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Vinyl Sulfides. I. A "One-Step" Synthesis from Halides

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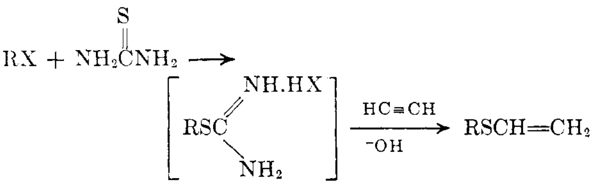
Vinyl sulfides (I) can be prepared by base-catalyzed reaction of isothiuronium salts (II) with acetylene without prior isolation of the mercaptan. As the isothiuronium salt need not be isolated after preparation, the technique constitutes essentially a "one-step" synthesis from alkyl halides.

The preparation of vinyl sulfides (I) by the base-catalyzed reaction of acetylene with a mercaptan is a straightforward, high yield reaction when conducted according to Reppe's procedure using an alcohol solvent.[1]

However, the scope of the synthesis is somewhat limited by the relative unavailability of mercaptans, particularly those which contain a second functional group. For many complex vinyl sulfides (I) desired for a study of their properties, it was necessary first to synthesize the mercaptan, usually either 1) by reaction of sodium hydrosulfide with an appropriate substrate[2a,b] or 2) by alkaline decomposition of an isothiuronium salt.[3]

As both of these preparative reactions, like the vinylation reaction, are performed in an alkaline medium, it became of interest to investigate the combination of the preparative and vinylation steps. We have studied several such techniques; one of the most satisfactory is a combined hydrolysis-vinylation of isothiuronium salts (II). As neither the mercaptan nor II need be isolated, the method is a convenient "one-step" conversion of halides to vinyl sulfides.



$$RX + NH_2\overset{\overset{S}{\|}}{C}NH_2 \longrightarrow \left[RSC\begin{matrix}\nearrow NH.HX\\ \searrow NH_2\end{matrix}\right] \xrightarrow[-OH]{HC\equiv CH} RSCH{=}CH_2$$

II I

This paper describes an application of the method to preparation of vinyl sulfides containing no other active functional group, a study which was preliminary to synthesis of aminoalkyl vinyl sulfides.[4]

The hydrolysis-vinylation reactions are accomplished most readily by heating an aqueous solution of II and sodium hydroxide with acetylene at elevated temperature and pressure. The reactions are extremely rapid and exothermic. The product I is readily isolated, since the crude reaction mixture usually consists of a two-phase system—an aqueous layer which contains inorganic salts, and the relatively pure, but slightly colored, vinyl sulfide as an oil layer, which can be purified by distillation to a mobile, water-white liquid.

A brief study of the scope of the technique showed that most satisfactory yields are obtained from alkyl halides having a relatively reaction halogen. Conversions of ethyl bromide, *n*-butyl bromide, *s*-butyl bromide, 2-ethylhexyl bromide, 1-bromotetradecane, benzyl chloride, and phenethyl bromide to the corresponding I are accomplished in good to excellent yields, as shown in Table I. Only polymeric products are obtained from allyl and methallyl chlorides, despite excellent conversions to the isothiuronium salts. These observations generally parallel results obtained in vinylation of the free mercaptans, and several attempts to prepare allyl vinyl sulfide from allyl mercaptan by the Reppe procedures[1] were unsuccessful. No effort was made to account for the low conversions of tetrahydrofurfuryl and thenyl chlorides.

The low yield of cyclohexyl vinyl sulfide was expected since the preparation of II from cyclohexyl bromide has been reported to proceed to a maximum yield of 50%.[5] *n*-Butyl vinyl sulfide was obtained as a by-product (15%). This is explained by the elimination of hydrogen bromide during the preparation of cyclohexylisothiuronium bromide in refluxing *n*-butyl alcohol with subsequent conversion of *n*-butyl alcohol, thiourea and hydrogen bromide to *n*-butylisothiuronium bromide.[6]

In addition to a small amount of phenoxyethyl vinyl sulfide, phenol was isolated (25% yield) from the crude vinylation products obtained from phenoxyethylisothiuronium bromide. The low yield of phenoxyethyl vinyl sulfide also reflects an involved and tedious work-up procedure.

