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Experimental and Theoretical Study of the Radical-Chain Addition of Benzenethiol to Heterosubstituted Allenes

Daniel J. Pasto* and Gaël L'Hermine

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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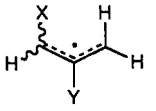
The radical-chain addition of benzenethiol to phenylallene (PHA), methoxyallene (MEOA), carbomethoxyallene (CBA), cyanoallene (CNA), chloroallene (ClA), and (phenylthio)- and [(4-methylphenyl)thio]allene (PHSA and MPHSA) has been studied. In all cases, except with ClA, the benzenethiyl radical undergoes attack at the central allene carbon atom to produce a heterosubstituted allyl radical (1). With ClA, the majority of attack occurs at the central carbon atom with a minor amount of attack occuring at C_3. The intermediate substituted allyl radicals undergo hydrogen atom transfer to produce only the 1-substituted-2-(phenylthio)-1-propenes as a mixture of *E* and *Z* isomers which, in general, become thermodynamically equilibrated under the reaction conditions. The *E*:*Z* product ratios vary considerably, being 18:82 from MEOA, 20:80 from ClA, 40:60 from PHSA and MPHSA, 49:51 from PHA, 61:39 from CNA, and 72:28 from CBA. Ab initio molecular orbital calculations have been carried out on models of the starting allenes, the substituted allyl and vinyl radical intermediates, and the product-substituted propenes. The regioselectivity of attack by the benzenethiyl radical on the substituted allenes appears not to be controlled by frontier molecular orbital (FMO) interactions, which is opposite to our earlier interpretation of the relative reactivities and regioselectivities of the radical-chain addition of benzenethiol to alkyl-substituted allenes. The relative reactivities and regioselectivities of the addition to the heterosubstituted allenes observed in this study indicate that the reaction is not FMO controlled but is thermodynamically controlled. The addition of the benzenethiyl radical occurs at C_2 of the substituted allenes, which is calculated to be quite exothermic (>20 kcal mol^{-1}), compared to the formation of the vinyl radical by attack at C_3, and which produces the more stable substituted allyl radical intermediates. Similarly, the regioselectivity of the hydrogen atom transfer to the substituted allyl radicals is also not controlled by FMO interactions but also occurs to produce the more thermodynamically stable 1-substituted-2-(phenylthio)-1-propenes. The relative stabilities of the anti- and syn-substituted allyl radicals and the (*E*)- and (*Z*)-1-substituted-2-(phenylthio)-1-propenes are discussed in terms of 1,4-long-range π-bonding and antibonding interactions and bond dipolar interactions.

Introduction

The results derived studies on reactions that involve the formation of heterosubstituted allyl radicals (1) have revealed a wide range of regioselectivities in the reactions of these intermediates. The reactions in which these substituted allyl radicals have been formed include the (2 + 2) cycloaddition reactions of heterosubstituted allenes with 1,1-dichloro-2,2-difluoroethene (1122)[1,2] and diethyl fumarate (DEF),[2,3] the cyclodimerization of heterosubstituted allenes,[1] and the reduction of 3-substituted-2-propen-1-yl bromides.[4] A summary of these regioselectivities is presented in Table I.



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In an effort to gain an understanding of the factors that affect the regioselectivities of the reactions of 1, as well as those governing the regioselectivity of radical addition to heterosubstituted allenes, we have undertaken an experimental and theoretical study of the free-radical, chain addition of benzenethiol to phenylallene (PHA), methoxyallene (MEOA), carbomethoxyallene (CBA), cyanoallene (CNA), chloroallene (ClA) and (phenylthio)- and [(4-methylphenyl)thio]allene (PHSA and MPHSA). The results of a previous study on the radical-chain addition of benzenethiol to alkyl-substituted allenes suggested that the relative reactivities and regioselectivities of addition were controlled by frontier molecular orbital interactions.[5]

Table I. Regioselectivities in the Reactions of Substituted Allyl Radicals

X	reaction	$X—C_1{=}{=}C_2{=}{=}C_3$	
C_2H_5	C_6H_5SH[a]	2	98
	1122[b]	17	83
	DEF[c]	56	44
C_6H_5	1122[d]	55	45
	DEF[d]	15	85
	CD[d]	100	0
	R_3SnH[e]	15	85
CH_3O	1122[f]	30	70
	DEF[g]	53	47
Cl	1122[f]	33	67
	DEF[g]	16	84
	CD[f]	56	44
	R_3SnH[e]	0	100
CN	1122[f]	24	76
	CD[f]	0	100
	R_3SnH[e]	4	96
C_6H_5S	1122[f]	38	62
	CD[f]	64	36

[a] Reference 6. [b] Reference 7. [c] Reference 8. [d] Reference 2. [e] Reference 4. [f] *Reference* 1. [g] Reference 3.

Table II. *E*:*Z* Thermodynamic Ratios of the 2-(Phenylthio)-1-substituted-1-propenes

substituted propene	*E*:*Z*	substituted propene	*E*:*Z*
3 (X = OCH_3)	18:82	2 (X = C_6H_5)	49:51
6 (X = Cl)		5 (X = CN)	61:39
8 (X = SC_6H_5)	40:60	4 (X = CO_2CH_3)	72:28

The results of the present study, however, indicate that FMO interactions do not control the relative reactivities or the regioselectivities of the addition of benzenethiyl to the heterosubstituted allenes.

Results

Phenylallene (PHA). Benzenethiol (BT) readily adds to PHA to produce a mixture of only the two adducts (*E*)-2 and (*Z*)-2 in a ratio of 49:51. Refluxing the mixture in $CDCl_3$ in the presence of a catalytic quantity of iodine

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(1) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1986**, *51*, 3611.
(2) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1986**, *51*, 1676.
(3) Pasto, D. J.; Yang, S.-H., unpublished results.
(4) Pasto, D. J.; Huang, N.-Z., unpublished results.
(5) Pasto, D. J.; Warren, S. E. *J. Org. Chem.* **1981**, *46*, 2842.
(6) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837.
(7) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670.
(8) Pasto, D. J.; Yang, S.-H. *J. Am. Chem. Soc.* **1984**, *106*, 152.

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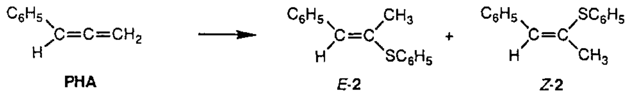
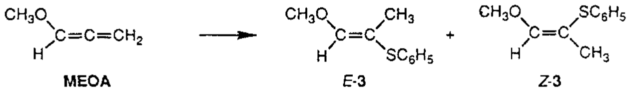
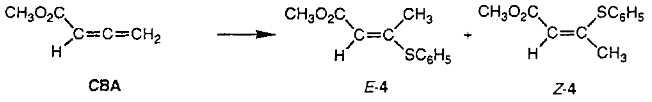


resulted in decomposition of the adducts. Thus, in this case, it is not possible to ascertain whether the ratio of (E)-**2** to (Z)-**2** is kinetically controlled or whether equilibration has occurred. The NMR spectra of the two stereoisomers were not sufficiently different that an accurate assignment of chemical shifts and coupling constants was possible. The mixture was separated by rotating-disk, thin-layer chromatography giving the pure stereoisomers. (These were the only benzenethiol adducts of the substituted allenes that could be separated by chromatographic techniques. The other systems underwent apparent hydrolytic decomposition or polymerization on attempted chromatographic separation.) The assignment of the stereochemistry in (E)-**2** and (Z)-**2** is based on the relative magnitudes of the allylic long-range coupling constants, which are generally larger when syn, and the relative chemical shifts of the vinyl hydrogens, which are calculated to appear at lower field in the Z isomers.[9] The long-range allylic coupling constants in (E)-**2** and (Z)-**2** are 1.26 and 1.30 Hz, while the chemical shifts are δ 6.675 and 6.707. Although the differences are not very large, the trends in coupling constants and chemical shifts are consistent with each other. However, in view of the fact that the two stereoisomers are formed in virtually the same amounts, the possible misassignment of stereochemistry will not have a critical impact on later arguements.

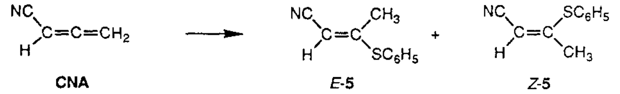
Methoxyallene (MEOA). BT cleanly adds to MEOA to produce only the two stereoisomeric adducts (E)-**3** and (Z)-**3** in a ratio of 18:82. Heating in the presence of iodine produced no change in the ratio of (E)-**3** to (Z)-**3**, indicating that the observed ratio represents that of the thermodynamic equilibrium between the two stereoisomers. In this case, unfortunately, both of the long-range allylic coupling constants are the same (1.34 Hz). The assignment of stereochemistry has been made on the basis that in the isomer assigned as (Z)-**3** the vinyl hydrogen appears at lower field in the NMR ($\Delta\delta$ = 0.18 ppm). Calculations of the chemical shifts of the vinyl hydrogens[9] indicates that the vinyl hydrogen of the Z isomer should appear at lower field by 0.23 ppm. The results of ab initio MO calculations on models for (E)- and (Z)-**3** indicate that the Z isomer is lower in energy and consistent with the experimental observations.



