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Radical-Chain Addition of Benzenethiol to Allenes. Analysis of Steric Effects and Reversibility

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The radical-chain addition of benzenethiol to the monoalkylallenes **1a–e** and the 1,1-dialkylallenes **6** and **8** has been studied. Attack by the benzenethiyl radical occurs at C_2 and C_3 of **1b–e** in a ratio of 83:17. Increased attack (25%) at C_3 occurs with *tert*-butylallene (**1a**). The 1,1-dialkylallenes undergo attack only at C_2. Deuterium-labeling studies indicate that the thiyl radical addition step is not detectably reversible under the reaction conditions. The internal alkene adducts **2**, **3**, **9**, and **10** are the kinetically favored products. Rapid and reversible addition of the thiyl radical to the adducts results in complete stereochemical equilibration during the course of the reaction. The hydrogen atom abstraction step is reversible under the reaction conditions with **1a** and **8** but not with **6** or the other monoalkylallenes. Treatment of the adducts derived from **1a** and **8** with a catalytic quantity of iodine results in isomerization to the more thermodynamically stable adducts **4** and **11**. The kinetics and thermodynamics of these reactions are discussed, and steric strain energies for the $CH_3 \cdots SC_6H_5$ and $t\text{-Bu} \cdots SC_6H_5$ interactions have been estimated to be 0.8–0.9 and 3.9–4.0 kcal/mol, respectively.

One of our main research efforts is directed toward differentiating between the $({}_{\pi}2_s + {}_{\pi}2_a)$ and $[{}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)]$[1] concerted and the two-step, diradical intermediate mechanisms for the cycloaddition reactions involving allenes. In these studies we have selected several addition reactions of allenes as models for a detailed comparison of the chemoselectivities (preference for attack on the two different π systems in unsymmetrically substituted allenes), stereoselectivities, relative reactivities, and kinetic isotope effects with those derived in the cycloaddition reactions of allenes which proceed via mechanistically questioned pathways.[1] As a model for the formation of the allyl radical portion of the diradical intermediate formed in the two-step process, we have initially investigated the addition of a radical to variously substituted allenes. Several radical and radical-chain additions to allene and a few substituted allenes have been studied, including methyl,[2] trifluoromethyl,[3] hydrogen bromide,[4] trimethyltin hydride,[5] and various thiols.[6,7] As the previous studies did not provide the necessary data for comparison purposes, the radical-chain addition of benzenethiol to a number of substituted allenes was selected for detailed study. Previously, the addition of benzenethiol had been investigated only with allene,[6,7] methylallene,[7] and 1,1-dimethylallene.[7] During the course of the present study, we have discovered an unexpectedly facile reversibility in the product-forming, chain-transfer step in which the ease of abstraction of a hydrogen atom from the product is a sensitive function of the steric strain in the adduct. The results of relative reactivity and kinetic isotope effect studies are reported in the accompanying paper.[8]

Results

Addition of Benzenethiol to Monoalkylallenes. *tert*-Butylallene. The reaction of a slight excess of benzenethiol with *tert*-butylallene (**1a**) at 25 °C in the absence of solvent resulted in the rapid, quantitative formation (by NMR) of a mixture of the adducts **2–5** in a 20:17:38:25 ratio (eq 1). No 2:1 adducts were indicated to be present by NMR and GC/MS. Adducts **2** and **5** were obtained pure by preparative GLC. Adducts **3** and **4** could not be separated and were isolated as a mixture. The gross structures of the adducts are assigned on the basis of their NMR and mass spectra, with the stereochemistries of **2** and **3** being assigned on the basis of NOE experiments (see

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[1] Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37.

[2] Rajbenbach, A.; Szwarc, M. *Proc. R. Soc. London, Ser. A* **1959**, *251*, 394.

[3] Haszeldine, R. N.; Leadham, K.; Steel, B. R. *J. Chem. Soc.* **1954**, 2040. Stefani, A. P.; Herk, L.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 4732; Meunier, H.; Abell, P. I. *J. Phys. Chem.* **1967**, *71*, 1430.

[4] Kovackic, D.; and Leitch, L. C. *Can. J. Chem.* **1961**, *39*, 363. Griesbaum, K.; Oswald, A. A.; Hall, D. N. *J. Org. Chem.* **1964**, *29*, 2404. Heiba, E.-A. I.; Haag, W. O. *Ibid.* **1966**, *31*, 3814. Tien, R. Y.; Abell, P. I. *Ibid.* **1970**, *35*, 956.

[5] Kuivila, H.; Rahman, W.; Fish, R. *J. Am. Chem. Soc.* **1965**, *87*, 2835.

[6] Griesbaum, K.; Oswald, A. A.; Quiram, E. R.; Naegele, W. *J. Org. Chem.* **1963**, *28*, 1952. Van der Ploeg, H. J.; Knotnerus, J.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 775.

