reaction occurred only *after* acetic acid was added to the mixture. Since we also observed the formation of by-products that contained boron bonded to the substrate, we suspected that diborane or a related species was involved. Although this hypothesis proved to be incorrect, it nevertheless led to the discovery that sodium borohydride with acetic acid is, in fact, a hydroborating agent.

It is well known that sodium borohydride in conjunction with various strong acids is an effective hydroborating agent.[2] Furthermore, Brown and Subba Rao[3] have shown that sodium borohydride and propionic acid probably react as follows:

$$CH_3CH_2CO_2H + NaBH_4 \longrightarrow H_2 + [CH_3CH_2CO_2BH_3]^{\ominus}Na^{\oplus}$$

We have noted that the analogous reaction between sodium borohydride and acetic acid produces a species which, perhaps by its decomposition into diborane and sodium acetate, is capable of effecting hydroboration. This fact was demonstrated by treating hexene-1 with a twofold excess of sodium borohydride and acetic acid. The product was then oxidized with hydrogen peroxide to give hexanol-1 in 75% yield.

The observation that a mixture of sodium borohydride and acetic acid can effect hydroboration is especially important in view of the fact that one of the frequently employed procedures for carrying out "conventional" reductions with sodium borohydride is to decompose the excess reagent with acetic acid. In view of our findings, this procedure affords the possibility of introducing serious complications when the aim is to effect selective hydride reduction in systems containing groups (such as olefinic linkages) that are susceptible to attack by diborane. Our findings may also serve to rationalize certain hitherto inexplicable reactions with sodium borohydride[4]—*e.g.*, the facile reduction of certain lactone to lactols and of the olefinic bond of α,β-unsaturated ketones. The vital role played by the acid would be either to protonate the substrate, thus rendering it more susceptible to attack by hydride as appears to be the case with enamines,[1] or to produce diborane, or a related species, which in turn attacks the substrate (or its protonated form).

Experimental

To a stirred suspension of 1.90 g. of sodium borohydride (Metal Hydrides, Inc.) and 2.10 g. of hexene-1 (Aldrich Chemical Co.) in 25 ml. of anhydrous tetrahydrofuran (distilled from lithium aluminum hydride) was added 3.00 g. of glacial acetic acid over a period of 45 min. The mixture was stirred under an atmosphere of nitrogen for 3 hr. at room temperature; then 25 ml. of 10% sodium hydroxide solution and 10 ml. of 30% hydrogen peroxide were very carefully added (violent gas evolution). The mixture was stirred for 1 hr. at room temperature, diluted with saturated brine, and thoroughly extracted with ether. The combined ether layers were washed with saturated brine and dried over anhydrous sodium sulfate. Most of the solvent was removed by distillation at atmospheric pressure through a 25-cm. Vigreux column. The residue was distil: led through a short column and afforded 1.36 g. of a liquid, b.p. 155–162°, which was identified as hexanol-1 by infrared and vapor phase chromatographic comparison with authentic material and by conversion to the α-naphthylurethane derivative, m.p. 57–59°.[5] The residue from the distillation amounted to 0.54 g. of nearly pure hexanol-1, identified as described above.

The infrared spectra of the forerun fractions from the distillation described above showed bands due to unreacted hexene-1, but no absorption in the 2.5–3.3-μ region was observed, indicating the absence of ethanol in the reduction mixture.

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Reactions of Epithioethylbenzene (Styrene Sulfide)

JOHN M. STEWART

Montana State University, Missoula, Montana

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The preparation of epithioethylbenzene (styrene sulfide) has been reported by Guss and Chamberlain,[1] using the reaction of epoxyethylbenzene with potassium thiocyanate in water–dioxane solution. These authors attempted the addition of piperidine and morpholine to the styrene sulfide, but obtained only sulfur-free products which were not identified. It was of interest to this investigator to verify these results, to attempt to find conditions under which amines and styrene sulfide would undergo addition reactions to furnish aminesubstituted mercaptans, and to determine which, if any, of the common ring opening reactions of olefin sulfides styrene sulfide would undergo.

