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SIGMATROPIC REARRANGEMENTS OF ALKENYL BENZOFURYL AND BENZOTHIENYL SULFIDES

A. V. Anisimov, V. S. Babaitsev, T. A. Kolosova, and E. A. Viktorova

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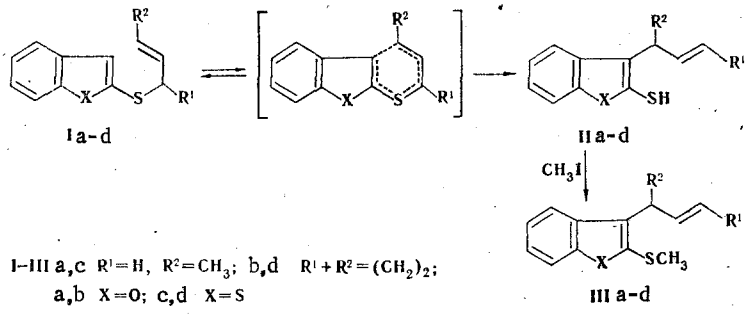
The thio Claisen rearrangement of 2-butenyl 2-benzofuryl sulfide, cyclopenten-2-yl 2-benzofuryl sulfide, 2-butenyl 2-benzothienyl sulfide, and cyclopenten-2-yl 2-benzothienyl sulfide was investigated. The rates, energies and entropies of activation of the process were calculated, and the effect of the structure of the sulfide, the polarity of the solvent, and the temperature was demonstrated by comparison of these values. The 1,3-thioallyl rearrangement of 1-methylallyl 3-methyl-2-benzothienyl sulfide was studied, and it was shown that this reaction competes with the thio Claisen rearrangement.

Transformations of allyl thienyl and allyl sulfides via a scheme involving a concerted [3,3]-sigmatropic shift lead to the formation of alkenylthiophenethiols and furanthiols [1], which undergo cyclization to condensed derivatives of thiophene and thiopyran [2]. The extension of this reaction to sulfides of the benzofuran and benzothiophene series makes it possible to expect the production of difficult-to-obtain benzofuranthiols and benzothiophenethiols, as well as benzothienothiophenes and benzothienothiopyrans.

When alkenyl 2-benzofuryl and alkenyl 2-benzothienyl sulfides Ia-d are heated in the presence of solvents with various polarities andwithout asolvent, theyundergo rearrangement to isomeric thiols IIa-d (Table 1):



In a number of cases thiols IIa-d are formed in significant yields (up to 19%) even when sulfides Ia-d are allowed to stand for a long time (10 days) at room temperature.

The rearrangement of all of the investigated sulfides proceeds irreversibly as a first-order reaction with inversion of the allyl group; this follows from the structures of thiols IIa,c and the methyl derivatives IIIa,c, which were isolated in the transformations of sulfides Ia,c.

A comparison of the kinetic parameters E_{act} and ΔS for the rearrangement of sulfides Ia-d indicates the absence of an effect of the heteroatom (S or O) on their resistance to re-

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TABLE 1. Results of Experiments on the Rearrangement of Sulfides

Sulfide	Solvent	Expti. time, min	Yields of thiols, %		
			110°	130°	180°
Ic	m-Xylene	20	—	60	65
	Dibutyl ether	20	—	68	37
Ib	m-Xylene	3	18	8	—
	Dibutyl ether	3	12	30	—
Ia	m-Xylene	5	17	35	—
	Dibutyl ether	5	38	50	—
Id	m-Xylene	20	—	40	14
	Dibutyl ether	20	—	45	12

TABLE 2. Kinetic Parameters of the Rearrangement of the Sulfides

Sulfide	Solvent	T, °C	$K_0 \cdot 10^{-3}$, sec^{-1}	E_{act}, kcal/mole, ±0.5	$-\Delta S$, kcal/mole deg
Ia	m-Xylene	120	3,64	13,4	34,0
	Dibutyl ether	120	2,26	11,8	43,0
Ib	The same	130	6,87	12,8	43,0
Ic	m-Xylene	130	1,15	13,7	44,5
	Dibutyl ether	130	0,67	12,0	41,5
Id	m-Xylene	130	3,03	14,6	36,5
	Dibutyl ether	130	0,83	11,7	46,5

TABLE 3. Results of Experiments on the Mutual Isomerization of 1-Methylallyl 3-Methyl-2-benzothienyl Sulfide (V) and 2-Butenyl 3-Methyl-2-benzothienyl Sulfide (VI)

Sulfide	T, °C	Expti. time, h	V : VI ratio
V	20	336	90 : 10
	20	2160	55 : 45
	75	1	80 : 20
	100	1	76 : 24
	150	1	35 : 65
	200*	1	5 : 95
VI	20	0,5	5 : 95
	200*	1	5 : 95

*Partial destruction of the sulfide with cleavage of the C—S bond is observed.

