The Addition of Thiyl Radicals to Allenic Hydrocarbons[1]

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Ethane- and benzenethiyl radicals add to allene, 1,2-butadiene, and 3-methyl-1,2-butadiene to give 1:1 and 2:1 adducts. Ethanethiol and allene yield allyl ethyl sulfide, 1,2-bis(ethylthio)propane, and 1,3-bis(ethylthio)-propane. Attack is 12.8% on the center carbon and 87.2% on terminal carbons. Attack of ethanethiyl radicals on 1,2-butadiene occurs at all three positions to give *cis-* and *trans*-crotyl ethyl sulfide, ethyl α-methylallyl sulfide, *cis-* and *trans*-2-ethylthio-2-butene, and *meso-* and *dl*-2,3-bis(ethylthio)butane. Interconversion of the allylic isomers occurs to a small extent under the reaction conditions making the relative amounts of attack on the ends of the allenic system slightly uncertain. Attack was 45.5:48.2:6.3 on carbons 1, 2, and 3. Ethane- and benzenethiyl radicals attack 3-methyl-1,2-butadiene exclusively at the center carbon of the allenic system. Additions of ethanethiyl radicals to propyne, 1- and 2-butyne, and 1,3-butadiene were studied. Additions to the allenes do not occur by prior rearrangement to these hydrocarbons and rapid addition of thiyl radicals to them, nor could these hydrocarbons be detected in allenes recovered from addition studies.

It was of interest to examine addition of free radicals to allenes because little is known about such allene reactions. The results are of special interest for research on allene polymerization and for comparison with the results of ionic additions.[2]

When the present research was started, the product of such an addition had been determined with certainty in only one instance. Attack on allene itself by trifluoromethyl radicals, produced photolytically from trifluoroiodomethane, occurs at a terminal position.[3]

$$\mathrm{CF_3I} \xrightarrow{h\nu} \cdot\mathrm{CF_3} + \mathrm{I}\cdot$$

$$\cdot\mathrm{CF_3} + \mathrm{CH_2{=}C{=}CH_2} \longrightarrow \mathrm{CF_3CH_2\dot{C}{=}CH_2}$$

$$\mathrm{CF_3CH_2\dot{C}{=}CH_2} + \mathrm{CF_3I} \longrightarrow \mathrm{CF_3CH_2CI{=}CH_2} + \cdot\mathrm{CF_3}$$

More recently attack by bromine atoms from hydrogen bromide or deuterium bromide on allene or deuterated allene was reported to occur at the center carbon of the allene system.[4,5]

Thiyl radicals offer several advantages for study of radical additions: it is usually easy to make certain that the addition occurs by a radical mechanism, fairly rapid addition is the rule, and the products usually can be separated by vapor phase chromatography. In the present work ethane- and benzenethiyl radicals were found to add smoothly to allene, 1,2-butadiene, and 3-methyl-1,2-butadiene. These three allenic hydrocarbons were chosen because they present a series of allenes in which substitution varies in a systematic fashion.

Addition of thiophenol to allene occurred slowly during irradiation to yield 50% of phenyl allyl sulfide and small amounts of higher boiling products. The reaction product failed to react with 2,4-dinitrophenylhydrazine reagent which indicates that no significant amount of phenyl isopropenyl sulfide was present. Thus thiophenyl radicals attack allene mainly at the terminal positions.

Addition of ethyl mercaptan was studied more carefully. The mercaptan and allene were heated for eight hours at 67° with 2,2′-azobisisobutyronitrile as chain initiator. Considerable unchanged allene (free from propyne) and mercaptan were recovered. Ethyl allyl sulfide (I) was isolated, and a higher boiling fraction was shown to contain mainly 1,3-diethylthiopropane (II) and a little of the 1,2-diadduct; the former was isolated as its disulfone.

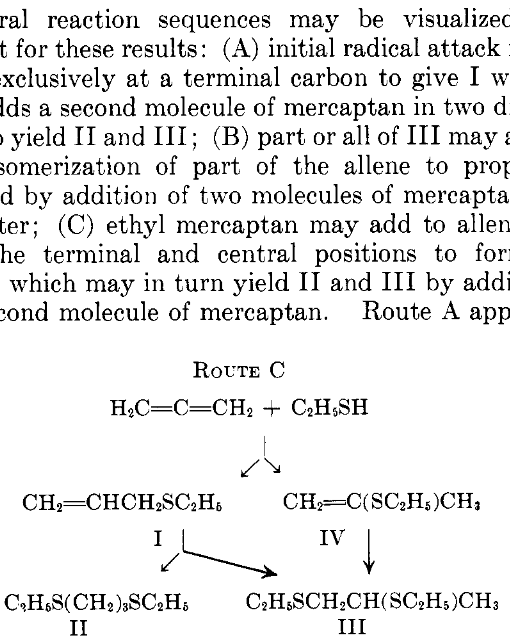
V.p.c. permitted analysis of this mixture and established that other mono- and diadducts were absent within the limit of error of the method. The results obtained from an analysis of two additional runs carried out under different conditions (variation of reaction time and relative concentration of reactants) are summarized in Table I.

TABLE I

Products	Run 1 (mole %)	Run 2 (mole %)
Ethyl allyl sulfide (I)	16.5	64.9
1,3-Bis(ethylthio)propane (II)	67.5	21.4
1,2-Bis(ethylthio)propane (III)	16.0	13.7

Several reaction sequences may be visualized to account for these results: (A) initial radical attack may occur exclusively at a terminal carbon to give I which then adds a second molecule of mercaptan in two directions to yield II and III; (B) part or all of III may arise from isomerization of part of the allene to propyne followed by addition of two molecules of mercaptan to the latter; (C) ethyl mercaptan may add to allene at both the terminal and central positions to form I and IV which may in turn yield II and III by addition of a second molecule of mercaptan. Route A appears to be relatively unimportant because the yield of III remains nearly constant when addition conditions are changed so that the yield of II varies widely. This was confirmed by addition of ethyl mercaptan to I; the mixture obtained was found to contain 95.7% II and 4.3% III.

ROUTE C



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[1] This paper is taken from the Ph.D. thesis of G. E. Illingworth, Jr. The research was supported by a contract with the Office of Ordnance Research, U. S. Army.

[2] T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).

