distilled to give 10.4 g (60.0%) of enamine IIa with bp 122-128°C (4 mm), n_D^{20} 1.4912, and d_4^{20} 1.0041. IR spectrum: 1650 cm^{-1} (C=C). PMR spectrum (CCl_4): 1.06 and 1.12 (6H, s, CH_3), 1.60 (4H, m, 3- and 5-CH_2), 2.50 (5H, m, 4-CH and CH_2OCH_2), 3.52 (6H, m, 6-CH_2 and CH_2NCH_2), and 2.00 ppm (3H, s, CH_3C=). Found: C 69.4; H 10.1; N 6.0%. $C_{13}H_{23}NO_2$. Calculated: C 69.3; H 10.3; N 6.2%.

β-(2,2-Dimethyltetrahydro-4-pyranyl)-β-oxopropionic Acid Anilide (IV). A 2.4-g (0.02 mole) sample of phenyl isocyanate was added with stirring to a solution of 4.5 g (0.02 mole) of enamine IIa in 40 ml of dry chloroform, after which stirring was continued for 4-5 h, and the mixture was then refluxed for 1 h. The solvent was removed by distillation, and the residue was dissolved in carbon tetrachloride. Pentane was added to the solution, and the precipitated crystals of N-phenylcarbamoylmorpholine (mp 157-158°C) were separated. The residual 5.4 g (78%) of III was hydrolyzed without further purification by acidification with 7% hydrochloric acid solution. The mixture was allowed to stand at room temperature for 24 h, after which it was extracted with benzene. The extract was dried with magnesium sulfate, the solvent was removed by distillation, and the residue was crystallized from ether. If necessary, the product was purified through the copper chelate (mp 125-126°C). Workup gave 5.2 g (82% based on III) of amide IV with mp 71-72°C. IR spectrum: 1710 (C=O, ketone), 1675 (C=O, amide), and 3300 cm^{-1} (N-H). PMR spectrum ($CDCl_3$): 1.2 (6H, s, 2-CH_3), 1.60 (4H, m, 3- and 5-CH_2), 2.80 (1H, m, 4-CH), 3.70 (2H, m, 5-CH_2), 3.60 (2H, s, $COCH_2CO$), and 7.4 (5H, m, C_6H_5). Found: C 70.1; H 7.7; N 5.0%. $C_{16}H_{21}NO_3$. Calculated: C 69.8; H 7.7; N 5.1%.

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MECHANISM OF THE THIO-CLAISEN REARRANGEMENT OF 3-METHYLALLYL PHENYL SULFIDE

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The thio-Claisen rearrangement of isomeric 3- and 1-methylallyl phenyl sulfides was investigated. It is demonstrated that the thio-Claisen rearrangement of the 3-methyl isomer is preceded by its thioallyl rearrangement to the 1-methyl isomer. The latter undergoes thio-Claisen rearrangement to o-(3-methylallyl)thiophenol, which is cyclized to 2-ethyl-2,3-dihydrobenzothiophene and 2-methylthiochroman under the reaction conditions.

We have previously reported [1-3] that the final product of the thio-Claisen rearrangement of 3-methylallyl phenyl sulfide (I) both in the presence of nitrogen bases [2, 3] and under heterogeneous acid-catalysis conditions [1, 3] is a mixture of two-ring compounds of the 2,3-dihydrobenzothiophene and thiochroman series. In the present research the sequence of the conversions of sulfide I to two-ring compounds was ascertained in a homogeneous medium in the presence of quinoline, since under these conditions the principal rearrangement process is not complicated by side and secondary reactions.

The realization of the rearrangement of sulfide I (Table I) showed that the composition of the resulting mixture of sulfides II-V is close to that obtained previously by Kwart and

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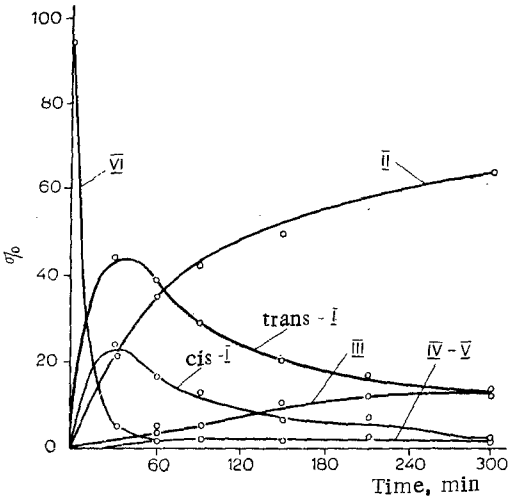


