

sodium salt of hydroxymethylene methyl isobutyl ketone was degraded to 2-isobutylpyridine. There seems to be no simple rule to predict the

point of condensation of ethyl formate with an unsymmetrical ketone.

EVANSTON, ILLINOIS

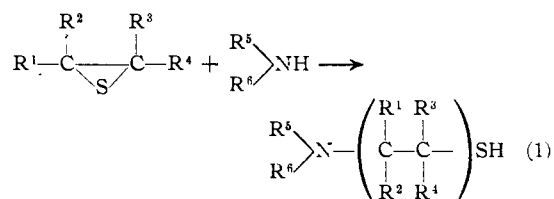
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Synthesis of Amino Mercaptans from Olefin Sulfides¹

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The need for large quantities of mercaptans in the synthetic rubber industry has prompted the investigation of various reactions of possible use in the large-scale production of these substances. The present report concerns a study of the preparation of amino mercaptans by the reaction of olefin sulfides and amines in accordance with equation 1.

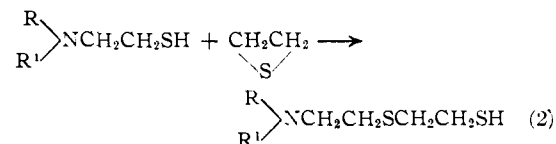


The reaction has been used previously for the preparation of certain amino mercaptans from ethylene sulfide or propylene sulfide and primary or secondary amines.³ A number of new amino thiols now have been prepared from these olefin sulfides and others have been obtained from isobutylene sulfide and cyclohexene sulfide.

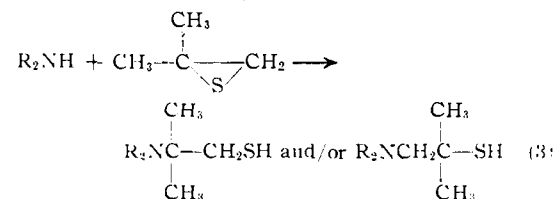
The cyclic sulfides were prepared by the reaction of the oxides with potassium thiocyanate in aqueous or dilute alcoholic solutions.⁴ The spontaneous polymerization of ethylene sulfide, noted by previous investigators⁵ to occur even at 0° was found to be effectively inhibited by the addition of a small amount of an aliphatic mercaptan.⁶ Cyclohexene sulfide could be stored in the refrigerator for periods of several days without polymerization, and samples of isobutylene sulfide have undergone no significant change on storage at room temperature for about three months.

Reactions of the cyclic sulfides with secondary amines were carried out without catalyst or solvent at temperatures near 100°, the period of reaction being ten to twenty hours. The yields were not improved by the addition of phenol,³ aluminum chloride or the sodium derivative of the amine. The yields of amino mercaptans were

adversely affected by the presence of bulky substituents on the nitrogen atom and by increasing degree of substitution in the sulfide ring. The product from ethylene sulfide and di-*n*-butylamine was obtained in 70–80% yields, whereas that from the same sulfide and di-*n*-heptylamine was obtained in only 40 to 55% yields. Only negative results were obtained from ethylene sulfide and diphenylamine or dicyclohexylamine. Isobutylene sulfide reacted with secondary amines such as di-*n*-butylamine only to the extent of 15 to 25%, but the yields from this sulfide and primary amines or cyclic secondary amines such as piperidine and morpholine were in the range of 55 to 75%. Propylene sulfide was treated with only one amine, di-*n*-amylamine, with which it reacted to the extent of 50 to 60%. From the one trial made with it, cyclohexene sulfide appears to be less reactive than isobutylene sulfide; only a 35% yield of the amino mercaptan was obtained from cyclohexene sulfide and piperidine. In most of the reactions small amounts of the products formed by reaction of the amino mercaptan with more of the sulfide were produced (equation 2).³ The presence of an excess of the amine repressed this side reaction.



Unsymmetrically substituted olefin sulfides might be expected to yield one or both of two isomeric products in the reaction with secondary amines. For example, the possible products from isobutylene sulfide are a primary and a tertiary mercaptan (equation 3). The Rheinboldt color test⁷ indicates the products to be tertiary mer-



captans. These amino mercaptans react with iodine to give sulfenyl iodides (equation 4) in good yields, indicating that the substances con-

(7) Rheinboldt, *Ber.*, **60**, 184 (1927).

