), 7.36 (d, *J* = 8.97 Hz, 2 H), 8.15 (d, *J* = 8.97 Hz, 2 H). ^{13}C NMR: ($CDCl_3$) δ 32.7, 122.0, 124.0, 127.3, 127.4, 145.6. HR EIMS (on mixture): exact mass calcd for $C_9H_8{}^{35}ClNO_2S$, 228.9964; found, 228.9966.

Preparation of a Mixture of the Methylallyl Dimers ***10a - 12a.*** A mixture of **10a - 12a** was prepared following the procedure of Doering et. al.[9] by refluxing 4.9 mL (50 mmol) of crotyl chloride with 0.9 g (37 mmol) of magnesium in anhydrous ether. The mixture of isomers was separated by preparative GC on a 12 ft x 1/4 in. SE-30 on Chromosorb P at 80 °C.

E,E-**10a**. ^{1}H NMR: ($CDCl_3$) δ 1.64 (m, 6 H), 2.02 (br s, 4 H), 5.40 - 5.45 (m, 4 H).

E,Z-**10a**. ^{1}H NMR: ($CDCl_3$) δ 1.60 (br d, *J* = 5.9 Hz, 3 H), 1.65 (br d, *J* = 6.5 Hz, 3 H), 2.00 - 2.05 (m, 4 H), 5.35 - 5.50 (m, 4 H).

Z,Z-**10a**. (Only a trace amount formed as suggested by GC, and could not be isolated and characterized by ^{1}H NMR.)

E-**11a**. ^{1}H NMR: ($CDCl_3$) δ 0.98 (d, *J* = 6.68 Hz, 3 H), 1.65 (ddd, *J* = 4.60, 1.20, 1.20 Hz, 3 H), 1.90 - 2.10 (m , 2 H), 2.16 (dddd, *J* = 13.50, 6.80, 6.80, 1.20 Hz, 1 H), 4.92 (ddd, *J* = 10.34, 1.50, 1.10 Hz, 1 H), 4.96 (ddd, *J* = 17.25, 1.70, 1.50 Hz, 1 H), 5.33-5.50 (m, 2 H),5.75 (ddd, *J* = 17.25, 10.34, 6.92 Hz, 1 H).

Z-**11a**. ^{1}H NMR: ($CDCl_3$) δ 1.05 (d, *J* = 6.65 Hz, 3 H), 1.60 (br d, *J* = 6.55 Hz, 3 H), 2.02 - 2.10 (m, 2 H), 2.18 (br ddd, *J* = 13.73, 6.85, 6.85 Hz, 1 H), 4.92 (ddd, *J* = 10.34, 1.50, 1.10 Hz, 1 H), 4.98, (ddd, *J* = 17.25, 1.70, 1.50 Hz, 1 H), 5.39 (dtq, *J* = 10.85, 7.00, 1.58 Hz, 1 H), 5.50 (dqt, *J* = 10.85, 6.65, 1.44 Hz, 1 H), 5.75 (ddd, *J* = 17.25, 10.34, 6.91 Hz, 1 H).

12a. ^{1}H NMR: ($CDCl_3$) δ 0.95 (d, *J* = 6.69 Hz, 6 H), 0.97 (d, *J* = 6.69 Hz, 6 H), 2.05 (m, 2 H), 2.15 (m, 2 H), 4.92 - 5.00 (m, 8 H), 5.60 - 5.80 (m, 4 H).

Preparation of a Mixture of the Phenylallyl Dimers ***10b*** *-* ***12b***. A mixture of **10b**, **11b** and **12b** was obtained in a ratio of 15:48:38 as side-reaction products in ~3% yield from the preparation of **5b** and was isolated by rotating-disk chromatography on silica gel. Identification of the individual isomers was made possible by correlation of the coupling constants in the NMR spectrum of the mixture. HR EIMS (of mixture): exact mass calcd for $C_{18}H_{18}$, 234.1409; found 234.1414.

E,E-**10b**. ^{1}H NMR: ($CDCl_3$) δ 2.38 (m, 4 H), 6.27 (br d, *J* = 15.84 Hz, 2 H), 6.38 (d, J = 15.84 Hz, 2 H), 7.00 - 7.20 (m, 10 H).

