SYNTHESIS AND SOME PROPERTIES OF THIOLS, SULFIDES, AND DISULFIDES OF THE SULFOLANE SERIES

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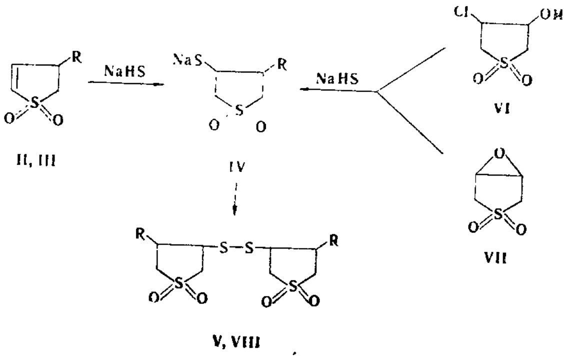
Sulfolanethiols, which were oxidized to 3,3'-disulfolanyl disulfide and 3,3'-bis(4-hydroxysulfolanyl) disulfide, were obtained by reaction of 3-sulfolene and 4-hydroxy-2-sulfolene with sodium hydrosulfide. Previously unknown cleavage of the sulfolanyl sulfides at the C–S bond of the sulfolane ring was observed during their oxidative chlorination and alkaline hydrolysis.

3,3'-Disulfolanyl disulfide is an efficient catalyst in the preparation of oligoester maleates [1]. The well-known method for the synthesis of sulfolanyl sulfides from sulfolene and mercaptans [2] is restricted by the available assortment of the latter. We have developed a method for the preparation of sulfolanethiols – the starting materials for the synthesis of disulfolanyl disulfides and various sulfides. It is known that 3-sulfolene (I) [2] and 4-hydroxy-2-sulfolene (II) [3] react with sodium hydrosulfide in aqueous solution to give sulfides. We have found that 3,3'-disulfolanyl sulfide, like 3,3'-disulfolanyl ether [4], is cleaved in the presence of bases to 2-sulfolene (III) and sulfolanyl mercaptan. However, if 3-sulfolenes or 2-sulfolenes are subjected to reaction with dilute (15%) aqueous sodium hydrosulfide [5], sulfolanethiols are formed in 80-90% yields. The addition of hydrosulfide to 3-sulfolene precedes migration of the double bonds to the 2 position [6].

According to the degree of isomerization, 2-sulfolene is rapidly converted to sulfolanethiol, and 3,3'-disulfolanyl sulfide is therefore not formed in the reaction of the thiol with 2-sulfolene. If 2-sulfolene is used, because of its increased concentration in solution, 3,3'-disulfolanyl sulfide is precipitated and rapidly disappears. Sulfolane-3-thiol (IV) was extracted from the acidified solution with chloroform and purified by vacuum fractionation.



II R=OH; III R=H; IV R=H; V R=OH; VIII R=H

Under similar conditions, 4-hydroxy-2-sulfolene (II) reacts to give the water-soluble 4-hydroxysulfolane-3-thiol, which was isolated from the solution in the form of 3,3'-bis(4-hydroxysulfolanyl) disulfide (V) by oxidation with hydrogen peroxide. The same compound was obtained by reaction of 3-chloro-4-hydroxysulfolane (VI) or 3,4'-epoxysulfolane (VII) with sodium hydrosulfide. Sulfolane-3-thiol was oxidized to 3,3'-disulfolanyl disulfide (VIII) by hydrogen peroxide, iodine, and air oxygen. A one-step method for

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TABLE 1. Characteristics of the Synthesized Compounds

