

cal electrolyses as outlined above. 5-Chlorovaleric acid (4.0 g.) and sodium (0.15 g., 0.0066 mole) were dissolved in methanol (50 ml.), and a current of 2.0 amp. applied. As the current started to drop, a methanolic solution of the remainder of the starting materials was slowly added to maintain the current at about 2.0 amp. Total time of the electrolysis was 2.6 hours. After the usual isolation, fractionation through a modified Podbielniak column yielded crude 13-fluorotridecyl chloride. This fraction was heated under reflux for one hour with concentrated hydrochloric acid (20 ml.) and then separated into neutral and acidic portions. The neutral fraction, upon distillation through the same column, yielded 3.05 g. (24.4%) of 13-fluorotridecyl chloride of b.p. 160.5° (14 mm.) and n_D^{25} 1.4407.

Anal. Calcd. for $C_{13}H_{26}ClF$: C, 65.97; H, 11.00; Cl, 15.01. Found: C, 65.74; H, 10.85; Cl, 14.98.

Methyl 18-Fluorostearate.—Methyl hydrogen sebacate (3.0 g., 0.014 mole) was added to a solution of sodium (0.15 g., 0.0066 mole) in methanol (50 ml.). A current of 1.5 amp. was applied. A solution of methyl hydrogen sebacate (11.4 g., 0.053 mole) and 10-fluorodecanoic acid (10 g., 0.053 mole) was added at such a rate as to maintain the current at 1.5 amp. The reaction was complete after 2.8 hours. After the usual isolation procedure, crude methyl 18-fluorostearate was obtained, of b.p. 143–148° (0.6 mm.), which solidified on standing. This was recrystallized from petroleum ether (60–80°) yielding 0.8 g. (4.8%) of pure methyl 18-fluorostearate, m.p. 33–34°. A small portion of this was hydrolyzed with 10% sodium hydroxide to 18-

fluorostearic acid, which after recrystallization from petroleum ether had m.p. 68–69°. An equal mixture of the samples obtained by this method and by the oxidation of 18-fluoroöctadecanol (see above) had m.p. 68–69°.

Anal. Calcd. for $C_{18}H_{37}O_2F$: C, 72.14; H, 11.70. Found: C, 72.25; H, 11.48.

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LONDON, ONTARIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Isomerization by Base of Alkyl Allyl Sulfides to Alkyl Propenyl Sulfides. The Mechanism of the Reaction¹

BY D. S. TARBELL AND WILLIAM E. LOVETT

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Allyl *n*-hexyl sulfide is isomerized to *n*-hexyl propenyl sulfide by refluxing with 3.7 *M* alcoholic sodium ethoxide; allyl *t*-butyl sulfide behaves similarly. Allyl *n*-hexyl ether is recovered after similar treatment. Diallyl sulfide is isomerized to dipropenyl sulfide, and is also converted in part to an unsaturated mercaptan, 3-mercapto-1,5-hexadiene, by a rearrangement of an allyl group. *N*-Sodiochloro-*p*-bromobenzenesulfonamide has been found to be superior to chloramine-T for characterization of sulfides by formation of sulfilimines. Isomerization of allyl *n*-hexyl sulfide by sodium ethoxide in deuterioethanol gives *n*-hexylpropenyl sulfide containing (by mass spectrometric analysis) considerable quantities of mono- and dideuterated products, indicating that the isomerization proceeds through a carbanion which can exchange with the solvent. The results of the study emphasize the ability of sulfide sulfur, not attached to an aromatic ring, to stabilize a negative charge on the adjacent carbon, presumably through contributions from resonance forms with a decet of electrons around sulfur.

It was shown previously² that aryl allyl sulfides (I, R = aryl or 2-pyridyl) are readily isomerized by aqueous or alcoholic base to the corresponding propenyl sulfides II. This behavior was interpreted as an indication of the ability of the sulfur atom to stabilize the carbanion III by contributions from resonance forms with a decet of electrons around sulfur. It was obviously desirable to know if the isomerization required the presence of an aromatic (or heterocyclic) group attached to sulfur; such groups might contribute to the stability of the carbanion by resonance involving the aromatic nucleus. In the present paper it is shown that the isomerization of alkyl allyl sulfides to alkyl propenyl sulfides does in fact occur readily. Experiments on the isomerization in deuterioethanol indicate that the reaction probably proceeds through a carbanion III which can exchange deuterium with the solvent.

The allyl sulfides I were prepared and characterized by analysis, refractive index, spectroscopic properties and by catalytic reduction to the corresponding *n*-propyl sulfides IV. The isomerization was followed by observing the refractive index, and the propenyl sulfides II were characterized by analysis, spectroscopic properties, preparation of crystalline sulfilimines and by catalytic reduction to the *n*-propyl sulfides IV. These were shown to be identical with authentic samples of the *n*-propyl sulfides by mixed melting points of the crystalline sulfilimines.

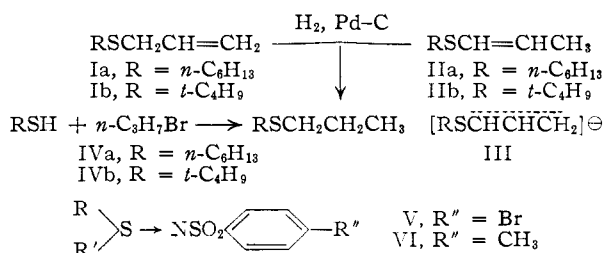
It was found in this work that sulfilimines V prepared from *N*-sodiochloro-*p*-bromobenzenesulfonamide³ were uniformly higher melting and more desirable as derivatives than the corresponding ones (VI) prepared from chloramine-T.

The *n*-hexyl propenyl sulfide (IIa) obtained by isomerization was apparently a mixture of *cis* and *trans* isomers, as was phenyl propenyl sulfide,² because the sulfilimine melted over a range (75–85°),

(1) This research was supported in part by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

(2) D. S. Tarbell and M. A. McCall, *THIS JOURNAL*, **74**, 48 (1952).