The hydrolysis-vinylation of II is adaptable to the synthesis of α,ω-bis(vinyl sulfides), $CH_2{=}CHSRSCH{=}CH_2$, and is particularly attractive

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[1] W. Reppe and F. Nicolai, U. S. Pat. **2,081,766** (May 25, 1937).

[2] (a) L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1685 (1932); cf. Connor "Organic Sulfur Compounds," Gilman's *Organic Chemistry*, Wiley, New York, 1st Ed., Vol. I, 1943, p. 841. (b) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 278–282 (1949).

[3] G. G. Urquhart, J. W. Gates, Jr., and Ralph Connor, *Org. Syntheses*, **21**, 36 (1941).

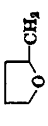
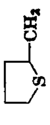
[4] H. J. Schneider, J. J. Bagnell, and G. C. Murdoch, *J. Org. Chem.*, **26**, 1982 (1961).

[5] J. Stanek, *Chem. Listy*, **46**, 383–384 (1952); *Chem. Abstr.*, **47**, 4296i (1953).

[6] R. L. Frank and P. V. Smith, *J. Am. Chem. Soc.*, **68**, 2103 (1946).

TABLE I

VINYL SULFIDES, $RSCH=CH_2$

R =	Formula	B.P.	Mm.	n_D^{25}	d_{25}^{25}	M_D		Carbon, %		Hydrogen, %		Sulfur, %		Yield, %
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
CH_3	C_3H_6S	68	760	1.4826	0.9002	23.59	23.69	48.59	48.32	8.16	8.24	43.24	43.27	89
C_2H_5	C_4H_8S	92	760	1.4735	0.8749	28.21	28.38							
n-C_4H_9	$C_6H_{12}S$	70	60	1.4738	0.8728	37.44	37.52	62.00	61.70	10.41	10.41	27.6	27.0	90
s-C_4H_9	$C_6H_{12}S$	74	115	1.4687	0.8581	37.44	37.78					27.6	27.4	75
$C_4H_9CH(C_2H_5)CH_2$	$C_{10}H_{20}S$	89	10	1.4602	0.8655	55.91	54.71					18.6	18.6	80
n-$C_{14}H_{29}$	$C_{16}H_{32}S$	105	0.15									12.5	11.9	91
C_6H_{11}	$C_8H_{14}S$	71	9	1.5097	0.9492	44.48	44.91	67.54	67.66	9.92	9.73	22.54	22.30	30
$C_6H_5CH_2$	$C_9H_{10}S$	98	10	1.5773	1.0378	47.69	48.15					21.3	21.4	91
$C_6H_5CH_2CH_2$	$C_{10}H_{12}S$	98	10	1.5612	1.0070	52.31	52.99	73.09	73.12	7.37	7.46	19.52	19.27	73
$C_6H_5OCH_2CH_2$	$C_{10}H_{12}OS$	89	0.65	1.5633	1.0791	54.44	53.95	66.63	66.25	6.71	6.73	17.79	17.72	12
$-(CH_2)_4SCH=CH_2$	$C_8H_{14}S$	80	0.6	1.5443	1.0116	54.2	54.6	55.12	55.00	8.09	8.09	36.79	36.66	68
	$C_7H_{12}OS$	84	10.5	1.5097	1.0393	41.50	41.60	58.29	57.63	8.39	8.01	22.23	22.10	25
	$C_7H_8S_2$	78	3	1.5972	1.1868	46.93	46.96	53.80	53.70	5.16	5.28	41.04	40.80	55

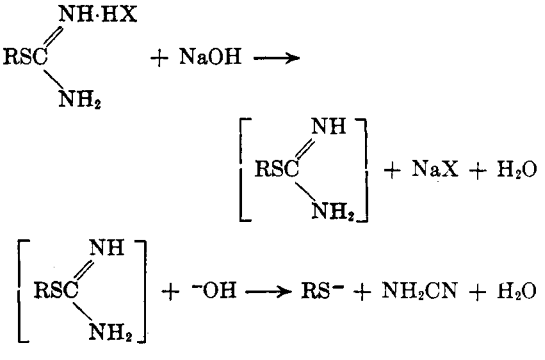
for the preparation of 1,4-bis(vinylthio)butane (3,8-dithia-1,9-decadiene). The parent mercaptan, 1,4-butanedithiol, is obtained readily only by reaction of the corresponding dihalide with thiourea. Tetrahydrothiophene results from reaction of 1,4-dihalides with sodium hydrosulfide.[7] The major exception in this series is the 1,2-isomer from which the major product was an intractable tar. In some respects this observation parallels the behavior of 1,2-ethanedithiol under Reppe conditions where considerable modification was required to define satisfactory conditions for preparation of 1,2-bis(vinylthio)ethane[8] (3,6-dithia-1,7-octadiene) in quantitative yield.