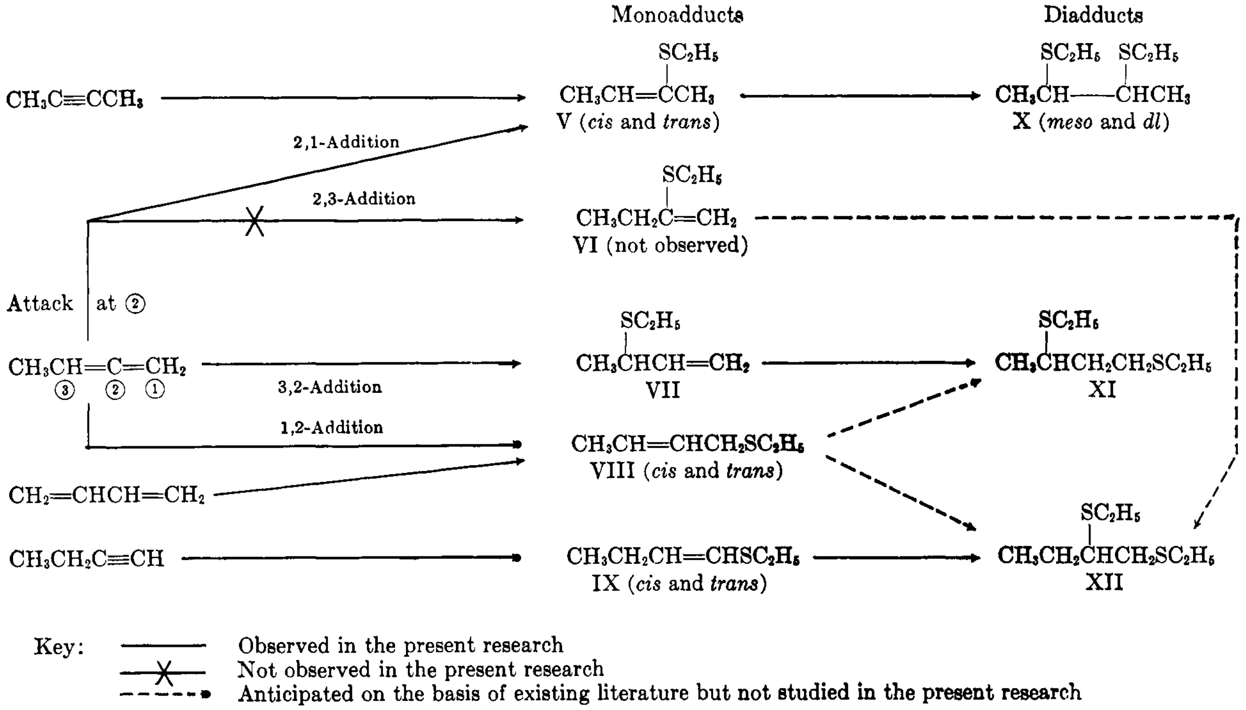
[3] R. N. Haszeldine, K. Leedham, and B. R. Steele, *J. Chem. Soc.*, 2040 (1954).

[4] D. Kovachic and L. C. Leitch, *Can. J. Chem.*, **39**, 363 (1961).

[5] L. C. Leitch and D. Kovachic, Abstracts of Papers, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959, p. 105-P.

Chart I

Reaction of C_4H_6 Isomers with C_2H_5SH



Ethyl mercaptan was added to propyne in order to assess possibility B. The reaction was carried out under the conditions used for addition to allene. V.p.c. analysis showed that the expected[6] diadduct III is the only one formed. The remaining products were *cis*- and *trans*-1-ethylthio-1-propene on the basis of comparison of v.p.c. retention times with those of authentic compounds prepared from propionaldehyde.[7] Monoadducts and diadduct were present in a weight ratio of 1.4 to 1. This experiment excludes route B for the allene addition.

If route C is to be accepted as the major route for addition of ethyl mercaptan to allene one must account for the absence of 2-ethylthio-1-propene (IV). IV was, therefore, prepared by pyrolysis of acetone diethylmercaptol[8,9] and competitive addition of ethyl mercaptan to I and IV (approximately 1:1) was carried out under the allene addition conditions. In each instance v.p.c. analysis of unchanged thioethers revealed the presence of I only, even with reaction times as short as one hour. Therefore, IV reacts far more rapidly with mercaptan than does I,[10] and the addition of ethyl mercaptan to allene follows route C.

The addition was inhibited to the extent of 99% by 4-*t*-butylpyrocatechol which establishes the chain nature of the reaction.

The per cent of center attack on allene can be obtained from Table I by subtracting from the per cent of III the per cent of this compound obtained by addition to ethyl allyl sulfide. Runs 1 and 2 give, respectively, 13.0 and 12.7%. The extent of attack at each position on allene by ethyl mercaptan radical is, therefore, the following.

$$\begin{array}{ccc} CH_2{=\!=} & C & {=\!=}CH_2 \\ \uparrow & \uparrow & \uparrow \\ 43.6\% & 12.8\% & 43.6\% \end{array}$$

The high reactivity of 2-ethylthio-1-propene in the addition reaction with ethyl mercaptan raises a question in connection with the addition of thiyl radicals to terminal alkynes. It has always been assumed[6] that these additions take the following course.

$$RC{\equiv}CH \xrightarrow{R'SH} RCH{=}CHSR' \xrightarrow{R'SH} RCH(SR')CH_2SR'.$$

It may well be, however, that substantial amounts of $RC(SR'){=}CH_2$ are formed but react immediately to give diadducts.

Addition of ethyl mercaptan to 1,2-butadiene was carried out under conditions similar to those employed with allene. A complex mixture of products including both mono- and diadducts was formed. V.p.c. methods of separating the mixture were worked out and the components were identified by comparison of retention times and infrared spectra with those of authentic samples. Chart I summarizes the qualitative results, and Table II gives quantitative results for a typical run.

Table II

Products	Mole %
Ethyl crotyl sulfide (VIII)	45.5
Ethyl α-methylallyl sulfide (VII)	6.3
2-Ethylthio-2-butene (V)	29.2
2,3-Bis(ethylthio)butane (X)	19.0
	100.0

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[6] A. T. Blomquist and J. Wolinsky, *J. Org. Chem.*, **23**, 551 (1958). This paper contains a bibliography of the addition reaction of mercaptans to acetylenes.

[7] H. J. Boonstra, L. Brandsma, A. M. Wiegman, and J. F. Arens, *Rec. trav. chim.*, **78**, 252 (1959).

[8] P. J. Wiezevich, L. B. Turner, and P. K. Froelich, *Ind. Eng. Chem.*, **25**, 295 (1933); L. B. Turner, U. S. Patent 2,066,199 (December 29, 1937) [*Chem. Abstr.*, **31**, 1038 (1937)].

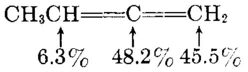
[9] A. Sporzynski, *Arch. Chem. Farm.*, **3**, 59 (1936).

