with three portions of benzene. The benzene-soluble material was washed through 50 g. of Florisil with 1.5 l. of benzene to give 0.98 g. of faintly yellow, oily solid. This was chromatographed on 30 g. of alumina collecting 300-ml. fractions. Elution with petroleum ether and two fractions of 20% benzene in petroleum ether gave 0.275 g. (28%) of cholestanone, m.p. 125.5–128°, identical with an authentic sample.[20] Elution with 50% benzene in petroleum ether and pure benzene gave 0.497 g. (50%) of recovered cholestanol, m.p. 141.5–142.5°.

Photoirradiation of PQ and 3β-Methoxy-5-cholestene (V).—A suspension of 2 g. of PQ and 0.91 g. of V[19] in 70 ml. of benzene was irradiated for 94 hr. The dark, wine red solution was concentrated on the steam bath to 10 ml., the 0.44-g. sample of unchanged PQ was filtered, and the filtrate washed through 50 g. of Florisil to give 1.19 g. of faintly yellow oil. This was dissolved in petroleum ether and chromatographed on 50 g. of Florisil, collecting 250-ml. fractions. Elution with four fractions of 10% benzene–petroleum ether, two of 20%, and one of 30% afforded 0.29 g. of nearly colorless oil, identical by infrared spectra with V.

Further elution with one fraction each of 30%, 50%, and 90% benzene–petroleum ether and one of pure benzene yielded 0.66 g. of faintly yellow oil; λ_{max} (dioxane) 251 mμ (sh) (39,000), 256 (47,500), 272 (sh) (18,800), 305 (7500), 318 (9100), 335 (6000), 373 (1500), 395 (770) (extinctions based on molecular weight of a 1:1 adduct); (CH_2Cl_2) 6.1 μ, 6.2, 9.1, no absorption at 2.5–3.1. Treatment of 287 mg. of the oil with aqueous acidic dioxane as described for the adducts of PQ and II afforded 262 mg. of crude product with essentially unchanged ultraviolet and infrared spectra. Repeated chromatography on Florisil failed to give any crystalline products.

Photoadduct (VI) of Tetrachloro-*o*-quinone and Dioxane.—A solution of 3 g. of quinone in 90 ml. of dioxane was irradiated for 14 hr. when the deep red color had faded to light orange. The excess dioxane was removed under reduced pressure without heating to give a tan solid which after one recrystallization from ethyl acetate gave 946 mg. (20%) of V as white needles, m.p. 159–161°. The analytical sample was obtained by crystallization from ethyl acetate, m.p. 167–168°; λ_{max} (dioxane) 291 mμ (sh) (2000), 298 (2400); (KBr) 3.05 μ, no strong maxima at 5.5–6.05.

Anal. Calcd. for $C_{10}H_8O_4Cl_4$: C, 35.96; H, 2.41; Cl, 42.46. Found: C, 35.78; H, 2.23; Cl, 42.28.

Attempted isolation of additional product yielded only solids with broad melting ranges.

Acknowledgment.—The author wishes to acknowledge the generous cooperation of Professor G. J. Mains and Dr. R. Doepker in the photoirradiation experiments and of Professor R. J. Kurland in the determination and interpretation of n.m.r. spectra.

Allene Chemistry. I. Free Radical Addition of Thiols to Allene

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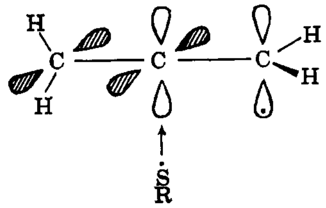
Methanethiol, benzenethiol, and thiolacetic acid added readily to allene under homolytic conditions. The initial attack of the corresponding thiyl radicals occurred quite selectively at the terminal positions of allene, to yield 1:1 and 2:1 adducts. The methanethiol–allene reaction has been studied in greater detail with the help of capillary gas chromatography, n.m.r., and infrared analysis. Allyl methyl sulfide, 1,3-bis(methylthio)propane, and 1,2-bis(methylthio)propane were the reaction products. The yield of the 1:1 adduct (allyl methyl sulfide) varied between 40 and 75 mole % when the reaction temperature was changed from −75 to +17°. 1,3-Bis(methylthio)propane was derived from allyl methyl sulfide, whereas 1,2-bis(methylthio)propane was mainly (>93%) derived from 2-methylthiopropene, the product of a center attack to allene. The selectivity of the initial attack of the thiyl radicals at the terminal positions of allene increased with decreasing reaction temperature. It was found to be 88% at 17° and 95% at −75°. In the addition of thiolacetic acid to allene terminal attack by the thiyl radical occurs with about 91% selectivity, whereas the benzenethiol–allene reaction is less selective. At 17° only about 80% terminal attack was observed.

Free radical reactions of diolefins containing isolated[3] and conjugated[4–6] double bonds have been examined previously in this laboratory. This paper reports about the consequent extension of these studies to the cumulative double bond system of allene.