Compound No.	Compound	mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
				C	H	Cl	S	C	H	Cl	S	
IV	$R^*—SH$	†	$C_4H_8O_2S_2$	31,5	5,4	—	42,3	31,6	5,3	—	42,1	85
V	$HO—R—S—S—R—OH$	205—206	$C_8H_{14}O_6S_4$	28,8	4,3	—	38,2	28,7	4,2	—	38,4	85
VIII	$R—S—S—R$	125—127	$C_8H_{14}O_4S_4$	31,9	4,3	—	42,3	31,8	4,7	—	42,4	80
IX	$R—SO_2—Cl$	118	$C_4H_7O_4S_2Cl$	22,2	3,3	16,3	29,3	21,9	3,2	16,2	29,3	90
X	$R—SO_2—S—R$	183—184	$C_8H_{14}O_6S_4$	28,6	4,2	—	38,3	28,7	4,2	—	38,4	80
XI	$Cl—R—S—R$	176—177	$C_8H_{13}O_4S_3Cl$	32,0	3,8	11,5	32,0	31,5	4,2	11,6	31,6	90
XII	$R—SO_2—CH_2\ C(Cl)—(CH_2)_3—CH_3$	113—115	$C_{10}H_{19}O_4S_2Cl$	40,5	6,0	12,3	21,4	40,0	6,3	11.7	21,2	80
XIII	$R—SO_2—C(C_6H_5)=CHCl$	154—155	$C_{12}H_{13}O_4S_2Cl$	44,6	3,8	11,2	20,3	44,9	4,0	11,0	20,0	40
XIV	$R—S—(CH_2)_2—S—R$	148	$C_{10}H_{18}O_4S_4$	36,5	5,6	—	38,5	36,3	5,5	—	38,8	90
XV	$R—SO_2—(CH_2)_2—SO_2R$	175	$C_{10}H_{18}O_8S_4$	30.4	4,6	—	32,6	30.4	4,6	—	32,5	90
XVI	$R—SO_2—CH_3$	131—132	$C_5H_{10}O_4S_2$	30,3	5,0	—	32,2	30,5	5.1	—	32.3	83
XVII	$R—SO_2—CH_2—CH=CH_2$	71—72	$C_7H_{12}O_4S_2$	37,2	5,4	—	28,8	37,5	5,4	—	28,6	85
XVIII	$R—SO_2—C_4H_9$	90	$C_8H_{16}O_4S_2$	40,2	6,7	—	26,6	40,0	6,7	—	26,7	95
XIX	$RSO_2—C_8H_{17}$	111	$C_{12}H_{24}O_4S_2$	48,5	7.8	—	21,7	48,6	8,2	—	21,6	83
XX	$R—SO_2—(CH_2)_2—Cl$	92	$C_6H_{10}O_4S_2Cl$	29,4	4,3	14,3	26,1	29,3	4,1	14,4	26,1	60

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*R = sulfolanyl.

† This compound had bp 152-153° (2 mm), n_D^{20} 1.5160, and d_4^{20} 1.1797; found: MR_D 39.50; calculated: MR_D 39.29.

the preparation of disulfide VIII from 3-sulfolene by oxidation of sulfolane-3-thiol by air oxygen has been developed [7]. Sulfolanesulfonyl chloride (IX), which was identified by alternative synthesis from sulfolane-3-sulfonic acid [8], was obtained by vigorous oxidation of 3,3'-disulfolanyl disulfide or sulfolane-3-thiol with chlorine. In the case of incomplete chlorination, the formation of sulfolanyl thiosulfonate (X) mixed with the sulfonyl chloride was observed. The oxidative chlorination of 4-hydroxysulfolane-3-thiol gives 4-hydroxysulfolane-3-sulfonic acid, which is identical to a previously obtained sample [9].

Anomalous cleavage of 3,3'-disulfolanyl sulfide by chlorine in alkaline media to 2-sulfolene and sulfolanesulfonyl chloride was observed. The latter is hydrolyzed under the reaction conditions to give sodium sulfolane-3-sulfonate. Inasmuch as the reaction proceeds only in the presence of alkali, the results can be explained by prior cleavage of the sulfide to 2-sulfolene and sulfolane-3-thiol and subsequent conversion of the thiol.

Sulfolanesulfenyl chloride, which is an orange-red oily liquid that fumes in air and reacts vigorously with olefins, was obtained by chlorination of sulfolane-3-thiol and the disulfide in absolute carbon tetrachloride. The corresponding chlorosulfides and sulfones (XI-XIII, Table 1) were isolated in the reaction of the sulfenyl chloride with 3-sulfolene, hexene, and phenylacetylene.

Sodium sulfolane-3-thiolate reacts vigorously with alkyl halides, for example CH_3I, C_3H_5Br, $Br(CH_2)_2Br$, C_4H_9Br, $C_8H_{17}Cl$, $C_6H_5CH_2Cl$, and $Cl(CH_2)_2OH$ to give the corresponding sulfides, which were identified in the form of sulfones XIV-XX (Table 1).

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. Chromatography was carried out in a thin loose layer of activity II Al_2O_3 with elution by ether–ethyl acetate (2 : 3) and development by iodine vapors.

Sulfolane-3-thiol (IV). A mixture of 2.7 mole of 3-sulfolene and 1.5 liter of 10-15% aqueous sodium hydrosulfide solution was heated at 50-60° with vigorous stirring for 8 h, after which it was neutralized with hydrochloric acid, and the resulting layers were separated. The upper aqueous layer was extracted with chloroform and combined with the lower layer. The combined layers were washed with acidified water and dried, and the solvent was removed. The residual solfolane-3-thiol was purified by vacuum fractionation. The IR spectrum contains the characteristic frequencies of the SO_2 group at 1130 cm^{-1} (ν_s) and 1310 cm^{-1} (ν_{as}) and ν_{SH} at 2575 cm^{-1}.

