(52.5 mmoles) of sodium hydroxide in 5 ml. of water. The reaction was refluxed for 30 min. (until positive halogen concentration diminished), then cooled to room temperature to yield a crystalline mass. The product was collected on a funnel, washed with methanol-water, and dried *in vacuo:* weight 4.3 g. (59%), m.p. 167–172°. An additional crop was obtained by removing much of the methanol *in vacuo:* 1.9 g. (26%), m.p. 161–167°. The combined crops (6.2 g.) were recrystallized from 400 ml. of boiling water to yield 5.1 g. (70%): m.p. 166–170° (lit.[7] m.p. 172°), λ_{max}^{MeOH} 281 mμ (ε 8,220).

Anal. Calcd. for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.58; H, 6.58; N, 19.45.

Methyl Thiazolyl-4-carboximidate Hydrochloride (VIII).—To a solution of 100 g. (0.908 mole) of 4-cyanothiazole[11] in 300 ml. of anhydrous methanol there was added with stirring a solution of 5.47 g. (0.101 mole) of sodium methoxide in 100 ml. of methanol. The solution was stirred for 17 hr. at room temperature, after which the catalyst was neutralized by the addition of 6.08 g. (0.101 mole) of glacial acetic acid. The reaction mixture was concentrated *in vacuo* to a crystalline mass and the product free base was extracted from sodium acetate with methylene chloride. The hydrochloride VIII was crystallized from 1 l. of methylene chloride by the addition of 99 ml. of 8.96 *N* methanolic hydrogen chloride: yield 148 g. (92%), m.p. 151–154° dec. Recrystallization from methanol–ether produces an analytical sample, m.p. 151–154° dec.

Anal. Calcd. for $C_5H_7ClN_2OS$: C, 33.62; H, 3.95; N, 15.68. Found: C, 33.54; H, 3.95; N, 15.81.

N′-(3-Pyridyl)-4-thiazolecarboxamidine Hydrochloride (VI).—A mixture of 20 g. (0.112 mole) of VIII and 10.5 g. (0.112 mole) of 3-aminopyridine in 50 ml. of ethanol was stirred at room temperature for 17 hr., after which the crystalline product was collected on a funnel, washed with ethanol, and dried *in vacuo.* The yield of crude product was 17.2 g. (64%), m.p. 214–217° dec. Recrystallization from methanol–ether produced 12.2 g. of pure product, m.p. 223–225°.

Anal. Calcd. for $C_9H_9ClN_4S$: C, 44.90; H, 3.77; Cl, 14.73; N, 23.28; S, 13.32; equiv. wt., 241. Found: C, 44.71; H, 3.83; Cl, 14.73; N, 23.79; S, 13.62; equiv. wt., 241.

N-Chloro-N′-(3-pyridyl)-4-thiazolecarboxamidine (IX).—A solution of 5.00 g. (20.8 mmoles) of VI in a mixture of 40 ml. of water and 40 ml. of methylene chloride was stirred at room temperature with 7.30 ml. of 2.85 *M* sodium hypochlorite[13] (20.8 mmoles) for 15 min. The organic layer was separated and the aqueous phase was extracted with two small portions of methylene chloride. After drying over sodium sulfate and removing the drying agent by filtration, the filtrate was concentrated to a small volume and the product was crystallized by the addition of petroleum ether: 4.42 g. (89%), m.p. 143–144° dec. Recrystallization from ethyl acetate yielded an analytical sample, m.p. 146–147°.

Anal. Calcd. for $C_9H_7ClN_4S$: C, 45.28; H, 2.96; Cl, 14.85; N, 23.47. Found: C, 45.47; H, 2.78; Cl, 14.83; N, 23.46.

2-(4-Thiazolyl)-4-azabenzimidazole (VII).—To a stirred suspension of 2.00 g. (8.38 mmoles) of IX in 24 ml. of 50% aqueous methanol there was added 0.98 g. (9.22 mmoles) of sodium carbonate as a saturated aqueous solution. The mixture was refluxed until the positive halogen test on potassium iodide–starch paper was negative (20 min.), after which it was cooled to room temperature, filtered, and washed with cold 50% aqueous methanol; then water to yield 0.39 g. (23%) of product, m.p. 304–307°. Recrystallization from methanol produced a sample melting 310–311°, $\lambda_{max}^{0.1\,N\ HCl}$ 321 mμ (ε 29,600), which was identical with the imidazole VII obtained by condensing 2,3-diaminopyridine and VIII by infrared, ultraviolet and n.m.r. analysis.

Anal. Calcd. for $C_9H_6N_4S$: C, 53.45; H, 2.99; N, 27.70. Found: C, 53.50; H, 2.70; N, 27.57.