(3) R. R. Baxter and F. D. Chattaway, *J. Chem. Soc.*, **107**, 1814 (1915).



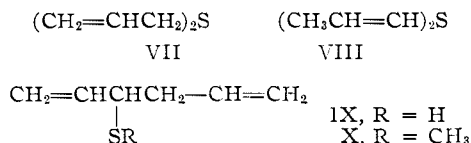
but had the proper percentage composition; it showed a band at 702 cm.^{-1} , which is characteristic of a *cis*-disubstituted double bond, and a band at 956 cm.^{-1} , characteristic of a *trans* disubstituted double bond.²

n-Hexyl propenyl sulfide (IIa) was hydrolyzed by boiling 6 *N* hydrochloric acid to propionaldehyde, which was isolated as the dinitrophenylhydrazone, in 63% yield.⁴

Treatment of allyl *n*-hexyl ether with refluxing sodium ethoxide in ethanol gave 58% of starting material, under conditions which brought about complete isomerization of the sulfide.⁵

The ultraviolet absorption spectra of the alkyl allyl sulfides I and the alkyl *n*-propyl sulfides IV are similar to those reported previously^{6,7}; isomerization of the allyl sulfides to the propenyl compounds leads to a bathochromic shift and increased intensity of absorption, as would be expected from the spectra of vinyl sulfides^{6,8} as compared to allyl sulfides.

Treatment of diallyl sulfide (VII) with sodium ethoxide in ethanol yielded a neutral product, which was apparently a mixture of diallyl (VII), allyl propenyl and dipropenyl (VIII) sulfides; a mercapto compound, probably IX, was also formed.



The diallyl, allyl propenyl and dipropenyl sulfide mixture was heated further with ethanolic sodium ethoxide until the refractive index showed no further change. The analysis agreed with the dipropenyl sulfide structure, and the infrared spectrum showed no bands in the regions (*ca.* 990 and 910 cm.^{-1}) characteristic of a terminal double bond.^{2,9} Further, material which from its refractive index was a mixture of the diallyl, allyl propenyl and dipropenyl sulfides, was reduced catalytically to di-*n*-propyl sulfide; this was shown to

(4) A similar hydrolysis of a substituted vinyl sulfide to a carbonyl compound is reported by G. Rosenkranz, S. Kaufmann and J. Romo, *THIS JOURNAL*, **71**, 3689 (1949).

(5) For a recent example of the greater acidity of a methylene adjacent to divalent sulfur, as compared to one adjacent to oxygen, see W. J. Brehm and T. Levenson, *ibid.*, **76**, 5389 (1954).

(6) H. P. Koch, *J. Chem. Soc.*, 387 (1949).

(7) E. A. Fehnel and M. Carmack, *THIS JOURNAL*, **71**, 84 (1949).

(8) C. C. Price and J. Zomlefer, *ibid.*, **72**, 14 (1950); H. Mohler and J. Sorge, *Helv. Chim. Acta*, **23**, 1206 (1940); K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(9) N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950), reported two strong bands at 986 and 916 cm.^{-1} in the spectrum of diallyl sulfide.

be identical, through the crystalline sulfilimine, with an authentic sample.

The base-soluble compound formed in the isomerization showed infrared absorption in the region characteristic of mercapto groups and of terminal double bonds, but none in the $-\text{CH}=\text{CHCH}_3$ region. The analysis also agreed with structure IX, which appears fairly certain. It is interesting to note that the action of potassium amide in ether on diallyl ether leads to the analogous product,¹⁰ $\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$.

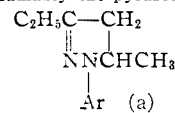
The mercapto group of IX was methylated, giving X. This sulfide was not reduced completely by repeated treatment with hydrogen and palladium-charcoal, as shown by the ultraviolet absorption spectrum. The sulfide X was partially isomerized and partially hydrolyzed to a ketone by refluxing with alcoholic sodium ethoxide. Treatment of this isomerized sulfide with aqueous alcoholic hydrochloric acid gave a carbonyl compound, which behaved, on treatment with dinitrophenylhydrazine, like ethyl propenyl ketone.¹¹

Mechanism of Isomerization.—The isomerization of allyl *n*-hexyl sulfide to the propenyl sulfide by sodium ethoxide was carried out in deuterioethanol,¹² to determine if the isomerization goes through a carbanion XI, which can exchange with the solvent (path 1), or if the isomerization is accomplished through a concerted process (path 2), involving a transition state such as XII. If the reaction is run in deuterioethanol, path 2 should lead to a maximum of one atom of deuterium in the product, and path 1 should lead to incorporation of a maximum of two deuterium atoms. This assumes that there is enough deuterioalcohol present so that the light ethanol produced does not enter into the exchange appreciably.

In the first isomerization of allyl *n*-hexyl sulfide with deuterioethanolic sodium ethoxide, the deuterioethanol apparently contained enough deuterium oxide (or water)¹² to reduce the concentration of

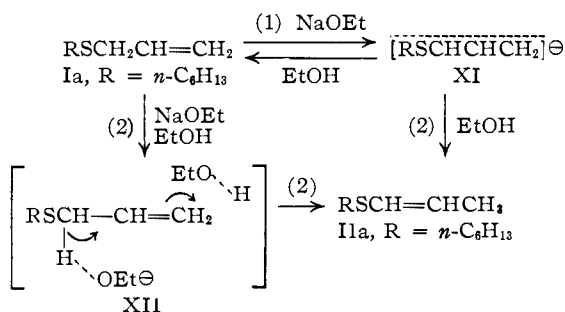
(10) C. R. Hauser and S. W. Kantor, *THIS JOURNAL*, **73**, 1437 (1951).