(1) This work was carried out under contract Ru RSR 95 between Rubber Reserve Company and the University of Illinois.

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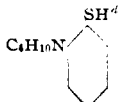
(3) German Patent 631,016; *C. A.*, **30**, 6908 (1936).

(4) French Patent 797,621; *ibid.*, **30**, 7122 (1936).

(5) Barr and Speakman, *J. Soc. Dyers Colourists*, **60**, 238 (1944).

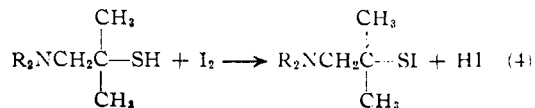
(6) U. S. Patent 2,185,660; *C. A.*, **34**, 2865 (1940).

TABLE I
 AMINO MERCAPTANS FROM AMINES AND OLEFIN SULFIDES

Amine	Structure of amino mercaptan	B. p. or m. p., °C. (mm.)	n_D^{20}	Analyses, %				Yield, %	
				Carbon		Hydrogen			Sulfur
				Calcd.	Found	Calcd.	Found	Calcd.	Found
A. From Ethylene Sulfide									
n -C ₇ H ₁₅ NH ₂	CH ₃ (CH ₂) ₆ NHCH ₂ CH ₂ SH	70-71 (2.5)	1.4703	61.65	61.93	12.08	11.87	17.29	16.86 ^a
	Acetyl derivative	160-162 (4)							
(n -C ₄ H ₉) ₂ NH	(n -C ₄ H ₉) ₂ NCH ₂ CH ₂ SH	74-75 (2)	1.4635						70-80
	Hydrochloride	M. p. 112-113		53.19	53.19	10.71	10.57		
(n -C ₅ H ₁₁) ₂ NH	(n -C ₅ H ₁₁) ₂ NCH ₂ CH ₂ SH	86-90 (2.5)	1.4643					14.75	14.91 ^a
	Hydrochloride	M. p. 85-86							
(n -C ₇ H ₁₅) ₂ NH	(n -C ₇ H ₁₅) ₂ NCH ₂ CH ₂ SH	127-128 (2)	1.4660					11.72	11.17 ^a
(n -C ₈ H ₁₇) ₂ NH	(n -C ₈ H ₁₇) ₂ NCH ₂ CH ₂ SH	146-148 (2)	1.4658					10.63	9.80 ^a
Piperidine	C ₆ H ₁₀ NCH ₂ CH ₂ SH	70-72 (9)	1.5015	57.87	57.63	10.41	10.53		77
		56-57 (4)							
C ₄ H ₉ NH ₂	C ₆ H ₅ NHCH ₂ CH ₂ SH	95-97 (2.5)	1.6040	62.70	62.49	7.24	7.31	20.92	20.88 ^a
	Acetyl derivative	M. p. 65-66		61.50	61.48	6.71	6.96		
	C ₆ H ₅ N(CH ₂ CH ₂ SH) ₂ ^b	138-140 (2)	1.6248	56.29	57.02	7.09	7.40		3
B. From Propylene Sulfide									
(n -C ₄ H ₉) ₂ NH	(n -C ₄ H ₉) ₂ CH ₂ CH(CH ₃)SH ^c (?)	86-87 (2)	1.4634	67.46	67.58	12.63	12.48	13.85	13.77 ^a
C. From Isobutylene Sulfide									
n -C ₇ H ₁₅ NH ₂	n -C ₇ H ₁₅ NHCH ₂ C(CH ₃) ₂ SH ^d	83-86 (2)	1.4630 ^e					15.76	15.82 ^a
	Acetyl derivative	128-131 (2.5)	1.4800 ^e						
	Sulfenyl iodide	Dec. 200-225°		40.12	40.09	7.35	7.61		
n -C ₁₁ H ₂₃ NH ₂	n -C ₁₁ H ₂₃ NHCH ₂ C(CH ₃) ₂ SH	138-141 (3)							52.5
	Sulfenyl iodide	Dec. 210-230°		48.11	47.95	8.58	8.93		
(C ₂ H ₅) ₂ NH	(C ₂ H ₅) ₂ NCH ₂ C(CH ₃) ₂ SH	94-95 (52)	1.4597 ^f	59.56	60.08	11.87	11.78		43
	Sulfenyl iodide	M. p. 175-177		33.45	33.58	6.32	6.53		
		(dec.)							
(n -C ₄ H ₉) ₂ NH	(n -C ₄ H ₉) ₂ NCH ₂ C(CH ₃) ₂ SH	89-90 (2)	1.4748 ^e						15-25 ^a
	Sulfenyl iodide	M. p. 176-178		41.98	41.82	7.63	8.30		
		(dec.)							
(n -C ₄ H ₉) ₂ NH	(n -C ₄ H ₉) ₂ NCH ₂ C(CH ₃) ₂ SH	85-90 (2)	1.4653 ^e						26.5 ^a
	Hydrochloride	M. p. 85-86							
	Sulfenyl iodide	M. p. 147-148		45.28	45.15	8.14	8.52		
(<i>iso</i> -C ₄ H ₉) ₂ NH	(<i>iso</i> -C ₄ H ₉) ₂ NCH ₂ C(CH ₃) ₂ SH	83-86 (2)	1.4677						13
	Sulfenyl iodide	M. p. 205-206		45.28	44.99	8.14	8.31		
		(dec.)							
Morpholine	C ₄ H ₈ ONCH ₂ C(CH ₃) ₂ SH	81-82 (6.5)	1.4886					18.29	17.63 ^a
Piperidine	C ₆ H ₁₀ NCH ₂ C(CH ₃) ₂ SH	47 (2.5)	1.4840	62.37	62.70	11.05	11.15		61
	Hydrochloride	M. p. 198-199		51.53	51.82	9.61	9.75	15.28	14.72 ^a
3-Methyl- piperidine	C ₆ H ₁₂ NCH ₂ C(CH ₃) ₂ SH	51-53 (2)	1.4782					17.11	16.67 ^a
4-Ethyl- piperidine	C ₇ H ₁₄ NCH ₂ C(CH ₃) ₂ SH	74-76 (2.5)	1.4894	65.61	65.80	11.51	11.62		77
Piperazine	HS(CH ₂) ₂ CCH ₂ NC ₄ H ₈ NCH ₂ C(CH ₃) ₂ SH ^b	M. p. 127-131		54.91	54.75	9.99	9.85		50
D. From Cyclohexene Sulfide									
Piperidine		97-99 (1)	1.5190					16.08	15.40 ^a

