Isotope Effects and Relative Reactivities in the Radical-Chain Addition of Benzenethiol to Substituted Allenes

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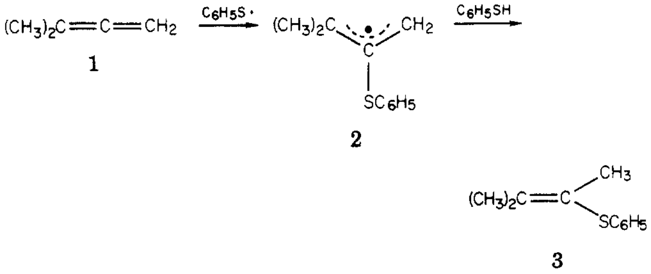
The relative reactivities of several monoalkyl- and 1,1-dialkylallenes, one trialkylallene, and one tetraalkylallene toward the addition of phenylthiyl radical have been measured. Isotope effects have been measured for the addition of the phenylthiyl radical to 1,1-dimethylallene and its 3,3-dideuterio and 1,1-bis(trideuteriomethyl) analogues and to ethylallene and its 3,3-dideuterio analogue. The results are interpreted in terms of a very early transition state in which very little rotation about one end of the allene system has occurred. The relative reactivities and product distributions are determined by frontier molecular orbital interactions between the singly occupied MO of the phenylthiyl radical and the occupied π MO's of the allene.

As part of our study of model reactions of allenes for comparison with the [2 + 2] cycloaddition reactions of allenes we have determined the chemo- and stereoselectivities, relative reactivities, and kinetic isotope effects in the radical-chain addition of benzenethiol to substituted allenes. The chemo- and stereoselectivity aspects are described in the previous paper.[1] In the present paper the relative reactivities and kinetic isotope effects are presented and are interpreted in terms of detailed mechanistic descriptions of the steps in the radical-chain addition process.

Results

Measurement of Kinetic Isotope Effects. 1,1-Dimethylallene (1). 3,3-Dideuterio-1,1-dimethylallene (1-d_2) and 1,1-bis(trideuteriomethyl)allene (1-d_6) were prepared, and the kinetic isotope effects were measured by using competitive reaction techniques. Approximate 1:1 mixtures of 1 and 1-d_2 and of 1 and 1-d_6 were prepared and the H_2/D_2 and H_6/D_6 ratios were determined by using mass spectral techniques (see Experimental Section). Accurately weighed portions of the mixtures of 1 and 1-d_2 and of 1 and 1-d_6 were reacted with ~0.5 molar equiv of benzenethiol. After completion of the addition reaction, as determined in control experiments, the unreacted allene mixtures were removed on a vacuum line and the H_2/D_2 and H_6/D_6 ratios were determined by mass spectrometry. The H_2/D_2 and H_6/D_6 ratios in the mixtures of the adducts 3 and 3-d_2 and the adducts 3 and 3-d_6 were determined by mass spectral techniques. The k_H/k_D values were calculated by an iterative computer program (see Experimental Section) and are given below the following reaction equation.



$$k_{H_2}/k_{D_2} = 0.977 \pm 0.005,\ 0.982 \pm 0.005$$
$$k_{H_6}/k_{D_6} = 1.30 \pm 0.01$$

Table I. Total and Partial Relative Reactivities for Phenylthiyl Radical Addition to Substituted Allenes

substituents	k_{rel}(total)	$k_{rel}(C_2)$	$k_{rel}(C_3)$
ethyl	1.00	0.83	0.17
butyl	0.95	0.79	0.16
isobutyl	0.95	0.79	0.16
isopropyl	0.69	0.58	0.11
tert-butyl	0.54	0.34	0.20
1,1-dimethyl	12.5 (1.00)[a]	12.5	[b]
1-ethyl-1-methyl	11.6 (0.93)	11.6	[b]
1-*tert*-butyl-1-methyl	6.4 (0.51)	6.4	[b]
3-ethyl-1,1-dimethyl	19.8	16.3	3.5
1,1,3,3-tetramethyl	9.5	9.5	[b]

[a] Numbers in parentheses are relative rates within the 1,1-dialkylallene series. [b] No C_3 attack product detected by NMR.

