The Role of Allylic Reversal in Free-Radical Thiol Additions to Allylic Halides[1]

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The free-radical addition of alkanethiols to 3-chloropropene and 2-methyl-3-chloropropene was found to yield 2-chloropropyl as well as the expected 3-chloropropyl alkyl sulfides. In contrast, the addition of reactive thiols such as benzenethiol to these chlorides forms only the expected 3-chloropropyl sulfides in good yields. The addition of benzenethiol to 3-bromopropene, however, produces in high yield 2-bromopropyl phenyl sulfide and none of the expected 3-isomer. In the methanethiol–3-chloro-2-methylpropene system it was shown that the ratio of 2- to 3-chloropropyl adduct formed varies with the reactant ratio used. An increase in thiol concentration leads to a decrease in the amount of 2-chloropropyl adduct formed; conversely, an increase in allylic chloride used leads to a decrease in the amount of 3-chloropropyl adduct formed. It is postulated that formation of 2-halopropyl isomers in these additions is the result of a β' elimination from the initial adduct radical (allylic reversal of thiol addition) followed by ionic hydrogen halide readdition to the allylic sulfide formed. Support for this hypothesis was provided by a crossover experiment in which benzenethiol was added to allyl bromide in the presence of β-methallyl methyl sulfide. The products of this reaction were those of a bromine atom crossover, allyl phenyl sulfide and 2-bromo-2-methylpropyl methyl sulfide.

During the course of research recently carried out in these laboratories on the addition of thiols to allylic sulfides,[2] alternate synthetic routes to unsymmetrical 1,3-bis(substituted thio)propanes, as exemplified by I, were considered. An appealing route appeared to

$$\underset{\text{I}}{\text{RSCH}_2\text{CH}_2\text{CH}_2\text{SR}'} \qquad \text{R} \neq \text{R}'$$

be the free-radical addition of a thiolic compound to an allyl halide to form a γ-halo sulfide followed by a nucleophilic displacement of the halide ion by a mercaptide

$$\text{RSH} + \text{CH}_2{=}\text{CHCH}_2\text{Cl} \longrightarrow \text{RSCH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{R}'\text{S}^-} \text{RSCH}_2\text{CH}_2\text{CH}_2\text{SR}'$$

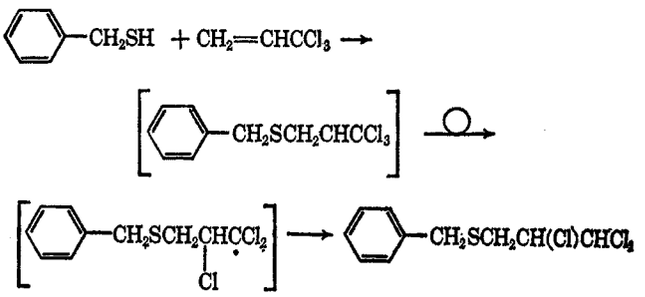
ion. The fact that such γ-halo or 3-chloropropyl sulfides were previously available only through relatively elaborate, low-yield sequences[3] and a feeling that they should be generally useful intermediates for the synthesis of a variety of 1,3-propanes with mixed terminal functionality added incentive to a study of these reactions.

Although seemingly a straightforward reaction, few examples of thiol additions to allylic halides were to be found in surveying the literature.[4,5] Sjoberg[6] first reported the thermally induced addition of thiolacetic acid to allyl chloride to produce in good yield 3-chloropropyl thiolacetate (II).

$$\text{AcSH} + \text{CH}_2{=}\text{CHCH}_2\text{Cl} \xrightarrow{80^\circ} \underset{\text{II}}{\text{AcSCH}_2\text{CH}_2\text{CH}_2\text{Cl}}$$

This reaction was later used by both Bordwell[7] and Dittmer[8] as part of a facile scheme for the synthesis of thiacyclobutanes through pyrolysis of II in the presence of base.

The only other reports of thiol additions to allylic halides occur in the studies of Nesmeyanov and his co-workers[9,10] concerned with the rearrangements ensuing from the addition of radicals to polyhalo olefins. Most pertinent to the present investigation, as it later developed, was the Russian workers' observation that the addition of α-toluenethiol to 3,3,3-trichloropropene produces 2,3,3-trichloropropylbenzyl sulfide, supposedly *via* an intramolecular chlorine atom shift.



The bulk of the Russian work[10] in this field, however, has definitely implied through both theoretical interpretation and practical experience that such rearrangements are unique to polyhalo systems, and, therefore, this precedent did not appear to constitute a deterrent to the contemplated scheme for 3-halopropyl sulfide synthesis involving only allylic monohalides.

Results

1. Thiol Additions to Allylic Chlorides.—It was found that the ultraviolet light catalyzed addition of methanethiol to 3-chloro-2-methylpropene (β-methallyl chloride) at a 1:2 reactant ratio proceeds readily to yield, in addition to the expected γ-chloro sulfide (IV) a significant amount of a second product. The major expected product, 3-chloro-2-methylpropyl methyl sulfide, was identified by its nmr spectrum and elemental analysis. The presence of a by-product was

(1) Presented before the Division of Organic Chemistry at the 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) D. N. Hall, A. A. Oswald, and K. Griesbaum, *J. Org. Chem.*, **30**, 3829 (1965).

(3) (a) E. Rothstein, *J. Chem. Soc.*, 309 (1937); (b) T. P. Dawson, *J. Am. Chem. Soc.*, **55**, 2070 (1933).

(4) F. W. Stacy and J. F. Harris, Jr., *Org. Reactions*, **13**, 150 (1963).

