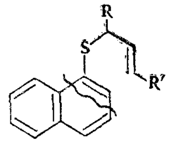
[3,3]-SIGMATROPIC REARRANGEMENT OF ALLYL AND 2-BUTENYL 1-NAPHTHYL SULFIDES

R. G. Aukharieva, T. A. Danilova,
A. V. Anisimov, and E. A. Viktorova

UDC 952:943.51:547.717'732'818

The [3,3]-sigmatropic rearrangement of alkenyl 1-naphthyl sulfides in solutions with various polarities was investigated at 138-190°C. The reaction proceeds through the formation of 2-alkenyl-1-naphthalene thiols, which subsequently undergo cyclization to compounds of the 2,3-dihydronaphtho[1,2-b]thiophene and naphtho[1,2-b]dihydrothiopyran series. 2-Butenyl 1-naphthyl sulfide, in addition to its passing directly through a [3,3]-sigmatropic rearrangement, to a considerable extent undergoes a prior [1,3]-sigmatropic rearrangement, which ultimately leads to the formation of four cyclic products. The kinetic parameters of the rearrangement of the sulfides were determined. The more negative entropies of activation constitute evidence for the high symmetry of the transition state.

Previously on the basis of our research [1] and the research of foreign authors [2] we expressed the assumption that as the lability of the π electrons in the aromatic portion of the sulfide molecule increases, its rearrangement is facilitated. The correlation obtained can be refined substantially by an investigation of the transformations of alkenyl naphthyl sulfides (Ia-c), regarding which the literature currently contains no information:

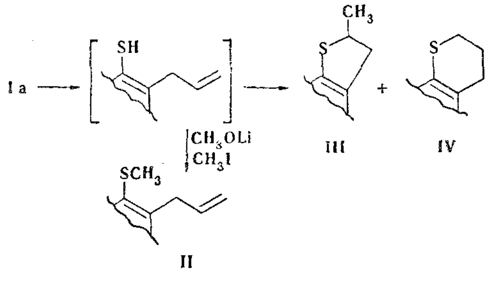


Ia-c

a $R=R'=H$;
b $R=H$, $R'=CH_3$;
c $R=CH_3$, $R'=H$

The rearrangement of sulfides Ia, b was carried out in solvents with various polarities at 138-190°C for 30-240 min.

In the absence of a solvent, sulfide Ia does not undergo any changes up to 170°C, whereas at 190°C it undergoes 23% rearrangement (Table 1). The nature of the solvent used has a substantial effect on the degree of conversion of the starting sulfide, the final products of which are two substances, to which the data from PMR spectroscopy and chromatographic mass spectrometry make it possible to assign 2-methyl-2,3-dihydronaphtho[1,2-b]thiophene (III) and naphtho[1,2-b]dihydrothiopyran (IV) structures:

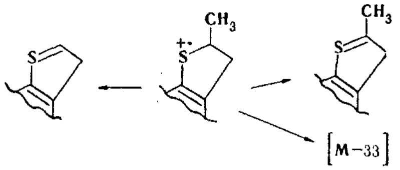


The principal pathway of mass-spectrometric fragmentation of III is characteristic for methyldihydrobenzothiophenes [3], viz., elimination of a hydrogen atom with the formation of a 199 ion,* a methyl radical with the formation of a 185 ion, and an SH radical:

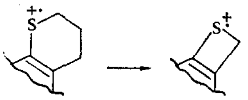
---

*Here and subsequently, the m/e values are given for the ion peaks.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotskilicheskikh Soedinenii, No. 5, pp. 611-614, May, 1981. Original article submitted June 26, 1980.



For IV, the isomer of III, the principal fragmentation pathway under the influence of electron impact is retrodiene ejection of a C_2H_4 group with the formation of a 172 ion, which makes it possible to assign the naphtho[1,2-b]dihydrothiopyran structure to IV:



It follows from Table 1 that the selectivity of the formation of sulfides III and IV increases as the temperature is raised due to suppression of the parallel reaction involving the formation of 1-naphthalenethiol.

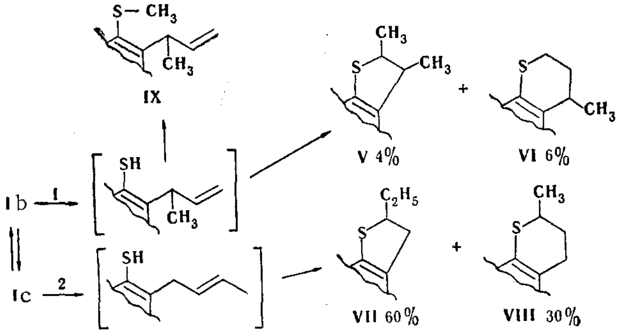
According to the data from chromatographic mass spectrometry, a mixture of four three-ring sulfides (V-VIII) is formed in the conversion of sulfide Ib (N,N-dimethylaniline, 165°C, 240 min).