Ethylallene. A mixture of ethylallene (4) and its 3,3-d_2 analogue was reacted with 0.5 molar equiv of benzenethiol. The H_2/D_2 ratio in the unreacted allene mixture was determined by mass spectrometry. The mixture of adducts was separated by preparative GLC, giving pure fractions of 7 and 10 and an inseparable mixture of 8 and 9. The H_2/D_2 ratios in 7 and 10 and in the mixture of 8 and 9 were determined by mass spectrometry. The H_2/D_2 ratio in 8 must be the same as that in 7 in that rapid *E–Z* isomerization takes place during the addition process.[1] The H_2/D_2 ratio in 9 was then calculated from the H_2/D_2 ratio for the mixture of 8 and 9 by assuming that the 7/8 ratio formed in the reaction is the same as that derived in the addition to unlabeled 4, the latter being readily determined by NMR.[1] The relative yields of the four adducts formed on addition to the unlabeled 4 are indicated beneath the structures in Scheme I, while the yields derived in the addition to the mixture of labeled and unlabeled 4 appear in parentheses.

As the H_2/D_2 ratio in the intermediate radical 6 must be the same as that in the adduct 10, the H_2/D_2 ratio in the radical 5 can then be calculated from the H_2/D_2 ratios in the starting and recovered allene and in radical 6. Sufficient data is thus available for calculation of the isotope effects in all of the reactions illustrated in Scheme I. The values of the isotope effects are given above or below the reaction arrows in Scheme I. A large uncertainty is associated with the isotope effect for formation of 9 because of its low yield and the estimated error in determining the yield of 9 (±1%) which greatly affects the H_2/D_2 ratio calculated for 9. In turn, the large uncertainty in the H_2/D_2 ratio for 9 increases the uncertainty limits of the isotope effect for formation of 7 and 8 to a value much larger than those associated with the other isotope effects. If calculated only for the formation of 7, the uncertainty limits would be slightly less than ±0.02.

Relative Reactivity Measurements. The relative reactivities of substituted allenes toward attack by phenylthiyl radical were determined by using competitive

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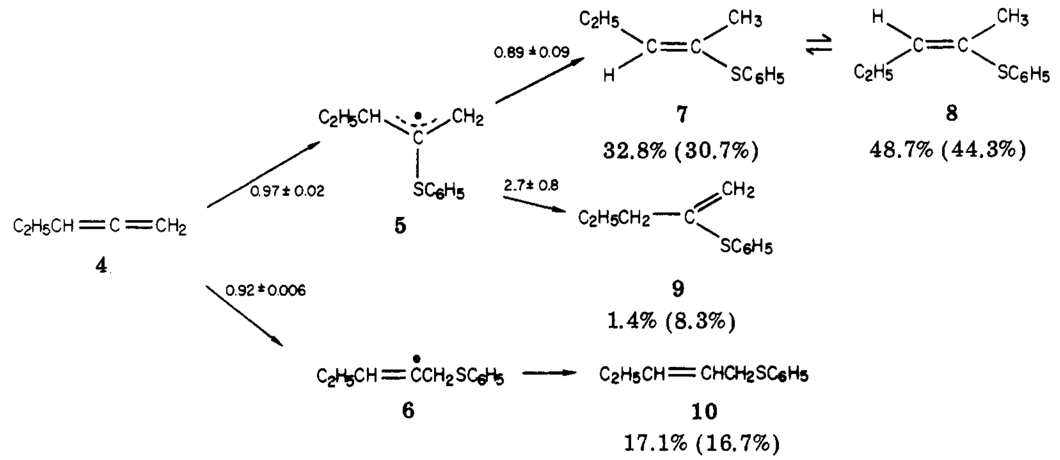
[1] Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.*, previous paper in this issue.

0022-3263/81/1946-2842$01.25/0

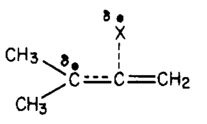
Scheme I



reaction techniques with an added internal standard for GLC analysis. The total relative reactivities relative to ethylallene are given in Table I. Partial relative reactivities for attack at C_2 and C_3 (no attack was observed at C_1 with any of the substituted allenes) have been calculated by using product distribution data[1] and are also given in Table I.

