mixture was maintained at 25.0°. Samples (9 ml.) were withdrawn at the intervals stated in Table III and immediately distributed between 75 ml. of benzene and 40 ml. of water. The organic phase was washed three times with sodium carbonate (5%) and five times with water and taken to dryness *in vacuo*. To complete the removal of water, acetone was added, and the distillation was repeated. To free the residue of acetone, the crystals were suspended twice in warm petroleum ether which was evaporated each time. The adequacy of this procedure for terminating the first stage of the reaction was tested by adding compound **7** in 0.7 ml. of benzene to a separatory funnel containing 75 ml. of benzene, 40 ml. of water, and 9 ml. of formic acid. The product isolated as above showed no change in spectrum. The residues from the first two samples were dissolved in carbon disulfide and analyzed by absorbance measurements at 780 and 673 cm.$^{-1}$. The later samples were dissolved in dioxane and their absorbances were measured at 263, 268, 274, and 300 mμ. A_{300} values served to correct for nonspecific absorption on the basis of the spectrum of a sample withdrawn after 26 hr. The weights entered in Table III represent the means calculated from the measurements at the three other wavelengths and the absorptivities of **8a**. The maximum difference between the mean and the individual values was less than 1.5% except at 8 hr. (3%). The infrared spectrum of the sample taken after 26 hr. agreed closely with that of purified **8b**.

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Reactions with Base of 2-Propargylthioethanol and the 2-(2-Haloallylthio)ethanols[1]

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Treatment of 2-propargylthioethanol (**1**) or a 2-(2-haloallylthio)ethanol (**2** or **3**) with sodium hydroxide in water, toluene, or dimethyl sulfoxide, or with sodium amide in ether, gave 2-methyl-1,4-oxathiene (**4**) as the only cyclic product. Further study of the reactions carried out in water and in ether showed that 2-allenylthioethanol (**5**) and 2-(1-propynylthio)ethanol (**6**) were also formed. **4** was prepared from **2** and **3** in deuterium oxide. The amount and location of deuterium in **4** from 2-(2-bromoallylthio)ethanol (**2**) were consistent with the hypothesis that **4** results from cyclization of **6**, which is formed exclusively by prototropic rearrangement of **1**, the dehydrohalogenation product of **2**. The amount and location of deuterium in **4** from 2-(2-chloroallylthio)ethanol (**3**) indicated that a significant amount of **6** was formed by dehydrochlorination of 2-(*trans*-2-chloropropenylthio)-ethanol (**8**), which was formed together with its *cis* isomer (**7**), by prototropic rearrangement of **3** at a rate competitive with dehydrochlorination of **3** to **1**.

Previous work has shown that the mode of base-induced cyclization of propargylaminoethanols,[2] propargyloxyethanol,[3] and their 2-haloallyl analogs is markedly dependent on solvent. In aprotic solvents, the principal cyclization products are formed by nucleophilic addition of alkoxide to the allene or internal acetylene formed by prototropic rearrangement of the propargyl compound. In water, wherein prototropic rearrangements occur relatively slowly, most of the cyclization products result from nucleophilic addition of alkoxide to the acetylenic carbons of the propargyl compound. Continuing work directed toward determining the scope and limitations of base-induced cyclization reactions of propargyl and 2-haloallyl compounds, we have examined reactions of 2-propargylthioethanol (**1**) and the 2-(2-haloallylthio)ethanols (**2** and **3**) with base in various solvents.

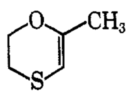
$HC{\equiv}CCH_2SCH_2CH_2OH$

1

$H_2C{=}\overset{X}{C}CH_2SCH_2CH_2OH$

2, X = Br
3, X = Cl

When the sulfides **1**–**3** were subjected to a variety of conditions similar to those used to effect cyclization of their amine[2] and ether[3] analogs, *i.e.*, sodium hydroxide in water, toluene, and dimethyl sulfoxide, and sodium amide in ether, only one cyclic product, **4**, was obtained. The infrared and nmr spectra of **4** clearly indicated that it was 2-methyl-1,4-oxathiene, and comparison of **4** with 2-methyl-1,4-oxathiene prepared from mercaptoethanol and chloroacetone[4] confirmed the structural assignment.