[7] Jacobs, T. L.; and Illingworth, G. E., Jr. *J. Org. Chem.* **1963**, *28*, 2692.

[8] Pasto, D. J.; Warren, S. E. *J. Org. Chem.*, following paper in this issue.

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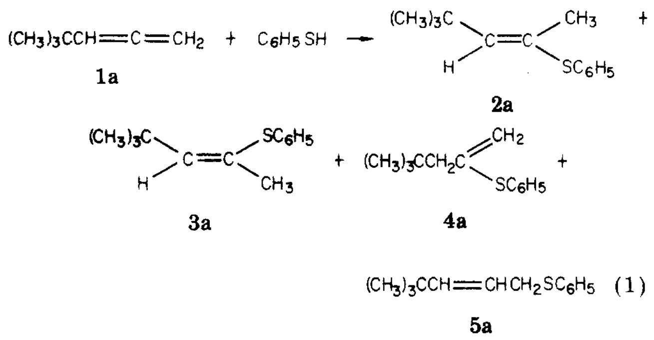


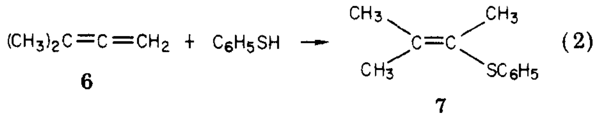
Experimental Section for details). Only a single stereoisomer of 5 was detected, that probably being the trans isomer.

In an attempt to determine the thermodynamic equilibrium constant between **2a** and **3a**, a sample of pure **2a** and a mixture of the adducts **2a**–**5a** were treated with a catalytic quantity of iodine in deuteriochloroform, and the NMR spectra were periodically recorded. When pure **2a** was treated in this manner, the resonance signals of **3a** appeared immediately, followed by the disappearance of the signals of **2a** and **3a** with concomitant appearance of the signals of **4a**. The vinyl resonances of **4a** appeared broadened and could be caused to coalesce on addition of larger quantities of iodine. (The addition of a drop of aqueous sodium bisulfite to destroy the iodine resulted in immediate sharpening of the vinyl resonances.) The appearance of the vinyl resonances of **5a** was unaffected by the presence of the iodine. When the mixture was allowed to stand for a prolonged period of time, no further changes occurred; i.e., there was no conversion of **4a** to **5a** or vice versa.

The addition of an equivalent amount of 4-methylbenzenethiol to a mixture of **2a**–**5a** resulted in a rapid exchange and equilibration of the phenylthio group with the 4-methylphenylthio group in **2a**–**4a**. No exchange of the phenylthio group of **5** was observed. The NMR and GC/MS of the equilibrated mixtures indicated no change in the relative quantities of the adducts.

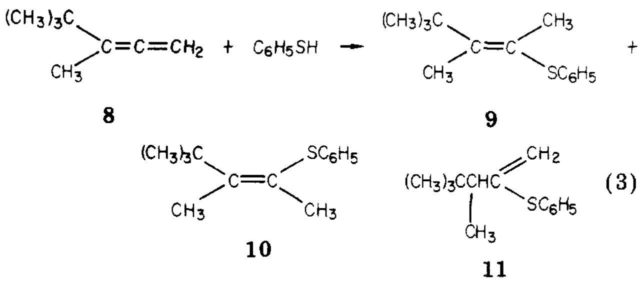
Other Monoalkylallenes. The relative yields of the products formed in the radical chain addition of benzenthiol to isobutyl- (**1b**), *n*-butyl- (**1c**), isopropyl- (**1d**), and ethylallene (**1e**) are given in Table I. The structures of the adducts have been assigned by comparison of chemical shifts with those of **2a**–**5a**.

Addition of Benzenethiol to 1,1-Dialkylallenes. 1,1-Dimethylallene (6). 1,1-Dimethylallene reacts very rapidly with benzenethiol to produce only **7**, consistent with the results reported previously.[7] Adduct **7** is unaffected by the presence of a catalytic quantity of iodine.



Addition of benzenethiol to a 54:46 mixture of **6** and **6**-*3,3*-d_2 resulted in the formation of **7** which on mass spectral analysis showed essentially no **7**-d_1 to be present, with the amount of **7**-d_2 slightly decreased.

1-*tert*-Butyl-1-methylallene (8). The addition of benzenethiol to **8** produces a mixture of the three adducts **9**–**11** (in a ratio of 42:40:18) which were separated by preparative GLC. The assignment of the methyl resonances in the NMR spectra of **9** and **10** was made on the basis of deuterium labeling by the addition of benzenethiol-*S*-*d*. The assignment of the stereochemistry of **9** and **10** was made by comparison of the relative chemical shifts



of the methyl groups attached to the carbon atoms bearing the phenylthio group with those in **2a** and **3a**.

The treatment of **9** or **10** with a catalytic quantity of iodine results in a rapid equilibration and a slower isomerization to form **11**. The addition of benzenethiol to a 56.6:43.4 mixture of **8** and **8**-*3,3*-d_2 resulted in the formation of **11** having a $d_0/d_1/d_2$ distribution of 62:32:6.