[10] After this work was completed, M. F. Shostakovskiĭ, E. P. Gracheva, and N. K. Kul'bovskaya, *Zh. Obshch. Khim.*, **30**, 383 (1960), reported that IV reacts rapidly with ethyl mercaptan to give 1,2-bis(ethylthio)propane.

cis and *trans* isomers of 2-ethylthio-2-butene (V) and ethyl crotyl sulfide (VII) were present and separated on the v.p.c. column. Both diastereomers of diadduct X, 2,3-bis(ethylthio)butane also were observed.

The evidence that all of the products arise directly from 1,2-butadiene and none from rearrangement of the allene to other hydrocarbons, followed by addition to the latter, is less complete than with allene, but is still quite convincing. The extent of addition in comparable runs on 1,2-butadiene, 1-butyne, 2-butyne, and 1,3-butadiene suggests that the rates of addition are not greatly different. Unchanged hydrocarbon was recovered in each instance and shown to contain no rearrangement products. For 1-butyne this evidence is supplemented by the observation that the monoadduct, 1-ethylthio-1-butene, is not present among the addition products from 1,2-butadiene.

Diadduct X results from addition of a second molecule of ethyl mercaptan to V. The sum of V and X thus represents the amount of attack on the center carbon of the allene system in 1,2-butadiene. Attack on this system can be summarized in the following manner.



$$\mathrm{CH_3}\underset{\substack{\uparrow\\6.3\%}}{\mathrm{CH}}=\underset{\substack{\uparrow\\48.2\%}}{\mathrm{C}}=\underset{\substack{\uparrow\\45.5\%}}{\mathrm{CH_2}}$$

These results are less certain than those for allene for two reasons: (1) allylic rearrangement VII $\rightleftharpoons$ VIII occurs to an uncertain extent; (2) the v.p.c. analytical method does not uniquely exclude diadducts XI and XII nor can monoadduct VI be excluded completely.

It was shown that the primary allylic isomer VIII rearranges partially to VII under addition conditions, but the extent of this rearrangement is not great enough to account for all of the VII found in the addition to 1,2-butadiene. Thus it is certain that some attack by thiyl radicals occurs at C-3 of the allenic system. The extent of attack at this position may be considerably greater than indicated, because VII undergoes extensive conversion to VIII under addition conditions. This rearrangement does not affect determination of the percentage of attack at the center carbon.

The difficulty with the diadduct analysis is probably of very little importance for determination of the extent of center attack, but it makes it uncertain that 2,3-addition can be ruled out completely. It seemed unlikely that VIII, which has an internal double bond, would add ethyl mercaptan rapidly, and this was shown to be correct. The thiol appears to add to VII somewhat more rapidly, but even here a separate experiment gave a low yield of adduct. Moreover, VII is not a major constituent of the reaction mixture, so no more than a small error in the percentage of center addition would result from this. Greatest difficulty involves VI, the monoadduct which was not observed, because by analogy with ethyl isopropenyl sulfide one would expect addition of ethyl mercaptan to occur rapidly. This would yield the 1,3-diadduct XII. No error is introduced into the figure for center attack by this because both V and VI involve such attack, but to the extent that XII might have been present, 2,3-addition might have occurred. It is believed that this error was small because the infrared spectrum of the mixture of adducts from 1,2-butadiene was essentially identical to that of authentic X. However, the other diadducts do not have sufficiently different spectra to exclude the possibility that they were present to the extent of 10 to 20%. Because only 19% of diadducts was obtained in the addition, orientation figures may be in error by 2 to 4% from this cause.

Small amounts of VI might also have escaped detection, because this compound was not prepared and examined separately. It was expected that pyrolysis of 2,2-bis(ethylthio)butane would yield VI and both geometrical isomers of V, but only the latter two were observed. *cis* and *trans* V also were obtained by addition of ethyl mercaptan to 2-butyne. The isomers from these two sources and from the 1,2-butadiene addition were separated by preparative v.p.c. and the infrared spectrum of each isomer was constant for all three samples. It seems most unlikely that VI could have been formed from 2-butyne, and, therefore, within the limits of detection by infrared, it was not present among the 1,2-butadiene adducts.

A spontaneous exothermic addition occurred when thiophenol was added dropwise to 3-methyl-1,2-butadiene. The product had a narrow boiling range and was shown by elemental analysis and molecular weight determination to correspond to a monoadduct, $C_{11}H_{14}S$. Acid hydrolysis gave methyl isopropyl ketone and ozonization followed by oxidative degradation produced acetone. The infrared spectrum of the product displayed a weak band at 1634 cm.$^{-1}$ suggesting the presence of a symmetrically substituted ethylene. Possible monoadducts, $(CH_3)_2C{=}CHCH_2SC_6H_5$ and $CH_2{=}CHC(CH_3)_2SC_2H_5$, were available and had quite different spectra.[11] Strong bands at 837 cm.$^{-1}$ and 908 cm.$^{-1}$, respectively, in the spectra of these compounds were absent in the spectrum of the monoadduct indicating that these allylic sulfides were not present in significant amount in the addition product. Thus radical addition of phenyl mercaptan to 3-methyl-1,2-butadiene occurs by attack at the central carbon of the allenic system to yield 3-methyl-2-phenylthio-2-butene.

Ethyl mercaptan was added to 3-methyl-1,2-butadiene utilizing azobisisobutyronitrile initiation as in previous cases. A 1:1 adduct was obtained in good yield. The infrared spectrum displayed weak bands at 1626 cm.$^{-1}$ and 1590 cm.$^{-1}$ and lacked bands attributable to a terminal methylene group. Hydrolysis of the adduct in 2,4-dinitrophenylhydrazine reagent produced the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone. This evidence suggests that 3-methyl-2-ethylthio-2-butene is the only product obtained from the addition reaction; however, no extensive effort was made to determine the presence of minor amounts of side products.

The most prominent feature of the results of this research is the increasing extent of center addition which accompanies methyl substitution of the allenic system. Table III summarizes this.

TABLE III

Compound	% Center addition
Allene	12.8
1,2-Butadiene	48.2
3-Methyl-1,2-butadiene	100

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[11] S. N. Lewis, Ph.D. dissertation, UCLA, 1959. We wish to thank Dr. Lewis for providing samples of these compounds.

It is interesting that ionic addition of hydrogen chloride to the same series of allenes[3] shows a similar trend although orientations are more clean cut with these.