4

$H_2C{=}C{=}CHSCH_2CH_2OH$ **5** $H_3CC{\equiv}CSCH_2CH_2OH$ **6**

Further examination of the aqueous and ethereal reaction mixtures[5] revealed that, in addition to 2-methyl-1,4-oxathiene (**4**), 2-propargylthioethanol (**1**) and 2-(2-bromoallylthio)ethanol (**2**) were converted to 2-allenylthioethanol (**5**) and 2-(1-propynylthio)ethanol (**6**) in varying amounts, depending on the conditions. Pure **6**, which was readily characterized by spectral means, was isolated from reaction mixtures that contained excess base. The presence of **5** in products isolated after a short reaction time or from mixtures that were deficient in base was indicated by the appearance in the infrared spectrum of a band at

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[1] Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963. This research was supported by Grant GM-10606 from the National Institute of General Medical Sciences of the U. S. Public Health Service.

[2] (a) W. J. Croxall and J. H. Mellema, U. S. Patent 2,960,508 (Nov 15, 1960); *Chem. Abstr.*, **55**, 14482 (1961); (b) A. T. Bottini, J. A. Mullikin, and C. J. Morris, *J. Org. Chem.*, **29**, 373 (1964).

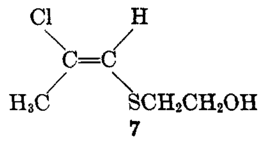
[3] A. T. Bottini, F. P. Corson, and E. F. Böttner, *ibid.*, **30**, 2988 (1965).

[4] I. R. Marshall and H. A. Stevenson, *J. Chem. Soc.*, 2360 (1959).

[5] Reactions of 2-haloallylaminoethanols and propargyloxyethanol carried out in water and ethers gave the greatest differences in product compositions.

1950 cm^{-1}, characteristic of allenes, and by the appearance in the 56.4-Mc spectrum of a triplet (1H) at 313 cps (downfield from TMS) and a doublet (2H) at 270 cps, both with $J \sim 6.8$ cps. Interestingly, because the intensity of the allene band at 1950 cm^{-1} is considerably greater than that of the internal acetylene band at 2050 cm^{-1}, examination of the infrared spectra of mixtures of **5** and **6** containing as little as 20% **5** gave the false impression that the mixtures were mainly **5**.[6]

Treatment of 2-(2-chloroallylthio)ethanol (**3**) with base in ether and water gave **4** in yields up to 30%. The major product from **3**, however, was an isomeric alcohol **7**, and the infrared and nmr spectra of **7** were consistent with the 2-(2-chloropropenylthio)ethanol structure. As base-induced rearrangements of allyl sulfides to propenyl sulfides are known to occur rapidly[7] under conditions that are considerably milder than those required to bring about similar rearrangements of allylamines[8] or allyl ethers,[7a,9] the conversion of **3** to 2-(2-chloropropenylthio)ethanol is not surprising. The simplicity of the nmr spectrum of the rearranged sulfide indicated that it consisted of only one of the two possible geometric isomers. As the material survived conditions that could be expected to effect *trans*-dehydrochlorination across a double bond,[10] we concluded that **7** was 2-(*cis*-2-chloropropenylthio)ethanol.