When the reactions of dimethylamine and piperidine with styrene sulfide were carried out in the absence of a solvent, hydrogen sulfide was evolved, no addition products could be obtained, and the products appeared to be polymeric in nature. However, when a solution of the sulfide in 90% benzene–10% ethanol was added slowly to an excess of secondary amine in the same solvent mixture and at various temperatures, aminomercaptan addition products (I) were obtained.

$$C_6H_5CHCH_2 + R_2NH \longrightarrow C_6H_5CHCH_2NR_2$$
$$\quad\diagdown\diagup\quad\qquad\qquad\qquad\quad|$$
$$\quad\ S\qquad\qquad\qquad\qquad\ SH$$

I

The yields obtainable seemed to be controlled mainly by steric factors—dimethylamine, piperidine, and morpholine giving good yields, diethylamine giving a much lower yield, and di-*n*-butylamine giving no addition product. Neither acidic nor basic types of catalysts appeared to improve the yields. The structure I shown is for the so-called "normal" cleavage of the sulfide ring, taking place at the primary carbon atom. This would be expected by analogy to reactions of epoxyethylbenzene (styrene oxide) with amines.[2] This structure was also proved for the reaction product of piperidine and styrene sulfide by desulfurizing the addition compound with Raney nickel and identifying the resulting product

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TABLE I

ADDITION COMPOUNDS (I) FROM AMINES AND STYRENE SULFIDE

Amine used	Yield, %	B.p., °C. (mm.)	Ref. index	Hydrochloride M.p., °C.	Hydrochloride % Carbon Calcd.	Hydrochloride % Carbon Found	Hydrochloride % Hydrogen Calcd.	Hydrochloride % Hydrogen Found
Piperidine	60	121–123 (0.5)	$n^{25}D$ 1.5577	174–175	60.56	60.40	7.82	7.68
Morpholine[a]	63	126–127 (0.4)	$n^{30}D$ 1.5584	175 dec.	55.48	55.37	6.98	6.82
Dimethylamine[b]	56–65	77–78 (0.5)	$n^{27}D$ 1.5458	184.5–185.5 dec.	55.15	55.29	7.40	7.31
Diethylamine	14–27	90–91 (0.5)	$n^{24}D$ 1.5378	Oil				

[a] Direct analysis of the morpholine adduct: Calcd. for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67. Found: C, 64.32; H, 7.53. [b] Ose and Yakugaku[3] report b.p. 94–97° (5 mm.); hydrochloride m.p. 185–186° dec.

as 1-(β-phenylethyl)piperidine. Furthermore, the amine addition product from dimethylamine formed a hydrochloride salt whose melting point agreed with that of the known compound, 1-phenyl 2-dimethylaminoethanethiol, previously prepared in another manner.[3] The main by-products of these reactions appeared to be polymers of styrene sulfide. Table I lists yields, constants, and analytical data for the amine adducts prepared.

No addition product was isolated from reactions of primary amines and styrene sulfide. Again both acidic and basic types of catalysts were tried without success. It appeared that in all of these attempted reactions polymerization of the cyclic sulfide took precedence over the desired addition reaction.

Halogens reacted readily with styrene sulfide in either anhydrous or aqueous solution, as has previously been shown with propylene sulfide.[4] A solution of the sulfide in chloroform can be titrated quantitatively to a color end point with a solution of bromine in chloroform to give a disulfide addition product of two moles of styrene sulfide with one mole of bromine. No attempt was made to prove the structure of this adduct. However, from the results of investigations on the reaction of aqueous chlorine with styrene sulfide described later, it appears very likely that the isomer formed would be bis(2-bromo 2-phenylethane) disulfide, $C_6H_5CHCH_2SSCH_2CHC_6H_5$ (Br on each CH). The reaction of styrene sulfide with a saturated solution of chlorine in aqueous acetic acid resulted in an excellent yield of 2-chloro 2-phenylethanesulfonyl chloride, $C_6H_5CHCH_2SO_2Cl$ (Cl on CH). The structure of this compound was proved by its conversion to the known compound[5], 2-phenylethene-1-sulfonamide by reaction with aqueous ammonia. Treatment of the chlorosulfonylchloride with secondary amines also readily converted it to *N*-substituted 2-phenylethene-1-sulfonamides.