Carboxymethoxyallene (CBA). BT reacts cleanly with CBA to produce a mixture of only the two adducts (E)-**4** and (Z)-**4** in a ratio of 72:28. Heating this mixture with a catalytic quantity of iodine does not result in a change in this ratio, indicating that the ratio represents the thermodynamic equilibrium between the two stereoisomers. In this case the assignment of stereochemistry is quite unambiguous, the long-range allylic coupling constant in (Z)-**4** (1.15 Hz) being larger that in (E)-**4** (1.00 Hz) and the chemical shift of the vinyl hydrogen in (Z)-**4** (δ 5.86) being at lower field that in (E)-**4** (δ 5.23).

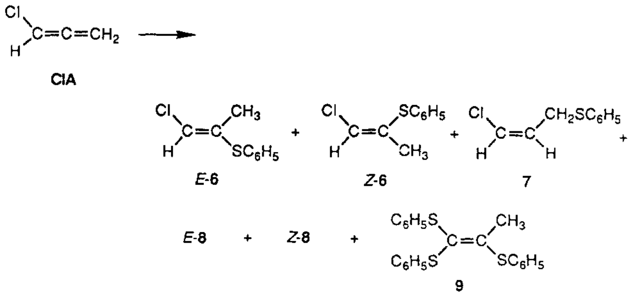


Cyanoallene (CNA). *Extreme caution must be exercised when working with CNA.*[10] CNA reacts with BT to produce a mixture of only (E)-**5** and (Z)-**5** in a ratio of 61:39. The stereochemistry of the two adducts is readily assigned on the basis of the allylic long-range coupling constants, 1.35 Hz in (Z)-**5** and 0.75 Hz in (E)-**5**, and the chemical shifts of the vinyl hydrogens, δ 5.24 in (Z)-**5** and 4.52 in (E)-**5**.



Chloroallene (ClA). ClA reacts very slowly with BT to produce a complex mixture of compounds. Photoinitiation using an ultraviolet lamp was required. The NMR spectrum of the crude reaction mixture indicated the presence of several products. Analysis by MS indicated the presence of 1:1 ClA:BT adducts, the presence of adducts in which the chlorine has been replaced by phenylthio, and the presence of 1:2 adducts with *m/e* 366. The lower molecular weight adducts could be removed by trap-to-trap distillation on a vacuum line, leaving behind the higher molecular weight products. Attempted rotating-disk, thin-layer chromatography resulted in the isolation of only one of the adducts, **7**. The assignment of the other structures has been accomplished by a combination of NMR and MS data and by comparing the NMR spectral characteristics with those of adducts derived in the addition of BT to PHSA.

The stereochemistry of (E)-**6** and (Z)-**6** has been assigned by comparison of the allylic long-range coupling constants and the results of theoretical calculations. The long-range coupling constant in the major isomer (J = 1.44 Hz) is larger than that in the minor isomer (J = 1.34 Hz), suggesting that the major isomer has the Z stereochemistry. However, a comparison of the chemical shifts of the vinyl hydrogens leads to the opposite assignment; the vinyl hydrogen in the major isomer appearing at higher field (δ 6.05) compared to the minor isomer (δ 6.30). In this case the relative values of the long-range coupling constants and the chemical shifts predict opposite stereochemistries. The results of ab initio MO calculations on the two isomers indicates that the Z isomer is lower in energy (see later section of Theoretical Calculations). As an excellent correlation is observed between the observed thermodynamic equilibrium constants for the other 2-(phenylthio)-1-substituted-1-propenes encountered in this study with the relative calculated total energies the stereochemistry of the major isomer is assigned as the Z isomer. The ratio of (E)-**6** to (Z)-**6** is 20:80.



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[9] Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhill, S. *Tetrahedron* **1969**, *25*, 2023.

[10] Extreme caution must be exercised in the handling of cyanoallene. It is capable of causing severe allergic reactions in some individuals. The authors suggest the use of double, heavy-duty rubber gloves when handling this material.

Table III. Relative Reactivities of Heterosubstituted Allenes toward Radical-Chain Addition of Benzenethiol

allene	rel reactivity[a]	allene	rel reactivity[a]
MEOA	2.34	PHA	0.55
MPHSA	1.44	ClA	0.15
DMA	1.00	CBA	<0.09
PHSA	0.88		

[a] Relative reactivity of 1,1-dimethylallene assigned as 1.00. See ref 5.

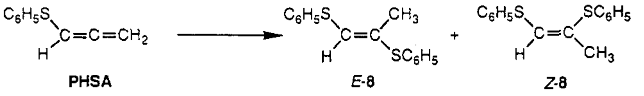
Table IV. Total (au) and π MO (eV) Energies of Substituted Allenes

		C_1=C_2		C_2=C_3	
substituent	E_{tot}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
H_2C=CH—	-192.470 75	-8.608	+3.497	-10.217	+4.881
HS—	-517.742 58	-8.909[a] -12.083[b]	+4.877	-10.207	+3.840
HO—	-190.433 50	-9.261	+5.409	-10.378	+4.269
Cl—	-574.099 13	-10.156[c]	+3.176	-10.807	+4.477
NC—	-207.289 23	-10.555	+2.963	-11.400	+3.875
HO_2C—[d]	-303.035 63	-10.747	+2.783	-10.908	+4.317
HO_2C—[e]	-303.035 84	-10.734	+2.797	-11.001	+4.294

[a] Predominantly sulfur nonbonded pair AO. [b] Predominantly C_1–C_2 MO. [c] Extensive contribution from the chlorine nonbonded pair AO. [d] Transoid conformation abut the system. [e] Cisoid conformation about the π system.

The structure of **7** is clearly evident from its NMR spectrum, which shows a double doublet for the methylene hydrogens and two double triplets for the vinyl hydrogens. The cis stereochemistry is assigned on the basis of the relatively small vicinal coupling constant of 7.30 Hz between the vinyl hydrogens. The ratio of (*E*)-**6**:(*Z*)-**6**:**7** formed in this reaction is 6.0:30.6:36.4. The structures of the two adducts in which the chlorine has been replaced by phenylthio has been assigned as (*E*)-**8** and (*Z*)-**8** and are formed in a ratio of 46.6:53.4. The structure of the 1:2 adduct is believed to be **9** on the basis of its mass spectrum, which shows a parent ion with *m*/*e* of 366, and its NMR spectrum, which shows only one high-field singlet.

(Phenylthio)allene (PHSA). BT adds to PHSA to produce a mixture of only (*E*)-**8** and (*Z*)-**8** in a ratio of 60:40.[11] Treatment with iodine results in partial decomposition and a change in the ratio of (*E*)- to (*Z*)-**8** to 40:60. The assignment of stereochemistry of the adducts is based on the relative magnitudes of the allylic long-range coupling constants of 1.20 Hz in (*Z*)-**8** and 1.00 Hz in (*E*)-**8** and the fact that the vinyl hydrogen of (*Z*)-**8** appears at lower field (δ 6.44) than that of (*E*)-**8** 6.40).

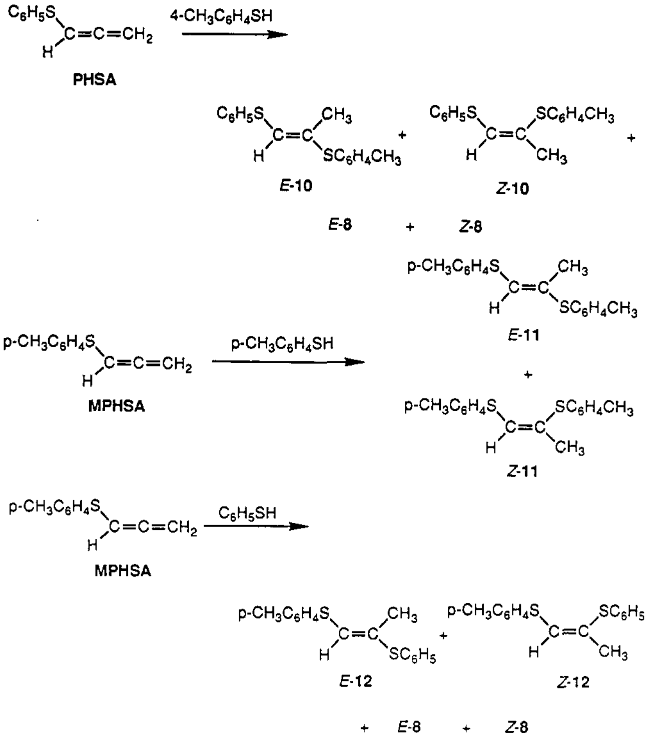


A series of crossover experiments were carried out to detect the extent of arylthio exchange that might be occurring during these addition reactions. PHSA was reacted with 4-methylbenzenethiol, producing a mixture of (*E*)-**10** and (*Z*)-**10** in a ratio of 38:62, accompanied by 9% of a mixture of (*E*)- and (*Z*)-**8** and <0.5% of a mixture of (*E*)- and (*Z*)-**11**. The mass spectrum of the reaction mixture confirmed the presence of the three sets of adducts. (An authentic mixture of (*E*)-**11** and (*Z*)-**11** was prepared by the addition 4-methylbenzenethiol to [(4-methylphenyl)-thio]allene, MPHSA.) The reaction of MPHSA with BT produced a mixture of (*E*)-**12** and (*Z*)-**12** in a ratio of 40:60, along with 5% of a mixture (*E*)- and (*Z*)-**11** and approximately 0.5% of a mixture of (*E*)- and (*Z*)-**8**. (Attempted isomerization with iodine led to decomposition.) The stereochemistry of the adducts **10**, **11**, and **12** has been assigned in a manner similar to that for **8**.