7

We believe that nearly all the 2-propargylthioethanol (**1**) is converted to 2-methyl-1,4-oxathiene (**4**) by cyclization of 2-(1-propynylthio)ethanol (**6**), which is formed by prototropic rearrangement of **1**. This mechanism is analogous to that proposed to explain base-induced cyclization of propargyloxyethanol to 2-methyl-1,4-dioxene.[3] Significantly, treatment of **6** with aqueous sodium hydroxide at 100° gives **4** in better than 70% yield.[11]

There are two reasonable mechanisms that can explain conversion of a 2-(2-haloallylthio)ethanol (**2** or **3**) by base to 2-methyl-1,4-oxathiene (**4**). The first is dehydrohalogenation to 2-propargylthioethanol (**1**) followed by prototropic rearrangement of **1** *via* 2-allenylthioethanol (**5**) to 2-(1-propynylthio)ethanol (**6**), which cyclizes to **4**. Significantly, the first step in most base-induced cyclization reactions of the amine[2b] and ether[3] analogs of **2** and **3** appears to be dehydrohalogenation to the corresponding propargyl compound. Another reasonable first step for the reaction of **2** or **3** is base-induced rearrangement to the corresponding 2-(*trans*-2-halopropenylthio)ethanol. 2-(*cis*-2-Chloropropenylthio)ethanol (**7**) is the major product of the reactions of 2-(2-chloroallylthio)ethanol (**3**) with base. As base-induced rearrangements of other allyl thio ethers give mixtures of *cis*- and *trans*-propenyl thio ethers,[7] it seems likely that 2-(*trans*-2-chloropropenylthio)ethanol (**8**) was formed together with its *cis* isomer. **8** could then undergo *trans*-dehydrochlorination to 2-(1-propynylthio)ethanol (**6**), which cyclizes to **4**. We should note that no 2-(2-bromopropenylthio)ethanol (**9**) was observed in the higher-boiling fractions obtained from 2-(2-bromoallylthio)ethanol (**2**) in water. Failure to observe any **9** indicates that this second mechanism is an unlikely one for conversion of **2** to **4**. Note also that substitution of bromine for chlorine should tend to favor the first mechanism because **2** can be expected to undergo dehydrohalogenation more rapidly than **3**, but the rates of prototropic rearrangement of **2** and **3** can be expected to be similar.

It appeared that the relative importance of these mechanisms could be assessed by examining 2-methyl-1,4-oxathiene (**4**) prepared from the 2-(2-haloallylthio)ethanols in deuterium oxide. If one makes the reasonable allowance that the acetylenic hydrogen of 2-propargylthioethanol (**1**) is equilibrated very rapidly with deuterium oxide in the presence of base,[12] formation of **4** *via* a mechanism in which the first step is dehydrohalogenation to **1** will give **4** with a fully deuterated methyl group as well as deuterium at C-3. (Note that each step in the sequence **1** → **5** → **6** results in replacement of one hydrogen by deuterium.) On the other hand, prototropic rearrangement of the 2-(2-haloallylthio)ethanol, followed by dehydrohalogenation to **6** and cyclization of **6**, will give **4** with deuterium at C-3 and only one deuterium on the methyl carbon.

It was readily determined that 2-methyl-1,4-oxathiene (**4**) and deuterium oxide do not undergo exchange catalyzed by deuterioxide. However, when 2-(1-propynylthio)ethanol (**6**) was treated with sodium deuterioxide solution,[13] the **4** obtained had an average of only 2.62 ± 0.04 hydrogens on the methyl carbon. This indicates that exchange of the methyl hydrogens of **6** occurs, but at a rate that is slow compared with cyclization of **6** to **4**.

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[6] Synthesis of propargyl, allenyl, and 1-propynyl sulfides have been reported recently. See L. Brandsma, H. E. Wijers, and J. F. Arens, *Rec. Trav. Chim.*, **82**, 1040 (1963); G. Pourcelot and C. Georgoulis, *Bull. Soc. Chim. France*, 866 (1964), and references cited therein.

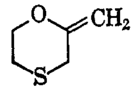
[7] (a) D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956); (b) C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

[8] C. C. Price and W. H. Snyder, *Tetrahedron Letters*, **No. 2**, 69 (1962).

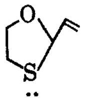
[9] (a) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960); (b) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); (c) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

[10] See S. I. Miller and R. M. Noyes, *ibid.*, **74**, 629 (1952).