(11) The dinitrophenylhydrazone of this ketone is reported (P. S. Stutsman and H. Adkins, *ibid.*, **61**, 3303 (1939)) to be red and to melt at $164\text{--}165^\circ$. In two runs, involving treatment of the methyl sulfide X with 3.7 *M* sodium ethoxide in ethanol followed by acid hydrolysis, we obtained a red derivative giving the correct analysis, m.p. $163\text{--}163.5^\circ$. Several synthetic samples of ethyl propenyl ketone (prepared by the method of E. E. Blaise, *Bull. soc. chim.*, **33**, 45 (1905); L. Coppens, *Bull. soc. chim. Belg.*, **38**, 310 (1929); W. G. Young, *et al.*, *THIS JOURNAL*, **68**, 295 (1946)) gave red-orange products, m.p. *ca.* $110\text{--}140^\circ$, when treated with dinitrophenylhydrazine; it was not possible to obtain pure material of m.p. 165° from this mixture, although by repeated recrystallization in two cases an orange product, m.p. $149\text{--}149.5^\circ$, was obtained. It was presumably the pyrazoline (a), Ar = 2,4-(NO₂)₂-



C₆H₄. *Anal.* Calcd. for C₁₂H₁₄N₂O₄: C, 51.78; H, 5.07. Found: C, 51.89; H, 5.30. The formation of pyrazolines from α,β - or β,γ -unsaturated ketones has been noted before (C. F. H. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 222 (1937); L. I. Braddock, *et al.*, *Anal. Chem.*, **25**, 301 (1953)). We also prepared ethyl propenyl ketone from crotonyl chloride and diethylcadmium, in spite of adverse indications from the literature (D. Nightingale and F. Wadsworth, *THIS JOURNAL*, **67**, 416 (1945)), but it gave the same type of derivative with dinitrophenylhydrazine as the ketone prepared by the Blaise method.

(12) Prepared by the method of J. D. Roberts, C. M. Regan and I. Allen, *ibid.*, **74**, 3683 (1952).



ethoxide ion below the lower limit necessary for complete isomerization of the allylic double bond. The refractive index and infrared spectrum indicated that about 50% isomerization had occurred. A weak band was present at 2165 cm.^{-1} , characteristic of the C-D stretching vibration,¹³ showing that some deuterium uptake had occurred. Treatment of the wet deuterioalcohol with more ethyl orthocarbonate gave dry deuterioethanol. Sodium ethoxide in this solvent gave complete isomerization of allyl *n*-hexyl sulfide, judging from the refractive index.

Run 1 was made with the allyl *n*-hexyl sulfide and dry deuterioethanol, whose refractive index and density agreed with the reported values.¹² Run 2 was carried out similarly, using as starting material the partially isomerized and deuterated material described above. In run 3, *n*-hexyl propenyl sulfide (which had been isomerized in the usual manner with sodium ethoxide in light ethanol) was subjected to the same sodium ethoxide-deuterioethanolic conditions used for the isomerizations in runs 1 and 2. Sample 4 was *n*-hexyl propenyl sulfide which had never been in contact with any deuterium-containing compound. The mass spectrometric analyses of these samples are indicated in the table.

MASS SPECTROMETRIC ANALYSES OF *n*-HEXYL PROPENYL SULFIDES FROM SODIUM ETHOXIDE-DEUTEROETHANOL ISOMERIZATION^a

	Samples ^b			
	1	2	3	4
C ₁₀ H ₂₂ S	<0.1	<0.1	0.1	1.0
C ₁₀ H ₂₀₋₂ O ₂ S	0.8	1.0	1.0	0.8
C ₉ H ₂₀ S	(0) ^c	(0) ^c	(0) ^c	1.3
C ₉ H ₁₈ S	34.8	31.0	90.2	96.9
C ₉ H ₁₇ DS	48.0	48.7	8.1	..
C ₉ H ₁₆ D ₂ S	15.6	19.2	0.78	..
C ₉ H ₁₅ D ₃ S	0.47	0.28	0.1	..
C ₉ H ₁₄ D ₄ S	<0.05	<0.05	<0.05	..

^a Mass spectrometric analyses through the courtesy of Dr. D. O. Schissler and Dr. D. P. Stevenson, Shell Development Company, Emeryville, Calif. ^b Results are the percentage of the respective species in the total sample. ^c Assumed.

The interpretation of these results is not entirely clear-cut, because it is not clear what the relative rate of the reaction of the carbanion XI with EtOH, compared to EtOD, should be.¹⁴ Since EtOH is

(13) H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 43.

(14) Ratios of about 5, and of about 12, have been obtained in similar cases for reaction of a carbanion with H₂O, as compared with D₂O (W. D. Walters and K. F. Bonhoeffer, *Z. physik. Chem.*, **A182**, 265 (1938), S. K. Hsü, C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*,

produced in the reaction, the molar ratios (at the concentrations used) are 4.6 EtOD:1 EtOH at 50% isomerization, and 1.75 EtOD:1 EtOH at 100% isomerization. Regardless of the exact value of the isotope effect, the percentage of dideuterated material in samples 1 and 2, compared to the control, indicates that some exchange with the solvent has occurred. Path 1 therefore is strongly indicated. It is conceivable that the exchange is due to some process unrelated to, but simultaneous with, the isomerization reaction; however, it is difficult to formulate such a process which would be different from path 1 or 2. The exchange of the propenyl sulfide with the solvent is clearly too slow to account for the deuterium uptake.