(5) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, pp 62–97.

(6) B. Sjoberg, *Ber.*, **74B**, 64 (1941).

(7) (a) F. G. Bordwell and W. A. Hewett, Abstracts of Papers, 126th National Meeting of the American Chemical Society, New York, N. Y., Sept 1954, pp 6–10; (b) F. G. Bordwell and W. A. Hewett, *J. Org. Chem.*, **23**, 636 (1958).

(8) D. C. Dittmer, W. R. Hertler, and H. Winicor, *J. Am. Chem. Soc.*, **79**, 4431 (1957).

(9) (a) A. N. Nesmeyanov, R. Kh. Freidlina, R. G. Petrova, and A. B. Terent'ev, *Dokl. Akad. Nauk. SSSR.*, **127**, 575 (1959); (b) A. N. Nesmeyanov, R. Kh. Freidlina, A. B. Terent'ev, and R. G. Petrova, *ibid.*, **138**, 859 (1961).

(10) R. Kh. Freidlina, V. N. Kost, and M. Ya Khorlina, *Russ. Chem. Rev.*, **31**, 1 (1962).

TABLE I

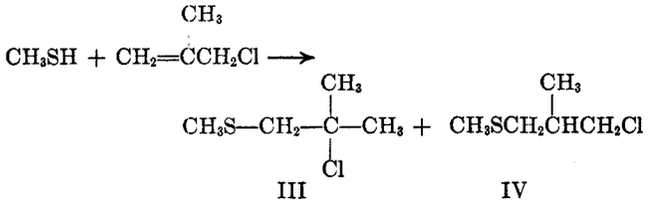
ULTRAVIOLET-CATALYZED THIOL ADDITIONS TO ALLYLIC HALIDES

Reactants		Concn,	Time,	Convn,	Product compn, mole %[a]		
RSH	$CH_2=C(Y)CH_2X$	RSH/halide	hr	%	$RSCH_2CH(Y)CH_2Cl$	$RSCH_2C(X)YCH_3$	$RSCH_2CH(Y)CH_2SR$
CH_3SH	$CH_2=C(CH_3)CH_2Cl$	0.5	20	100[b]	59	41	Nil
CH_3SH	$CH_2=C(CH_3)CH_2Cl$	1.0	20	100[b]	69	31	Nil
CH_3SH	$CH_2=C(CH_3)CH_2Cl$	2.0	20	100[b]	70	5	25
CH_3SH	$CH_2=C(CH_3)CH_2Cl$	6.0	24	100[b]	77	Nil	23
CH_3SH	$CH_2=C(H)CH_2Cl$	0.8	4	79[c]	86	14	Nil
CH_3CH_2SH	$CH_2=C(CH_3)CH_2Cl$	1	9	79[c]	72	28	Nil
C_6H_5SH	$CH_2=C(CH_3)CH_2Cl$	1	9	77[c]	100	Nil	Nil
$CH_3C(O)SH$	$CH_2=C(H)CH_2Cl$	1	9	76[c]	100	Nil	Nil
C_6H_5SH	$CH_2=C(H)CH_2Br$	1	23	57[c]	Nil	78[d]	Nil
C_6H_5SH	$CH_2=C(H)CH_2Br$	2.0	20	100[b]	Nil	77[e]	Nil

[a] Based on nmr analysis of crude reaction mixture. [b] Based on absence of limiting reagent in the reaction mixture. [c] Yield of adduct mixture isolated by distillation. [d] 22% of presumably 2-(1-bromopropyl) phenyl sulfide was present. [e] 23% of presumably 2-(1-bromopropyl) phenyl sulfide was present.

shown by extraneous nmr signals in the spectrum of the product mixture, appearing as singlets at 2.90, 2.20, and 1.64 of relative intensities 2:3:6 [δ given in parts per million (ppm) downfield shift from tetramethylsilane as an internal standard]. The difficulty experienced in separating this by-product from the major product by distillation, the nature of extraneous nmr signals, and the agreement of the elemental analysis of a mixture of the unknown material with the 3-chloropropyl sulfide with that calculated for pure 3-chloropropyl sulfide all implied that the second product was an isomer of the major one.

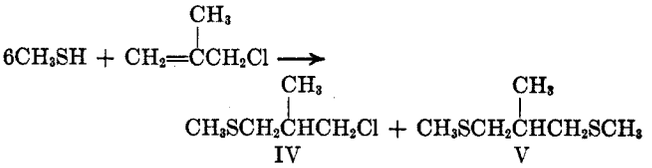
Such an isomer, 2-chloro-2-methylpropyl methyl sulfide, was synthesized by the ionic addition of hydrogen chloride to β-methallyl methyl sulfide. This compound exhibits nmr signals corresponding exactly to those observed for the unknown by-product. A comparison of the infrared spectrum of the independently synthesized 2-chloropropyl sulfide with that of a fraction isolated from methanethiol addition to β-methallyl chloride enriched in the by-product confirmed that it was indeed 2-chloro-2-methylpropyl methyl sulfide. Thus, the addition of methanethiol to β-methallyl chloride surprisingly yields the 2-chloropropyl sulfide III as well as the expected 3-chloropropyl sulfide IV.



Changes in the reactant proportions in methanethiol addition to β-methallyl chloride led to a variation in the proportion of β- and γ-chloro sulfides produced as shown in the first four entries of Table I.

These differences in product composition were clearly evident from the nmr spectra. Since all of the signals of the β-chloro sulfide appeared as clean singlets at unobscured chemical shifts, it was possible to use their integrated intensities to determine the molar ratio of γ- to β-chloro sulfide in the mixture. The intensity of the upfield doublet from the β-methyl group in the 3-chloro-2-methylpropyl isomer provided confirmation for these calculations.