[11] Cyclization of 2-propargylthioethanol (**1**) to 2-methylene-1,4-oxathiane (i), followed by prototropic rearrangement of i to 2-methyl-1,4-oxathiene (**4**), is also conceivable. This mechanism is analogous to those by which propargylaminoethanols and propargyloxyethanol are converted to 2-methylenemorpholines[2b] and 2-methylenedioxane.[3] In aqueous sodium hydroxide at 100°, 20 hr is required for *ca.* 50% conversion of propargylaminoethanols or propargyloxyethanol to cyclic products, but only 2 hr is required for a comparable conversion of **1** to **4**. As there is no apparent reason why **1** should cyclize more rapidly than its amine or ether analog, we believe that very little **4** is formed *via* i. Another conceivable mechanism is cyclization of 2-allenylthioethanol (**5**) to 2-methyl-1,4-oxathiene (**4**) (or to i followed by rearrangement to **4**). By analogy with the allenylamine[2] and allenyl ether[3] analogs of **5**, it can be argued that cyclization of **5** would give 2-vinyl-1,3-oxathiolane (ii) as the major product. No trace of ii was observed as a product from any reaction of the hydroxyethyl sulfides **1-3**.



i



ii

[12] See H. B. Charman, D. R. Vinard, and M. M. Kreevoy, *J. Am. Chem. Soc.*, **84**, 347 (1962), and references therein.

[13] A similar control experiment was not carried out with **5** because we were unable to obtain a reasonably pure sample of that compound.

The 2-methyl-1,4-oxathiene (**4**) obtained from 2-(2-bromoallylthio)ethanol (**2**) had 0.19 ± 0.01 hydrogen on the methyl carbon and 0.06 ± 0.01 hydrogen at C-3. As all of the hydrogen (and deuterium) at C-3 was incorporated from the solvent,[14] and as there was three times as much hydrogen on the methyl group, it appears that all of the hydrogen on the methyl group was also incorporated from the solvent. This indicates that the only important mechanism by which **2** is converted to **4** is *via* **1**, **5**, and **6**.

The 2-methyl-1,4-oxathiene (**4**) obtained from 2-(2-chloroallylthio)ethanol (**3**) had 0.45 ± 0.02 hydrogen on the methyl carbon and 0.04 ± 0.01 hydrogen at C-3.[14] As the **4** formed from **3** *via* 2-(propargylthio)-ethanol (**1**) will have 0.12 hydrogen on the methyl carbon and that formed *via* 2-(*cis*-2-chloropropenylthio)ethanol (**8**) could be expected to have $(2 \times 2.6/3.0 =)$ 1.7 hydrogens on the methyl carbon, it appears that ~20% of the **4** is formed *via* initial prototropic rearrangement to **8** and that ~80% is formed *via* initial dehydrochlorination to **1**.

The presence of a small amount (~6%) of 2-(2-chloroallylthio)ethanol (**3**) in the higher-boiling fraction from the reaction of **3** in sodium deuterioxide solution was indicated by the presence in the nmr spectrum of the vinyl hydrogen bands of **3**. Interestingly, the nmr band characteristic of the allyl hydrogens of **3** was not present in the spectrum. In order to allow greater recovery of **3**, the reaction was carried out at 65 ± 5° instead of at ~100°. Examination of the nmr spectrum of the resulting higher-boiling fraction revealed that the ratio of intensities of the allyl and vinyl bands of recovered **3** was 0.26. This indicated that **3** undergoes exchange of its allyl hydrogens more rapidly than it rearranges. In other words, the stepwise mechanism proposed for the isomerization of allyl *n*-hexyl sulfide to propenyl *n*-hexyl sulfide[7a] appears to be operative for the isomerization of **3** to the 2-(2-chloropropenylthio)ethanols (**7** and **8**).

