The gas–liquid partition chromatogram showed two partially resolved peaks in area ratio of about 85:15, presumably owing to the two geometrical isomers, **12a** and **12b**.

Reduction of the Alkylidenecyclopropanes.—A typical procedure is given.

Into a flask fitted with stirrer, condenser, and dropping funnel was placed 19 g (0.074 mole) of 1,1-dibromo-2,2-dimethyl-3-ethylidenecyclopropane. The contents were cooled in an ice bath and 21.7 g (0.074 mole) of tri-*n*-butyltin hydride was added over 2 hr. The reaction mixture was then warmed to about 35° and allowed to stand until a test of an aliquot with acid indicated disappearance of the hydride (*ca.* 24 hr). Distillation provided 9.2 g (70%) of 1-bromo-2,2-dimethyl-3-ethylidenecyclopropane, bp 47° (10 mm). A residue of 27.2 g of tri-*n*-butyltin bromide remained in the distillation flask.

The reduction was also attempted with trimethyltin hydride. Although the reaction appeared to proceed more rapidly than with tri-*n*-butyltin hydride, difficulties were encountered in separating all of the trimethyltin bromide from the product. Thus, no advantage accompanied the use of this hydride.

Reduction of the Alkylidenebromocyclopropanes.—The procedure was essentially the same as that for the reduction of the dibromo derivatives with the difference that longer time was required for complete reaction.

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The Chemistry of Allene. I. Factors Governing the Orientation of Free-Radical Addition

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The kinetics of free-radical addition of benzenethiol to allene has been studied and a reaction mechanism consistent with the results is proposed. At high thiol concentrations the ratio of products (M_1/M_2) resulting from thiyl radical addition to the terminal (M_1) and the central carbon (M_2) is a measure of the corresponding rate constants k_1/k_2. The difference between the corresponding activation energies $E_{k_1} - E_{k_2} = -1100$ cal/mole. Reversibility of the initial thiyl-radical addition to the terminal carbon explains the effects of the reaction temperatures and thiol concentrations on the ratio of the terminal and central isomers.

The orientation of the addition of free radicals or electrophilic reagents to allene has been the subject of several investigations and has been reviewed recently.[1] Factors governing the point of attack and the distribution of the products of addition, however, are not well understood. For example, addition of trifluoromethyl radicals, produced photochemically from trifluoroiodomethane, occurs at the terminal carbon.[2] More recently, attack by thiyl radicals from benzenethiol, methanethiol, or ethanethiol was reported to occur with high selectivity at the terminal carbon.[3,4] In a different study[5] the products from the free-radical addition of 1-propanethiol, benzenethiol, and α-toluenethiol to allene were attributed to the indiscriminate attack of thiyl radicals on the terminal or the central carbon atoms.

Factors governing the orientation of bromine atoms to allene are equally obscure. It has been reported that bromine atoms from hydrogen bromide in the liquid[6] and in the gas[7] phase attack allene at the central carbon. The addition of hydrogen bromide at room temperature and in the liquid phase proceeds similarly and gives 2-bromopropene as the major product, but selectivity of central carbon attack decreases with a decrease in the reaction temperature.[1] Three different mechanisms were proposed to account for the observed results.

The present investigation has been undertaken to obtain quantitative analysis of the orientation of free-radical additions to allene. The kinetics of free-radical addition of benzenethiol to allene has been studied, and effects of temperatures and thiol concentrations on the proportions of the terminal and central adduct were determined. The results have been compared with those obtained from the addition of trichloromethyl radicals from bromotrichloromethane.

Results

Benzenethiol Addition to Allene.—Benzenethiol in benzene as a solvent reacted smoothly with allene in the presence of either ultraviolet light or peroxides. Unreacted allene showed no isomerization to methylacetylene under the reaction conditions. In all the runs, phenylallyl sulfide, phenylisopropenyl sulfide, 1,2- and 1,3-bisphenylthiopropane, and phenyl disulfide were the only observed reaction products. There was complete absence of 1-phenylthiopropene which would be the expected product from the free-radical addition of benzenethiol to methylacetylene.

It was reported that some ionic addition of benzenethiol to phenylallyl sulfide took place at 82°.[5] Under our experimental conditions, however, there was no evidence of ionic addition to either phenylallyl sulfide or to allene. This was supported by (1) the absence of 2,2-bisphenylthiopropane and (2) the absence of 1,2-bisphenylthiopropane from blank runs of the addition of benzenethiol to phenylallyl sulfide. For the above reasons the products of the reactions were considered throughout to be derived from the thiyl-radical

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[1] K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, **29**, 2404 (1964).