^a Mercaptan sulfur, by method of Kolthoff and Harris. ^b Prepared from two moles of sulfide per mole of amine. ^c Prepared from 1.25 moles of amine per mole of sulfide. ^d Used two moles of amine per mole of sulfide. ^e n_D^{20} .

sist largely, if not solely, of the tertiary mercaptan isomers. The structure of the product from propylene sulfide and di-*n*-amylamine was not



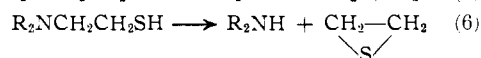
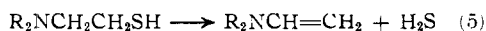
investigated. By analogy with the products from isobutylene sulfide it would be expected to consist largely of the secondary mercaptan; however, the product from *n*-butylamine and two molecules of propylene sulfide has been described³ as the primary dimercaptan (C₄H₉N[CH(CH₃)CH₂SH]₂).

The primary mercaptans prepared from ethyl-

ene sulfide and secondary amines are less stable in the atmosphere than simple unsubstituted mercaptans, but they can be stored under nitrogen. Most of the compounds were analyzed by the Kolthoff amperometric titration⁸ of mercaptan groups. Samples which had been allowed to stand in alcohol solutions without protection from the atmosphere had low mercaptan sulfur contents; treatment of such solutions with zinc

(8) The authors are indebted to Dr. H. A. Laitinen and Mr. W. P. Jennings for the mercaptan analyses; mixtures of primary and tertiary mercaptans were analyzed by an argentimetric-iodimetric titration and total mercaptan sulfur by an amperometric titration, both devised by Professor I. M. Kolthoff of the University of Minnesota (Kolthoff, private communication; Kolthoff and Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946)).

amalgam increased the mercaptan sulfur content. The higher-boiling amino mercaptans derived from either ethylene sulfide or isobutylene sulfide could not be obtained in the pure state by distillation under pressures as low as 2 mm. Successive redistillations of such substances gave distillates of successively lower mercaptan sulfur content, indicating that the amino mercaptans undergo thermal decomposition probably according to either or both of the reactions shown in equations 5 and 6.