In the other addition reactions of styrene sulfide which were accomplished, no effort was made to prove the structure of the product formed. Hydrochloric acid (12 *N*) or a solution of 12 *N* hydrochloric acid in ethanol caused polymerization of the sulfide. However, addition of styrene sulfide to a saturated solution of hydrogen chloride gas in glacial acetic acid resulted in formation of the desired chloromercaptan addition product in fairly good yield. From the results of the work on propylene sulfide and chloropropylene sulfide,[6,7] and by analogy to the structure of products obtained from the reaction of styrene oxide and hydrogen chloride,[8] it would appear very likely that the sulfide ring is cleaved in the "abnormal" manner at the secondary carbon to give 2-chloro-2-phenylethanethiol. This compound proved to be quite unstable on standing. Samples sealed under an argon atmosphere and submitted for analysis decomposed in transit. Titration with alcoholic iodine solution within a short time after distillation established quantitatively the nature of the compound through oxidation of the thiol group to a disulfide.

Acetyl chloride reacted readily with styrene sulfide and again, based on the work of Davies and Savige[6,7] on propylene sulfide and chloropropylene sulfide, it is assumed likely that the cleavage of the sulfide ring proceeded "abnormally" at the secondary carbon to yield 2-chloro-2-phenylethyl thioacetate,

$$C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2S\overset{\displaystyle O}{\overset{\|}{C}}CH_3$$

Only one reaction between a mercaptan and styrene sulfide was tried. Butanethiol-1 in the presence of boron trifluoride–ethyl ether complex as catalyst gave a 33% yield of adduct which could be either or both of the isomers, $C_6H_5CHCH_2SC_4H_9$ (SH on CH) and $C_6H_5CHCH_2SH$ (SC_4H_9 on CH).

Experimental[9]

Epithioethylbenzene (Styrene Sulfide).—A modification of the method of Guss and Chamberlain[1] was used. Following their procedure of simply stirring a 50% aqueous dioxane solution of potassium thiocyanate with styrene oxide at 0° for varying periods of time, yields no higher than 42% were obtained. In the modified procedure, after stirring the initial reaction mixture for 2 hr. at 60°, the top layer of mixed sulfide and oxide was separated and then stirred for an additional hour at 60° with a fresh aqueous dioxane solution of potassium thiocyanate. By this procedure yields of up to 72% were obtained. Due to the tendency of styrene sulfide to polymerize slowly on standing, it was used as soon as possible after distillation.

Method of Amine Addition Reactions.—To a rapidly stirred 2.5 times comparative molar amount of the amine in four times its volume of 90% benzene–10% ethanol was added dropwise a solution of styrene sulfide in three times its volume of the same solvent mixture. The additions were usually carried out at room temperature, but in the case of dimethylamine both original solu-

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(7) W. Davies and W. E. Savige, *ibid.*, 774 (1951).

(8) J. R. Clark and M. Pugliese, *J. Org. Chem.*, **24**, 1088 (1959).

(9) Melting points are uncorrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn.

tions were first chilled in the refrigerator and then the addition was carried out in the laboratory, the temperature of the reaction mixture slowly rising somewhat during this addition. In the case of one experiment with piperidine, the yield was improved very slightly by adding the sulfide solution to the piperidine solution maintained at 60°. In all cases the reaction mixtures after the addition was completed were corked in flasks and allowed to stand at room temperature for a period of 1 or more days. The solvents were then removed at reduced pressure, and the product was isolated by vacuum distillation. Since these products seemed to be somewhat unstable on standing at room temperature, hydrochloride salts were prepared for analysis by bubbling dry hydrogen chloride through an ether or benzene solution of the aminothiol and recrystallizing the precipitated hydrochloride from ethanol–ether or chloroform–carbon tetrachloride mixtures. The following amine adducts of structure I were prepared: 1-phenyl 2-piperidinoethanethiol, 1-phenyl 2-morpholinoethanethiol, 1-phenyl 2-dimethylaminoethanethiol, and 1-phenyl 2-diethylaminoethanethiol.