The over-all course of free radical addition reactions to allene is obviously dependent on the point of initial attack of the radical species which starts the chain. In the case of unsymmetrically substituted mono-[7a] and diolefins,[5] it has been generally demonstrated that the reaction path involving the more stable of the possible radical intermediates is preferred. On this basis it might at first glance seem that initial attack at the center carbon of allene should be favored, since one can write a resonance-stabilized allylic radical intermediate (I), whereas terminal attack leads to a vinylic radical (II). However, in view of the special geometry of the allene molecule, such a representation of the initial attack is certainly oversimplified. The incipient radical from a center attack resembles a primary radical rather than an allylic one, since the orbital of the odd electron does not overlap with the π-orbitals of the remaining double bond.



This complication, though it might cause an increase of the activation energy for the center attack and possibly favor terminal addition, has never been discussed in previous publications on this subject.

The question of terminal and center attack in free radical additions to allene has been answered differently by previous workers. Szwarc and co-workers[8] have

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[3] A. A. Oswald and F. Noel, *J. Org. Chem.*, **26**, 3948 (1961).

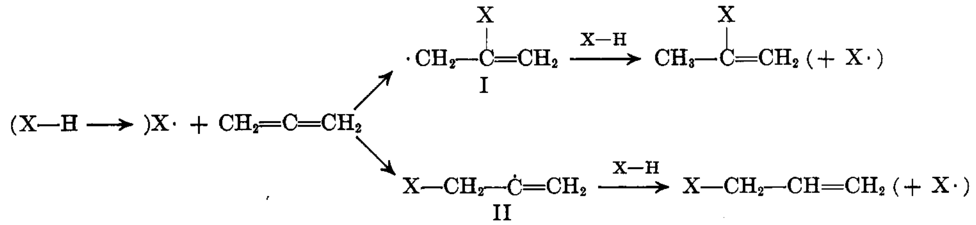
[4] A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *ibid.*, **27**, 2439 (1962).

[5] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).

[6] A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 1262 (1963).

[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) p. 314; (b) pp. 321–323.

[8] A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).



studied the rate constants for the addition of CF_3 and CH_3 radicals to allene and substituted allenes. They concluded from their work that the point of initial attack to the unsubstituted allene is dependent upon the polarity of the starting radical. Thus, the slightly nucleophilic[9] methyl radicals were reported to attack at the center carbon atom, whereas the highly electrophilic trifluoromethyl radical was assumed to attack at the terminal positions.

On the other hand, Pullman[10] suggested that free radicals generally attack at the terminal positions of allene. His prediction was based on a calculation of the radical polarization energies of the carbon atoms in allene.

Aside from these theoretical considerations and some thermally[11,12] and photochemically[13] induced reactions which yielded polymers of unidentified structures, there was only one known definitely free radical addition to allene when this work was started. Haszeldine and co-workers[14] found that the photochemical addition of trifluoroiodomethane yields 4,4,4-trifluoroiodobut-1-ene by an exclusively terminal attack of the starting CF_3 radical on allene.

$$(F_3CI \longrightarrow)F_3C\cdot + CH_2{=}C{=}CH_2 \longrightarrow$$
$$F_3C{-}CH_2{-}\dot{C}{=}CH_2 \xrightarrow{F_3CI} F_3C{-}CH_2{-}CI{=}CH_2(+F_3C\cdot)$$

Kovachic and Leitch[15] claim to have added hydrogen bromide and deuterium bromide to allene and deuterated allenes by a free radical mechanism. The main reaction products were the corresponding 2-bromopropenes. Their formation was assumed to be the consequence of a preferential center attack by the bromine atom in the first propagation step.

$$(HBr \longrightarrow)Br\cdot + CH_2{=}C{=}CH_2 \longrightarrow$$
$$CH_2{=}CBr{-}CH_2\cdot \xrightarrow{HBr} CH_2{=}CBr{-}CH_3(+Br\cdot)$$

However, the 2-bromopropenes also could have been formed by an ionic mechanism, analogous to the one reported for the addition of hydrogen chloride to allene.[16]

$$CH_2{=}C{=}CH_2 \xrightarrow{H^+} CH_2{=}\overset{+}{C}{-}CH_3 \xrightarrow{X^-}$$
$$CH_2{=}CX{-}CH_3\ (X = Cl, Br)$$

Having this somewhat conflicting literature information, we selected thiols[17] as adding agents, since their reactions with diolefins in general can be carried out readily by an exclusively free radical mechanism to yield stable compounds.

Results

Mixtures containing 0.1 mole of a thiol, 0.3 mole of allene, and 0.001 mole of *t*-butyl hydroperoxide were irradiated in quartz tubes for different lengths of times and at different temperatures (Table I). The crude reaction mixtures were analyzed by gas–liquid chromatography as well as n.m.r. and infrared spectroscopy.