With decreasing thiol concentration, increasing amounts of β-chloro sulfide were formed. Conversely, by using a sixfold excess of methanethiol it was possible to suppress completely β-chloro sulfide formation although formation of a new by-product, 1,3-bis(methylthio)-2-methylpropane (V), was observed in this case.

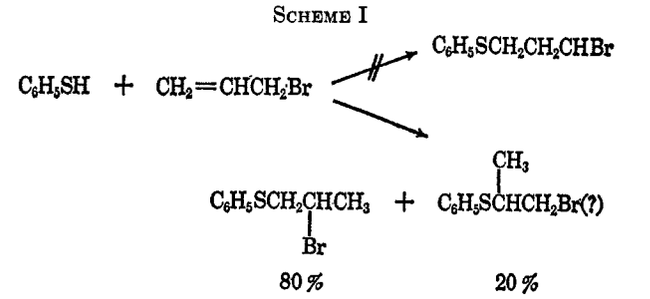


The presence of this latter by-product was demonstrated by nmr analysis of the crude product mixture and a nearly pure sample was isolated by repeated distillation.

Equimolar addition of ethanethiol to β-methallyl chloride gave the same product distribution observed with methanethiol (Table I). Methanethiol addition to allyl chloride at a 1:1 ratio gave somewhat more of the γ-chloropropyl isomer than resulted in the β-methallyl chloride case. Similar additions of benzenethiol and thiolacetic acid to these chlorides led only to the expected γ-chloro products. These latter additions could also be induced by heat alone as Sjoberg's[6] results suggest.

2. Thiol Additions to Allylic Bromide.—In contrast to its addition to allylic chlorides, benzenethiol addition to allyl bromide at an equimolar ratio gave none of the expected 3-bromopropyl phenyl sulfide, but instead a 57% yield of a 4:1 mixture of the 2-bromo isomer and a second, unidentified compound which was inseparable by distillation (Scheme I). Since the combustion analysis of this mixture agreed with that calculated for

SCHEME I

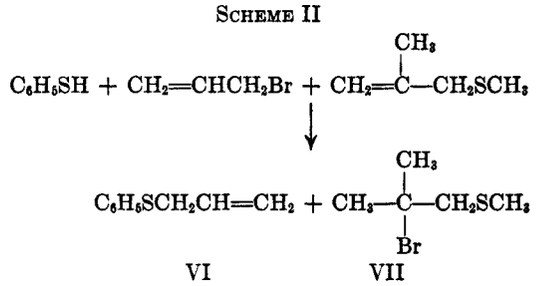


pure 1-(2-bromopropyl) phenyl sulfide, it is likely that this unidentified compound is the third isomer 2-(1-bromopropyl) phenyl sulfide. A mixture of the 2-bromopropyl sulfide with the same contaminant was

produced by ionic hydrogen bromide addition to allyl phenyl sulfide as shown by comparison of both infrared and nmr spectra. Reaction of a twofold excess of benzenethiol with allyl bromide did not lead to any change in the product distribution. Substitution of heat for ultraviolet light as an initiator was unsuccessful; only 8% reaction was observed under conditions that gave >90% reaction with allyl chloride.

Addition of benzenethiol to allyl bromide under free-radical conditions in the presence of an equivalent amount of β-methallyl methyl sulfide led to an entirely different reaction mixture, consisting of only allyl phenyl sulfide (VI) and (2-bromo-2-methylpropyl) methyl sulfide (VII) (Scheme II). These products were separated by distillation and identified by comparison of their infrared and nmr spectra with those of independently synthesized authentic samples. In a control experiment, it was found that ultraviolet irradiation of an equimolar mixture of β-methallyl methyl sulfide and 2-bromopropyl phenyl sulfide failed to induce any reaction.

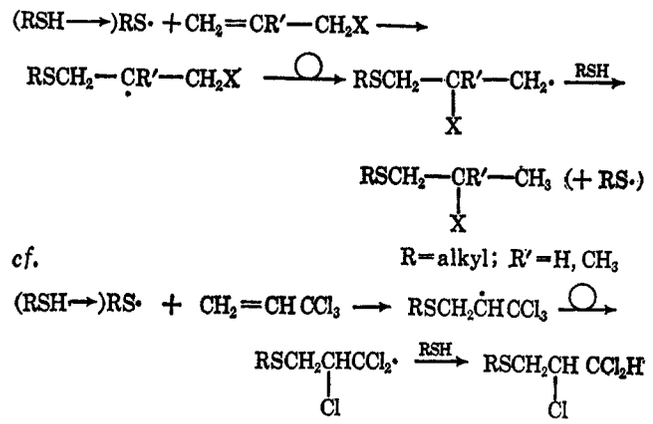
SCHEME II



VI VII

Discussion

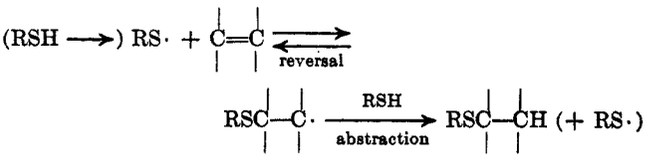
Superficially, the formation of β-halo sulfides by thiol additions to allylic halides appears to be analogous to the intramolecular halogen atom migrations observed by Nesmeyanov and co-workers in the addition of α-toluenethiol to 3,3,3-trichloro-1-propene.[9a] On the basis of this previous work, an intramolecular halogen atom shift mechanism can be written to explain β-halo sulfide formation in thiol additions to allylic halides. On closer examination, however, it is apparent



that this analogy is not valid. In the trichloropropene reaction, the effect of chlorine atom migration is to transfer the unpaired electron from a less stable (CĊHC) to a more stable (Cl_2ĊC) position while in the allylic monohalide cases the unpaired electron is transferred from a more stable (CĊRC) to a less stable (H_2ĊC) position. Furthermore, the fact that β-methallyl methyl sulfide can intercept the "migrating" bromine in benzenethiol addition to allyl bromide clearly demonstrates the β-halo sulfide formation in this case is not the result of an intramolecular process.