Compound VII from 2,3-Diaminopyridine.—A suspension of 2,3-diaminopyridine (15 g., 0.137 mole) and 24.5 g. (0.137 mole) of VIII in 63 ml. of ethanol was stirred at room temperature for 18 hr., after which the crystalline product was collected and washed with ethanol (25 ml.) and water. After drying *in vacuo,* the product weighed 4.36 g., m.p. 308–309°. The mother liquors deposited an additional sample weighing 6.30 g., m.p. 290–292°. Recrystallization from methanol yielded a sample: m.p. 310–312.5°, $\lambda_{max}^{0.1\,N\ HCl}$ 320 mμ (ε 30,200). The product was identical with VII obtained from compound IX by infrared, ultraviolet, n.m.r., and microchemical analysis.

2-Phenyl-1,3,3a-triazaindene (V).—To a solution of 10 g. (50.7 mmoles) of N′-(2-pyridyl)benzamidine[8] (IV) in a mixture of 50 ml. of methylene chloride and 50 ml. of water at 5° there was added with stirring 50.7 ml. of 1 *N* hydrochloric acid followed by 18.1 ml. of 2.81 *M* sodium hypochlorite[13] (50.7 mmoles). After stirring 30 min. at 10°, the organic layer was removed and the aqueous layer was extracted with three 5-ml. portions of methylene chloride. The combined organic layers were washed with water and then dried over anhydrous sodium sulfate. Filtration and concentration yielded a crystalline N-chloro intermediate which was washed with ethanol and dried *in vacuo:* 9.43 g., m.p. 85–87°. Five grams (21.6 mmoles) of the intermediate was suspended in 60 ml. of 50% aqueous methanol and treated with 2.75 g. (25.9 mmoles) of sodium carbonate in the usual manner. The product weighed 3.90 g. (74%) based on starting amidine IV: m.p. 135–137.5°. Recrystallization from acetone produced a sample: m.p. 138–139° (lit.[9] m.p. 141°); picrate m.p. 164–166° (lit.[9] m.p. 168°). The ultraviolet spectrum of V in cyclohexane was identical with reported values.

Anal. Calcd. for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.52; H, 4.41; N, 21.39.

Allene Chemistry. III.[1] Free-Radical Addition of Hydrogen Sulfide to Allene

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Hydrogen sulfide and allene have been allowed to react in varying relative ratios under typical free-radical conditions in the liquid phase at −70°. The reactions occurred selectively by terminal attack of the sulfhydryl radicals on allene. 3-Propenethiol was formed as the primary reaction product. If hydrogen sulfide was used in an excess, 3-propenethiol reacted further to form 1,3-propanedithiol in good yield. When allene was used in excess, diallyl sulfide was formed in moderate yield, along with oligomers of 3-propanethiol and other by-products.

The first definitely free-radical addition of hydrogen sulfide to an olefinic double bond was reported by Vaughan and Rust[3] in 1942. They found that under the influence of ultraviolet light addition occurred very rapidly even at −78° and was highly selective yielding "anti-Markownikoff" products. Based on their results and the similar course of thiol–olefin additions,[4] they proposed the following mechanism for the reaction.

$$(H_2S \longrightarrow)HS\cdot + CH_2{=}CHR \longrightarrow$$
$$HSCH_2\dot{C}HR \xrightarrow{H_2S} HSCH_2CH_2R + HS\cdot$$

The generality of this mechanism has subsequently been confirmed by the similar course of the free-radical

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(2) Author to whom correspondence should be addressed.

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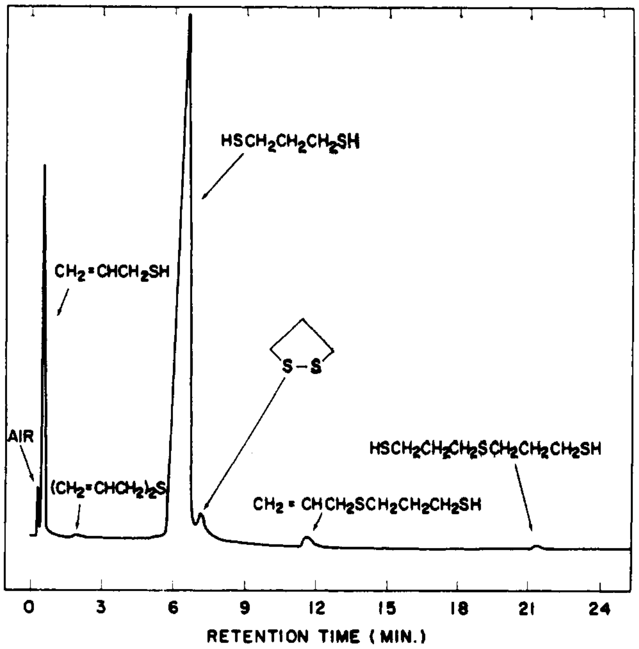
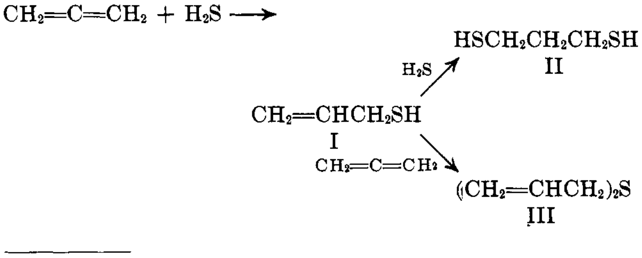