Experimental¹⁵

Allyl *n*-Hexyl Sulfide (Ia).¹⁶—A mixture of *n*-hexyl mercaptan (118 g.), ethyl alcohol (250 ml.) and sodium hydroxide (40 g.) was heated on a steam-bath with stirring until the sodium hydroxide had dissolved. The solution was cooled, allyl bromide (121 g.) was added dropwise with stirring, the solution was refluxed for 10 min., and the alcohol was removed by distillation at atmospheric pressure. The residue was diluted with 200 ml. of water, the layers were separated, and the aqueous layer was extracted with three 40-ml. portions of ether. The water-insoluble layer and ether extracts were combined, washed with water until neutral, dried, the solvent removed and the residue distilled *in vacuo*, with addition of 0.1% hydroquinone. The yield was 127 g. (80%) of material with the following properties: b.p. 78–78.5° (9–10 mm.), *n*_D²⁰ 1.4638, *d*₄²⁰ 0.8626; the ultraviolet spectrum was similar to that of allyl propyl sulfide⁸; the infrared spectrum showed the bands at 987 and 912 cm.⁻¹ characteristic of a —CH=CH₂ group.¹⁷

Anal. Calcd. for C₉H₁₈S: C, 68.29; H, 11.46; *M*_D, 51.26.¹⁸ Found: C, 68.60; H, 11.59; *M*_D, 51.09.

A product of the same b.p. and *n*_D was obtained by the action of allyl bromide on *n*-hexyl lead mercaptide¹⁹; this showed that the alkali used in the first procedure had not brought about partial isomerization.

Allyl *t*-Butyl Sulfide (Ib).—This compound was prepared in 54% yield by the first procedure given above, from 90.2 g. of *t*-butyl mercaptan, 350 ml. of alcohol, 40 g. of sodium hydroxide and 121 g. of allyl bromide; it had the following properties: b.p. 139–141.5°, *n*_D²⁰ 1.4638, *d*₄²⁰ 0.8479; spectroscopic properties similar to those of allyl *n*-hexyl sulfide.⁸

Anal. Calcd. for C₇H₁₄S: C, 64.55; H, 10.83; *M*_D, 42.03. Found: C, 64.76; H, 10.92; *M*_D, 42.31.

Isomerization of the Alkyl Allyl Sulfides to Alkyl Propenyl Sulfides. A. *n*-Hexyl Propenyl Sulfide (IIa).—*n*-Hexyl allyl sulfide (8.0 g., *n*_D²⁰ 1.4688) was refluxed for 12 hr. under nitrogen in a solution prepared from 7.0 g. of sodium and 100 ml. of absolute alcohol. The reaction mixture was diluted with 400 ml. of water and extracted four times with ether. The ether extracts were washed with water until neutral and dried with calcium chloride. Distillation yielded 4.89 g. (61%) of the propenyl sulfide of the

78 (1938)). Deuterium isotope effects are reviewed by K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955), who reports only a small difference for rates of some carbanion reactions with ROH compared to ROD (p. 723).

(15) Melting points corrected; analyses by Miss Annette Smith and by Microtech Laboratories.

(16) General procedure of H. J. Backer and G. J. de Jong, *Rec. trav. chim.*, **67**, 889 (1948).

(17) All attempts to prepare a solid sulfilimine from allyl *n*-hexyl sulfide were unsuccessful. Similarly, the sulfilimine of diallyl sulfide is unstable and likewise unsuitable for characterization (F. Challenger and D. Greenwood, *J. Chem. Soc.*, 26 (1950); A. S. F. Ash, F. Challenger and D. Greenwood, *ibid.*, 1877 (1951)).

(18) Using the value of 7.97 for sulfur (T. S. Price and D. F. Twiss, *ibid.*, **101**, 1264 (1912)), and other values from F. Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911).

(19) E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1529 (1947).

following properties: b.p. 79.5–80.5° (9.5 mm.), n_D^{20} 1.4760, d_4^{20} 0.8646; ultraviolet absorption, 226 (3.73).

Anal. Calcd. for $C_9H_{18}S$: C, 68.29; H, 11.46; *M_D*, 51.26. Found: C, 68.43; H, 11.51; *M_D*, 51.58.

Further heating of the above product with sodium ethoxide under the same conditions for an additional 12 hr. did not change the refractive index, and hence the isomerization was complete. Refluxing allyl hexyl sulfide with 20% alcoholic potassium hydroxide for 3 hr. did not change the refractive index appreciably. The use of more dilute sodium ethoxide than that used above (1.67 *M* compared to 3.70 *M*) gave little isomerization after 12 hr. It was found that 25 cc. of 3.7 *M* sodium ethoxide in ethanol was just as effective as the 100 cc. used above for isomerizing the allyl sulfide.

The sulfilimine, S-propenyl-S-*n*-hexyl-N-*p*-bromobenzenesulfonylsulfilimine,²⁰ was prepared from a solution of 1.70 g. of the sulfide IIa in 15 cc. of alcohol by heating with a solution of 6.7 g. of N-sodiochloro-*p*-bromobenzenesulfonamide (see below) in 80 ml. of 1:1 water-alcohol for 60 min. on the steam-bath. The solid which formed after cooling the mixture in an ice-bath was dissolved in benzene, washed three times with 5% sodium hydroxide solution, and crystallization was induced by adding heptane to the hot benzene solution. The product, obtained after one crystallization from benzene-heptane in 62% yield (2.62 g.), melted at 74–82° and after repeated crystallization from benzene-heptane and alcohol-water mixtures melted over the same range.

Anal. Calcd. for $C_{16}H_{22}BrNO_2S_2$: C, 45.91; H, 5.65. Found: C, 46.08; H, 5.41.

B. *t*-Butyl Propenyl Sulfide (IIb).—Allyl *t*-butyl sulfide (32.0 g., n_D^{20} 1.4638) was isomerized by the procedure described above, using a solution of 28 g. of sodium in 400 ml. of absolute alcohol. The product, 21.1 g. (66%), had the following properties: b.p. 139.1–140.8°, n_D^{20} 1.4700, d_4^{20} 0.8522; ultraviolet absorption, 224 (3.49) and 248 (3.41).

Anal. Calcd. for $C_7H_{14}S$: C, 64.55; H, 10.83; *M_D*, 42.03. Found: C, 64.74; H, 10.90; *M_D*, 42.60.