TABLE I

EXPERIMENTAL AND ANALYTICAL DATA OF THIOL–ALLENE ADDITIONS

R	Thiols used	Peroxide added	Temp., °C.	Time, hr.	Conversion of thiols, %	Yield[a] of adduct mixture	Amount of components in mixture, mole %: $RS{-}CH_2{-}CH{=}CH_2$	$RS{-}(CH_2)_3{-}SR$	$RS{-}\overset{\overset{CH_3}{\vert}}{C}H{-}CH_2{-}SR$	Center attack[b] on allene, %
CH_3	Methanethiol	Yes	15–17	56	100	88	66[c]	19[d]	15[e]	14
CH_3	Methanethiol	Yes	17	4.66	100	87	76	12	12	11
CH_3	Methanethiol	Yes	17	1.5	100	86	76	13	11	10
CH_3	Methanethiol	Yes	17	15 min.	58	54	74	13	13	12
CH_3	Methanethiol	No	−45	25	...	..	39	53	8	8
CH_3	Methanethiol	Yes	−75	12	100	71	57	37	6	6
$CH_3{-}CO$	Thiolacetic acid	Yes	17	15 min.	...	92	73	18	9	9
C_6H_5	Benzenethiol	Yes	17-18	52	100	..	70	11	19	19
C_6H_5	Benzenethiol	No	Ambient	35	100	75	73	10	17	17
C_6H_5	Benzenethiol	Yes	17	3.5	100	83	72	7	21	21

[a] Based on thiol conversion and product distribution. [b] Based on the amount of VI in the product mixture less the amount of VI formed from III. [c] Retention time, 6.8 min. [d] Retention time, 24.4 min. [e] Retention time, 22.7 min.

The peaks in the gas chromatograms have been individually identified by authentic compounds. The g.l.c. results have been supported by semiquantitative n.m.r. analyses. These were based on the relative areas of peaks which were characteristic of the individual components and which did not interfere with each other in the spectra of the reaction mixtures (Fig. 1).

The free radical character of these peroxide- and

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[9] A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc.* (London), **251A**, 349 (1959).

[10] B. Pullman, *J. chim. phys.*, **55**, 790 (1958).

[11] S. Lebedew, *Chem. Zentr.*, **I**, 1410 (1914).

[12] J. B. Harkners, G. B. Kistiakowski, and W. H. Mears, *J. Chem. Phys.*, **5**, 684 (1937).

[13] S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, **55**, 1038 (1933).

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

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

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

[17] When the experimental studies of this work were finished, we learned of a similar investigation by T. L. Jacobs and G. E. Illingworth at the University of California.

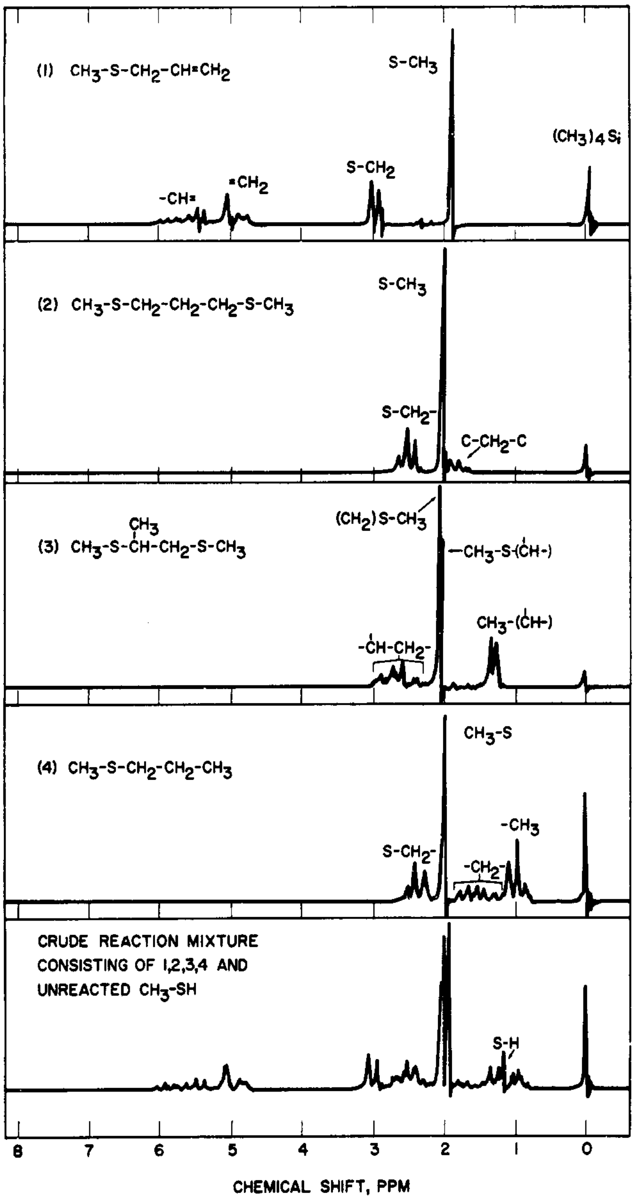


Fig. 1.—Nuclear magnetic resonance spectra of methanethiol–allene adducts.

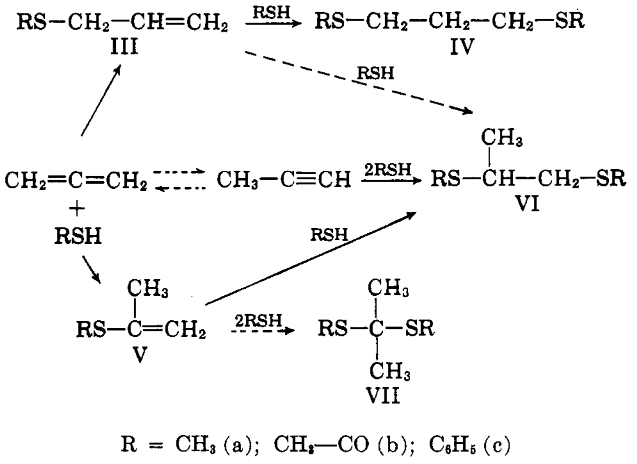
ultraviolet-catalyzed reactions has been demonstrated in the case of the benzenethiol–allene additions. Mixtures of allene and benzenethiol have been treated without any initiation, with ultraviolet initiation, and with a combined peroxide and ultraviolet initiation. The relative rates, based on the thiol decrease, were 1:5.5:7.5, respectively.