Experimental Section[15]

2-Propargylthioethanol (**1**).—To a stirred, ice-cold solution of 120 g (1.0 mole) of propargyl bromide and 100 ml of ethanol was added dropwise in 1.5 hr a solution prepared from 78 g (1.0 mole) of 2-mercaptoethanol, 300 ml of ethanol, and 40 g (1.0 mole) of sodium hydroxide. When the addition was complete, the mixture was allowed to warm to room temperature and to stand for 20 hr. Most of the ethanol (375 ml) was distilled from the stirred mixture. The residue was cooled, and 200 ml of water and 150 ml of ether were added. The phases were separated, and the aqueous phase was extracted with 100 ml of ether. The ether extracts were combined, dried with sodium sulfate, and distilled to give 85.5 g (74%) of **1**, bp 80–83° (3 mm). Noted in the infrared spectrum were strong bands at 3370 (OH) and 3300 cm^{-1} ($\equiv CH$), and a weak band at 2120 cm^{-1} ($C\equiv C$). The nmr spectrum of **1** containing ~2% TMS consisted of a broadened singlet at 227 cps (OH), a triplet (J ~ 6.4 cps) at 209 cps (CH_2O), a doublet (J ~2.4 cps) at 183 cps ($\equiv CCH_2$), a triplet (J ~6.4 cps) at 158 cps ($OCCH_2S$), and a triplet (J ~2.4 cps) at 138 cps ($HC\equiv$).

Anal. Calcd for C_5H_8OS: C, 51.69; H, 6.94; S, 27.60. Found: C, 51.42; H, 6.94; S, 27.62.

The 2-(2-Haloallylthio)ethanols (2 and 3).—The following procedure, which is typical, is patterned after that described by Tarbell and Lovett[7a] for the preparation of allyl *n*-hexyl sulfide. To a stirred solution prepared from 150 ml of ethanol, 39 g (0.50 mole) of 2-mercaptoethanol, and 20 g (0.50 mole) of sodium hydroxide was added dropwise 100 g (0.50 mole) of 2,3-dibromopropene in 40 min. Upon the addition of less than 2 ml of dibromopropene, a white precipitate formed. During the addition, the temperature was maintained below 30° by cooling with an ice bath. (During another reaction, the temperature was allowed to exceed 55°, the yield was diminished, and the **2** obtained was contaminated with **5** and **6**.) When addition was complete, the mixture was allowed to stand for 1 hr; it was then heated at reflux with stirring for 30 min. The condenser was set for downward distillation, and 140 ml of ethanol was distilled. The residue was cooled, 150 ml of water was added to dissolve the salt, and the two-phase mixture that resulted was separated. The aqueous solution was extracted twice with 40-ml portions of ether. The organic solutions were combined, dried with sodium carbonate, and most of the ether was removed by distillation at atmospheric pressure. Hydroquinone (~100 mg) was added to the residue, which was distilled rapidly to give 65 g (66%) of **2-(2-bromoallylthio)ethanol** (**2**), bp 105–107° (3 mm), n^{26}_D 1.5555. The infrared spectrum possessed strong bands at 3370 (OH), 1635 (C=C), and 900 cm^{-1} ($CH_2=$). The nmr spectrum of **2** as a 20% solution in carbon tetrachloride consisted of bands centered at 327 and 309 cps ($=CH_2$), a singlet at 185 cps (OH), a triplet (J ~6.5 cps) at 204 cps (CH_2O), a narrow band centered at 194 cps ($=C-CH_2S$), and a triplet (J ~6.5 cps) at 144 cps ($OCCH_2S$).

Anal. Calcd for C_5H_9BrOS: C, 30.47; H, 4.60; Br, 40.54. Found: C, 30.48; H, 4.60; Br, 40.48.

2-(2-Chloroallylthio)ethanol (**3**), bp 92–95° (3 mm), n^{22}_D 1.5300, was obtained in 83% yield from 111 g (1.0 mole) of 2,3-dichloropropene, 78 g (1.0 mole) of mercaptoethanol, and 40 g (1.0 mole) of sodium hydroxide. The infrared spectrum possessed strong bands at 3355 (OH), 1635 (C=C), and 897 cm^{-1} ($CH_2=$). The nmr spectrum of **3** containing 2% TMS consisted of bands centered at 300 and 293 cps ($CH_2=$), a broadened singlet at 242 cps (OH), a triplet (J ~6.6 cps) at 204 cps (CH_2O), a narrow band centered at 188 cps ($=C-CH_2S$), and a triplet (J ~6.6 cps) at 144 cps ($OCCH_2S$).