Table V. π MO Coefficients of the Substituted Allenes

		C_1=C_2		C_2=C_3	
substituent	MO[a]	C_1	C_2	C_2	C_3
H_2C=CH—	O	0.421	0.432	0.560	0.570
	U	0.435	0.615	0.737	0.768
HS—	S[b]	0.369	0.428		
	O[c]	0.455	0.289	0.490	0.538
	U	0.818	0.721	0.561	0.679
HO—	O	0.492	0.542	0.526	0.558
	U	0.831	0.721	0.592	0.701
Cl—	O[d]	0.475	0.466	0.521	0.537
	U	0.801	0.776	0.565	0.547
NC—	O	0.522	0.440	0.541	0.554
	U	0.5611	0.748	0.715	0.775
HO_2C—[e]	O	0.572	0.451	0.491	0.535
	U	0.438	0.692	0.774	0.816
HO_2C—[f]	O	0.577	0.443	0.516	0.541
	U	0.445	0.703	0.762	0.812

[a] O designates the occupied π MO; U designates the unoccupied π MO. [b] The predominantly nonbonded pair on sulfur MO with a coefficient of 0.710. [c] The predominantly C_1–C_2 π MO. [d] The coefficient on chlorine is 0.561. [e] Transoid conformation of the conjugated π system. [f] Cisoid conformation of the conjugated π system.



Determination of Relative Reactivities. The relative reactivities of the substituted allenes were measured in a series of competition experiments. Equimolar quantities of the substituted allenes were reacted with a deficient amount of BT, and the extent of reaction of the two substituted allenes was determined by integration of the NMR spectrum using an internal standard for comparison of the amounts of the two substituted allenes before and after reaction. The results are given in Table III.

Theoretical Calculations. Ab initio MO calculations have been carried out on models for the starting substituted allenes, the intermediate substituted allyl and vinyl radicals, and the final product propenes using the

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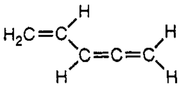
[11] The ratios of (*E*)- to (*Z*)-**8**, -**11**, and -**13** varied somewhat from run to run, indicating that complete thermodynamic equilibration had not been achieved.

Table VI. Total (au) and SOMO (eV) Energies of 1-Substituted-allyl (21) and 1-Substituted-2-mercaptoallyl (27) Radicals

X	X—CH⩵CH⩵CH$_2$ E_{tot}	X—CH⩵CH⩵CH$_2$ E_{SOMO}	X—CH⩵C(SH)⩵CH$_2$ E_{tot}	X—CH⩵C(SH)⩵CH$_2$ E_{SOMO}
syn H$_2$C=CH—	-193.098 87	-8.628	-590.141 43	-8.926
anti H$_2$C=CH—	-193.095 44	-8.680	-590.140 39	-9.002
syn HO—	-191.049 68	-8.362	-588.0933 39[a]	-8.666[a]
			-588.092 86	-8.726
anti HO—	-191.050 32	-8.340	-588.094 55[a]	-8.713[a]
			-588.094 28	-8.718
syn HS—	-513.352 79	-8.307	-910.393 73	-8.533
anti HS—	-513.353 08	-8.405	-910.396 66	-8.655
syn Cl—	-547.710 05	-9.431	-971.749 54	-9.727
anti Cl—	-547.711 03	-9.474	-971.753 27	-9.809
syn NC—	-207.908 40	-10.095	-604.949 46	-10.530
anti NC—	-207.907 60	-10.089	-604.950 73	-10.568
t-syn HO$_2$C—	-303.649 08	-9.940	-700.670 66	-10.400
t-anti HO$_2$C—	-303.644 70	-9.858	-700.687 53	-10.383
c-syn HO$_2$C—	-303.649 49	-9.942	-700.678 24	-10.372
c-anti HO$_2$C—	-303.646 12	-9.853	-700.689 51	-10.389

[a] Geometry optimized.

GAUSSIAN86 package of programs.[12] Calculations have been carried out on ClA and CNA and on **13–16** as models for



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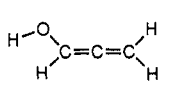

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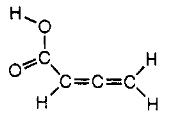

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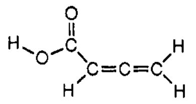

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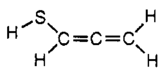

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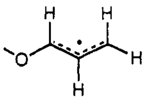
the other substituted allenes at the 4-31G level with full geometry optimization. The conformations shown in structures **13–16** were considered to be the least sterically congested in the parent more highly substituted systems. The total energies and the energies of the occupied and unoccupied π MO's are given in Table IV, and the coefficients are given in Table V. The calculated structural parameters are given in Table I of the supplementary material (see paragraph at end of paper).

Preliminary calculations on the substituted allyl radicals were carried out on the *syn* and *anti*-hydroxyallyl radicals **17** and **18** and on the 2-mercapto-substituted hydroxyallyl radicals **19** and **20** to determine the effect of substitution



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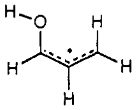

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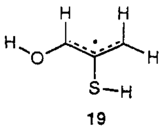

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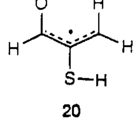

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of H by SH at C_2. Although the conformations about the C=C—S—H in **19** and **20** may not be the lowest in energy, these orientations of the O–H and S–H preclude any intermolecular hydrogen bonding between the groups which would result in a lower energy and affect the difference

Table VII. SOMO Coefficients of 1-Substituted-allyl (21) and 1-Substituted-2-mercaptoallyl (27) Radicals

X	X—CH⩵CH⩵CH$_2$ C_1	C_2	C_3	X—CH⩵C(SH)⩵CH$_2$ C_1	C_2	C_3
syn H$_2$C=CH—	-0.600	-0.005	+0.518	-0.618	-0.020	+0.450
anti H$_2$C=CH—	-0.610	-0.008	+0.510	-0.623	-0.021	+0.412
syn HO—	-0.703	-0.082	+0.575	-0.722	-0.091	+0.504[a]
				-0.722	-0.089	+0.509
anti HO—	-0.693	-0.075	+0.590	-0.725	-0.075	+0.502[a]
				-0.722	-0.083	+0.493
syn HS—	-0.609	-0.071	+0.450	-0.600	-0.089	+0.413
anti HS—	-0.607	-0.084	+0.440	-0.613	-0.087	+0.333
syn Cl—	-0.642	-0.019	+0.578	-0.645	-0.036	+0.553
anti Cl—	-0.641	-0.012	+0.590	-0.671	-0.030	+0.444
syn NC—	-0.601	+0.074	+0.636	-0.635	+0.053	+0.326
anti NC—	-0.605	+0.082	+0.641	-0.636	+0.065	+0.346
t-syn HO$_2$C—	-0.599	+0.073	+0.657	-0.655	+0.065	+0.519
t-anti HO$_2$C—	-0.584	+0.100	+0.666	-0.644	+0.068	+0.419
c-syn HO$_2$C—	-0.601	+0.074	+0.657	-0.662	+0.059	+0.518
c-anti HO$_2$C—	-0.588	+0.098	+0.666	-0.644	+0.065	+0.403

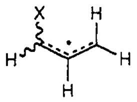
[a] Geometry optimized.

Table VIII. Total Energies of the Substituted Vinyl Radicals 28

X	E_{tot}, au	X	E_{tot}, au
(*E*)-HO	-191.008 39	(*Z*)-HS	-513.318 57
(*Z*)-HO	-191.010 34	(*Z*)-Cl	-574.678 06

in energy between the *E* and *Z* isomers. (This was encountered in the calculations on the substituted propenes which will be discussed later.) These calculations were carried out at the UHF 4-31G level with full geometry optimization. As expected, the substitution of H by SH resulted in only minor changes in the energies and coefficients of the SOMOs of the hydroxyallyl radicals. On substitution of H by SH the energies of the SOMOs of **17** and **18** were slightly lowered from -8.362 to -8.666 eV and -8.340 to -8.713 eV, respectively, due to the increase in the nuclear potential field. Similarly, only slight changes were observed in the coefficients at C_1 and C_3, changing from 0.703 and -0.575 in **17** to 0.722 and -0.504 in **19** and 0.693 and -0.590 in **18** to 0.725 and -0.502 in **20**.

In view of these minor changes in the energies of the SOMOs and the coefficients and to conserve computer time, full geometry optimization calculations were first carried out at the 4-31G level on the substituted allyl radicals **21–26**[13] (Chart I), followed by single-point calcu-



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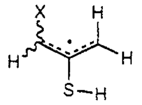

27

lations on the mercapto-substituted allyl radicals **27** in which the C–S and S–H bond lengths and the C–S–H bond angle were assigned the optimized values calculated for **19** and **20**. The total and SOMO energies of the substituted allyl radicals are given in Table VI, and the coefficients of the SOMOs are given in Table VII. The calculated structural parameters are given in Table II of the supplementary material.