The hydrolysis-vinylation of II requires a minimum catalytic excess of sodium hydroxide above that required for neutralization of the hydrohalide. Variation in yield of benzyl vinyl sulfide with reduction of base is shown in Table II. No extensive investigation of alkali requirements was conducted; in all preparations in Table I two moles of sodium hydroxide per mole of isothiuronium salt were employed. Both the hydrolysis and vinylation reactions must be catalytic in hydroxide. Following neutralization of II with the first mole of base, the reaction can proceed by regeneration of hydroxide ion.

TABLE II

YIELDS OF BENZYL VINYL SULFIDE

Moles NaOH Mole Isothiuronium Salt	$C_6H_5CH_2SCH=CH_2$
2	86.0
1.1	87.3
1.05	83.9
1.0	39.3



$$RSC(=NH\cdot HX)NH_2 + NaOH \longrightarrow [RSC(=NH)NH_2] + NaX + H_2O \quad (1)$$

$$[RSC(=NH)NH_2] + {}^-OH \longrightarrow RS^- + NH_2CN + H_2O \quad (2)$$

$$RS^- + HC\equiv CH + H_2O \longrightarrow RSCH=CH_2 + {}^-OH \quad (3)$$

In related studies[9] it has been shown that sodium carbonate and amines catalyze vinylation of mercaptans. Replacement of sodium hydroxide

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[7] W. P. Hall and E. E. Reid, *J. Am. Chem. Soc.*, **65**, 1466 (1943).

[8] R. C. Morris and G. W. Conklin, U. S. Pat. **2,664,414** (Dec. 29, 1953).

[9] H. J. Schneider, U. S. Pat. **2,910,480** (Oct. 27, 1959).

with these materials in the present study gave generally unpromising results.

EXPERIMENTAL

Materials. Methyl bromide, ethyl bromide, *n*-butyl bromide, *s*-butyl bromide, 2-ethylhexyl bromide, 1-bromotetradecane, cyclohexyl bromide, 1,2-dibromoethane, 1,4-dibromobutane, and phenethyl bromide were Distillation Products white label grade, used as received. Benzyl chloride was commercial grade and was redistilled (40–41°/6 mm.) before use. Phenoxyethyl bromide,[10] tetrahydrofurfuryl chloride,[11] and chloromethyl thiophene[12] were prepared by published procedures. Methylmercaptan was purchased from Mathieson; ethyl mercaptan, from Distillation Products. Commercial grade (Monsanto) thiourea was employed throughout. Ethanol (2B) was obtained from Publicker Industries, *n*-butyl alcohol was Baker and Adamson reagent grade. Acetylene was drawn from Air Reduction Co. cylinders, compressed and scrubbed with carbon and activated alumina.

Isothiuronium salts were prepared by the standard procedure,[3] refluxing the halide with thiourea in water or ethanol. In most cases conversions were followed by titration for X^- and were complete in 4–6 hr. Cyclohexyl bromide was refluxed with thiourea in butanol for 30 hr., and water was observed in the reflux condensate in the latter stages; the butanol was replaced by water before reaction with acetylene. Thenylisothiuronium chloride was isolated (61%) and redissolved in water for vinylation.

Anal. Calcd. for $C_6H_9ClN_2S_2$: N, 13.4; S, 30.7; Cl, 17.0. Found: N, 13.5; S, 30.5; Cl, 17.0.

Vinyl sulfides. The vinylations were performed in a 1-l. stirred autoclave.[13] The solutions of isothiuronium salts were charged to the autoclave along with aqueous sodium hydroxide (2 moles/mole isothiuronium salt). Water content of the mixture was usually adjusted to 250 c.c./mole of isothiuronium salt. After flushing with nitrogen and acetylene, the reactor was heated with steam to 95–100° and acetylene was pressed in at 400–450 p.s.i.g. until adsorption ceased. Reaction times varied from 8–30 min.

