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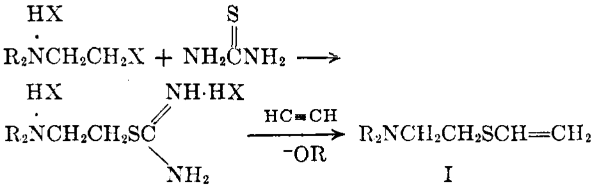
Hydrolysis-vinylation of aqueous dialkylaminoalkyl isothiuronium halides yields dialkylaminoalkyl vinyl sulfides in good yield. Cyclization of the isothiuronium salt reduces the yield when primary or secondary amino groups are present.

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.



$$\overset{HX}{\cdot}R_2NCH_2CH_2X + NH_2\overset{S}{\overset{\|}{C}}NH_2 \longrightarrow \overset{HX}{\cdot}R_2NCH_2CH_2SC\begin{cases}NH\cdot HX\\NH_2\end{cases} \xrightarrow[-OR]{HC\equiv CH} \underset{I}{R_2NCH_2CH_2SCH=CH_2}$$

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).

TABLE I

AMINO VINYL SULFIDES

R	Formula	B.P.	Mm.	n_D^{20}	n_D^{25}	d_{20}^{20}	d_{25}^{25}	M_D Calcd.	M_D Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Neut. Equiv. Calcd.	Neut. Equiv. Found	Yield, %
$(C_2H_5)_2NCH_2CH_2$	$C_8H_{17}NS$	92	20	1.4853	1.4833	0.9027	0.8996	50.6	50.8	60.32	60.39	10.76	10.60	20.13	20.29	8.79	8.90	159	159	78
$(CH_3)_2NCH_2CH_2$	$C_6H_{13}NS$	68	17	1.4906	1.4882	0.9139	0.9114	41.4	41.6	54.91	54.81	9.98	9.85	24.43	24.40	10.68	10.63	131	132	67
$CH_3NHCH_2CH_2$	$C_5H_{11}NS$	71	24	1.5046	1.5022	0.9544	0.9514	36.4	36.5	51.23	51.75	9.46	9.28	27.35	26.94	11.95	11.86	117	117	27
$NH_2CH_2CH_2$	C_4H_9NS	67	20	—	1.5196	—	0.9984	31.6	31.7	—	—	—	—	31.07	30.2	13.58	13.2	103	105	14
$NH_2CH_2CH_2CH_2$	$C_5H_{11}NS$	68	7	1.5179	1.5155	0.9795	0.9765	36.2	36.3	51.23	52.02	9.46	9.29	27.35	26.52	11.95	11.96	117	117	30
$(CH_3)_2NCH(CH_3)$- CH_2	$C_7H_{15}NS$	76	16	1.4925	1.4904	0.9194	0.9188	46.0	45.9	57.88	57.96	10.41	9.98	—	—	9.64	9.76	145	147	39
$(CH_3)_2NCH_2CH_2CH_2$	$C_7H_{15}NS$	79	18	1.4860	1.4839	0.9048	0.9017	46.0	46.2	57.88	57.80	10.41	10.51	—	—	—	—	145	145	75
$(CH_3)_2NCH_2CH_2$- SCH_2CH_2	$C_8H_{17}NS_2$	83	0.3	1.5305	1.5205	1.0092	1.0069	58.6	58.7	50.21	50.82	8.96	8.93	33.5	32.6	7.32	7.41	191	192	—

despite an extremely rapid rate of vinylation. In the preparation of *N*-methylaminoethyl vinyl sulfide considerable unsuccessful experimental effort, including temperature and solvent changes and variation in addition and ratio of reagents, was devoted to circumventing the intramolecular cyclization. Substitution of ethylene thiourea for thiourea did not improve the yield of *N*-methylaminoethyl vinyl sulfide.