Methanethiol.—The main part of the work has been carried out using methanethiol as the adding agent. This resulted in reaction mixtures consisting of relatively low boiling components which could be easily analyzed by capillary gas chromatography. Furthermore, in the semiquantitative n.m.r. analysis of these mixtures the interference of the signals arising from the alkyl group of the starting thiol was reduced to a minimum (Fig. 1).

At 17° the reaction was half completed in fifteen minutes. After ninety minutes no unchanged mercaptan could be detected. The colorless liquid reaction mixture consisted of allyl methyl sulfide (IIIa), 1,3-bis(methylthio)propane (IVa), and 1,2-bis(methylthio)propane (VIa) in the average molar ratio of 6.5:1:1. Methyl propyl sulfide also was formed from a propylene impurity in the starting allene. Only trace amounts of unidentified impurities showed up in the gas chromatograms, and none of the other possible reaction products Va or VIIa were present.

If the reaction was carried out at lower temperatures, much longer reaction times were required. The mixtures again consisted of the same components; however, their ratio was considerably changed. Thus, at −75° the yield of the monoadduct IIIa had dropped in favor of the 1,3-diadduct IVa and the actual ratio (IIIa:IVa:VIa) was 10:6.4:1.

These results can be generally explained by the following reaction sequences.



R = CH_3 (a); CH_3—CO (b); C_6H_5 (c)

It is obvious that the allyl methyl sulfide (IIIa) and the 1,3-bis(methylthio)propane (IVa) originally are derived from a terminal attack of the thiyl radical on the allene molecule. The third reaction product, 1,2-bis(methylthio)propane (VIa), however, can arise by three different routes.

Center attack of the thiyl radical on allene would lead to methyl 2-propenyl sulfide (Va), which could react subsequently with methanethiol to form the diadduct VIa. If this were the exclusive reaction path, the per cent of VIa in the reaction mixture could be related directly to the amount of center attack. The fact that no monoadduct Va was ever found is not surprising, since it has been shown recently by Shostakowskii and co-workers[18] that the corresponding ethyl 2-propenyl sulfide is very reactive towards ethanethiol and readily forms the corresponding 1,2-bis(diethylthio)propane.

An alternate route to form VIa starts out with a possible isomerization of allene to methylacetylene under the influence of ultraviolet irradiation or thiyl radicals. We showed in an independent experiment that methylacetylene reacts readily with methanethiol to form the diadduct VIa. Therefore, the critical step would be the isomerization reaction. It was known that allene does not isomerize below 320–400° in the absence of a catalyst.[12] However, the combined effect of ultraviolet light and thiyl radicals on allene isomerizations was not known. Therefore, the excess of allene from the addition reaction was analyzed by g.l.c. It could be shown that no methylacetylene was present. Of course, this evidence is conclusive only if the thiol

[18] M. F. Shostakovskii, E. P. Gracheva, and N. N. Kul'bovskaya, *Zh. Obsch. Khim.*, **30**, 383 (1960).

is added with about equal rates to allene and methylacetylene.

This could be confirmed by treating a mixture of the two with less than the required amount of thiol and analyzing the unchanged gaseous allene–methylacetylene mixture as well as the liquid products formed. We can, therefore, rule out this route to VIa under the prevailing reaction conditions.

The third route to VIa, namely thiol addition to IIIa, is highly improbable in view of the general direction of free radical additions of thiols to olefins.[7a] In independent experiments we could indeed show that this "reverse" addition occurs to less than 7%.

On the basis of these results it can be concluded that at least 93% of the 1,2-bis(methylthio)propane formation occurs through the vinyl sulfide Va and, therefore, reflects the amount of center attack to allene. At 17° center attack occurs with 12%, at −45° it occurs with only 8%, and at −75° the ratio drops to 6%. The situation is, however, just the reverse for the ratio of mono- (IIIa) to diadduct (IVa). At 17° this ratio was about 5:1 as compared to 1.5:1 at −75°.

Thiolacetic Acid.—Addition of thiolacetic acid to allene also occurred readily under the conditions described before. A mixture of the monoadduct IIIb and two diadducts IVb and VIb was formed (Table I). With the assumption that the previous conclusion concerning the mode of formation of the diadduct VIb can be generalized, terminal attack was found to occur with 91%. The molar ratio of the mono- (IIIb) to the diadduct VIb is 4:1.

Benzenethiol.—The peroxide- and ultraviolet-catalyzed addition of benzenethiol to allene was completed in three and a half hours.