Figure 1.—Gas chromatogram of a crude adduct mixture from reactions of excess hydrogen sulfide with allene.

addition of hydrogen sulfide to mono- and diolefins,[5-8] chlorinated[3,9] and fluorinated[10] olefins, vinyl[11] and allyl[3] ethers, and allylamines.[12] Quite recently this reaction has been extended to substituted acetylenes[13] and it was shown that it followed the same pattern as the corresponding free-radical additions of thiols to acetylenes do.[14] However, similar reactions with allene remained heretofore unexamined.

As established by previous work in this laboratory[15] and by an independent investigation of Jacobs and Illingworth,[16] thiols can be selectively added to the terminal positions of allene. Assuming a similar reaction course for the addition of hydrogen sulfide to allene, this should open a direct synthetic route to such difunctional compounds as 3-propenethiol (I), 1,3-propanedithiol (II), and diallylsulfide (III). In the following, we report the results of such a study.



Results and Discussion

Allene was treated with hydrogen sulfide in the liquid phase between −70 and −80°. A combination of 2,2′-azobisisobutyronitrile (AIBN) or *t*-butyl hydroperoxide and ultraviolet light irradiation initiated the reactions effectively (Table I). However, in order to keep the reaction free from any by-products that could arise from decomposition of an added initiator, some reactions were also carried out with ultraviolet light irradiation alone. Effective stirring of the reaction mixture had a pronounced influence on the reaction rate, particularly when hydrogen sulfide was used in a large excess over allene.

The crude adduct mixtures were examined by a combination of gas–liquid chromatography and time-of-flight mass spectrometric analysis[17] (g.l.c./t.o.f., Table II). This procedure allowed us to obtain the retention time, the molecular weight, and a typical mass spectrum of each individual component as well as a quantitative evaluation of the crude adduct mixture in one run. After this preliminary analysis, the peaks in the gas chromatograms were further identified by the admixture of authentic compounds to the crude reaction products. The g.l.c. results were supported by semiquantitative n.m.r. analyses, based on the relative areas of signals which were characteristic of the individual components and which did not interfere with each other in the spectra of the reaction mixtures.

The addition of excess hydrogen sulfide to allene produced 1,3-propanedithiol (II) and 3-propenethiol (I) as the major reaction products, comprising 90–95% of the total reaction mixture (Table I, Figure 1).[18] In the initial stages of the reaction the two compounds were present in approximately equimolar ratios while, after prolonged reaction times, the ratio of 1,3-propanedithiol increased at the expense of that of 3-propenethiol.

Trimethylene disulfide (IV) was consistently found as a by-product in the analysis of the adduct mixtures. However, the combined g.l.c./t.o.f. method always gave higher values for IV than ordinary g.l.c. analysis did. G.l.c. analysis of a synthetic blend of II and IV[19] established that IV has a longer retention time than II, and that the two compounds can be readily separated from each other. Nevertheless, g.l.c./t.o.f. analysis showed that the material eluted at the retention time of II contained considerable amounts of IV.

We rationalized this discrepancy by assuming that the amount of trimethylenedisulfide which showed up as a separate peak in the gas chromatogram (amount shown in Table I) either was present in the original adduct mixture or it was formed in the injection block of the chromatograph before the mixture entered the

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(18) For some reactions, commercial allene, containing 2–5% of 2-chloropropene, was used. In these cases the amount of 2-chloropropanethiol formed was subtracted from the total reaction mixture and the relative amounts of the products derived from allene were recalculated in order to make the results comparable with those obtained from hydrogen sulfide addition to pure allene.

(19) Trimethylene disulfide has been reported to be an oil which readily di- and polymerizes [J. A. Barltrop, P. M. Hayes and M. Calvin, *J. Am. Chem. Soc.*, **76**, 4348 (1954), and literature cited there]. Our reference sample had the properties of the reported "dimer"; however, its g.l.c./t.o.f. analysis afforded a parent peak of 106, corresponding to the molecular weight of the monomer. Since the molecular weight had no bearing on our problem, we did not examine in which phase of the analytical procedure (*i.e.*, in the gas chromatogram or in the heated connecting line) monomer formation occurred.

