REACTION OF SULFOLENES AND THEIR DERIVATIVES WITH SOME SULFUR-CONTAINING NUCLEOPHILES

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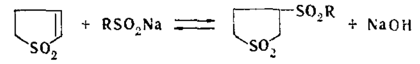
Reaction of 2-sulfolene, 4-hydroxy-2-sulfolene, 4-bromo- and 3-chloro-2-sulfolenes, 3-chloro-4-hydroxysulfolane, and 3,4-dibromo(dichloro)sulfolanes with sodium methane-, hexane-, allene-, benzene-, and p-toluenesulfinates and magnesium gave 3-methyl-, 3-hexyl-, 3-allyl-, 3-phenyl-, and 3-(p-tolylsulfonyl)sulfolanes, 3-methyl-, 3-phenyl-, and 3-(p-tolylsulfonyl)-4-hydroxysulfolanes, and 3-phenyl- and 4-phenylsulfonyl-2-sulfolenes.

The base-catalyzed addition of mercaptans to 2-sulfolenes and 3-sulfolenes, which gives sulfolanyl sulfides, is well known [1]. Sulfolanyl sulfones were synthesized by oxidation of the latter [2]. The method does not extend to sulfides that contain readily oxidized groups. It has been proposed [2] that such sulfones be synthesized by reaction of the salts of sulfinic acids with halogen derivatives of sulfolane. Considering the limited accessibility of β-halosulfolanes [3-5], we worked out a one-step method for the preparation of sulfolanyl sulfones by reaction of sulfinic acid salts with 2-sulfolene [6].

A study of the properties of β-derivatives of sulfolane that contain heteroatoms [7] showed that in the presence of bases sulfolanyl sulfones are almost completely converted to 2-sulfolene and sulfinic acid salts, so that their addition cannot be realized in aqueous media.



If the alkali formed is removed from the reaction by means of an acetate or phosphate buffer, the sulfolanyl sulfones are formed in good yields (see Table 1). 4-Hydroxy-2-sulfolene reacts similarly to give 3-alkyl(aryl)sulfonyl-4-hydroxysulfolanes. These same products are obtained by reaction of sulfinic acid salts with 3-chloro-4-hydroxysulfolane.

A product identified as 4-phenylsulfonyl-2-sulfolene (X) was isolated in the reaction of 3,4-dibromo (chloro)sulfolanes and 4-bromo-2-sulfolene with sodium benzenesulfinate in aqueous media and in acetic acid. In acetic acid 3,4-diphenylsulfonylsulfolane (XI) was also obtained in 25% yield. The products were identified by chemical and spectral methods – by IR spectroscopy from the presence in the spectrum of X of the characteristic C–H absorption band for a cis-disubstituted double bond at 645 cm^{-1}, which is absent in the case of XI, and by UV spectroscopy for X and PMR spectroscopy (Fig. 2). The ratio of the integral intensities of the signals of the protons in the 4- and 5-positions (τ 6.25 ppm and 5.87 ppm, respectively) of the proton in the 3-position (τ 5.66 ppm, M), and of the protons in the 2-position (τ 2.73 ppm, M) is 1 : 1 : 1 : 2 for sulfolene X.

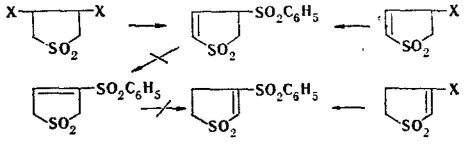


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TABLE 1. Sulfolanyl Sulfones $R-SO_2-R'$

Compound	R (in the 3-position)	R′	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	S	C	H	S	
I	CH_3	Sulfolanyl	133—134	$C_5H_{10}O_4S_2$	30,3	5,0	32,2	30,5	5,1	32,3	50
II	$CH_2{=}CH{-}CH_2$		71—72	$C_7H_{12}O_4S_2$	37,2	5,4	28,8	37,5	5,4	28,6	50
III	C_6H_{13}		86,5—87	$C_{10}H_{20}O_4S_2$	45,2	8,0	23,7	45,1	7,5	23,9	70
IV	C_6H_5		160	$C_{10}H_{12}O_4S_2$	46,0	4,5	24,6	46,2	4,6	24,6	70
V	C_7H_7		117	$C_{11}H_{14}O_4S_2$	48,7	5,3	23,2	48,2	5,1	23,4	70
VI	CH_3	4-Hydroxy-sulfolanyl	192—193	$C_5H_{10}O_5S_2$	29,2	4,7	29,9	28,0	4,7	29,9	30
VII	C_6H_5		153	$C_{10}H_{12}O_5S_2$	43.5	4,7	23,2	43,5	4,4	23,2	90
VIII	C_7H_7		142—143	$C_{11}H_{14}O_5S_2$	44.6	5,0	22,5	45,5	4,9	22,1	80
IX	C_6H_5	2-Sulfolenyl	153—154	$C_{10}H_{10}O_4S_2$	46,4	3,7	24,9	46,5	3,9	24,8	70
X	C_6H_5	2-Sulfol-enyl*	138	$C_{10}H_{10}O_4S_2$	46,7	4,1	25,0	46,5	3,9	24,8	85
XI	C_6H_5†		284—285	$C_{16}H_{16}O_6S_3$	47,5	4,1	23,9	47,9	4,0	24,0	55

* Substituent R in the 4-position.

†Substituent R in the 3- and 4-positions.