The extent of the cyclization reaction of secondary and primary aminoalkyl isothioureas depends upon the relative positions of the nitrogen and sulfur. The yield of 3-aminopropyl vinyl sulfide was double that of the ethyl homolog under identical conditions, and additional improvement could be expected as the length of carbon chain between nitrogen and sulfur was further increased. Higher boiling materials of the "sulphurane" type,[6] $R_2NCH_2CH_2SCH_2CH_2SCH{=}CH_2$, were obtained as by-products in the preparation of dialkylaminoethyl vinyl sulfides. Their mode of formation has not been established. Their appearance recalls the decomposition of dialkylaminoethyl mercaptans with the formation of dialkylaminoethylthioethyl mercaptans, which has been suggested as the reason for the difficulty in isolation of the higher boiling members of the series.[7]

EXPERIMENTAL

Materials. Dimethylaminoethyl chloride hydrochloride, diethylaminoethyl chloride hydrochloride, dimethylaminopropyl chloride hydrochloride, and dimethylaminoisopropyl chloride hydrochloride were used as received from Michigan Chemical Co. Aminoethyl bromide hydrobromide was purchased from Distillation Products Co. and was not further purified. *N*-Methylaminoethyl chloride hydrochloride was prepared in 81% yield from *N*-methylaminoethanol and thionyl chloride and 3-aminopropyl chloride hydrochloride in 51% yield from 3-aminopropanol, using a published procedure for the *N,N*-dimethylamino homologs.[8]

Reaction of 2-amino-2-methylpropanol-1 with thionyl chloride under a variety of conditions produced only the hydrochloride of the amino alcohol rather than the expected chloride hydrochloride.[9a]

N-Methylaminoethanol and 3-aminopropanol were Carbide & Carbon commercial grade and thionyl chloride was used as received from Hooker Electrochemical Co. 2-Bromopyridine was DPI reagent grade.

Isothiuronium salts were prepared by standard procedures in water or ethanol. Conversion of covalent to electrovalent halogen was followed by argentometric-potentiometric titration.[9b] Analytical results were more satisfactory with the bromides; some interference from thiourea was noted when chlorides were employed.

In general, reaction of the aminoalkyl halide hydrohalide with thiourea was vigorous and, if desired, the crystalline

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(6) P. E. Spielmann, Richter's *Organic Chemistry*, Vol. I, 2nd Ed. (Revised), Blakiston, 1919, p. 323.

(7) H. R. Snyder *et al.*, *J. Am. Chem. Soc.*, **69**, 2672 (1947).

(8) L. Hall, V. Stephens, and J. H. Burckhalter, *Org. Syn.*, **31**, 37 (1951).

(9) (a) G. D. Jones, *J. Org. Chem.*, **9**, 484–499 (1944).

(9) (b) R. P. Yeck and G. H. Kissin, *Ind. Eng., Chem., Anal. Ed.*, **17**, 692 (1945).

isothiuronium salt could be isolated. However, 1-methyl-2-(dimethylamino)ethyl chloride hydrochloride gave a sirupy isothiuronium salt from which I was prepared in low yield.

Dimethylaminoethyl vinyl sulfide. A solution (477 g.) of dimethylaminoethyl isothiuronium chloride hydrochloride was prepared by refluxing dimethylaminoethyl chloride hydrochloride (144 g., 1 mole) and thiourea (83 g., 1.1 moles) in water (250 cc.) for 6 hr. A portion of this solution (465 g., 415 cc.) was charged to the 1-l. autoclave with 50% aqueous sodium hydroxide (250 g., 160 cc., 3 moles).

The reactor was flushed with acetylene and heated to 120° in 16 min. The reaction was maintained at 120–132° for a period of 1 hr. under a maximum acetylene pressure of 480 psig. The total acetylene absorption was 1.73 moles. The reactor was cooled to room temperature and the products removed under nitrogen pressure. The crude products (744 g.) were in two layers. The upper oil layer (173 g.) was separated and flash distilled to give 145 g. of distillate (including 15 g. of water) and 25 g. of dry salt-like residue. The dry distillate (123 g.) was fractionated through a 12″ Vigreux to give dimethylaminoethyl vinyl sulfide (85 g., 0.65 mole, 66.7%) and dimethylaminoethylthioethyl vinyl sulfide (15 g., 0.079 mole, 16.2%).

The presence of the vinyl sulfide group was supported by infrared absorption at 1585 cm.$^{-1}$ (C=C stretching), 852 cm.$^{-1}$, and 958 cm.$^{-1}$ (—CH wagging) in agreement with correlations previously developed for vinyl sulfides.

Benzyl chloride (11.2 g., 0.089 mole) was added at room temperature to dimethylaminoethyl vinyl sulfide (12.5 g., 0.095 mole) in anhydrous ethanol (100 cc.). After standing overnight, ethanol was evaporated. The residue was recrystallized from benzene to yield 2-vinyl thioethyl benzyl dimethyl ammonium chloride (21.8 g., 0.085 mole, 96%), as white platelets, m.p. 126–129.5°C.

Anal. Calcd. for $C_{13}H_{20}NSCl$: S, 12.4. Found: S, 12.2.

