Allene Chemistry. IV. Unsymmetrical Terminal Thiol–Allene Diadducts. The Effect of Allylic Reversal[1]

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The synthesis of unsymmetrical 1,3-bis(substituted mercapto)propanes by the sequential radical diaddition of two different thiols to allene was studied. The major by-products were found to be the corresponding two symmetrical thiol diadducts of allene. These arise by an allylic scission mechanism during the reversible addition of thiyl radicals to the allyl sulfide monoadduct intermediates. As predicted by the proposed mechanism, by-product formation can be suppressed by adding an excess of the thiol of high hydrogen-donating ability to the allyl sulfide monoadduct in the critical second step of the addition sequence. An examination of the literature shows that similar allylic reversal mechanisms satisfactorily explain several reactions where direct radical displacements have been proposed.

In preceding papers of this series[2] it was shown that thiols can be added to allene in a free-radical manner to yield symmetrical 1,3-bis(substituted thio)propanes.

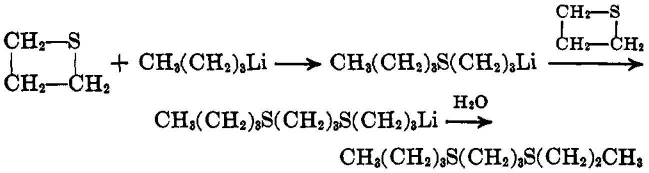
$$H_2C{=}C{=}CH_2 \xrightarrow{RSH} RSCH_2CH{=}CH_2 \xrightarrow{RSH} RSCH_2CH_2CH_2SR$$

These reactions could be carried out in high yields since thiyl radicals selectively attack the terminal carbon atoms of the allene molecule. The present paper describes the extension of this previous work to the synthesis of unsymmetrical 1,3-bis(substituted thio)propane, mixed thiol–allene diadducts by the sequential addition of two different thiols to allene.

$$H_2C{=}C{=}CH_2 \xrightarrow{RSH} RSCH_2CH{=}CH_2 \xrightarrow{R'SH} RSCH_2CH_2CH_2SR'$$

No general method for the synthesis of such unsymmetrical compounds is known. Only two compounds of this type have been described previously in the literature. The first, 1-benzylthio-3-ethylthiopropane, was obtained in 43% yield by Rothstein[3] *via* the laborious ionic sequence shown. The second compound, 1-*n*-butylthio-3-*n*-propylthiopropane, was isolated by Bordwell and co-workers[4] from the reaction of thiacyclobutane with *n*-butyl lithium.

$$ClCH_2CH_2CH_2OH \xrightarrow{C_2H_5SNa} C_2H_5SCH_2CH_2CH_2OH \xrightarrow{SOCl_2} \longrightarrow C_2H_5SCH_2CH_2CH_2Cl \xrightarrow{PhCH_2SNa} C_2H_5SCH_2CH_2CH_2SCH_2Ph$$



$$\begin{matrix} CH_2{-}S \\ | \quad\; | \\ CH_2{-}CH_2 \end{matrix} + CH_3(CH_2)_3Li \longrightarrow CH_3(CH_2)_3S(CH_2)_3Li \xrightarrow{\begin{matrix} CH_2{-}S \\ | \quad\; | \\ CH_2{-}CH_2 \end{matrix}} CH_3(CH_2)_3S(CH_2)_3S(CH_2)_3Li \xrightarrow{H_2O} CH_3(CH_2)_3S(CH_2)_3S(CH_2)_2CH_3$$

Other routes to unsymmetrical 1,3-bis(substituted thio)propanes using selective displacement reactions of symmetrical 1,3-disubstituted propanes are also conceivable. However, such reactions would be expected to require a large excess of the difunctional reactant and to lead to by-product formation.[4] In contrast,

$$\begin{tikzcd}
NaS(CH_2)_3SNa \arrow[r, "RCl"] & RS(CH_2)_3SNa \arrow[dr, "ClR'"] & \\
& & RS(CH_2)_3SR' \\
Cl(CH_2)_3Cl \arrow[r, "RSNa"] & RS(CH_2)_3Cl \arrow[ur, "NaSR'"'] &
\end{tikzcd}$$

sequential thiol additions to allene seemed to offer a simple route and, therefore, appeared worthy of study.

Since we had shown previously that a variety of thiols can be added to allene to form allyl sulfides with high selectivity,[2] it was only necessary for the present purpose to study the reaction of various thiols with allyl sulfides. In this study, therefore, a variety of simple thiols was added to different allyl sulfides at 15–20° without solvent under ultraviolet light irradiation. The reaction mixtures were analyzed by gas–liquid partition chromatography (g.l.p.c.). Nuclear magnetic resonance (n.m.r.) spectroscopy was used for semiquantitative analysis and for identification.

Results

The addition of thiols to equimolar amounts of allyl sulfides with ultraviolet irradiation occurs readily. The reaction of simple aliphatic and aromatic thiols at 17° is essentially complete in 9.5 hr. (Table I). In the absence of ultraviolet light or peroxide, the reaction is very slow; g.l.p.c. analyses of reaction mixtures, stored several days at ambient temperatures, showed no evidence of product formation. These observations confirm the free-radical nature of these reactions.

