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).

Early efforts to obtain α-(alkylmercapto)styrenes were based upon the assumption that phenylacetylene could be made to react with mercaptans under standard vinylation conditions to yield terminally-unsaturated products. Methylacetylene has been reported[4] to yield isopropenyl ethers by base-catalyzed reaction with alcohols, and isolation of both α- and β-styryl derivatives has been reported by reaction of phenylacetylene with mercaptoacetic acid.[5] During this study a paper appeared which suggests that base-catalyzed addition of mercaptans to 1-alkynes invariably produces a vinyl sulfide with internal unsaturation.[6]

Phenylacetylene reacted exothermally with mercaptoethanol containing a small quantity of dissolved sodium to yield a single product in 59% yield (purified). That the reaction product is the

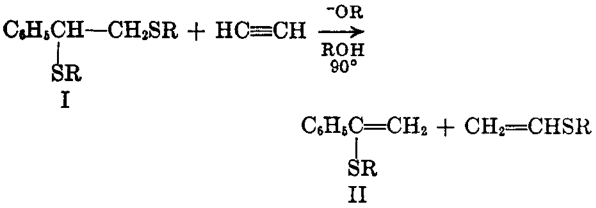
$$C_6H_5C\equiv CH + HSCH_2CH_2OH \xrightarrow[125^\circ]{^-OR} C_6H_5CH=CHSCH_2CH_2OH$$

β-isomer was demonstrated by hydrolysis and reaction with 2,4-dinitrophenylhydrazine to phenyl acetaldehyde 2,4-dinitrophenylhydrazone.

Hydrolysis with subsequent conversion of the derived carbonyl compound to the corresponding 2,4-dinitrophenylhydrazone[7] offers a fairly clean-cut method of distinction between the α- and β-styryl ethers, leading, respectively, to derivatives of acetophenone and phenyl acetaldehyde. Qualitative experiments with each isomer indicate that the rate of hydrolysis of the α-isomer is extremely more rapid and clean-cut than that of the β-isomer. The appearance of acetophenone 2,4-dinitrophenylhydrazone is rapid and quantitative. The appearance of phenylacetaldehyde 2,4-dinitrophenylhydrazone is slow and semi-quantitative.

Similarly, β-(ethylmercapto)styrene was obtained by reaction of phenylacetylene with ethyl isothiuronium bromide hydrobromide, from which the mercaptide ion was generated *in situ*.[8] Apparently, addition of mercaptans to phenyl acetylene, under most conditions, will be controlled by the most stable resonance form of the intermediate anion ($C_6H_5\bar{C}=CHSR$) to yield the β-isomer, and therefore, α-(alkylmercapto)styrenes cannot be prepared by direct vinylation procedures from phenylacetylene.

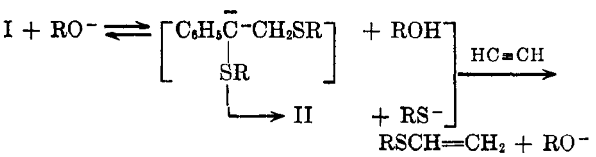
A successful method for preparation of α-(alkyl mercapto)styrenes (II) involves the base-catalyzed elimination of a mercaptan from 1-phenyl-1,2-bis(alkylmercapto)ethanes (I) in the presence of acetylene.



$$\underset{\text{I}}{C_6H_5\underset{SR}{CH}-CH_2SR} + HC\equiv CH \xrightarrow[\substack{ROH\\ 90^\circ}]{^-OR} \underset{\text{II}}{C_6H_5\underset{SR}{C}=CH_2} + CH_2=CHSR$$

In most experiments, *t*-butyl alcohol, which vinylates rather slowly, was employed as a solvent. Reaction conditions, however, are relatively mild and primary alcohols may also be used. No extensive study of the temperature variable has been made. At 90–100° yields are excellent; at 150° yields appear to be lowered either by polymerization or by further chemical reaction.