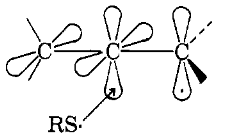
For radical addition of ethyl mercaptan to allene, alternative paths may be formulated.

$$\text{A}\left\{\begin{array}{l} CH_2{=}C{=}CH_2 + C_2H_5S\cdot \longrightarrow CH_2{=}\dot{C}{-}CH_2SC_2H_5 \\ CH_2{=}\dot{C}{-}CH_2SC_2H_5 + C_2H_5SH \longrightarrow \\ \qquad\qquad CH_2{=}CHCH_2SC_2H_5 + C_2H_5S\cdot \end{array}\right.$$

$$\text{B}\left\{\begin{array}{l} CH_2{=}C{=}CH_2 + C_2H_5S\cdot \longrightarrow CH_2{=}C(SC_2H_5)\dot{C}H_2 \\ CH_2{=}C(SC_2H_5)\dot{C}H_2 + C_2H_5SH \longrightarrow \\ \qquad\qquad CH_2{=}C(SC_2H_5)CH_3 + C_2H_5S\cdot \end{array}\right.$$

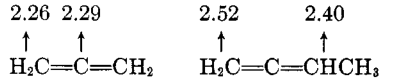
Orientation-controlling competition between A and B depends upon both of the rate constants involved in each path.

To the extent that one can correlate the stability of intermediates with the free energies of activation it should be possible to make predictions about orientations by considering these intermediates. Looking at the first step in A and in B one sees that terminal attack A yields a vinyl radical and central attack B yields what appears to be an allylic radical. However as central attack is occurring the geometry of the allenic system prevents overlap of the orbital in which the odd electron is to be accommodated with the π orbital of the double bond unless rotation occurs to make the terminal substituents coplanar.



Thus activation energy for central attack may be considerably higher than for terminal attack on allene because the transition state may resemble that for formation of a primary radical. One would then predict that the first step of A would be faster than the first step of B.

It is often possible to predict the position of attack of radicals on unsaturated systems by molecular orbital calculation of radical localization energies. Such calculations have been carried out[12] for allene and 1,2-butadiene with the following results (given in β units).



$$\overset{2.26}{\underset{\uparrow}{}}H_2C{=}\overset{2.29}{\uparrow}C{=}CH_2 \qquad \overset{2.52}{\uparrow}H_2C{=}C{=}\overset{2.40}{\uparrow}CHCH_3$$

This lends support to the prediction that the first step of A is faster than the first step of B.

Even if the radical formed in the first step in B is nonallylic, it seems quite likely that it would have time to assume the geometry of the stable allylic radical before it enters into the displacement step to give product. The observation that thiol additions are nonstereospecific[13] supports this view.

Very little is known about the stability of vinyl radicals such as that produced in the first step of A. However, the marked "poisoning" or decelerating effect of small amounts of acetylenes on ordinary vinyl polymerizations suggests that acetylenic bonds are fairly readily attacked by radicals and that the deceleration stems from the slow attack of the resulting vinyl radicals on ordinary double bonds. If vinyl radicals are also unreactive in a displacement reaction such as step 2 of A, it would be difficult to predict the relative rates of the second steps in A and B. The relative rates of addition of ethyl mercaptan to propyne and allene were not determined in our work, but the additions with these compounds were carried out under very similar conditions and suggest that propyne reacts slightly more slowly than allene. Thus the second step in both A and B may be quite slow.

A more exact analysis of orientation of radical addition to allene will only be possible after further investigation; this study will be undertaken. It is perhaps not surprising that the orientation varies as much as reported when different reagents are added (*i.e.*, trifluoromethyl iodide[3] and hydrogen bromide[4]).

Substituted allenes are more complicated because attack can occur at three sites. Increasing attack on the center carbon of the allenyl system would be expected if orientation were controlled by the first steps in the alternative paths, because with 1,2-butadiene a secondary radical would result (assuming no twisting) and with 3-methyl-1,2-butadiene a tertiary radical. Pullman's calculations[12] predict that attack at position 3 of 1,2-butadiene will predominate over attack at 1. Allylic rearrangement makes it impossible to tell whether this actually occurs. Even if rearrangement has not been extensive enough to reverse the orientation, one still does not know the relative rates of attack at positions 1 and 3 because the relative rates of the second steps are not known.

It has been reported[14] that 2-methyl-1-butene is 1.2 times more reactive than 1-octene toward dodecanethiyl radicals. The relative reactivity of thiyl radicals toward a series of olefins such as ethylene, propylene, and isobutylene appears not to have been determined, but, to the extent that Walling's result is general, one would expect reactivity to increase in the order shown. This is the order observed[15] with trifluoromethyl radicals. At least on the basis of ultraviolet spectra the allene system appears to behave as though it possessed two noninteracting double bonds.[16,17] One might, therefore, expect that the ease of attack of the center carbon of allenes by thiyl radicals would increase in the series allene < 1,2-butadiene < 3-methyl-1,2-butadiene. Qualitatively it appears from our results that the over-all rate of attack by thiyl radicals increases through this series in this order, and that the shift from terminal to central attack is the result of increase of rate of attack at the center rather than decrease at terminal positions.

Szwarc[18] devised a technique for determining relative rates of attack of methyl radicals on aromatic and unsaturated compounds. Initially the technique was applied to a study of the addition of methyl radicals to a large number of aromatic hydrocarbons, and good correlation with the localization energies was obtained. Later the technique was extended to a variety of unsaturated compounds. In the series ethylene, propylene, and isobutylene the relative rates were 1, 1.2, 2.12

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(12) B. Pullman, *J. chim. phys.*, **55**, 790 (1958).

(13) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **82**, 5354 (1960).

(14) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).

(15) A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

(16) W. D. Celmer and I. A. Solomons, *ibid.*, **75**, 1372 (1953).

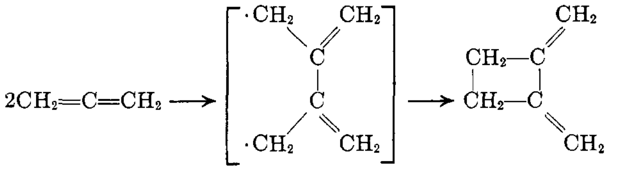
(17) T. L. Jacobs and D. Dankner, *J. Org. Chem.*, **22**, 1424 (1957).

(18) For a recent review of this technique, see M. Szwarc and J. H. Birks, "Theoretical Organic Chemistry," (Kekulé Symposium), Butterworths Publications Ltd., London, 1959, p. 262.