Desulfurization of Piperidine–Styrene Sulfide Adduct for Proof of Structure.—To a solution of 7.5 g. of the piperidine–styrene sulfide adduct in 100 ml. of benzene was added 80 g. of Raney nickel (no. 28, active nickel catalyst from the Raney Catalyst Co., Chattanooga, Tenn.). The mixture was stirred and heated at reflux in a water bath for 1.5 hr. It was then cooled and filtered and two extractions were made with 3 *N* hydrochloric acid. The combined acid extracts were made basic with 3 *N* sodium hydroxide solution, and the resulting mixture was extracted with ether twice. After drying of the ether extracts over anhydrous potassium carbonate and stripping of the ether, distillation gave 2 g. of colorless liquid, b.p. 115–116° (3 mm.); $n^{25}D$ 1.5235. [Paden and Adkins[10] reported b.p. 127–128° (10 mm.), for 1-(β-phenylethyl)-piperidine.] A picrate was prepared and recrystallized from ethanol, m.p. 144–145°. This agrees with that reported[11] for the picrate of 1-(β-phenylethyl)piperidine, 144–145°, and does not correspond to that reported for 1-(α-phenylethyl)piperidine, 140–142°.[12,13] The hydrochloride derivative was also prepared and was recrystallized first from ethanol and ether and then from chloroform and carbon tetrachloride, m.p. 218–220° after each recrystallization. This is clearly not in agreement with the melting point, 178°, reported[13] for the hydrochloride of 1-(α-phenylethyl)piperidine and thus supports the previous evidence for the structure of the adduct. It is, however, somewhat lower than the melting point, 232–233°, previously reported[10] for the hydrochloride of 1-(β-phenylethyl)piperidine.

Reaction of Anhydrous Bromine and Styrene Sulfide.—A solution of 4.1 g. (0.03 mole) of styrene sulfide in 25 ml. of chloroform was cooled in an ice bath and a cold solution of 2.4 g. (0.015 mole) of bromine in 25 ml. of chloroform was added dropwise with shaking. A light permanent yellow color indicated the end point of the reaction just before the last few drops were added. The solvent was stripped at room temperature under reduced pressure. The crude product weighed 7 g., indicating that a small amount of solvent was still present. When this thick oil was left in the refrigerator for a week, it slowly crystallized. The solid was recrystallized twice from ligroin (Eastman 0.67 to 0.69 density) to give colorless crystals, m.p. 89–91°.

Anal. Calcd. for $C_{16}H_{16}Br_2S_2$: Br, 36.97. Found: Br, 36.95

Reaction of Aqueous Chlorine and Styrene Sulfide.—A saturated solution of chlorine in 100 ml. of 80% acetic acid was cooled externally with an ice bath and stirred while 5.4 g. (0.04 mole) of styrene sulfide was added dropwise below the surface. At the same time chlorine was passed slowly into the mixture. After addition of the sulfide was completed and the solution was yellow, more water was added to make the concentration 50%. The yellow color disappeared, and more chlorine was passed into the mixture until a permanent yellow color again was attained. The mixture was then poured into 150 ml. of water, 15 ml. of chloroform was added with shaking, and the lower layer was separated. A second extraction of the aqueous layer with 15 ml. of chloroform was made, and the chloroform extracts were combined, washed twice with water, and dried over calcium chloride. Removal of solvent under reduced pressure left 8.9 g. of crude product. Distillation gave 8 g. (84%) of 2-chloro 2-phenylethanesulfonyl chloride, b.p. 126–128° (0.6 mm.). A redistillation was performed and a center cut, b.p. 116–118° (0.3 mm.); $n^{27}D$ 1.5630 was taken for analysis.

Anal. Calcd. for $C_8H_8Cl_2O_2S$: C, 40.18; H, 3.37. Found: C, 40.45; H, 3.44.

