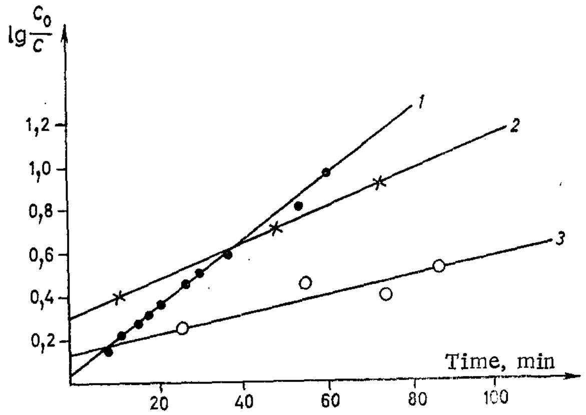

Fig. 1. Dependence of log C_0/C on the reaction time: 1) adduct VI, 2) adduct VIII, 3) adduct IX.

graph, for the construction of which we recorded the dependence of the intensity of the signal of the NH group on the nitrone concentration. The log $C_0/C = f(t)$ dependence is presented in Fig. 1 (C_0 is the initial concentration, and C is the nitrone concentration at time t).

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EFFECT OF THE SUBSTITUENT IN THE THIOPHENE RING ON THE [3,3]-SIGMATROPIC REARRANGEMENT OF ALLYL THIENYL SULFIDES

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The thio Claisen rearrangement of a number of 5-substituted allyl 2-thienyl sulfides was studied. On the basis of kinetic data it is shown that substituents that decrease the aromatic character of the transition state decrease the reactivity of the sulfide.

The thio Claisen rearrangement of allyl thienyl sulfides proceeds under relatively mild conditions and to a lesser extent than in the case of allyl phenyl sulfides and is complicated by side processes [1, 2]. 5-Substituted allyl 2-thienyl sulfides are therefore convenient subjects for the study of the effect of substituents in the aromatic ring on the thio Claisen rearrangement.

Sulfides Ia-f undergo rearrangement to isomeric 5-X-3-allylthiophene-2-thiols (IIIa-f), which were isolated in individual form. A study of the kinetics of the rearrangement of all

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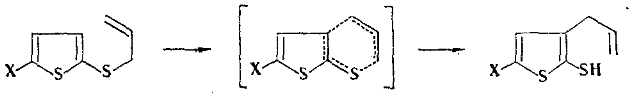
TABLE 1. Kinetic Parameters of the Rearrangement of Sulfides

Sulfide	Solvent	Temp., °K	$K \cdot 10^4$, sec^{-1}	E_a, kcal/mole	$-\Delta S^{\neq}$, cal/mole-deg
Ia	Hexametapol	343	0,12	18,5	29,4
		350	0,20		
		358	0,38		
Ib	Hexametapol	362	0,23	19,5	28,3
		372	0,49		
		380	0,82		
Ic	Hexametapol	360	0,12	21	25,1
		370	0,28		
		380	0,60		
	Dibutyl ether	343	0,83	17	29,9
		349	1,23		
		353	1,67		
Id	Dibutyl ether	363	0,05	19	32,8
		370	0,09		
		378	0,14		
	m-Xylene	353	0,04	19	31,7
		363	0,07		
		378	0,28		
		391	0,70		
Ie	Dibutyl ether	363	0,04	20	30,5
		370	0,07		
		376	0,10		
	m-Xylene	353	0,03	19	32,3
		363	0,05		
		376	0,11		
		386	0,18		
If	Dibutyl ether	400	0,13	25	21,0
		411	0,29		
		418	0,50		
	m-Xylene	390	0,16	22,5	25,3
		398	0,29		
		404	0,42		

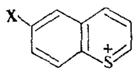
of the sulfides in various solvents showed that it is a first-order reaction and has a high negative entropy of activation and that the polarity of the solvent has a slight effect on the reaction rate.



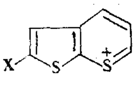
I a-f II a-f III a-f

I-III a $X = CH_3O$; b $X = CH_3$; c $X = CH_3S$; d $X = H$; e $X = Cl$; f $X = Br$

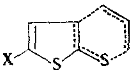
A comparison of the kinetic parameters (Table 1) of the rearrangement of the sulfides showed that their reactivities decrease in the order Ia > Ib > Ic > Id > Ie > If. To explain the effect of the substituent on the rate of the thio Claisen rearrangement of chloro-substituted allyl thienyl sulfides we have previously [3] successfully used the Dewar approach [4], which consists in the fact that the factors that decrease the aromatic character of the transition state hinder the rearrangement. Unfortunately, it is difficult to directly evaluate the effect of a substituent in the thiophene ring on the aromatic character of the six-membered ring of the transition state. However, in addition to this, in the case of 6-substituted thiachromylium salts IVa-f it has been shown [5] that the series of substituents in the order indicated above decreases the aromatic character of the thiapyrylium ring, for which a six-membered transition state has been proposed isoelectronically.



