

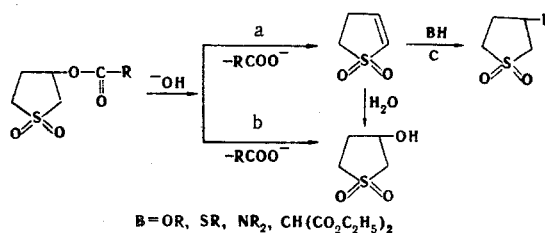
# REACTIONS OF 3-ACYCLOXYSULFOLANES WITH NUCLEOPHILIC REAGENTS

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In contrast to alkyl esters of carboxylic acids, 3-acyloxysulfolanes on reaction with nucleophilic reagents readily split out a carboxylic acid to give 2-sulfolene, which then reacts with compounds containing a labile hydrogen atom. On the basis of data on the kinetics of alkaline hydrolysis of benzoates, a scheme for elimination of the acid that includes the intermediate formation of a transition state of the  $E_1cB$  type is proposed.

3,4-Diacyloxysulfolanes are recommended as auxiliary substances for the finishing of cotton fabrics in alkaline media [1]. In order to ascertain the scheme of the chemical transformations of the preparations and the possibility of finishing protein fibers with them, in the present research we studied the hydrolysis of 3-acetoxysulfolane (I) and substituted 3-benzoxysulfolanes (IIa-e) and their base-catalyzed reactions with alcohols, amines, and mercaptans. It was found that, in contrast to esters of aliphatic alcohols, 3-acyloxysulfolanes are titrated by alkali and give 2-sulfolene containing up to 8% 3-hydroxysulfolane in the case of 3-acetoxysulfolane (I) and traces of 3-hydroxysulfolane in the case of 3-benzoxysulfolane (IIa). The percentage of 3-hydroxysulfolane increases as the alkali concentration, reaction time, and temperature are increased and reaches 20% when equimolar amounts of NaOH and sulfolane I are heated at 50° for 12 h. In a control experiment at low alkali concentration (0.05 N) 2-sulfolene does not add water, and the formation of 3-hydroxysulfolane upon titration can therefore be explained by partial hydrolysis of the ester via general scheme b, whereas it is additionally formed by hydration (c) of 2-sulfolene upon prolonged heating with alkali [2].



3-Alkoxy-sulfolanes, sulfides, and 3-(dicarbethoxymethyl)sulfolane, which were previously described in [3], were isolated from reactions with alkoxides, mercaptides, and sodiomalonic ester (BH), respectively. Their formation can be explained by elimination of RCOOH via scheme a with subsequent addition of BH to 2-sulfolene. The presence of 2-sulfolene, identified by thin-layer chromatography (TLC), constitutes evidence in favor of this assumption. 3-Hydroxysulfolane is also formed. The ratio of the products depends on the nature of the reagent. The yields of alkoxy-sulfolanes are 70-90% with alkoxides of primary alcohols (C<sub>1</sub>-C<sub>4</sub>) of normal and isomeric structure in the case of equimolar ratios of the reagents and change only slightly as the length of the chain increases. Appreciable resinification is observed with secondary alcohols such as sec-C<sub>4</sub>H<sub>9</sub>OH, the yield of 3-sec-butoxy-sulfolane decreases to 50-55%, and the yield of 3-

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TABLE 3. Results of the Hydrolysis of 3-Benzoxysulfane in H<sub>2</sub>O Containing KOH and in D<sub>2</sub>O Containing NaOD