G.l.p.c. and n.m.r. analysis of the reaction mixtures indicated that, in general, these additions led to complex mixtures of products. To identify the components, the possible products were synthesized independently. The desired unsymmetrical 1,3-bis(substituted thio)propanes were prepared by the reaction sequence shown. The symmetrical trimethylene bis-sulfide by-products were obtained from 1,3-dibromopropane with the corresponding sodium mercaptides using the general method of Mann and Purdie.[5]

$$ClCH_2CH{=}CH_2 \xrightarrow[\text{ultra-violet}]{RSH} RSCH_2CH_2CH_2Cl \xrightarrow{R'SNa} RSCH_2CH_2CH_2SR'$$

$$BrCH_2CH_2CH_2Br \xrightarrow{2RSNa} RSCH_2CH_2CH_2SR$$

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[1] Presented before the Division of Petroleum Chemistry, 149th National Meeting at the American Chemical Society, Detroit, Mich., April 1965.

[2] K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1964).

[3] E. Rothstein, *J. Chem. Soc.*, 309 (1937).

[4] F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1083 (1954).

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

TABLE I

ADDITION OF EQUIMOLAR AMOUNTS OF THIOLS TO ALLYL SULFIDES

Reactants[a] Compounds used Allyl sulfide $R'S—CH_2CH{=}CH_2$	Mercaptan RSH	In the reaction mixture,[b] mole % $R'SCH_2CH{=}CH_2$	RSH	Product distribution, mole %[b] $R'S—(CH_2)_3—SR$	$R'S—(CH_2)_3—SR'$	$RS—(CH_2)_3—SR$	$RSCH_2CH{=}CH_2$	Unidentified[c]
Ethyl	Phenyl	2.6[d]	9[e]	93	2	2	3	2
Phenyl	Ethyl	...[f]	27	6	32	0	63	0
Ethyl	*n*-Propyl	4	Trace	61	18	15	5	5
n-Propyl	Ethyl	2	Trace	62	19	14	5	4
Ethyl	Isopropyl	7	Trace	55	20	15	10	1
Isopropyl	Ethyl	0	Trace	74	16	11	0	4
Ethyl	*t*-Butyl	6	11	56	22	22	1	4
t-Butyl	Ethyl	2	5	71	13	7	10	3
Phenyl	Benzyl	35	21	17	42	9	33	3
Benzyl	Phenyl	22	20	89	4	2	5	0

[a] In general, 0.05 mole of each reactant was used. [b] Determinations were made by g.l.p.c. except where stated otherwise. [c] As per cent area of all the g.l.p.c. peaks. [d] N.m.r. gives 2.6%. [e] N.m.r. gives 2%. [f] N.m.r. gives 7%.

TABLE II

PHYSICAL AND ANALYTICAL DATA OF 1,3-BIS(SUBSTITUTED THIO)PROPANES

Formula Structural	Empirical	B.p., °C. (mm.)	Calcd., % C	H	S	Found, % C	H	S
$C_2H_5S(CH_2)_3SPh$	$C_{11}H_{16}S_2$	120–121 (1.2)	62.25	7.60	30.15	62.56	7.63	29.78
$C_2H_5S(CH_2)_3S(CH_2)_2CH_3$	$C_8H_{18}S_2$	72–73 (0.25)	53.91	10.18	35.91	53.81	10.05	35.31
$C_2H_5S(CH_2)_3SCH(CH_3)_2$	$C_8H_{18}S_2$	58–59 (0.25)	53.91	10.18	35.91	53.60	9.95	36.14
$C_2H_5S(CH_2)_3SC(CH_3)_3$	$C_9H_{20}S_2$	68–71 (0.65)	56.22	10.49	33.29	56.26	10.55	33.49
$C_2H_5S(CH_2)_3SCH_2Ph$	$C_{12}H_{18}S_2$	130–132 (0.05)	63.70	8.62	28.29	63.64	8.06	28.29
$PhCH_2S(CH_2)_3SPh$	$C_{16}H_{18}S_2$	165–167 (0.25)	70.05	6.61	23.33	70.07	6.64	23.22
$CH_3(CH_2)_2S(CH_2)_3S(CH_2)_2CH_3$	$C_9H_{20}S_2$	84–85 (1.2)	56.22	10.49	33.29	56.27	10.50	32.71
$(CH_3)_2CHS(CH_2)_3SCH(CH_3)_2$	$C_9H_{20}S_2$	87–88 (3.0)	56.22	10.49	33.29	56.51	11.05	32.16

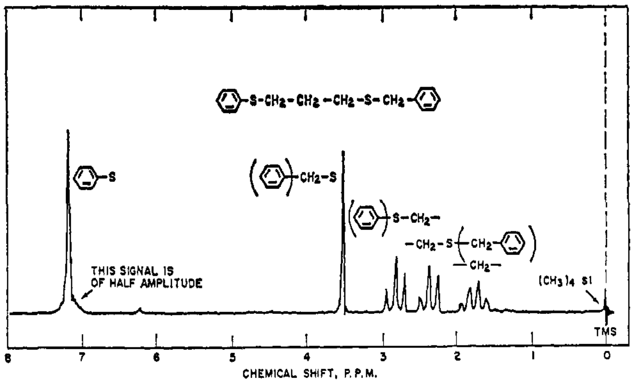
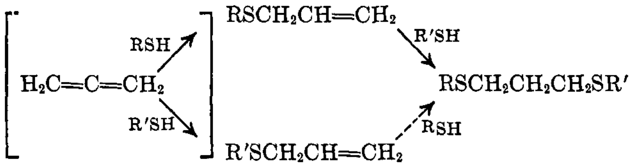


Figure 1.—Proton magnetic resonance spectrum of 1-benzylthio-3-phenylthiopropane.