Discussion

Kinetic Isotope Effects. In our detailed study of the mechanism of the cycloaddition reactions of allenes we felt it was necessary to determine the values of the kinetic isotope effects for the formation of an intermediate allyl radical formed by the addition of a free radical to an allene, as well as in the reactions of the intermediate allyl radical to form the final products, for comparison with isotope effects derived with diradical intermediate and the mechanistically questionable cycloaddition reactions of allenes. In order to exert control over which π system of an allene was undergoing attack, we selected 1,1-dimethylallene (1) for our initial studies. (Previous studies had shown that attack by a radical on 1 occurred only at C_2.)[2] In 1, attack by a free radical should be strongly favored at the p AO on C_2 of the C_1–C_2 double bond because of the greater stability of the incipient radical center at C_1 relative to C_3; i.e., 11 is favored over 12. During the attack illustrated in 11, two important processes occur within the allene portion of 11: (1) rotation of the $(CH_3)_2C$ portion of the allene must occur to form the planar allyl radical intermediate; (2) disruption of the delocalization of the C_1–C_2 π system into the π-type σ MO of the terminal methylene group occurs due to the C···X bond formation and the rotation and bending motions required of the $(CH_3)_2C$ portion of 11 (see 13). The rotation of the $(CH_3)_2C$ portion of 1 in 11 will give rise to a rotational isotope effect,[3] the maximum value of which will be the ratio of the masses of the labeled to the unlabeled groups, i.e., $(CH_3)_2/(CD_3)_2$, or 1.20. The disruption of the delocalization will give rise to a secondary isotope effect due to a change in the stretching and bending force constants of the C–H bonds. In an allene the C–H bond is an "allyl-vinyl"-type hybrid which on going to the allyl radical intermediate becomes a vinyl-type C–H bond. This change results in an increase in the force constants and, thus, a less-than-unity isotope effect. Stretching force constants derived from geometry optimization calculations by using the GAUSSIAN 70 package of programs[5,6] on allene and the allyl radical support this qualitative analysis. The $=CH_2$ coupled symmetrical stretching force constant in allene is 11.79 mdyn/Å (or 5.90 mdyn/Å per C–H bond) and 6.21 mdyn/Å for both the inner and outer C–H bonds of allyl radical (4-31G calculations).[6] However, because of the very early transition state, the character of the C–H bonds in the allyl radical may not be a good representation of the C–H bonds in the transition state. Calculations on 11, in which the original geometry of the allene is retained, also indicate that the C–H stretching force constants increase on radical attack at C_2 (12.29 mdyn/Å for the coupled, symmetrical stretch of the $=C^3H_2$).



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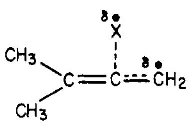

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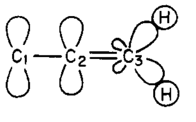

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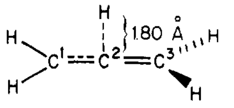

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The k_{H_2}/k_{D_2} for addition of the phenylthiyl radical to the central carbon atom of 1 is less than unity. The small value of the isotope effect (0.98) is consistent with the fact that the reaction is very fast at room temperature and must be occurring via a very early transition state.[7]

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(2) Jacobs, T. L.; Illingworth, G. E. *J. Org. Chem.* **1963**, *28*, 2692.

(3) Rotational isotope effects have been discussed previously;[4] however, no rotational isotope effect uncontaminated by other contributing isotope effects has been reported.

(4) Gajewski, J. J.; Chou, S.-K. *J. Am. Chem. Soc.* **1977**, *99*, 5696. Crawford, R. J.; Cameron, D. M.; Tokunaga, H. *Can. J. Chem.* **1974**, *52*, 4025.

(5) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QPCE* **1973**, *10*, 236.

(6) It has been demonstrated that C–H bond-stretching force constants calculated by geometry-optimization calculations using the 4-31G basis set correlate well with gas-phase equilibrium isotope effects for reactions in which a methyl group is attached to an atom bearing a nonbonded pair of electrons, but not particularly well when a vacant orbital is generated adjacent to the methyl group. Although the systems discussed in this paper differ substantially in structure, similar correlations appear to work well. See: DeFrees, D. J.; Taagepera, M.; Levi, B. A.; Pollak, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5532.

