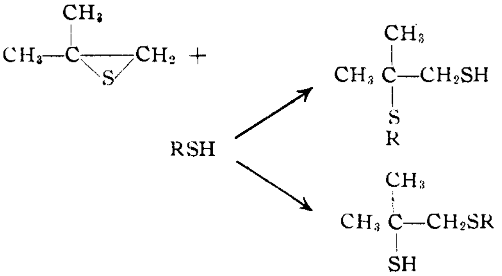
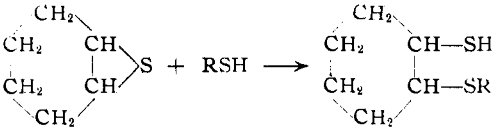
[Contribution from the Noyes Chemical Laboratory of the University of Illinois]

The Synthesis of Mercaptans from Olefin Sulfides. II[1,2]

By H. R. Snyder, John M. Stewart[3a] and J. B. Ziegler[3b]

In a study of methods of preparation of mercaptans[2] the reactions of certain olefin sulfides with compounds containing hydroxyl and sulfhydryl groups have been investigated. The reactions of ethylene sulfide and propylene sulfide with mercaptans have been reported[4] to occur when the reactants are heated in inert solvents. In the present work the reactions could be effected only in the presence of catalysts, such as sodium ethoxide or boron fluoride (added as the ether or acetic acid compound). The sulfides of greatest interest were isobutylene sulfide and cyclohexene sulfide. Both primary and tertiary mercaptans are formed from the first reagent (equation 1); only secondary mercaptans can be formed from cyclohexene sulfide (equation 2). Reaction products from either sulfide are capable of reacting further to give mercaptans containing more than one thioether group (equation 3).


(1)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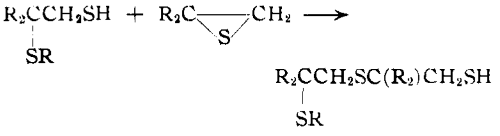
(3)

Only primary aliphatic mercaptans were added to the sulfides. The total yields from isobutylene sulfide and mercaptans such as *n*-amyl mercaptan were in the neighborhood of 75% when the mercaptan was used in 100% excess (to suppress reaction 3) as compared to about 40% when the theoretical amount of mercaptan was employed. 2-Ethylhexyl mercaptan and isobutylene sulfide reacted to give only about 30% of the addition product, the low yield probably to be ascribed to steric hindrance. Mercaptans such as β-ethoxyethyl mercaptan, having an oxygen atom in the β-position, reacted to give about 65% of the addition products. The yields referred to here were of the mixtures of primary and tertiary mercaptans. The primary mercaptans were the major constituents[5] (60–80%) of the mixtures when the original reagents were primary saturated mercaptans in the range of butyl to octyl; however, the product from dodecyl mercaptan was mostly (58%) tertiary. Mercaptans containing an oxygen atom in the β-position led to products containing about 60% of the primary isomer. The products were richer in primary mercaptans when the alkaline catalyst (sodium ethoxide) was used rather than the acidic catalyst (boron fluoride).

The yields of products from cyclohexene sulfide were in the range of 30–40% when the other reagent was a saturated mercaptan and about 55% when the mercaptan contained an ether oxygen atom in the β-position. Attempts to cause the addition of mercaptans to tetramethylethylene sulfide were unsuccessful.

Reactions of olefin sulfides with alcohols apparently have not been attempted previously. When heated with an excess of a primary saturated alcohol and a little boron fluoride (added as the ether or acetic acid compound) isobutylene sulfide reacted to give β-alkoxy mercaptans. The yields obtained ranged from 35–40% from 1-octanol or 2-ethylhexanol to about 20% from 1-butanol. Cellosolve, benzyl alcohol and α-phenylpropyl alcohol gave very poor yields in the reaction with isobutylene sulfide. Little or no reaction occurred between secondary alcohols, such as 2-octanol or cyclohexanol, and isobutylene sulfide, or between primary alcohols and propylene sulfide or cyclohexene sulfide. The products from isobutylene sulfide and saturated alcohols contained but little of the tertiary mercaptan, as shown by titration,[5] by the Rheinboldt color test,[6] and by reaction with alcoholic iodine to give disulfides in high yields; however, the product from cellosolve was largely the tertiary mercaptan. Reactions of the products with more of the sulfide (analogous to reaction 3) occur, leading to high boiling materials.

The ordinary procedures for the conversion of mercaptans to solid derivatives led to oils when applied to many of the substituted mercaptans

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

[2] For the preceding paper see This Journal, **69**, 2672 (1947).