The sulfilimine was prepared by shaking the sulfide (0.56 g.) with an aqueous solution of N-sodiochloro-*p*-bromobenzenesulfonamide (1.34 g.) for 30 min. The product, which solidified on standing overnight, was worked up as above. The yield, after several recrystallizations at room temperature from benzene-heptane, was 0.13 g. (8%), m.p. 93.5–95.5° dec. The compound appears to decompose when heated in benzene solution, and must be recrystallized from cold solvents.

Anal. Calcd. for $C_{13}H_{18}BrNO_2S_2$: C, 42.86; H, 4.98. Found: C, 42.88; H, 5.18.

N-Sodiochloro-*p*-bromobenzenesulfonamide.—The preparation of this compound is described because it may be useful for characterizing sulfides. *p*-Bromobenzenesulfonamide (91.6 g., crude material satisfactory) was dissolved in 3050 ml. of a saturated solution of calcium hypochlorite, prepared by adding well-ground chlorinated lime to water until undissolved solid remained in the bottom and filtering off the solid. To the filtered solution, cooled in an ice-bath, was added 1000 cc. of 50% aqueous acetic acid with slow stirring, until the precipitation was complete. The product was filtered, washed with a little water and dried well. The crude material was suitable for conversion to the sodium salt.²¹ Recrystallization of a sample of the crude material from chloroform-petroleum ether yielded a product of m.p. 108–109.5°; the reported³ value is 108°.

The crude dry N,N-dichloro compound (94.2 g.) was added in small quantities to 900 ml. of 10% aqueous sodium hydroxide solution which was heated to about 80°. After each addition, the mixture was stirred gently until the solution became clear. When the addition was complete, the solution was cooled, the resulting crystals were filtered, washed with a little brine and dried in a desiccator over calcium chloride. The yield was 109 g. The first crop of crystals showed 91% of the theoretical oxidizing power by the iodide-thiosulfate procedure.

S,S-Di-*n*-butyl-N-*p*-bromobenzenesulfonylsulfilimine.—This was prepared as described above for *t*-butyl propenyl sulfide, from 1.3 g. of di-*n*-butyl sulfide and 2.4 g. of N-

sodiochloro-*p*-bromobenzenesulfonamide, and was recrystallized from benzene-heptane and alcohol-water, m.p. 104–105°. The di-*n*-butylsulfilimine derived from *p*-toluenesulfonamide²² melts at 65.5°.

Anal. Calcd. for $C_{14}H_{22}BrNO_2S_2$: C, 44.20; H, 5.83. Found: C, 44.44; H, 5.94.

Reduction of *n*-Hexyl Allyl Sulfide (Ia) to *n*-Hexyl *n*-Propyl Sulfide.²—Palladium-on-Norite catalyst²³ (10 g., 10%) was stirred with hydrogen in 125 cc. of alcohol until there was no further absorption. The catalyst was filtered by suction, washed with alcohol and returned to the reduction flask; allyl *n*-hexyl sulfide (15.0 g., n_D^{20} 1.4688) in 125 cc. of alcohol was added, and the mixture was stirred for 24 hr. at which time 2300 cc. (98%) of hydrogen had been absorbed. The catalyst was removed by filtration, and the alcohol was removed by distillation at atmospheric pressure. Water (200 ml.) was added to the residue, the layers were separated, and the aqueous layer was extracted with three portions of ether. The combined water-insoluble layers were washed three times with aqueous sodium hydroxide, washed with water until neutral, and dried. The solution yielded after distillation *in vacuo*, 8.3 g. of *n*-hexyl propyl sulfide, b.p. 79.5–79.7° (9.5 mm.), n_D^{20} 1.4555, d_4^{20} 0.8448.

Anal. Calcd. for $C_9H_{20}S$: C, 67.43; H, 12.58. Found: C, 67.15; H, 12.57.

The *p*-toluenesulfonylsulfilimine was prepared by shaking the sulfide with an aqueous solution of chloramine-T. The product (43%) was crystallized and purified as described in other cases, and melted at 65–65.5°.

Anal. Calcd. for $C_{16}H_{27}NO_2S_2$: C, 58.32; H, 8.26. Found: C, 58.66; H, 8.39.

The *p*-bromobenzenesulfonylsulfilimine, prepared similarly, crystallized more readily than the above derivative, and melted at 101.5–102.5°.

Anal. Calcd. for $C_{15}H_{24}BrNO_2S_2$: C, 45.68; H, 6.13. Found: C, 45.93; H, 6.19.

Both of these sulfilimines were prepared from samples of *n*-hexyl *n*-propyl sulfide prepared in three ways: (1) as above, (2) by reduction of the propenyl compound and (3) by reaction of *n*-hexyl mercaptan and propyl bromide. The derivatives from the three sources were shown to be identical by mixed m.p. determinations.

***n*-Hexyl *n*-Propyl Sulfide. A. By Reduction of the Propenyl Sulfide.**—Reduction of 15.3 g. of the propenyl sulfide IIa by the procedure described above gave 72% of the propyl sulfide, b.p. 78.8–79.5° (9 mm.), n_D^{20} 1.4554.

B. By Alkylation.—Hexyl mercaptan (14.7 g.), alcohol (35 ml.), sodium hydroxide (5.0 g.) and *n*-propyl bromide (15.3 g.) were treated as described for the preparation of allyl *n*-hexyl sulfide. The hexyl propyl sulfide, obtained in 74% yield, had the physical properties reported above.

Allyl *n*-Hexyl Ether.—*n*-Hexyl iodide (101 g.) was added slowly with stirring to a solution of 11.5 g. of sodium in dry allyl alcohol (50 g., n_D^{20} 1.4135), and the mixture was refluxed for 22 hr. The reaction mixture was worked up in the usual way, and yielded 37.1 g. (55%) of allyl *n*-hexyl ether, b.p. 159–165°, n_D^{20} 1.4204, d_4^{20} 0.8064. The product was refractionated three times for analysis, and showed the properties b.p. 161.0–161.3°, n_D^{20} 1.4200.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.69; H, 12.87.