The k_{H_6}/k_{D_6} of 1.30 for the addition to 1 is *larger* than the theoretical maximum of 1.20. As thiyl radicals are known to be electrophilic[8] and polar effects have been shown to be present in radical addition reactions,[9] the observed k_{H_6}/k_{D_6} must be a product of a rotational and a polarization-induced (delocalization of partial positive charge into the orbitals of the methyl groups) isotope effect. The development of partial positive charge on C_1 of 1 will result in a greater-than-unity isotope effect.[10] Analysis of the relative reactivity data in Table I indicates that the rotational isotope effect contribution must be very small. For example, the change from ethyl to *n*-butyl or isobutyl, which is a mass ratio change of 1.97, results in only a 4.8% reduction in rate of attack at C_2! The change from 1,1-dimethyl- to 1-ethyl-1-methylallene, a mass change of 1.47, results in a reduction in rate of 7%. The relative reactivity data are consistent with a very early transition state in which little rotation about C_1 has occurred and are in agreement with the conclusions derived from the k_{H_2}/k_{D_2} isotope effect.

Attack by the phenylthiyl radical on ethylallene occurs at both C_2 and C_3. The attack at C_2 is associated with a kinetic isotope effect of 0.97, very similar to that observed with 1,1-dimethylallene. Attack at C_3 is associated with a k_{H_2}/k_{D_2} of 0.92. This value is very similar to those observed in the addition of methyl[11] and cyclopropyl[12] radicals to 1,1-dideuteriopropene (k_{H_2}/k_{D_2} = 0.89 and 0.92, respectively) and in the radical polymerization of styrene-β,β-d_2[13] (0.88).

Hydrogen atom abstraction by the intermediate radical 6 to form 7 and 8 is characterized with a k_{H_2}/k_{D_2} of 0.89. This isotope effect is similar to that for the thiyl radical attack at C_3 of ethylallene. Both reactions involve an atom transfer to a sp^2-hybridized carbon atom and, thus, would be expected to possess similar isotope effects.

The k_{H_2}/k_{D_2} calculated for the formation of 9 from 5 is unrealistically large and is associated with a large uncertainty; however, the isotope effect must certainly be substantial to cause the significant change in the yield of 9.[14] At the present time the origin of this isotope effect is unknown. Preliminary calculations on 12 suggest that the C–H stretching force constants increase slightly (6.24 and 6.25 mdyn/Å for the inner and outer C–H bonds, respectively) which should give rise to a less-than-unity isotope effect. It is obvious that there are other internal motions that are involved along the reaction coordinate which could give rise to the significant isotope effect, for example, the shortening of the C^2=C^3H_2 bond length which will give rise to a greater-than-unity isotope effect. Further calculations are necessary to gain a better understanding of the changes involved in going to the transition state.

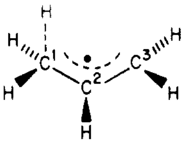

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Table II. Calculated (STO-3G) and Observed Orbital Energies (eV) of Allenes

	occupied MO's		unoccupied MO's	
	C_1=C_2	C_2=C_3	C_1=C_2	C_2=C_3
allene	−8.7960 (10.07)[a,b]	−8.7960 (10.64)	8.6605	8.6605
methylallene	−8.3015 (9.33)	−8.5903 (10.06)	8.7982	8.7459
1,1-dimethylallene	−7.9545 (8.95)	−8.4185 (9.86)	8.8531	8.8130
trimethylallene	−7.7907 (8.69)	−7.9759 (9.24)	8.9075	8.9151
tetramethylallene	−7.6565 (8.47)[b]	−7.6565 (8.96)	8.9518	8.9518

[a] Photoelectron ionization potentials taken from ref 17 are given in parentheses. [b] Jahn–Teller split bands.