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[4] German Patent 696,774 [*C. A.*, **35**, 5909 (1941)].

[5] 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).

[6] Rheinboldt, *Ber.*, **60**, 184 (1927).

Table I

Mercaptan Addition Products

Mercaptan	Formula of product	B. p., °C.	at mm.	$n^{20}D$	Analyses,[i] % Calcd. C	Calcd. H	Calcd. S^a	Found C	Found H	Found S^a	% Tertiary RSH
				A. From Isobutylene Sulfide							
n-$C_4H_9SH^b$	$C_8H_{16}S_2$	52–53	2	1.4938	53.87	10.17	17.98	53.69	10.38	17.33	28.7
n-$C_4H_9SH^c$	$C_8H_{18}S_2$	67–71	3	1.4988	...	...	17.98	...	...	16.67	49.3
n-C_4H_9SH	$C_{12}H_{26}S_3{}^d$	145–149	4	1.5784	...	...	12.03	...	...	12.38	63.4
n-C_4H_9SH	$C_{16}H_{34}S_4{}^e$	170–195	3–3.5	1.5300	...	...	9.04	...	...	9.40	52.3
n-$C_5H_{11}SH$	$C_9H_{20}S_2$	82–84	3	1.4920	...	...	16.66	...	...	17.20	39.2
n-$C_6H_{13}SH$	$C_{10}H_{22}S_2$	101–102	2.5	1.4908	58.19	10.75	...	58.58	11.16	...	41.4
n-$C_7H_{15}SH$	$C_{11}H_{24}S_2$	109	4	1.4856[f]	59.94	10.97	14.55	59.82	10.87	14.55	16.7
$C_8H_{17}SH^g$	$C_{12}H_{26}S_2$	119–121	4.5	1.4885[f]	61.48	11.18	13.68	61.70	11.05	13.60	19.7
n-$C_{12}H_{25}SH$	$C_{16}H_{34}S_2$	167–170	3	1.4845	...	...	11.03	...	...	11.16	57.9
$C_2H_5OCH_2CH_2SH$	$C_8H_{18}OS_2$	84–85	4.5	1.4948	49.45	9.34	16.50	49.56	9.51	16.22	42.8
$C_6H_{13}O_2SH^h$	$C_{10}H_{22}O_2S_2$	140	5	1.4900	50.38	9.30	13.45	50.18	9.37	13.43	38.4
				B. From Cyclohexene Sulfide							
n-C_4H_9SH	$C_{10}H_{20}S_2$	109–111	2.5	1.5234	58.76	9.86	15.68	58.81	9.61	15.17	..
n-$C_5H_{11}SH$	$C_{11}H_{22}S_2$	123–126	3.5	1.5186	60.49	10.16	14.68	60.66	10.31	15.46	..
n-$C_6H_{13}SH$	$C_{12}H_{24}S_2$	130–133	3	1.5135	62.00	10.41	13.80	62.18	10.71	13.45	..
n-$C_7H_{15}SH$	$C_{13}H_{26}S_2$	141–144	3	1.5113	63.34	10.63	13.01	64.35	10.48	12.91	..
$C_2H_5OCH_2CH_2SH$	$C_{10}H_{20}OS_2$	112–114	4.5	1.5195	54.49	9.15	14.55	54.46	9.19	14.53	..

[a] Mercaptan sulfur (determined by amperometric analysis). [b] Sodium ethoxide catalyst. [c] Boron fluoride catalyst. [d] The product from 1 mole of mercaptan and 2 of sulfide, probably a mixture of the 4 possible isomers. [e] The product from 1 mole of mercaptan and 3 of sulfide, probably a mixture of the 8 possible isomers. [f] The temperature was 21°. [g] 2-Ethylhexyl mercaptan. [h] 2-(2′-Ethoxyethoxy)-ethyl mercaptan. [i] Reference 5.

prepared in this work. Several of the new mercaptans were converted to solid mercaptoacetaldehyde dinitrophenylhydrazones by application of the reactions shown in equation 4. The procedure may prove useful in the characterization of other mercaptans.

$$RSH + ClCH_2CH(OC_2H_5)_2 \xrightarrow{NaOC_2H_5}$$

$$HCl + RSCH_2CH(OC_2H_5)_2 \xrightarrow[HCl]{H_2O}$$

$$RSCH_2CHO \longrightarrow RSCH_2CH{=}NNHC_6H_3N_2O_4 \quad (4)$$

Experimental

I. **Reagents.**—Isobutylene sulfide and cyclohexene sulfide were prepared as described previously.[2] Tetramethylethylene sulfide was prepared by the method of Youtz and Perkins.[7] The mercaptans used as reagents were prepared by the method of Urquhart, Gates and Connor.[8] Only 2-(2′-ethoxyethoxy)-ethyl mercaptan appears to be new; the bromide used in its preparation was prepared by the method of Blicke and Zienty[9] for 2-ethoxyethyl bromide. The mercaptan, obtained in 71% yield, boiled at 90° (20 mm.), $n^{20}D$ 1.4540.