Fig. 1

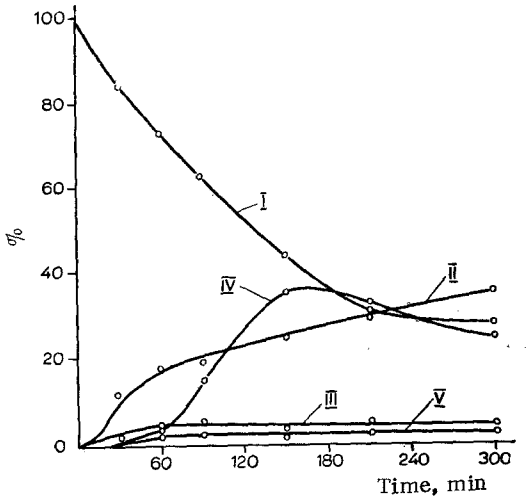


Fig. 2

Fig. 1. Accumulation of the products of transformation of 1-methyl-allyl phenyl sulfide (VI) in quinoline at 237°C.

Fig. 2. Accumulation of the products of transformation of 3-methyl-allyl phenyl sulfide (I) in quinoline at 237°C.

TABLE 1. Transformations of 3- and 1-Methylallyl Phenyl Sulfides in Quinoline (for a sulfide to quinoline ratio of 1:5 and a reaction time of 5 h)

Sulfide	Temp., °C	Ratio of the reaction products				
		VI	II	III	IV	V
I (Kwart [4])	250	—	57,5	10	27	5,5
I	237	—	54	5	37	4
VI	237	Traces	80	16		4
I*	350	—	77—60	13—16	5—13	5—11

*These data are presented for comparison; the reaction was carried out in the presence of Al_2O_3 and $ZnCl_2/Al_2O_3$ [1, 3].

Cohen [4]. The structures of sulfides II and III, which are the principal reaction products, constitute evidence that the thio-Claisen rearrangement of sulfide I proceeds either without inversion of the side chain* or with thioallyl rearrangement to 1-methylallyl phenyl sulfide (VI), which precedes the thio-Claisen rearrangement of sulfide I. The latter assumption was expressed by Kwart, who presented indirect evidence in favor of it in [4, 6, 7]. At the same time, Kwart and Johnson [7] presented data on the greater thermodynamic stability of sulfide I. Thus at 130°C under chromatographic conditions the I $\rightleftarrows$ VI equilibrium is shifted markedly to favor the formation of cis- and trans-I.

We have established that the thioallyl rearrangement of sulfide VI proceeds considerably more readily than was previously noted in [7]. Thus, even when sulfide VI is stored in a sealed ampul at room temperature, after 3 weeks it undergoes 15% isomerization to sulfide I, and after 18 months the percentages of sulfides I and VI in the mixture are, respectively, 45 and 55%. However, the equilibrium ratio of these sulfides is 95:5, in agreement with the data of Kwart [6].

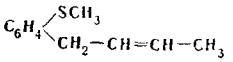
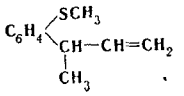
In order to obtain more accurate information regarding the thio-Claisen rearrangement of sulfide I we identified o-(3-methyl-allyl)thiophenol (VII) in the reaction mixture in the form of its methyl ether. When we carried out the rearrangement of sulfide VI in quinoline, we recorded the character of the accumulation of its transformation products with time (Fig. 1). It follows from Fig. 1 that sulfide VI initially undergoes rapid isomerization to a mixture of cis- and trans-I; however, after a certain maximum is reached, this process gradually slows

*A similar case was described in [5].