The crude reaction mixtures consisted of the monoadduct IIIc, the two diadducts IVc and VIc, very little phenyl propyl sulfide, and between 5–10% unidentified impurities. The main impurity showed a single peak in the n.m.r. at the same position (1.45 p.p.m.) as the diadduct VIIc. V.p.c. analysis of a blend, containing synthetic VIIc and the crude benzenethiol–allene adduct, demonstrated, however, that VIIc was not a product of the addition reaction. Fractional distillation of the reaction mixture largely confirmed the results of the g.l.c. and n.m.r. analyses. The per cent of the diadduct VIc in the reaction mixture was higher than in the two previous cases (Table I). It was shown that less than 2% of VIc arises from the allyl phenyl sulfide IIIc. Assuming that benzenethiyl radicals do not isomerize allene, the amount of terminal attack is thus only 80%.

Discussion

The present work has shown that thiyl radicals add selectively to the terminal positions of allene. In the second propagation step, the vinylic type radical intermediate then abstracts hydrogen from the thiol to yield alkyl (or aryl) allyl sulfides. The over-all reaction is, therefore, a 1,2-addition of a thiol to allene.[19a] This reaction course is largely in line with Pullman's theory. Since thiyl radicals are electrophilic species,[19b] one would expect, however, the same results on the basis of Szwarc's prediction. Therefore, the information which was obtained in the present investigation does not allow a decision between the two conflicting theories. Nevertheless, the thiol addition reaction might be a potential means of solving this question, using various *para*-substituted benzenethiols as adding reagents. A correlation between the nature of the substituent and its effect on the selectivity of the reaction should give an indication as to the validity of Szwarc's prediction.

The observed difference in selectivity between the thiyl radicals derived from methanethiol and thiolacetic acid on one side and benzenethiol on the other side is somewhat puzzling. Since the latter thiyl radicals are resonance stabilized and less reactive[7b] than the former ones, one might have anticipated an increased selectivity for the benzenethiol–allene addition. Even though the reverse has been observed, the effect is too small to suggest any definite conclusion.

The yield of the diadduct IVa is increasing at the expense of the monoadduct IIIa with falling reaction temperatures. It is believed that this effect reflects the higher reactivity of the monoadduct over that of allene. The first propagation step in this diadduct formation might involve a fast equilibrium of the following type.

$$\mathrm{RS{-}CH_2{-}CH{=}CH_2 + \cdot SR \overset{\text{fast}}{\rightleftarrows}}$$

$$\mathrm{RS{-}CH_2{-}\dot{C}H{-}CH_2{-}SR \xrightarrow[\text{slow}]{\text{RSH}} RS{-}CH_2{-}CH_2{-}CH_2{-}SR}$$

The lower ratio of the diadduct IVc relative to the monoadduct IIIc in the benzenethiol–allene addition reaction seems to support this assumption. The enhanced stability of the resonance-stabilized thiyl radical, derived from benzenethiol, would favor the reversibility of the first propagation step and thus decrease the over-all yield of the diadduct IVc.

Experimental

Materials.—The allene and methylacetylene used were Matheson products. Allene contained 0.038% of propane and between 0.5 and 7.3% (depending on the batch) of propylene; however, no methylacetylene was present. The thiols used were C.P. chemicals. All reference samples have been prepared by known methods, starting from the corresponding bromides or chlorides and sodium mercaptides. Characteristic n.m.r. parameters of them are listed in Table II.

Method of Analyses.—The adduct mixtures of methanethiol, thiolacetic acid, and allene have been analyzed by capillary gas chromatography. A Perkin-Elmer Model 226 linear programmed temperature gas chromatograph with a 200-ft., 0.02-in. i.d. Golay column coated with a mixture of 50% phenylsilicone and 50% nitrilesilicone was used. Temperatures of the injection block and detector were 270° and 190°, respectively. The temperature of the column was first held for 10 min. at 50°; afterwards, it was programmed at a rate of 10° per min. up to 160° and then maintained at that temperature isothermally until the end of the analyses. A CRS-1 digital chromatogram integrator (supplied by Infotronics Co., Houston, Tex.) was used for recording the peak areas. Data from the integrator were automatically transferred to a printer which in turn printed out peak retention times and peak areas on a printer tape.

The higher boiling benzenethiol–allene adducts were separated on a F & M Model 500 linear programmed temperature gas chromatograph with a 2-ft., 0.25-in. o.d. column. The column

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(19) (a) NOTE ADDED IN PROOF.—After this work was submitted for publication we learned that workers at Shell [H. J. Van der Ploeg, J. Knoterus, and A. F. Bickel, *Rec. trav. chim.*, **81**, 775 (1962)] concluded that thiol additions to allene are rather indiscriminate. We feel that their conclusion is valid only when a large excess of allene is used. (b) W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 85.