The conversion of I to II probably proceeds in two distinct but simultaneous chemical steps. While we have speculated with regard to incorporation of acetylene in an activation complex, the synthetic sequence is perhaps best described by a series of consecutive reactions involving base-catalyzed elimination, followed by base-catalyzed vinylation of the eliminated species. The latter reaction is irreversible and promotes complete conversion of I to II. The utility of acetylene in the reaction sequence was demonstrated by control experiments. Distillation of ethyl mercaptan from 1-phenyl-1,2-bis(ethylmercapto)ethane (Ia) gave only 31% yield of the substituted styrene, compared to 89% yield when acetylene was employed as an aid to elimination. When Ia was heated in a closed reactor with potassium *t*-butoxide (10 mole per cent) in *t*-butyl alcohol in the absence of acetylene, α-(ethylmercapto)styrene was obtained in 9.0% conversion, approximately equivalent to the catalyst employed. The greater portion (87%) of Ia was recovered unchanged. It might be observed that acetylene is not the only substance which can be employed as an aid to elimination in this reaction sequence, but the irreversibility of the vinylation reaction and the stability of the by-product vinyl sulfides under reaction conditions suggested acetylene as being most suitable.



$$\text{I} + RO^- \rightleftharpoons \left[\left[C_6H_5\underset{SR}{\overset{-}{C}}-CH_2SR\right] \begin{matrix} + ROH \\ \\ + RS^- \end{matrix}\right] \xrightarrow{HC\equiv CH} RSCH=CH_2 + RO^-$$

$$\left[C_6H_5\underset{SR}{\overset{-}{C}}-CH_2SR\right] \longrightarrow \text{II}$$

I is readily available from the reaction of styrene with a disulfide in the presence of iodine.[9] The reaction proceeded in good yield in all cases examined, except di-*t*-butyl disulfide, where no stable product could be obtained. Where possible, the crude reaction mixture was freed from iodine by washing with sodium hydroxide, and I was distilled. Where I was expected to present diffi-

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[4] M. F. Shostakovskii, *Chem. Abstr.*, **48**, 9899 (1954).

[5] B. Holmberg, *Chem. Abstr.*, **46**, 100 (1952).

[6] W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **78**, 2760 (1956).

[7] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2nd ed., Wiley, 1940, p. 65.

[8] H. J. Schneider and J. J. Bagnell, *J. Org. Chem.*, in press.

[9] B. Holmberg, *Chem. Abstr.*, **34**, 2341^9 (1940); *Chem. Abstr.*, **32**, 4155^5 (1938).

culties during distillation because of an exceptionally high boiling point, *e.g.* 1-phenyl-1,2-bis-(2-hydroxyethylmercapto)ethane (Ic), the crude I was stirred with solid potassium hydroxide to destroy elemental iodine and reacted with acetylene without further purification.

EXPERIMENTAL

Reaction of phenylacetylene with mercaptoethanol. Phenylacetylene (51 g., 0.5 mole) was added dropwise to mercaptoethanol (39 g., 0.5 mole) containing dissolved sodium metal (1.15 g., 0.05 g.-atom). The reaction was conducted with stirring under nitrogen and temperature was maintained at 125–140° by alternate heating and cooling over a period of 45 min. The crude reaction product was flash distilled into a Dry Ice–acetone cooled receiver to give a clear, light yellow distillate (72 g., b.p. 132–160°/0.9 mm., pot temp. 149–210°), and a dark residue (8 g.). After preliminary removal of low boiling materials (2 g.), β-styryl 2-hydroxyethyl thioether (53 g., 0.294 mole, 59% yield) was recovered by distillation through a 12-inch Vigreux column as an off-white, mobile liquid, b.p. 124–126°/0.6 mm., n_D^{25} 1.6260–1.6278 (refractometer reading difficult).