TABLE I

ADDITION OF EXCESS AND EQUIMOLAR AMOUNTS OF HYDROGEN SULFIDE TO ALLENE

Hydrogen sulfide–allene, mole	Catalyst	Reaction time	Conversion, %	Relative amounts of liquid components in the adduct mixtures, mole %						
				$CH_2{=}CHCH_2SH$	$HS(CH_2)_3SH$	$(CH_2{=}CHCH_2)_2S$		$CH_2{=}CHCH_2S(CH_2)_3SH$	$HS(CH_2)_3S(CH_2)_3SH$	$HSCH_2CH(CH_3)SH$[a]
13	Ultraviolet	24 hr.	32[b]	21.8	72.5	0.2	4.0	1.2	0.2	. . .
10	Ultraviolet–*t*-BuOOH	5 days[c]	57[d]	20.6	69.0	. . .	6.9	0.9	2.6	. . .
10	Ultraviolet–AIBN	5 hr.	32[e]	45.6	47.7	. . .	2.0	2.0	0.4	2.2
10	Ultraviolet	5 hr.	21[f]	44.0	50.4	0.2	2.6	1.7	. . .	1.0
7.5	Ultraviolet–*t*-BuOOH	6.5 days[c]	67[g]	17.3	75.2	. . .	5.4	0.8	. . .	1.1
1	Ultraviolet	67 hr.	26[h]	11.2	54.8	1.4	11.6	11.8	9.1	. . .

[a] Represents the amount of center attack occurred on allene. [b] No other by-products detected by g.l.c. or n.m.r. [c] Stirring was not effective. [d] 2-Chloropropanethiol (10.6%) and three higher boiling components, comprising 3.5% together, were also detected by g.l.c. [e] 2-Chloropropanethiol (6.2%) and three higher boiling components, comprising 2% together, were detected. [f] 2-Chloropropanethiol (13.7%) and 1.4% of a higher boiling component were also detected by g.l.c. [g] 2-Chloropropanethiol (11.6%) and 0.6% of a higher boiling component were also detected by g.l.c. [h] Three higher boiling components, comprising 6% together, were also detected by g.l.c. The reaction also produced 11% of a solid, polymeric material.

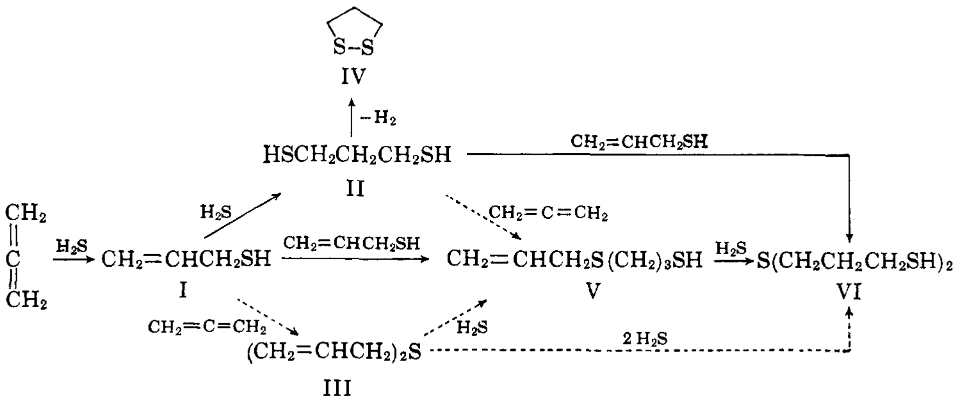
TABLE II

TIME-OF-FLIGHT ANALYSES OF THE CRUDE ADDUCT MIXTURES DERIVED FROM REACTIONS OF ALLENE AND HYDROGEN SULFIDE

Compd.[a]	Mol. wt., calcd.	Characteristic ion masses detected, m/e									
		Molecular ion		Fragment ions, all structures assumed[b]							
H_2S	34	H_2S	34	HS	33	S	32				
$CH_2{=}C{=}CH_2$[c]	40	C_3H_4	40	C_3H_3	39	C_3H_2	38	C_3H_1	37		
$CH_2{=}CHCH_2SH$	74	C_3H_6S	74	$HSCH_2$	47	$CH_2{=}CHCH_2$	41				
$(CH_2{=}CHCH_2)_2S$	114	$C_6H_{10}S$	114	$CH_2{=}CHCH_2S$	73	$CH_2{=}CHCH_2$	41				
$HSCH_2CH_2CH_2SH$	108	$C_3H_8S_2$	108	$CH_2{=}CHCH_2S$	74	$HSCH_2$	47	$CH_2{=}CHCH_2$	41		
$\overline{SCH_2CH_2CH_2S}$	106	$C_3H_6S_2$	106	C_3H_6S	74	S_2	64	CHS	45		
$CH_2{=}CHCH_2SCH_2CH_2CH_2SH$	148	$C_6H_{12}S_2$	148	$HS(CH_2)_3S$	107	$S{=}CHCH_2CH_2SH$	106	$CH_2{=}CHCH_2S$	73	$HSCH_2$ 47	$CH_2{=}CHCH_2$ 41
$CH_2{=}CHCH_2SCH_2CH(CH_3)SH$	148	$C_6H_{12}S_2$	148	$CH_2{=}CHCH_2SCH_2$	87	CH_3CHSH	61				
$HSCH_2CH_2CH_2SCH_2CH_2CH_2SH$	182	$C_6H_{14}S_3$	182	$HS(CH_2)_3S$	107	$HSCH_2$	47				

[a] Arranged in the order of increasing retention times. [b] Observation of the characteristic sulfur doublets due to the sulfur isotopes S^{32} and S^{34} in the fragment ions was of help in assigning these fragment ion structures. [c] Residual allene from the reaction; it was also detected by n.m.r.