Some physical and analytical data of these products are given in Table II.

The n.m.r. parameters of the unsymmetrical 1,3-bis(substituted thio)propanes are listed in Table III. As shown by the table, the chemical shift values of the three methylene groups are very similar to those of the symmetrical compounds[1,2] whenever the two substituents are either both aliphatic or aromatic. However, when one of the substituents is aliphatic and the other aromatic, the two methylene groups α to the sulfur exhibit significantly different chemical shifts. As expected, the inductive effect of the aromatic group caused a considerable paramagnetic shift of the methylene hydrogens next to its sulfur resulting in a higher chemical shift. This difference in the α-methylene chemical shifts is illustrated by Figure 1 and allows a rapid check of the purity of such unsymmetrical bis-sulfides, and, furthermore, a semiquantitative determination in admixtures with either one of the corresponding bis-sulfides.

The reaction of different thiols with equimolar amounts of various allyl sulfides results in widely different reaction selectivities for the desired unsymmetrical bis-sulfides (17–93%). In general, the more highly divergent in structure the thiyl group of the thiol and that of the allyl sulfide, the greater was the difference in selectivity between the two superficially equivalent synthetic sequences. Thus the addition of



benzenethiol to allyl ethyl sulfide occurred with a selectivity to the mixed diadduct of 93%, while the

$$C_2H_5SCH_2CH{=}CH_2 \xrightarrow{PhSH} C_2H_5SCH_2CH_2CH_2SPh$$

addition of ethanethiol to allyl phenyl sulfide gave only 5% selectivity (Table I). The major products of the latter reaction were allyl ethyl sulfide (63%) and diphenyl trimethylene bis-sulfide (31%). When the two thiyl groups were both aliphatic, and therefore more similar, the sequence of addition had less of an effect on the over-all selectivity to the unsymmetrical diadducts. In all such cases, moderate selectivities (52–80%) were observed. The principal by-products were again the corresponding allyl sulfides and symmetrical trimethylene bis-sulfides.

The effect of changing reactant ratios was also examined in the ethyl allyl sulfide–benzenethiol system. The data in Table IV show that an increasing relative concentration of the thiol addend results in a higher selectivity. A fivefold molar excess of the thiol resulted in the exclusive formation of the desired un-

TABLE III

CHARACTERISTIC PROTON N.M.R. PARAMETERS OF 1,3-BIS(SUBSTITUTED THIO)PROPANES[a]

Structure of $RSCH_2CH_2CH_2SR'$	-RS-			$-CH_2-$	$-CH_2-$	$-CH_2-$	-SR'-		
$CH_3CH_2S(CH_2)_3SPh$		1.20[b] t	2.5 m	2.58 m	1.85[b] p	2.98[b] t	7.29 m		
$CH_3CH_2S(CH_2)_3S(CH_2)_2CH_3$		1.22[c] t	2.58 m	2.58 m	1.78[d] p	2.58 m	2.58 m	1.54 m	0.97[c] t
$CH_3CH_2S(CH_2)_3SCH(CH_3)_2$		1.21[c] t	2.52 m	2.52 m	1.78[d] p	2.52 m	2.75[c] m	1.22[c] d	
$CH_3CH_2S(CH_2)_3SC(CH_3)_3$		1.23[b] t	2.52 m	2.52 m	1.78[d] p	2.52 m	1.29 s		
$CH_3CH_2S(CH_2)_3SCH_2Ph$		1.16[b] t	2.39 m	2.39 m	1.69[c] p	2.39 m	3.59 s	7.21 s	
$PhCH_2S(CH_2)_3SPh$		7.15[d] m	3.52 s	2.36[d] m	1.81[d] p	2.81[d] m	7.15 m		
$CH_3CH_2CH_2S(CH_2)_3SCH_2CH_2CH_3$	0.96[d] t	1.53 m	2.54[c] t	2.54[c] t	1.78[d] p	2.54[c] t	2.54[c] m	1.53 m	0.96[d] t
$(CH_3)_2CHS(CH_2)_3SCH(CH_3)_2$		1.26[d] d	2.78[d] m	2.56[c] t	1.82[c] p	2.56[c] t	2.78[d] m	1.26[e] d	

[a] Chemical shifts of structural units, p.p.m. downfield from tetramethylsilane internal reference in carbon tetrachloride solution: s, singlet; d, doublet; t, triplet; q, quadruplet; p, pentuplet; m, multiplet. [b] J = 7.5 c.p.s. [c] J = 7.0 c.p.s. [d] J = 6.5 c.p.s. [e] J = 6.0 c.p.s.