Concentration [KOH]	% Diox- ane in water	10°			18°			23°		
		$k_1 \cdot 10^{-3} \text{ sec}^{-1}$	$k_2, \text{ liter} \cdot \text{mole}^{-1} / \text{sec}^{-1}$	[KOH]	$k_1 \cdot 10^{-3} \text{ sec}^{-1}$	$k_2, \text{ l} \cdot \text{mole}^{-1}$	[KOH]	$k_1 \cdot 10^{-3} \text{ sec}^{-1}$	$k_2, \text{ l} \cdot \text{mole}^{-1} / \text{sec}^{-1}$	[KOH]
0.0092	50	2.28 ± 0.20	0.248	0.0134	5.76 ± 0.14	0.430	0.0092	5.89 ± 0.11	0.675	0
0.0134		2.83 ± 0.22	0.218	0.0166	7.20 ± 0.14	0.434	0.0134	9.06 ± 0.14	0.671	
0.0166		3.63 ± 0.16	0.218	0.0204	9.63 ± 0.18	0.472	0.0204	13.70 ± 0.18	0.671	
0.029		7.22 ± 0.18	0.248	0.029	1.27 ± 0.16	Av. 0.443		0	Av. 0.672	
0.012	10	1.94 ± 0.21	0.162	0.0382	3.33 ± 0.07	0.406	0.0064	3.92 ± 0.10	0.613	0
0.0168		3.60 ± 0.11	0.214	0.012	4.93 ± 0.14	0.413	0.012	7.22 ± 0.14	0.602	
0.0253		5.36 ± 0.14	0.212	0.0168	6.96 ± 0.17	0.414	0.0168	10.60 ± 0.14	0.631	
NaOD			Av. 0.196	0.020	8.36 ± 0.15	Av. 0.413			Av. 0.615	
0.008	50	2.40 ± 0.11	0.300	NaOD	4.46 ± 0.14	0.558	NaOD	6.83 ± 0.07	0.854	0
0.01		2.90 ± 0.14	0.290	0.008	5.23 ± 0.17	0.523	0.01	8.05 ± 0.15	0.805	
0.0103		2.76 ± 0.16	0.268	0.01	5.16 ± 0.10	0.501	0.0103	7.44 ± 0.14	0.723	
0.0132		4.33 ± 0.20	0.328	0.0132	10.10 ± 0.09	0.565	0.0132	11.20 ± 0.08	0.847	
			Av. 0.296			Av. 0.527			Av. 0.807	

TABLE 1. Characteristics of 3-(4-Substituted Benzoxy)sulfolanes

Compound	x	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	S	C	H	S	
Ila	H	164—165	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub> S	54.8	5.2	13.4	55.0	5.1	13.4	70
Ilb	4-CH <sub>3</sub>	125—126	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub> S	56.9	5.6	12.6	56.7	5.6	12.6	51
Ilc	4-Cl	162—164	C <sub>11</sub> H <sub>11</sub> ClO <sub>4</sub> S	47.5	4.2	11.5	48.0	4.0	11.7	35
Ild	4-NO <sub>2</sub>	202—203	C <sub>11</sub> H <sub>11</sub> NO <sub>6</sub> S	46.2	3.6	10.9	46.7	3.9	11.2	61
Ile	2-NO <sub>2</sub>	118	C <sub>11</sub> H <sub>11</sub> NO <sub>6</sub> S	46.8	3.9	11.3	46.7	3.9	11.2	80

TABLE 2. Results of the Hydrolysis of 3-(4-Substituted Benzoxy)sulfolanes at 18° in a 10% Solution of Dioxane in Water

Substituent	[KOH]	k <sub>1</sub> · 10 <sup>-3</sup> , sec <sup>-1</sup>	k <sub>2</sub> , l · mole <sup>-1</sup> /sec <sup>-1</sup>
H	0,0082	3,33 ± 0,17	0,406
	0,0120	4,96 ± 0,13	0,413
	0,0168	6,96 ± 0,08	0,414
	0,0200	8,36 ± 0,14	0,418
			Av. 0,413
CH <sub>3</sub>	0,0036	0,73 ± 0,15	0,304
	0,0099	3,09 ± 0,08	0,312
	0,0120	3,43 ± 0,10	0,286
	0,0153	4,56 ± 0,14	0,297
	0,0216	6,53 ± 0,17	0,301
		Av. 0,300	
Cl	0,0036	1,24 ± 0,14	0,544
	0,0099	5,20 ± 0,10	0,525
	0,0120	6,80 ± 0,14	0,566
	0,0153	8,93 ± 0,07	0,582
	0,0217	11,77 ± 0,09	0,543
		Av. 0,552	
NO <sub>2</sub>	0,0036	4,46 ± 0,14	1,239
	0,0043	5,20 ± 0,18	1,209
	0,0082	10,00 ± 0,16	1,219
	0,0097	12,00 ± 0,20	1,242
		Av. 1,227	

hydroxysulfolane increases to 25%. 3-Allyloxysulfolane (53%) and 3-hydroxysulfolane (40%) were isolated from the reaction with allyl alcohol. Up to 70% of a mixture of 2-sulfolene and 3-sulfolene and ~ 30% 3-hydroxysulfolane are formed in the reaction with sodium tert-butoxide in tert-butyl alcohol. Starting sulfolane I is regenerated in the reaction with sodium phenoxide in excess phenol (2 : 1) at 50°, and the product contains a small amount of sulfolene and 3-hydroxysulfolane, which were detected by TLC; at 100° after 24 h, ~ 10% 3-phenoxy sulfolane is additionally obtained, and this is in agreement with data on the elimination of esters at increased temperatures [4] and on the addition of phenols to 2-sulfolene [5].