[2] R. N. Haszeldine, K. Leedham, and R. B. Steele, *J. Chem. Soc.*, 2020 (1954).

[3] K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1963).

[4] T. L. Jacobs and G. E. Illingworth, Jr., *ibid.*, **28**, 2692 (1963).

[5] H. J. Van der Ploeg, J. Knotnerus, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 775 (1962).

[6] D. Kovachic and H. C. Leitch, *Can. J. Chem.*, **39**, 3636 (1961).

[7] P. I. Abell and R. S. Anderson, *Tetrahedron Letters*, **No. 49**, 3727 (1964).

TABLE I

FREE-RADICAL ADDITION OF BENZENETHIOL TO ALLENE IN LIQUID PHASE[a]

Solvent	Isomer %[c] 20° M_2	20° M_1	80° M_2	80° M_1	120° M_2	120° M_1	140° M_2	140° M_1
None[d]	19.8	80.2	24.0	76.0	26.3	73.7	29.9	70.1
Benzene	19.8	80.2	43.0	57.0	62.9	37.1	96	4
Acetonitrile	...	...	28.6	71.4	62.3	37.7	...	...
Anisole	19.1	80.9	...	...	...	...	...	...
Benzonitrile	20.9	79.1	34.5	65.5	...	...	...	...
Chlorobenzene	...	...	37.9	62.1	67.2	32.8	...	...
Tetrachloroethylene	...	...	35.1	64.9	67.5	32.5	...	...
Trichloroethane	...	...	37.4	62.6	...	...	...	...

[a] All the runs were carried out in triplicate and the results were reproducible to about ±5%. [b] In all solvent runs benzenethiol and allene concentrations were 1.0 M each. [c] M_2 represents mole per cent central isomer in 1:1 and 2:1 adducts; M_1, terminal isomer in 1:1 and 2:1 adducts. [d] Molar ratio of thiol to allene = 4.0.

addition to either the terminal or central carbons of allene.

In all the kinetic runs at 80° the reactions were stopped after about 20% of allene had reacted. Analyses were carried out by vapor phase chromatography (vpc) and comparison of the reaction mixtures with synthetic mixtures of known composition showed good material balance, thus indicating that oligomeric compounds could be only present in very minor yields.

At high thiol concentrations the relative rate of the thiyl radical attack on the center carbon of allene increased slowly as the reaction temperature was raised. At 140° it was almost equal to the rate of attack at each of the terminal carbon atoms (Table I, no solvent). A plot of the logarithm of the ratio of the rate constants for thiyl-radical attack at the terminal and central carbons (k_1/k_2), respectively, *vs.* $1/T$ (Figure 1) showed a linear dependence of the rate of attack on the central carbon with temperature. A further increase in the relative yield of the central isomer was obtained at low molar concentrations of benzenethiol in solvents (Table I). A plot of the ratio of the terminal and the central carbon adduct (M_1/M_2) against the averages of the initial and final molar concentrations of benzenethiol in a 1 M solution of allene in benzene or heptane at 80° (Figure 2), showed a linear increase in the proportion of central-carbon isomer with decrease in thiol concentration below about 1 M. At benzenethiol concentrations above 3 M, the ratio leveled at about 3.0 and became independent of thiol concentration. This dependence of central-carbon isomer on thiol concentration was not observed at 20° and lower.

The data of Table I indicate little effect of solvent polarity on isomer distribution at 20 or at 120° and above. Some slight effect appears at 80°.

The ratio of M_1/M_2 (Table II) was constant at various degrees of conversion. Some runs, however, carried out at 140° and at low thiol concentrations revealed (Table II) that part of the 2:1 adduct, 1,2-bisphenylthiopropane, reverts to the corresponding 1:1 adduct at the higher conversions. This was substantiated by direct conversion of 1,2-bisphenylthiopropane to phenylisopropenyl sulfide under the reaction conditions normally used. This did not influence the ratio M_1/M_2 (M_1 and M_2 refer throughout to the terminal or central carbon isomers, respectively, and M_1 and M_2 refer to the yield based on the mole per cent of the 1:1 adduct plus the mole per cent of the 1:1 adduct in the corresponding 2:1 adduct).

