REACTION OF SULFOLANYL SULFONATES WITH SOME NUCLEOPHILIC REAGENTS

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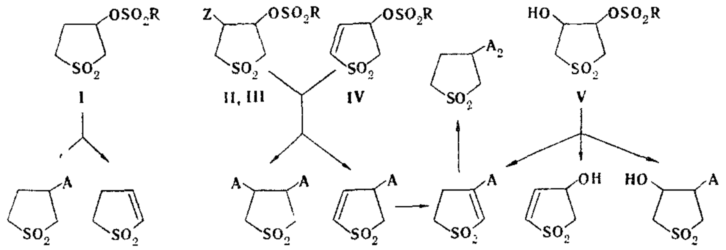
The corresponding β-substituted sulfolane derivatives were isolated in the reaction of 3-sulfolanyl arene(alkane)sulfonates with amines, alcohols, and mercaptans. Depending on the nature of the nucleophile, 3,4-disubstituted sulfolanes and 4- and 3-substituted 2-sulfolenes were obtained with 3,4-sulfolanyl disulfonates and 4-sulfolen-2-yl sulfonates.

The preparation of sulfolanyl and sulfolenyl arene(alkane)sulfonates [1, 2] and their use as convenient sulfolanylating agents for aromatic hydrocarbons [3, 4] have been reported. In the present research we investigated the reactions of these compounds with amines, alcohols, and mercaptans.



Z = halogen OSO_2R, where $R = C_6H_5$, C_7H_7, CH_3

The corresponding 3-substituted sulfolanes, which were identified by their IR spectra and mixed-melting-point determinations with the previously described compounds, were obtained in 70-90% yields in the reaction of I with butylamine, morpholine, butyl and allyl alcohols, and n- and tert-butyl mercaptans. 2-Sulfolene, the presence of which in small amounts in all of the remaining cases was noted by thin-layer chromatography (TLC) (R_f 0.38), was isolated in 96% yield in the reaction with diethylamine.

Considering the increased α-C–H acidity of β-derivatives of sulfolanes [5] and the appreciable activation of cleavage of CH_3O^- and PhO^- groups [6] from the corresponding sulfolanyl ethers, it might be assumed that the reaction of I with nucleophilic reagents is also realized completely or partially via an elimination–addition scheme with the formation of substitution products or 2-sulfolene if addition of the nucleophile is hindered.

Sulfonates II-V react in a more complex manner. A mixture of products, which Prochazka and Horak were unable to completely identify, was obtained in the reaction of III and IV

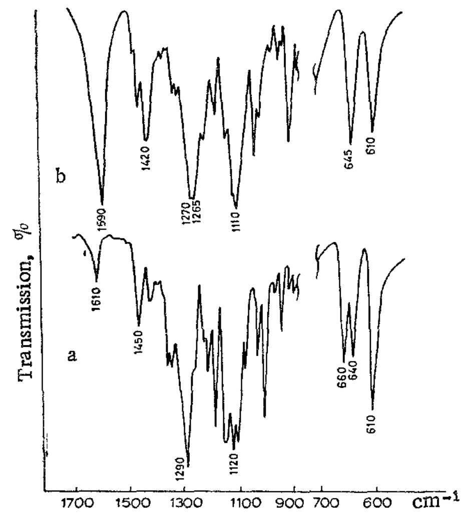


Fig. 1. IR spectra: a) 4-morpholino-2-sulfolene; b) 3-morpholino-2-sulfolene.

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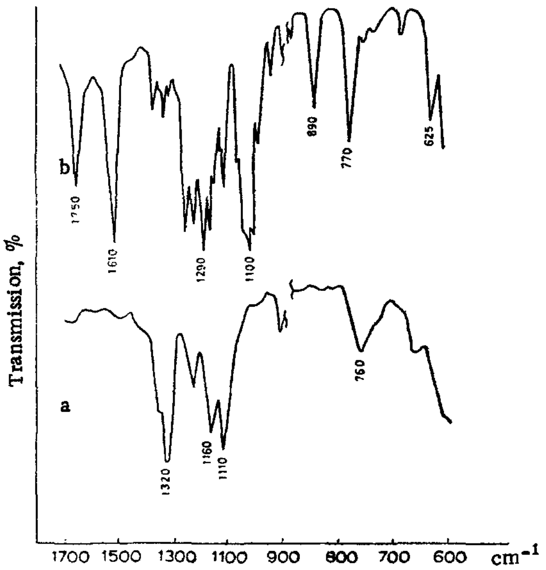