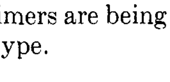
which also correlates with localization energies. Szwarc observed that methyl groups located at a reaction center greatly lower reactivity apparently by blocking the approach of the attacking radical. For example the methyl affinities of propylene, *trans*-, and *cis*-2-butene were 21.9, 6.9, and 3.4, respectively. Isobutylene and trimethylethylene gave values of 35.6 and 5.6. The following values for methyl affinities of allenes were obtained[19] at 65°: allene, 17.6 ± 0.2; 1,2-butadiene, 14.8 ± 2.0; 1,2-pentadiene, 19.2; 2,3-pentadiene, 13.8; tetraphenylallene, 52. Since the presence of blocking groups on the terminal carbons of the allenic system does not lower reactivity, Szwarc concluded that addition occurs on the center carbons of the allenes. This conclusion ignores the possibility that orientation varies between different allenes. The methyl affinities are not inconsistent with predominance of terminal attack in allene itself and increased proportions of central attack on the more substituted allenes. Furthermore, the failure to observe more attack at C-3 than at C-1 of 1,2-butadiene may be explained by the blocking effect of the methyl on C-3.

Little can be said on the basis of these addition studies about orientation during radical polymerization of allenes, because such polymerization has not been studied. Investigations along these lines will be reported later.

Dimerization of allenes was found to yield cyclobutane derivatives.[20] Allene yields 1,2-dimethylenecyclobutane in low yield at 140–150°; none of the 1,3-isomer was detected.[20] At higher temperatures in a flow system both 1,2- and 1,3-adducts are formed in 85:15 ratio.[21] Roberts[22] writes the following dimerization.

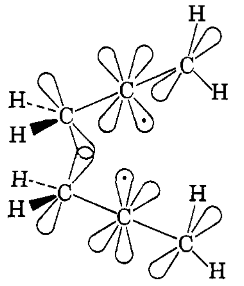


This implies that center attack of the allenic system is preferred. It would appear that one should consider the possibility that dimers are being formed from biradicals of the following type.



$$\begin{array}{l} CH_2{-}\underset{\cdot}{C}{=}CH_2 \\ | \\ CH_2{-}C{=}CH_2 \end{array}$$

If biradicals are formed by reaction of two allene molecules, the main course of the reaction would have to involve either bond formation between central carbons or between terminal carbons. If no twisting of the allene molecules occurs before or at the transition state, terminal–terminal attack would appear to give the preferred route on the basis of our addition results. A geometry such as the following seems possible.



There seems no reason for twisting to occur before four-membered ring is formed, and of course the simultaneous formation of both bonds has not been ruled out. Even if both are forming, the extent of formation need not be the same in both.

For 3-methyl-1,2-butadiene which yields at least two of the three head-to-head products[20] (none of the 1,3 dimethylenecyclobutane isomers has been detected), an intermediate diradical in which the center carbons of two allenes are involved (see Roberts[22]) is more consistent with our results on additional reactions. Models suggest that a transition state geometry in which one linear allene system is at or near right angles to the other is better stereochemically as Roberts pointed out. The results of investigations of allene dimerizations will be reported later.

Experimental

Boiling points and melting points are uncorrected. Melting points determined on a Fisher-Johns melting point apparatus are labeled "block," and those determined in a modified Hershberg apparatus (total immersion Anschütz thermometers) are labeled "bath." Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam recording spectrophotometer (sodium chloride optics) or a Beckmann Model IR-4 recording spectrophotometer (lithium fluoride optics). Ultraviolet spectra were obtained on a Cary Model 11 recording spectrophotometer.

In the vapor phase chromatographic analyses peak areas were assumed to be proportional to weight % of components unless unusual operating conditions required the use of empirical correction factors.

Materials.—Thiophenol and ethyl mercaptan were Eastman White Label chemicals. 2,2′-Azobisisobutyronitrile was supplied by the Polychemicals Department of E. I. du Pont de Nemours and Co. Commercially available allene (Dow Chemical Co. or Columbia Organic Chemicals Co.) was found to contain 2 to 5% of propylene (v.p.c., 20-ft. dimethylsulfolane column on firebrick at room temperature). Allene of greater than 99% purity was prepared from 2-bromo-3-chloropropene by a modification of a conventional procedure.[23] 2-Bromo-3-chloropropene (Columbia Organic Chemicals Co.) was distilled through a 17-in. helix column within 1 hr. of use; b.p. 42–44° (50 mm.); $n^{25}D$ 1.4978 [lit.[24] b.p. 45.7° (50 mm.); $n^{25}D$ 1.4968].

Propyne (Air Reduction Chemical Co.) was free from allene within the precision of v.p.c.

1,2-Butadiene was prepared by the Bouis synthesis.[25,26] 2,3-Dibromobutene was obtained in 33% yield based on crotyl alcohol and debrominated with zinc in refluxing Methyl Cellosolve (dropwise addition of the dihalide) to yield 88% of 1,2-butadiene. V.p.c. (20-ft. dimethylsulfolane column, room temperature) showed 0.7% 1-butene and 0.2% 2-butene; 1,3-butadiene, 1-butyne, and 2-butyne were absent. 1-Butyne and 2-butyne were obtained from Farchan Laboratories. V.p.c. showed that 4-carbon impurities were absent except for a trace and 0.4% of

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1,2-butadiene, respectively. 1,3-Butadiene (Matheson Co.) contained no 4-carbon impurities.

3-Methyl-1,2-butadiene was prepared from dimethylethynylcarbinol (Air Reduction Co.) *via* the chloride[27]; v.p.c. indicated 98.3% purity.

General Procedure for Additions to Allene.—Allene was liquefied in a graduated container and the required amount (usually 6 to 9 ml.) allowed to vaporize into a reaction ampoule; recorded amounts may be in error by 10%. Thiol and initiator were added, the ampoule sealed at −78°, and the reaction carried out with heating or irradiation as required. The ampoule was cooled, opened, unreacted allene allowed to distil, and remainder analyzed by v.p.c. The mixture was distilled to recover products.

Addition of Thiophenol to Allene.—A quartz ampoule containing 13.5 g. (0.12 mole) of thiophenol and 6.0 g. (0.15 mole) of allene was irradiated for 2 months (Ultra Violet Products Co. "Mineralight" SL 2537, filter with maximum transmission at 2537 Å., operating at 1 to 2 in.). Allene (2.3 ml.) was recovered and 8.9 g. of phenyl allyl sulfide [b.p. 55–64° (0.2–0.5 mm.), n^{25}_{D} 1.5720, d^{29}_{4} 1.020] isolated by distillation through a short Vigreux column. The infrared spectrum of this product was identical with that of authentic material.[28] Higher boiling material (3.0 g., n^{25}_{D} 1.5938–1.6000) was obtained in two fractions by vacuum transfer at full pump; infrared spectra were very different from the spectrum of the sulfide, but further identification was not attempted.