TABLE IV

EFFECT OF RELATIVE REACTANT CONCENTRATION ON THE ADDITION OF BENZENETHIOL TO ETHYL ALLYL SULFIDE[a]

Thiol–allyl sulfide ratio	Reactants				Products, mole %[b]			
	$C_2H_5SCH_2CH{=}CH_2$		PhSH					
	mmole	Conversion[c]	mmole	Conversion[c]	$C_2H_5S(CH_2)_3SPh$	$C_2H_5S(CH_2)_3SC_2H_5$	$PhS(CH_2)_3SPh$	$PhSCH_2CH{=}CH_2$
0.2	50	...	10	100	77	11	0	12
0.5	20	47	10	79	88	7	0	5
1.0	50	66	50	70	93	2	2	3
2.0	10	65	20	43	96	1	0	3
5.0	10	100	50	...	100[d]	0	0	0

[a] At 17°C. for 6.5 hr. with ultraviolet irradiation. [b] Determined by g.l.p.c. G.l.p.c. showed up to 2 wt. % unidentified compounds in the reaction mixtures. [c] On the basis of n.m.r. spectra of reaction mixtures. [d] G.l.p.c. showed the presence of 2.5 wt. % of diphenyl disulfide and of 1 wt. % of unidentified compounds in the reaction mixture.

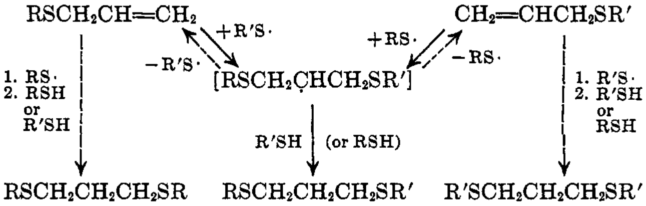
symmetrical diadduct. A high excess of either reactant effected a complete conversion of the other within 6.5 hr.

Discussion

The synthesis of unsymmetrical terminal thiol–allene diadducts by sequential radical-type diaddition of thiols is complicated by side reactions which occur when the second thiol is added to the allyl sulfide monoadduct. We propose that the observed by-products arise *via* the combination of conventional, reversible additions shown in Scheme I.

SCHEME I

PROPOSED MECHANISM OF THIOL ADDITIONS TO ALLYL SULFIDES



Disregarding the commonly accepted reversibility of thiol–olefin free-radical additions, an anti-Markovnikov addition of a thiol to an allyl sulfide would be expected to lead to the desired unsymmetrical 1,3-bis(substituted thio)propane *via* the route indicated by the solid arrows in Scheme I.

Considering now the possible reversible steps denoted by the dashed arrows of the figure, it becomes apparent that the reversal of thiyl-radical addition to an allyl sulfide has not one but two possible courses. The initially formed unsymmetrical diadduct radical intermediate has two sulfide groups in β positions to the carbon radical. Therefore, the radical can be stabilized by homolytic elimination of either of the two thiyl radicals. Scission of the adding thiyl radical merely reconstitutes the original reactants (simple reaction reversal), but elimination of the other thiyl groups leads to a different thiyl radical–allyl sulfide pair (allylic reversal). The net result of this second process is *formally* a "radical displacement." The

$$R'S\cdot + CH_2{=}CH{-}CH_2{-}SR \longrightarrow R'S{-}CH_2{-}CH{=}CH_2 + \cdot SR$$

formation of a second thiyl radical (derived from the original allyl sulfide) and a second allyl sulfide (derived from the starting thiol) ultimately lead to the symmetrical by-products observed in the reactions reported above. Addition of the new thiyl radical to the original allyl sulfide followed by hydrogen abstraction results in a symmetrical trimethylene bis-sulfide having the substituents of the original allyl sulfide as shown by the dotted line on the left side of Scheme I. The addition of the starting thiol to the allyl sulfide resulting by allylic reversal, shown on the right side, yields the other possible symmetrical bis-sulfide with the thiyl substituents of the starting thiol.

This picture of the various reactions occurring agrees not only with the kind but also with the amounts of the various products observed. The desired reaction product (unsymmetrical bistrimethylene sulfide) is obtained from the unsymmetrical bis(substituted thio)propyl radical intermediate by hydrogen abstraction from the original thiol. Its rate of formation, therefore, should be directly proportional to the hydrogen availability of the adding thiol. One measure of the hydrogen-donor ability of thiols is known from the literature in terms of chain-transfer constants.[6-8] A

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(6) F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).

(7) J. L. O'Brien and F. Gornick, *ibid.*, **77**, 4757 (1955).

(8) R. A. Gregg, D. M. Alderman, and F. R. Mayo, *ibid.*, **70**, 3740 (1948).

comparison of selectivities to the unsymmetrical bis-sulfides observed in the addition of various thiols to ethyl allyl sulfide with the chain transfer constants of the thiols[7] (Table V) supports this hypothesis.