TABLE II

PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF THIOL–ALLENE ADDUCTS

(Chemical shifts of structural units, p.p.m. downfield from tetramethylsilane internal reference; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet)

	$RS-CH_2-CH=CH_2$				$RS-CH_2-CH_2-CH_2-SR$			$RS-CH_2-CH(CH_3)-S-R$				
R	RS—	$-CH_2-$	—CH=	$=CH_2$	RS—	$-S-CH_2$	$-CH_2-$	RS—	$-CH_2-$	—CH—	$(-CH_3)$	—SR
CH_3	s 1.94	d 3.05[a]	m 5.77[b]	m 5.02 m 5.04 [c]	s 2.07	t 2.57[a]	m 1.82[a]	s 2.08	q 2.53 q 2.80 [h]	m 2.86[e]	d 1.32[d]	s 2.07
CH_3CO—	s 2.23	d 3.49[a]	m 5.82[b]	m 5.03 m 5.16 [c]	s 2.29	t 2.90[a]	m 1.79[a]	s 2.32	d 3.10 d 3.12 [f]	m 3.67[g]	d 1.27[a]	s 2.27[a]
C_6H_5	m 7.0–7.5	d 3.38[a]	m 5.82[b]	m 4.93 m 5.00 [c]	m 6.8–7.4	t 2.84[a]	m 1.77[a]	m 7.0–7.4	q 2.68 m *ca.* 3.0 [i]	m ~3.0[j]	d 1.33[d]	m 7.0–7.4

[a] $J = 7$ c.p.s. [b] X part of an $ABXY_2$ spin system, $J = 9$ c.p.s., 17 c.p.s., and 7 c.p.s. [c] AB part of an $ABXY_2$ spin system, $J_{AB} = 3$ c.p.s., remote coupling constant 1 c.p.s. [d] $J = 6$ c.p.s. [e] X part of an $ABXY_3$ spin system, $J_{AX} = 9$ c.p.s., $J_{BX} = 12$ c.p.s., $J_{XY} = 7$ c.p.s. [f] AB part of an $ABXY_3$ spin system. [g] X part of an $ABXY_3$ spin system, $J_{AX} = 9$ c.p.s., $J_{BX} = 7$ c.p.s. [h] AB part of an $ABXY_3$ spin system. [i] AB part of an $ABXY_3$ spin system not sufficiently resolved for detailed assignments. [j] X part of an $ABXY_3$ spin system not sufficiently resolved for detailed assignments.

packing consisted of 3% Dowfax 9N40 (obtainable from Dow Chemical Co., Midland, Mich.) on 60–80-mesh Gas Chrom P.

Operating conditions were as follows: detector cell temperature, 370°; detector cell current, 150 ma.; injector part temperature, 295°; helium flow at exit, 60 cc./min.; column heating rate, 5.6°/min.; starting column temperature, 100°; finished column temperature, 225°; sample size, 0.5 µl.

The crude reaction mixtures were analyzed as such or after removal of the excess thiol. The components were identified by comparison of their retention times with those of the pure compounds. In addition to that, blends, containing the reaction mixture and the authentic compound, were individually run for each component. The added components showed up in the area of the respective peaks and did not cause any change (broadening or splitting) in the shape of the peaks.

The response factors for the adducts of methanethiol and allene have been determined with synthetic blends of the individual components. It was found that the relative areas can be directly related to the weight per cent.[20]

Allene and the allene–methylacetylene mixtures were analyzed on the F & M Model 500 gas chromatograph, using a 10-ft. column, packed with 20% dimethyl sulfolane on Chromosorb P. The column temperature was maintained at 30°.

N.m.r. spectra were recorded and integrated on a Varian Model A-60 proton resonance spectrometer. The infrared spectra were obtained using a Baird recording spectrophotometer, Model B.

Addition of Thiols to Allene.—In a 100-ml. quartz tube 12 g. (0.3 mole) of allene was condensed at −80°; 0.1 mole of a mercaptan and 0.001 mole of *t*-butyl hydroperoxide were added. The sealed tube was placed into a temperature-controlled water (17 ± 1°) or "Freon 11" bath. A 100-w. Hanovia ultraviolet immersion lamp was placed about 5 cm. from the reaction tube. If the reaction was carried out below room temperature, the lamp was surrounded by a quartz mantle to avoid excessive cooling of the lamp.

After an arbitrary period of reaction time the tubes were opened at −80°. If methanethiol was the adding agent, the excess gases subsequently were passed through a saturated methanol solution of lead acetate and a wet test meter to determine the unreacted thiol and allene selectively. The lead–bismethyl sulfide was determined gravimetrically. In the benzenethiol–allene reaction mixtures the excess thiol was titrated potentiometrically with silver nitrate and was removed by washing with a 5% aqueous sodium hydroxide solution. The remaining crude reaction mixtures were in all cases colorless or slightly yellow liquids, depending on the reaction times.

In one experiment, 9.1 g. of a crude benzenethiol–allene adduct mixture was distilled to yield 4.7 g. (51.7 wt. % as compared to 56% by g.l.c. analysis) of allyl phenyl sulfide, b.p. 68–69° (1 mm.). The remaining mixture of higher boiling diadducts was subsequently analyzed by g.l.c. and n.m.r.

Addition of Methanethiol to Methylacetylene.—A mixture of 4 g. (0.1 mole) of methylacetylene, 9.6 g. (0.2 mole) of methanethiol, and 90 mg. of *t*-butyl hydroperoxide was irradiated in a sealed quartz tube for 4.5 hr. at 15°. The crude reaction product (11.8 g., 86%) was a colorless liquid. G.l.c. analysis showed that it consisted with 93% of the diadduct, VIa, b.p. 84° (20 mm.).

