[Contribution from the Department of Chemistry, Duquesne University]

The Behavior of Some Disulfides in the Presence of Acids. Attempted Preparation of Phenethyl Disulfide

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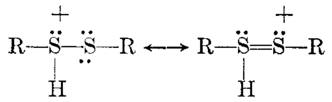
Phenyl disulfide failed to rearrange in the presence of sulfuric acid or boron trifluoride but gave deeply colored solutions unlike benzyl disulfide. During attempted preparations of phenethyl disulfide there was observed a transient color and the distillates deposited 2-phenethylsulfinyl-1-phenylethanol which was also synthesized from phenethyl mercaptan, styrene, and air.

In view of the known ability of sulfides to become protonated[1] it was of interest to investigate the possibility that the protonation of phenyl disulfide (I) may lead to a rearrangement analogous to the benzidine rearrangement of protonated hydrazobenzenes.[2] While I readily dissolved in cold 100 per cent sulfuric acid, only starting material could be isolated when the solution was poured on ice.[3] Similarly, a treatment of a refluxing solution of I in chloroform with gaseous boron trifluoride failed to cause any rearrangement of the disulfide.

The failure of the cleavage of the sulfur-sulfur bond can be attributed to the resonance possibility of the monoprotonated species:



$$R—\underset{H}{\overset{+}{\ddot{S}}}—\ddot{S}—R \longleftrightarrow R—\underset{H}{\overset{+}{S}}=\ddot{S}—R$$

This phenomenon would be expected to inhibit the double protonation required for the benzidine rearrangement of hydrazobenzenes, and also to strengthen the sulfur-sulfur bond.

During the experiments with I it was observed that the addition of sulfuric acid or boron trifluoride produced a deep violet or blue color, respectively, and that the color disappeared when the mixtures were poured on ice. In order to determine whether the formation of color depends on conjugation of the protonated disulfide with the aryl groups or simply results from the above mentioned resonance of the protonated disulfide moiety, there was also investigated the behavior of benzyl disulfide in cold sulfuric acid. This disulfide was found to be soluble in cold sulfuric acid without sulfonation but the solution was only slightly discolored (pale yellow). Thus it may be concluded that the production of color when disulfides are treated with acids (under conditions which do not cause sulfonation or other pronounced changes) requires conjugation of an aryl group with the protonated disulfide function.

It was our intention to extend the observation of halochromy of disulfides to phenethyl disulfide (II) but the preparation of this compound in the pure state proved fruitless. Previous investigators[4,5] also reported difficulties in the purification of II and the more recent workers[6] who claimed to have prepared pure II failed to substantiate their claim by analytical data. In our hands the product of the oxidation of phenethyl mercaptan by either sodium hypoiodite or by hydrogen peroxide gave, when subjected to vacuum distillation, colorless vapor which unexpectedly turned purple upon reaching the cold part of the distillation apparatus. The purple distillate upon standing gradually faded and returned to a colorless state. The distillates, purple or colorless, upon repeated distillations gave erratic change in boiling ranges so that no constant-boiling fraction could be obtained, and the transient purple color was always apparent. Furthermore, the distillates upon standing precipitated a solid which by analysis and by comparison with an authentic sample proved to be 2-phenethylsulfinyl-1-phenylethanol (III). The formation of III indicates the instability of II under attempted vacuum distillations and can be visualized to result from the following sequence of reactions.

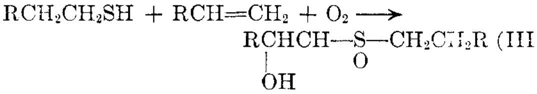
$$(R = C_6H_5)$$

$$RCH_2CH_2SSCH_2CH_2R \longrightarrow 2\ RCH_2CH_2S\cdot \qquad (1)$$

$$RCH_2CH_2S\cdot \longrightarrow RCH_2CH_2\cdot + S \qquad (2)$$

$$RCH_2CH_2\cdot + RCH_2CH_2S\cdot \longrightarrow RCH{=}CH_2 + RCH_2CH_2SH \qquad (3)$$

$$2\ RCH_2CH_2\cdot \longrightarrow RCH{=}CH_2 + RCH_2CH_3 \qquad (4)$$



$$RCH_2CH_2SH + RCH{=}CH_2 + O_2 \longrightarrow \underset{OH}{RCH}CH—\underset{O}{S}—CH_2CH_2R\ (III) \qquad (5)$$

$$S + S \longrightarrow S_2 \longrightarrow S_x \qquad (6)$$

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[1] Szmant and Brost, *J. Am. Chem. Soc.*, **73**, 4175 (1951).