TABLE V

SELECTIVITY TO UNSYMMETRICAL BIS-SULFIDE IS DEPENDENT ON HYDROGEN DONOR ABILITY OF THIOL

$$RSH \xrightarrow{C_2H_5SCH_2CH=CH_2} C_2H_5SCH_2CH_2CH_2SR$$

Thiol, reactant with ethyl allyl sulfide		
Structure	Chain transfer constant[a]	Selectivity to unsymmetrical bis-sulfide, %
PhSH	2.7	93
$CH_3CH_2CH_2SH$	~0.66[b]	61
$(CH_3)_2CHSH$	0.38	52
$(CH_3)_3CSH$	0.18	55

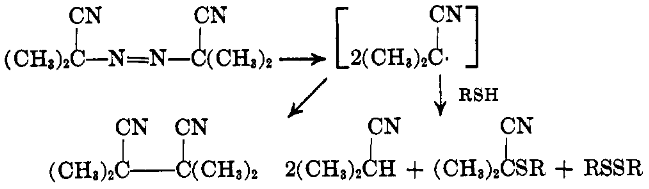
[a] See ref. 7. [b] No chain transfer constants for *n*-propanethiol were available. The constant for *n*-butanethiol, 0.66, should certainly be similar to that of *n*-propanethiol since the molecular weight of primary thiols reportedly has little effect on their chain transfer constants (see ref. 8).

TABLE VI

Thiol		Yield of $(CH_3)_2CHCN$,
Type	Formula	%
Aromatic	PhSH	60
n-Aliphatic	$C_{16}H_{33}SH$	52
Secondary aliphatic	$CH_3(CH_2)_5CH(CH_3)SH$	40
Tertiary aliphatic	$(CH_3)_3CCH_2C(CH_3)_2SH$	32
	No thiol	0

The above correlation between hydrogen-donor ability and chain-transfer constant is qualitatively supported by a study of azobisbutyronitrile in the presence of various types of thiols.[9] Such decompositions led to isopropyl cyanide or bis(2-cyano)isopropyl dimer depending on the reactivity of the thiol hydrogen (Scheme II). As expected, the yield of isopropyl cyanide decreased with decreasing hydrogen reactivity of the thiol (Table VI).

SCHEME II



The large differences between the chain-transfer constants of the aromatic thiol and the aliphatic thiols are matched by large differences between the corresponding selectivities of their reactions with allyl sulfides. As expected, a *n*-alkyl mercaptan shows smaller but significant differences from secondary and tertiary aliphatic thiols. No strict comparison with 2-methyl-2-propanethiol can be made since both it and its products underwent a partial decomposition on the g.l.p.c. column. However, even exact analytical data would not give much support for our hypothesis in view of the possible steric hindrance effect.

The availability of thiol hydrogen for abstraction can be increased simply by increasing the relative concentration of the thiol. As expected this results in increased selectivity as shown by Table V.

An examination of the selectivities observed in the reactions of the same thiol with different allyl sulfides suggests that another important factor in these reactions is the stability of the thiyl radical formed by allylic reversal. There is a decreasing stability of thiyl radicals from aryl through benzyl to alkyl substitution.[10] This effect should result in decreased rates of allylic reversal in the corresponding allyl sulfide–ethanethiol reactions. Less allylic reversal is reflected by a higher selectivity to the unsymmetrical diadduct, as shown in Table VII.

TABLE VII

SELECTIVITY TO UNSYMMETRICAL BIS-SULFIDE IS DEPENDENT ON ALLYL SULFIDE

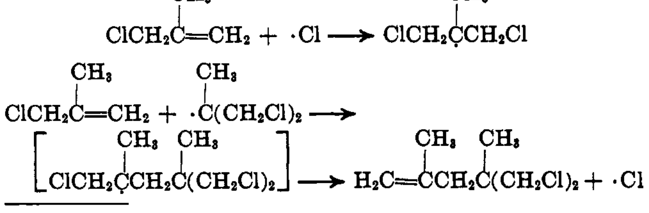
$$RSCH_2CH=CH_2 \xrightarrow{C_2H_5SH} RSCH_2CH_2CH_2SC_2H_5$$

Allylsulfide reactant with ethanethiol	Selectivity to unsymmetrical bis-sulfide, %
$PhSCH_2CH=CH_2$	5
$CH_3CH_2CH_2SCH_2CH=CH_2$	62
$(CH_3)_2CHSCH_2CH=CH_2$	73
$(CH_3)_3CSCH_2CH=CH_2$	71

On the basis of the proposed correlations, it becomes apparent that the two possible sequences of mixed thiol additions to allene should indeed lead to different product distributions. For a high yield of unsymmetrical 1,3-bis(substituted thio)propanes, the poorer hydrogen-donating thiol should first be added to allene. This will result in a higher yield of the desired allyl sulfide monoadduct than addition of the better hydrogen donor since the selectivity for terminal addition to allene is inversely related to the hydrogen donor ability of the adding thiol.[2,11] The resulting allyl sulfide should then be allowed to react with an excess of the better hydrogen-donating thiol to suppress the formation of symmetrically substituted trimethylene bis-sulfides *via* allylic scission. The side reactions of this step are even less likely using this sequence since the thiol of poorer hydrogen-donor ability usually gives a less stable thiyl radical. The thiyl group of the allyl sulfide monoadduct intermediate of the recommended sequence, therefore, is a poorer leaving group, *i.e.*, less subject to scission during further thiol addition.

A search of the literature showed that several free-radical reactions have been observed to yield products that arose from allylic reversal.