Attempted Isomerization of Allyl *n*-Hexyl Ether.—This ether (8.0 g., n_D^{20} 1.4200) was refluxed under nitrogen for 12 hr. with 3.7 *M* sodium ethoxide in ethanol. The mixture was worked up as described above for the isomerization of allyl hexyl sulfide, and yielded, as sole product, 58% (4.66 g.) of starting material, b.p. 159.5–161°, n_D^{20} 1.4200.

***t*-Butyl *n*-Propyl Sulfide. A. By Alkylation.**—*t*-Butyl mercaptan (25.0 g.) was alkylated using 80 ml. of alcohol, 9.1 g. of sodium hydroxide and 28.0 g. of *n*-propyl bromide, using the procedure described above for Ia. The product obtained after one distillation (18.8 g., 62%) was refractionated, and then showed the following properties: b.p. 138–138.1°, n_D^{20} 1.4452, d_4^{20} 0.8268.

Anal. Calcd. for $C_7H_{16}S$: C, 63.56; H, 12.20. Found: C, 63.69; H, 12.16.

(22) C. W. Todd, J. H. Fletcher and D. S. Tarbell, *THIS JOURNAL*, **65**, 350 (1943).

(23) R. Mozingo, *Org. Syntheses*, **26**, 78 (1946).

(20) For naming of sulfilimines, see C. A., **39**, 5929 (1945).

(21) Cf. F. D. Chattaway, *J. Chem. Soc.*, **87**, 148 (1905).

The *p*-toluenesulfonylsulfilimine melted, after several crystallizations from benzene-heptane, at 81.5–82.5°.

Anal. Calcd. for $C_{14}H_{23}NO_2S_2$: C, 55.78; H, 7.69. Found: C, 55.69; H, 7.74.

The *p*-bromobenzenesulfonylsulfilimine melted, after several crystallizations from benzene-heptane, at 115–116° dec.

Anal. Calcd. for $C_{13}H_{20}BrNO_2S_2$: C, 42.62; H, 5.50. Found: C, 42.29; H, 5.61.

The infrared spectrum of this *p*-bromobenzenesulfonylsulfilimine was identical with that obtained from the corresponding sulfilimine prepared from the reduced *t*-butyl propenyl sulfide (see below). Mixed meltings of samples of these two sulfilimines obtained from samples of *t*-butyl *n*-propyl sulfide, prepared by the preceding method and by the two succeeding methods showed that the three samples of the sulfide were identical.

B. By Reduction of Allyl *t*-Butyl Sulfide (Ib).—This sulfide (15 g., n_D^{20} 1.4638) was reduced catalytically in alcohol, using 15 g. of 5% palladium-on-Norite, by the described procedure. The product (7.65 g., 51%) had a slightly higher refractive index (1.4473) than the synthetic sulfide (1.4452), but yielded the same crystalline sulfilimine.

C. By Reduction of *t*-Butyl Propenyl Sulfide (IIb).—The sulfide (15 g., n_D^{20} 1.4700) was reduced catalytically, using 20 g. of 5% palladium-on-Norite. The distilled product (5.22 g., 35%) showed n_D^{20} 1.4458.

Acid Hydrolysis of *n*-Hexyl Propenyl Sulfide (IIa) to Propionaldehyde.—*n*-Hexyl propenyl sulfide (5 g., n_D^{20} 1.4760) in 250 ml. of ethanol was refluxed on a steam-bath for 2 hr. with 37 ml. of 6 *N* hydrochloric acid. During the heating, nitrogen was passed over the solution and into a trap containing dinitrophenylhydrazine in aqueous alcoholic sulfuric acid.²⁴ After refluxing for 5 min., an orange precipitate started to form in the trap. After 2 hr., the precipitate in the trap was collected and crystallized twice from water-alcohol. The product (0.93 g., 63%) melted at 153–153.5° and gave no depression on mixed m.p. with an authentic sample of propionaldehyde 2,4-dinitrophenylhydrazone.²⁵

Action of Ethanolic Sodium Ethoxide on Diallyl Sulfide; 3-Mercaptohexadiene-1,5.—Diallyl sulfide²⁶ (19.0 g., n_D^{20} 1.4896) was refluxed under nitrogen for 12 hr. in a solution of 16 g. of sodium in 240 ml. of absolute alcohol. The reaction mixture was diluted with water and extracted four times with ether; the extracts were washed with water, dried and fractionated *in vacuo*, giving 1.9 g. of material with the following properties: b.p. 61.5–62° (40 mm.), n_D^{20} 1.4938; ultraviolet spectrum, 236 (3.78). The infrared spectrum showed a strong band at 992, and a broad band in the range 956–909 cm^{-1} (center at 934 cm^{-1}), indicating the presence of both allyl and propenyl groups. Further isomerization of this material to dipropenyl sulfide is described below.

The basic layer from the extraction of the reaction mixture was acidified with concd. hydrochloric acid, extracted four times with ether, and the extracts were washed with water and dried. Fractionation of the product yielded 3.47 g. (18%) of material, b.p. 63.5–64.5° (39 mm.), which, after refractionation, had the following properties: b.p. 61.5–62.5° (37 mm.), n_D^{20} 1.5029; ultraviolet absorption, 234 (3.56); infrared bands, among others, at 2532, 995 and 915 cm^{-1} .

Anal. Calcd. for $C_8H_{10}S$: C, 63.10; H, 8.83. Found: C, 63.01; H, 9.07.

In subsequent isomerizations, yields of neutral material were 17 and 28%, and of mercaptan, 24 and 31%. There was a higher boiling residue, probably disulfide.