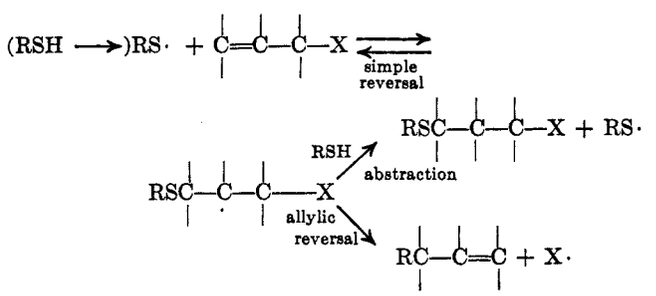
An alternate and, in view of the present observations, preferable mechanism for the formation of β-halo sulfides from the addition of thiols to allylic halides is provided by the concept of allylic reversal.[2]

Ordinarily, the addition of a radical species to a double bond leads to a β-substituted radical intermediate which can react further by abstraction and chain transfer (propagation to form product) or it can undergo β elimination (*i.e.*, reversal of addition) to re-form the starting species.[11] In the case of addition to an



allylically substituted olefin, however, the intermediate radical formed is β,β′ disubstituted. Thus, if the original allylic substituent has a radical-leaving ability comparable with that of the group derived from the addend, the alternative reaction path to abstraction can be either β elimination or β′ elimination. This third course of reaction (β′ elimination) is termed allylic reversal of radical addition to contrast it with simple reversal (Scheme III). Such situations arising from allylic reversals have been recently shown to occur in the addition of thiyl radicals to allyl sulfides[2] and *a priori* it was expected to occur in similar additions to allylic halides.[12] Its result is to introduce a new radical species and allylically substituted olefin into the system which can react further to give by-products.

SCHEME III



An outline to explain 2-halopropyl sulfide formation in thiol–allylic halide reactions incorporating an allylic reversal as the pivotal step is shown in Scheme IV.

Allylic reversal forms a halogen atom which, by hydrogen abstraction from a thiol, can subsequently form a hydrogen halide. Ionic addition of this acid to the allylic sulfide also formed by allylic reversal leads to the observed β-halo sulfide products.

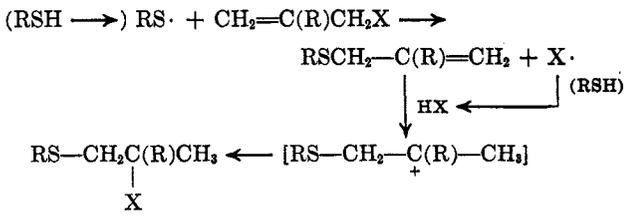
(11) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

(12) Walling[13] has predicted that such "rearrangements" can occur in the addition of radical species to an allylically substituted olefin and that the complications thus introduced can obscure the primary processes in such reactions. A number of authors[14] have parenthetically noted the intervention of allylic reversal in a variety of systems, but, to our knowledge, no one has yet systematically investigated the factors that influence their extent and ultimate consequences.

(13) C. Walling in "Molecular Rearrangements," Vol. 2, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 439.

(14) See ref 2 and 13 for summaries and H. Muramatsu and P. Tarrant, *J. Org. Chem.*, **29**, 1796 (1964), for a recent example.

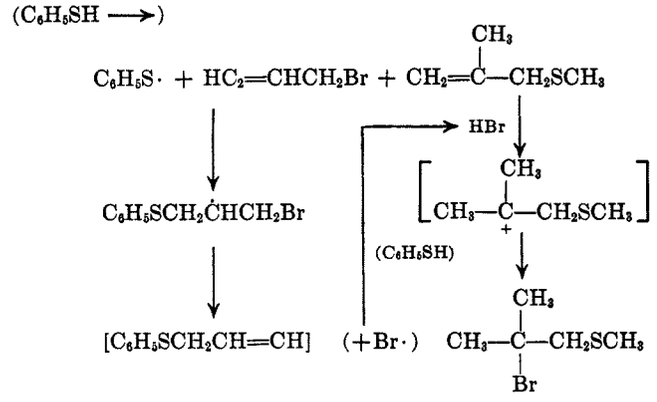
SCHEME IV



Since bromine is a better radical leaving group than chlorine and thus more prone to undergo allylic reversal, this mechanism correctly predicts the difference between the extent of β-halo sulfide formed in benzenethiol addition to allyl chloride and allyl bromide. The scheme outlined above also correctly predicts the observed effect of varying the adding thiol concentration on the extent of 2-halopropyl formation. Increasing the concentration of thiol in the reaction makes more hydrogen atoms available for abstraction by the intermediate adduct radical thus favoring hydrogen abstraction over allylic reversal. The same effect explains the difference in extent of 2-halopropyl sulfide formation observed between an alkanethiol and benzenethiol or thiol–acetic acid. The latter compounds are better hydrogen atom donors than the former and, therefore, facilitate abstraction.