TABLE II

FREE-RADICAL ADDITION OF BENZENETHIOL TO ALLENE IN BENZENE SOLUTION AT 1 M CONCENTRATION OF THIOL AT 140°

Conversion,[a] mole %	Product composition, mole % M_2[b] 1:1 adduct	2:1 adduct	Total	M_1 1:1 adduct	2:1 adduct
5.6	80.7	13.4	94.1	...	5.7
10.7	84.0	11.7	95.7	...	4.2
12.6	88.7	8.3	97.0	...	3.0
13.17	88.6	7.9	96.5	...	3.4
31.3	90.0	6.4	96.4	...	3.2

[a] Based on thiol consumed. [b] M_2 represents central carbon isomers; M_1, terminal carbon isomers.

The Addition of Bromotrichloromethane to Allene.—Bromotrichloromethane reacted with allene when initiated with ultraviolet light or by peroxides to yield a mixture of 1:1 and 2:1 adducts. Vpc showed only the two products of $\cdot CCl_3$ attack at the terminal carbons of allene. This selectivity was not altered over a reaction temperature range of −10 to 135°. The 1:1 adduct underwent dehydrohalogenation with triethylamine to yield 1 mole of triethylamine hydrochloride and a diene believed to be 1,1-dichloro-3-bromo-1,3-butadiene. The ultraviolet absorption spectrum of the diene showed a maximum at λ 249 mμ (ϵ_{max} 10,000), which are characteristic of a substituted 1,3-butadiene.

The infrared spectrum of the diaddition product showed no unsaturation. This compound was found to be identical with that obtained from the ultraviolet-induced addition of $BrCCl_3$ to the 1:1 adduct. The nmr spectrum of the diadduct showed a singlet resonance at τ 5.77 (tetramethylsilane reference).

$$BrCCl_3 + CH_2{=}C{=}CH_2 \longrightarrow$$

$$Cl_3CCH_2CBr{=}CH_2 \xrightarrow{BrCCl_3} Cl_3CCH_2CBr_2CH_2CCl_3$$

$$Cl_3CCH_2CBr{=}CH_2 \xrightarrow[Et_3N]{} Cl_2C{=}CHCBr{=}CH_2 + Et_3N\cdot HCl$$

Discussion

The methylene groups in allene are orthogonal and the π orbitals are similarly arranged. Because of such geometry the transition state for free-radical attack on the center carbon resembles that of a primary rather than allylic radical. Since there is no large energetic advantage for attack at either carbon, steric and statistical factors apparently are dominating in controlling the orientation of addition. This could

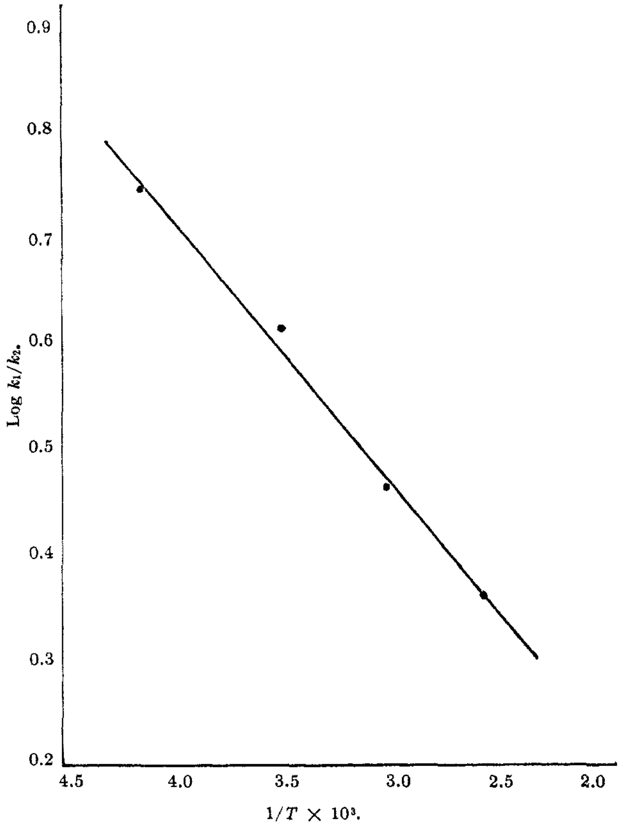


Figure 1.—Determination of $E_1 - E_2$: $\Delta E = 1108$ cal/mole. The effect of the reaction temperature on the rate constants of attack at the terminal (k_1) and central carbon (k_2) of allene at high thiol concentration.