The principal peak in the mass spectra of V, VI, and VIII with a molecular mass of 214 is the $[M-CH_3]^+$ ion peak. The virtually identical intensities (78%) of the molecular-ion peak and the $[M-30]^+$ ion peak observed only in the mass spectrum of V constitutes evidence for the presence in the V molecule of two methyl groups. This makes it possible to propose the 2,3-dimethyl-2,3-dihydronaphtho[1,2-b]thiophene structure for V.

In the case of VI and VIII the most intense peaks with respect to the molecular-ion peak are the $[M-CH_3]^+$ ion peaks. This constitutes evidence for the presence in VI and VIII of one methyl group. In addition, peaks of 172 ions, which correspond to retrodiene fragmentation with the ejection of a C_2H_4 group, are present in the mass spectra of these compounds. The 2- and 4-methylnaphtho[1,2-b]dihydrothiopyran structures are the most likely structures for VI and VIII.

The $[M-C_2H_5]^+$ ion peak has the maximum intensity in the mass spectrum of VII with the same molecular mass of 214 as sulfides V, VI, and, VIII. This makes it possible to assign the 2-ethyl-2,3-dihydronaphtho[1,2-b]thiophene structure to VII.

The formation of sulfides VII and VIII can be represented as being the result of cyclization of 2-butenyl-1-naphthalenethiol. Evidently, as in the transformations of 2-butenyl phenyl sulfide [4], the [3,3]-sigmatropic rearrangement of Ib is preceded by its [1,3]-sigmatropic rearrangement to isomer Ic, and thus the conversion of starting sulfide Ib is realized via two pathways, in which pathway "2" prevails:



The formation of sulfides III-VIII occurs during rearrangement of Ia, b through the formation of the corresponding thiols, which is confirmed by the fact that we obtained their methyl derivatives II and IX.

The rearrangement of sulfides Ia, b in quinoline and diphenyl ether is a first-order reaction. The E_a value (Table 2) in quinoline for Ia, b is lower than the corresponding E_a values for the reaction in diphenyl ether, which reflects the role of the nitrogen bases as nucleophilic agents [2] that facilitate cleavage of the C—S bond in the starting

TABLE 1. Rearrangement of Allyl 1-Naphthyl Sulfide (Ia) (at a sulfide–solvent volume ratio of 1:2)

Solvent	Temp., °C	Time, min	Mass percentage in the reaction mixture, %				
	—		Ia	III	IV	1-naphthalene thiol	unident. comp.
—	170	30	93	1	1	2	3
	170	60	88	3	2	5	2
	170	120	87	4	3	5	1
	190	120	77	8	7	5	3
Quinoline	138	30	83	5	5	5	2
	138	60	74	10	7	7	2
	155	60	40	26	24	8	2
	165	60	34	32	29	3	2
	190	60	—	59	41	—	—
Tetralin	190	150	100	—*	—*	—	—
	190	240	74	11	8	7	—
Diphenyl ether	190	60	92	—*	—*	8	—
	190	120	84	6	—*	10	—
	190	240	82	6	4	7	1
o-Xylene	140	90	97	3	—*	—	—
	140	120	95	3	2	—	—
Valeric acid	155	60	97	1	1	1	—*

*Trace amounts.

TABLE 2. Kinetic Parameters for the Rearrangement of Allyl and 2-Butenyl 1-Naphthyl Sulfides (Ia, b)

Sulfide	Solvent	Temp., °C	$K \times 10^4$ sec^{-1}	E, kcal/mole	$-\Delta S^{\neq}$, cal/mole · deg
Ia	Quinoline	138	1,48	12	49,5
		146	1,95		
		155	2,70		
		165	3,67		
Ia	Diphenyl ether	170	1,10	20	34,2
		178	1,61		
		190	3,02		
		200	5,20		
Ib	Quinoline	152	1,43	15	44,2
		158	1,68		
		165	1,99		
		175	2,46		
Ib	Diphenyl ether	180	1,20	23	28,8
		190	1,93		
		202	4,30		
		210	6,46		

sulfide. A comparison of the rate constants for the rearrangement of sulfides Ia, b in the same solvent shows that sulfide Ia undergoes rearrangement more readily. This is associated with the fact that the methyl group attached to the γ-carbon atom in the Ib molecule slows down electrophilic attack of C_γ at the β-carbon atom of the naphthalene ring. The latter also leads to a decrease in the rate constant and an increase in E_a for the rearrangement of sulfide Ib. The more negative entropies of activation constitute evidence for the high symmetry of the transition state in the rearrangement of sulfides Ia, b to thiols.

The results confirm the conclusion [1] regarding the effect of the aromatic character of the sulfide on the rate of [3,3]-sigmatropic rearrangement. The ease of the rearrangement decreases in the following order: allyl 2-furyl sulfide > allyl 2-thienyl sulfide > allyl 1-naphthyl sulfide > allyl phenyl sulfide.