The corresponding 3-substituted sulfolanes were isolated in yields up to 85% from the reaction with sodium butylmercaptide and sodiomalonic ester. On the other hand, up to 85% 3-hydroxysulfolane containing 3-butylamino(morpholyl)sulfolane, which were identified by TLC with known samples [3], is formed in the reaction of sulfolanes I and IIa with amines (butylamine and morpholine). If addition to the carbonyl group of 3-acyloxysulfolane is hindered, for example, in the case of o-nitrobenzoxy sulfolane (Ile), the reaction proceeds via an elimination-addition scheme (a-c) to give 2-sulfolene, 3-butylaminosulfolane, and traces of 3-hydroxysulfolane. Sulfolane I does not react with aniline acetate at 50°, whereas acetanilide and 3-hydroxysulfolane are formed at 180° via scheme b, and the products contain 2-sulfolene as an impurity.

We have previously proved [5] a carbanion mechanism for the formation of 2-sulfolene during the elimination of PhOH in the alkaline hydrolysis of 3-aryloxysulfolanes. In order to ascertain the mechanism of elimination of RCOOH (a), in the present research we investigated the kinetics of the alkaline (NaOH an NaOD) hydrolysis of IIa and of p-substituted 3-benzoxysulfolanes (IIb-d, Table 1). The hydrolysis was carried out in 10 and 50% solutions of dioxane in H<sub>2</sub>O and D<sub>2</sub>O. The pseudomonomolecular (k<sub>1</sub>) and bimolecular (k<sub>2</sub>) rate constants found are presented in Tables 2 and 3. The activation parameters (log A and E) were calculated from the temperature dependence of the bimolecular rate constant for the reaction of IIa

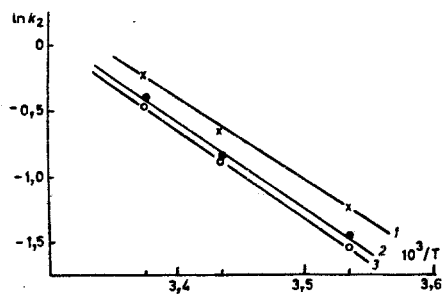


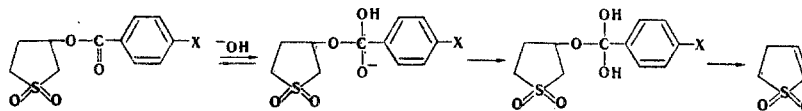
Fig. 1. Arrhenius dependence  $\ln k_2$  on  $1/T$  for the reaction of IIa; 1) in a 50% solution of dioxane in water; 2) in 50%  $D_2O$ ; 3) in 10%  $D_2O$ .

at 10, 18, and 23° (Fig. 1) from the Arrhenius equation; correlation coefficient  $r = 0.999$ , and the error in the calculation  $s = 0.02$ . The activation parameters found (Table 4) are close to the literature values for base-catalyzed carbanion reactions [5, 6] and differ from the  $E$  and  $\log A$  values peculiar to alkaline hydrolysis reactions of phenyl and alkyl benzoates [7, 8].

A comparison of the  $k_2$  values (Table 2) for IIa-d shows that electron-donor substituents in the para position of the phenyl ring retard the reaction, whereas electron-acceptor substituents accelerate it. The change in  $k_2$  under the influence of substituents is described by the Hammett equation with  $\sigma^D$  substituent constants [9]:

$$\lg k = -0.384 + 0.646\sigma^D \\ (r=0.996; s=0.031)$$

The sign of reaction constant  $\rho$  coincides with the sign of  $\rho$  found for the elimination of aryloxysulfolanes ( $\rho = +1.47$ ) [5] in a 10% solution of dioxane in water at 18°, but the magnitude of  $\rho$  is smaller. A similar dependence of  $\rho$  on the character of the leaving group was observed in elimination reactions of 4-(4-substituted phenoxy)-2-butanones [5] and 4-(4-substituted benzoxy)-2-butanones [9], for which an  $E_1cB$  carbanion mechanism was proved. In reactions of this type  $\rho$  is theoretically zero for elimination of groups that leave readily [11]. The increased  $\rho$  value, the linear dependence of the rate on the alkali concentration, and the preexponential factor make it possible to assume initial addition of  $OH^-$  at the carbonyl groups to give an unstable ortho ester in which a sulfolanyloxy anion is not split out via the general scheme, but, because of the increased  $\alpha$ -CH acidity of sulfolanes I and II, the C-O bond attached to the sulfolane ring is cleaved either through a transition state similar to the  $E_1cB$  state or via an  $E_1cB$  mechanism:



Evidence in favor of this assumption is the linear dependence of the rate constant for elimination of  $XPhCOO^-$  in the reaction of IIa-d on the  $pK_a$  values of the corresponding substituted acetic acids  $XPhCOOCH_2COOH$  (Fig. 2, curve a). These values, which were taken from [12], correlate well with the parameters of the substituents in the benzene ring and serve as a measure of transmission of the effect on the acidity of the leaving group through the methylene bridge. A similar dependence of the rate constant on the  $pK_a$  values of  $XPhOCH_2COOH$  is observed for the elimination of 3-aryloxysulfolanes (Fig. 2, curve b), which react via an  $E_1cB$  mechanism [5]. The identical slopes of the lines indicate identical effects of the  $\alpha$ -CH acidity on the rates of both reactions. The acceleration of the hydrolysis of sulfolane IIa in  $D_2O$  (Table 3) and in dimethyl sulfoxide (DMSO) ( $k_2 = 0.492$  and  $1.42$  liter  $\cdot$  mole $^{-1}$ /sec $^{-1}$  at 18°, respectively, in 10 and 50% DMSO) relates to the nature of the transition state of type  $E_1cB$ .

#### EXPERIMENTAL METHOD

The products were chromatographed in a thin loose layer of activity II  $Al_2O_3$  with elution by ether and chloroform (for the aminolysis of sulfolane II) and development with iodine vapors. The KOH solutions were prepared from standardized solutions by dilution with twice-distilled water.

**3-Acetoxy-sulfolane (I) and Benzoxy-sulfolanes (IIa-d).** These compounds were obtained by refluxing equimolar amounts of 3-hydroxy-sulfolane with the appropriate acid chlorides in absolute chloroform. The physical constants of IIa-d are presented in Table 1. Sulfolane I had mp 74-75° [14].

**Hydrolysis of Sulfolane I.** A) A solution of 0.8 g (0.02 mole) of sodium hydroxide in 15 ml of water was added with stirring to a solution of 3.56 g (0.02 mole) of 3-acetoxy-sulfolane in 35 ml of water at such a rate that the pH of the solution was no higher than 8-8.4. The mixture was then extracted with chloroform, during which the degree of extraction of 2-sulfolene was monitored by TLC. The solvent was evaporated to give 2 g (85%) of sulfolene. The aqueous layer was vacuum evaporated, and the residue was extracted with acetone to give 0.22 g (8.5%) of 3-hydroxy-sulfolane.

B) The hydrolysis was carried out with an equimolar ratio of reagents, which were mixed simultaneously and heated at 50 deg for 12 h. Workup gave 1.74 g (74%) of 2-sulfolene and 0.55 g (20%) of 3-hydroxysulfolane.

Hydrolysis of Sulfolanes IIa-d: Kinetic Measurements. A spectrometric method was used for the kinetic measurements. The absorption spectra of IIa-d without alkali and in the course of alkaline hydrolysis were recorded with an SF-16 spectrophotometer, the thermostated cuvette of which served as the reaction vessel. The reaction was carried out in 10% dioxane-water mixtures, inasmuch as the benzoates are insoluble in water. The addition of dioxane did not affect the form of the UV spectrum. 2-Sulfolene and 3-hydroxysulfolene, which absorb below 220 nm, did not interfere with the determination. A working wavelength ( $\lambda$ ) was selected for each ester: 280 nm for IIa, 248 nm for IIb, and 260 nm for IIc; at this working wavelength the change  $\Delta D = (D_0 - D_\infty)$ , where  $D_0$  is the optical density corresponding to the initial sulfolanyl benzoate concentration and  $D_\infty$  is the optical density of the potassium benzoates, has its maximum value during the reaction. Inasmuch as the hydrolysis of IIa-d to 3-hydroxysulfolane is insignificant, no correction for consumption of the benzoates via scheme b was introduced.