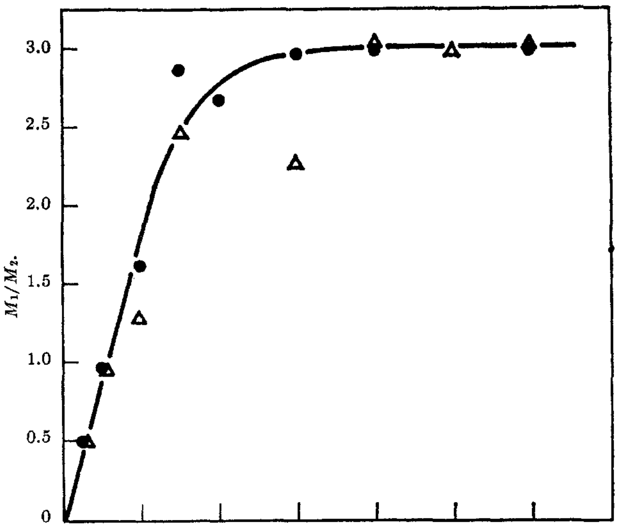


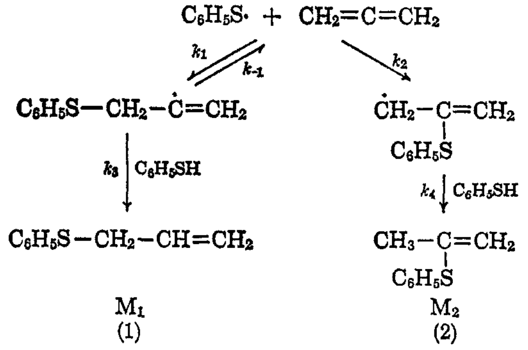
Figure 2.—Effect of thiol concentration on the ratio of terminal and central isomers (M_1/M_2) at 80° in benzene (△) or heptane (●) as a solvent.

be also predicted from the molecular orbital calculations of radical localization energies for allene.[8]

Radicals that can undergo fast reversible addition to a double bond, however, represent an exception to these generalizations. Thiyl and bromine radicals are species that fall under these exceptions, and under kinetically controlled conditions products resulting from their attack on the center carbon of allene predominate. This is due to their reversible attack on the terminal carbons compared with the relatively nonreversible attack on the central carbon atom of allene. The reversible attack of Br· on an olefin is well known, as are the addition of thiyl radicals. Thiol free-radical reactions have appreciable negative energy of activation and Sivertz[9] has shown recently that reversibility with thiyl-radical additions actually occurs in the gas phase. Evidence was based on the determination of the over-all negative activation energies for gas phase photochemical additions of CH_3SH to isobutylene, propylene, and ethylene. Also, the isomerization of pure *cis*- and *trans*-butene-2 has been given as evidence for the reversibility of the addition step.[10,11]

Our results show that initial reversible free-radical attack can kinetically favor the formation of the central isomer in addition reactions of allene and are consistent with the following mechanism. It involves (a) an initial attack of benzenethiyl radical, followed by (b) hydrogen transfer to the transient intermediate as represented in Scheme I.

SCHEME I



The free-radical intermediate formed *via* route 1 should undergo the reverse reaction, which is characteristic of α-thioalkyl radicals.[9-11] However, the initial radical intermediate formed *via* route 2, although it may be initially nonallylic, undergoes rapid rotation of 90° about the C–C axis to assume the conformation of the stable allylic radical. Such a rotation must have a very low activation energy and the gain of the resonance energy will render the reverse of thiyl-radical addition highly endothermic.

From Scheme I and with the usual steady-state approximation, the ratio of the two isomers can be expressed as

$$\mathrm{d}M_1/\mathrm{d}M_2 = \frac{k_1k_3}{k_2}\,\frac{[\mathrm{C_6H_5SH}]}{(k_{-1} + k_3[\mathrm{C_6H_5SH}])}$$

where M_1 and M_2 represent mole fractions of terminal and central carbon isomers, respectively.