Discussion

The results described above are consistent with the mechanism outlined in Scheme I for the addition of benzenethiol to a monoalkylallene. The data suggest that the attack by the phenylthiyl radical on both the internal and terminal carbon atoms of the allene to form the intermediate radicals **12**–**14** is irreversible. The iodine atom catalyzed isomerization of **2a** and **3a** to **4a**, via **12a** and **13a**, occurs without resulting in any detectable increase in **5a**. If the attack by the phenylthiyl radical was reversible, one must then observe an increase in **5a** during the isomerization process. The addition of the thiyl radical to the central carbon atom of the allene must be quite exoergic, on the order of 25 kcal/mol.[9] This value would represent the *minimum* activation energy for the reverse of the addition reaction, a value too high to be observed in the present reaction.

Evidence for the reversible formation of **12** and **13** from **2** and **3** during the course of the free radical chain addition process is provided by the observation that **11** derived from the addition of benzenethiol to a 54:46 mixture of **8** and **8**-*3,3*-d_2 possessed a distribution of $d_0/d_1/d_2$ of 62:32:6. The decrease in **11**-d_2 and the formation of **11**-d_1 can only be rationalized by the reformation of the intermediate allyl radicals by loss of a deuterium atom from **9** and **10** followed by abstraction of a hydrogen atom to form **11**. Considering that the H–D kinetic isotope effect in hydrogen atom abstraction reactions is of the order of 2–5,[13] the reduction in **11**-d_2 to **11**-d_1 and **11**-d_0 represents a substantial rate in the formation of the intermediate allyl radicals by deuterium (or hydrogen) atom loss from the adducts. The estimated changes in energy for the phenylthiyl and iodine atom abstraction reactions with **2** and **3** are ~0[14] and ~7[16] kcal/mol, respectively, representing

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(9) Calculated on the basis of the following bond-dissociation and radical-stabilization energies: C=C of allene, 146 kcal (assigned the same as in ethylene on the basis of their essentially identical spectroscopic and calculated molecular orbital properties);[1] $C_6H_5S\cdot$ stabilization energy, 9.6 kcal;[10] C–S, 75 kcal (67.5 kcal for $C_6H_5S–CH_3$ plus 8 kcal for the change from sp^3 to sp^2 carbon); allyl radical stabilization energy ~10–14 kcal.[11]

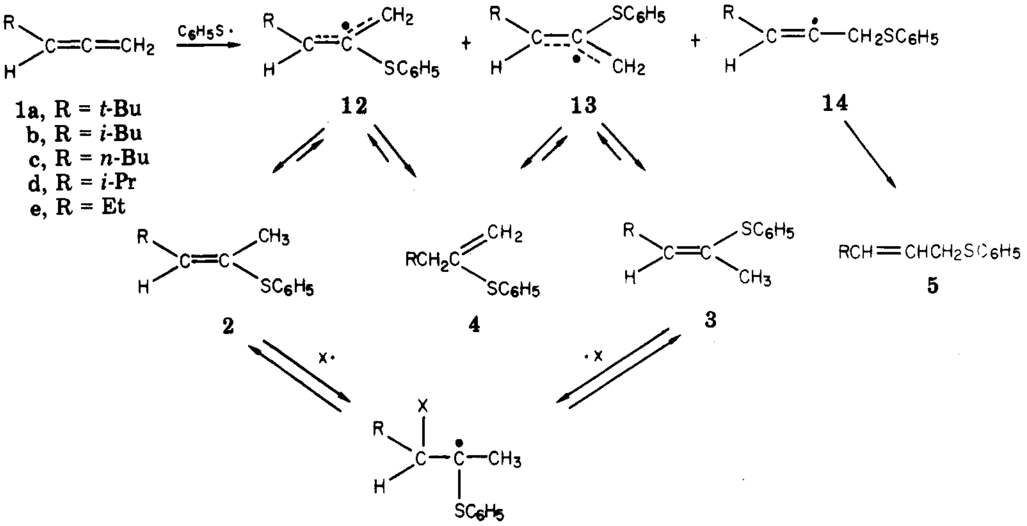
(10) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 295.

(11) A range of values from 9 to 21 kcal/mol has been reported for the stabilization energy of the allyl radical, the value of ~10 kcal/mol[12] appears to be reasonable, and ~14 kcal/mol for the 1,1-dimethylallyl radical (see: Krusic, P. J.; Meakin, P.; Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 6211 and references therein).

(12) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125. Golden, D. M.; Rodgers, A. S.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 3196.

(13) The k_H/k_D for chlorine atom abstraction of a hydrogen atom from toluene is 2.0 (Brown, H. C.; Russell, G. A. *J. Am. Chem. Soc.* **1952**, *74*, 3995) and for bromine atom abstraction ~5.0 (Wiberg, K. B.; Slaugh, L. H. *J. Am. Chem. Soc.* **1958**, *80*, 3033).