Anal. Calcd. for $C_{10}H_{12}OS$: S, 17.78; OH No., 311. Found: S, 17.78; OH No., 317.

Treatment of β-styryl 2-hydroxyethyl thioether with acidified 2,4-dinitrophenylhydrazine gave a heterogeneous 2,4-dinitrophenylhydrazone. After some difficulty in recrystallization, the 2,4-dinitrophenylhydrazone of phenylacetaldehyde was obtained as yellow needles, m.p. 118–118.4°. The mixed melting point with an authentic sample (m.p. 119.9–121°) was 119.8–120.4°.

Reaction of phenylacetylene with ethyl isothiuronium bromide. A solution of ethyl isothiuronium bromide in ethanol (120 ml.) was prepared by refluxing ethyl bromide (1.0 mole) and thiourea (80 g., 1.05 moles) for 4.75 hr. Phenylacetylene (102 g., 1.0 mole) was added and the resulting solution was heated under nitrogen pressure (100 psig.) to 120°. Over a period of 12 min. a solution of sodium hydroxide (120 g., 3.0 moles) in water (160 ml.) was added by means of a positive displacement pump. The alkali was followed by a water wash (85 ml.) and the reaction was continued for an additional hour.

The heterogeneous reaction mixture (670 g., two layers and salt) was separated, the water layer extracted with ether, and the combined organic materials were flash distilled. Rectification of the flash distillate through a Vigreux column gave β-(ethylmercapto)styrene (130 g., 0.79 mole, 79% yield) as a water-white liquid, b.p. 70–75°/0.2 mm., n_D^{25} 1.6097.

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.36; S, 19.52. Found: C, 72.93; H, 7.53; S, 19.41.

1-Phenyl-1,2-bis(alkylmercapto)ethanes (I). Styrene (107.8 g., 1.04 moles), ethyl disulfide (122.2 g., 1.0 mole), and iodine (2 g.) were mixed and stirred at room temperature for 5 days. The dark reaction mix was washed with 1*N* aqueous sodium hydroxide (500 ml.) until the iodine color disappeared. The organic layer was separated and distilled through a modified Claisen to give Ia (195 g., 0.86 mole, 86% yield) as a white, mobile liquid, b.p. 109°/0.2 mm., n_D^{25} 1.5641, d_{25}^{25} 1.0463.

Anal. Calcd. for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01; S, 28.33; M_D, 70.02. Found: C, 63.64; H, 8.08; S, 28.31; M_D, 70.60.

Similarly, 1-phenyl-1,2-bis(methylmercapto)ethane (Ib) was prepared in 86% yield as a water-white liquid, b.p. 85°/0.14 mm., n_D^{25} 1.5855, d_{25}^{25} 1.0938.

Anal. Calcd. for $C_{10}H_{14}S_2$: C, 60.55; H, 7.11; S, 32.33; M_D, 60.78. Found: C, 60.56; H, 6.95; S, 32.35; M_D, 60.99.

1-Phenyl-1,2-bis(phenylmercapto)ethane was obtained in 87% yield as a white solid, m.p. 56–57°.

Anal. Calcd. for $C_{20}H_{18}S_2$: C, 74.49; H, 5.63; S, 19.89. Found: C, 74.79; H, 5.62; S, 19.60.

α-(Alkylmercapto)styrenes (II). A solution of 1-phenyl-1,2-bis(ethylthio)ethane (Ia) (93 g., 0.41 mole) in *t*-butyl alcohol (50 ml.) containing dissolved potassium metal (1.6 g., 0.041 g.-atom) was charged to a 240 ml. magnetically stirred autoclave. The gas space was swept with nitrogen and acetylene, and the reactor and contents were heated to 100°. Acetylene (11 g., 0.423 mole) was pressed in from a calibrated reservoir over a period of 35 min.