After integration the above expression is reduced to

$$\frac{M_1}{M_2} = \frac{k_1k_3}{k_2}\,\frac{[\mathrm{C_6H_5SH}]}{(k_{-1} + k_3[\mathrm{C_6H_5SH}])}$$

Here, it is assumed that the decomposition of thiyl radical intermediate (k_{-1}) is a unimolecular process. If the thiyl-radical transfer to allene is bimolecular such as

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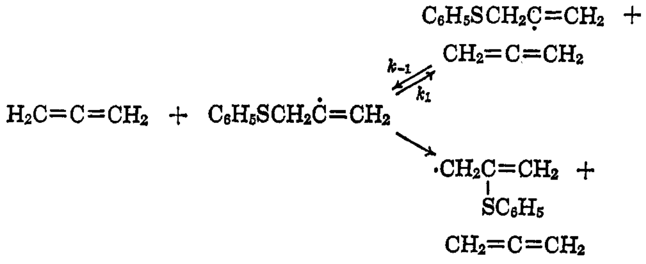
[8] B. Pullman, *J. Chim. Phys.*, **55**, 790 (1958).

[9] C. Sivertz and W. Andrews, *J. Polymer Sci.*, **19**, 587 (1956).

[10] C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

[11] N. P. Neureiter and F. G. Bordwell, *ibid.*, **82**, 5354 (1960).



the over-all expression will be

$$\frac{M_1}{M_2} = \frac{k_1k_3}{k_2}\frac{[C_6H_5SH]}{(k_{-1}'[\text{allene}] + k_3[C_6H_5SH])}$$

The two equations acquire similar forms for allene concentration of 1 *M*. However, such bimolecular dissociation of the vinyl radical intermediate is unlikely.[12]

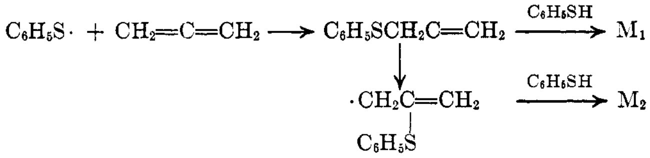
At any given temperature there are two limiting cases.

(A) At high thiol concentrations $k_3[C_6H_5SH] >> k_{-1}$. This leads to the expression

$$\frac{M_1}{M_2} = \frac{k_1k_3[C_6H_5SH]}{k_2k_3[C_6H_5SH]} = \frac{k_1}{k_2} \quad (3)$$

Under these conditions the ratio of M_1/M_2 is constant and is independent of the thiol concentration. This is in good agreement with the experimental results (Figure 2) and M_1/M_2 gives directly the ratio of rate constants of the initial thiyl-radical attack at the terminal and central carbon atoms of allene k_1/k_2.

The finding that for one particular reaction temperature M_1/M_2 is constant at high thiol concentrations rules out the formation of M_1 and M_2 *via* an initial attack of the thiyl radical at the terminal carbon followed by its migration to the central carbon. A



similar mechanism has been proposed[7] for Br· addition from HBr to allene. Such a mechanism would require that M_1/M_2 to increase linearly with C_6H_5SH at all concentrations.

(B) At low thiol concentrations, where $k_3[C_6H_5SH] << k_{-1}$

$$\frac{M_1}{M_2} = \frac{k_1}{k_2}\frac{k_3[C_6H_5SH]}{k_{-1}} \quad (4)^{13}$$

In this event the ratio of M_1/M_2 is a linear function of the thiol concentration. This is experimentally verified as illustrated in Figure 2. Moreover, at 80°, from the plot of Figure 2 and eq 3, $k_1/k_2 = 3.0$. Using this value, the measured slope, and eq 4

$$\frac{k_3}{k_{-1}} = \frac{\text{slope}}{k_1/k_2} = 0.6 \pm 0.2 \text{ mole/l.}$$

Thus, at thiol concentration less than 1.67 *M*, the composite thiyl radical from the terminal attack on allene undergoes the reverse of addition at a faster rate than the hydrogen abstraction from the benzenethiol. This ultimately leads to a higher proportion of the central carbon isomer. The proposed kinetic scheme is also consistent with the observed temperature dependence of M_1/M_2. The decomposition of the thiyl-radical intermediate (k_{-1}) is expected to have the highest activation energy of the four reactions; therefore, at low thiol concentrations (4), M_1/M_2 decreases considerably with increase in temperature (Table I and II). The almost exclusive formation of M_2 at higher temperatures is understandable; *i.e.*, there will be a ceiling temperature for the "terminal product," M_1, but not for the "central product," M_2. At high thiol concentrations (3) the ratio of M_1/M_2 decreases linearly with increase in temperature (Figure 1) and k_1/k_2 is equal to 2 at about 140° indicating at these temperatures that the thiyl-radical addition to C_1 or C_2 ofa llene is indiscriminate. The Arrhenius plot (Figure 1) shows only a small difference (1.1 kcal/mole) in the activation energies of the two addition reactions (E_{k_1} and E_{k_2}, respectively).