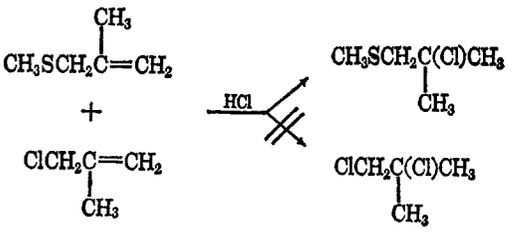
Further, compelling evidence for the allylic reversal mechanism is found in the effect of added β-methallyl methyl sulfide on the course of benzenethiol addition to allyl bromide (Scheme V). Interception of the hydrogen halide reveals the intermediacy of an allyl sulfide in the reaction. The great reactivity of β-methallyl methyl sulfide as a substrate for electrophilic addition allows it to effectively remove the hydrogen bromide in the system before it can add back to the allyl sulfide to form *n*-(2-bromopropyl) phenyl sulfide. A similar trapping of allylic sulfide by methanethiol free-radical additions accounts for the appearance of 1,3-bis(methylthio)-2-methylpropane in the reaction of β-methallyl chloride with a high excess of methanethiol. The alternate possibility of an ionic displacement of a chloride ion by methanethiol is less likely on the basis of an independent experiment in which a mixture of a 3-chloropropyl sulfide with methanethiol was irradiated for 24 hr by ultraviolet light. Only 7% displacement of chloride was observed in this experiment.

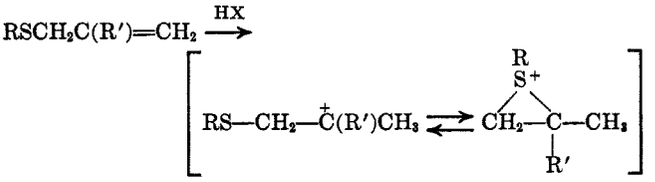
SCHEME V



The fact that similar halogen atom crossovers to form 1,2-dihalides were not observed in reactions containing excess allylic halide can be attributed to a preferential scavenging of the hydrogen halide by the allyl sulfide in the system. The preference was independently confirmed by allowing β-methallyl methyl sulfide to compete with β-methallyl chloride in ionic hydrogen chloride addition (Scheme VI). Nmr analysis of the reaction mixture after the addition of 1 mole of hydrogen chloride showed that completely selective addition to the sulfide had occurred. This enhanced reactivity of allyl sulfides as substrates for electrophilic addition can be explained by stabilization of the carbonium ion intermediate through both neighboring-group participation and inductive effects of the adjacent thio ether group.[15,16]

SCHEME VI





Conclusions

The results described above show that the free-radical addition of a thiol to an allylic halide is not necessarily the straightforward reaction it at first appears to be. Although it proceeds as expected to produce 3-chloropropyl sulfides with thiols of high hydrogen donor ability (such as benzenethiol) and allylic chlorides, with other thiols (such as methanethiol) or with allylic bromides, deceptive complications arise. Thiols of low hydrogen-donor ability lead to 2-chloropropyl as well as 3-chloropropyl sulfides unless used in excess. Allylic bromides lead almost exclusively to 2-bromopropyl sulfide formation under all the conditions tried.

These drawbacks, however, are not without compensation. The addition of thiols to allylic bromides may prove to be a useful route to 2-bromopropyl sulfides, particularly in view of the accessibility of the former from olefin brominations. A similar possibility exists in directing the addition of alkyl mercaptans to allylic chlorides to yield 2-chloropropyl sulfides.

On the more theoretical side, the present work has cast further light on some of the factors which can influence the selectivity of free-radical reactions. Such knowledge is necessary both for devising efficient synthetic sequences using these reactions and in drawing the correct conclusions from the results of model studies.

(15) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 16, 17.

(16) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 25, 26, 144, 145.

TABLE II

NUCLEAR MAGNETIC RESONANCE PARAMETERS OF β- AND γ-HALO SULFIDES AND THIOL ACETATES

Structure of $RSCH_2CX(Y)CH_2Z$	Chemical shift, ppm[a] RS		CH_2	CX	(Y)	CH_2Z
$CH_3SCH_2CH(CH_3)CH_2Cl$	2.08 s	...	2.65 m	2.04 o	1.09 d	3.58 d
$CH_3SCH_2CH(H)CH_2Cl$	2.08 s	...	2.62 t	2.06 o	...	3.63 t
$CH_3SCH_2CCl(CH_3)CH_2H$	2.20 s	...	2.90 s	...	1.64 s	1.64 s
$CH_3CH_2SCH_2CCl(CH_3)CH_2H$	1.24 t	2.62 q	2.90 s	...	1.61 s	1.61 s
$C_6H_5SCH_2CH(CH_3)CH_2Cl$	7.20 m	...	2.84 m	2.00 m	1.03 d	3.47 d
$CH_3C(O)SCH_2CH(H)CH_2Cl$	2.31 s		2.98 t	2.02 m	...	3.58 t
$C_6H_5SCH_2CH(Br)CH_2H$	7.18 m	...	3.23 m	3.99 m	...	1.69 d
$CH_3SCH_2CBr(CH_3)CH_2H$	2.21 s		3.07 s	...	1.83 s	1.83 s
$CH_3CH_2SCH_2CH(CH_3)CH_2Cl$	1.25 t	2.51 m	2.51 m	1.95 m	1.07 d	3.54 d

[a] Of structural units downfield from internal tetramethylsilane in carbon tetrachloride. Shapes of nmr signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, o = five-line multiplet, m = multiplet.