Addition of Ethyl Mercaptan to Allene.—Authentic samples of possible monoadducts were separated by v.p.c. on an 8-ft. didecyl phthalate column (100°, 15-p.s.i. helium), diadducts on a 4-ft. Apiezon "M" column (180°, 15-p.s.i. helium), and a mixture of both separated into monoadduct and diadduct fractions on the Apiezon column (140°, 15 p.s.i.). Table IV lists compounds examined and retention times in minutes. Retention times for the components of a mixture of ethyl allyl sulfide, 1,2-, and 1,3-bis(ethylthio)propanes were 0.7, 9.1, and 13.2; the monoadduct peak area was empirically corrected (factor 0.64).

An ampoule containing 7.1 g. (0.11 mole) of ethyl mercaptan, 3.6 g. (0.09 mole) of allene, and 20 mg. of azobisisobutyronitrile was heated at 67° for 8 hr. Unchanged allene was removed at room temperature and shown to contain no propyne (v.p.c., 20-ft. dimethylsulfolane column). The residue (10.2 g.) was distilled at reduced pressure to give unchanged ethyl mercaptan, 0.5 g. of **ethyl allyl sulfide** [b.p. 37° (95 mm.), n^{25}_{D} 1.4670], and 5.3 g. [b.p. 47–50° (0.3 mm.)] shown by infrared and v.p.c. to be a mixture of a little ethyl allyl sulfide with **1,2- and 1,3-bis(ethylthio)propane**. The pot residue was negligible. Ethyl allyl sulfide was identified by infrared and v.p.c. comparison with authentic material. The diadduct mixture (0.5 ml.) was evaporated to dryness with 2 ml. of 30% hydrogen peroxide and 2 ml. of glacial acetic acid. A crystalline disulfone, m.p. 187.5–188.2°, was obtained after one recrystallization from 96% ethanol. This product did not depress the melting point of authentic disulfone of 1,3-bis(ethylthio)propane. Infrared spectra were identical.

TABLE IV

Compound	Retention time, min.
Ethyl isopropenyl sulfide	26.4
Ethyl allyl sulfide	29.5
Ethyl propenyl sulfide[a]	31.5, 35.2
1,2-Bis(ethylthio)propane	3.3
1,3-Bis(ethylthio)propane	4.6

[a] *cis* and *trans* isomers were separated, but no attempt was made to relate geometrical configuration and peak identity.

Anal. Calcd. for $C_7H_{16}S_2O_4$: C, 36.82; H, 7.06. Found: C, 37.05; H, 7.03.

Similar runs were made to give the results recorded in Table I: run 1, 6.8 g. (0.11 mole) of ethyl mercaptan, 2.8 g. (0.07 mole) of allene, 20 mg. of azobisisobutyronitrile, 70°, 8 hr.; run 2, 7.0 g. (0.11 mole) of ethyl mercaptan, 4.3 g. (0.11 mole) of allene, 20 mg. azobisisobutyronitrile, 70°, 6 hr. A run of this size to which 1.0 g. of 4-*t*-butylpyrocatechol had been added was completely inhibited.

Authentic samples of various adducts were prepared by known displacement reactions. Ethyl allyl sulfide (b.p. 114–116°, $n^{25.2}_{\mathrm{D}}$ 1.4650) was obtained in 50% yield as described[29] except that allyl chloride was used and the reaction mixture refluxed for 1.5 hr.; infrared (neat), 3065, 2950, 2900, 1827, 1631, 1450, 1425, 1402, 1374, 1265, 1224, 1045, 1030, 985, 910, 862, 742 cm.⁻¹ V.p.c. showed less than 1% of low boiling impurity. **1,3-Bis(ethylthio)propane** was prepared similarly from 1,3-dibromopropane. The product was a faintly yellow oil, b.p. 66–83° (1.2 mm.); n^{25}_{D} 1.5025; infrared (neat), 2940, 2900, 2860, 1450, 1372, 1337, 1293, 1249, 1195, 1045, 965, 832, 775, and 750 cm.$^{-1}$ [lit.[30] b.p. 107° (10 mm.), n^{20}_{D} 1.5052]. The disulfone had m.p. 188.3–189.0° (bath) (lit.[29] m.p. 183.2–184.5°). **1,2-Bis(ethylthio)propane** was prepared similarly; b.p. 62–63° (1.6 mm.); $n^{25.5}_{\mathrm{D}}$ 1.5013; infrared (neat), 2940, 2900, 2850, 1450, 1370, 1302, 1261, 1220, 1174, 1103, 1065, 1045, 995, 967, 887, 822, and 776 cm.$^{-1}$. It failed to give a crystalline derivative under conditions used for preparation of the disulfone of 1,3-bis(ethylthio)propane.

Some difficulty attended the preparation of **ethyl isopropenyl sulfide** (IV). Preliminary attempts to repeat the pyrolysis of acetone diethylmercaptol, which was reported[8,9] to yield the desired product, were unsuccessful. Sufficient sulfide for our purpose was obtained by pyrolysis of 13 g. of the mercaptol (prepared by passage of hydrogen chloride through a solution of ethyl mercaptan and acetone in 2:1 molar ratio) in a 100-ml. flask under an insulated 20-cm. Vigreux column. An oil bath was used to heat the flask, and decomposition was evident at 140°, but the distillate came over only at 170° and above; final heating was at 220–230°. The distillate was washed with 50 ml. of 10% sodium hydroxide and water, dried over anhydrous magnesium sulfate, and distilled to yield 1 g. of a colorless liquid, b.p. 116–126°; n^{25}_{D} 1.4707 [lit.[10] b.p. 114–115° (750 mm.), n^{20}_{D} 1.4750]; infrared (neat), 3085, 2945, 2910, 2855, 1786, 1711, 1607, 1548, 1372, 1260, 1193, 1120, 1050, 1027, 968, 836, 785, and 760 cm.$^{-1}$. V.p.c. indicated the presence of 1.6% of a low boiling impurity.

Attempts to pyrolyze acetone diethylmercaptol under milder conditions gave only traces of IV. When distillation occurred at 140° through a short Claisen head, neither distillate nor pot residue contained isolable amounts of IV. Such modifications as pyrolyses under reduced pressure, or under nitrogen and catalysts such as hydrochloric acid, phosphoric acid, potassium pyrosulfate, potassium bisulfate, potassium hydroxide, or aluminum *t*-butoxide failed to effect improvement.