3,3'-Disulfolanyl Disulfide (VIII). A mixture of 2 moles of 3-sulfolene in 500 ml of water and 500 ml of commerical 25% NaHS was heated to 50-60° and stirred for 8 h. Stirring was continued, and 200 ml of hydrochloric acid and 200 ml of 28% hydrogen peroxide were added slowly dropwise in succession. After 5 h, 209 g (78%) of a white precipitate of VIII with mp 125° (from acetone) was separated.

3,3'-Bis(4-hydroxysulfolanyl) disulfide (V) was similarly obtained from 4-hydroxy-2-sulfolene.

Sulfolane-3-sulfonyl Chloride (IX). A mixture of 112 g (1 mole) of 3-sulfolene in 250 ml of water and 250 ml of 25% NaHS was stirred at 60-80° for 1-8 h, after which a stream of chloride and air (1 : 10) was bubbled into the mixture until sulfolanesulfonyl chloride precipitated. The precipitated sulfonyl chloride was removed by filtration, washed with water, and dried to give IX with mp 115-116° (from carbon tetrachloride) [8]. When the amount of chloride was inadequate, the sulfolanyl thioester of sulfolane-3-sulfonic acid (X) with mp 183-184° (from acetone) was formed.

Oxidative Chlorination of 3,3'-Disulfolanyl Sulfide. A 0.007-mole sample of 3,3'-disulfolanyl sulfide was chlorinated at room temperature in 30 ml of a 10% aqueous solution of alkali for 3-12 h, after which the precipitate was removed by filtration and identified (by mixed-melting-point determination) as sulfolane-3-sulfonyl chloride (mixed mp 115-116°). The aqueous solution was extracted with chloroform, and the chloroform was removed to give 0.8 g of a mixture of 2-sulfolene and 3-sulfolene, which were identified by TLC.

Sodium sulfolane-3-sulfonate, which was present in the aqueous layer, was identified from the IR spectrum in the form of sulfolane-3-sulfonic acid [8] by conversion of the salt on KU-2 ion-exchange resin. The degree of conversion of the disulfolanyl sulfide was 97%.

Sulfolane-3-sulfenyl Chloride and Its Reaction with Unsaturated Compounds. A solution of 0.06 mole of sulfolane-3-thiol or 0.03 mole of 3,3'-disulfolanyl disulfide in 200 ml of absolute carbon tetrachloride was chlorinated at room temperature until the precipitate vanished. The solid was removed, and 0.06 mole of 1-hexene in CCl_4 was added to the residual sulfolane-3-sulfenyl chloride at such a rate that the temperature of the mixture did not exceed 50°. The mixture was then stirred for 1-2 h, the solvent was removed by distillation, and the residual 1-(sulfolanyl-3-thio)-2-chlorohexane was identified in the form of sulfone XII by oxidation with 28% hydrogen peroxide in glacial acetic acid. 4-Chlorosulfolanyl-3-thiosulfolane (XI) was similarly obtained from sulfolane-3-sulfenyl chloride and 3-sulfolene in CCl_4. Under the same conditions, 1-phenyl-1-(sulfolanyl-3-thio)-2-chloroethylene, which was identified in the form of sulfone XIII, was obtained with phenylacetylene.

Reaction with Alkyl Halides. A 17.2-ml (0.2 mole) sample of dibromoethane was added to 50° with vigorous stirring in the course of 1 h to 128 ml (0.2 mole) of an aqueous solution of sodium sulfolane-3-thiolate. The water was removed by vacuum distillation, and the residue was extracted with acetone to give 31.2 g (0.094 mole) of white crystalline XIV with mp 148° (from methanol). 3-Methyl-, 3-allyl-, 3-butyl-, 3-octyl-, 3-benzyl-, and 3-(β-hydroxyethylthio)sulfolanes were similarly obtained. The latter sulfide was converted to 3-(2-chloroethylthio)-sulfolane by refluxing in concentrated HCl. Crystalline 3-benzylthiosulfolane was crystallized from diethyl ether and had mp 62-63° (mp 61-63° [10]). The liquid sulfides were purified by vacuum distillation and were identified in the form of the sulfones (XV-XX) by oxidation with 28% hydrogen peroxide in glacial acetic acid. The sulfones were crystallized from methanol.

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