EXPERIMENTAL

The analysis of the reaction products was carried out with an LKhM-8 MD chromatograph with detection by thermal conductivity; the carrier gas was helium, the liquid phase was SE-30 on Chromosorb W (30-40 mesh), and the column temperature was 220°C. Chromatographic mass-spectrometric analysis was carried out with a Varian MAT-111 (Gnom) apparatus. The PMR spectra of solutions in CCl_4 were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard.

Synthesis of Allyl 1-Naphthyl Sulfide (Ia). This synthesis was carried out by the classical method for the preparation of mixed sulfides [5] by the reaction of potassium thionaphtholate with allyl bromide. The product was obtained in 64% yield and had bp 135-137°C (5 mm), n_D^{20} 1.6583, and d_4^{20} 1.1200 [bp 153.3-155.3°C (4.2 mm)]. PMR spectrum: 7.6 (7H, m, $C_{10}H_7$), 5.7 (1H, m, $=CH-$), 4.6 (2H, m, $=CH_2$), and 3.4 ppm (2H, d, $-CH_2-$).

2-Butenyl 1-Naphthyl Sulfide (Ib). This compound was obtained by the reaction of 1-naphthalenethiol with 1,3-butadiene in the presence of ethylsulfuric acid and without it, as in the preparation of 2-butenyl phenyl sulfide [7]. The product was obtained in 75% yield and had bp 121-123°C (4 mm), n_D^{20} 1.6389, and d_4^{20} 1.100. PMR spectrum: 7.6 (7H, m, $C_{10}H_7$), 5.6 (2H, m, $-CH=CH-$), 3.4 (2H, d, $-CH_2-$), and 1.6 ppm (3H, d, $-CH_3$). Found: C 78.0; H 6.6; S 15.6%. $C_{14}H_{14}S$. Calculated: C 78.50; H 6.54; S 14.96%.

1-Methylallyl 1-Naphthyl Sulfide (Ic). This compound was obtained by the method used to prepare Ia and had bp 95-97°C (3 mm). PMR spectrum: 7.6 (7H, m, $C_{10}H_7$), 5.4 (1H, m, $-CH=$); 4.6 (2H, m, $=CH_2$); 3.3 (1H, d, $>CH-$); 1.4 ppm (3H, d, $-CH_3$).

Methyl 1-(2-Allylnaphthyl) Sulfide (II). This compound was identified from its PMR spectrum: 7.4 (6H, m, $C_{10}H_6$), 5.7 (1H, m, $=CH-$), 4.6 (2H, m, CH_2), 3.4 (2H, d, $-CH_2-$), and 2.4 ppm (3H, s, $-CH_3$).

Methyl 1-[2-(1-Methylallyl)naphthyl] Sulfide (IX). This compound was identified from its PMR spectrum: 7.4 (6H, m, $C_{10}H_6$), 5.4 (1H, m, $=CH-$), 4.6 (2H, m, $=CH_2$), 2.8 (1H, m, $>CH-$), 2.1 (3H, s, $-CH_3$ attached to the S atom), and 1.3 ppm (3H, d, $-CH_3$).

2-Methyl-2,3-dihydronaphtho[1,2-b]thiophene (III). This compound had bp 145-147°C (4 mm), while naphtho[1,2-b]dihydrothiopyran (IV) had bp 163-165°C (4 mm). They were obtained by rearrangement of sulfide Ia in quinoline at 190°C. PMR spectrum of III: 7.6 (6H, m, $C_{10}H_6$), 3.8 (1H, m, $>CH-$), 2.8 (2H, m, $-CH_2-$), and 1.4 ppm (3H, d, $-CH_3$). PMR spectrum of sulfide IV: 7.6 (6H, m, $C_{10}H_6$), 2.8 (2H, m, $-CH_2-$), and 2.1 ppm (2H, m, $-CH_2-$).

Rearrangement of Sulfides Ia, b. The rearrangement was carried out in a thermostatted flask in a stream of nitrogen or in ampuls at 138-210°C. The concentration of the starting sulfide during the reaction was determined by chromatography with the use of n-butylnaphthalene 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 determined at that instant at which the contribution of side processes was minimal.

LITERATURE CITED

1. A. V. Anisimov, V. F. Ionova, V. K. Govorek, V. S. Babaitsev, and E. A. Viktorova, Dokl. Akad. Nauk SSSR, 244, 362 (1979).
2. H. Kwart and J. L. Schwarts, J. Org. Chem., 39, 1575 (1974).
3. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972), p. 189.
4. A. V. Anisimov, R. G. Aukharieva, E. A. Viktorova, and T. A. Danilova, Summaries of Papers Presented at the 9th International Symposium on the Chemistry of Organic Sulfur Compounds [in Russian], Riga (1980), p. 72.
5. F. Krüger, J. Prakt. Chem., 14, 206 (1876).
6. A. H. Weinstein and R. M. Pierson, J. Org. Chem., 23, 554 (1958).
7. T. A. Danilova, T. Abdin, and E. A. Viktorova, Neftekhimiya, 11, 444 (1971).