Anal. Calcd. for $C_5H_{12}S_2$: C, 44.07; H, 8.87; S, 47.06. Found: C, 44.31; H, 8.86; S, 47.06.

Addition of Methanethiol of a Mixture of Allene and Methylacetylene.—A mixture, containing 0.05 mole of allene and methylacetylene each, 90 mg. of *t*-butyl hydroperoxide, and 0.05 mole of methanethiol was irradiated in a sealed quartz tube for 1 hr. at 15°. The unchanged gaseous allene–methylacetylene mixture and the liquid reaction product were analyzed by g.l.c.

	Allene	Methylacetylene
Mole % at start	48	52
Mole % after reaction	53	47
Mole % product derived from	52	48

The discrepancy in the analyses of the unchanged gases and of the liquid reaction mixture might be due to the fact that two different chromatographic instruments were used.

Addition of Methanethiol to Allyl Methyl Sulfide.—Mixtures containing 2 g. (0.023 mole) of allyl methyl sulfide, 1.2 g. (0.025 mole) of methanethiol, and 10 mg. of *t*-butyl hydroperoxide were irradiated in sealed quartz tubes for the indicated lengths of time at 17°. The reaction products were analyzed by g.l.c. and n.m.r.

Reaction time, hr.	Yield of crude adduct, %	Ratio of the diadducts in mixture IVa	VIa
2	94	93	7
18	100	94	6

Relative Rates of Benzenethiol–Allene Additions Dependent on the Initiation.—Mixtures of 0.3 mole of allene and 0.1 mole of benzenethiol reacted for 20 min. at 17° under the indicated different conditions. At the end the amount of unchanged benzenethiol in the liquid reaction mixture was potentiometrically titrated with a silver nitrate solution.

Reaction vessel	Ultraviolet irradiation	*t*-Butyl hydroperoxide	Thiol reacted, %	Relative rates
Glass tube	No	No	11.7	1
Quartz tube	Yes	No	65	5.5
Quartz tube	Yes	0.001%	87.5	7.5

Addition of Benzenethiol to Allyl Phenyl Sulfide.—Allyl pheny sulfide (7.5 g., 0.05 mole) and benzenethiol (5.5 g., 0.05 mole) were irradiated in the presence of 10 mg. of *t*-butyl hydroperoxide at 17°. After 2 hr. only 53% of the thiol had disappeared. The crude reaction product was washed with a 5% aqueous solution of sodium hydroxide and water. The dried (over sodium sulfate) product was analyzed by g.l.c. It consisted of 98% of 1,3-bis(phenylthio)propane and 2% of 1,2-bis(phenylthio)propane.

Independent Syntheses of the G.c. Reference Samples.—

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[20] See also N. D. Nogare and R. S. Juvet, Jr., "Gas Liquid Chromatography," Interscience, New York, N. Y. 1962, p. 197.

The **monoadducts** have been prepared by the method of Price and Gillis.[21] Allyl methyl sulfide[21]: b.p. 93.5–95°; infrared,[22] 3.27 (=CH),[23a] 5.45 (overtone to =CH$_2$),[23b] 6.14 (C=C),[23c] 10.95 μ (=CH$_2$ deform.).[23d] Allyl acetyl sulfide: b.p. 48–49° (27 mm.) (*Anal.* Calcd. for C_5H_8OS: C, 51.69; H, 6.94. Found: C, 51.98; H, 6.97); infrared, 3.26 (=CH),[23a] 5.45 (overtone to =CH$_2$),[23b] 6.13 (C=C),[23c] 10.90 μ (=CH$_2$ deform.).[23d] Allyl phenyl sulfide[24]: b.p. 51–52° (0.4 mm.); infrared, 6.12 (C=C olefinic),[23c] 10.90 μ (=CH$_2$ deform.).[23d]

The **diadducts** have been prepared by the general method of Mann and Purdie.[25] 1,3-Bis(methylthio)propane[26]: b.p. 99–100° (27 mm.); infrared, 3.45, 7.0, 7.95, 8.04, 10.50 μ. 1,3-Bis-(acetylthio)propane: b.p. 105–106° (2 mm.) (*Anal.* Calcd. for $C_7H_{12}O_2S_2$: C, 43.73; H, 6.29. Found: C, 43.53; H, 6.25); infrared, 3.40, 5.90, 6.97, 7.39, 8.07, 8.80 μ. 1,3-Bis(phenylthio)propane[25]: b.p. 170–171° (0.3 mm.). 1,2-Bis(methylthio)-propane: b.p. 90.5–91° (27 mm.) (*Anal.* Calcd. for $C_5H_{12}S_2$: C, 44.06; H, 8.87; S, 47.06. Found: C, 44.45; H, 9.01; S, 47.1); infrared, 3.36 and 3.43, 6.99, 7.29, 7.60, 7.94, 8.17, 8.43, 9.05, 9.38, 9.83, 10.47, 14.82 μ. 1,2-Bis(acetylthio)propane: b.p. 70–72° (0.2 mm.) (*Anal.* Calcd. for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29. Found: C, 43.59; H, 6.15). 1,2-Bis(phenylthio)-propane: b.p., 158–160° (0.3 mm.) (*Anal.* Calcd. for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19; S, 24.63. Found: C, 69.50; H, 6.36; S, 24.75); infrared, 3.29, 3.40, 3.45, 6.34, 6.77, 6.97, 7.32, 8.50, 9.20, 9.77, 13.50, 14.50 μ.