Fig. 2

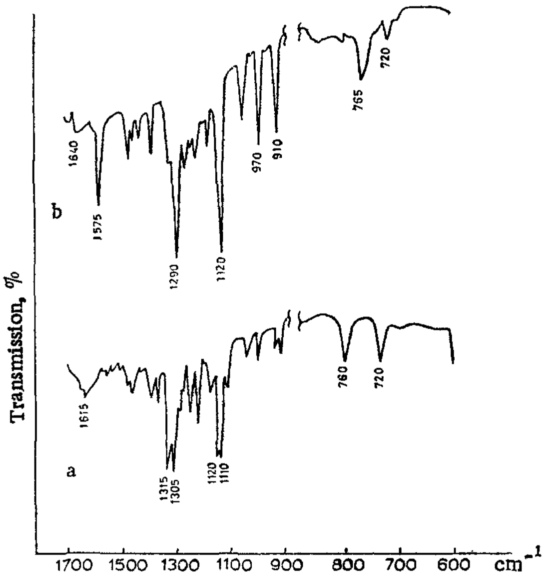
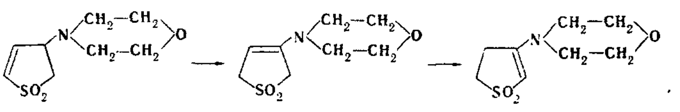


Fig. 3

Fig. 2. IR spectra: a) 4-butoxy-2-sulfolene; b) 3-butoxy-2-sulfolene.

Fig. 3. IR spectra: a) 4-tert-butylthio-2-sulfolene; b) 4-n-butylthio-2-sulfolene.

with liquid ammonia [7], while the corresponding 4-N-substituted 2-sulfolenes, identified as the hydrochlorides, are obtained with morpholine, butylamine, and diethylamine in tetrahydrofuran (THF) and methanol. The position of the double bond in the ring was proved by the presence of the IR spectrum of the δ_{C-H} frequency characteristic for a cis double bond at 660 cm^{-1}, which is absent in the IR spectrum of the isomerized product (Fig. 1). It was established that 4-N-substituted 2-sulfolenes are isomerized to 3-N-substituted 2-sulfolenes in 1 N aqueous alkali solutions.



Although we were unable to isolate 3-N-substituted 3-sulfolenes, the isomerization probably proceeds by successive migration of the double bond from the 4 position to the 3 position and then to the 2 position, which is stabilized by the donor–acceptor interaction of the unshared pair of electrons of the nitrogen atom with the d orbitals of the sulfur atom of the sulfonyl group.

3-Butylamino- and 3-morpholino-4-hydroxysulfolanes were obtained in yields of 86 and 92%, respectively, in the reaction of V with butylamine and morpholine. As in the case of I, elimination of a sulfonate group was observed with diethylamine, and 4-hydroxy-2-sulfolene, which was identified by TLC (R_f 0.1), was isolated.

The composition of the products of the reaction of sulfonates IV–V with alkoxides and mercaptides depends on the nature of the nucleophilic reagent and the conditions. At room temperature, II–IV reacted with the alkoxides of allyl and butyl alcohols to give 3,4-dialkoxysulfolanes, but the yields of ethers were lower with iso- and sec-butyl alcohols. The nature of the alcohol had a similar effect on the yield of 3-alkoxy-4-hydroxysulfolanes in the reaction with sulfonate V. The yields of hydroxy ethers fell successively in the order allyl alcohol, n-, iso-, and sec-butyl alcohols. In all cases, the presence of traces of 3,4-dialkoxysulfolanes was detected by TLC. Mixtures of two products with R_f 0.65 and 0.50 and 0.65 and 0.25, respectively, which were separated by column chromatography, were obtained in the reaction of IV with sodium butoxide in excess butanol at −10 and 70–80°. The product with R_f 0.65 was identified as 3,4-dibutoxysulfolane. The products with R_f 0.50 and 0.25 were butoxysulfolenes in which the position of the double bond was established by comparison of their IR spectra (Fig. 2). As in the case of Ib, an appreciable shift of the asymmetrical stretching absorption of the SO_2 group as a consequence of the donor–acceptor interaction of the heteroatom with the sulfonyl group and the presence of the intense absorption band of a double bond, which is characteristic for 3-substituted 2-sulfolenes [9, 11], are characteristic for 3-butoxy-2-