Other syntheses examined briefly without success included thermal decarboxylation of β-ethylthiocrotonic acid[31] and propynylation of sodium ethylthiolate (160°, 12 hr.); a successful synthesis by the second of these methods has now appeared.[10] Attempts to prepare **2-chloro-2-ethylthiopropane** (from acetone, ethyl mercaptan and hydrogen chloride) for dehydrohalogenation gave only acetone mercaptol; this compound recently has been reported[10] and found to decompose below 0° with liberation of hydrogen chloride and formation of a complex mixture from which only ethyl mercaptan was isolated and identified.

Vinyl thioethers have been prepared by dehydration of β-hydroxysulfides.[32,33] 2-Chloro-1-propanol prepared by a modification of Lucas' method[34] was added dropwise to ethyl mercaptan in ethanolic potassium hydroxide with refluxing to yield 2-ethylthio-1-propanol. The crude product appeared to dehydrate when dropped onto molten potassium hydroxide[32] (250°) and v.p.c. indicated a low yield of IV.

Addition of Ethyl Mercaptan to Propyne.—From equimolar amounts of ethyl mercaptan and propyne (68°, 8 hr., 20 mg. of azobisisobutyronitrile) were obtained 40% 1,2-bis(ethylthio)-propane and 56% *cis*- and *trans*-1-ethylthio-1-propene (ratio of geometric isomers, 56:44). Ethyl allyl sulfide and 1,3-bis(ethylthio)propane were absent. The remaining 4% was probably ethyl disulfide.

Addition of Ethyl Mercaptan to 1,2-Butadiene, 1-Butyne, 2-Butyne, and 1,3-Butadiene.—A 20-ft. dimethylsulfolane column separated the four hydrocarbons at room temperature. Several v.p.c. columns (didecyl phthalate, Carbowax 4000, or 3-methyl-3-nitropimelonitrile) could separate a given pair of monoadduct geometrical isomers (*cis* and *trans* V or VIII or IX), but complete

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separation of a known mixture of all monoadducts (including VII but not VI) was not accomplished. The best was a 4-m. 3-methyl-3-nitropimelonitrile column operated at 89° and 20-p.s.i. helium, with which separation was complete except that one geometrical isomer of V and one of IX came off as a single peak; retention times in minutes were as follows: VII, 14.3; V, 17.2, 22.5; IX, 18.6, 22.5; VIII, 24.7, 28.1. Several columns (Apiezon M, sucrose acetate isobutyrate, and Dow Corning phenyl methyl silicone fluid 550) separated 1,4-bis(ethylthio)butane from mixtures containing 1,2; 1,3; 2,3; and 1,4 diadducts at 160–190°, but this was the only unique separation attained. Pure X was separated into *dl* and *meso* isomers on a 4-m. Carbowax 4000 column at 154°. Separation of addition products into mono- and diadduct fractions was effected on a 2-m. Carbowax 4000-on-Fluoropak column (145°, 3-p.s.i. helium).

An ampoule containing 3.8 g. (0.07 mole) of 1,2-butadiene, 4.35 g. (0.07 mole) of ethyl mercaptan, and 15 mg. of azobisisobutyronitrile was heated at 70° for 19 hr. After unchanged 1,2-butadiene (1.3 g.) was recovered, the products were shown to consist of 81 mole % monoadducts and 19% diadducts (assuming peak areas proportional to weight per cents). Table II records the results of v.p.c. analysis of the monoadducts. The crude reaction mixture (6.9 g.) was distilled to give 3.2 g. of monoadducts, b.p. 54–58° (31 mm.), and 1.4 g. of diadducts, b.p. 123.5–128°. An intermediate fraction (1 g.) probably contained mainly monoadducts.

Addition to 1-butyne was conducted similarly (0.1 mole scale, 25 mg. azobisisobutryronitrile, 70°, 11 hr.). V.p.c. separation (1-m. Carbowax 4000 column, 79°) showed about equal amounts of *cis* and *trans* IX and a small peak with the retention time of ethyl disulfide. A v.p.c. at 138° gave a peak believed to be XII, a small unknown peak, and a single peak for the isomers of IX. The reaction product (10.3 g.) was fractionally distilled to give 3.2 g., b.p. 55–58° (31 mm.), $n^{25}_{\rm D}$ 1.4743, and 3.2 g., b.p. 115–125° (31 mm.), $n^{25}_{\rm D}$ 1.4981. The lower boiling fraction was a mixture of *cis* and *trans* IX of greater than 99% purity (v.p.c.); a trace of diethyl sulfide was present.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41. Found: C, 61.74; H, 10.31.

Infrared spectrum (neat) showed bands at 2960, 2925, 2868, 1712, 1610, 1455, 1378, 1352, 1318, 1301, 1264, 1222, 1065, 1054, 1020, 967, 938, 888, 831, 818, 756, 733, 685 cm.$^{-1}$.

The higher boiling fraction consisted of greater than 96% XII; impurities in order of elution were 1-ethylthio-1-butene, ethyl disulfide, and the unknown compound previously mentioned.

Anal. Calcd. for $C_8H_{18}S_2$: C, 53.87; H, 10.17. Found: C, 54.07; H, 10.24.

Infrared spectrum (neat) showed bands at 2950, 2915, 2859, 1452, 1376, 1342, 1263, 1205, 1171, 1093, 1047, 968, 915, 823, 781, 755, 731 cm.$^{-1}$.

Addition of ethyl mercaptan to 2-butyne was conducted similarly (0.1 mole scale, 20 mg. azobisisobutyronitrile, 70°, 15 hr.). Both 2-butyne and ethyl mercaptan (2.0 g.) were recovered. Fractional distillation at 31 mm. gave 4.0 g. of V, b.p. 52°; 1.2 g., b.p. 52–111°, $n^{25}_{\rm D}$ 1.4938; and 2.6 g. of X, b.p. 111–121°. Redistilled V had b.p. 52–53.5° (31 mm.), $n^{25}_{\rm D}$ 1.4780.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41. Found: C, 61.99; H, 10.64.

Infrared spectrum (neat) showed bands at 2960, 2930, 2860, 2733, 1636, 1605, 1450, 1377, 1308, 1263, 1156, 1140, 1080, 1053, 1026, 998, 968, 902, 800, 785, 762 cm.$^{-1}$.

Redistilled X had b.p. 112–121° (31 mm.), $n^{25}_{\rm D}$ 1.4990.

Anal. Calcd. for $C_8H_{18}S_2$: C, 53.87; H, 10.17. Found: C, 54.04; H, 10.00.

Infrared spectrum (neat) showed bands at 2965, 2930, 2860, 2736, 1452, 1376, 1264, 1242, 1212, 1175, 1135, 1101, 1045, 972, 781, 756 cm.$^{-1}$.