Very similar results have been obtained in the free-radical addition of HBr to allene which also follows the proposed mechanism and k_1/k_2 was found to be equal to 2 at −78°.[14] The dependence of M_1/M_2 ratio on the reaction temperatures and thiol concentrations does not support a proposed mechanism[15] which involves the initial formation of a bridged thiyl radical which can react directly or undergo opening of the three-membered ring to give a vinyl or an allylic radical (or both). For such a mechanism to be consistent with our results requires that the opening of the three-membered ring to have higher activation energy than that of the hydrogen transfer from benzenethiol which is unlikely. This will be also inconsistent with the relative ease of the isomerization of olefins with thiols in general.

It is instructive to compare the direction of radical additions to allene. The selectivity for addition at the terminal carbon atom increases in the order Br· < RS· < ·CCl_3, which is the same order reported for the activation energies of these radicals to olefins in general. The high selectivity for ·CCl_3 addition to C_1 of allene, however, could be partly due to steric reasons.[16]

The Effects of Solvents.—The effects of solvents on the over-all ratio of M_1/M_2 is not very conclusive, but still some points can be drawn. The runs carried out at low temperature (20°), the temperature range where there is little evidence of the reversibility of the initial thiyl-radical attack on allene, showed no effect of solvents. At 80°, however, where the reversibility of the initial thiyl-radical attack is evident, solvents influenced the over-all ratio of M_1/M_2. These effects were no longer observed when the reactions were carried out at 120°. It might not be coincidental that the effects of solvents reported in Table II are somewhat parallel to those reported by Walling on the effect of solvents on stabilizing β scission for *t*-butoxy radical over that of hydrogen abstraction.[17] Exact

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[12] Our preliminary results show that M_1/M_2 is independent of allene concentrations. This is in accord with the reported unimolecular dissociation of α-bromoalkyl radicals [H. Steimetz and R. N. Noyes, *J. Am. Chem. Soc.*, **74**, 4141 (1952)] which is independent of large concentrations of olefins.

[13] In the event of a bimolecular decomposition the ratio of M_1/M_2 will be a linear function of C_6H_5SH/allene ratio.

[14] W. O. Haag and E. I. Heiba, to be published.

[15] H. G. Kuivila, W. Rahman, and R. H. Fish, *J. Am. Chem. Soc.*, **87**, 2835 (1965).

[16] Comparison of the rate constant for ·CCl_3 addition to cyclohexene and the corresponding activation energy [H. W. Melville, J. C. Robb, and R. C. Trutton, *Discussions Faraday Soc.*, **14**, 150 (1953)] with those of RS· from *n*-butanethiol to pentene-1[9] indicates a relatively low preexponential factor for ·CCl_3 addition to olefins.

[17] C. Walling, P. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963).

analysis of the effects of solvents on the product distribution of free-radical additions to allene, however, has to await further investigations.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 237 double-beam recording spectrophotometer (sodium bromide optics). Ultraviolet spectra were obtained on a Beckman DK-2A recording spectrophotometer. In the vapor phase chromatographic analyses, peak areas were assumed to be proportional to weight per cent of components and were compared with synthetic mixtures of known compositions. Boiling points and melting points are uncorrected.

Materials.—Commercially available allene (Dow Chemical Co.) used in these studies contained 5–8% propylene. All other reactants and activators had a purity level above 98%.

General Procedure for Addition of Benzenethiol to Allene.—In a typical experimental run a 50-ml benzene solution was made of 0.025 mole (or as specified) of benzenethiol and 0.005 mole of peroxide. The mixture was transferred into a thick-walled Pyrex ampoule fitted with a ground joint and flushed with nitrogen for about 5 min. The ampoule was connected to a vacuum line, cooled in liquid nitrogen, and evacuated to remove traces of dissolved oxygen. Allene (0.025 mole) was condensed and the ampoule was sealed while connected to the vacuum line. In the runs carried out at room temperature the reactants were sealed in a quartz ampoule fitted internally with a condenser coil for cold-water circulation. Hanovia ultraviolet 200-w lamp was used for initiation. Benzoyl peroxide was used for the runs carried out at 80° and di-*t*-butyl peroxide for the runs carried out at 115, 120, and 140°.