In 1948, Wilzbach, Mayo, and Van Meter[12] found that methallyl chloride dimerized on irradiation in the presence of tetraethyl lead, probably by the following mechanism.



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(9) P. Bruin, A. F. Bickel, and E. C. Kooyman, *Rec. trav. chim.*, **71**, 1115 (1952).

(10) U. Schmidt, A. Müller, and K. Markau, *Chem. Ber.*, **97**, 405 (1964).

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

(12) K. E. Wilzbach, F. R. Mayo, and R. Van Meter, *J. Am. Chem. Soc.* **70**, 4069 (1948).

In 1949, Kharasch and Sage[13] reported that the free-radical addition of bromotrichloromethane to allyl bromide led to 4,4,4-trichloro-1-butene and 1,2,3-tribromopropane as the main products. The formation of these products, was explained by the following mechanism.

$$BrCH_2CH{=}CH_2 \xrightarrow{Cl_3C\cdot} BrCH_2\underset{\cdot}{C}HCH_2CCl_3 \longrightarrow CH_2C{=}HCH_2CCl_3\ (+\ Br\cdot)$$

$$BrCH_2CH{=}CH_2 \xrightarrow{Br\cdot} BrCH_2\underset{\cdot}{C}HCH_2Br \xrightarrow{Cl_3CBr} BrCH_2CH(Br)CH_2Br\ (+\ Cl_3C\cdot)$$

Kharasch and Büchi[14] found that the decomposition of diacetyl peroxide in allyl bromide yielded 46% of 1-butene and several bromoalkanes.

$$BrCH_2CH{=}CH_2 \xrightarrow{H_3C\cdot} BrCH_2\underset{\cdot}{C}HCH_2CH_3 \longrightarrow H_2C{=}CHCH_2CH_3\ (+\ Br\cdot)$$

In 1953, Kharasch, Simon, and Nudenberg[15] found that the addition of bromotrichloromethane to α-methylstyrene yields α-(2,2,2-trichloroethyl)styrene possibly *via* the following mechanism.

$$CH_3{-}C(Ph){=}CH_2 \xrightarrow{Cl_3C\cdot} CH_3{-}\underset{\cdot}{C}(Ph){-}CH_2CCl_3 \longrightarrow CH_2{=}C(Ph){-}CH_2CCl_3\ (+\ H\cdot)$$

Concurrently with the latter work, Gaylord and Eirich[16] found that the polymerization of allyl esters with benzoyl peroxide led to allyl benzoate. The same

$$RCO_2CH_2CH{=}CH_2 \xrightarrow{PhCO_2\cdot} RCO_2CH_2\underset{\cdot}{C}HCH_2O_2CPh \longrightarrow H_2C{=}CHCH_2O_2CPh\ (+\ RCO_2\cdot)$$

authors[17,18] also found the occurrence of degradative chain transfer in allyl ester polymerizations, which may be due to a similar scission mechanism.

Kharasch[14] and Gaylord[16,17] have pointed out that a direct radical displacement could also explain these

$$XCH_2CH{=}CH_2 + Y\cdot \longrightarrow YCH_2CH{=}CH_2 + X\cdot$$

results on the allyl sulfide reaction product distributions. However, the effect of the structure and the concentration of thiol addends, we feel, definitely support the alternative allylic cleavage reversal mechanism. This mechanism correctly predicts that high hydrogen-donor ability and/or high concentration of thiol should lead to lower amounts of allylic cleavage product. The direct radical displacement mechanism, on the other hand, predicts that these same factors would favor the formation of by-products by increasing the concentration of attacking thiyl radicals. The well-known facility of the addition of thiyl radicals to olefinic bonds, the reversibility of such reactions,[11] and the propensity of radicals to stabilize themselves by β elimination all support this mechanism. Therefore, we believe that some of the reactions reported in the literature may also take place by the allylic reversal mechanisms given above. Further work is still necessary, however, to provide data that will allow a clear-cut distinction between the two possible mechanisms in these cases.

Experimental Section

Materials and Equipment.—All chemicals used were purchased from Matheson Coleman and Bell, with the exception of 2-propane- and 2-methyl-2-propanethiols which were obtained from the Eastman Kodak Co. Their purity was determined by g.l.p.c. or in some cases n.m.r. and found to be higher than 95%. Ultraviolet irradiations were carried out with a 100 W Hanau medium pressure mercury immersion lamp (from G. W. Gates and Co.), placed approximately 5 cm. from the reaction vessel in a water bath held between 15 and 20°. Tightly stoppered quartz test tubes equipped with magnetic stirrers were used as reaction vessels.

Methods of Analyses.—Compounds derived solely from aliphatic thiols were chromatographed on a 100-ft., 0.02-in.-i.d., coated (50% phenylsilicone–50% nitrile silicone) capillary Golay column. The g.l.p.c. equipment used has been already described in this series.[1,2] Higher boiling compounds derived from aryl thiols were analyzed on a 3-ft., 0.25-in.-o.d. column packed with 60–80-mesh Gas Chrom P coated with 3% Dowfax 9N-40 with equipment previously described.[1,2]

The crude reaction mixtures were analyzed as such. Components were identified by comparison of their retention times with those of pure samples run under the same conditions. In cases of doubt, pure reference compounds were added to the crude reaction mixtures and the samples rerun to verify identifications.