Anal. Calcd. for $C_6H_{14}O_2S$: C, 47.98; H, 9.39; S, 21.34. Found: C, 48.10; H, 9.61; S, 21.33.

II. **Reactions of Mercaptans with Olefin Sulfides. A. Sodium Ethoxide as Catalyst.**—The procedure used in most preparations consisted of adding 0.05 mole of the mercaptan and 0.05 mole of the sulfide to 13 ml. of absolute ethanol containing sodium ethoxide equivalent to 0.01 g. of sodium. After an initial period during which the temperature of the reaction mixtures invariably rose spontaneously, heat was applied and refluxing was continued for ten to twenty hours. The product was isolated by extraction with ether, washing of the extract with water and saturated sodium chloride solution, drying, and distillation under diminished pressure. In some preparations the proportion of mercaptan was doubled.

B. Boron Fluoride as Catalyst.—A mixture of 0.11 mole of the mercaptan and two drops of boron fluoride etherate was stirred and heated on a steam-bath while 0.05 mole of the sulfide was added dropwise (over about forty-five minutes). The mixture was heated for two hours after completion of the addition and worked up as described above.

The mercaptans prepared by these procedures are listed in Table I.

III. **Reactions of Alcohols with Olefin Sulfides.**—A mixture of 0.10 mole of the alcohol, 0.05 mole of the sulfide and 10 drops of boron fluoride–acetic acid was heated on a steam-bath for twenty hours. The cooled mixture was dissolved in ether and the solution was washed with aqueous sodium carbonate solution and saturated sodium chloride solution. The product was recovered from the dried solution by distillation under diminished pressure.

The mercaptans prepared by this method are listed in Table II.

IV. **Mercaptoacetaldehyde Dinitrophenylhydrazones.**—To a solution prepared from 0.023 g. (0.01 mole) of sodium and 20 ml. of absolute ethanol was added 0.01 mole of the alkoxy thiol, followed by 1.5 g. (0.01 mole) of diethyl monochloroacetal. The resulting solution was refluxed on the steam cone for four hours. The end of the reaction was indicated by the clarification of the solution, which remained cloudy during the precipitation of sodium chloride. The precipitated salt was then collected on a Hirsch funnel and washed with ethanol. The combined filtrate and washings were treated with 10 ml. of water and acidified to congo red paper with concentrated hydrochloric acid. The resulting solution was evaporated on the steam cone, to an orange-yellow oil. This oil was taken up in ether and washed with water and sodium bicarbonate solution. After removal of the ether the crude mercaptoacetaldehyde was obtained as an orange-yellow oil with a characteristic, fern-like odor.

The crude aldehyde was converted to the 2,4-dinitro-

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(7) Youtz and Perkins, This Journal, **51**, 3508 (1929).

(8) Urquhart, Gates and Connor, *Org. Syn.*, **21**, 36 (1941).

(9) Blicke and Zienty, This Journal, **63**, 2779 (1941).

TABLE II

ALCOHOL ADDITION PRODUCTS FROM ISOBUTYLENE SULFIDE

Alcohol	Formula of product	B. p., °C.	at mm.	$n^{20}D$	Analyses,[f] % Calcd. C	Calcd. H	Calcd. S[a]	Found C	Found H	Found S[a]
n-C_4H_9OH	$C_8H_{18}OS^b$	59–61	4.5	1.4493	...	...	19.75	...	...	18.90
n-$C_5H_{11}OH$	$C_9H_{20}OS^b$	58–59	2	1.4543	61.32	11.44	...	61.14	11.15	...
n-$C_6H_{13}OH$	$C_{10}H_{22}OS^b$	73–74	2	1.4536	63.11	11.66	16.85	63.70	11.54	16.34
n-$C_7H_{15}OH$	$C_{11}H_{24}OS^b$	84–86	3	1.4551	64.82	11.87	15.68	65.20	12.10	15.23
n-$C_6H_{17}OH$	$C_{12}H_{26}OS^b$	98–102	3.5	1.4548	...	...	14.68	...	...	14.02
$C_8H_{17}OH^c$	$C_{12}H_{26}OS^b$	75–80	2	1.4550	65.98	12.00	14.68	66.03	12.11	14.00
	$C_{16}H_{34}OS_2^d$	119–121	2	1.4831	62.68	11.15	10.46	62.81	11.18	10.25
$C_2H_5OCH_2CH_2OH$	$C_{12}H_{26}O_2S_2^{d,e}$	110–125	3	1.5006	54.09	9.84	12.03	54.10	9.71	11.49