Calculations have been carried out on a few of the substituted vinyl radicals **28** for comparison of their total energies with those of similarly substituted allyl radicals **21**. All of the substituted vinyl radicals **28** were calculated to possess considerably higher energies than the corresponding allyl radicals (see Table VIII), and calculations

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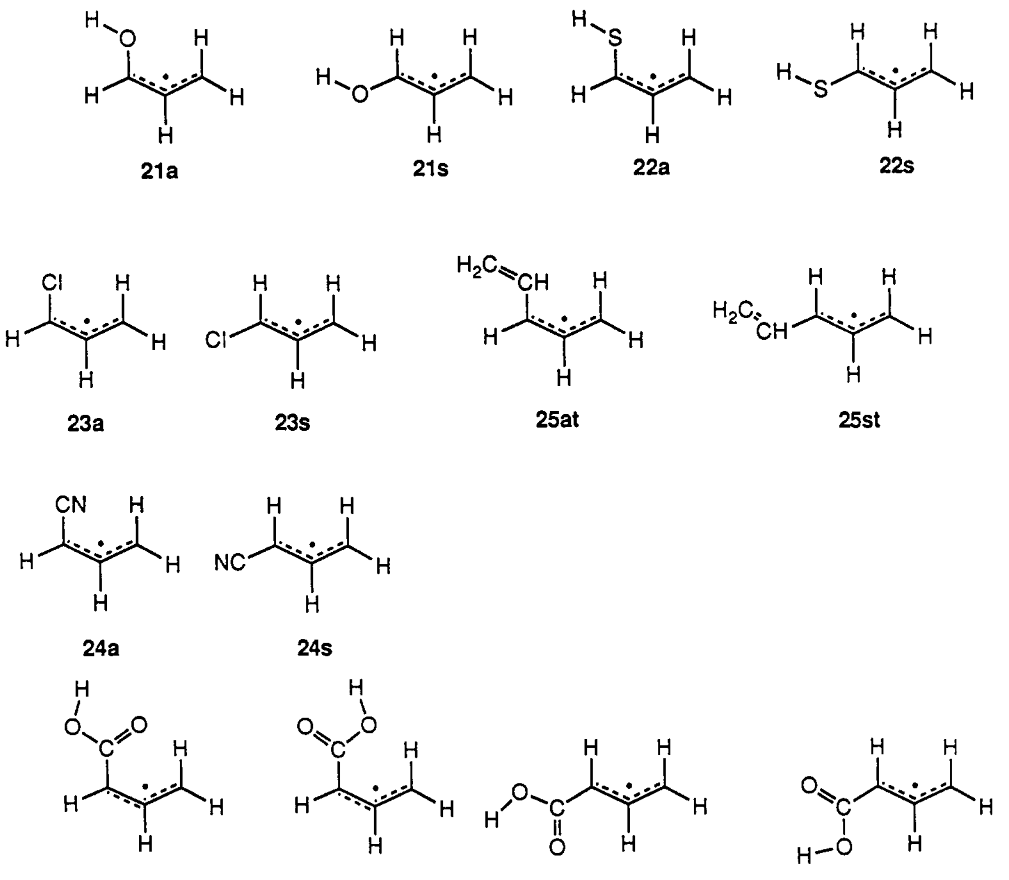
[12] GAUSSIAN86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburg, PA, 1984.

[13] The letters indicating stereochemistry are a for anti and s for syn stereochemistry of the allyl radical and c for cisoid and t for transoid conformations about the conjugated π system.

Chart I



21a **21s** **22a** **22s**

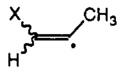
23a **23s** **25at** **25st**

24a **24s**

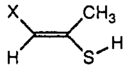
26ac **26at** **26sc** **26st**

on the other stereoisomers and on the other substituted vinyl radicals were not carried out. Calculations were not carried out on the 3-substituted-1-propen-2-yl radicals in view of the fact that they should be very close in energy to **28** and thus higher in energy than the substituted allyl radicals.

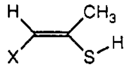
Calculations have been carried out on the *E* and *Z* isomers of the 2-mercapto-1-substituted-1-propenes **30** and **31**. Initial calculations were carried out on the various



28

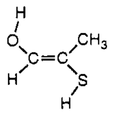


30

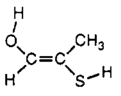


31

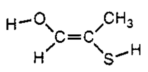
conformational isomers of 1-hydroxy-2-mercapto-1-propene (**29a–g**) at the fully geometry-optimized 4-31G level. The two potentially hydrogen-bonded conformations **29e** and **29g** are calculated to be lowest in energy (−588.698 43 and −588.699 31 au, respectively). As these conformations are not considered to be realistic for the 1-methoxy-2-(phenylthio)-1-propene, these conformations have been ignored. For the most reasonable comparisons of the conformations of (*E*)- and (*Z*)-**29** we have selected **29c** and **29f** in which



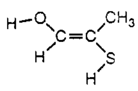
29a



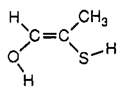
29b



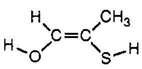
29c



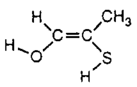
29d



29e



29f



29g

Table IX. 4-31G/6-31G* Total Energies of the (*E*)- and (*Z*)-2-Mercapto-1-substituted-1-propenes 30 and 31

X	ΔE_{tot}, au 30	 31
HO—	−589.425 95 (1.6)[a,b]	−589.428 50 (0.0)
	−589.428 76 (1.5)[c]	−589.431 15 (0.0)
Cl—	−973.473 43 (1.4)[b]	−973.475 64 (0.0)
	−973.478 28 (1.1)[c]	−973.480 09 (0.0)
HS—	−912.082 44 (0.7)[b]	−912.083 62 (0.0)
H_2C=CH—	−591.462 30 (1.3)[b]	−591.464 43 (0.0)
NC—	−606.315 18 (0.0)[b]	−606.314 27 (0.6)
HO_2C—[d]	−702.192 99 (1.2)[b]	−702.194 94 (0.0)
HO_2C—[e]	−702.196 95 (0.6)[b]	−702.197 90 (0.0)
HO_2C—[d]	−702.202 15 (0.0)[c]	−702.201 27 (0.6)

[a] Relative energies in kcal mol^{-1} are given in parentheses. [b] 6-31G* single-point calculation on the 4-31G optimized structures. [c] 6-31G* optimized energies. [d] Transoid conformation about the conjugated π system. [e] Cisoid conformation about the conjugated π system.

no intramolecular hydrogen bonding is possible and also in which the groups attached to the oxygen and sulfur atoms are oriented in the least sterically congested direction with respect to each other.[14] The difference in energy between **29c** and **29f** at the 4-31G level was much smaller than the experimental value of Δ*G* for the equilibrium between (*E*)- and (*Z*)-**3** (0.10 versus 0.90 kcal mol^{-1}, respectively). Calculations were then carried out on **29c** and **29f** at the 6-31G* level with full geometry optimization resulting in a difference in energy of 1.50 kcal mol^{-1}, somewhat closer to the experimental value. Single-point

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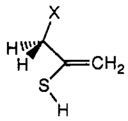
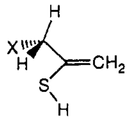
[14] The 4-31G geometry optimized energies for the other isomers of **29** are **29a**, −588.694 88; **29b**, −588.693 37; **29c**, −588.694 54; **29d**, −588.694 88; and **29f**, −588.604 70.

calculations at the 6-31G* level on the 4-31G optimized structures gave a difference in energy of 1.60 kcal mol^{-1}, very close to that derived from the 6-31G* geometry optimization calculations. To conserve computer time, the remaining substituted propenes having the conformations about the X substituents shown in **21**–**26** were optimized at the 4-31G level, and then single-point calculations were carried out at the 6-31G* level. In all cases, except with X = CO_2H, the differences in total energy at this level corresponded well with the experimental ΔG's for the equilibria between **30** and **31**. At the optimized 4-31G level **30** (X = CO_2H) is calculated to be lower in energy, but at the 4-31G/6-31G* level **31** (X = CO_2H) is calculated to be lower in energy. However, geometry optimization calculations on **30** and **31** (X = CO_2H) at the 6-31G* level again indicated that **30** (X = CO_2H) is lower in energy. The total energies are given in Table IX. The calculated structural parameters are given in Table III of the supplementary material.

