

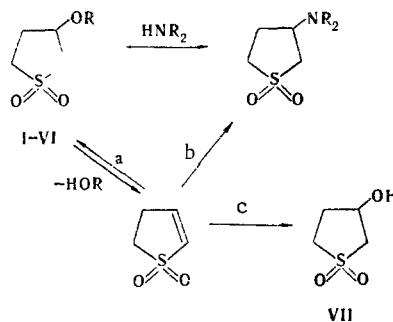
REACTION OF 3-AR(ALK)OXYSULFOLANES WITH AMINES

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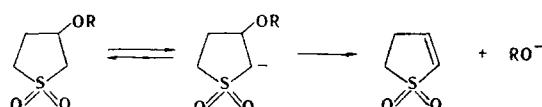
On the basis of data on the kinetics of the hydrolysis of 3-aroxy sulfolanes in aqueous solutions of tertiary amines and in acetonitrile it is shown that the elimination of phenols is subject to specific base catalysis and occurs via an (E1cB)R carbanion mechanism. The exchange of aroxy and alkoxy groups of sulfolanyl ethers on reaction with nucleophilic reagents is explained by an elimination-addition scheme.

It has been shown [1] that sulfolanyl ethers in reactions with nucleophilic reagents exchange an alkoxy substituent. The reaction occurs with amines only in aqueous or alcoholic media, does not take place in absolute acetonitrile, and is accelerated appreciably by OH^- and OR^- ions. Moreover, the corresponding 3-aminosulfolanes are formed with primary amines in aqueous solution, a mixture of aminosulfolane and 3-hydroxysulfolane is formed with secondary amines, and 2-sulfolene containing 3-hydroxysulfolane is formed with tertiary amines. These results can be explained if it is assumed that the amination of sulfolanyl ethers occurs through elimination-addition (a, b) and is accompanied by partial hydration of 2-sulfolene (c) in aqueous solution.



I $\text{R}=\text{CH}_3$; II $\text{R}=\text{C}_4\text{H}_9$; III $\text{R}=\text{C}_4\text{H}_7\text{O}_3\text{S}$; IV $\text{R}=\text{C}_6\text{H}_5$; V $\text{R}=\text{C}_7\text{H}_7$; VI $\text{R}=\text{C}_6\text{H}_4\text{Br}$

In the hydrolysis of 3-methoxysulfolane (I) under the influence of NaOD in D_2O we proved [2] by means of the PMR spectra that splitting out of methanol precedes the isotopic exchange of the hydrogen atoms of the methylene group in the 2 position. This and data [3] on the kinetics of alkaline hydrolysis of 3-aroxy sulfolanes (IV-VI) make it possible to assume that elimination of the RO^- groups occurs through the formation of a carbanion via the scheme



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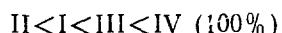
TABLE 1. Results of the Hydrolysis of 3-Aroxysulfolanes
in 10% Aqueous Dioxane at 40°C

Compound	Amine *	Compound concn., mole ⁻¹ · 10 ³	Amine concn., mole liter ⁻¹	pH	$k_{\text{obs}}^{\text{found}} \cdot 10^6$ mole ⁻¹ sec ⁻¹	Average $k_{\text{obs}}^{\text{found}}$	$k_{\text{obs}}^{\text{calc}} \cdot 10^6$ mole ⁻¹ sec ⁻¹
IV	A	4,10	0,003	9,95 ± 0,05	28	25	26
IV	A		0,062		21		
IV	A	4,10	0,004	10,10 ± 0,01	38	46	37
IV	A		0,074		54		
IV	A	4,10	0,006	10,49 ± 0,01	130	117	90
IV	A		0,132		104		
IV	B	4,10	0,007	9,97 ± 0,03	18,0	18	20
IV	B		0,255		18,0		
IV	B	4,10	0,008	10,18 ± 0,01	38	40	43
IV	B		0,316		42		
IV	B	4,10	0,022	10,62	150	150	130
IV	B		0,34		150		
IV	C	4,10	0,12	9,95 ± 0,05	23	21	24
IV	C		0,25		19		
IV	C	4,10	0,015	10,10 ± 0,05	40	44	41
IV	C		0,199		48		
V	A	4,23	0,004	10,20 ± 0,02	33	33,5	35
V	A		0,074		34		
V	A	4,23	0,006	10,41 ± 0,03	61	53	54
V	A		0,132		46		
V	B	4,23	0,022	10,35 ± 0,02	42	37	45
V	B		0,262		32		
VI	A	4,89	0,003	9,90 ± 0,05	57	65	57
VI	A		0,062		73		
VI	A	4,89	0,004	10,13 ± 0,02	97	93	80
VI	A		0,064		90		
VI	B	4,89	0,007	9,78 ± 0,02	38	33	35
VI	B		0,273		29		
VI	B	4,89	0,0104	9,95 ± 0,02	61	62	54
VI	B		0,232		64		
VI	C	4,89	0,015	9,80 ± 0,05	30	36	37
VI	C		0,25		42		
VI	C	4,89	0,009	10,0 ± 0,01	79	69	60
VI	C		0,322		58		