The reactants were cooled to room temperature. The oil layer was separated and distilled to give the vinyl sulfides as water-white, mobile liquids.

Isolation of cyclohexyl vinyl sulfide was preceded by recovery of the by-product *n*-butyl vinyl sulfide.

The crude oil layer recovered in the preparation of phenoxyethyl vinyl sulfide reverted to a mush during attempted distillation. The vinyl sulfide was extracted from the semisolid with ether, and recovered by distillation. The residual solid was dissolved in water and saturated with carbon dioxide. Phenol was recovered from the resulting solution by extraction with ether and subsequent distillation.

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(10) L. Luskin, U. S. Pat. 2,569,423 (Sept. 25, 1951).

(11) L. A. Brooks and H. R. Snyder, *Org. Syntheses*, Coll. Vol. III, 84 (1945).

(12) K. B. Wiberg and H. F. McShane, *Org. Syntheses*, Coll. Vol. III, 29, 31 (1949).

(13) Autoclave Engineers, Inc., Erie, Pa.

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Vinyl Sulfides. II. Aminoalkyl Vinyl Sulfides

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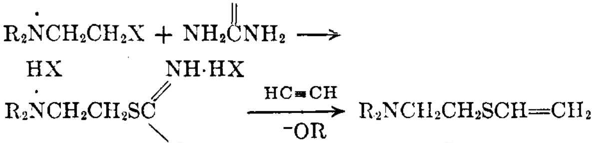
Hydrolysis-vinylation of aqueous dialkylaminoalkyl isothiuronium halides yields dialkylaminoalkyl vinyl sulfides in good yield. Cyclization of the isothiuronium salt reduces the yield when primary or secondary amino groups are present.

Aminoalkyl vinyl ethers, while convertible to a number of readily polymerizable derivatives,[1] are themselves sluggish monomers in the presence of free radical catalysts. Since vinyl sulfides, as a class, polymerize more readily than vinyl ethers, the preparation of a number of aminoalkyl vinyl sulfides (I) was desired for a study of their properties. Direct vinylation of mercaptans[2] is a preferred route to vinyl sulfides but relatively few aminoalkyl mercaptans are available.[3]

Preparative methods for aminoalkyl mercaptans are most often low yield reactions, largely because of disulfide formation. As the hydrolysis-vinylation of isothiuronium salts[4] gives high yields of vinyl sulfides from reactive halides without isolation of the salt or the mercaptan and aminoalkyl halide hydrohalides were readily available, preparation of I by this route was of practical interest. Amino vinyl sulfides (I) prepared are listed in Table I.



$$\overset{HX}{R_2\dot{N}}CH_2CH_2X + NH_2\overset{S}{\overset{\|}{C}}NH_2 \longrightarrow \overset{HX}{R_2\dot{N}}CH_2CH_2SC(=NH\cdot HX)NH_2 \xrightarrow[{}^-OR]{HC\equiv CH} R_2NCH_2CH_2SCH{=}CH_2$$

I

Best yields were obtained when the nitrogen was fully substituted. When the amine group was secondary or primary, intramolecular cyclization of the free isothiourea[5] could not be prevented

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(1) *Cf.* S. Melamed and B. F. Aycock, U. S. Pat. 2,727,020 (Dec. 13, 1955) for isocyanato derivatives; N. Bortnick and S. Melamed, U. S. Pat. 2,734,890 (Feb. 14, 1956) for ureido derivatives and P. L. de Benneville and S. Melamed, U. S. Pat. 2,694,687 (Nov. 16, 1954) for melamino derivatives.

(2) J. W. Reppe and F. Nicolai, U. S. Pat. 2,081,766 (May 25, 1937).

(3) Aminobenzenethiol was available from American Cyanamid Co.; diethylaminoethyl, dimethylaminoethyl, and aminoethyl mercaptan have become available from Evans Chemetics Co. since this study was completed.

(4) H. J. Schneider, J. J. Bagnell, and G. C. Murdoch, *J. Org. Chem.*, 26, 1980 (1961).

(5) W. Marckwald and O. Frobenius, *Ber.*, 34, 3549 (1901).