[a] Mercaptan sulfur (determined by amperometric analysis). [b] The product contains traces of the tertiary mercaptan. [c] 2-Ethylhexanol. [d] The product from 1 mole of alcohol and 2 of sulfide. [e] Contains 57.4% of tertiary mercaptan. [f] Reference 5.

TABLE III

DERIVATIVES OF ALCOHOL AND MERCAPTAN ADDITION PRODUCTS OF ISOBUTYLENE SULFIDE

Alcohol or mercaptan	Derivative	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
n-C_4H_9OH	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	62–63	$C_{16}H_{24}O_5N_4S$	50.00	6.29	50.20	6.37
n-$C_5H_{11}OH$	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	52–53.5	$C_{17}H_{26}O_5N_4S$	51.24	6.58	51.21	6.50
n-$C_7H_{15}OH$	RSSR	[a]	$C_{22}H_{46}O_2S_2$	64.96	11.40	64.79	11.49
	$RSCH_2CH_2C_6H_5$	[b]	$C_{19}H_{32}OS$	73.96	10.46	73.85	10.29
n-$C_8H_{17}OH$	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	40–41	$C_{20}H_{32}O_5N_4S$	54.52	7.32	54.79	7.55
$C_6H_{17}OH^c$	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	48–50	$C_{20}H_{32}O_5N_4S$	54.52	7.32	54.38	7.43
n-$C_7H_{15}SH$	RSSR[d]	[d]	$C_{22}H_{46}S_4$	60.61	10.57	60.69	10.74

[a] Liquid boiling at 195–202° (2.5). [b] Liquid boiling at 150–154° (2). [c] 2-Ethylhexanol. [d] The disulfide presumably is related to the primary mercaptan only. [e] Liquid boiling at 185° (2.5 mm.).

phenylhydrazone by means of the procedure of Shriner and Fuson.[10] The ethanol solubility of the derivative is appreciable and in some instances crystallization occurred only after long chilling of the solution. The product was recrystallized from ethanol, methanol or high-boiling petroleum ether.

The derivatives prepared are listed in Table III along with a few of other types which were prepared and analyzed.

Summary

The preparation of a number of mercaptans by the reaction of alcohols or mercaptans with olefin sulfides in the presence of catalysts is described.

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[10] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 143.

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Some β-Keto Esters

BY S. B. SOLOWAY AND F. B. LAFORGE

For the synthesis of dihydrocinerone (2-butyl-3-methyl-2-cyclopenten-1-one)[1] by a procedure of Hunsdiecker,[2] β-oxocaprylic acid ester is required as the starting material. Hauser and Hudson[3] list three methods which have been used for the synthesis of this β-keto ester: (1) the acylation of ethyl acetoacetate with caproyl chloride and the subsequent ammonolysis of the product (yield "excellent"); (2) the hydration of 2-octynoic acid and esterification (yield, 50–80%); and (3) the forced condensation of 2-heptanone with ethyl carbonate by the agency of sodium ethoxide (yield, 65%). Recently, Anderson and coworkers[4] have employed a modification of the third method, developed by Levine and Hauser,[5] which substitutes sodium amide as the condensing agent (yield, 57%).

Under the first method Hauser and Hudson[3] mention the alcoholysis of the acylacetoacetic ester but without giving references. Hunsdiecker[2] has employed the alcoholysis procedure successfully (yield, 65–70%), and in our hands good yields were likewise obtained with the employment of commercial sodium methoxide and commercial anhydrous methanol. The procedure

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[1] LaForge and Barthel, *J. Org. Chem.*, **10**, 222 (1945).

[2] Hunsdiecker, *Ber.*, **75B**, 447, 455, 460 (1942).

[3] Hauser and Hudson, "Organic Reactions," Adams, editor-in-chief, vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, chap. 9, p. 266.

[4] Anderson and co-workers, THIS JOURNAL, **67**, 2197 (1945).

[5] Levine and Hauser, *ibid.*, **66**, 1768 (1944).