E-**11b**. ^{1}H NMR: ($CDCl_3$) δ 2.64 (m, 2 H), 3.42 (m, 1 H), 5.06 (ddd, J = 16.49, 1.40, 1.40, 1 H), 5.07 (ddd, J = 9.29, 1.40, 1.00 Hz, 1 H), 6.02 (ddd, J = 16.49, 9.29,7.43 Hz, 1 H), 6.12 (dt, J = 15.78, 7.07, 1 H), 6.44 (d, J = 15.78 Hz, 1 H).

1:1 mixture of *dl*- and *meso*-**12b**. ^{1}H NMR: ($CDCl_3$) δ 3.59 - 3.66 (m, 4 H), 4.78 (br d, *J* = 16.89 Hz, 2 H), 4.86 (br d, *J* = 10.25 Hz, 2 H), 5.03 (br d, *J* = 16.71 Hz 2 H), 5.08 (br d, *J* = 10.08 Hz, 2 H), 5.85 (ddd, *J* = 16.89, 10.25, 7.75 Hz, 1 H), 5.05 (ddd, *J* = 16.71, 10.08, 7.75 Hz, 1 H).

General Procedure for the Photolysis of the Substituted-Homoallylic 4-Nitrobenzenesulfenates. Approximately 10 - 20 μL of the substituted sulfenate was dissolved in 0.7 mL of C_6D_6 in a capped Pyrex NMR tube and subjected to irradiation in a Rayonet Photochemical Chamber Reactor, Model RPR-100, at 350 nm at 35 °C. Periodic NMR analysis was carried out until the NMR spectrum showed the complete disappearance of the sulfenate. During the photolysis there was a continual disappearance of the reddish color of the 4-nitrobenzenesulfenate, and the precipitation of bis-(4-nitrophenyl)disulfide. The NMR spectra of the final reaction mixtures were recorded. The products were identified by the comparison with the ^{1}H NMR chemical shifts of the authentic materials whose syntheses were described above, and the products described below. The ratios of the products were determined by the integration of the NMR spectra. The results of the photolysis experiments have been given in the Results section of this article.

*Photo-Induced Decomposition of E- and Z-5-Carbomethoxy-2-methyl-4-penten-2-yl 4-Nitrobenzene-sulfenates E-***16a** *and Z-***16a**). Irradiation of *E*-**16a** and *Z*-**16a** produced identical mixtures of products composed of bis-(4-nitrophenyl)disulfide, E-1carbomethyxy-1-propen-3-yl 4-nitrophenyl sulfide (E-20a) and a mixture of the carbomethoxyallyl dimers **17a** - **19a** which were isolated by column chromatography on Silica gel eluting with a 1:4 mixture of ether-pentane. The structures of **17a** - **19a** were easily assigned on the basis of the NMR spectrum of the mixture.

E-**16a**. ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H), 3.78 (dd, *J* = 6.63, 1.43 Hz, 2 H), 6.03 (dt, *J* = 15.50, 1.43 Hz, 1 H), 6.96 (dt, *J* = 15.50, 6.63 Hz, 1 H), 7.34 (d, *J* = 8.93 Hz, 2 H), 8.14 (d, *J* = 8.93 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 33.4, 51.8, 124.1, 124.2, 127.2, 145.2, 145.7, 166.0. HR EIMS: exact mass calcd for $C_{11}H_{11}NO_4S$, 253.0409; found, 253.0406.

dl- and *meso*-**19a**. ^{1}H NMR ($CDCl_3$) δ 3.50 (m, 4 H), 3.70 (s, 3 H), 5.21 (br d, *J* = 17.36 Hz, 2 H), 5.24 (br d, *J* = 10.55, 2 H), 5.77 (ddd, *J* = 17.36, 10.55, 6.10 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 34.3, 48.7, 51.5, 52.1, 118.3, 123.1, 134.6, 145.1, 166.5, 167.0.