[2] Hine, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, 1956, p. 345.

[3] The solution of I (and of sulfides)[1] in *cold* concentrated sulfuric acid is the result of protonation and not sulfonation. The insolubility of phenyl ether in sulfuric acid seems to be commonly misinterpreted (see Shriner, Fuson, and Curtin, *Systematic Identification of Organic Compounds*, 4th Ed., John Wiley & Sons, New York, 1956, p. 85) and attributed to slow sulfonation rather than lack of protonation.[1]

[4] von Braun, *Ber.*, **45**, 1565 (1912).

[5] Holmberg, *Ark. Kemi, Minerol. Geol.*, **12A**, No. 14, 10 (1937).

[6] McMillan and King, *J. Am. Chem. Soc.*, **70**, 4143 (1948).

Reaction (1) is well known and does not require any comment. Reactions (2) and (3) may well occur simultaneously, and the formation of resonance-stabilized styrene could be the driving force of reaction (3). The disproportionation shown in (4) is a prominent reaction of the phenethyl radical.[7] Reaction (5) was utilized for the preparation of III in excellent yield and was shown previously[8] in the case of styrene and a variety of mercaptans. Finally, we believe that reaction (6) explains the production of the transient purple color during vacuum distillations of II. When gaseous monomeric sulfur reaches the cold part of the distillation apparatus it would be expected to dimerize slowly (because of dilution with the liquid organic distillate) and thus to produce the S_2 molecules which were recently shown by Rice[9] to be purple. The dimeric sulfur subsequently polymerizes to give colorless colloidal sulfur.

EXPERIMENTAL

Attempted rearrangements of I. Compound I, 5 g., was dissolved in 50 cc. of 100% sulfuric acid while the mixture was cooled in an ice-bath. The purple solution after 30 minutes was poured on ice and I was recovered in almost quantitative yield, m.p. and mixture m.p. 59–60°.

I, 5 g., was dissolved in 50 cc. of chloroform and the refluxing solution was treated with gaseous boron trifluoride for 4 hours. The blue solution containing also a bluish oil was extracted with aqueous potassium fluoride and the chloroform layer after drying was concentrated. Addition of ethanol to the residue gave only I (90%; m.p. and mixture m.p. 59–60°).

Attempted rearrangement of benzyl disulfide. Benzyl disulfide, 5 g., was dissolved in ice-cold 100% sulfuric acid and the essentially colorless solution was kept at ice temperature for 30 minutes. When the solution was poured into a large quantity of ice-water there was recovered 85% of the initial disulfide, m.p. and mixture m.p. 69–70°.

Attempted preparation of II. The previously described procedure[6] gave an oil which upon distillation gave two fractions: b_1 165–174° and b_5 163°. Redistillation of these fractions gave fractions b_1 90–140° and b_1 140–170° and decomposition was apparent since the boiling points were erratic when the distillations were repeated. During distillations there were observed the color changes mentioned in the Discussion. The distillates upon standing gradually deposited 5–10% of a white solid, m.p. 163–163.5° after crystallization from methanol and petroleum ether.

Anal. Calc'd for $C_{14}H_{14}O_2S$: C, 70.00; H, 6.61; S, 11.69. Found: C, 69.87; H, 6.90; S, 11.49.

The preparation of II was also attempted by treating 50 g. of phenethyl mercaptan with a solution of 45.8 g. of iodine in 150 cc. of water containing 15 g. of sodium hydroxide. The mixture was extracted with benzene and the benzene solution was washed with dilute hydrochloric acid, dilute sodium hydroxide, and finally with water. The dried benzene solution was concentrated and the residual oil was fractionated. After removal of a low-boiling fraction consisting of unreacted phenethyl mercaptan there were collected fractions b_3 170–180° and b_2 170–180°. Redistillations of these fractions gave erratic boiling ranges and the transient purple color was observed. Upon standing at room temperature for several days the distillates deposited 5–10% of the white solid described above.

Preparation of III. An equimolar (0.1 mole) mixture of phenethyl mercaptan and redistilled styrene in heptane was treated with oxygen for a period of 23 hrs. by passing air into the solution to give a quantitative yield of a white solid which upon crystallization proved to be identical with the product obtained from the distillates in the attempted preparation of II.

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(7) Hey, *Reactions of Free Radicals in Solution*, Reilly Lectures, v. IX, Notre Dame Press, 1954, p. 8.

(8) Kharasch, Nudenberg, and Mantell, *J. Org. Chem.*, **16**, 524 (1951).

(9) Rice and Sparrow, *J. Am. Chem. Soc.*, **75**, 848 (1953).