TABLE 1. Characteristics of R–X–R'

Compound No.	R	R'	X	mp or bp (mm), °C	Empirical formula	Found, %				Calculated, %				Yield, %
						C	H	N	S	C	H	N	S	
1	H	$NHC_4H_9 \cdot HCl$	4-Substituted 2-sulfolene	182—183	$C_8H_{16}NClO_2S$	42,3	7,2	6,4	14,4	42,6	7,1	6,3	14,3	88
2	OH	NHC_4H_9	3,4-Disubstituted sulfolane	112—113	$C_8H_{17}NO_3S$	46,3	8,2	7,0	15,7	46,4	8,3	6,7	15,5	86
3	H	NC_4H_8O	4-Substituted 2-sulfolene	130—131	$C_8H_{13}NO_3S$	47,4	6,4	6,8	15,4	47,3	6,4	6,9	15,7	83
4	H	NC_4H_8O	3-Substituted 2-sulfolene	179—180	$C_8H_{13}NO_3S$	47.2	6,4	7,1	15,9	47,3	6,4	6,9	15,7	95
5	H	$N(C_2H_5)_2 \cdot HCl$	4-Substituted 2-sulfolene	208—209	$C_8H_{16}NClO_2S$	42,4	7,1	6,4	14,2	42,6	7,1	6,2	14,6	61
6	OH	NC_4H_8O	3,4-Disubstituted sulfolane	154—155	$C_8H_{14}NO_4S$	43,5	6,7	6,6	14,7	43,6	6.2	6,4	14,5	92
7	H	OC_4H_9	4-Substituted 2-sulfolene	143—145 (1)	$C_8H_{14}O_3S$	50,5	7,3		16.7	50,4	7,4		16,8	52
8	H	OC_4H_9	3-Substituted 2-sulfolene	86—87	$C_8H_{14}O_3S$	50,7	7,4		16.9	50,4	7,4		16,8	50
9	OH	OC_4H_9	3,4-Disubstituted sulfolane	170—172 (1,5)	$C_8H_{16}O_4S$	46,2	7,6		15,2	46,1	7,7		15,4	80
10	OH	OC_4H_9-*iso*	3,4-Disubstituted sulfolane	150—152 (1,5)	$C_8H_{16}O_4S$	46,1	7.6		15.4	46,1	7,7		15,4	50
11	OC_4H_9	OC_4H_9	3,4-Disubstituted sulfolane	160—162 (1.5)	$C_8H_{16}O_4S$	55,2	9.5		12,3	55,1	9,6		12,3	90
12	OC_4H_9-*iso*	OC_4H_9-*iso*	3,4-Disubstituted sulfolane	145—147 (1)	$C_{12}H_{25}O_4S$	55,1	9.1		12,4	55,1	9.6		12,3	85
13	OH	OC_4H_9-*sec*	3,4-Disubstituted sulfolane	*	$C_8H_{16}O_4S$	46,3	7,6		15,4	46.1	7,7		15,4	30
14	OC_4H_9-*sec*	OC_4H_9-*sec*	3,4-Disubstituted sulfolane	†	$C_{12}H_{25}O_4S$	54,9	9,1		12,4	55,1	9,6		12,3	66
15	OH	$OCH_2—CH═CH_2$	3,4-Disubstituted sulfolane	170—172 (2)	$C_7H_{12}O_4S$	42,8	6,2		16,0	43,7	6,3		16,6	90
16	H	SC_4H_9-*tert*	4-Substituted sulfalene	55—56	$C_8H_{14}O_2S_2$	46.6	6,8		30,8	46,6	6.8		31,0	96
17	H	$SO_2C_4H_9$	4-Substituted 2-sulfolene	105—106	$C_8H_{14}O_4S_2$	40,5	6,8		26,7	40,3	5,9		26,9	90
18	OH	$SO_2C_4H_9$	3,4-Disubstituted sulfolane	83—84	$C_8H_{16}O_5S_2$	37,5	6,3		25,1	37,5	6,3		25,0	94
19	$SO_2C_4H_9$	$SO_2C_4H_9$	3,4-Disubstituted sulfolane	174—175	$C_{12}H_{24}O_6S_3$	39,9	6,6		26,6	40,0	6.7		26,7	70

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*n_D^{20} 1.6966.