The chromatographic peak areas were determined by planimetry. The correspondence of the observed relative areas to the mactual weight per cents of the reaction mixtures was confirmed using accurately weighed synthetic blends of the pure components. In general, there was close agreement with mixtures containing only trimethylene bis-sulfides. In these cases, the differences between relative areas and theory weights were no greater than 3%. Mixtures containing both allylic mono- and bis-sulfide diadducts gave somewhat poorer agreement (maximum difference 6%). Estimation of thiol concentrations by g.l.p.c. was generally not attempted, since the narrowness of peaks made planimetry difficult and since 2-methyl-2-propanethiol decomposed on the capillary column.

N.m.r. spectra were recorded on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. N.m.r. was used to verify the identities of reactants. This method was also useful in estimating the relative amounts of thiols, monoadducts, and diadducts in the reaction mixtures and in confirming the diterminal structure of the major diadduct components.

Infrared spectra were recorded with a Baird recording spectrophotometer Model B, using a neat thin film of sample.

Additions of Thiols to Allyl Sulfides.—A mixture of thiol and allyl sulfide[19] (Tables I and IV) was weighed into a quartz test tube equipped with a magnetic stirrer. The tube was then chilled and the air was displaced with nitrogen. After being tightly stoppered, the tubes were immersed into a stirred water bath maintained at 15–20°, approximately 5 cm. from the ultraviolet source. The contents of the tubes were then irradiated and analyzed as described above.

Isolation of 1-Ethylthio-3-phenylthiopropane.—A mixture of 110 g. (1 mole) of benzenethiol and 20.4 g. (0.2 mole) of allyl ethyl sulfide was irradiated for 12 hr. at 17°. N.m.r. analyses of samples (a total of 7.9 g.) withdrawn during the reaction showed that the reaction was essentially complete after 4 hr. The reaction mixture was diluted with ether, extracted with 10% aqueous sodium hydroxide, washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent at atmospheric pressure, the remainder was distilled *in vacuo* to give two fractions, 3.6 g., b.p. 99–121° (1.2 mm.), and 29.6 g., b.p. 121° (1.2–1.5 mm.), respectively. The first fraction was shown by g.l.p.c. to be substantially 1-ethylthio-3-phenylthiopropane contaminated with a material of similar retention time (possibly a 1,2 isomer). The second fraction was the pure unsymmetrical 1,3 diadduct. The distillation residue (3.0 g.) was found by n.m.r. to contain about 70% of this compound and 30% phenyl disulfide. The over-all yield was, therefore, 88% of theory.

3-Chloropropyl Ethyl Sulfide (1-Chloro-4-thiahexane).—A mixture of 408 g. (6.6 moles) of ethanethiol and 507 g. (6.6 moles) of allyl chloride (3-chloro-1-propene) was placed in a 1-l. flask equipped with a water-jacketed quartz immersion well containing a Hanau ultraviolet lamp. The reaction mixture

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[13] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 79 (1949).

[14] M. S. Kharasch and G. Büchi, *ibid.*, **14**, 84 (1949).

[15] M. S. Kharasch, E. Simon, and E. W. Nudenberg, *ibid.*, **18**, 328 (1953).

[16] N. G. Gaylord and F. R. Eirich, *J. Am. Chem. Soc.*, **74**, 334 (1952).

[17] N. G. Gaylord and F. R. Eirich, *ibid.*, **74**, 337 (1952).

[18] N. G. Gaylord, *J. Polymer Sci.*, **22**, 71 (1956).

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

was irradiated for 4 hr. under nitrogen at 17–27°. N.m.r. analysis of the raw product showed that 85% of the allyl chloride had reacted. Fractional distillation of the crude product yielded 671 g. (73%) of 3-chloropropyl ethyl sulfide between 58 and 64° at 10 mm. Kretov and Toropova[20] reported b.p. 58–72° (18 mm.). An n.m.r. spectrum of the product in carbon tetrachloride showed signals (parts per million from internal tetramethylsilane) as follows: 3.43 t (chloromethylene), 2.38 m (mercaptomethylenes), 1.80 p (middle methylene), and 1.11 t (methyl).

3-Chloropropyl Phenyl Sulfide.—A stirred mixture of 550 g. (5.0 moles) of benzenethiol and 382.5 g. (5.0 moles) of allyl chloride was irradiated for 9 hr. at 17–30° under a nitrogen atmosphere. N.m.r. analysis indicated that 66 mole % of the allyl chloride had been consumed. Fractional distillation of the crude product *in vacuo* produced 413.8 g. (44%) of 3-chloropropyl phenyl sulfide, b.p. 95–96° (0.45 mm.), n^{26}_{D} 1.5717 [lit.[21] b.p. 124–125° (7 mm.), n^{26}_{D} 1.5714]. An n.m.r. spectrum of the product in carbon tetrachloride showed signals (parts per million from internal tetramethylsilane) as follows: 7.17 s, 7.20 s (phenyl), 3.49 t (chloromethylene), 2.93 t (mercaptomethylene), and 1.91 p (middle methylene).