Finally, calculations were carried out on a few selected examples of the 2-mercapto-3-substituted-1-propenes **32** and **33**. The calculations on the initially selected **32** and


32

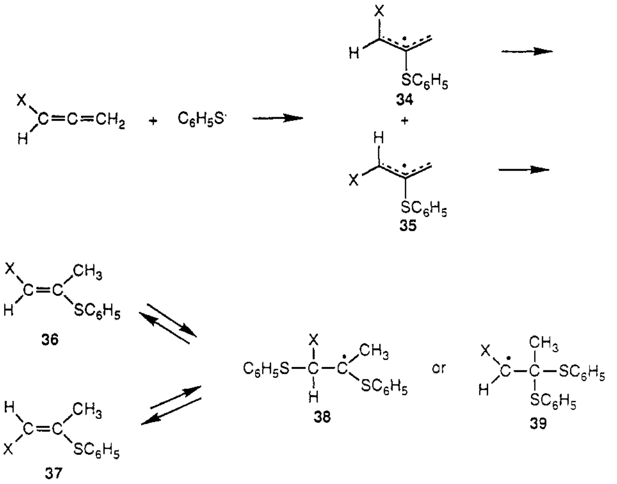

33

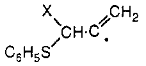
33 (X = OH) were carried out at the 4-31G level with full geometry optimization followed by single-point calculations at the 6-31G* level so that the total energies of **32** and **33** (X = OH) could be directly compared with those of **30** and **31** (X = OH). The initial calculations indicated that **32** and **33** were considerably higher in energy than **30** and **31**, and, due to the fact the 4-31G geometry optimization calculations required considerable computer time because of the difficulty in reaching the threshold parameters for the conformation about the C_2–C_3 bond, calculations were not carried out on all of the substituted **32** and **33**. For example, the lowest energy H-eclipsed conformations of the 2-mercapto-1-substituted-1-propenes **33** (X = OH) were higher in energy compared to the lowest energy conformations of the 2-mercapto-1-substituted-1-propenes **31** by 4.8 (X = OH), 3.1 (X = SH), 2.3 (X = Cl), 5.1 (X = CN), and 8.7 kcal mol^{-1} (X = CH=CH_2).

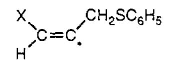
Discussion

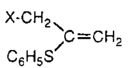
Addition of Benzenethiyl Radical to the Substituted Allenes. Regioselectivity. The benzenethiyl radical undergoes addition to the substituted allenes utilized in this study only to the central allene carbon atom, except in the case of ClA, in which a minor amount of addition occurs at C_3, to produce the substituted anti- and syn-substituted allyl radicals **34** and **35** (see Scheme I). If the addition of benzenethiyl radical to the substituted allenes is controlled by frontier molecular orbital (FMO) interactions, the dominant interaction will be between the HOMO of the allene and the SOMO of the benzenethiyl radical (SOMO energy of −9.661 eV at the non-geometry-optimized 4-31G level). The observed regioselectivity of the addition of the benzenethiyl radical to PHA, PHSA, and MEOA is consistent with a FMO-controlled reaction (as was also the case with the alkyl-substituted allenes),[5] the largest coefficients in the HOMOs of these allenes being at the central allene carbon atom (C_2) of the C_1–C_2 double bond. In ClA, CNA, and CBA, however, the largest coefficient in the HOMO is at C_1, suggesting that if the attack by the benzenethiyl radical is controlled by FMO interactions, addition should occur at C_1 to produce the vinyl radical **40**. No products are

Scheme I




40


41


42

derived from ClA, CNA, or CBA involving initial attack at C_1. (See the later discussion on the reaction of benzenethiyl with ClA and the arylthioallenes). It is conceivable that attack at C_1 is fast and reversible and that the intermediate vinyl radical **40** is not trapped by hydrogen atom transfer. However, this does not seem reasonable in view of the fact that the vinyl radical **41** formed by attack of benzenethiyl at C_3 of ClA is trapped by hydrogen atom transfer. Thus, the regioselectivity observed in the addition of BT to ClA, CNA, and CBA suggests that the addition of benzenethiyl radical to these substituted allenes is not controlled by FMO interactions and, by extension, that the regioselectivity of the addition of benzenethiyl radical to the other substituted allenes is also probably not controlled by FMO interactions.

Relative Reactivity. The relative reactivities of the substituted allenes toward free-radical addition of benzenethiol (Table III) shows no direct correlation with E_{HOMO} or C_i/E_{HOMO} of the substituted allene, or with $E_{HOMO-SOMO}$. The relative reactivity data also suggest that the addition of the benzenethiyl radical to the substituted allenes is not controlled by FMO interactions.

Thermodynamic Considerations. The results of the ab initio MO calculations on the substituted allyl and vinyl radicals **21** and **28** indicate that the substituted allyl radicals are significantly lower in energy. Thus, the substituted allyl radicals are expected to be thermodynamically favored in the addition of the benzenethiyl radical to the substituted allenes. The changes in total energy for the reaction in eq 1 have been calculated (the optimized 4-31G energy of HS$^\bullet$ is −397.61665 au) and are given in Table X.

$$XCH{=}C{=}CH_2 + HS^\bullet \rightarrow \mathbf{27} \qquad (1)$$

In all cases the reactions are calculated to be quite exothermic (>20 kcal mol^{-1}). It must be noted, however, that there is no correlation between the relative reactivities given in Table III with the ΔE_{tot}'s given in Table X.

The thermodynamics of the addition process has also been evaluated by using the method of Benson[15] for the calculation of the heats of formation of chemical species. Unfortunately, not all of the necessary group values are available for the calculation of the ΔH_f for a reaction in

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(15) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

Table X. Calculated ΔE_{tot}'s for the Reactions in Eq 1

X	ΔE_{tot}, kcal mol^{-1}		X	ΔE_{tot}, kcal mol^{-1}	
	anti	syn		anti	syn
HO—	-27.75	-26.86	*t*-HO_2C—	-22.17	-11.54
HS—	-23.54	-21.70	*c*-HO_2C—	-23.28	-16.21
Cl—	-23.58	-21.24	*t*-H_2C=CH—	-31.39	-32.04
NC—	-28.20	-27.40			

Table XI. ΔE_{tot}'s between Anti and Syn Configurations of 1-Substituted-allyl and 2-Mercapto-1-substituted-allyl Radicals

X	ΔE_{tot}(*anti*) − ΔE_{tot}(*syn*), kcal mol^{-1}	
	allyl	2-mercaptoallyl
HO—	+0.40	+0.89 (0.73)[a]
HS—	+0.18	+1.84
Cl—	+0.62	+2.34
H_2C=CH—	-2.15	+0.65
NC—	-0.50	+0.80
t-HO_2C—	-2.75	+10.58
c-HO_2C—	-2.11	+7.07

[a] Geometry optimized structures.

eq 1. Instead, the ΔH_f is calculated for the reaction shown in eq 2[16] in which $CH_3^•$ replaces $HS^•$. (The ΔH_f's for $CH_3^•$

$$HOCH{=}C{=}CH_2 + CH_3^• \rightarrow HOCH{=}C(CH_3){-}CH_2^• \quad (2)$$

and $HS^•$ are very similar, being 34.3 and 34.0 kcal mol^{-1} respectively). The ΔH_f calculated for the reaction in eq 2 is −17.2 kcal mol^{-1}. (The calculated ΔH_f's for the other substituted systems will be the same since the XCH= portion in the allene and the radical remain the same.) This calculated value is in reasonable agreement with the values of ΔE_{tot}'s given in Table X. The exothermicity of the radical addition to an allene is due to the highly positive heat of formation of the allenic carbon atom (34.2 kcal mol^{-1}),[15] which is lost on going to the allyl radical (the group values for sp^2-hybridized carbon atoms are in the range of +6 to +10 kcal mol^{-1}).[15]

Summary. The regioselectivity and relative reactivity data indicate that the addition of the benzenethiyl radical to the substituted allenes employed in this study is not controlled by FMO interactions. Theoretical and thermodynamic calculations indicate that the addition process is quite exothermic, and it must be concluded that the addition process is controlled by thermodynamic factors. The Hammond postulate,[17] however, would then suggest that the transition state for the addition process should occur rather early along the reaction coordinate. This being the case, however, the transition state cannot be occurring so early along the reaction coordinate that FMO interactions become dominant in controlling the regioselectivity and relative reactivity of the addition process.

Thermodynamic Stereochemical Preference of the Intermediate Substituted Allyl Radicals. The addition of the benzenethiyl radical to the substituted allenes is expected to produce the anti-substituted allyl radical **34** as the kinetically favored intermediate.[7] This is due to the fact that during the approach of the benzenethiyl radical to the 2p AO on C_2 of the substituted double bond the substituent will preferentially rotate away from the approaching benzenethiyl radical to produce **34** instead of rotating toward the approaching benzenethiyl to produce **35**. Unfortunately, the stereoselectivity of the addition process is ultimately lost due to the thermodynamic equilibration of the product-substituted propenes **36** and **37** (see Scheme I).