SCHEME I



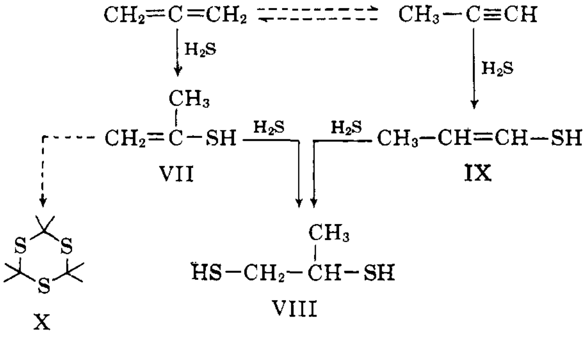
separation column. The amount of IV, which was eluted together with II, on the other hand, was probably formed by dehydrogenation of the dithiol (II) in the chromatography column or in the detector cell. This could be substantiated by a model experiment. Freshly distilled 1,3-propanedithiol produced only one peak in the gas chromatogram while its subsequent t.o.f. analysis again detected both the dithiol II and the disulfide IV in the eluted product.

It may be inferred from this that conversion of 1,3-propanedithiol to its corresponding disulfide is not a significant side reaction under the prevailing free-radical conditions.

Other by-products in the reaction of excess hydrogen sulfide with allene were allyl(3-mercapto propyl) sulfide (V) and bis(3-mercapto propyl) sulfide (VI). Their possible modes of formation are shown in the general reaction scheme, Scheme I, the most likely ones being indicated by solid arrows.

Less than 1% of diallyl sulfide (III) was present in the crude reaction mixtures. Of course some of it may theoretically be masked by subsequent reactions with hydrogen sulfide to form V and VI, as we have shown by independent experiments. However, in the allene–hydrogen sulfide addition reaction, V and VI were probably mainly derived from 3-propenethiol (I) and 1,3-propanedithiol (II) which both were present in rather high concentrations. At any rate, the over-all maximum yield of III, V, and VI places an upper limit of less than 5% to the formation of diallyl sulfide.

All of the compounds I–VI were derived from an initial terminal attack of the sulfhydryl radicals on allene. The corresponding center-attack reaction apparently was quite insignificant. Only 1 to 2% of a compound having a retention time identical with that of authentic 1,2-propanedithiol (VIII) was detected in the gas chromatogram. This compound could theoretically arise either *via* a direct center attack on allene or *via* isomerization of allene to methylacetylene and subsequent diaddition of hydrogen sulfide.[13]



Since it had been reported previously that no isomerization could be detected during the free-radical addition of thiols[15,16] and hydrogen bromide[1] to allene, we believe that VIII probably arose *via* a direct center addition to allene. At any rate, the low occurrence of VIII places an upper limit of approximately 2% for a center attack of hydrogen sulfide on allene. Isomerization of the intermediate vinylic monoadduct VII to trithioacetone (X) apparently did not occur, since none of the peaks in the gas chromatograms of the adduct mixtures lined up with that of authentic trithioacetone.

Vacuum distillation of a typical adduct mixture produced approximately 90% of liquid fractions and 10% of a nondistillable, viscous, yellow residue. On the basis of its infrared and n.m.r. spectrum, this residue consisted mainly of a mixture of thiol-terminated oligomers and/or polymers of the general type $H(-SCH_2CH_2CH_2-)_nSH$, probably formed by the same types of reactions that led to VI. Whether these side reactions occurred during the addition of hydrogen sulfide to allene or during the distillation could not be determined.

In conclusion, it has been shown that the free-radical addition of excess hydrogen sulfide to allene occurs with high selectivity (>95%) at the terminal positions of allene and produces 1,3-propanedithiol in better yields than previously reported methods did.[20-23]

Reaction of equimolar amounts of hydrogen sulfide and allene produced essentially the same liquid components although in a different ratio, as the addition of excess hydrogen sulfide to allene did (Table I). The reaction could not be optimized towards the formation of 3-propenethiol (I), although this might have been anticipated on the basis of the stoichiometry. 1,3-Propanedithiol was still the main product; however, more of the dimeric thiol V was formed than in cases where excess hydrogen sulfide was used. Approximately 10% of a polymeric material was also formed in these reactions.