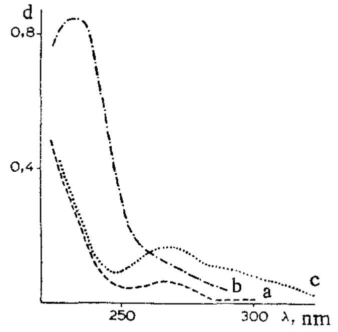

Fig. 1

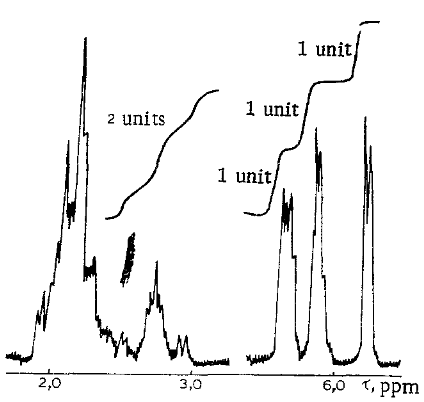

Fig. 2

Fig. 1. UV spectra in 10% aqueous dioxane of 4-phenylsulfonyl-2-sulfolane (a); 3-phenylsulfonyl-2-sulfolene (b); and 4-phenylsulfonyl-2-sulfolene containing KOH (c).

Fig. 2. PMR spectrum of a 10% solution of 4-phenylsulfonyl-2-sulfolene.

The isomeric 3-substituted sulfonyl-3-sulfolenes and sulfonyl-2-sulfolenes were not detected. 3-Phenylsulfonyl-2-sulfolene was isolated in the reaction of sodium benzenesulfinate with 3-chloro-2-sulfolene and was identified by thin-layer chromatography (R_f 0.43), IR and UV spectroscopy, and a mixed melting point determination with previously described products [8]. It was established by means of UV spectroscopy (Fig. 1) that 4-phenylsulfonyl-2-sulfolene is not isomerized in alkaline media. A smooth reaction between o-nitrophenyl-2,3-dibromo(dichloro)propyl sulfone and sodium p-toluenesulfinate, which leads to the trisulfone $ArSO_2CH_2CH(SO_2Ar)CH_2SO_2Ar$, has been reported [9]. On the other hand, α,β-unsaturated sulfones $ArSO_2CH{=}CHCH_2SO_2Ar$ are formed in good yields with p-chloro-, p-bromo-, and p-iodophenyl 2,3-dibromopropyl sulfones. The reaction with 3,4-dibromosulfolane proceeds similarly.

The data obtained in this study can be explained if one assumes that the substitution reaction proceeds via an elimination–addition scheme leading to the formation of 4-phenylsulfonyl-2-sulfolene, which does not add a second sulfinate molecule in alkaline media but forms a trisulfone (XI) in acetic acid.

EXPERIMENTAL

The UV spectra of ethanol and 10% aqueous dioxane solutions of the compounds were recorded with an SF-16 spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ and dimethyl sulfoxide (DMSO) solutions were recorded with a Varian-60A spectrometer with an operating frequency of 60 MHz and cyclohexane as the internal standard.

2-Sulfolene, 3-chloro-2-sulfolene, and 4-hydroxy-2-sulfolene were obtained by isomerization of 3-sulfolene, 3-chloro-3-sulfolene [10], and 3,4-epoxysulfolane [11], respectively. The 3,4-dihalosulfolanes and 3-chloro-4-hydroxysulfolane [12] were synthesized by bromination and chlorination of 3-sulfolene, while 4-bromo-2-sulfolene [13] was synthesized by reaction of 3,4-dibromosulfolane with pyridine. The products were chromatographed in a loose thin layer of activity II Al_2O_3; the eluent was diethyl ether, and the chromatograms were developed with iodine vapors.

3-Aryl(alkyl)sulfonylsulfolanes. An equimolar mixture of 2-sulfolene and the sulfinic acid salt was heated at 100° in an aqueous solution of phosphate (acetate) buffer or in acetic acid for 5-6 h. Sulfones III-V were isolated from the cooled (to 0°) solutions by filtration. An additional amount of the product was isolated by evaporation of the filtrate and recooling. Sulfones I and II were isolated by evaporation of the solvent and crystallization of the residue from methanol.

3-Aryl(methyl)sulfonyl-4-hydroxysulfolanes (VI-VIII). These compounds were obtained by a procedure similar to that used in the preceding experiment by reaction of sulfinic acid salts with 4-hydroxy-2-sulfolene and 3-chloro-4-hydroxysulfolane. They were isolated as sulfones I and II.

3-Phenylsulfonyl-2-sulfolene (IX). A 3.8-g (0.025 mole) sample of 3-chloro-2-sulfolene and 4.1 g (0.025 mole) of sodium benzenesulfinate were refluxed in a solution of 15 ml of CH_3COOH in 40 ml of water for 5-6 h. The products isolated were sulfones III-V.

4-Phenylsulfonyl-2-sulfolene (X). This compound was obtained in 80-85% yield by reaction of sodium benzenesulfinate with 3,4-dibromo(dichloro)sulfolanes and 4-bromo-2-sulfolene in molar ratios of 2:1 and 1:1, respectively. The product depressed the melting point of IX, and its IR, UV (Fig. 1), and PMR (Fig. 2) spectra differed from those of IX. Its spectrum (Fig. 1) did not change in 0.1 N KOH at 50°.

3,4-Diphenylsulfonylsulfolane (XI). This compound was obtained: a) in 55% yield (mp 284-285°) by reaction of sodium benzenesulfinate with X in acetic acid in a molar ratio of 1:1 and (b) in 25% yield in a mixture containing X by reaction of sodium benzenesulfinate with 3,4-dibromo(dichloro)sulfolanes and 4-bromo-2-sulfolene in a molar ratio of 2:1.

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