Relative Reactivities. In the monoalkylallene series the very small decrease in the rate on increasing the mass of the alkyl group, i.e., *n*-butyl and isobutyl vs. ethyl, has been interpreted in terms of a very early transition state in which little rotation about C_1 has occurred. Thus, very little stabilization energy of the ultimate allyl radical should be felt in the transition state. The 12.5-fold increase in the rate of reaction of 1,1-dimethylallene over ethylallene might be attributed to the additional stabilizing effect of the incipient radical by the second alkyl group. Alkyl substitution at a radical center, however, provides relatively little stabilization of the radical, being on the order of 0–3 kcal/alkyl group.[15] In a very early transition state only a small portion of this stabilization will be felt which, in turn, should have little effect on the rate of reaction. Relative rate factors of only 1.4–2.3 have been reported for carbon-based radical additions to propene and isobutene.[16] Furthermore, as alkyl stabilization of the incipient radical plays the dominant role in determining the relative reactivity of the allene, the introduction of an alkyl group at C_3 should not affect the reactivity for attack at the 2p AO on C_2 of the C_1–C_2 double bond. Inspection of the relative reactivity data for 1,1-dimethylallene and 3-ethyl-1,1-dimethylallene in Table I, however, shows that the introduction of the alkyl group at C_3 *increases* the relative reactivity at C_2 by ~30% despite a rate-retarding steric effect introduced by that group!

The relative reactivity data for attack at C_2 and for attack at C_3 relative to that at C_2 are easily understood on the basis of frontier MO theory. The dominant interaction between the electrophilic phenylthiyl radical and an allene must involve the interaction of the singly occupied MO on sulfur of the phenylthiyl radical with the occupied π MO's of the allene. The introduction of an alkyl group onto the allene chromophore not only raises the energy of the π system to which it is attached but also raises the energy of the remote π system (see Table II). This arises because

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[7] A substantially larger k_{H_2}/k_{D_2} (0.88 ± 0.02) has been observed for the formation of the diradical intermediate from 1 and 1,1-dichloro-2,2-difluoroethene. This reaction requires 12–16 h at 160 °C and must involve a later transition state than that encountered in the phenylthiyl radical addition (Pasto, D. J.; Warren, S. E., unpublished results).

[8] Cadogen, J. I.; Sadler, I. H. *J. Chem. Soc. B* **1966**, 1191.

[9] Walling, C. "Free Radicals in Solution"; Wiley: New York, 1967; pp 132–491.

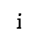
[10] Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109.

[11] Feld, M.; Stefani, A. P.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 4451.

[12] Stefani, A. P.; Chuang, L.-Y. Y.; Todd, H. E. *J. Am. Chem. Soc.* **1978**, *92*, 4168.

[13] Pryor, W. A.; Henderson, R. W.; Ratsiga, R. A.; Carroll, N. *J. Am. Chem. Soc.* **1966**, *88*, 1199.

[14] We have also observed an unusually large isotope effect and associated product distribution effect in the ring closure of the diradical intermediate i formed from ethylallene and 1,1-dichloro-2,2-difluoroethene.



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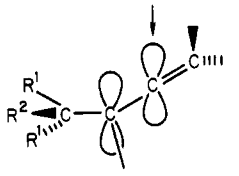
[15] Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1537.

[16] Trotman-Dickenson, A. F. "Free Radicals, An Introduction"; Wiley: New York, 1959; pp 110–112.

of the mixing of certain of the MO's of the alkyl group with the remote π system which have the same symmetry. On the average, the elevation in the energy of the remote π system is approximately 40% of that experienced by the π system to which the alkyl group is attached. (Little differences are noted in the energies of the lowest unoccupied MO's of the substituted allenes.) In ethylallene the difference in energy between the two π systems should be similar to that in methylallene (0.73 eV from PES measurements[17] and 0.29 eV from STO-3G calculations), and competitive attack on the two π systems is to be expected. That attack at C_3 of the C_2–C_3 π bond occurs instead of at C_2 can also be rationalized. The introduction of an alkyl group at C_1 increases the coefficient of the 2p AO on C_3 of the C_2–C_3 π bond (c_{C_3} = 0.6518 and c_{C_2} = 0.5453 in methylallene). In 1,1-dimethylallene the difference in energy between the two π systems is greater [0.91 eV (PES),[17] 0.47 eV (STO-3G)], and attack at C_2 is further favored. With 3-ethyl-1,1-dimethylallene the difference in energy is smaller [0.55 eV (PES),[17] 0.18 eV (STO-3G)], and competitive attack at C_2 and C_3 is again observed. In addition, the relative reactivities at C_2 and C_3 are greater than those in 1,1-dimethylallene and ethylallene, respectively, due to the elevation in the energy of the remote π systems on introduction of the alkyl groups.