The amount of diallyl sulfide (III) formed was again low. This is interesting since the preparation of thiols by the free-radical addition of hydrogen sulfide to olefins is often complicated by the concurrent formation of dialkyl sulfides, unless the reaction is carried out with an

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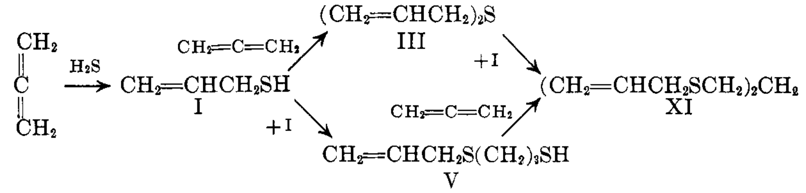
Scheme II



excess of hydrogen sulfide.[24] It may be inferred from these results that 3-propenethiol shows a higher reactivity towards hydrogen sulfide to form 1,3-propanedithiol and toward itself to yield V, than it does toward allene. In view of this, the selective preparation of diallyl sulfide III from hydrogen sulfide and allene in the liquid phase does not seem to be feasible.

Reaction of excess allene with hydrogen sulfide indeed yielded only 25 to 30% of diallyl sulfide. 3-Propenethiol (I), its dimer (V), and 1,3-bis(allyl mercapto)propane (XI) were always present as the major byproducts. Together these four compounds accounted for 70–90% of the adduct mixture.

The possible modes of formation of these products are shown in Scheme II. It can be seen from this scheme that dimerization of the intermediate 3-propenethiol and subsequent reactions of diallyl sulfide draw heavily on the yield of III and probably prevent its effective synthesis from allene and hydrogen sulfide in a liquid phase batch reaction.

The remainder of the adduct mixtures could not be completely analyzed. 1,3-Propanedithiol and its corresponding disulfide IV were detected in some of the reactions along with higher boiling components, possibly telomers.

Owing to the incomplete analysis of the adduct mixtures only a lower limit of approximately 70–90% (*i.e.*, amount of I, III, V, and XI present) can be set for the selectivity of the reaction towards a terminal attack. We have demonstrated that 1,2-bis(allylmercapto)propane, isomeric with XI, was not present in the reaction mixture, while time-of-flight analysis (Table II) indicated that one of the higher boiling components was the thiol $CH_2=CHCH_2SCH_2CH_2(CH_3)SH$, which would be a product derived from a center attack on allene. However, its presence in the reaction mixture could not be unequivocally proven.

In summary, the present work has established that hydrogen sulfide adds with high selectivity to the terminal positions of allene as thiols[15,16] and trifluoroiodomethane[25] do, thus leaving hydrogen bromide the only addend so far that prefers a center attack on allene under similar conditions.[1]

Experimental

Materials.—Allene from Matheson contained between 2 and 5% of 2-chloropropene. For some of the reactions allene of 99.5+% purity was used. Hydrogen sulfide from Matheson was of C.P. grade. The reference samples 3-propenethiol, 1,2-propanedithiol, 1,3-propanedithiol, and diallyl sulfide from Wateree Chemical Co. were all redistilled before use.

Method of Analyses. Gas–Liquid Chromatography.—Allene was analyzed on the F and M Model 500 gas chromatograph, using a 10-ft. column, packed with 20% dimethylsulfolane on Chromosorb P. The column temperature was maintained at 30°.

The crude adduct mixtures were separated on a F and M Model 500 linear programmed temperature gas chromatograph with a 3-ft., 0.25-in.-o.d. column. The column packing consisted of 3% Dowfax 9N40 (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, 50°; finished column temperature, 225°; sample size, 1.5 μl.

Gas–Liquid Chromatography/Time-of-Flight Mass Spectroscopy Analysis (g.l.c./t.o.f.).—After the conditions for effective separation had been established (*vide supra*) the crude adduct mixtures were submitted to a combined g.l.c./t.o.f. analysis.[17] A gas chromatograph (type, column, and conditions used were the same as above) was ganged to a time-of-flight mass spectrometer. The effluent from the gas chromatograph was metered into the spectrometer through a connecting line and a metering valve (Vari-vac Model VV-500C, manufactured by Vactronic Laboratory Equipment, Inc.) heated to 200°.

The spectrometer was a Bendix Instrument, Type 12-101, which has been modified so as to include a 1.66-m. flight tube, multigate recording, and improved electron-beam focusing. A multichannel Minneapolis–Honeywell Visi-corder was used to record the mass spectral data obtained.

N.m.r. and Infrared Spectra.—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 Hydrogen Sulfide to Allene.—All the additions were carried out according to the same general procedure. Differences existed only in the relative reactant ratios, the sample sizes, the type of stirring (magnetic or vigorous mechanical stirring), and the type of initiation used. The following is a typical example. Allene (11.2 g., 0.28 mole) and 128 g. (3.8 mole) of hydrogen sulfide were condensed into a 200-ml. cylindrical quartz tube, equipped with an effective, air-tight, mechanical stirrer. The tube was placed into a Freon bath which was kept between −70 and −80° by means of a low-temperature circulating unit (from Lawler Electrical Manufacturing Co., Bayonne, N. J.). A 100-w. Hanau ultraviolet immersion lamp (from G. W. Gates and Co., Inc., Franklin Square, Long Island, N. Y.) was placed about 5 cm. from the reaction tube. The lamp was surrounded by a quartz mantle in order to insulate it against excessive cooling.