Dipropenyl Sulfide (VIII).—The neutral fraction (33.1 g., n_D^{20} 1.4955) from isomerization of diallyl sulfide as above, was refluxed for 12 hr. in a solution of 36 g. of sodium in 400 ml. of absolute alcohol. The product, obtained in

the usual way, was 10.1 g. (31%), n_D^{20} 1.5092. This product (7.8 g.) was refluxed again with 3.7 *M* sodium ethoxide, and yielded 3.4 g. of material, n_D^{20} 1.5101. Refractionation yielded dipropenyl sulfide of the following properties: b.p. 62.9–63.2° (38 mm.), n_D^{20} 1.5108, d_4^{20} 0.9012; ultraviolet absorption, 238–239 (3.94); infrared, strong band at 941–934 and at 1610 cm^{-1} , but no absorption in the 990 and 910 cm^{-1} regions, and hence no terminal double bonds.

Anal. Calcd. for $C_8H_{10}S$: C, 63.10; H, 8.83; *M_D*, 36.94. Found: C, 63.09; H, 8.80; *M_D*, 37.95.

Reduction to Di-*n*-propyl Sulfide.—A sample of incompletely isomerized allyl propenyl sulfide (4.8 g., n_D^{20} 1.5010) was reduced with hydrogen and 5% palladium-on-Norite (12.5 g.). After 39 hr., 86% of the calculated amount of hydrogen had been adsorbed. The product (1.38 g., n_D^{20} 1.4473) was obtained by distillation in a short-path still and was shown to be di-*n*-propyl sulfide by preparation of the crystalline sulfilimine, m.p. 110–111.5°; a mixed m.p. with an authentic sample showed no depression.

Hexadienyl Methyl Sulfide (X).—To a cooled solution of the mercaptohexadiene IX (15.0 g., n_D^{20} 1.5025) in 5.25 g. of sodium hydroxide in 50 ml. of alcohol was added during 1 hr. 18.7 g. of methyl iodide, and the mixture was refluxed for 2 hr. The mixture was diluted with water, extracted with four portions of ether; the ether extracts were washed with aqueous alkali, and were then dried and distilled. The yield of once-distilled material was 8.1 g.; redistillation yielded an analytical sample with the following properties: b.p. 78.2–78.8° (38 mm.), n_D^{20} 1.5017; ultraviolet absorption, 232 (3.79).

Anal. Calcd. for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.75; H, 9.34.

Ethyl Propenyl Ketone.²⁷—To a cold solution of ethylmagnesium bromide (from 21.8 g. of ethyl bromide and 4.9 g. of magnesium in 100 ml. of ether) was added 29.3 g. of anhydrous cadmium chloride with stirring over a 5-min. period. After stirring and refluxing gently for 30 min., the reaction mixture gave a negative Gilman test for the Grignard reagent. Most of the ether was removed by distillation, 65 ml. of benzene was added and an additional 10–15 ml. of solvent was removed. Crotonyl chloride (10.4 g.) dissolved in 70 ml. of benzene was added to the cooled reaction mixture. Some heat was evolved, and the mixture was kept around 40° by cooling. After the addition was complete, the reaction mixture was stirred for 10 min., refluxed for 1 hr., and then cooled in an ice-bath, while it was decomposed with 120 g. of ice, followed by 50 ml. of cold 20% sulfuric acid. The layers were separated, the aqueous layer was extracted twice with ether, and the combined water-insoluble layers were washed four times with sodium carbonate, with water and dried. Distillation yielded 1.45 g. of product, with b.p. 137.5–138°, n_D^{20} 1.4398; ultraviolet absorption, 221 (4.0). The physical properties agree well with those reported¹¹ for material prepared by the modified Blaise method (allyl bromide, zinc and propionitrile), and the method is more convenient. The yield probably can be improved.

Preparation of Deuteroethanol.—Ethyl orthocarbonate was prepared according to Tieckelmann and Post²⁸ from 185 g. of sodium, 4 l. of absolute ethanol and 262 g. of perchloromethyl mercaptan.²⁹ The yield was 207 g. (77%) of material, b.p. 159–161.5°, n_D^{20} 1.3933; reported³⁰ values are b.p. 158–161, n_D^{20} 1.3905.

The reported preparation¹² of deuteroethanol from ethyl orthocarbonate was modified as follows: Freshly distilled ethyl orthocarbonate (214 g., n_D^{20} 1.3933), containing one drop of concentrated sulfuric acid was placed in a 500-ml. Claisen flask with a water condenser attached. Deuterium oxide (19.9 g., 99.8%) was added in 4- or 5-drop portions to this solution. The reaction mixture was heated gently on a steam-bath after each addition, until the deuterium oxide had reacted (and the solution appeared homogeneous). It is important to add the deuterium oxide slowly so that the reaction does not get out of control. As the reaction proceeded, slightly larger amounts of the deuterium oxide could be added safely. After about half of the deu-

(27) General procedure of J. Cason, *THIS JOURNAL*, **68**, 2078 (1946); *Chem. Revs.*, **40**, 15 (1947).

(28) H. Tieckelmann and H. W. Post, *J. Org. Chem.*, **13**, 265 (1948).

(29) We are indebted to the Stauffer Chemical Co. for this material.

(30) J. D. Roberts and R. E. McMahon, *Org. Syntheses*, **32**, 68 (1952).

(24) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(25) C. F. H. Allen, *THIS JOURNAL*, **52**, 2955 (1930).