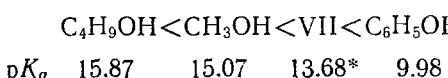
*Triethylamine (A), diethylethanol amine (B), and dimethyl-ethanolamine (C).

To prove the proposed two-step carbanion preequilibrium mechanism of cleavage $[(\text{ElcB})_R]$, in the present research we investigated the sensitivity of the reaction to the strength of the catalyzing base.

In the preparative reaction of aroxysulfolanes I-IV with triethylamine in the presence of water we obtained 2-sulfolene, the yield of which increases in the following order:



This same sequence of the reactivities of the ethers is retained in the reaction with butylamine and corresponds to an increase in the acidity of the alcohol split out:



The effect of the catalyzing base on the rate was investigated in the reaction of sulfolanes IV-VI with the tertiary amines $\text{N}(\text{C}_2\text{H}_5)_3$, $\text{N}(\text{C}_2\text{H}_5)_2\text{C}_2\text{H}_4\text{OH}$, and $\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$. The data from the kinetic measurements are presented in Table 1. The observed rate constants for elimination of PhO^- from IV-VI at a constant solution pH depend only slightly on the amine concentration and change linearly as the activity of the hydroxide ions changes.

The $k_{\text{obs}}^{\text{found}}$ constants coincide satisfactorily with the $k_{\text{obs}}^{\text{calc}}$ values according to the equation

$$k_{\text{obs}}^{\text{calc}} = k_2 \cdot K_w / a_{\text{H}}$$

where k_2 is the bimolecular rate constant for IV-VI at 40° in alkaline hydrolysis [3]. At the same time, the reaction does not occur in absolute acetonitrile with the same amines. This constitutes evidence for specific base catalysis and, according to the data in [5], serves as evidence in favor of the proposed elimination scheme.

A comparison of the results of the present research and the results obtained in [6] shows that the sensitivity of the reaction of 3-hydroxysulfolanes to the strength of the catalyzing base is considerably higher than for 4-hydroxy-2-butanones; this is in agreement with the lower C-H acidity of sulfones.

The data from the kinetic studies show that the reaction rate is determined by the basicity of the hydroxyl group, whereas the principal product is determined by the nucleophilicity of the amines. This makes it possible to suppose that the reaction of sulfones I-VI with primary and secondary amines does not proceed by direct substitution of OR^- by the amine but rather via scheme a, b. In addition, a similar dependence of the yields of the 3-amino-sulfolanes on the character of the amine is observed in the reaction of I and 2-sulfolene [7] with various primary and secondary amines; in this case the steric structure of the amine has a greater effect than the basicity.

EXPERIMENTAL

Compounds I-VI were previously described in [3, 7]. Buffer solutions of the amines were prepared from weighed samples of freshly distilled amines and their hydrochlorides in 1 M KCl solution for maintenance of a constant ionic strength.

The kinetic measurements were made with an SF-16 spectrophotometer, the 1-cm-thick thermostatted cuvette of which was used as the reaction vessel. The course of the reaction was followed from the change in the concentration of the potassium phenoxides at the absorption maxima λ_r 288, 295, and 299 nm, respectively, for $\text{C}_6\text{H}_5\text{O}^-$, $\text{C}_7\text{H}_7\text{O}^-$, and $\text{BrC}_6\text{H}_4\text{O}^-$. 2-Sulfolene does not absorb in this region, whereas the difference in the absorption of the phenoxides and ethers IV-VI is very great, and the absorption of the ethers was therefore disregarded in the calculations. The experiments were repeated no less than three times, and the arithmetic mean was found from the data with a scatter of $\pm 5\%$. The pH values were measured with a glass electrode with an LPU-01 pH-meter. The activity of the hydroxide ions was calculated from the K_w/a_{H} ratio, where $K_w = 1.41 \cdot 10^{-14}$ is the self-dissociation constant of water in 10% aqueous dioxane at 40° [8]. The rate of hydrolysis was investigated at a constant pH, and the $k_{\text{obs}}^{\text{found}}$ rate constants were therefore calculated from a first-order equation [9], regardless of the reagent ratio.