Addition of ethyl mercaptan to 1,3-butadiene was conducted similarly (0.11-mole scale, 25 mg. azobisisobutyronitrile, 70°, 12 hr.). Much butadiene (unrearranged) and ethyl mercaptan were recovered. The reaction products were distilled to yield 1.8 g. of monoadducts, b.p. 45–53.5° (31 mm.), $n^{25}_{\rm D}$ 1.4711. V.p.c. on the 3-methyl-3-nitropimelonitrile column at 84° showed this to contain mainly VIII (ratio of *cis–trans* isomers 20:80) plus 1% VII. In a larger run, VIII, b.p. 52.5–54° (31 mm.), was isolated and a small fraction, b.p. 107° (31 mm.), obtained; this had infrared peaks at 1690, 1660, and 1637 cm.$^{-1}$, and gave two v.p.c. peaks with retention times intermediate to those of the $C_6H_{12}S$ and $C_8H_{18}S_2$ isomers obtained previously. Trace components with the behavior of $C_8H_{18}S_2$ isomers also were observed.

Authentic 1,4-bis(ethylthio)-butane was prepared by displacement on 1,4-dichlorobutane; v.p.c. indicated that it was absent from the mixture of adducts. This compound had b.p. 143–148° (31 mm.), $n^{25}_{\rm D}$ 1.5000. The disulfone was prepared as for II, m.p. 128.4–129° (bath).

Anal. Calcd. for $C_8H_{18}S_2O_4$: C, 39.64; H, 7.84. Found: C, 39.93; H, 7.71.

Radical addition (ultraviolet light catalyzed) of ethyl mercaptan to 1,3-butadiene has been reported[35] since our work was completed. The product was mainly **ethyl crotyl sulfide** believed to be *trans;* the minor product (4%) was reported to be **4-ethylthio-1-butene**, but the possibility that it contained 3-ethylthio-1-butene does not appear to have been excluded.

Syntheses of authentic samples of adducts were carried out by known methods. VIII and VII were prepared from sodium thioethoxide and crotyl chloride (3 hr. standing at room temperature) or α-methylallyl chloride (9 hr. standing at room temperature) essentially as for ethyl allyl sulfide. VIII contained 1.2% VII (v.p.c. 8-ft. didecyl phthalate column at 124°; *cis* and *trans* VIII not resolved). Crude VIII distilled into two fractions, b.p. 142–142.5° and 142.5–143°, $n^{25}_{\rm D}$ 1.4712 and 1.4720, respectively.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.59. Found: C, 61.83; H, 10.52; S, 27.27.

Infrared (neat) showed bands at 3025, 2965, 2925, 2735, 1664, 1452, 1422, 1377, 1305, 1266, 1222, 1175, 1061, 1047, 1035, 960, 924, 780, 757, 745, 695 cm.$^{-1}$.

Similarly VII was redistilled and collected as two fractions, b.p. 126.0–127.0° and 127.0–128.0°; $n^{25}_{\rm D}$ 1.4586 and 1.4606. The second fraction was mainly VII but contained some VIII (v.p.c. on 3-methyl-3-nitropimelonitrile column).

Anal. Found: C, 61.86; H, 10.46; S, 27.99.

Infrared (neat) showed 3080, 2960, 2920, 2860, 1830, 1634, 1450, 1415, 1371, 1265, 1217, 1157, 1023, 985, 962, 907, 750, 715 cm.$^{-1}$.

2-Ethylthio-2-butene (V), was prepared by pyrolysis of the diethyl mercaptol of 2-butanone (pot temp. 162–217°). It was expected that 2-ethylthio-1-butene also would result from this pyrolysis, but the only products revealed by v.p.c. were *cis* and *trans* V, also obtained from 2-butyne. Distillation gave fractions contaminated with 2-butanone and then material, b.p. 137–140°; the infrared of the latter was very similar in peak positions to that of V from 2-butyne.

Ethyl mercaptan (0.045 mole) was added to VII (0.048 mole) in an attempt to prepare XI (25 mg. azobisisobutyronitrile, 70°, 18 hr.). Recovered VII (0.033 mole) was shown by v.p.c. to consist of 79% VIII and 21% VII. The fraction, b.p. 59–133°, 1.2 g., which would contain XI could not be distinguished by v.p.c. from X and XII; its infrared showed bands at 2962, 2930, 2870, 1455, 1430, 1378, 1265, 1222, 1168, 1101, 1049, 966, 918 and 754 cm.$^{-1}$.

Similar addition of ethyl mercaptan to VIII (25 mg. of azobisisobutyronitrile, 70°, 13 hr.) containing 1.2% of VII permitted recovery of VIII containing 5% of VII.

Addition of Mercaptans to 3-Methyl-1,2-butadiene.—Dropwise addition of 0.25 mole of thiophenol to 0.22 mole of the allene produced an exothermic reaction after half completion; addition was completed with ice cooling. Distillation gave 37.5 g., b.p. 52.5–57° (0.2 mm.), $n^{25}_{\rm D}$ 1.5700. Redistillation gave b.p. 64° (0.7 mm.), $n^{25}_{\rm D}$ 1.5696, d^{29}_4 0.998.

Anal. Calcd. for $C_{11}H_{14}S$: C, 74.09; H, 7.91; S, 17.99, mol. wt., 178. Found: C, 74.11; H, 7.85; S, 18.09; mol. wt., 176 (cryoscopic in benzene).

Infrared (neat) showed bands at 3070, 2990, 2915, 2359, 2732, 1943, 1865, 1791, 1714, 1632, 1585, 1477, 1441, 1371, 1326, 1299, 1272, 1233, 1177, 1154, 1129, 1082, 1024, 999, 896, 823, 735, 688 cm.$^{-1}$.

Addition of ethyl mercaptan was carried out as for the other allenes [6.7 g. (0.1 mole) of 3-methyl-1,2-butadiene, 4.4 g. (0.07 mole) of mercaptan, 100 mg. of azobisisobutyronitrile, 72°, 5 hr.]. Distillation at atmospheric pressure gave material, b.p. 55° (15 mm.), $n^{25}_{\rm D}$ 1.4841.

Anal. Calcd. for $C_7H_{14}S$: C, 64.54; H, 10.84. Found: C, 64.33; H, 11.02.

Infrared (neat) showed bands at 2950, 2910, 2854, 2718, 1626, 1588, 1447, 1368, 1257, 1228, 1124, 1036, 1048, 964, 837, 817, 775, 757 cm.$^{-1}$.

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