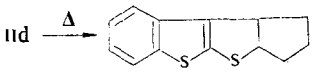
arrangement (Table 2).

The slight change in the K_0 rate constants calculated in the initial sections of the kinetic curves from a first-order equation and the E_{act} values on passing from m-xylene to dibutyl ether constitutes evidence for a small degree of separation of the charges in the transition state; the large negative ΔS values also indicate the high symmetry of the latter.

According to the IR spectroscopic data, thiols IIa-d formed as a result of the reaction are stabilized due to the formation of associates with the solvent (a broad band at 2400-2550 cm^{-1} in the case of dibutyl ether) or undergo cyclization to give difficult-to-separate mixtures of derivatives of thieno[2,3-b]thiophene and thieno[2,3-b]thiopyran in the case of IIa-c. Unstable ammonium salts of the corresponding thiols are formed when the reaction is carried out in nitrogenous bases.

The cyclization of thiol IId proceeds selectively to give cyclopentano-2,3-dihydrobenzothieno[2,3-b]thiophene, since in this case the formation of an isomeric sulfide with a six-

membered ring requires considerable distortion of the bond angles and the interatomic distances in thiol IId:

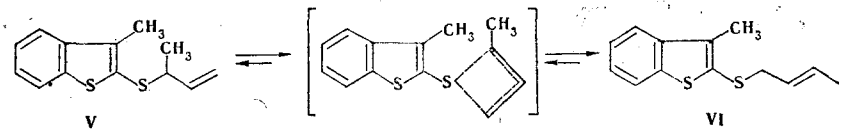


IV

[1,3]-Sigmatropic rearrangement of allyl phenyl sulfides in a number of cases proceeds simultaneously with the principal process, viz., the thio Claisen rearrangement, and complicates its study substantially [3-5]. 1-Methyl-allyl 3-methyl-2-benzothienyl sulfide (V) and 2-butenyl 3-methyl-2-benzothienyl sulfide (VI), for which [3,3]-sigmatropic rearrangement is impossible by virtue of their structural peculiarities [6], are convenient subjects for the study of their [1,3]-sigmatropic rearrangement.

According to the PMR spectroscopic data, sulfide V undergoes 5-95% isomerization to sulfide VI when it is heated without a solvent at 20-200°C (Table 3), while sulfide VI undergoes no more than 5% reversible isomerization to sulfide V under these conditions. Thus an equilibrium exists between sulfides V and VI and is shifted to a significant degree to favor sulfide VI.

Partial destruction of sulfides V and VI with cleavage of the C–S bond and the formation of bis(3-methyl-2-benzothienyl) disulfide is observed at temperatures above 175°C. Considering the absence of intermolecular processes in the rearrangements of allyl hetaryl sulfides [7], it may be assumed that the [1,3]-thioallyl rearrangement of sulfides V and VI occurs as an intramolecular concerted reaction through a four-center transition state:



V VI

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded at 20°C with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard.

2-Butenyl 2-Benzofuryl Sulfide (Ia). This compound was obtained in 34% yield by the action of 1,3-butadiene on 2-benzofuranthiol at −5°C in the presence of ethylsulfuric acid and had n_D^{20} 1.6200 and d_4^{20} 1.1045. PMR spectrum: 1.70 (3H, d, CH_3), 3.51 (2H, d, CH_2), 5.48 (2H, m, CH = CH), 6.70 (1H, s, benzofuran β-H), and 7.23 ppm (4H, m, aromatic). Found: C 71.4; H 6.0; S 15.6%. $C_{12}H_{12}OS$. Calculated: C 70.69; H 5.9; S 15.7%.

Cyclopenten-2-yl 2-Benzofuryl Sulfide (Ib). This compound was obtained in 48% yield by the method in [8] by the action on benzofuran of n-butyllithium, sulfur, and 3-chlorocyclopent-1-ene in absolute ether and had n_D^{20} 1.6240 and d_4^{20} 1.1840. PMR spectrum: 2.15 (4H, m, CH_2CH_2), 3.95 (1H, m, CH), 5.65 (2H, s, CH = CH), 6.53 (1H, s, benzofuran β-H), and 7.13 ppm (4H, m, aromatic).