Methyl iodide (32.1 g., 0.23 mole) was added dropwise over a period of 1 hr. to a soluton of 2-dimethylaminoethyl vinyl sulfide (32.5 g., 0.25 mole) in 75% aqueous ethanol (9.8 g.). The reaction temperature was controlled at 35–37° by intermittent cooling. The quaternary salt crystallized overnight. The methiodide, a white solid melting at 227–228° with decomposition, was obtained by recrystallization from 75% ethanol.

Anal. Calcd. for C_7H_6NSI: S, 11.7. Found: S, 11.9.

N-Methylaminoethyl vinyl sulfide. A 1-l. autoclave was charged with 50% aqueous sodium hydroxide (122.4 g., 1.53 moles), water (77 g.), dimethoxyethane (100 g.), swept with nitrogen and acetylene, heated to 105°, and pressurized to 465 psig. with acetylene. Over a period of 20 min., a solution of *N*-methylaminoethyl isothiuronium chloride hydrochloride (105 g., 0.51 mole) in water (200 cc.) was pumped (21 cc./min.) into the reactor by means of a Milton-Roy Model MM1C Minipump. During the addition, the temperature was maintained at 104–106° and the pressure at 410–465 p.s.i.g. When addition was complete, the temperature was raised to 127° over a period of 25 min. Acetylene absorption was small.

The removal of the products (568 g.) was impeded by the presence of salts. The crude product contained two liquid phases with precipitated salt. Both layers were saturated with potassium hydroxide and a final dry oil layer of 148 g. was obtained. This material was flash distilled to give 133 g. of distillate and 13 g. of polymeric residue. After removal of the dimethoxyethane, *N*-methylaminoethyl vinyl sulfide (20 g., 0.17 mole, 33.5%) was obtained.

The presence of the secondary amino group was supported by a medium, sharp adsorption band at 3280 cm.$^{-1}$

Residues from similar preparations were collected and distilled through a 12″ Vigreux column to give 2-imino-3-methyl-1,3-thiazolidine[10] as a light yellow liquid, b.p. 57–58°/0.4 mm.

Anal. Calcd. for $C_4H_8N_2S$: C, 41.37; H, 6.89; N, 24.14; S, 27.59; neut. equiv., 116. Found: C, 41.83; H, 6.93; N, 23.85; S, 27.25; neut. equiv., 119.

The picrate of 2-imino-3-methyl-1,3-thiazolidine recrystallized from ethanol as yellow platelets, m.p. 204–205° (lit.[10] m.p. 200–203°).

Anal. Calcd. for $C_{10}H_{11}N_5O_7S$: C, 34.78; H, 3.21; N, 20.28; S, 9.28. Found: C, 34.30; H, 3.09; N, 19.38; S, 8.70.

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(10) S. Gabriel, *Ber.*, **22**, 146 (1889).

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Vinyl Sulfides. III. α-Mercaptostyrenes

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α-Phenyl vinyl sulfides (α-mercaptostyrenes) have been prepared in excellent yield by the reaction of acetylene with 1-phenyl-1,2-bis(alkylmercapto)ethanes under mild vinylation conditions.

In every series of vinyl monomers, the presence of a substituent on the α-carbon of the vinyl group brings about marked changes in monomer properties. The comparative properties of acrylates and methacrylates, of styrene and α-methylstyrene, for example, are well known. In a general study of vinyl sulfides, therefore, it became of interest to study the properties of monomers of the general structure, $CH_2{=}C(Y)SR$. This report describes the preparation of α-mercaptostyrenes ($Y = C_6H_5$); another report[1] describes the preparation of ketene mercaptals ($Y = SR$). α-(Phenylmercapto)styrene has been prepared[2] by decarboxylation of 3-(phenylmercapto)cinnamic acid. Another synthesis,[3] not specifically described, can be inferred from a study of ketones with thiophenol, involving elimination of thiophenol from α,α-di(phenylmercapto)ethylbenzene. No reference to α-(alkylmercapto)styrenes appears to be available.

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(1) H. J. Schneider, J. J. Bagnell, and G. C. Murdoch, *J. Org. Chem.*, **26**, 1987 (1961).

(2) S. Ruhemann, *Ber.*, **46**, 3384 (1913); W. S. Emerson, *Chem. Rev.*, **45**, 118 (1949).

(3) E. Campaigne and J. Leal, *J. Am. Chem. Soc.*, **76**, 1272 (1954).