E-**18a**. ^{1}H NMR ($CDCl_3$) δ 2.48 (m, 1 H), 2.66 (m, 1 H), 3.19 (m, 1 H), 3.70 (s, 3 H), 3.72 (s, 3 H), 5.18 (br d, J = 15.77, 1 H), 5.20 (br d, *J* = 10.99 Hz, 1 H), 5.80 (ddd, *J* = 16.34, 10.99, 8.35 Hz, 1 H), 5.87 (dt, *J* = 15.77, 1.40 Hz, 1 H), 6.86 (ddd, *J* = 16.34, 7.26, 7.23 Hz, 1 H).

E,E-**17a**. ^{1}H NMR ($CDCl_3$) δ 2.40 (m, 4 H), 3.75 (s, 6 H), 5.85 (d, *J* = 15.60 Hz, 2 H), 6.94 (dt, *J* = 15.60, 5.60 Hz, 2 H).

Photo-Induced Decomposition of the Mixture of E- and Z-5-Cyano-2-methyl-4-penten-2-yl 4-Nitroben-zenesulfenates (E- and Z-16b). The irradiation of the mixture of *E*- and *Z*-**16b** produces a mixture of bis-(4-nitrophenyl) disulfide, acetone, and a mixture of the *E*- and *Z*-1-cyano-1-propen-3-yl 4-nitrophenyl sulfides (*E*- and *Z*-**20b**). There was no evidence for the formation of **17b**, **18b**, or **19b**. A mixture of *E*- and *Z*-**20b** was isolated by column chromatography on silica gel.

E-**20b**. ^{1}H NMR ($CDCl_3$) δ 3.95 (dd, *J* = 7.70, 1.24 Hz, 2 H), 5.44 (dd, *J* = 10.72, 1.24 Hz, 1 H), 6.49 (dt, *J* = 10.72, 7.70 Hz, 1 H), 7.45 (d, *J* = 8.98 Hz, 2 H), 8.33 (d, *J* = 8.95 Hz, 2 H).

Z-**20b**. ^{1}H NMR ($CDCl_3$) δ 3.78 (dd, *J* = 6.42, 1.64 Hz, 2 H), 5.57 (dt, *J* = 16.15, 1.64, 1 H), 6.75 (dt, *J* = 16.15, 6.42 Hz, 1 H), 7.35 (d, *J* = 8.95 Hz, 2 H), 8.24 (d, *J* = 8.95 Hz, 2 H). No parent ion could be observed by EIMS or CIMS.

Photo-Induced Decomposition of 3-Chloro-2-methyl-4-penten-2-yl 4-Nitrobenzenesulfenate (**21**). The irradiation of **21** produced a mixture of bis-(4-nitrophenyl) disulfide, acetone, *E*- and *Z*-3-chloro-2-propen-1yl 4-nitrophenyl sulfide (*E*- and *Z*-**25**), a mixture of the chloroallyl dimers **22** - **24**, and a small amount of the bis-sulfide **26**. The volatile components were removed on a vacuum line. Because of the small amount of **22** - **24** formed they could not be separated from the solvent. Silica gel chromatography of the nonvolative residue using ether as eluent afforded a mixture of *E*- and *Z*-**25** and **26**.

22 - **24** could be identified by their ^{1}H NMR spectral characteristics in the aliphatic C-H region. **22**: δ 2.02 - 2.04 (m). **23**: δ 2.42 - 2.49 (m) and 3.03 (m) in a 2:1 ratio. **24**: δ 3.13 - 3.16 (m). The ratio of the regioisomers was easily determined by integration of the cited regions in the NMR spectrum.

E-**26**. ^{1}H NMR ($CDCl_3$) δ 3.76 (dd, *J* = 6.20, 0.75 Hz, 2 H), 5.73 (dt, *J* = 15.72, 0.75 Hz, 1 H), 5.89 (dt, J = 15.72, 6.20 Hz, 1 H), 7.33 (d, *J* = 8.83 Hz, 2 H), 8.13 (d, *J* = 8.83 Hz, 2 H). HR EIMS: exact mass calcd for $C_{15}H_{12}N_2O_4S_2$, 348.0238; found, 348.0236.

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