Scheme I



15, X = I, ArS·

Table I. Yields of Benzenethiol Addition Products with Monoalkylallenes (1, $RCH{=}C{=}CH_2$)

	% yield			
	2	3	4	5
a, R = $(CH_3)_3C$	20	17	38	25
b, R = $(CH_3)_2CHCH_2$	35	45	3	17
c, R = $CH_3CH_2CH_2CH_2$	32	49	2	17
d, R = $(CH_3)_2CH$	33	48	2	17
e, R = CH_3CH_2	32	49	2	17

the minimum activation enthalpies for the abstraction reactions. The partial relief of the steric strain energies of the adducts (see later Discussion) on lengthening of the C=C bond, compared to that in the allyl radical, results in a reduction in the energy barriers to a value where these reactions should occur very rapidly at room temperature.

There is no evidence indicating that the formation of **5** from **14** is detectably reversible. No doubt this is due to the stronger vinyl C–H bond in **5** and the lack of stabilization in the intermediate vinyl radical **14**.

The ratios of **2** to **3** (see Table I) represent the thermodynamically controled product ratios as indicated by the iodine-catalyzed and 4-methylbenzenethiol-equilibration experiments. These stereoisomerizations probably proceed via the radical addition product **15**. (The line broadening of the vinyl hydrogen resonances of **4a** arises from a similar rapid iodine atom addition–rotation–elimination sequence.) The observed **2**:**3** product ratios allow calculation of the equilibrium constants and relative strain energies of the addition products. The present studies suggest that the R···SC_6H_5 strain energies are ~0.3–0.4 kcal/mol less than the R···CH_3 strain energies. The *t*-Bu···CH_3 and CH_3···CH_3 strain energies have been found to be 4.29 and 1.0 kcal/mol,[18] giving values for the *t*-Bu···SC_6H_5 and CH_3···SC_6H_5 strain energies of 3.9–4.0 and 0.8–0.9 kcal/mol, respectively.

The relative strain energies in the variously substituted adducts is manifest in the relative rates of hydrogen atom abstraction from the adducts. Qualitatively, the rate of hydrogen atom abstraction, as measured by the rate of isomerization from internal to terminal alkene adducts, occurs most rapidly with **9** and **10** and somewhat slower with **2a** and **3a**, while rearrangement of **7** was not detectable. In **9** and **10** there is partial relief of the *t*-Bu···CH_3 and CH_3···SC_6H_5 and of the *t*-Bu···SC_6H_5 and CH_3···CH_3 strain energies, respectively, which total ~5.1 kcal/mol in both **9** and **10**. The total strain energies in **2a** and **3a** are ~4.3 and ~4.0 kcal/mol, while that in **7** is only ~2.1 kcal/mol.

The strain energies are also reflected in the (**2** + **3**)/**4** product ratios (see Table I). The product distributions derived from isobutyl-, *n*-butyl-, isopropyl-, and ethylallene are essentially identical. With *tert*-butylallene there is considerably more hydrogen atom abstraction by **12a** and **13a** at the *more* sterically hindered end of the allyl radical; however, this mode of reaction produces the *least* strained product (**4a**).

The ratios of attack at C_2 and C_3 in **1b–e** are essentially identical. With *tert*-butylallene, however, there is significantly more attack occurring at C_3. In the monoalkylallenes **1b–e** the alkyl groups can adopt conformations which present the same steric hindrance to attack at C_2. In *tert*-butylallene, however, attack at C_2 is more sterically hindered, resulting in an increase in the attack at C_3. There is also a concomitant decrease in the overall reactivity of the *tert*-butyl-substituted allenes which will be discussed in the accompanying paper.

Experimental Section

Synthesis of Allenes. 1,1-Dimethylallene (3-Methyl-1,2-butadiene). 1,1-Dimethylallene (**6**) was prepared by lithium aluminum hydride reduction of 3-chloro-3-methyl-1-butyne in refluxing tetrahydrofuran[19] by using a slightly modified procedure[20] in which the propargyl chloride is slowly added to the refluxing lithium aluminum hydride–tetrahydrofuran mixture and allowing the allene to distill out (along with some tetrahydrofuran) at 50–55 °C. The distillate is repeatedly washed with cold water until the tetrahydrofuran is not detectable by NMR analysis. The allene is dried over anhydrous potassium carbonate and is then distilled (bp 42 °C).

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[14] Calculated on the basis of C–H and C_6H_5S–H bond energies of 88.6[12] and 88[17] kcal/mol, an allyl radical stabilization energy of ~10 kcal/mol,[12] and a phenylthiyl stabilization energy of 9.6 kcal/mol.[10]

[15] Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

[16] Calculated on the basis of C–H and H–I bond energies of 88[12] and 71[17] kcal/mol and the allyl radical stabilization energy of ~10 kcal/mol.[11]

[17] Bailey, W. J.; Pfeiffer, C. R. *J. Org. Chem.* **1955**, *20*, 95.