Conversion of 2-Chloro-2-phenylethanesulfonyl Chloride to 2-Phenylethenesulfonamides.—Addition of 2-chloro-2-phenylethanesulfonyl chloride to aqueous ammonia with vigorous shaking resulted in precipitation of a white solid. This was recrystallized three times from ethanol to give 2-phenylethenesulfonamide m.p. 139.5–141°, lit.,[5] m.p. 140–142°.

Anal. Calcd. for $C_8H_9NO_2S$: C, 52.44; H, 4.95. Found: C, 52.70 H, 5.21.

The reactions of amines with 2-chloro-2-phenylethanesulfonyl chloride were carried out in ether solution, using an excess of the amine. Immediate reaction occurred, with precipitation of the amine hydrochloride. The mixtures were allowed to stand several hours, then washed three times with water, and the ether solutions were dried over calcium chloride. Removal of the ether left oils which crystallized on standing in the refrigerator. The solids were recrystallized several times from ligroin (Eastman 0.67 to 0.69 density) containing a few drops of benzene. The following sulfonamides were obtained: *N,N*-Diethyl-2-phenylethenesulfonamide—m.p. 76–77°. *Anal.* Calcd. for $C_{12}H_{17}NO_2S$: C, 60.23; H, 7.12. Found: C, 60.36; H, 7.11. 2-Phenylethenesulfonpiperidide–m.p. 84–86°. *Anal.* Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82. Found: C, 61.94; H, 6.63.

Reaction of Hydrogen Chloride and Styrene Sulfide.—A solution of 7 g. (0.059 mole) of styrene sulfide in 25 ml. of 90% benzene–10% ethanol solution was added dropwise with stirring at room temperature to a saturated solution of hydrogen chloride in 100 ml. of glacial acetic acid. When approximately half of the sulfide had been added, the mixture was resaturated with hydrogen chloride and the addition then was continued. After the addition was completed, the mixture was corked in a flask and let stand for 6 days. It was then poured into 250 ml. of saturated sodium chloride solution and two ether extractions were made. The combined ether extracts were washed three times with water and dried over anhydrous magnesium sulfate. Distillation gave 4.5 g. (50%) boiling from 77–82° (0.3 mm.). Redistillation gave a center cut for analysis, b.p. 86–87° (0.4 mm.); $n^{25}D$ 1.5779. Since samples decomposed on standing, analysis was carried out on a freshly distilled sample by titration with alcoholic iodine of the thiol group.

Anal: Calcd. for C_8H_9ClS: equiv. wt., 172.66. Found: equiv. wt., 171.5.

Reaction of Acetyl Chloride and Styrene Sulfide.—To 4.0 g. (0.05 mole) of acetyl chloride was added dropwise with shaking 3.4 g. (0.025 mole) of styrene sulfide. The mixture was allowed to stand at room temperature overnight and then poured into about 40 ml. of water. Two ether extractions were made and the combined ether extracts were washed three times with water and dried over calcium chloride. Distillation gave 3 g. (55.5%) of colorless oil, b.p. 127–129° (0.7 mm.). Redistillation gave a center cut for analysis, b.p. 121° (0.3 mm.); $n^{27}D$ 1.5620.

Anal. Calcd. for $C_{10}H_{11}ClOS$: C, 55.93; H, 5.17. Found: C, 55.69; H, 5.08.

Reaction of Butanethiol-1 and Styrene Sulfide.—To 7.2 g. (0.08 mole) of butanethiol-1 containing 2 drops of boron trifluoride–ethyl ether complex as catalyst and maintained at 60–70° with a water bath was added dropwise with stirring 5.4 g. (0.04 mole) of styrene sulfide. Stirring and heating was continued for 2 hr. and then the mixture was allowed to stand overnight at room temperature. Distillation gave 3 g. (33.3%), b.p. 100–103° (0.7 mm.). Redistillation gave a center cut for analysis, b.p. 107–108° (1.2 mm.); $n^{30}D$ 1.5586.

Anal. Calcd. for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.84; H, 8.17.

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