Experimental

I. Preparation of the Sulfides

A. Isobutylene Sulfide.—To a vigorously stirred solution of 97 g. (1 mole) of potassium thiocyanate in 100 ml. of water was added dropwise 72 g. of isobutylene oxide. The addition required five hours. The top layer was then separated from the aqueous layer and stirred with a fresh solution of 50 g. of potassium thiocyanate in 100 ml. of water for an additional five-hour period. The temperature of the reaction mixture was kept below 40°. The crude sulfide was dried over calcium chloride and fractionally distilled. The yield was 64 g. (73%) of clear, colorless liquid boiling at 84–86°, n_D^{20} 1.4641.

Anal. Calcd. for C_4H_8S : C, 54.49; H, 9.14. Found: C, 54.49; H, 9.45.

B. Cyclohexene Sulfide.—To a solution of 130 g. of potassium thiocyanate in 100 ml. of water was added 70 ml. of ethanol and then 60 g. of cyclohexene oxide. This mixture was stirred vigorously for four hours. During this period the temperature rose to 45°. A 40-g. portion of cyclohexene oxide was added, the mixture was cooled to 20°, and stirred vigorously for an additional twenty hours. The mixture was then saturated with salt and the top layer was separated. The crude sulfide was washed twice with 100-ml. portions of water and dried over magnesium sulfate, and distilled under reduced pressure. The yield was 70 g. (60%, based on the oxide) of clear, colorless liquid boiling at 83–87° at 46 mm.; n_D^{20} 1.5292.

Anal. Calcd. for $C_6H_{10}S$: C, 63.0; H, 8.8. Found: C, 62.2; H, 8.6.

C. Ethylene Sulfide.—Ethylene sulfide was prepared in about 50% yield by a slight modification of the procedure given in French Patent 797,621.⁴ About five drops of *n*-butyl mercaptan ordinarily was added to 50-g. portions as a stabilizer. The stabilized sulfide was stored at about 0°.

D. Propylene Sulfide.—Propylene sulfide, prepared by the same method, was stored at about 0° without the addition of a stabilizer.

II. Preparation of the Amino Mercaptans

A. From Ethylene Sulfide.—A mixture of equimolar amounts of the amine and olefin sulfide in a glass-lined bomb was heated for sixteen to eighteen hours at 90–100°. The reaction mixture was then fractionated *in vacuo* in a flask of the modified Claisen type. A current of nitrogen was admitted at a slow rate through the capillary ebulliator during the distillation.

B. From Isobutylene and Cyclohexene Sulfides.—A mixture of equimolar amounts of the amine and olefin sulfide was heated under reflux on the steam cone for sixteen to eighteen hours. The products were isolated by fractionation as described in (A) above.

III. Derivatives of Amino Thiols

A. Hydrochlorides.—These compounds were made in most cases by saturating a solution of the base in alcohol with dry hydrogen chloride gas. Addition of ether precipitated the salt which was recrystallized from alcohol-ether or alcohol-acetone. Some hydrochlorides were prepared by direct addition of concentrated aqueous hydrochloric acid to the base.

B. Sulfenyl Iodides.—The amine-isobutylene sulfide addition product was dissolved in alcohol and an alcoholic solution of iodine was added dropwise with shaking until a faint yellow color persisted. The derivative was precipitated by the addition of ether and recrystallized by dissolving in warm absolute ethanol and chilling, or by precipitating from a saturated solution in absolute ethanol by the addition of ether. Some decomposition with the formation of a yellow color was occasionally caused by heating the solution too strongly during recrystallization.

C. Acetyl Derivatives.—An excess of acetic anhydride was added to the primary amine-olefin sulfide addition product and the mixture was allowed to stand for about one hour. It was then poured into water and if the resulting oil solidified, the material was recrystallized from high-boiling petroleum ether. If the oil did not solidify, it was taken up in ether, washed with water and dried over anhydrous sodium sulfate. It was then purified by distillation *in vacuo*.

Summary

The preparation of a number of amino mercaptans by the reaction of amines with olefin sulfides is described. The effects of variations in the structures of the reactants upon the yields of the products are reported. During the course of the work two apparently hitherto undescribed olefin sulfides, cyclohexene sulfide and isobutylene sulfide, and a number of new amino mercaptans have been prepared.

URBANA, ILLINOIS

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