Experimental Section

Reagents.—Allyl chloride, β-methallyl chloride, allyl bromide, sodium methoxide, hydrogen chloride, hydrogen bromide, benzenethiol, and methanethiol were supplied by the Matheson Co. Reagent grade methane and ethanethiol from Eastman were also used. The halides were distilled under nitrogen and were shown by nmr to be >90% pure before use.

Methods of Analysis.—Nmr spectra were recorded on 30–50% solutions in carbon tetrachloride containing 5% tetramethylsilane on a Varian Model A-60 proton resonance spectrometer. Nmr parameters for various halo sulfides isolated during this study are shown in Table II. Infrared spectra were taken as neat samples on a Baird recording spectrophotometer, Model B.

Additions of Methanethiol to β-Methallyl Chloride.—Methanethiol (12 g, 0.25 mole) was condensed in a quartz tube (equipped with a Teflon-clad screw seal and magnetic stirring bar) containing 45.3 g (0.5 mole) of β-methallyl chloride (3-chloro-2-methyl-1-propene). The sealed tube was placed in a water bath (15 ± 3°) approximately 5 cm from a 100-w Hanau medium-pressure ultraviolet lamp. After 20 hr of irradiation, the tube was opened, the methanethiol was allowed to evaporate, and the residue was analyzed by nmr. Analysis indicated that the mixture contained 41 mole % β-methallyl chloride, 34% 3-chloro-2-methylpropyl methyl sulfide (3 isomer), and 24% 2-chloro-2-methylpropyl methyl sulfide (2 isomer). Distillation of the reaction mixture provided a forerun of 20.2 g of β-methallyl chloride and major fraction, 26.0 g, bp 69–78° (23 mm), which was shown by nmr to contain 58 mole % of the 3 and 42% of the 2 isomer. An infrared spectrum of this fraction showed only bands present in the spectra of either the pure γ or β isomer. Mixtures of 12 g (0.25 mole), 24.6 g (0.5 mole), and 60 g (1.25 mole) of methanethiol with 22.6 g (0.25 mole), 22.6 g (0.25 mole), and 18.1 g (0.2 mole) of β-methallyl chloride, respectively, were treated and analyzed in a similar manner. Two distillations of the first of these reactions provided a substantially pure sample of 3-chloro-2-methylpropyl methyl sulfide, bp 54° (9 mm).

Anal. Calcd for $C_5H_{11}ClS$: C, 43.31; H, 8.00; Cl, 25.57; S, 23.12. Found: C, 43.62; H, 7.79; Cl, 25.19; S, 23.44.

Addition of Methanethiol to Allyl Chloride.—A mixture of 19.4 g (0.4 mole) of methanethiol and 38.7 g (0.51 mole) of allyl chloride (3-chloro-1-propene) was irradiated in a quartz tube for 4 hr. Nmr analysis of the reaction mixture, after venting of the excess methanethiol, showed that it consisted of 28% allyl chloride, 63% 3-chloropropyl methyl sulfide, and 10% 2-chloropropyl methyl sulfide. Distillation of the reaction mixture provided two major fractions, bp 158–164° (760 mm) and 69–71° (23–27 mm) [lit.[17] bp 71.2° (29 mm)], of combined weight 3.92 g which was shown by nmr to be 3-chloropropyl methyl sulfide.

Synthesis of 2-Chloro-2-methylpropyl Methyl Sulfide.—β-Methallyl methyl sulfide prepared essentially by the method of Barnard, *et al.*,[18] had bp 113–114° (760 mm) [lit.[18] bp 113.0–113.2° (758 mm)]. Gaseous hydrogen chloride was slowly passed through a mixture of 30.6 g (0.3 mole) of the sulfide and 0.1 ml of boron trifluoride until 9.8 g (0.27 mole) had been absorbed (41 hr). The red reaction mixture was distilled to provide 34.5 g (92%) of the β-chloro sulfide, bp 46–47° (15 mm). An infrared spectrum exhibited major bands at 3.37, 3.42, 6.85, 6.95, 7.24, 7.31, 8.05, 8.14, 8.27, 8.62, 9.02, 10.19, 10.42, 11.61, 12.25, 13.47, and 14.33 μ.

Anal. Calcd for $C_5H_{11}ClS$: C, 43.31; H, 8.00; Cl, 25.57; S, 23.12. Found: C, 43.78; H, 8.05; Cl, 25.41; S, 23.1.

Addition of Ethanethiol to β-Methallyl Chloride.—A mixture of 31.0 g (0.5 mole) of ethanethiol and 45.3 g of β-methallyl chloride were irradiated in quartz with ultraviolet light for 9 hr. Nmr analysis showed that the reaction product mixture consisted of 19% β-methallyl chloride, 58% 3-chloro-2-methylpropyl ethyl sulfide, and 23% 2-chloro-2-methylpropyl ethyl sulfide.

This mixture was distilled *in vacuo* to give two major fractions, the first (17.3 g), bp 83–87° (25 mm), and the second (9.0 g), bp 87–105° (25 mm). Redistillation of the first fraction gave an analytical sample of chloro-2-methylpropyl ethyl sulfide. An infrared spectrum showed major peaks at 3.43, 3.51, 6.87, 6.93, 7.28, 7.60, 7.92, 8.07, 10.30, 10.52, 10.68, 11.15, 11.65, 12.25, 12.38, 12.75, 13.75, and 14.60 μ.

Anal. Calcd for $C_6H_{13}ClS$: C, 47.20; H, 8.58; Cl, 23.22; S, 21.00. Found: C, 47.26; H, 8.35; Cl, 23.39; S, 21.4.

