[3,3]-SIGMATROPIC REARRANGEMENT OF ALLYL 2-BENZOTHIENYL SULFIDE

A. V. Anisimov, V. S. Babaitsev,
S. Ya. Grobovenko, T. A. Danilova,
and E. A. Viktorova

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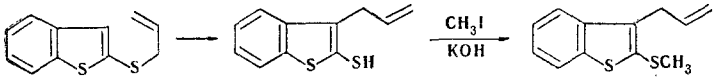
Allyl 2-benzothienyl sulfide at 20-120°C undergoes a [3,3]-sigmatropic rearrangement to give 3-allylbenzothiophene-2-thiol. The kinetic parameters of the reaction were studied. Under the experimental conditions the thiol undergoes cyclization to give 2-methyl-2,3-dihydrobenzothieno[2,3-b]thiophene, 2-methylbenzothieno[2,3-b]thiophene, and benzothieno[2,3-b]dihydrothiopyran. Allyl 3-methyl-2-benzothienyl sulfide does not form a thiol even at 150-190°C but rather forms only bis(3-methyl-2-benzothienyl) disulfide.

The transformations of allyl thienyl and allyl furyl sulfides upon moderate heating in various solvents, which proceed as intramolecular concerted [3,3]-sigmatropic shifts, constitute a convenient preparative method for the synthesis of substituted heteroaromatic thiols [1, 2]. In the present research we studied the rearrangement of allyl 2-benzothienyl sulfide (I) and also made an attempt to use the cyclization of 3-allyl-benzothiophene-2-thiol (II) for the preparation of condensed sulfur-containing heterocyclic compounds.

The rearrangement of sulfide I to its isomeric thiol II takes place even at room temperature: After standing for 30 days, it undergoes 26% conversion to thiol II, and methyl 3-allyl-2-benzothienyl sulfide (III) was isolated by the action on it of an alkaline solution of methyl iodide.

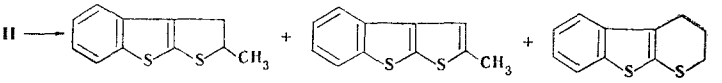


I II III

The polarity of the solvent used does not have a substantial effect on the course of the rearrangement of sulfide I, as evidenced by the virtual equality of the rate constants calculated from a first-order equation, as well as of the apparent energies of activation of the rearrangement in m-xylene and dibutyl ether (Table 1). The large negative activation entropies constitute evidence for the high symmetry of the transition state of the rearrangement, which is characteristic for concerted processes.

The maximum yield of thiol II was obtained in dibutyl ether at 130°C after 10 min (Table 2). A further increase in the experimental time, as well as an increase in the temperature, lowers the yield of the thiol because of its cyclization.

According to the data from PMR and chromatographic mass spectrometry, the products of cyclization of thiol II are 2-methyl-2,3-dihydrobenzothieno[2,3-b]thiophene (IV), 2-methylbenzothieno[2,3-b]thiophene (V), and benzothieno[2,3-b]dihydrothiopyran (VI):



IV V VI

The most intense peaks in the mass spectra of IV-VI are the molecular-ion peaks, whereas the intensity of the [M + 2] peak, which amounts to ~9% of the molecular-ion peak, constitutes evidence for the presence of two sulfur atoms in the molecules. The molecular ion

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 615-618, May, 1981. Original article submitted June 26, 1980.

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TABLE 1. Some Kinetic Parameters of the Rearrangement of Sulfide I

Solvent	T, °K	$k_0 \cdot 10^3$	Apparent E_a, kJ	$-\Delta S^{\neq}$, cal/mole/deg or eu
m-Xylene	363	0,48		
	373	0,68		
	383	1,12	56,4	39,20
	393	1,44		
	403	2,70		
Dibutyl ether	363	0,49		
	373	0,68		
	383	0,94	47,2	45,15
	393	1,53		
	403	2,33		

TABLE 2. Results of Experiments on the Rearrangement of Sulfide I (experimental time 10 min)

Solvent	Exptl. temp., °C	Yield of thiol II, %
Dibutyl ether	90	19
	100	30
	110	45
	120	61
	130	75
m-Xylene	120	64
N,N-Dimethylaniline	120*	5
Without a solvent	120*	4

*Experimental time 60 min.

TABLE 3. Results of Experiments on the Cyclization of Thiol II (experimental time 2 h at 120°C)

Solvent	Comp. of the cyclic products, %		
	IV	V	VI
Hexametapol	57	38	5
Quinoline	53	38	9
N,N-Dimethylaniline*	51	32	16
Tributylamine	42	39	19
m-Xylene	23	11	66
Without a solvent	15	9	76

*Experimental time 1 h at 118°C.

that is formed from sulfide IV under the influence of electron impact undergoes fragmentation with splitting out of a hydrogen atom to give a 205 ion* or splitting out of CH_3 and SH groups to give 191 and 173 ions. Elimination of a hydrogen atom with the formation of a 203 ion with subsequent detachment of S, C_2H_2, or CS fragments to give 171, 177, and 159 ions is characteristic for the mass-spectrometric fragmentation of V. In the case of sulfide VI the principal fragmentation pathway under the influence of electron impact is retrodiene ejection of a C_2H_4 group to give a 178 ion.