Anal. Calcd for C_5H_9ClOS: C, 39.34; H, 5.94; Cl, 23.23. Found: C, 39.47; H, 5.95; Cl, 23.26.

Reactions of 1,2, and 3 with base were conducted following procedures patterned after those used to convert N-alkyl-N-(2-haloallyl)ethanolamines and N-alkyl-N-propargylethanolamines to 3-alkyl-2-vinyloxazolidines and 4-alkyl-2-methylenemorpholines.[2] Reactions of more than routine interest and characterization of the products obtained are given below.

1 and Aqueous Sodium Hydroxide.—A heterogeneous mixture of 17.4 g (0.15 mole) of **1** and 150 ml of 1 *N* sodium hydroxide solution was heated under reflux with stirring for 2 hr. The mixture was cooled and extracted with 50 ml of ether, and the ether solution was dried with sodium carbonate. Distillation gave 8.7 g (50%) of a fraction with bp 80–83° (76 mm), n^{23}_D 1.5251, and 2.8 g (16%) of a fraction with bp 85–87° (6 mm), n^{22}_D 1.5283. The residue weighed 1.1 g.

The infrared spectrum of the first fraction possessed a strong band at 1645 cm^{-1} (polar C=C), but it possessed no bands in the 3350 (OH) or 900 ± 15 cm^{-1} ($=CH_2$) regions. The nmr spectrum of the first fraction containing 2% TMS consisted of a quartet (J ~ 1.0 cps) at 265 cps (=CH), two sets of bands resembling triplets at 238 (CH_2O) and 158 cps (CH_2S), and a doublet (J ~1.0 cps) at 96 cps (CH_3). These spectra were identical in every respect with those of 2-methyl-1,4-oxathiene (**4**), bp 62° (18 mm), n^{24}_D 1.5238 [lit.[4] bp 56° (10 mm), n^{16}_D 1.5288], prepared in 8% yield from chloroacetone and mercaptoethanol.[4]

The infrared and nmr spectra of the second fraction were notably different from those of **1**. The infrared spectrum possessed a very weak band at 2050 cm^{-1} ($C\equiv C$) and a band at 1385 cm^{-1} (CH_3). The nmr spectrum consisted of a broad band at 246 cps (OH), a triplet (J ~ 6.5 cps) at 205 cps (CH_2O), a triplet (J ~ 6.5 cps) at 153 cps (CH_2S), and a singlet at 106

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(14) The main source of the hydrogen in the solvent was the unlabeled 2-(2-haloallylthio)ethanol.

(15) Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 spectrophotometer. Nmr spectra were obtained at 56.4 Mc, using a Varian Associates HR-60 system equipped with electronic integrator and base-line stabilizer. Integrals are averages of at least eight determinations. Resonance frequencies in nmr spectra were determined relative to internal tetramethylsilane (TMS) using the side-band technique with a Packard CD-200 audiooscillator and are reported in cycles per second downfield from the TMS resonance (resonances frequencies were subsequently checked using a Varian Associates A-60A system). Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, Calif.

cps (CH_3). These spectra indicated that the material was 2-(1-propynylthio)ethanol (**6**).

Anal. Calcd for C_5H_8OS: C, 51.69; H, 6.94. Found: C, 51.73; H, 6.83.

1 and Sodium Amide in Ether.—To a magnetically stirred slurry of 3.9 g (0.10 mole) of sodium amide in 120 ml of dry ether was added dropwise 11.6 g (0.10 mole) of **1** in 20 min. Ammonia was evolved, and within 30 min of the final addition the mixture became dark brown. After 24 hr, 20 ml of water was added cautiously, and the two-phase mixture was separated. The ether solution was dried with sodium sulfate and distilled to give 4.9 g (42%) of **4**, bp 69–72° (35 mm), $n^{24}\mathrm{D}$ 1.5248, and 2.3 g (20%) of **6**, bp 70–75° (3 mm), $n^{24}\mathrm{D}$ 1.5278.