Unsymmetrical 1,3-Bis(substituted thio)propanes from 3-Chloropropyl Ethyl Sulfide.—The appropriate thiol (0.4 mole) was slowly added to a solution of 21.6 g. (0.4 mole) of sodium methylate in 200 ml. of methanol contained in a four-neck flask under a nitrogen atmosphere. Then 54.6 g. (0.4 mole) of 3-chloropropyl ethyl sulfide was slowly added to the mercaptide solution. The resulting mixture was refluxed for 2 hr. while a white precipitate formed. Methanol was then distilled from the reaction mixture, and water (150 ml.) and ether (100 ml.) were added to the distillation residue. The organic phase was separated and washed three times with water and dried over anhydrous sodium sulfate. Ether was stripped from the solution and the residue was distilled under high vacuum to obtain the purified product (Tables II and III).

1-Benzylthio-3-phenylthiopropane was prepared from 3-chloropropyl phenyl sulfide by the general procedure given above using benzylmercaptan and sodium methylate. After solvent removal, n.m.r. indicated greater than 95% purity of the crude product. Analytical and n.m.r. data of a distilled sample are shown in Tables II and III, respectively.

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[20] A. E. Kretov and E. M. Toropova, *J. Gen. Chem. USSR*, **7**, 2009 (1937); *Chem. Abstr.*, **32**, 518 (1938).

[21] W. H. Vinton, U. S. Patent 2,604,657 (1952); *Chem. Abstr.*, **47**, 1516*d* (1953).

Fluoro Ketones. III. Preparation and Thermal Decomposition of Fluoroacetone Hemiketal Esters[1]

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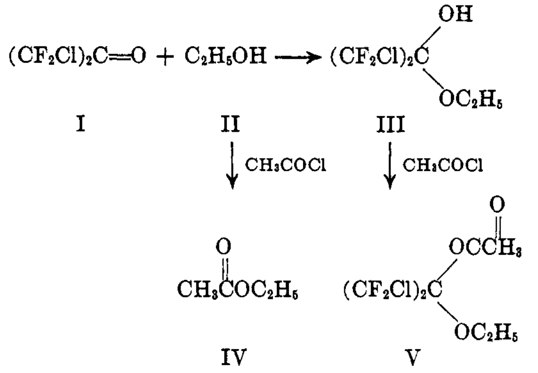
The preparation and properties of novel fluoroacetone hemiketal esters and carbonates are reported. Thermal decomposition of these esters gave the corresponding fluoroacetones and simple esters. A possible mechanism for these decompositions is presented.

The facile reaction of fluoroacetones with a wide variety of nucleophiles has been reported to give good yields of the corresponding adducts.[1b,2–4] These adducts are hydrolytically unstable, giving the fluoroacetone hydrate and starting nucleophile. For practical reasons, it was desired to convert these adducts to more stable derivatives.

Attempts to prepare esters of the amide–fluoroacetone adducts were unsuccessful,[1b] but esters, sulfonates, and carbamates of fluoroacetone cyanohydrins have recently been synthesized.[5] These results are in accord with the findings of Mill and co-workers.[4d]

Alcohols are known to react with fluoroacetones in an equilibrium reaction to give hemiketals such as III.[3b]



Distillation of these hemiketals was tedious and always accompanied by a considerable amount of the fluoroacetone (recovered from a cold trap). Consequently, crude hemiketals were largely used in the work reported in this paper.

Acetylation of III with acetyl chloride and pyridine was carried out in dry diethyl ether or tetrahydrofuran,[6] with distillation of the crude product at atmospheric pressure giving both IV and V. The formation of IV could be rationalized either by the acetylation of II (using the principle of microscopic reversibility) or by the decomposition of V. Distillation of the

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[1] (a) Part I: B. Farah and S. Horensky, *J. Org. Chem.*, **28**, 2494 (1963); (b) part II: P. E. Newallis and E. J. Rumanowski, *ibid.*, **29**, 3114 (1964); (c) presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstracts, p. 23K.

[2] (a) C. Woolf, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1957, p. 23 M; (b) A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950); (c) A. T. Morse, P. B. A. Ayscough, and L. C. Leitch, *Can. J. Chem.*, **33**, 453 (1955).

[3] (a) I. L. Knunyants and Yu. A. Cherburkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 678 (1960); (b) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960); (c) I. L. Knunyants, C. Ch'ing-yun, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 686 (1960); (d) R. G. Koshyanovskii, *Proc. Acad. Sci. USSR, Chem. Sect.*, **137**, 379 (1961).

[4] (a) I. L. Knunyants, Yu. M. Rokhlin, N. P. Gambaryan, Yu. A. Cherburkov, and C. Tsin-Yun, *Khim. Nauka i Promy.*, **4**, 802 (1959); (b) F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, **28**, 1825 (1963); (c) S. Andreades, *ibid.*, **27**, 4157 (1962); (d) T. Mill, J. O. Rodin, R. M. Silverstein, and C. Woolf, *ibid.*, **29**, 3715 (1964).

[5] E. J. Rumanowski, unpublished results.

[6] Dissolving III in ether or tetrahydrofuran liberated a considerable amount of heat, probably due to the formation of strong hydrogen bonds. Hexafluoroisopropyl alcohol, for example, has been recently reported to form strong hydrogen bonds with tetrahydrofuran [see W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964)].