TABLE 2. Kinetic Parameters of the Rearrangement of 3- and 1-Methyl-allyl Phenyl Sulfides (I and VI) in Quinoline

Sulfide	Temp., °C	$K \cdot 10^{-4}$, sec^{-1}	E_a, kcal/mole
I	235	4,00	15
	245	4,74	
	255	5,96	
VI	155	5,23	10
	165	6,80	
	185	11,80	

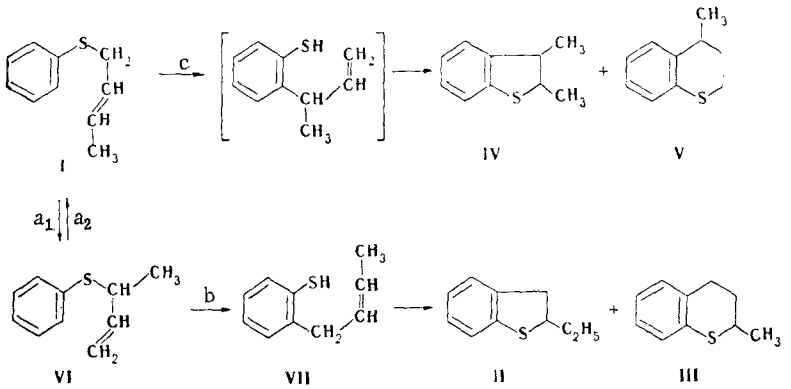
TABLE 3. Chemical Shifts of the Protons of the Methyl Derivatives of o-Alkenylthiophenols (δ, ppm)

Sulfide	Type of protons	Literature data [10]	Exptl. data
	C=C—CH$_3$	1,5—2,1	1,52, 3H, d
	C=C—CH$_2$—C$_6$H$_5$	3,4—3,6	3,5, 2H, d
	C=CH	5,1—5,3	5,3, 1H, m
	S—CH$_3$	2,47	2,47, 3H, s
	C$_6$H$_5$S	7,27	7,2, 5H, m
	C$_6$H$_5$—C—CH$_3$	1,3	—
	C=C—CH—C$_6$	2,8	—
	C=CH$_2$	4,6—4,8	—

down, and the yields of two-ring compounds II and III increase rapidly. The corresponding curves change antibatically.

Similar data for sulfide I, which demonstrate a steady increase in the formation of sulfides II and III vis-à-vis a simultaneous decrease in the yields of trans- and cis-I and sulfides IV and V, are presented in Fig. 2. The thio-Claisen rearrangement of sulfides I and VI in the initial segments of the kinetic curves is described by a first-order equation; the kinetic parameters are presented in Table 2.

A comparison of the data obtained makes it possible to conclude that the transformations of sulfide I proceed via the scheme:



Despite the fact that at the examined temperatures the thermodynamic equilibrium of the thioallyl rearrangement is shifted virtually completely to favor sulfide I, there is a certain temperature threshold at which the rate of conversion of sulfide VI via pathway b increases sharply, while the irreversibility of the step involving the cyclization of thiophenol VII shifts the entire process in the a_1—b direction, i.e., the thio-Claisen rearrangement of sulfide I is kinetically controlled. The formation of sulfides IV and V is associated with the partial transformation of sulfide I via pathway c.

Thus we were able to obtain direct experimental confirmation of the occurrence of thio-Claisen rearrangement of sulfide I through a step involving thioallyl rearrangement. The data presented in Table 1 on the transformations of sulfide I in the presence of nitrogen bases and in the presence of heterogeneous acid catalysts are identical; however, in the latter case sulfide II is formed more selectively.

EXPERIMENTAL

The transformations of 1- and 3-methylallyl phenyl sulfides in quinoline were carried out as in [8]. The synthesis of o-(3-methylallyl)thiophenol methyl ether was accomplished by the method in [9].

The reaction products were analyzed by gas–liquid chromatography (with a column filled with SE-30 on Chromosorb W, a temperature of 220°C, helium as the carrier gas, a flow rate of 10 ml/min, a column length of 2 m, and a column diameter of 3 mm; with a column filled with Apiezon L (15%) on Chromaton, a temperature of 200°C, helium as the carrier gas, a flow rate of 10 ml/min, a column length of 3 m, and a column diameter of 3 mm), PMR spectroscopy with a Varian T-60 spectrometer with CCl_4 as the solvent and hexamethyldisiloxane as the internal standard, and chromatographic mass spectrometry with a Varian MAT-111 (Gnom) spectrometer.

The structure of the side chain of the o-alkenylthiophenol methyl ether was proved by PMR spectroscopy (Table 3).

Kinetic Measurements. The concentration of the starting sulfide during the reaction was determined by chromatography by means of n-butylbenzene as the internal standard. Prior calibration of the mixtures showed that the accuracy in the determination of the sulfide concentration was ±1%. The reaction rate was calculated by graphical differentiation of the curves at the initial moment of the reaction, at which point the contribution of the side processes is minimal.

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