Synthesis of 2-Chloro-2-Methylpropyl Ethyl Sulfide.—The compound prepared in a manner similar to that used for its methyl analog had bp 71–74° (25 mm). An infrared spectrum exhibited major peaks at 3.35, 3.40, 6.84, 7.22, 7.30, 7.91, 9.00, 10.20, 11.53, 12.20, 13.65, and 15.00 μ.

Anal. Calcd for $C_6H_{13}ClS$: C, 47.20; H, 8.58; Cl, 23.22; S, 21.00. Found: C, 47.45; H, 8.48; Cl, 22.34; S, 21.33.

Synthesis of 3-Chloro-2-Methylpropyl Phenyl Sulfide.—A mixture of 55 g (0.5 mole) of benzenethiol and 45.3 g (0.5 mole) β-methallyl chloride in a quartz tube were irradiated for 9 hr. Nmr analysis indicated that 74 mole % of the allylic chloride had been consumed. Distillation provided a total of 66.4 g (66%) of product, the major fraction having bp 84–89° (0.35 mm). An infrared spectrum showed bands at 3.27, 3.39, 3.47, 6.30, 6.75, 6.85, 6.94, 7.27, 7.50, 7.58, 7.87, 8.05, 9.17, 9.33, 9.72, 10.50, 11.15, 11.60, 12.23, 12.42, 13.40, and 14.40 μ.

Anal. Calcd for $C_{10}H_{13}ClS$: C, 59.83; H, 6.53; S, 15.97. Found: C, 60.16; H, 6.50; S, 16.18.

Addition of Thiolacetic Acid to Allyl Chloride.—Ultraviolet irradiation of a mixture of 38 g (0.5 mole) of thiolacetic acid and 38.3 g (0.5 mole) of allyl chloride in a quartz tube for 9 hr followed by distillation gave 57.6 g (65%) of 3-chloropropyl thiolacetate, bp 101–102° (27 mm) [lit.[6] bp 83–84° (10 mm)]. An infrared spectrum exhibited bands at 3.41, 5.87, 6.96, 7.39, 7.65, 7.88, 8.77, 9.00, 10.60, 11.63, 12.85, 13.85, 14.35, and 15.37 μ.

Addition of Benzenethiol to Allyl Bromide.—A mixture of 22.0 g (0.2 mole) of benzenethiol and 24.2 g (0.2 mole) of allyl bromide in a quartz tube was irradiated with ultraviolet light for 23 hr. Nmr analysis of the orange reaction mixture indicated that 77% of allyl bromide was consumed. The reaction mixture was decanted from a small amount of viscous, red liquid and distilled to yield 26.2 g (57%) of product mixture, bp 84–86° (0.35 mm). The material's infrared spectrum showed bands at 3.27, 3.37, 3.43, 6.30, 6.75, 6.94, 7.28, 8.06, 8.21, 8.55, 8.96, 9.17, 9.35, 9.50, 9.74, 10.00, 11.15, 11.97, 13.45, and 14.46 μ.

Anal. Calcd for $C_9H_{11}BrS$: C, 46.76; H, 4.80; Br, 34.57; S, 13.87. Found: C, 46.86; H, 4.80; Br, 34.44; S, 13.81.

Irradiation of a mixture of 22.0 g (0.2 mole) of benzenethiol and 12.1 g (0.1 mole) of allyl bromide in the same manner for 20 hr resulted in complete consumption of allyl bromide. The nmr spectrum of the reaction mixture indicated that the same products were formed as those obtained from the 1:1 reaction.

(17) W. R. Kirner, *J. Am. Chem. Soc.*, **50**, 2446 (1928).

(18) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

Heating of a mixture of 11.0 g (0.1 mole) of benzenethiol and 12.1 g (0.1 mole) of allyl bromide in the dark under nitrogen for 16 hr induced 8% reaction (based on nmr) yielding the same products.

Synthesis of 2-Bromopropyl Phenyl Sulfide.—Gaseous hydrogen bromide was slowly passed into 30.4 g (0.2 mole) of allyl pheny sulfide in flask wrapped securely in metal foil. After 13.4 g (0.17 mole) was absorbed, the reaction mixture was distilled to yield 13.3 g (33%) of product, bp 84–90° (0.35 mm). An infrared spectrum exhibited bands at 3.26, 3.37, 3.42, 6.29, 6.75, 6.92, 7.28, 8.52, 9.72, 11.15, 12.00, 13.43, and 14.45 μ.

Anal. Calcd for $C_6H_{11}BrS$: C, 46.76; H, 4.80; Br, 34.57; S, 13.87. Found: C, 46.69; H, 4.92; Br, 34.39; S, 13.8.

Reaction of Benzenethiol with Allyl Bromide in the Presence of β-Methallyl Sulfide.—A mixture of 6.7 g (0.06 mole) of benzenethiol, 7.4 g (0.06 mole) of allyl bromide, and 6.2 g (0.06 mole) of β-methallyl sulfide in a quartz tube was irradiated for 20 hr. Distillation of the reaction mixture provided two major fractions weighing 7.6 g (67%) and 4.6 g (50%), bp 56–68° (11 mm) and 86–88° (11 mm), respectively. Nmr and infrared spectra of the first fraction were virtually identical with those of 2-bromo-2-methylpropyl methyl sulfide and those of the second fraction of those of allyl phenyl sulfide. Ultraviolet irradiation of a mixture of 5.1 g (0.05 mole) of β-methallyl methyl sulfide and 11.6 g (0.05 mole) of 2-bromo-1-(phenylthio)propane for 20 hr produced absolutely no change in the mixture's nmr spectrum.