2 and Sodium Amide in Ether.—To a magnetically stirred slurry of 3.9 g of sodium amide in 120 ml of ether was added dropwise 19.6 g (0.10 mole) of 2-(2-bromoallylthio)ethanol (**2**). Ammonia was evolved, and a flocculent precipitate formed within 1 hr. After 24 hr, 35 ml of water was added cautiously, and the mixture that resulted was shaken in order to dissolve the precipitated salts. The two-phase mixture was separated, and the ether solution was dried with sodium sulfate and distilled to give a 5.2-g (45%) fraction with bp 74–76° (4 mm), $n^{22}\mathrm{D}$ 1.5366.[16] The infrared and nmr spectra of this material were similar to those of **6**, except that the infrared spectrum possessed a band of moderate intensity at 1950 cm^{-1} (C=C=C), and the nmr spectrum possessed a triplet ($J \sim 6.8$ cps) at 313 cps (C=C=CHS), and a doublet ($J \sim 6.8$ cps) at 270 cps ($C=C=CH_2$). The results of electronic integration indicated that the material consisted of 81 ± 2% **6** and 19 ± 2% 2-allenylthioethanol (**5**).

3 and Aqueous Sodium Hydroxide.—A heterogeneous mixture of 22.9 g (0.15 mole) of 2-(2-chloroallylthio)ethanol (**3**) and 150 ml of 2 *N* sodium hydroxide solution was stirred vigorously and heated under reflux for 2 hr. The reaction mixture was cooled and extracted successively with 75- and 50-ml portions of ether. The ether solutions were combined, dried with sodium sulfate, and distilled to give 4.9 g (28%) of **4**, bp 74–76° (35 mm), $n^{22}\mathrm{D}$ 1.5260, and 9.4 g (41%) of a fraction with bp 117–119° (12 mm), $n^{25}\mathrm{D}$ 1.5342, which proved to be **2-(*cis*-2-chloropropenylthio)ethanol** (**7**). The infrared spectrum of **7** differs most notably from that of **3** in that it possesses a band of moderate intensity at 1385 cm^{-1} (CH_3) and does not possess a band at 900 cm^{-1} ($=CH_2$). The nmr spectrum of **7** containing 2% TMS consisted of a quartet ($J \sim 1.3$ cps) at 341 cps (=CH), a broadened band at 246 cps (OH), a triplet ($J \sim 6.6$ cps) at 204 cps (CH_2O), a triplet ($J \sim 6.6$ cps) at 152 cps (CH_2S), and a doublet ($J \sim 1.3$ cps) at 115 cps (CH_3).

Anal. Calcd for C_5H_9ClOS: C, 39.34; H, 5.94. Found: C, 39.28; H, 6.11.

3 and Sodium Amide in Ether.—Using essentially the same procedure described for the reaction of **2** with sodium amide, 15.3 g (0.10 mole) of **3** and 3.9 g of sodium amide in 120 ml of ether gave, in addition to 1.6 g of **4**, a 7.3-g fraction with bp 80–100° (3 mm), $n^{22}\mathrm{D}$ 1.5334. Examination of the nmr spectrum showed that the fraction was a mixture of **3**, **6**, and **7**, and electronic integration of the spectrum showed further that the mixture was 35% **3**, 22% **6**, and 43% **7**. The absence of **4** from the mixture was indicated by gas–liquid partition chromatography (glpc).

Attempted Exchange of 4 with Deuterium Oxide.—A solution prepared from 2.0 g (0.05 mole) of sodium hydroxide, 50 ml of 99.8% deuterium oxide, and 5.8 g (0.05 mole) of **4** was stirred and heated under reflux for 3 hr. The reaction mixture was cooled and extracted three times with 10-ml portions of ether. The ether extracts were combined, dried with sodium sulfate, and distilled to give 4.8 g (83% recovery) of **4**, the infrared and nmr spectra of which were identical with those of unlabeled **4**.