†n_D^{20} 1.6957.

sulfolene (R_f 0.25) (Fig. 2b). The 3,4-dibutoxysulfolanes and butoxysulfolenes were identified by TLC in the reactions of sulfonates II and III with excess (1 : 2) sodium butoxide.

It has been reported [8] that 3,4-dichlorosulfolane reacts with mercaptides to give 3,4-dithio ethers. Refluxing of sulfonates II–IV with excess (1 : 2) sodium butylmercaptide in methanol for 4–5 h gave 3,4-di-(butylthio)sulfolane (R_f 0.40) containing butylthiosulfolene (R_f 0.45). The products were isolated and identified as the sulfones. At −10 to −5° a mixture of sulfides with R_f 0.62 and 0.45 and a disulfide with R_f 0.40 were obtained with the same reagents. To establish the structures of the compounds obtained we carried out the reaction of IV with sodium tert-butylmercaptide under similar conditions. At low temperature we obtained the previously undescribed 4-tert-butylthio-2-sulfolene, which differed from known isomers with respect to melting point, R_f value (0.55), and IR spectrum (Fig. 3). The positions of the frequencies of the SO_2 groups in the IR spectra of 4-tert-butylthio-2-sulfolene and the sulfide isolated in the reaction of IV with n-C_4H_9SNa at −10° were similar.

The corresponding 3-butylthio-2-sulfolenes, which had identical IR spectra and of which 3-tert-butylthio-2-sulfolene was previously described in [9], were obtained by refluxing IV with sodium tert- and n-butylmercaptides.

EXPERIMENTAL

The starting sulfonates (I–V) were previously obtained in [1, 2]. Thin-layer and column chromatography on activity II aluminum oxide with elution by diethyl ether were used to identify and separate the products. The thin-layer chromatograms were developed with iodine vapors. The IR spectra of KBr pellets or liquid films between KBr plates were recorded with a UR-20 spectrometer.

Reaction of Sulfolanyl Sulfonates with Amines. A mixture of 0.03 mole of sulfolanyl sulfonate and 0.06 mole of amine in 40 ml of dry THF was stirred at room temperature for 2 h, after which the precipitate was removed by filtration, the filtrate was evaporated, and the residue was recrystallized from methanol. The liquid aminosulfolanes were identified as the hydrochlorides.

Reaction of Sulfolanyl Sulfonates with Alcohols. A 0.03-g-atom sample of sodium metal was dissolved in 40 ml of alcohol, and 0.03 mole of sulfolanyl sulfonate was added. The mixture was then stirred at room temperature for 4–6 h, after which it was acidified to pH 6 with hydrochloric acid, and the precipitate was removed by filtration. The filtrate was evaporated, and the residue was extracted with three 25-ml portions of diethyl ether. The ether extracts were dried over anhydrous sodium sulfate, the ether was removed by distillation, and the residue was vacuum distilled.

4-Butoxy-2-sulfolene. This compound was obtained by the above method, except that the mixture was stirred at −10° for 3 h, and the mixture of 3,4-dibutoxysulfolane and 4-butoxy-2-sulfolene was separated with a column filled with aluminum oxide with monitoring by TLC.

3-Butoxy-2-sulfolene. This compound was similarly obtained, except that the mixture was stirred at 70° for 3 h.

Reaction of Sulfolanyl Sulfonates with Thiols. The reactions were carried out as in the case of the reactions with alcohols. The sulfides were isolated by crystallization from methanol or by vacuum distillation. The liquid sulfides were oxidized to sulfones in glacial acetic acid with 30% H_2O_2 solution. The sulfones were crystallized from methanol.

The compounds obtained for the first time are presented in Table 1.

Isomerization of 4-Morpholino-2-sulfolene. A mixture of 2 g of 4-morpholino-2-sulfolene and 10 ml of a 1 N KOH solution was refluxed for 1 h. It was then cooled, and the precipitate was recrystallized from water. The physical constants of 3-moropholino-2-sulfolene are presented in Table 1.

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