2-Butenyl 2-Benzothienyl Sulfide (Ic). This compound was obtained in 5% yield from 2-benzothiophenethiol and 1,3-butadiene by a method similar to that used to prepare Ia and had bp 125-126°C (1 mm) (with decomposition), n_D^{20} 1.6465, and d_4^{20} 1.1845. PMR spectrum: 1.52 (3H, m, CH_3), 3.35 (2H, m, CH_2), 5.42 (2H, m, CH = CH), and 7.4 ppm (5H, m, aromatic). Found: C 65.8; H 5.2; S 30.0%. $C_{12}H_{12}S_2$. Calculated: C 65.5; H 5.5; S 29.1%.

Cyclopenten-2-yl 2-Benzothienyl Sulfide (Id). This compound was obtained in 87% yield by the action on benzothiophene of n-butyllithium, sulfur, and 3-chlorocyclopent-1-ene in absolute ether by a method similar to that used to prepare Ib and had bp 131-132°C (1 mm) (with decomposition), n_D^{20} 1.6012, and d_4^{20} 1.2530. PMR spectrum: 2.32 (4H, m, CH_2CH_2), 4.20 (1H, m, CH), 5.85 (2H, m, CX = CH), and 7.48 ppm (5H, m, aromatic). Found: C 67.5; H 5.0; S 27.5%. $C_{13}H_{12}S_2$. Calculated: C 67.2; H 5.2; S 27.6%.

1-Methylallyl 3-Methyl-2-benzothienyl Sulfide (V). This compound was obtained in 84% yield from potassium 3-methyl-2-benzothiolate and 3-chloro-1-butene in dimethylformamide (DMF) at 0°C and had bp 125-126°C (1 mm) (with decomposition), n_D^{20} 1.6331, and d_4^{20} 1.2084. PMR spectrum: 1.50 (3H, d, allyl CH_3), 2.45 (3H, s, thiophene ring CH_3), 3.67 (1H, m, CH), 4.92 (2H, m, $=CH_2$), 5.85 (1H, m, CH=), and 7.48 ppm (4H, m, aromatic). Found: C 66.8; H 6.0; S 26.9%. $C_{13}H_{14}S_2$. Calculated: C 66.7; H 6.0; S 27.4%.

2-Butenyl 3-Methyl-2-benzothienyl Sulfide (VI). This compound was obtained in 80% yield from 3-methyl-2-benzothiophenethiol and 1,3-butadiene in the presence of 20% (by weight) of ethylsulfuric acid at 5°C and had bp 131-132°C (2 mm), n_D^{14} 1.6465, and d_4^{20} 1.1765. PMR spectrum: 1.55 (3H, d, allyl CH_3), 2.28 (3H, s, thiophene ring CH_3), 3.32 (aH, d, CH_2), 5.37 (2H, m, CH=CH), and 7.43 ppm (4H, m, aromatic). Found: C 66.8; H 5.9; S 27.4%. $C_{13}H_{14}S_2$. Calculated: C 66.7; H 6.0; S 27.4%.

Rearrangement of Sulfides Ia-d. The rearrangement was carried out in sealed ampuls in an argon atmosphere (Table 1). At the end of the reaction, the ampuls were cooled with dry ice, the contents were dissolved in ether, and the ether solution was washed three times with 10% aqueous KOH solution. The alkaline extracts were acidified with 10% HCl, and the liberated thiol was extracted with ether. The ether solution was washed with water and dried with $MgSO_4$, the ether was removed, and the residue was analyzed by TLC and PMR spectroscopy. If the thiol cyclized rapidly under the rearrangement conditions, it was isolated in the form of the S-methyl derivative by treatment of an alkaline solution of the thiolate with a threefold excess of CH_3I.

Isomerization of Sulfides V and VI. This process was carried out without a solvent in sealed ampuls in an argon atmosphere. At the end of the reaction, the ampul was cooled with dry ice, and the PMR spectrum of the reaction mixture was recorded.

3-(1-Methylallyl)-2-benzofuranthiol (IIa). This compound was obtained in 25% yield. PMR spectrum: 1.50 (3H, d, CH_3), 3.4 (1H, s, SH), 3.75 (1H, m, CH), 5.05 (2H, d, $=CH_2$), 5.95 (1H, m, CH=), and 6.55 ppm (4H, m, aromatic). Found: C 70.6; H 6.1; S 15.8%. $C_{12}H_{12}OS$. Calculated: C 70.6; H 5.9; S 15.7%.

3-(Cyclopent-2-yl)-2-benzofuranthiol (IIb). This compound was obtained in 37% yield. PMR spectrum: 2.25 (4H, m, CH_2CH_2), 3.35 (1H, s, SH), 4.20 (1H, m, CH), 5.72 (2H, m, CH=CH), and 7.15 ppm (4H, m, aromatic).