The experiments were carried out under pseudomonomolecular conditions in the presence of excess (no less than tenfold) KOH with repetition no less than three times. The pseudomonomolecular rate constants ( $k_1$ ) at several alkali concentrations were found from the slope of the line of the dependence of  $\log [D_0 - D_\infty / D_t - D_\infty]$  on time. The second-order rate constants were determined from the slope of the lines in coordinates of  $k_1$  (in reciprocal seconds) and [KOH] (Table 2).

Alcoholysis of Sulfolane I. A) A 3.56-g (0.02 mole) sample of 3-acetoxysulfolane was added to a solution of 0.46 g (0.02 g-atom) of sodium in 40 ml of absolute methanol, after which the mixture was stirred at 50° for 24 h and diluted with dry ether. The sodium acetate was removed by filtration, the solvent was removed in vacuo, and the 3-methoxysulfolane and 3-hydroxysulfolane in the residue (2.9 g) were determined by TLC. Chromatography with a column filled with  $Al_2O_3$  yielded 1.96 g (65%) of 3-methoxysulfolane (elution by ether) and 0.9 g (34%) of 3-hydroxysulfolane (elution with methanol).

B) The reaction with butanol was carried out similarly to give 3.24 g (85%) of 3-butoxysulfolane and 0.27 g (9.5%) of 3-hydroxysulfolane.

C) The reaction with sec-butyl alcohol under similar conditions yielded 2.58 g (55%) of 3-sec-butoxysulfolane (55%) and 0.27 g (9.5%) of 3-hydroxysulfolane.

D) The reaction with tert-butyl alcohol gave 1.4 g (60%) of 2-sulfolene containing 3-sulfolene and 0.76 g (25%) of 3-hydroxysulfolane.

E) The reaction with allyl alcohol gave 1.9 g (63%) of 3-allyloxysulfolane and 1.1 g (40%) of 3-hydroxysulfolane.

F) The reaction with phenol gave 0.6 g (10%) of phenoxysulfolane, which was identified by TLC and its melting point [4], and a mixture of 2-sulfolene with 3-hydroxysulfolane.

Mercaptolysis of Sulfolane I. A mixture of 3.56 g (0.02 mole) of I and sodium butylmercaptide, obtained by dissolving 0.46 g (0.02 g-atom) of sodium in 40 ml of butyl mercaptan, was heated at 50° for 24 h, after which it was acidified, and the excess mercaptan was removed by distillation. The mixture was then diluted with ether, and the sodium chloride was removed by filtration. The solvent was removed by vacuum distillation to give 3.35 g (85%) of butyl sulfolanyl sulfide, which was identified by TLC and oxidation to the sulfone with hydrogen peroxide.

Reaction of Sulfolanes I and IIa with Sodiomalonic Ester. Equimolar mixtures of acyloxysulfolanes and sodiomalonic ester were heated in excess absolute ethanol at 50° for 20 h, after which they were cooled and diluted with ether. The sodium benzoate (or acetate) was removed by filtration, the solvent was removed by distillation, and the sulfolanyl malonate was crystallized from alcohol and identified by TLC and a mixed-melting-point determination with an authentic sample. The yield of 3-(dicarbethoxymethyl)-sulfolane in the reaction with sulfolane I was 65%, as compared with 85% in the reaction with sulfolane IIa.

Reaction of Sulfolanes I and II with Amines. A 3.56-g (0.02 mole) sample of I was heated at 50° for 24 h in 50 ml of butylamine (morpholine), after which the excess amine was removed by vacuum distillation. According to TLC, the residue contained 3-hydroxysulfolane and the corresponding butylamino(morpholy)sulfolane. Chromatography with a column filled with  $Al_2O_3$  gave 2.43 g (85%) of 3-hydroxysulfolane. Under similar conditions, sulfolane IIc reacts with butylamine to give 2-sulfolene, 3-butylaminosulfolane, and traces of 3-hydroxysulfolane.

Starting sulfolane I was isolated from the reaction with aniline under similar conditions, whereas acetanilide and 3-hydroxysulfolane containing 2-sulfolene were obtained at 180°.

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