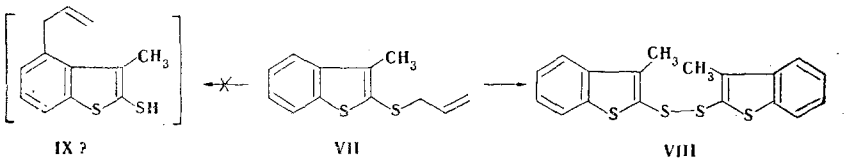
Thiol II undergoes cyclization at an appreciable rate even at room temperature. Upon standing for 30 days, the overall yield of IV-VI reached 66%. In aprotic solvents with various polarities (hexametapol, quinoline, and dibutyl ether) thiol II is converted primarily to a mixture of IV and V, whereas without a solvent or in m-xylene it is converted to VI (Table 3). As in the case of allylthiophenethiols [3], the primary course of the 5-exo- or 6-endocyclization of thiol II will evidently be determined by the possibility of attaining a transition state, the geometry of which is favorable for the formation of compounds with a five- or six-membered ring.

The most noteworthy fact in the cyclization is the formation of V (also obtained by heating sulfide IV with chloranil in chlorobenzene), which may be associated with processes involving intermolecular redistribution of hydrogen between II and IV. However, the mechanism of the formation of V requires further detailed study.

Allyl 3-methyl-2-benzothienyl sulfide (VII), in which the position adjacent to the allylthio group is occupied by a methyl group, forms only bis(3-methyl-2-benzothienyl) disulfide (VIII) and diallyl disulfide (according to the mass spectrum) even upon prolonged

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

heating at 150-190°C. The conversion of VII to its isomeric thiol (IX), which includes two successive [3,3]-sigmatropic shifts, requires surmounting a rather high energy barrier associated with twofold disruption of the aromatic system and is therefore not realized:



IX ? VII VIII

EXPERIMENTAL

The chromatographic analysis of the products of cyclization of thiol II was carried out with a model No. 1 LKhM-8MD chromatograph with a thermal conductivity detector with a column (l = 3 m, d = 0.4 cm) with SE-30 (5%) applied to silanized Chromaton N (0.2-0.3 mm) as the stationary phase; the column temperature was 250°C. 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. Chromatographic mass-spectrometric analysis was carried out with a Varian MAT-111 (Gnom) apparatus at an ionizing-electron energy of 80 eV and an emission current of 270 mA with a chromatographic column (l = 2 m, d = 0.4 cm) with SE-30 (5%) applied to silanized Chromaton N (0.2-0.3 mm) as the stationary phase and programmed heating from 80 to 250°C; the temperature-rise rate was 10°/min.

Allyl 2-Benzothienyl Sulfide (I). This compound was obtained by the general method for the synthesis of allyl hetaryl sulfides [4], except that after the addition of sulfur to an ether solution of 2-benzothienyllithium, the 2-benzothiophenethiol was extracted with a 10% solution of KOH, and the resulting solution was treated with allyl bromide. The reaction product was extracted with ether, the ether solution was dried and cooled to 0°C, and the precipitated crystals of sulfide I were recrystallized from ethanol to give a product with mp 78-79°C in 50% yield. PMR spectrum: 7.3 (5H, m, C_6H_5), 5.5 (1H, m, —CH=), 4.75 (2H, m, $=CH_2$), and 3.4 ppm (2H, d, $—CH_2—$). Found: C 64.0; H 4.6; S 31.4%. $C_{11}H_{10}S_2$. Calculated: C 64.1; H 4.8; S 31.1%.

The rearrangement of I was carried out by constant shaking in a sealed ampul in an argon atmosphere. At the end of the reaction, the ampul was cooled with dry ice, and the contents were dissolved in ether. The ether solution was treated with a 20% solution of KOH, and the alkaline extract was acidified with 2 N HCl. The liberated thiol was extracted with ether, the ether was removed by distillation, and the thiol was purified by passing through a column filled with silica gel (elution with hexane).

3-Allylbenzothiophene-2-thiol (II). This compound had n_D^{16} 1.6663 and d_4^{20} 1.2375. PMR spectrum: 7.5 (4H, m, C_6H_5), 5.95 (1H, m, —CH=), 5.15 (2H, m, $=CH_2$), 3.65 (2H, m, $—CH_2—$), and 3.23 ppm (1H, s, SH). Found: C 63.6; H 4.8; S 31.1%. $C_{11}H_{10}S_2$. Calculated: C 64.1; H 4.8; S 31.1%.

In the investigation of the kinetics of rearrangement of sulfide I the resulting thiol II after dilution of the reaction mixture with ether was titrated with a 0.0297 mole/liter solution of KOH with respect to phenolphthalein.