Acknowledgment.—The authors wish to thank A. M. Palmer and G. F. Shea for technical help and Miss M. J. Doolan for the g.c. analyses.

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(21) C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4750 (1953).

(22) For the monoadducts the bands characteristic of the double bond are reported. For the diadducts the strongest bands of the spectrum are reported without correlating them to particular structural elements.

(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959: (a) p. 43; (b) p. 50; (c) pp. 35–38; (d) pp. 49–51.

(24) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **52**, 3356 (1930).

(25) F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1557 (1935).

(26) See also S. Mathias, *Bol. Fac. Filosof., cienc. letras, Univ. São Paulo; Quim. No. 1*, **14**, 75 (1942).

Transannular Sulfoxide–Ketone Salt Formation across a Seven-Membered Ring[1]

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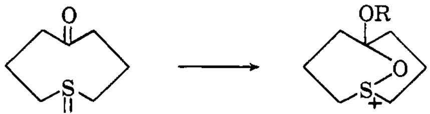
This investigation has established for the first time the occurrence of a transannular reaction between sulfoxide and ketone groups, with protonation, across a seven-membered ring: 1-thiacycloheptan-4-one 1-oxide (III) with perchloric or fluoboric acid gave the corresponding 5-hydroxy-8-oxa-1-thioniabicyclo[3.2.1]octane salt (IVa,b), with an oxygen bridge between the sulfur and the carbonyl carbon. The bicyclic fluoborate was methylated with 2,2-dimethoxypropane to give 5-methoxy-8-oxa-1-thioniabicyclo[3.2.1]octane fluoborate (IVc). Hydrolysis of both the bridgehead hydroxy and methoxy salts occurred so readily that all operations had to be conducted in a dry box. We found it hazardous to work with the perchlorate salts in this bicyclic series.

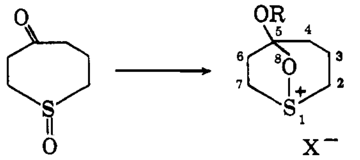
In an investigation of the occurrence of transannular interactions and reactions of diametric sulfoxide and ketone groups in medium rings (eight–eleven members), monocyclic 1-thiacyclooctan-5-one 1-oxide (I) was converted to a bicyclic perchlorate salt by transannular reaction involving protonation of the carbonyl oxygen.[2] The protonic salt and its methoxy and acetoxy derivatives were shown to have 1-thioniabicyclo[3.3.1]nonane structures (II), with an oxygen bridge between the sulfur and the carbonyl carbon. This type of bridging generates two six-membered rings from an eight-membered ring rather than two five-membered rings, as would have been the case had sulfur acted as the donor. The action of oxygen of the sulfoxide as the donor suggested that in the seven-membered ring system, 1-thiacycloheptan-4-one 1-oxide (III), similar bridging could lead to a probable structure of the 1-thioniabicyclo[3.2.1]octane type (IV) consisting of a five- and a six-membered ring, whereas the result of direct sulfur–carbon bridging would be a structure consisting of four- and five-membered rings, thermodynamically unstable under the reversible conditions of salt formation.



I

II

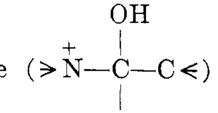
IIa, R = H
b, R = CH_3
c, R = $COCH_3$



III

IV

IVa, R = H, X = ClO_4
b, R = H, X = BF_4
c, R = CH_3, X = BF_4

A test of the ability of III, and possibly of a six-membered-ring compound of the 1-thiacyclohexan-4-one 1-oxide type, to undergo transannular reaction is also of theoretical interest because it should provide information concerning the lower limits of ring size for this phenomenon to occur. The lower limit for transannular bond formation, accompanying protonation, between diametric tertiaryamine and ketone[3] or sulfide and ketone functions[4,5] is presently at the eight-membered ring. However, when an additional atom is introduced between amino nitrogen and the 4-carbon of a six-membered ring in configuration and conformation favorable for reaction, a bridge may be formed creating two five-membered rings in an azoniabicyclo[2.2.1]heptane system. Thus, Bell and Archer[6] have shown that the salt of 3α-phenyl-3β-tropanyl phenyl ketone exists mainly in a transannular bridged structure  $(>\overset{+}{\mathrm{N}}-\underset{|}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}-\mathrm{C}<)$ and Polonovski and Polonovski[7] reported that scopin-

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(1) Support of this work by research grants (NSF-G6040 and NSF-G14121) from the National Science Foundation is gratefully acknowledged.

(2) N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).

(3) N. J. Leonard, R. C. Fox, and M. Ōki, *ibid.*, **76**, 5708 (1954).

(4) N. J. Leonard, T. L. Brown, and T. W. Milligan, *ibid.*, **81**, 504 (1959); **82**, 4075 (1960).

(5) C. G. Overberger and A. Lusi, *ibid.*, **81**, 506 (1959).

(6) M. R. Bell and S. Archer, *ibid.*, **82**, 151 (1960).