After 24 hr. of continuous irradiation and stirring the reaction was stopped. The unchanged hydrogen sulfide and allene were carefully removed by allowing the mixture to warm gradually to room temperature. The evaporating gases were passed through a trap at −20° to withhold volatile products other than H_2S or allene. The outlet of this trap was connected to a drying tower, filled with anhydrous $CaSO_4$ to prevent moisture from entering into the cold adduct mixture. A pale yellow liquid (11.4 g.) remained in the reaction tube after all the excess reactants were removed. This adduct mixture was analyzed as such by g.l.c., t.o.f., n.m.r., and infrared spectroscopy.

On standing in the refrigerator for several days approximately 30 mg. of a white solid precipitated from the crude adduct mixture. This solid did not show any functionality in its infrared spectrum beyond C–H stretching (3.43 μ) and deformation (7.11 μ) bands and two strong peaks in the fingerprint region (at 8.4 and 8.95 μ, respectively). Formation of amorphous solids from polymethylene mercaptan solutions have been observed previously and have been attributed to oxidation reactions, leading to "disulfides."[26]

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[24] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 315.

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

[26] N. B. Tucker and E. E. Reid, *J. Am. Chem. Soc.*, **55**, 775 (1933).

Distillation of 3.6 g. of the crude mixture afforded the following fractions: (1) b.p. 25° (30 mm.), 0.15 g.; (2) b.p. 24° (0.15 mm.), 0.8 g.; (3) 24–26° (0.15 mm.), 1.7 g.; (4) 26° (0.15 mm.), 0.5 g.; and residue, 0.4 g., viscous oil.

The fractions were characterized by g.l.c. and n.m.r. spectroscopy. Fraction 1 consisted of 70% of 3-propenethiol and 30% of its dimer V; fraction 2 consisted of 87% of 1,3-propanedithiol and 13% of 3-propenethiol; fraction 4 consisted mainly of 1,3-propanedithiol; the residue showed a S–H band at 3.94 μ in the infrared. The n.m.r. spectrum in CS_2 showed the following characteristic signals: multiplet, δ = 1.88 (center methylene group of $—CH_2CH_2CH_2—$), and multiplet, 2.78 p.p.m. (methylene groups attached to sulfur in $S—CH_2CH_2CH_2—S$).

Preparation of Trimethylene Disulfide "Dimer."[19]—To a solution of 10.8 g. (0.1 mole) of 1,3-propanedithiol, and 100 mg. (0.0013 mole) of *t*-butyl amine in 50 ml. of methanol, 10 g. (0.11 mole) of *t*-butyl hydroperoxide was added within 30 min. The mixture was stirred overnight and the white precipitate (9.6 g., 90%) was filtered off. Recrystallization from benzene yielded a compound, melting at 77–78° (lit.[23] m.p. 77–78°). N.m.r. (in CS_2) gave a multiplet, δ = 2.09, and a triplet, 2.77 p.p.m.

Addition of Hydrogen Sulfide to Diallyl Sulfide.—A mixture of 10.7 g. (0.983 mole) of diallyl sulfide, 17 g. (0.5 mole) of hydrogen sulfide, and 100 mg. (0.006 mole) AIBN was irradiated by ultraviolet light at −70° for 41 hr. When the unchanged hydrogen sulfide and diallyl sulfide were removed, 12.3 g. of a pale yellow liquid remained, consisting of 60% of V, 31% of VII, and three minor, unidentified components (according to g.l.c.). Distillation of this mixture afforded the following fractions: (1) b.p. ~25° (1 mm.), 1.3 g.; (2) b.p. 25–47° (0.3 mm.), 0.8 g.; (3) b.p. 44–46° (0.3 mm.), 3.2 g.; (4) b.p. 46–96° (0.3 mm.), 1.8 g.; (5) b.p. 96–98° (0.3 mm.), 1.7 g.; and (6) b.p. 98–102° (0.3 mm.), 0.3 g. Fraction 3 was the 3-propenethiol dimer V. N.m.r. (neat) gave a triplet, δ = 1.52 (J = 8 c.p.s.) (S—H); multiplet, 1.70 (J = 6.5 c.p.s.) ($S–CCH_2C–S$); multiplet, 2.60 ($—S—CH_2—C—CH_2S—$); doublet, 3.11 (J = 6.5 c.p.s.) (CH_2 of $S—CH_2—CH=$); multiplet, 5.08 (J = 9, 17, and 6.5 c.p.s.) ($=CH_2$); and a multiplet, 5.83 p.p.m. ($=CH—$).

Anal. Calcd. for $C_6H_{12}S_2$: C, 48.59; H, 8.16; S, 43.25. Found: C, 48.61; H, 8.39; S, 43.28.