Steric effects also play an important role on the reactivity of the allene system. In ethyl-, *n*-butyl-, and isobutylallene the alkyl groups can adopt conformations in which approach to C_2 is unimpeded. In isopropylallene, the isopropyl group can adopt a conformation in which one face of the C_1–C_2 π system is not sterically shielded (the top face of **13**, R^2 = H), while attack at the other face is sterically hindered by a methyl group, resulting in an overall reduction in the rate of attack at C_2 of isopropylallene. In *tert*-butylallene (and also with 1-*tert*-butyl-1-methylallene) approach to either face of the C_1–C_2 π system is sterically hindered resulting in a further reduction in the rate of attack at C_2. The size of the alkyl group at C_1 has little, or no, affect on the rate of attack at C_3.



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The moderate reduction in reactivity on going from the tri- to the tetrasubstituted allene is due to the fact that attack at C_2 on either face of either π bond of tetramethylallene is sterically impeded.

Summary

The detailed analysis of the isotope effects and the relative reactivities in the addition of phenylthiyl radical to substituted allenes indicate that the reaction occurs via a very early transition state in which little rotation of the orthogonal groups at the termini of the allene has occurred. The relative reactivities and chemoselectivities are governed by early frontier molecular orbital interactions between the SOMO of the phenylthiyl radical and the occupied π molecular orbitals of the allene.

Experimental Section

General Methods. Measurement of Isotopic Compositions. H_2/D_2 and H_6/D_6 isotopic composition ratios were determined by using an AEI MS 9 mass spectrometer operating at an ionization voltage of 14 eV with opened slits sufficient to produce flat-topped peaks. Under the operating conditions very little fragmentation was observed to produce M − 1 and M − 2 peaks. Pressures were maintained low enough to avoid ion–molecule reactions. Approximately 40–50 rapid scans were recorded in the parent ion region and the H_2/D_2 and H_6/D_6 ratios were calculated on the basis of peak height measurements. Values of the ratios differing by more than 2σ from the average value were discarded (on the average less than 5% of the measured ratios), and the average value was recalculated along with the uncertainty value. The H_2/D_2 ratios were then corrected for M + 2 and M − 2 contributions determined from similar mass spectral measurements carried out on the nondeuterated system.

Calculation of Kinetic Isotope Effects and Relative Reactivities. Rate ratios, both k_H/k_D's and relative rate ratios for pairs of substituted allenes, have been calculated by using an iterative computer program employing Δ concentration and time functions in the kinetic expressions. Starting with the initial concentrations of all reactants, the program iteratively adjusts the relative rate constants until the calculated product distribution(s) corresponded to the observed product distribution(s) to within preset limits (generally ±0.1%). Calculations were carried out to 99.8% completion with changes in the concentration of the benzenethiol of 0.05%. Uncertainty values in the k_H/k_D's are estimated from calculations using the high-end and low-end values for the H–D distributions in the allene and adduct(s).

1,1-Bis(trideuteriomethyl)allene. To 2.4 g (0.348 mol) of lithium in 200 mL of ether was slowly added 25 g (0.172 mol) of trideuteriomethyl iodide (>99.5% D). After the addition was completed, the solution was cooled to 0 °C, and 8.4 g (0.082 mol) of ethyl propiolate was slowly added. At the end of the addition 30 mL of water was added, and the ether layer was decanted, washed with saturated aqueous sodium chloride, and dried over magnesium sulfate. The solvent was removed by distillation, and the residue was distilled (bp 95–108 °C), giving 3.2 g of product alcohol.

To the 3.2 g of labeled alcohol was added 3.0 g of unlabeled 3-methyl-1-butyn-3-ol. The mixture was slowly added to a suspension of 5 g of calcium chloride in 20 mL of concentrated hydrochloric acid at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and then at 25 °C for 15 min. The reaction mixture was extracted with two 30-mL portions of ether. The extracts were combined, washed with saturated aqueous sodium chloride, and dried over potassium carbonate. The solvent was removed by fractional distillation.