The results of the theoretical calculations on the substituted allyl radicals **21**[18] and **27** reveal some very interesting trends in the preferred configurations which are dependent on the nature of the substituent X. In **21**, when X = OH, SH, and Cl, the anti configurations are calculated to be lower in energy (see Table XI). The results of the calculations on the hydroxyallyl radical are consistent with the experimental observation by Sustmann[19] that the methoxyallyl radical prefers the anti configuration (0.48 versus 0.40 kcal mol^{-1} calculated for the hydroxyallyl radical). In contrast when X = CH=CH_2, CN, and CO_2H the syn configuration is calculated to be lower in energy. (Sustmann has reported that the cyanoallyl radical prefers the anti configuration by 0.1 kcal mol^{-1}.)[19]

The two groups of substituents possess very different types of π systems. When X = OH, SH, and Cl the π system is butadiene-like, while when X = CH=CH_2, CN, and CO_2H the π system is pentadienyl-like. The butadiene- and pentadienyl-type π systems possess significantly different long-range interactions. When X = OH, SH, and Cl the butadiene-type Ψ_1 and Ψ_2 MOs are doubly occupied with Ψ_3 being singly occupied. Ψ_1 and Ψ_3 possess 1,4-long-range bonding interactions while Ψ_2 is antibonding. The 1,4-long-range bonding interaction is greater than the long-range antibonding, thus favoring the anti configuration because of the shorter distance between the X group and C_3 than in the syn configuration. This is nicely illustrated by the π Mulliken populations (given in Table XII) which show considerably greater 1,4-long-range bonding interactions in the anti configurations when X = HO, HS, and Cl. A further analysis of the long-range Mulliken populations also reveals that the interaction of the in-plane nonbonded pair on the heteroatom and the AOs on C_3 is attractive, which also favors the anti configuration.

In the pentadienyl systems, the long-range π interactions are more complex, involving additional 1,4- and 1,5-interactions, the latter being considerably less than the former. In the pentadienyl π system, Ψ_1 is 1,4-bonding, Ψ_2 is 1,4-antibonding, and Ψ_3 is 1,4-nonbonding, resulting in a net overall antibonding 1,4-interaction. This is illustrated by the 1,4-π Mulliken populations between the attachment atoms of the X groups and C_3, which are more negative in the anti configurations. The greater antibonding interactions in the anti configurations result in the syn configurations of **21** (X = CH=CH_2, CN, and CO_2H) being lower in energy.

In **27** the situation is even more complicated. In these systems there are two 1,4-long-range interactions, one between the X group and C_3 and one between the X group and the sulfur atom. When X = OH, SH, and Cl, the anti configuration is more highly favored than in the case of **21** (see Table XII). (It must be pointed out that complete geometry optimization calculations were carried out only when X = OH and that the values for the other systems are probably qualitatively but not quantitatively correct.) An analysis of the 1,4-π Mulliken populations given in Table XII, however, is not consistent with the trend in the

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(16) Group values are not available for atoms in delocalized radical species. The H_f for the allyl radical resonance contributing structure H_2C=CH—CH_2 is +38.1 kcal mol^{-1} versus the reported value of +40.6 kcal mol^{-1} (Table A.12, ref 15).

(17) Hammond, G. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(18) MNDO calculations have been reported on the methoxy and cyanoallyl radicals.[19]

(19) Sustmann, R. Allylic Radicals—An ESR Spectroscopical Study. In *Substituent Effects in Radical Chemistry*; NATO ASI Ser. C; D. Reidel: 1986; Vol. 189, pp 143–166.

Table XII. 1,4-π Mulliken Populations in 21 and 27

	Mulliken populations					
	21		27			
	X–C$_3$		X–C$_3$		X–S	
X	anti	syn	anti	syn	anti	syn
HO—	+0.001 20	+0.000 08	+0.001 20	+0.000 09	+0.000 07	+0.001 59
HS—	+0.000 98	+0.000 06	+0.000 87	+0.000 07	+0.000 08	+0.001 62
Cl—	+0.000 75	+0.000 04	+0.000 68	+0.000 04	+0.000 04	+0.001 29
$H_2C{=}CH$—	-0.001 34	+0.000 60	-0.001 20	-0.000 39	-0.000 02	-0.001 43
NC—	-0.001 00	-0.000 27	-0.000 84	-0.000 27	-0.000 02	-0.001 10
HO_2C—[a]	-0.000 83	-0.000 25	-0.000 68	-0.000 20	-0.000 05	-0.000 17
HO_2C—[b]	-0.000 85	-0.000 23	-0.000 68	-0.000 20	-0.000 06	-0.001 00

[a] Transoid conformation of the conjugated π system. [b] Cisoid conformation of the conjugated π system.

Table XIII. Calculated Dipole Moments of Substituted Allyl and 2-Mercapto-1-substituted Allyl Radicals

	dipole moment			
	allyl radicals[a]		2-mercaptoallyl radicals[b]	
X	anti	syn	anti	syn
HO—	2.14	2.03	1.02[c] 0.94	3.15[c] 3.15
HS—	1.60	1.59	0.17	2.87
Cl—	2.27	2.40	2.04	3.57
$H_2C{=}CH$—	0.01	0.05	1.68	1.45
NC—	3.86	4.10	3.39	5.31
t-HO_2C—	2.15	2.23	3.18	2.47
c-HO_2C—	1.43	1.76	0.79	2.79

[a] 4-31G geometry optimized structures. [b] 4-31G single-point calculation unless otherwise noted. [c] 4-31G optimized structures.

Table XIV. ΔE_{tot}'s for the Reactions in Eq 3

	ΔE_{tot}, kcal mol^{-1}	
X	*anti*-allyl **30**	*syn*-allyl **31**
HO—	-9.07	-8.08
HS—	-10.24	-8.46
Cl—	-11.27	-9.17
$H_2C{=}CH$—	-0.52	+0.45
NC—	-5.92	-5.65
HO_2C—[a]	-18.45	-8.05
HO_2C—[b]	-9.23	-13.69

[a] Transoid conformation about the π system. [b] Cisoid conformation about the π system.

total energies, there existing slightly more 1,4-long-range π bonding in the syn configurations than in the anti configurations, leading one to expect that the syn configurations would be favored. However, there is another important difference between the anti and syn configurations, that being their calculated dipole moments. The dipole moments of the anti configurations are considerably lower than those of the syn configurations (see Table XIII) which, in the gas phase, would favor the anti configurations. This dipolar effect is not important in the substituted allyl radicals **21** because the dipole moments of the anti and syn configurations are very similar.

The replacement of hydrogen by sulfur in **21** when X = $CH{=}CH_2$, CN, and CO_2H results in a change in the preference for the syn configuration to the anti configuration. The 1,4-π Mulliken populations between the attachment atom of the X group and C_3 are more negative in the anti configuration, thus favoring the syn configuration. The 1,4-interactions between the X group and the sulfur atom in the syn configuration, however, are more negative than the X–C_3 interactions in the anti configuration, thus tipping the balance toward the anti configuration. In addition, this is enforced by the much lower calculated dipole moments of the anti configurations compared to the syn configurations (see Table XIII).

Hydrogen Atom Transfer to the Substituted Allyl Radicals. The substituted allyl radicals formed on addition of benzenethiyl to the substituted allenes abstract a hydrogen atom from benzenethiol to form only the 1-substituted-2-(phenylthio)-1-propenes **36** and **37**. The results of the theoretical calculations on the substituted allyl radicals **27** show that in all of the allyl radicals the largest coefficient in the SOMO is at C_1,[20] which, if the hydrogen atom abstraction reaction is FMO controlled, will result in the formation of the 3-substituted-2-(phenylthio)-1-propenes **42**. The experimental results strongly indicate that the hydrogen atom transfer process is not controlled by FMO interactions.

The results of the theoretical calculations on **30** and **31** and **32** and **33** indicate that **30** and **31** are considerably lower in energy (see earlier discussion). The changes in total energies for the process shown in eq 3 indicate that

$$XCH{=}\dot{C}(SH){=}CH_2 + H_2S \rightarrow XCH{=}C(SH)CH_3 + HS^\bullet \quad (3)$$

these reactions are exothermic by approximately 10 kcal mol^{-1} (see Table XIV). (The calculated exothermicities would be expected to be slightly greater in the real reactions with benzenethiol due to the stabilization of the product thiyl radical by the phenyl group.) It must be concluded that the transition state for the hydrogen atom transfer process occurs late enough along the reaction coordinate so that the thermodynamic stability of the product determines the regioselectivity of the process and not FMO interactions.

***E*:*Z* Product Ratios.** During the hydrogen atom transfer reactions the stereochemistry of the intermediate substituted allyl radicals will be retained, and the *E*:*Z* product ratios will directly reflect the anti:syn ratios of the substituted allyl radicals formed in the addition of the benzenethiyl radical to the substituted allenes. This information would provide valuable insights on the factors that affect the stereoselectivity of the radical addition process. Unfortunately, however, this information is lost due to the thermodynamic equilibration of the products **36** and **37**.[21] The equilibration of **36** and **37** undoubtedly occurs by the reversible addition of benzenethiyl radical to **36** and **37** to produce **38** or **39** (Scheme I), which live long enough to undergo rotation about the C_1–C_2 bond before eliminating the benzenethiyl radical to re-form **36** and **37**. For reasons to be outlined later, it is believed that **38** is the intermediate formed in these isomerization processes.

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[20] Hyperfine coupling constant data for the methoxy and cyanoallyl radicals also indicate a greater spin density at C_1 than at C_3.[19]

[21] A similar isomerization of products has been observed previously in the radical-chain addition of benzenethiol to alkyl-substituted allenes (see ref 5).

Table XV. 1,4-π Mulliken Populations between X and Sulfur in 30 and 31

X	Mulliken population	
	30	31
HO—	+0.000 39	+0.004 03
HS—	+0.000 74	+0.004 71
Cl—	+0.000 41	+0.003 50
H_2C=CH—	+0.000 13	+0.001 52
NC—	+0.000 05	+0.000 71
HO_2C—[a]	−0.000 11	−0.000 42
HO_2C—[b]	−0.000 15	−0.000 93

[a] Transoid conformation about the π system. [b] Cisoid conformation about the π system.