Fraction 5 was the dithiol VII (lit.[21] b.p. 138–140° at 6 mm.). N.m.r. (in $CDCl_3$) gave a triplet, δ = 1.49 (J = 8 c.p.s.) (S—H); multiplet, 1.86 (J = 6.5 c.p.s.) ($S—C—CH_2—C—S$); and a multiplet, 2.66 p.p.m. ($S—CH_2—C—CH_2S$).

Trithioacetone (**X**) was prepared in 50% yield,[27] b.p. 59–61° (0.25 mm.). N.m.r. (neat) gave a singlet, δ = 1.70 p.p.m.

Preparation of 1,3-Bis(allylmercapto)propane (**XI**).—Diallyl sulfide (34.2 g., 0.33 mole) and 7.4 g. of freshly distilled 3-propenethiol, containing 25% of its dimer V, were allowed to react in a quartz flask in the presence of 90 mg. of *t*-butyl hydroperoxide and ultraviolet light irradiation at ambient temperatures. After 14 hr. the reaction was discontinued and the crude adduct mixture was fractionated to yield 11% of XI, boiling at 73–75° (0.2 mm.). N.m.r. (in CCl_4) gave a multiplet, δ = 1.78 (J = 7 c.p.s.) ($S—C—CH_2—C—S$); triplet, 2.50 ($S—CH_2CCH_2—S$); doublet, 3.09 (CH_2 of $SCH_2CH=CH_2$); multiplet, 5.08 (J = 7 c.p.s.) ($=CH_2$); and a multiplet, 5.83 p.p.m. (J = 9, 17, and 7 c.p.s.) ($—CH=$).

Anal. Calcd. for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 56.87; H, 8.55; S, 34.14.

Preparation of 2-Chloropropanethiol.—A mixture of 7.6 g. (0.1 mole) of 2-chloropropene, 6.8 g. (0.2 mole) of hydrogen sulfide, and 90 mg. (0.001 mole) of *t*-butyl hydroperoxide was irradiated at −70° for 36 hr. The reaction produced 8.7 g. of a dark mobile liquid. Distillation of 6.2 g. of the latter afforded 2 g. of 2-chloropropanethiol, b.p. 41–42° (18 mm.) (lit.[28] b.p. 125–125.5° at 764 mm.). N.m.r. (neat) gave a doublet, δ = 1.59 (J = 7 c.p.s.) (CH_3); multiplet, 2.83 (CH_2); and a multiplet, 4.13 p.p.m. (CH).

Preparation of 1,2-Bis(allylmercapto)propane.—To a solution of 21.6 g. (0.4 mole) of sodium methoxide in 100 ml. of methanol 21.6 g. (0.2 mole) of 1,2-propenedithiol was added under stirring. Then 48.4 g. (0.4 mole) of allylbromide was added and the mixture was kept at reflux for 2 hr. Stirring was continued without heating overnight. Upon addition of twice its volume of water the reaction mixture separated in two layers. The upper layer was separated, washed with water, and dried over anhydrous sodium sulfate. Distillation afforded 27 g. (72%) of 1,2-bis-(allylmercapto)propane, b.p. 69–73° (0.25 mm.). N.m.r. (neat) gave a doublet, δ = 1.29 (J = 6.5 c.p.s.) (CH_3); doublet, 2.17 (J = 9 c.p.s.) (CH_2 of $—CH—CH_2S$); multiplet, 2.58 (CH of $—CH—CH_2$); doublets at 3.12 and 3.18 (J = 6.5 c.p.s.) (CH_2 of $S—CH_2—CH=CH_2$); multiplets at 4.09 and 5.10 ($=CH_2$); and multiplets at 5.88 and 5.90 p.p.m. ($—CH=$).

Anal. Calcd. for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.41; H, 8.49; S, 34.13.

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7- and 12-Thienylbenz[*a*]anthracenes[1]

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The title compounds were prepared and their properties as well as mode of formation were studied. Analysis of the spectral patterns have also been made.

Much work has been done in recent years on the synthesis of polynuclear aromatic compounds containing sulfur. A notable example is the paper of Tilak[3] concerning 15 years of work on carcinogenesis by thiophene isosteres of polycyclic hydrocarbons. Because of our long interest in benz[*a*]anthracene chemistry,[4] and because of the obvious importance of the title compounds, we sought to prepare them by a simple extension of a known reaction route.[4] The problem turned out to be far from a simple extension of known reactions and several interesting observations came to light.

Two methods may be considered as practical approaches to the synthesis of the ketones, **9–12**, that are cyclized to the final aromatic products, **13–16**. Method A (see Chart I) offers the advantage that the aryl nitriles used may be easily prepared by a Rosenmund–von Braun reaction on the appropriate aryl chlorides which are easier to obtain than the aryl bromides which

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(2) Taken from the Ph.D. Theses of S. G. Quo and P. Polss presented to the Virginia Polytechnic Institute in 1959 and 1962, respectively.

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(4) For a recent example of syntheses in this area, see F. A. Vingiello, E. B. Ellerbe, T. J. Delia, and J. Yanez, *J. Med. Chem.*, **7**, 121 (1964).