The crude chloride from above was dissolved in 10 mL of tetrahydrofuran and was slowly added to 2.5 g of lithium aluminum hydride in 50 mL of refluxing tetrahydrofuran. During the addition the product allene was continuously allowed to distill from the reaction (along with some tetrahydrofuran) at ~55 °C. The distillate was repeatedly washed with cold water, and the allene mixture was purified by preparative GLC on a 12-ft silver nitrate/propylene glycol on Chromosorb P column at 40 °C. Analysis by mass spectrometry gave a ratio of 1 to 1-d_6 of 1.197 ± 0.012.

Addition of Benzenethiol to the Mixture of 1 and 1-d_6. The mixture of 1 and 1-d_6 (0.0798 g) was added 0.0484 g of benzenethiol. The reaction mixture was thoroughly mixed and was allowed to stand at room temperature for 30 min. The sample was placed on a vacuum line and the unreacted allene was removed. Analysis of the recovered allene by mass spectrometry as described gave a H_6/D_6 ratio of 1.062 ± 0.016.

Preparation of 3,3-Dideuterio-1-ethylallene. To a mixture of 19 mL of deuterium oxide and 9 mL of tetrahydrofuran in which a small piece of sodium had been dissolved was added 9.45 g of 3-chloro-1-pentyne. The reaction mixture was stirred for 15 min at 25 °C and was then extracted with ether, and the ether was removed by fractional distillation. This process was repeated six

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[17] Brogli, F.; Crandall, J. K.; Heilbronner, E.; Kloster-Jensen, E.; Sojka, S. A. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 455.

[18] Attempted preparation of 3 by the addition of lithium acetylide–ethylenediamine complex to acetone-d_6, to be followed by conversion of the alcohol to the chloride and reduction by lithium aluminum hydride, resulted in extensive H–D exchange between the acetone-d_6 and the ethylenediamine.

times, after which analysis by NMR showed no detectable ≡CH.

To 0.76 g of lithium aluminum deuteride in 30 mL of refluxing tetrahydrofuran was slowly added 1.88 g of 3-chloro-1-deuterio-1-pentyne in 10 mL of tetrahydrofuran. During the addition process the product allene was allowed to slowly distill from the reaction mixture (along with some tetrahydrofuran) at 55 °C. The distillate was repeatedly washed with cold water until no tetrahydrofuran was detectable by NMR. To the final product (~0.42 g) was added 0.405 g of unlabeled ethylallene, and the resulting mixture was analyzed by mass spectrometry, giving a H_2/D_2 ratio of 0.957 ± 0.003.

Addition of Benzenethiol to a Mixture of 4 and 4-d_2. Benzenethiol (0.0337 g) was added to 0.0550 g of the mixture of 4 and 4-d_2 (H_2/D_2 ratio of 0.957 ± 0.003). The reaction mixture was placed in direct sunlight for 30 min and was then allowed to stand overnight. The unreacted allene was removed on a vacuum line and was analyzed by mass spectrometry, giving a H_2/D_2 ratio of 1.015 ± 0.012.

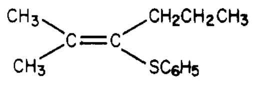
The adduct mixture was separated by preparative GLC on a 15 ft × $^3/_8$ in. Carbowax 20M on Chromosorb P column at 230 °C. The first peak, comprised of **8** and **9**, had a H_2/D_2 ratio of 0.998 ± 0.005 (corrected for P + 2 and P − 2 contributions determined with unlabeled **8**). The second peak (**7**) had a H_2/D_2 ratio of 0.922 ± 0.005, while the third peak (**10**) had a H_2/D_2 ratio of 0.893 ± 0.007.

The yields of the products were determined by a combined GLC and NMR analysis. The yields of the adducts derived from 4 and the mixture of 4 and 4-d_2 are given below the structures in Scheme I. The overall deuterium balance was within 0.1% of the starting amount of 4-d_2.