[18] Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.

[19] When the allene is not removed from the refluxing reaction mixture as it is formed, overreduction occurs (up to ~12%) to form 2-methyl-2-butene. Reduction of 3-chloro-1-deuterio-3-methyl-1-butyne with lithium aluminum deuteride results in the formation of 2-methyl-2-butene-d_4, indicating that the overreduction occurs via a radical-chain process.

[20] Kleinberg, K., Ed. *Inorg., Synth.* **1963**, *7*, 10.

Ethylallene (1,2-Pentadiene). Ethylallene (**1e**) was prepared by the lithium aluminum hydride reduction of 3-chloro-1-pentyne using the modified procedure described above (bp 42–44 °C).

Isopropylallene (4-Methyl-1,2-pentadiene). Isopropylallene (**1d**) was prepared by the lithium aluminum hydride reduction of 3-chloro-4-methyl-1-pentyne using the modified procedure described above.

1-*tert*-Butyl-1-methylallene (3,4,4-Trimethyl-1,2-pentadiene, 8). To 9.88 g (25.2 mmol) of bis(tributylphosphine)copper(I) iodide[21] in 50 mL of pentane at −78 °C (dry ice–acetone bath) under a nitrogen atmosphere was added 46 mL of 1.1 M *tert*-butyllithium. The reaction mixture was stirred for 1 h, and 2.07 g (23.4 mmol) of 1-chloro-2-butyne was added. The reaction mixture was stirred at −78 °C for 1 h, was then allowed to warm to room temperature, and was allowed to stir overnight. The reaction mixture was hydrolyzed by the addition of 50 mL of saturated aqueous ammonium chloride. The pentane layer was decanted and washed with aqueous ammonium chloride until no evidence of copper salts (blue color) remained. The extract was dried over anhydrous potassium carbonate. The pentane was removed by fractional distillation, and the product was distilled at 100–107 °C, giving 1.7 g (62%) of **8**: NMR ($CDCl_3$) δ 1.08 (s, 9 H), 1.68 (t, J = 3.0 Hz, 3 H), 4.58 (q, J = 3.0 Hz, 2 H). The allene was further purified by preparative GLC on a 10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb P column: exact mass calcd for C_8H_{14} *m/e* 110.110, found *m/e* 110.109.

***tert*-Butylallene (4,4-Dimethyl-1,2-pentadiene, 1a).** To 6.6 g (0.06 mol) of thiophenol in 80 mL of tetrahydrofuran at −40 °C was added 28 mL of 2.17 M *n*-butyllithium in hexane. The reaction mixture was stirred for 10 min and 11.4 g (0.06 mol) of copper(I) iodide was added. The mixture was allowed to warm to room temperature for 10 min and was then cooled to −70 °C and 46.2 mL of 1.3 M *tert*-butyllithium in pentane was added. The reaction mixture was allowed to warm to −40 °C for 10 min and was again cooled to −70 °C. Propargyl chloride (4.5 g, 0.06 mol) was added and the reaction mixture was allowed to warm to 25 °C and was stirred for 30 min. Saturated aqueous ammonium chloride (150 mL) was added. The organic layer was decanted, and the aqueous layer was washed with 50 mL of pentane. The combined organic fraction was washed five times with water (50 mL) and was dried over magnesium sulfate. The organic solvents were removed by fractional distillation, and the product was distilled (bp 73–75 °C). Pure **1a** was isolated by preparative GLC on a 10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb P column: NMR ($CDCl_3$) δ 1.06 (s, 9 H), 4.75 (B_2 portion of an AB_2 system, $J \approx 6$ Hz, 2 H), 5.17 (A portion of an AB_2 system, 1 H); exact mass calcd for C_7H_{12} *m/e* 96.094, found *m/e* 96.093.

***n*-Butylallene (1,2-Heptadiene, 1c).** *n*-Butylallene was prepared by the ferric chloride catalyzed coupling of *n*-butylmagnesium bromide with propargyl chloride[22] and was purified by preparative GLC.

Isobutylallene (5-Methyl-1,2-hexadiene, 1b). Isobutylallene was prepared by the ferric chloride catalyzed coupling of isobutylmagnesium bromide with propargyl chloride[22] and was purified by preparative GLC.

Preparation of 3-Chloro-1-pentyne. To a cooled (~10 °C) solution of 31 mL of thionyl chloride in 35 mL of pyridine was added 30 mL of 1-pentyn-3-ol with the temperature maintained at 10–20 °C. After completion of the addition of the alcohol, the reaction mixture was allowed to warm to room temperature. Water (100 mL) was cautiously added, and the organic layer was isolated. The organic phase was washed twice with 100-mL portions of 5% sodium bicarbonate and finally with water. The product was dried over potassium carbonate and was distilled: bp 55–58 °C (65 mm); 70% yield.