2 and 2 *N* Sodium Deuterioxide.—A mixture of 120 g (6.0 moles) of 99.7% deuterium oxide, 4.8 g (0.12 mole) of sodium hydroxide, and 11.6 g (0.059 mole) of 2-(2-bromoallylthio)ethanol (**2**) was stirred vigorously and heated under reflux for 2 hr. The mixture was cooled and extracted twice with 75-ml portions of ether. The ether extracts were combined, dried with sodium sulfate, and distilled to give 2.1 g (31%) of labeled **4**, bp 74–75° (32 mm).[17] The relative intensities of the nmr bands were 0.06 ± 0.01 (=CH), 1.94 ± 0.06 (CH_2O), 2.00 (CH_2S), and 0.190 ± 0.012 (CH_3).

3 and 2 *N* Sodium Deuterioxide at 100°.—A mixture of 100 g of 99.7% deuterium oxide, 8 g (0.20 mole) of sodium hydroxide, and 15.2 g (0.10 mole) of 2-(2-chloroallylthio)ethanol (**3**) was stirred vigorously and heated under reflux for 1 hr, cooled, and extracted with 25 ml of chloroform. The chloroform solution was dried with sodium sulfate and distilled to give 3.2 g (28%) of labeled **4**, bp 76–78° (35 mm),[17] and 4.9 g of a fraction with bp 78–80° (2 mm). The relative intensities of the nmr bands in **4** were 0.04 ± 0.01 (=CH), 1.98 ± 0.05 (CH_2O), 2.00 (CH_2S), and 0.45 ± 0.02 (CH_3).

Examination of the infrared and nmr spectra of the higher-boiling fraction indicated that it was mainly labeled **7** together with small amounts of **3** and **6**. The relative intensities of the nmr bands of the mixture were 0.169 ± 0.006 (=CH), 0.126 ± 0.008 ($=CH_2$), 2.01 ± 0.02 (CH_2O), 2.00 (CH_2S), 0.956 ± 0.010 (CH_3 of **7**), and 0.161 ± 0.005 (CH_3 of **6**).

3 and 2 *N* Sodium Deuterioxide at 65 ± 5°.—The preceding procedure was repeated, but at 65 ± 5° for 27 hr. Labeled **4** (140 mg, ~1%) was collected at 63–70° (15 mm),[17] and a 10.3-g fraction with bp 78–82° (2 mm) was also collected. The relative intensities of the nmr bands of **4** (in chloroform) were 0.05 ± 0.01 (=CH), 1.96 ± 0.04 (CH_2O), 2.00 (CH_2S), and 0.614 ± 0.018 (CH_3).

Examination of the infrared and nmr spectra of the higher-boiling fraction indicated that it was mainly **3** together with significant amounts of **6** and **7**. The relative intensities of the nmr bands of the mixture were 0.172 ± 0.006 (=CH), 1.02 ± 0.02 ($=CH_2$), 2.00 ± 0.02 (CH_2O), 0.266 ± 0.008 ($=C-CH_2S$), 2.00 (CH_2S), 0.600 ± 0.010 (CH_3 of **7**), and 0.074 ± 0.006 (CH_3 of **6**).

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[16] Brandsma, Wijers, and Arens[6] have noted that the refractive index of 1-ethylthio-1,2-propadiene ($n^{20}\mathrm{D}$ 1.520–1.521) is considerably greater than that of either 1-ethylthiopropyne ($n^{20}\mathrm{D}$ 1.4950) or 3-ethylthiopropyne ($n^{20}\mathrm{D}$ 1.4872).

[17] Assay of this material by glpc using a Loe Model 1 Chromato-O-Flex with a 0.25 in. × 6 ft column packed with Silicone No. 550 on firebrick indicated that it was >99% pure.