Measurement of the Relative Rates. Approximately 0.4 mmol of ethylallene and 0.4 mmol of the monoalkylallene or 1,1-dimethylallene, or 0.4 mmol of 1,1-dimethylallene and 0.4 mmol of the other di-, tri-, and tetraalkylallenes, were carefully weighed into a small reaction vessel equipped with a Minert valve (Kontes Glass Co.). Approximately 20–25 mg of pentane or heptane as an internal standard (depending on the relative GLC retention times of the allenes and the standards) was added, and the reaction vessel was carefully weighed. Several 0.15-μL samples were removed and analyzed by GLC on a 10-ft Apeizon M on Chromosorb P column at 70 °C, and the ratios of allene to internal standard were calculated. The reaction vessel was again weighed, and the initial amounts of the allenes added to the vessel were corrected for the losses incurred during the GLC analyses. Approximately 0.4 mmol of benzenethiol was added, and the reaction vessel was again carefully weighed to determine exactly the amount of the benzenethiol added. The reaction vessel was placed in direct sunlight for 30 min. Aliquots were then removed and analyzed by GLC, and the ratios of the allenes to internal standard were calculated. The changes in the allene–internal standard ratios were used to calculate the number of millimoles of each allene reacted, and the relative rates were calculated by using an iterative computer program.

Product distributions were determined from reactions carried out with pure allenes as reported in the previous paper[1] or as reported herein. Mass balance calculations agreed to within ±2% of the complete utilization of the benzenethiol.

Addition of Benzenethiol to 3-Ethyl-1,1-dimethylallene. To 53.6 mg (0.56 mmol) of the allene was added 47.4 mg (0.43 mmol) of benzenethiol. The mixture was allowed to stand in direct sunlight for 2 h, and then the excess allene was removed on a vacuum line. The NMR spectrum of the residue indicated the presence of two adducts I and II by comparison of the chemical shifts with those reported in the accompanying article for similar adducts: adduct I, NMR characteristic peaks ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz), 1.91 and 2.02 (s, $=C(CH_3)_2$); adduct II, NMR δ 1.13 (t, J = 6.8 Hz), 5.97 (d, J = 6.9 Hz). The NMR spectrum of the mixture also contained overlapping multiplets at δ 1.56 and 2.23. Integration of the NMR spectrum indicated a ratio of I/II of 84.7:15.3. Analysis by GC/MS indicated the presence of two adducts in a ratio of 80.3:19.7. Exact mass on the mixture calcd for $C_{13}H_{18}S$ 206.113, found 206.112.



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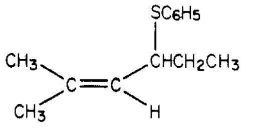
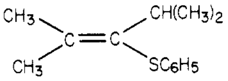


II

Addition of Benzenethiol to Tetramethylallene.[2] To 31.7 mg (0.33 mmol) of tetramethylallene was added 26.2 mg (0.24 mmol) of benzenethiol. The reaction mixture was allowed to stand in direct sunlight for 2 h, and then the excess unreacted allene was removed on a vacuum line. The NMR showed the presence of a single adduct having structure III:[2] NMR δ ($CDCl_3$) 1.22 (d, J = 6.8 Hz, 6 H), 2.32 and 2.36 (s, 3 H each), 3.81 (septet, J = 6.8 Hz, 1 H), 7.62 (br s, 5 H).



III

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Registry No. 1, 598-25-4; 4, 591-95-7; 3-ethyl-1,1-dimethylallene, 29212-09-7; tetramethylallene, 1000-87-9; butylallene, 2384-90-9; isobutylallene, 13865-36-6; isopropylallene, 13643-05-5; *tert*-butylallene, 26981-77-1; 1-ethyl-1-methylallene, 7417-48-3; 1-*tert*-butyl-1-methylallene, 7417-50-7; allene, 463-49-0; trimethylallene, 3043-33-2; benzenethiol, 108-98-5; deuterium, 7782-39-0.

Nickel(0)-Catalyzed Reactions of Bicyclo[2.1.0]pentane and Electron-Deficient Olefins[1,2]

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In the presence of a catalytic amount of bis(acrylonitrile)nickel(0), bicyclo[2.1.0]pentane suffers from the cleavage of the central σ bond and cycloadds to electron-deficient olefins such as methyl acrylate, acrylonitrile, dimethyl maleate, and dimethyl fumarate to give bicyclo[2.2.1]heptane derivatives. The stereochemistry and mechanism of the catalyzed cycloadditions have been elucidated by use of deuterated bicyclo[2.1.0]pentanes.

In connection with the activation of saturated hydrocarbons via homogeneous catalysis, we have examined reactions of various strained hydrocarbon systems which have unique steric and electronic structures.[1-4] Strained

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