Synthesis of 2-Bromo-2-methylpropyl Methyl Sulfide.—Gaseous hydrogen bromide was slowly passed into 20.4 g (0.2 mole) of β-methallyl methyl sulfide in a foil-wrapped flask. During the reaction the 18.4 g (0.23 mole) of gas was absorbed and the solution temperature rose to 50°. The red reaction mixture was distilled to give 28.4 g (76%) of product, bp 52–54° (10 mm). An infrared spectrum showed major bands at 3.39, 3.44, 6.85, 6.95, 7.24, 7.31, 8.13, 8.30, 8.68, 9.10, 10.20, 10.45, 11.70, 12.38, and 13.58 μ.

Anal. Calcd for $C_5H_{11}BrS$: C, 32.79; H, 6.05; Br, 43.64; S, 17.51. Found: C, 32.90; H, 6.07; Br, 43.71; S, 17.95.

Competitive Hydrochlorination of β-Methallyl Chloride and β-Methallyl Methyl Sulfide.—A mixture of 15.3 g (0.15 mole) of β-methallyl methyl sulfide and 13.7 g (0.15 mole) of β-methallyl chloride was treated with gaseous hydrogen chloride until 4.6 g (0.13 mole) was absorbed. Nmr analyses of the reaction mixture showed that more than 90 mole % of the sulfide had reacted to form the 2-chloropropyl sulfide, while only a trace of 1,2-dichloro-2-methylpropane was formed.

Attempted Methanethiol Displacement of Chloride from 3-Chloro-2-methylpropyl Phenyl Sulfide.—A stirred mixture of 20.0 g (0.1 mole) of the chloropropyl phenyl sulfide and 5.0 g (0.12 mole) of methanethiol was sealed in a quartz tube and subjected to ultraviolet irradiation for 24 hr. The tube was then opened and nitrogen was drawn through the reaction mixture at room temperature under moderate vacuum. Nmr analysis of the residue showed only a small amount (7%) of signal from a (methylthio) moiety (at δ 2.27).

Registry No.—II, 13012-54-9; III, 13012-55-0; IV, 13012-56-1; VI, 5296-64-0; VII, 13012-58-3; 3-chloropropyl methyl sulfide, 13012-59-4; 2-chloro-2-methyl propyl ethyl sulfide, 13012-60-7; 3-chloro-2-methyl propyl phenyl sulfide, 13012-61-8; 2-bromopropyl phenyl sulfide, 13012-62-9; 3-chloro-2-methyl propyl ethyl sulfide, 13012-63-0; 1-chloro-2-methyl propyl methyl sulfide, 13012-64-1; benzenethiol, 108-98-5; allyl bromide, 106-95-6.

The Structures of the Camphene Sultones[1]

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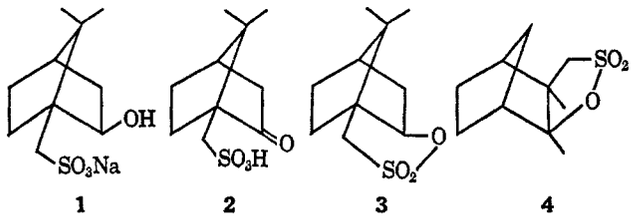
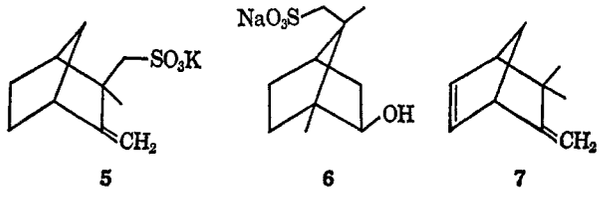
The sulfonation of camphene with sulfuric acid in acetic anhydride gave, initially, 10-isobornyl sultone (**3**) and, after work-up, a 4:1 inseparable mixture of sultones **4** and **16**. Neutralization of the initially formed reaction mixture with sodium carbonate afforded the acetoxysulfonate **35**. Camphene and dioxane–sulfur trioxide gave sultone **3** and the unsaturated sulfonate **30**. Upon heating sultone **3** rearranges to give pure sultone **4**. The structures of **3**, **4**, **16**, and **35** were established by lithium aluminum hydride reduction to isoborneol, camphene hydrate, 3,3,4-trimethyl-2-*exo*-norbornanol, and isoborneol, respectively. The structures of **3** and **35** were further verified by conversion into a derivative of 10-camphorsulfonic acid. The *exo,cis* ring juncture in sultone **4** was shown by conversion into 3-*endo*-methyl-3-*exo*-propyl-2-norbornanone (**26**), a compound synthesized by another stereospecific route.

While attempting to acylate camphene with acetic anhydride in the presence of sulfur trioxide, Lipp[3] observed the production of a crystalline, 1:1 adduct of camphene and sulfur trioxide, mp 133°. Acidification of the hydroxy sulfonate salt **1**, obtained by the sodium–alcohol reduction of camphor sulfonic acid (**2**), also gave the same adduct and led Lipp to conclude that the structure of "camphene sultone" was represented by formula **3**.

In 1938, Asahina[4] showed that basic hydrolysis of camphene sultone gave an unsaturated sulfonate salt **5** and proposed that the double bond was produced by dehydration of a tertiary alcohol, and the original sultone was best represented by gross structure **4**. Asahina also demonstrated that facile rearrangement of the bornyl ring system must occur since acidification of optically active sodium 10- and 9-(2-hydroxy)bornanesulfonates (**1** and **6**) gave rise to the same optically inactive sultone **4**, mp 133°.



1 2 3 4



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