Preparation of 3-Chloro-4-methyl-1-pentyne.[23] To a mixture of 0.13 mol of 4-methyl-1-pentyn-3-ol and 4.2 mL of pyridine at 0 °C was slowly added 4.5 mL (0.05 mol) of phosphorus trichloride. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The chloride was directly distilled from the reaction mixture: bp 98–100 °C; 80% yield.

1-*tert*-Butyl-3,3-dideuterio-1-methylallene (1,1-Dideuterio-3,4,4-trimethyl-1,2-pentadiene). To 2.25 g of lithium aluminum deuteride suspended in 95 mL of diethyl ether was added 7.95 g of ethyl 2-butynoate. After being stirred for 1 h at 25 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride. The ether layer was decanted and dried over anhydrous magnesium sulfate, and the ether was removed by distillation. Distillation of the residue gave 4.22 g (90%) of 1,1-dideuterio-2-butyn-1-ol, bp 138–143 °C. The alcohol was converted to the chloride (74%) by using the thionyl chloride procedure described above, and the chloride was converted to the desired allene by using lithium bis(tributylphosphine)-di-*tert*-butylcuprate.

3,3-Dideuterio-1,1-dimethylallene.[23] To 30 mL of deuterium oxide and 15 mL of tetrahydrofuran, in which 0.1 g of sodium had been dissolved, was added 30 g of 3-chloro-3-methyl-1-butyne. The mixture was stirred vigorously for 30 min at 25 °C. The reaction mixture was allowed to separate, and the organic layer was removed and subjected to the foregoing procedure three more times. The NMR spectrum showed greater than 98% exchange. The organic layer was dried over anhydrous potassium carbonate and was distilled.

To 2.0 g of lithium aluminum deuteride in 20 mL of tetrahydrofuran was added 9.3 g of the monodeuterated chloride. The reaction mixture was maintained at reflux, and allene and tetrahydrofuran were allowed to slowly distill from the reflux column at 50–55 °C. The distillate was washed repeatedly with ice-cold water until free of tetrahydrofuran. The allene was purified by preparative GLC on a 10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb column.

Reaction of *tert*-Butylallene (1a) with Benzenethiol. Compound **1a** (41.8 mg, 0.43 mmol) and benzenethiol (46.3 mg, 0.42 mmol) were mixed in a heavy-walled, Kontes Microflex tube reaction vessel which was placed in direct sunlight[24] at 25 °C. (At this reaction scale there was no apparent increase in the temperature of the reaction mixture.) Analysis by NMR indicated that the reaction had gone to completion within 5 min. The NMR spectrum of the product indicated the quantitative formation of four adducts. Preparative GLC on a 15 ft × $^3/_8$ in. 20% Carbowax 20M on Chromosorb P column gave three fractions: the first fraction (severely overlapping peaks) was a mixture of **3a** and **4a**, the second was **2a**, and the third was **5a**. Integration of the gas chromatogram and NMR spectrum indicated a product ratio of **2a**/**3a**/**4a**/**5a** of 20:17:38:25.

3a: NMR ($CDCl_3$) δ 1.25 (s, 9 H), 1.85 (d, $J \approx 1.5$ Hz, 3 H), 5.87 (q, $J \approx 1.5$ Hz, 1 H), 7.3 (m, 5 H); irradiation of the δ 5.87 resonance resulted in an 83% enhancement in the intensity of the δ 1.85 doublet; mass spectrum (GC/MS of second of the overlaping peaks), *m/e* (relative intensity) 206 (parent ion, 55), 191 (P − CH_3, 100), 110 (C_6H_5SH, 8); exact mass calcd for $C_{13}H_{18}S$ (as a mixture of **3a** and **4a**) *m/e* 206.113, found *m/e* 206.110.

4a: NMR ($CDCl_3$) δ 1.00 (s, 9 H), 2.18 (br s, 1 H), 4.82 (br s, 1 H), 5.05 (br s, 1 H), and 7.3 (m, 5 H); mass spectrum, *m/e* (GC/MS of the first of the overlapping peaks) 206 (P, 46), 191 (P − CH_3, 22), 150 (100), 110 (75).

2a: NMR ($CDCl_3$) δ 1.17 (s, 9 H), 2.00 (d, $J \approx 1.5$ Hz, 3 H), 6.02 (q, $J \approx 1.5$ Hz, 1 H), 7.3 (m, 5 H); irradiation of the δ 6.02 resonance resulted in a 23% enhancement in the intensity of the δ 2.00 doublet; mass spectrum (GC/MS), *m/e* (relative intensity) 206 (P, 40), 191 (P − CH_3, 100), 149 (20), 110 (5); exact mass calcd for $C_{13}H_{18}S$ *m/e* 206.113, found *m/e* 206.110.