(26) We have prepared a solid derivative by the action of 2,4-dinitrobenzenesulfonyl chloride on diallyl sulfide (*cf.* N. Kharasch and C. M. Buess, *THIS JOURNAL*, **71**, 2724 (1949)) in ethylene chloride; the product, after several crystallizations from absolute alcohol, melted at 92–93°. *Anal.* Calcd. for $C_{12}H_{14}ClN_2O_4S_2$: C, 41.32; H, 3.76. Found: C, 41.49; H, 3.93.

terium oxide had been added, some deuterioalcohol was distilled out of the reaction mixture, b.p. 79.5–80°. After all the deuterium oxide had been added, the crude deuterioalcohol was distilled from the reaction mixture, b.p. 79–83°. The yield was 82.3 g. (88%). The crude deuterioalcohol was then heated at reflux successively: with 38 g. of freshly distilled ethyl orthocarbonate, containing one drop of concentrated sulfuric acid for 12.5 hours; and finally with 75 g. of freshly distilled ethyl orthocarbonate containing one drop of concentrated sulfuric acid for 14.5 hours. After this treatment, the deuterioalcohol was purified by fractional distillation using a ten-inch, helices-packed column, b.p. 77.5–79°, n_{D}^{20} 1.3635. This main fraction was redistilled using the same column, b.p. 77–78°, n_{D}^{20} 1.3620, d_{4}^{25} 0.804. The yield was 49.2 g. (53%). The reported¹² values are b.p. 78.5–79°, n_{D}^{25} 1.3583,¹² d_{4}^{25} 0.801.³¹

Isomerization of Allyl *n*-Hexyl Sulfide with Sodium Ethoxide in Deuterioalcohol.—The sulfide (8.0 g., n_{D}^{20} 1.4688)

(31) T. Chang and Y. Wei, *C. A.*, **42**, 7236 (1948).

was refluxed for 14.5 hr. under nitrogen in a solution prepared from 1.4 g. of sodium and 20 ml. of deuterioalcohol (n_{D}^{20} 1.3620). The solution was worked up as described above, and the product (5.03 g., 63%) was obtained after two distillations; the center cut, which was taken for the mass spectrometric analyses, had the following properties: b.p. 86.7–86.9° (12.5–13 mm.), n_{D}^{20} 1.4762.

The other runs in deuterioethanol were carried out similarly.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

gem-Dihalides from the Hofmann Degradation of α -Haloamides¹

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α -Haloamides of acetic, propionic, butyric, isobutyric, methylethylacetic and diethylacetic acids were treated with sodium hypobromite to give *gem*-dihalides. The yields varied from 95% to less than 10%. Cyanate ion formation was found to accompany *gem*-dihalide formation. An α -haloisocyanate was prepared independently and shown not to be an intermediate in the formation of the *gem*-dihalides. Since the corresponding *N*-bromo- α -chloroamide under Hofmann conditions gave the *gem*-dihalide, but the *N*-bromoamide in the presence of bromide ion and absence of base did not react, the *N*-bromoamide ion is indicated as the intermediate which reacts to give the *gem*-halide.

During a previous investigation, which involved the characterization of α -halonitriles, Hofmann degradations of the corresponding amides to ketones were used to show that the halogen atoms were in the α -position.⁴ When α -chloro- α -methylbutyramide was subjected to the Hofmann reaction, only a 10% yield of ketone resulted. The identification of the main product from the reaction as a *gem*-dihalide led to the present investigation, which indicates that the reaction has more than limited applicability and, more important, that the conditions of the Hofmann reaction can be varied to increase either the yield of ketone or the yield of *gem*-dihalide.

Kishner,⁵ in 1905, attempted the preparation of cyclobutanone *via* a Hofmann degradation of α -bromocyclobutanecarboxamide. The yield of ketone was low, and the other product isolated was considered by Kishner to be 1,1-dibromocyclobutane. To confirm his belief he subjected α -bromo-isobutyramide to the same conditions and obtained in 12% yield an oil which contained a small amount of material assumed to be 2-bromopropylene. The main constituent of the oil was the *gem*-dihalide, 2,2-dibromopropane, which was identified by physical constants and by conversion to acetone.

A recent report by Rodionov, Alekseyeva and Vaver⁶ on an investigation of the Hofmann degra-

dation with α -bromoaliphatic amides describes the isolation of the corresponding ketones with no mention of *gem*-dihalides. However, Husted and Kohlhas⁷ in a study of the Hofmann degradation of aliphatic perfluoroamides report further examples of the formation of *gem*-dihalides (perfluorohalides) and indicate that the reaction proceeds through the *N*-bromoamide.

In the present study, Kishner's first experiments with α -bromo-isobutyramide were repeated and his results verified. Approximately 10% of 2,2-dibromopropane and 68% of acetone could be isolated from the Hofmann degradation. *Significantly*, a fivefold increase in the yield of *gem*-dihalide was gained by a simple variation of the experimental technique. In the latter experiment, 54% of *gem*-dihalide, 10% of acetone and 31% of α -hydroxyisobutyric acid were isolated. The two procedures differed only in that the first reaction mixture consisting of amide and sodium hypobromite was steam distilled immediately (procedure B) while the latter reaction mixture was allowed to remain at 0–5° for 66 hours (procedure A).

The corresponding α -chloro-isobutyramide, when subjected to the latter procedure, gave 95% of 2-chloro-2-bromopropane; procedure B gave only 29% yield of the mixed *gem*-dihalide.

Table I records the yields of *gem*-dihalides obtained from α -haloamides of acetic, propionic, butyric, isobutyric, methylethylacetic and diethylacetic acids. The carbonyl compounds were isolated and identified as 2,4-dinitrophenylhydrazone derivatives. The α -hydroxyacids were isolated by con-

(7) D. R. Husted and W. L. Kohlhas, *THIS JOURNAL*, **76**, 5141 (1954).

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(2) Supported in part by a Grant-in-aid from the Research Corporation of New York.

(3) Ethyl Corporation Predoctoral Fellow.

(4) C. L. Stevens and T. H. Coffield, *THIS JOURNAL*, **73**, 103 (1951).

(5) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **37**, 103, 106 (1905); *Chem. Centr.*, **76**, 1, 1219, 1220 (1905).

(6) V. M. Rodionov, E. N. Alekseyeva and V. A. Vaver, *Zhur. Obschei Khim.*, **23**, 1842 (1953).