Methyl 3-Allyl-2-benzothienyl Sulfide (III). This compound was obtained by treatment of an aqueous solution of potassium 3-allyl-benzothiophenethiolate with methyl iodide. The product was extracted with ether and was obtained in 70% yield; n_D^{20} 1.5537, d_4^{20} 1.1937. PMR spectrum: 7.45 (4H, m, C_6H_4), 5.5 (1H, m —CH=), 4.75 (2H, m, $=CH_2$), 3.4 (2H, d, $—CH_2—$), and 2.4 ppm (3H, s, CH_3).

The neutral part of the products of rearrangement of I that remained after treatment of the reaction mixture with KOH solution was washed with water, dried with magnesium sulfate, and, where necessary, was subjected to fractional distillation *in vacuo*. The product was analyzed by GLC, PMR, and chromatographic mass spectrometry. Fractions containing 73% VI, 27% (IV + V) (1), 93% (IV + V) and 7% (VI) (2) were isolated by fractional distillation.

2-Methyl-2,3-dihydrobenzothieno[2,3-b]thiophene (IV). PMR spectrum: 7.5 (4H, m, C_6H_4), 4.53 (1H, m, CH), 2.55 (2H, m, CH_2), and 1.4 ppm (3H, d, CH_3).

2-Methylbenzothieno[2,3-b]thiophene (V). Fraction (2) (0.57 g) was heated with 0.5 g of chloranil in 5 ml of chlorobenzene at 120°C for 5.5 h, after which the reaction mixture

was filtered, the chlorobenzene was removed by distillation, and the residue was dissolved in ether. The ether solution was cooled to 0°C and filtered, the ether was removed by distillation, and the residue was dissolved in acetone–hexane (1:5) and purified by passage through a column filled with silica gel. PMR spectrum: 7.44 (5H, m, C_6H_5), and 2.43 ppm (3H, s, CH_3).

Benzothieno[2,3-b]dihydrothiopyran (VI). PMR spectrum: 7.44 (4H, m, C_6H_4), 2.63 (4H, m, $-CH_2CH_2-$), and 1.70 ppm (2H, m, $-CH_2-$).

Allyl 3-Methyl-2-benzothienyl Sulfide (VII). This compound was obtained in 52% yield by the method described for sulfide I starting from 3-methylbenzothiophene and had n_D^{20} 1.5492 and d_4^{20} 1.2018. PMR spectrum: 7.55 (4H, m, C_6H_4), 5.7 (1H, m, $-CH=$), 5.04 (2H, m, $=CH_2$), 3.36 (2H, d, $-CH_2-$), and 2.33 ppm (3H, s, CH_3). Found: C 65.3; H 5.6; S 29.4%. $C_{12}H_{12}S_2$. Calculated: C 65.4; H 5.4; S 29.2%.

Sulfide VII was heated at 150-190°C in a sealed ampul in an argon atmosphere for 1 h, after which the mixture was dissolved in ether, and the ether solution was washed with 10% KOH solution. The ether was removed from the residue by distillation, and the residue was dissolved in hexane and chromatographed on silica gel elution with CCl_4–hexane–ether (47:43:10). Removal of the solvent gave sulfide VIII. PMR spectrum: 7.55 (8H, m, $C_{16}H_8$) and 2.55 ppm (6H, s, $2CH_3$).

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MASS-SPECTROMETRIC STUDY OF SUBSTITUTED TETRAHYDRO-4-THIOPYRONES

A. V. Serbin, P. I. Zakharov, Yu. I. Blokhin, and B. V. Unkovskii

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The mass spectra of 16 methyl- and phenyl-substituted tetrahydro-4-thiopyrones that differ with respect to the position of the substituents in the ring and some of their deutero derivatives were studied. The principal pathways of dissociative ionization of these compounds are due to cleavage of the α bonds with respect to the heteroatom and the carbonyl group. Analytical features that make it possible to determine the position of the substituents in the tetrahydro-4-thiopyrone ring and distinguish the structural and spatial isomers in this series of compounds were found.

In [1-5] we described new simple and convenient methods for the preparation of various derivatives of tetrahydro-4-thiopyrones from the bases and salts of alkenyl and styryl β-dialkylaminoalkyl ketones [1-3], as well as from 4-ketodecahydroquinolines [4, 5]. In the present research we studied the mass-spectral behavior of the tetrahydro-4-thiopyrones obtained by the indicated methods [1-5] and their previously known representatives and established the principles of the dissociative ionization of these compounds under the influence of electron impact. Up until now, data on the mass spectra of compounds of this type were limited to the data in [6-9], in which the fragmentation of unsubstituted tetrahydro-4-thiopyrone and its sulfoxide [6] and sulfone [6, 7] is described. Data on the mass spectra of 2,2-di and 2,3-dimethyl-, 2,2,6,6-tetramethyl-, and trans-2,5-dimethyltetrahydro-4-thiopyrone are presented in [8, 9] without analysis and discussion. The mass-spectral

M. V. Lomonosov Moscow Institute of Fine Chemical Technology, Moscow 119831.

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