Light ends were removed from the crude reaction product (144 g.), leaving a semi-solid residue. Water (30 ml.) was added to dissolve the precipitated alkoxide. The water layer was separated and washed with ether (3 × 30 ml.). The organic layer, the ether extracts and the flash distillate were recombined and distilled through a Vigreux column to give IIa (60 g., 0.37 mole, 89% yield) as a water-white, mobile liquid, b.p. 69°/1.5 mm., n_D^{25} 1.5742, d_{25}^{25} 1.0187.

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.36; S, 19.52; M_D, 52.31. Found: C, 73.08; H, 7.60; S, 19.67; M_D, 53.38.

Similarly, α-(methylmercapto)styrene (IIb) was prepared in 60% yield as a water-white liquid, b.p. 98°/1.6 mm., n_D^{25} 1.5910, d_{25}^{25} 1.048.

Anal. Calcd. for $C_9H_{10}S$: C, 71.95; H, 6.71; S, 21.34; M_D, 47.69. Found: C, 71.74; H, 6.52; S, 21.19; M_D, 48.58.

α-(2-Hydroxyethylmercapto)styrene (IIc). Iodine (4 g.) was added to a heterogeneous mixture of dithiodiglycol (commercial grade, $n_D^{25.2}$, 1.5632) and styrene (commercial grade, inhibited, 215 g., 2.06 mole). The mixture was stirred rapidly for a period of 7 days at room temperature. Additional increments of iodine (2 g.) were added after 5 hr. and 13.5 hr. The mixture slowly became homogeneous and after this stage was reached, the reaction mixture was allowed to stand an additional 12 days. The reaction product was a dark brown viscous liquid with a small amount of solid (14 g.) which was removed by filtration. The solid material was insoluble in ethanol—the liquid filtrate (500 g.) soluble. The filtrate was stirred with potassium hydroxide pellets (5 g., 0.089 mole) for 2 hr., during which time the color changed from brown to yellow-white. After another filtration to remove the inorganic solids, crude bissulfide (487 g.) was added to a solution of potassium metal (7.8 g., 0.2 g.-atom) in *t*-butyl alcohol (200 ml.).

The solution was contacted with acetylene (330–450 p.s.i.g.) in a 1-l. stirred autoclave. Over a period of 5 hr., the reaction mixture absorbed 42 g. (1.61 moles) of acetylene. The crude reaction product (638 g.) was flash distilled to give a yellow distillate (451 g., b.p. 122°/1.45 mm., pot temperature <187°) and a viscous, brown residue (180 g.). The flash distillate was redistilled into small fractions in a modified Claisen to give a) 2-hydroxyethyl vinyl sulfide (68 g., 0.65 mole, 32% yield) and b) IIc (117 g., 0.64 mole, 32% yield) as a light yellow liquid, b.p. 90–91°/0.07 mm., n_D^{25} 1.5908.

Base-catalyzed decomposition of 1-phenyl-1,2-bis(ethylthio)-ethane at atmospheric pressure. Ethyl mercaptan (18.3 g., 0.295 mole, 72.5%) was distilled from a solution of 1-phenyl-1,2-bis(ethylthio)ethane (92 g., 0.407 mole) in octanol-1 (50 ml., n_D^{25} 1.4275) containing dissolved potassium (1.6 g., 0.041 mole). The distillation was conducted under nitrogen. The mercaptan did not distill until the reaction temperature reached 171°. The ethyl mercaptan was collected in aqueous sodium hydroxide, and the distillation was continued to the boiling point of octanol-1 (189° in overhead, pot temperature, 217°). The ethyl mercaptan was isolated by acidification of the aqueous caustic after extraction with ether to recover the distilled octanol-1. No losses were sustained on the distillation.

All organic materials other than the ethyl mercaptan were recombined with the distillation residue and flash distilled *in vacuo* to a dry pot. After recovery of the ether and octanol-1, α-(ethylmercapto)styrene (21 g., 0.128 mole, 31.5%) was obtained.

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