Reaction of Ethers I-VI with Amines. A mixture of the ether and amine in a molar ratio of 1:3 was heated in the presence of 0.25-1% KOH solution (0.1 mole) at 70° for 6 h, after which the aqueous alkali layer was separated with benzene. The benzene layer was evaporated, and the percentage of 3-substituted aminosulfolanes, which were identified as the hydrochlorides (previously described in [7]), was determined in the residue by titration. The hydrochlorides were obtained by bubbling hydrogen chloride through an acetone solution of the residue. The yields of aminosulfolanes in the reaction of ether I with piperidine, butylamine, isobutylamine, allylamine, cyclohexylamine, and benzylamine were, respectively, 37, 52, 22, 33, 16, and 9%. 3-Butylaminosulfolane was obtained in 52, 28, 89, and 100% yields in the reaction of I-IV with butylamine.

Determination of the pK_a of 3-Hydroxysulfolane. The hydrocinnamic acid ester was obtained by esterification of 3-hydroxysulfolane with the acid chloride in absolute chloroform. The product was crystallized from methanol to give the ester, with mp 94-96°, in 98% yield. Found: C 58.2; H 6.1; S 12.1%. $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$. Calculated: C 58.2; H 6.0; S 11.9%.

The IR spectrum of a solution of the ester in CCl_4 ($7.5 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$ M) was recorded with a UR-20 spectrometer. The pK_a value was calculated from the equations [4]

$$\text{pK}_a = -1.316\sigma^*(R) + 15.74,$$

$$\sigma^*(R) = 0.08996v - 156.000.$$

The ν_{CO} frequency of the ester was 1751.5 cm^{-1} .

*The pK_a value of 3-hydroxysulfolane VII was found by an approximate method [4] from the frequency of the carbonyl group of the hydrocinnamic acid ester.

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REACTION OF 3-PHENYLSULFONYLBENZOTHIAZOLONE WITH AMINES

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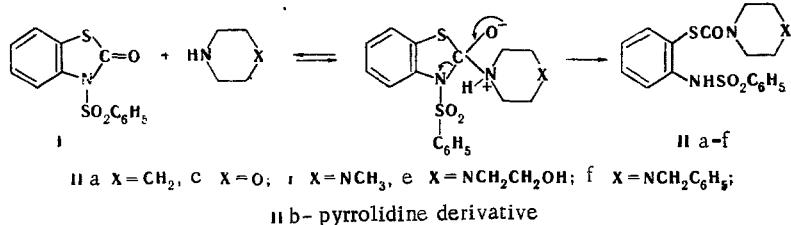
UDC 547.863'867.5

A phenylsulfonyl group in the 3 position accelerates and changes the direction of aminolysis of benzothiazolone and leads to the formation of 2-phenylsulfonylamino-S-phenyl esters of N-substituted thiocarbamic acids. 2,2'-Bis(phenylsulfonylamino)diphenyl disulfide and the corresponding symmetrical ureas were obtained in the reaction with several primary amines.

In our preceding studies [1, 2] we established that the corresponding 2,2'-bis(3-alkylureido)diphenyl disulfides are formed in the reaction of benzothiazolone and some of its benzene-substituted derivatives with primary and secondary amines at 100°C. This sort of decyclization is realized more readily in the case of the benzothiazolone analog benzoxazolone [2, 4].

In the present research we investigated the effect of an electron-acceptor substituent attached to the N₍₃₎ atom on the course and rate of the above-indicated reaction. In this connection, we studied the reaction of 3-phenylsulfonylbenzothiazolone (I) with several primary and secondary amines in ethanol.

The reaction with cyclic amines such as piperidine, pyrrolidine, morpholine, 1-methylpiperazine, 1-(β -hydroxyethyl)piperazine, and 1-benzylpiperazine leads to the production of the previously unknown 2-phenylsulfonylamino-S-phenyl esters of N-substituted thiocarbamic acids (II) in 45-75% yields.



Chemistry Department, K. Ohridskii Sofia University, Bulgaria. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 9, pp. 1192-1195, September, 1976. Original article submitted December 18, 1975.

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