Table XVI. Dipole Moments of 30 and 31

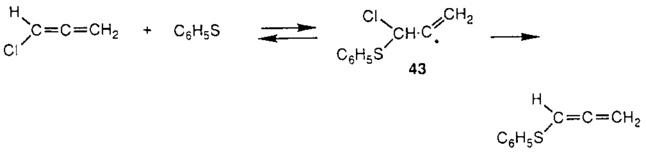
X	dipole moment[a]	
	30	31
HO—	1.24	3.15
HS—	0.53	3.06
Cl—	2.18	3.59
H_2C=CH—	1.86	1.74
NC—	4.25	6.01
HO_2C—[b]	3.93	3.45
HO_2C—[c]	1.10	3.34

[a] 6-31G* single-point calculations on the 4-31G optimized structures except as noted. [b] Transoid conformation about the π system. [d] Cisoid conformation about the π system.

The *E*:*Z* ratios vary considerably depending on the nature of the X group (see Table II). When X = OH, SH, and Cl, the *Z* stereoisomer is favored. An analysis of the 1,4-π Mulliken populations of **30** and **31** indicates that when X = OH, SH, and Cl, there is a substantial attractive interaction between the X group and the sulfur atom in the *Z* isomer (see Table XV). This appears to more than offset the effect of the considerably larger dipole moments of the *Z* isomers (see Table XVI). When X = CN and CO_2H, the *E* isomer **30** is more stable. The 1,4-π Mulliken populations indicate that the interactions between the carbon atoms of the cyano and carboxy groups and the sulfur atom are very small, thus favoring the *Z* isomer **31** when X = cyano and the *E* isomer when X is carboxy. In these two cases it appears that the much larger dipole moments of the *Z* isomers result in the favoring of the *E* isomers **30**.

There is an amazingly good correlation between the ΔG's for the equilibria between **36** and **37** and the calculated ΔE_{tot}'s, which is shown in Figure 1. The only point that does not correlate well is that for phenylallene. This could be due to an inaccurate thermodynamic equilibrium constants (see Results) and/or the possibility that the vinyl group is not a good model for the phenyl group in the calculations. Although the calculations were reasonable for the calculation of HOMO coefficients, this substitution does not give good correlations of changes in total energies.

Chloroallene and (Phenylthio)allene Systems. The free-radical chain addition of benzenethiol to ClA produces substantial quantities of the diphenylthio products (*E*)- and (*Z*)-**8**. There are two reasonable mechanisms for the formation of these products. It is conceivable that the benzenethiyl radical undergoes addition to C_1 to form **43**



in view of the fact that the largest coefficient of the HOMO of ClA is at C_1. The loss of chlorine atom from **43** would then form (phenylthio)allene (PHSA), which would then undergo further reaction to form **8**. A careful inspection of the NMR spectra of the mixtures of products derived from the reactions of ClA with BT did not show the presence of (*E*)- or (*Z*)-**8**. The lack of detection of PHSA, however, does not absolutely rule out this mechanistic pathway for the formation of (*E*)- and (*Z*)-**8**.

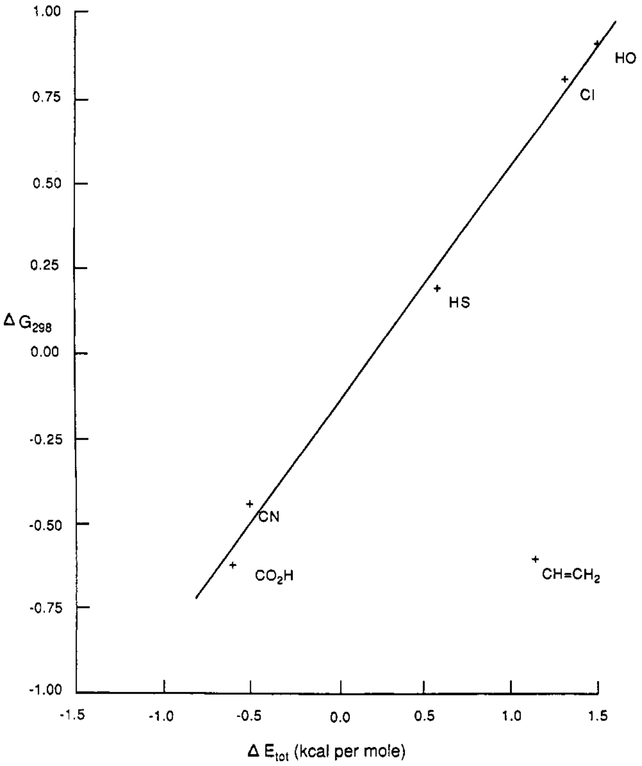


Figure 1. Plot of ΔG_{298} for the equilibria between **30** and **31** versus the difference in total energy between **30** and **31**.

A second mechanism for the formation of **8** involves loss of chlorine from **38** (X = Cl), which is one of the possible intermediates involved in the isomerization of **36** and **37**. Since the isomerization of **36** and **37** does occur and in the reaction of ClA with benzenethiol (*E*)- and (*Z*)-**8** are formed, it is most reasonable that **38** is involved in both of these processes. Also, the formation of **38** should be favored over **39** on the basis of the relative stability of the radical center[22] and steric effects.

In the addition of benzenethiol to [(4-methylphenyl)-thio]allene and 4-methylbenzenethiol to (phenylthio)allene, arylthio exchange also occurs to a minor extent. Again, this would be consistent with the formation of intermediates such as **38**, which would result in isomerization and exchange. The exchange of the X group in the reactions of the other substituted allenes is not observed, undoubtedly due to the extremely poor radical-leaving abilities of the other groups.

Experimental Section

General Procedures. Previously published procedures were used for the synthesis of PHA,[23] CNA,[24] MEOA,[25] ClA,[26] and CBA.[27]

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(Phenylthio)allene (PHSA).[28] To 6.6 g (0.06 mol) of benzenethiol dissolved in 80 mL of ether in a 250-mL round-bottomed flask equipped with a magnetic stirrer was added 75 mL of 1.25 M methyllithium in ether at −60 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 10 min and then cooled to −40 °C. Copper(I) bromide (8.6 g, 0.06 mmol) and 4.4 g (0.06 mol) of propargyl bromide were added, and the reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The reaction mixture was quenched by the addition of 50 mL of saturated aqueous ammonium chloride. The organic layer was decanted, and the aqueous phase was extracted with 50 mL of ether. The combined organic solution was washed twice with water and dried (MgSO$_4$). The ether was removed by distillation, leaving a 75:25 mixture of PHSA and phenyl propargyl sulfide, which was distilled at 70 °C/0.01 mmHg. The mixture was separated by column chromatography on silica gel with Skellysolve B as eluent; ^{1}H NMR (CDCl$_3$) δ 4.99 (d, J = 6.24 Hz, 2 H), 5.95 (t, J = 6.24 Hz, 1 H), 7.0–7.5 (m, 5 H).

[(4-Methylphenyl)thio]allene (MPHSA). The procedure described above was used to prepare MPHSA. NMR analysis of the crude product indicated it be pure MPHSA: ^{1}H NMR (CDCl$_3$) δ 2.30 (s, 3 H), 4.96 (d, J = 6.28 Hz, 2 H), 5.92 (t, J = 6.28 Hz, 1 H), 7.0–7.5 (m, 4 H); MS, exact mass calcd for C$_{10}$H$_{10}$S 162.0503, found 162.0501.

General Procedure for the Addition of Benzenethiol to the Substituted Allenes. To 30 μL of the substituted allene dissolved in 0.75 mL of CDCl$_3$ in an NMR tube was added 1 mol equiv of benzenethiol. The NMR tube was capped and placed in sunlight for 1 day (except for ClA, which required irradiation with a sun light to accomplish sufficient reaction). The NMR spectra of the reactions mixtures were recorded. Not all reactions went to completion. (Reproductions of the NMR spectra are provided in the supplementary material.) Attempts to isolate the benzenethiol adducts by chromatographic techniques resulted in decomposition. The volatiles were removed on a vacuum line, and the mass spectra of the mixtures were recorded.

General Procedure for the Iodine-Catalyzed Isomerization of the Benzenethiol Addition Products. To a portion of the reaction mixture dissolved in 0.75 mL of CDCl$_3$ in an NMR tube was added on small crystal of iodine. The NMR tube was capped and heated at 65 °C, and the NMR spectrum was periodically recorded and the ratio of *E*:*Z* stereoisomers was determined by integration of the vinyl hydrogen region peaks.

Phenylallene: *E*:*Z* ratio 49:51. (*E*)-**2**: ^{1}H NMR (CDCl$_3$) δ 2.133 (d, J = 1.26 Hz, 3 H), 6.675 (m, 1 H), 7.0–7.5 (m, 10 H). (*Z*)-**2**: ^{1}H NMR (CDCl$_3$) δ 2.032 (d, J = 1.30 Hz, 3 H), 6.707 (m, 1 H), 7.0–7.5 (m, 10 H). MS (of mixture) exact mass calcd for C$_{15}$H$_{14}$S 226.0816, found 226.0814. Attempted iodine-catalyzed isomerization of the product mixture resulted in decomposition.