For the kinetic runs at 80° another set of experiments was carried out using ultraviolet light as initiator and the results were comparable with those when benzoyl peroxide was used. Most of the runs were conducted in *triplicate* and *analyses* were carried out in duplicate. The ampoules in the experiments at elevated temperatures were placed in a constant-temperature bath (±2°) and the reaction time was controlled, by several attempts, and stopped after about 15–20% of allene had reacted (with ultraviolet light as initiator the reaction time ranges from 15–30 min and with peroxides from 30–60 min). The ampoules were cooled in Dry Ice bath in the dark and unreacted allene was vented. The reaction mixtures were analyzed by gas chromatography using a 6- or 10-ft column packed with a 425 methyl silicone GE SF-96 on Diatoport P. Helium was the carrier gas and a temperature increase of 11°/min was programmed over the range of 80–300° or 125–350° when the 10-ft column was used. Retention time and infrared spectra of all reaction products were compared with those of authentic samples.

Some runs at elevated temperatures were made in an autoclave using substantially the same procedure. The autoclave was fitted with a side outlet for samples every 3 min to determine the ratio of the two isomeric adducts at various degrees of conversion.

Addition of Bromotrichloromethane to Allene.—Bromotrichloromethane (0.3 mole) in a quartz ampoule was flushed with nitrogen and cooled in a Dry Ice bath at 78°, and 0.1 mole of allene was liquified and then sealed under nitrogen atmosphere. Irradiation with ultraviolet light was required to initiate the reaction. The reaction tube was cooled during irradiation with an internal water condenser. Benzoyl peroxide was used as an initiator for the runs carried out at 80° and di-*t*-butyl peroxide for those at 135°. After each run the reaction ampoule was cooled, unreacted allene was vented, the excess of bromotrichloromethane was evaporated, and the residue was fractionated under vacuum to give two products. (a) One was a colorless liquid, bp 78° (15 mm). *Anal.* Calcd for $C_4H_4BrCl_3$: C, 20.1; H, 1.7; halogen, 77.6. Found: C, 20.6; H, 1.78; halogen, 77.2. The infrared spectrum showed a strong absorption at 6.14 μ. This compound was characterized as 3-trichloromethyl-2-bromopropene. (b) The second was a colorless liquid, bp 110–114° (0.1 mm), $n^{25}\text{D}$ 1.5762. *Anal.* Calcd for $C_5H_4Br_2Cl_6$: C, 13.72; H, 0.91; halogen, 85.35. Found: C, 13.96; H, 1.14; halogen, 84.96. This product analyzed for 2:1 $BrCCl_3$–allene adduct and was assigned the structure of 1,1,1,5,5,5-hexachloro-3,3-dibromopentane, $CCl_3CH_2CBr_2CH_2CCl_3$. Its infrared spectrum was simple and showed no bands characteristic of unsaturation, and the nmr spectrum showed only one type of hydrogen. This material was also found to be identical with that obtained from the ultraviolet-induced addition of $BrCCl_3$ to the 1:1 adduct.

Dehydrohalogenation of the $BrCCl_3$–Allene Addition Product.—3-Trichloromethyl-2-bromopropene (22.5 g) was dissolved in 200 ml of triethylamine and refluxed for 2 hr. The reaction mixture was filtered to yield 13.1 g of a solid of mp 253° and mmp 253° with triethylamine hydrochloride. The filtrate was evaporated and the residue was distilled under vacuum as a colorless oil, bp (bath temperature) 72–74° (45 mm); gas chromatographic analysis over a 6-ft column packed with 2,4-dimethylsulfolene and dipropyl sulfone on Chromosorb at 80° showed only one major component. *Anal.* Calcd for $C_4H_3BrCl_2$: C, 23.76; H, 1.48; halogen, 74.75. Found: C, 23.43; H, 1.52; halogen, 74.28. Its ultraviolet absorption spectrum showed a maximum in 95% ethanol at λ 249 mμ (ϵ_{max} 10,000), characteristic for a substituted 1,3-butadiene.

Acknowledgment.—The author is grateful to his colleagues, Drs. R. F. Bridger, P. D. Caesar, and W. O. Haag, for suggestions and helpful discussion. The skillful technical assistance of Mr. G. A. Cudhea in carrying out experiments is acknowledged.