5a: NMR ($CDCl_3$) δ 0.93 (s, 9 H), 3.49 (d, J = 3.2 Hz, 2 H), 5.42 (m, 2 H), 7.2 (m, 5 H); mass spectrum (GC/MS), *m/e* (relative intensity) 206 (P, 50), 191 (P − CH_3, <2), 150 (13), 110 (49), 97 (64), 57 (100); exact mass calcd for $C_{13}H_{18}S$ *m/e* 206.113, found *m/e* 206.111.

Iodine-Catalyzed Isomerization of 2a. Approximately 10 mg of **2a** was dissolved in 0.75 mL of deuteriochloroform in an NMR tube, and one small crystal (~1 mg) of iodine was added.

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[21] Pasto, D. J.; Chou, S.-K.; Waterhouse, A.; Shults, R. H.; Hennion, G. F. *J. Org. Chem.* **1978**, *43*, 1385.

[22] Attempted use of the thionyl chloride/pyridine procedure resulted in an extremely low yield of product.

[23] Exchange of the acetylenic hydrogen (and hydroxyl) in basic deuterium oxide followed by conversion to the chloride with concentrated hydrochloric acid/calcium chloride resulted in extensive exchange of ≡CD by ≡CH. Very little solvolysis of the 3-chloro-3-methyl-1-butyne was observed under the reaction conditions described herein.

[24] No reaction occurred in the dark or when both reactants were triply freeze-degassed and then mixed in the dark.

The tube was capped and was allowed to stand at room temperature. The NMR spectrum of the sample was recorded periodically. Within 2 h the methyl doublet of **2a** had disappeared, and two very broad resonances representing the vinyl protons of **4a** had grown in intensity. (The resonances of **5a** were not broadened.) Continued monitoring over the course of 12 days showed no further change.

Reaction of a 2a–5a Adduct Mixture with 4-Methylbenzenethiol. A mixture of **2a**–**5a** was prepared as described above from 13.2 mg (0.135 mmol) of **1a** and 10.8 mg (0.098 mmol) of benzenethiol. After completion of the reaction, the excess **1a** was pumped off on a vacuum line. The adduct mixture was dissolved in 1.0 mL of deuteriochloroform, and 7.8 mg (0.063 mmol) of 4-methylthiophenol was added. The NMR spectrum was recorded after 30 min and showed the vinyl hydrogen quartets of **2a** and **3a** at δ 6.03 and 5.87 and two new quartets at δ 6.12 and 5.94 representing the (4-methylphenyl)thio adducts similar to **2a** and **3a**. The GC/MS of the mixture showed the three characteristic peaks of **3a** plus **4a**, **2a**, and **5a** with parent ions at *m/e* 206 and three peaks with parent ions at *m/e* 220 representing similar (4-methylphenyl)thio adducts.

Addition of Benzenethiol to the Monoalkylallenes 1b–e. Approximately 50-mg portions of **1b**–**e** and 0.7 molar equiv of benzenethiol were mixed and allowed to stand 30 min in direct sunlight. The excess **1b**–**e** was removed on a vacuum line. The adduct mixtures were analyzed by GC/MS, and their NMR spectra were recorded. Structural assignments were made by comparison of chemical shifts with those of **2a**–**5a** (all chemical shifts of comparable protons were with ±0.03 ppm of those in **2a**–**5a**). Integration of the NMR spectra provides product ratios which are tabulated in Table I. High-resolution mass spectral, exact masses were recorded for all adduct mixtures and were consistent to within *m/e* ±0.003.

Addition of Benzenethiol to 1,1-Dimethylallene (6). Compound **6** (32.0 mg, 0.47 mmol) and benzenethiol (41.6 mg, 0.38 mmol) were mixed in a Microflex reaction vessel, and the mixture was allowed to stand in direct sunlight for 20 min. The excess **6** was pumped off on a vacuum line. The NMR spectrum of the product showed the presence of a single product, **7**: ($CDCl_3$) δ 1.88 (br s, 3 H), 1.96 (br s, 3 H), 2.03 (br s, 3 H), 7.2 (m, 5 H).

Attempted Iodine-Catalyzed Isomerization of 7. Approximately 150 mg of **7** was dissolved in 1.0 mL of deuteriochloroform and placed in an NMR tube. Iodine (~2 mg) was added, the contents of the tube were triply freezed-degassed, and the tube was sealed under a vacuum. The NMR spectrum was periodically recorded over a period of 22 days. There was no evidence of isomerization, and the methyl resonances showed no exchange broadening. Similarly, no isomerization was evident after 24 days at 80 °C in benzene-d_6.

Addition of Benzenethiol to a Mixture of 6 and 6-*3,3-d*$_2$. To a mixture of 0.187 g of **6** and 0.158 g of **6**-*3,3-d*$_2$ was added 0.213 g of benzenethiol, and the reaction mixture was allowed to stand in direct sunlight for 15 min. The unreacted allene was recovered on a vacuum line. The mass spectrum of the unreacted allene showed no increase in **7**-d_1 over that in the starting mixture. The mass spectrum of the addition product similarly showed no increase in **7**-d_1 over that expected from the starting allene mixture.