Methoxyallene: *E*:*Z* ratio 18:82. (*E*)-**3**: ^{1}H NMR (CDCl$_3$) δ 1.756 (d, J = 1.34 Hz, 3 H), 3.675 (s, 3 H), 6.352 (q, J = 1.34 Hz, 1 H), 7.0–7.5 (m, 5 H). (*Z*)-**3**: ^{1}H NMR (CDCl$_3$) δ 1.851 (d, J = 1.34 Hz, 3 H), 3.690 (s, 3 H), 6.535 (q, J = 1.34 Hz, 1 H), 7.0–7.5 (m, 5 H). MS (of mixture), exact mass calcd for C$_{10}$H$_{12}$OS 180.0608, found 180.0603. Iodine-catalyzed isomerization of the mixture resulted in no change in the ratio of stereoisomeric adducts.

Carbomethoxyallene: *E*:*Z* ratio 72:28. (*E*)-**4**: ^{1}H NMR (CDCl$_3$) δ 2.44 (d, J = 1.00 Hz, 3 H), 3.52 (s, 3 H), 5.23 (q, J = 1.00 Hz, 1 H), 7.0–7.5 (m, 5 H). (*Z*)-**4**: ^{1}H NMR (CDCl$_3$) δ 1.82 (d, J = 1.15 Hz, 3 H), 3.49 (s, 3 H), 5.86 (q, J = 1.15 Hz, 1 H), 7.0–7.5 (m, 5 H); MS (of mixture), exact mass calcd for C$_{11}$H$_{12}$O$_2$S 208.0558, found 208.0554. Treatment of the reaction mixture with iodine did not result in a change in the ratio of the adducts.

Cyanoallene: *E*:*Z* ratio 61:39. (*E*)-**5**: ^{1}H NMR (CDCl$_3$) δ 2.27 (d, J = 0.75 Hz, 3 H), 4.52 (m, 1 H), 7.0–7.5 (m, 5 H). (*Z*)-**5**: ^{1}H NMR (CDCl$_3$) δ 1.85 (d, J = 1.35 Hz, 3 H), 5.24 (m, 1 H), 7.0–7.5 (m, 5 H); MS (of mixture), exact mass calcd for C$_{10}$H$_9$NS 175.0456, found 175.0455.

Chloroallene: (*E*)-**6**:(*Z*)-**6**:**7**:(*E*)-**8**:(*Z*)-**8** ratio 6.0:30.6:36.4:9.4:17.6. (*E*)-**6**: ^{1}H NMR (CDCl$_3$) δ 2.00 (d, J = 1.34 Hz, 3 H), 6.30 (q, J = 1.34 Hz, 1 H), 7.0–7.5 (m, 5 H). (*Z*)-**6**: ^{1}H NMR (CDCl$_3$) δ 1.77 (d, J = 1.44 Hz, 3 H), 6.05 (q, J = 1.44 Hz, 1 H), 7.0–7.5 (m, 5 H). **7**: ^{1}H NMR (CDCl$_3$) δ 3.74 (dd, J = 7.30, 1.33 Hz, 2 H), 5.87 (dt, J = 7.30, 7.30 Hz, 1 H), 6.10 (dt, J = 7.30, 1.33 Hz, 1 H), 7.0–7.5 (m, 5 H), MS, parent ion *m*/*e* 184. **9**: MS, parent ion *m*/*e* 366.

(Phenylthio)allene with benzenethiol: *E*:*Z* ratio 60:40. (*E*)-**8**: ^{1}H NMR (CDCl$_3$) δ 2.06 (d, J = 1.00 Hz, 3 H), 6.40 (q, J = 1.00 Hz, 1 H), 7.0–7.5 (m, 10 H). (*Z*)-**8**: ^{1}H NMR (CDCl$_3$) δ 1.97 (d, J = 1.20 Hz, 3 H), 6.44 (q, J = 1.20 Hz, 1 H), 7.0–7.5 (m, 10 H). MS, exact mass calcd for C$_{15}$H$_{14}$S$_2$ 258.0537, found 258.0536. Iodine-catalyzed isomerization resulted in a change in the *E*:*Z* ratio to 40:60 accompanied by some decomposition.

(Phenylthio)allene with 4-methylbenzenethiol: (*E*)-**10**:(*Z*)-**10** ratio 38:62. (*E*)-**10**: ^{1}H NMR (CDCl$_3$) δ 2.05 (d, J = 0.95 Hz, 3 H), 2.30 (s, 3 H), 6.24 (q, J = 0.95 Hz, 1 H), 7.0–7.5 (m, 9 H). (*Z*)-**10**: ^{1}H NMR (CDCl$_3$) δ 1.93 (d, J = 1.15 Hz, 3 H), 2.30 (s, 3 H), 6.35 (q, J = 1.15 Hz, 1 H), 7.0–7.5 (m, 9 H). The NMR spectrum also showed the presence of resonances characteristic of (*E*)- and (*Z*)-**8** (9%) and (*E*)- and (*Z*)-**11** (<0.5%). MS, exact mass calcd for C$_{16}$H$_{16}$S$_2$ 272.0693, found 272.0693. The mass spectrum also showed parent ion peaks at *m*/*e* 286 for **11** and 258 for **8**. Attempted iodine-catalyzed isomerization did not result in any change in the product distribution.

[(4-Methylphenyl)thio]allene with 4-methylbenzenethiol: *E*:*Z* ratio 39:61. (*E*)-**11**: ^{1}H NMR (CDCl$_3$) δ 2.03 (d, J = 1.05 Hz, 3 H), 2.30 (s, 6 H), 6.28 (q, J = 1.05 Hz, 1 H), 7.0–7.5 (m, 8 H). (*Z*)-**11**: ^{1}H NMR (CDCl$_3$) δ 1.92 (d, J = 1.20 Hz, 3 H), 2.30 (s, 6 H), 6.33 (q, J = 1.20 Hz, 1 H), 7.0–7.5 (m, 8 H). Attempted iodine-catalyzed isomerization did not result in any change in the product distribution.

[(4-Methylphenyl)thio]allene with benzenethiol: (*E*)-**12**:(*Z*)-**12** ratio 40:60. (*E*)-**12**: ^{1}H NMR (CDCl$_3$) δ 2.05 (d, J = 1.02 Hz, 3 H), 2.30 (s, 3 H), 6.426 (q, J = 1.02 Hz, 1 H), 7.0–7.5 (m, 9 H). (*Z*)-**12**: ^{1}H NMR (CDCl$_3$) δ 1.96 (d, J = 1.24 Hz, 3 H), 2.30 (s, 3 H), 6.416 (q, J = 1.24 Hz, 1 H), 7.0–7.5 (m, 9 H). In addition to the formation of (*E*)- and (*Z*)-**12**, the NMR spectrum of the reaction product indicated the formation of approximately 5% of a mixture of (*E*)- and (*Z*)-**11** and 0.5% of a mixture of (*E*)- and (*Z*)-**8**. Attempted iodine-catalyzed isomerization resulted in extensive decomposition of the products.

Determination of Relative Reactivities. Solutions were prepared containing 0.24 mmol of two different substituted allenes, 0.18 mmol of benzenethiol, and 0.12 mmol of either dibromo- or dichloromethane (as internal integration standards) in 0.75 mL of CDCl$_3$. The NMR integral was immediately recorded, and the sample was then set in the sunlight for 1 day. The NMR integral was then rerecorded, and the relative amounts of the two substituted allenes remaining was calculated.

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Registry No. **13**, 10563-01-6; **14**, 81788-96-7; **15**, 5732-10-5; **16**, 81788-93-4; **17**, 15338-29-1; **19**, 124128-14-9; **22**, 112775-21-0; **23**, 40905-10-0; **24**, 62528-89-6; **25**, 3808-35-3; **26**, 90439-83-1; **27** (X = SH), 124128-26-3; **27** (X = Cl), 124128-27-4; **27** (X = CH=CH$_2$), 124128-28-5; **27** (X = CN), 124128-29-6; **27** (X = CO$_2$H), 124128-30-9; (*E*)-**29**, 124128-15-0; (*Z*)-**29**, 124128-31-0; **30** (X = CO$_2$H), 124128-16-1; **30** (X = Cl), 124128-18-3; **30** (X = SH), 124128-20-7; **30** (X = CH=CH$_2$), 124128-22-9; **30** (X = CN), 124128-24-1; **31** (X = CO$_2$H), 124128-17-2; **31** (X = Cl), 124128-19-4; **31** (X = SH), 124128-21-8; **31** (X = CH=CH$_2$), 124128-23-0; **31** (X = CN), 124128-25-2; BT, 108-98-5; MEOA, 13169-00-1; CBA, 18913-35-4; CNA, 1001-56-5; CIA, 3223-70-9; PHSA, 1595-38-6; MPHSA, 124128-13-8.

Supplementary Material Available: Tables of the calculated structural parameters for the substituted allenes, allyl and vinyl radicals and the substituted propenes, and NMR spectra of the reaction mixtures derived from the addition of benzenethiol to the substituted allenes (40 pages). Ordering information is given on any current masthead page.

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