IV a-f



V a-f



II a-f

TABLE 2. Data from the PMR (ppm) and IR (cm^{-1}) Spectra of the Investigated Compounds

Compound	Thiophene ring protons	Allyl group protons			SH	Protons of the other groups	$\nu_{C=C}$	ν_{S-H}
		$-CH=$	$=CH_2$	$-CH_2-$				
I a	6,9 d 6,15 d	5,9 m	5,1 m	3,3 d		3,9 s (CH_3O)	1650	
I b	6,85 m 6,6 m	5,7 m	4,9 m	3,3 d		2,4 s (CH_3)	1650	
I c	7,0 m	5,9 m	5,05 m	3,4 d		2,4 s (CH_3S)	1650	
I f	7,05 m	6,0 m	5,1 m	3,4 d			1650	
IIIa	5,85 s	5,75 m	4,95 m	3,3 d	2,95 s	3,6 s (CH_3O)	1650	2590
IIIb	6,6 s	5,7 m	4,9 m	3,3 d	3,0 s	2,4 s (CH_3)	1650	2580
IIIc	7,0 s	5,9 m	5,1 m	3,4 d	3,2 s	2,5 s (CH_3S)	1650	2590
IIIf	6,9 s	5,85 m	4,95 m	3,4 d	3,1 s		1650	2600

The aromatic character of the thiapyrylium ring is easily evaluated from the resistance of thiapyrylium salts of one series to hydrolysis and is expressed numerically by the magnitudes of hydrolysis constants pK_{R^+}, which have the following values for 6-subsituted thiachromylium perchlorates [5]:

X	CH_3O	CH_3	CH_3S	H	Cl	Br
pK_{R^+}	4.39	4.09	3.40	3.15	1.95	1.74

Since the hydrolyses of thienothiapyrylium salts Va-f and thiachromylium salts IVa-f proceed via the same mechanism [6], from the pK_{R^+} values presented above one may conclude that the aromatic character of the thiapyrylium ring in 5-substituted thienothiapyrylium salts and, consequently, the six-membered transition state in the rearrangement of 5-substituted allyl thienyl sulfides decreases in the order indicated above. The [3,3]-sigmatropic rearrangement of sulfides Ia-f also is hindered in the same order.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of films were recorded with an IKS-22 spectrometer. The data from the PMR and IR spectra are presented in Table 2.

The experimental method for the study of the kinetics of the rearrangement and the rearrangement of sulfides Id and Ie were previously described in [2, 3].

The purity of the thiols obtained was monitored by thin-layer chromatography (TLC) on Silufol [elution with hexane—CCl_4—ether (47:43:10)].

Allyl 2-(5-Methoxythienyl) Sulfide (Ia). This compound was synthesized by the general method for the synthesis of allyl hetaryl sulfides [7] by the reaction of 5-methoxythiophene-2-thiol and allyl bromide in aqueous alkali. 5-Methoxythiophene-2-thiol was obtained by the successive action of butyllithium, sulfur, and water on 2-methoxythiophene. The sulfide was obtained in 60% yield (based on 2-methoxythiophene) and had bp 76-78°C (1 mm), n_D^{20} 1.5759, and d_4^{20} 1.0972. Found: C 50.7; H 5.3; S 34.5%. $C_8H_{10}OS_2$. Calculated: C 51.6; H 5.4; S 34.4%.

Allyl 2-(5-Methylthienyl) Sulfide (Ib). This compound was synthesized in 54% yield in the same way as sulfide Ia from 2-methylthiophene and had bp 64-65°C (1 mm), n_D^{20} 1.5780, and d_4^{20} 1.0881. Found: C 57.0; H 5.7; S 36.9%. $C_8H_{10}S_2$. Calculated: C 56.6; H 5.9; S 37.7%.

Allyl 2-(5-Methylthiothienyl) Sulfide (Ic). This compound was similarly synthesized in 69% yield and had bp 100-101°C (1 mm), n_D^{20} 1.6251, and d_4^{20} 1.1968. Found: C 47.9, H 4.9, S 46.7%. $C_8H_{10}S_3$. Calculated: C47.5; H 5.0; S 47.5%.

Allyl 2-(5-Bromothienyl) Sulfide (If). This compound was synthesized from 5-bromothiophene-2-thiol, which was obtained by the successive action of magnesium metal, sulfur, and water on 2,5-dibromothiophene. The product was obtained in 42% yield and had bp 91-93°C (1 mm), n_D^{20} 1.6182, and d_4^{20} 1.4588. Found: C 35.4; H 3.1; S 27.4%. $C_7H_7BrS_2$, Calculated: C 35.7; H 3.0; S 27.2%.

5-Methoxy-3-allylthiophene-2-thiol (IIIa). This compound was obtained by rearrangement of sulfide Ia. A mixture of 2.2 g of the sulfide and 15 ml of hexametapol was heated at 125°C for 10 min, after which the thiol was isolated by alkaline treatment as described in [3] to give 0.7 g (32%) of the thiol with n_D^{20} 1.5875. The thiol underwent cyclization to a considerable degree upon vacuum distillation.

5-Methyl-3-allylthiophene-2-thiol (IIIb). This compound was obtained by heating 3 g of sulfide Ib in 15 ml of hexametapol at 130°C for 20 min as in the preparation of thiol Ia. Workup gave 0.6 g (20%) of a product with bp 86-87°C (1 mm) and n_D^{20} 1.5912.

5-Methylthio-3-allylthiophene-2-thiol (IIIc). This compound was similarly obtained by heating 3 g of sulfide Ic in 20 ml of dibutyl ether at 80°C for 15 min. Workup gave 0.3 g (10%) of a product with bp 102-103°C (1 mm) and n_D^{20} 1.6127.

5-Bromo-3-allylthiophene-2-thiol (IIIf). This compound was also isolated by alkaline treatment after heating 4 g of sulfide If in 20 ml of m-xylene at 140°C for 1.5 h in sealed ampuls in an argon atmosphere. Workup gave 0.7 g (17%) of a product with n_D^{20} 1.6258, which decomposed upon vacuum distillation.

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