Addition of Benzenethiol to 1-*tert*-Butyl-1-methylallene (8). Compound **8** (73.9 mg, 0.67 mmol) and benzenethiol (105.6 mg, 0.68 mmol) were placed in a stoppered, Pyrex vessel and allowed to stand in direct sunlight for 15 min. The mixture of adducts was separated by preparative GLC on a 15 ft × $^3/_8$ in. 20% Carbowax 20M on Chromosorb P column, giving pure fractions of **11**, **10**, and **9** in a 17.9:40.2:41.9 ratio.

9: NMR ($CDCl_3$) δ 1.27 (s, 9 H), 2.09 (s, 3 H), 2.13 (s, 3 H), 7.2 (m, 5 H); mass spectrum (GC/MS), *m/e* (relative intensity) 220 (P, 13), 164 (34), 110 (100), 78 (12), 57 (16); exact mass calcd for $C_{14}H_{20}S$ *m/e* 220.129, found *m/e* 220.125.

10: NMR ($CDCl_3$) δ 1.32 (s, 9 H), 1.86 (s, 3 H), 1.95 (s, 3 H), 7.2 (m, 5 H); mass spectrum (GC/MS), *m/e* (relative intensity) 220 (P, 95), 205 (P – CH_3, 100), 163 (22), 111 (82), 110 (41), 78 (34), 57 (24); exact mass calcd for $C_{14}H_{20}S$ *m/e* 220.129, found *m/e* 220.130.

11: NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.15 (d, *J* = 6.7 Hz, 3 H), 2.21 (q, *J* = 6.7 Hz, 1 H), 4.61 (br s, 1 H), 5.01 (br s, 1 H), 7.2 (m, 5 H); mass spectrum (GC/MS), *m/e* (relative intensity) 220 (P, 95), 205 (P – CH_3, 100), 163 (23), 111 (87), 110 (46), 95 (41), 78 (37), 57 (40); exact mass calcd for $C_{14}H_{20}S$ *m/e* 220.129, found *m/e* 220.127.

Addition of Benzenethiol-*S-d* to 8. Compound **8** (32.5 mg, 0.48 mmol) and 46.4 mg (0.42 mmol) of benzenethiol-*S-d* (prepared by the multiple exchange–extraction procedure from benzenethiol and deuterium oxide) were mixed in an NMR tube and allowed to stand in direct sunlight for 20 min. The NMR spectrum ($CDCl_3$ solution) of the resulting adduct mixture showed a singlet at δ 1.86 (3 H) and broad 1:1:1 triplet at δ 1.95 (2 H) for **10** and a singlet at δ 2.09 (3 H) and a broad 1:1:1 triplet at δ 2.13 (2 H) for **9**.

Addition of Benzenethiol to a Mixture of 8 and 8-*3,3-d*$_2$. To 107.1 mg (1.56 mmol) of a mixture of **8** and **8**-*3,3-d*$_2$ (56.6 ±0.1% d_0 with <1% d_1) was added 47.0 mg (0.43 mmol) of benzenethiol. After completion of the reaction, the unreacted allene was pumped off on a vacuum line, and the mixture of adducts was separated by preparative GLC. Analysis of **11** by mass spectrometry showed the presence of 62.0 ± 0.5% **11**, 31.8 ± 0.4% **11**-d_1, and 6.02 ± 0.5% **11**-d_2.

Iodine-Catalyzed Isomerization of a Mixture of 9–11. To 70 mg of a freshly prepared mixture of **9**-**11** in 1.0 mL of deuteriochloroform in an NMR tube was added ~1 mg of iodine. The contents of the tube were freezed-degassed, and the tube was sealed under vacuum. The NMR spectrum was recorded immediately and showed the vinyl hydrogen resonances as very broad singlets (~12-Hz width at half-height). The addition of greater quantities of iodine resulted in coalescence of the vinyl hydrogen resonances. The methyl resonances of **9** and **10** were not apparent in the spectrum. No further changes were noted after 15 days.

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Registry No. 1a, 26981-77-1; **1b**, 13865-36-6; **1c**, 2384-90-9; **1d**, 13643-05-5; **1e**, 591-95-7; **6**, 598-25-4; **8**, 7417-50-7; 1-chloro-2-butyne, 3355-17-7; propargyl chloride, 624-65-7; 1-pentyn-3-ol, 4187-86-4; 3-chloro-1-pentyne, 14035-68-8; 3-chloro-4-methyl-1-pentyne, 56698-97-6; 4-methyl-1-pentyn-3-ol, 565-68-4; 1,1-dideuterio-3,4,4-trimethyl-1,2-pentadiene, 77494-70-3; 3,3-dideuterio-1,1-dimethylallene, 53730-66-8; benzenethiol, 108-98-5.