3-(1-Methylallyl)-2-benzothiophenethiol (IIc). This compound, with bp 50-51°C, was obtained in 65% yield. PMR spectrum: 1.45 (3H, d, CH_3), 3.20 (1H, s, SH), 3.30 (1H, m, CH), 4.95 (2H, m, $=CH_2$), 5.90 (1H, m, CH=), and 7.25 ppm (4H, m, aromatic). Found: C 65.1; H 5.1; S 30.0%. $C_{12}H_{12}S_2$. Calculated: C 65.5; H 5.5; S 29.1%.

3-(Cyclopent-2-yl)-2-benzothiophenethiol (IId). This compound, with bp 35-36°C, was obtained in 67% yield. PMR spectrum: 1.45 (3H, d, CH_3), 3.20 (1H, s, SH), 3.30 (1H, m, CH), 4.95 (2H, m, $=CH_2$), and 7.35 ppm (4H, m, aromatic). Found: C 67.4; H 5.6%. $C_{13}H_{12}S_2$. Calculated: C 67.2; H 5.2%.

Methyl 2-[3-(1-Methylallyl)benzofuryl] Sulfide (IIIa). This compound, with bp 110-112°C (2 mm), n_D^{20} 1.6040, and d_4^{20} 1.0650, was obtained in 85% yield. PMR spectrum: 1.50 (3H, d, allyl CH_3), 2.45 (3H, d, CH_3), 3.4 (1H, m, CH), 5.05 (2H, d, $=CH_2$), 5.95 (1H, m, CH=), and 7.2 ppm (4H, m, aromatic). Found: C 70.9; H 5.9; S 14.6%. $C_{13}H_{14}OS$. Calculated: C 71.2; H 6.42; S 14.7%.

Methyl 2-[3-Cyclopent-2-yl)benzofuryl] Sulfide (IIIb). This compound, with n_D^{20} 1.5980 and d_4^{20} 1.1306, was obtained in 88% yield. PMR spectrum: 2.41 (3H, s, CH_3), 3.4 (1H, m, CH), 3.90 (4H, m, CH_2CH_2), 5.60 (2H, m, CH=CH), and 6.90 ppm (4H, m, aromatic).

Methyl 2-[3-(1-Methylallyl)benzothienyl] Sulfide (IIIc). This compound, with bp 131-132°C (1 mm), n_D^{20} 1.6309, and d_4^{20} 1.1805, was obtained in 89% yield. PMR spectrum: 1.50 (3H, d, allyl CH_3), 2.50 (3H, d, CH_3), 4.35 (1H, m, CH), 5.10 (2H, m, $=CH_2$), 6.20 (1H, m, CH=), and 7.38 ppm (4H, m, aromatic). Found: C 66.5; H 6.2; S 28.1%. $C_{13}H_{24}S_2$. Calculated: C 66.7; H 6.0; S 27.4%.

Methyl 2-[3-(Cyclopent-2-yl)benzothienyl] Sulfide (IIId). This compound, with bp 132-133°C (2 mm), n_D^{20} 1.6218, and d_4^{20} 1.2005, was obtained in 70% yield. PMR spectrum: 1.95 (4H, m, CH_2CH_2), 2.4 (3H, d, CH_3S), 4.05 (2H, m, CH), 5.8 (2H, m, CH=CH), and 7.3 ppm (4H, m, aromatic). Found: C 67.6; H 6.0; S 26.0%. $C_{14}H_{14}S_2$. Calculated: C 68.3; H 6.0; S 26.0%.

Cyclopentano-2,3-dihydrobenzothieno[2,3-b]thiophene (IV). A mixture of 0.2 g of 3-(cyclopenten-2-yl)-2-benzothiophenethiol (IId) and 0.4 ml of quinoline was heated in an argon atmosphere in a sealed ampul at 120°C for 2 h, after which the ampul was cooled, and the contents were dissolved in 100 ml of ether. The ether solution was washed three times with 50-ml portions of 10% aqueous KOH solution and water until the wash waters were neutral. The ether solution was then dried with calcined magnesium sulfate, after which the ether was removed by distillation, and the residue was purified by chromatography on silica gel by elu-

tion with hexane. PMR spectrum: 2.14 (6H, m, aliphatic), 4.10 (1H, m), 4.65 (1H, m), and 7.40 (4H, m, aromatic).

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INVESTIGATION OF THE STEREOCHEMICAL DIRECTION OF THE CYANOETHYLATION OF SIX-MEMBERED HETEROCYCLIC KETONES AS A FUNCTION OF THE NATURE OF THE HETEROATOM

K. Kh. Tokmurzin, V. V. Kozyrev, and A. Sh. Sharifkanov

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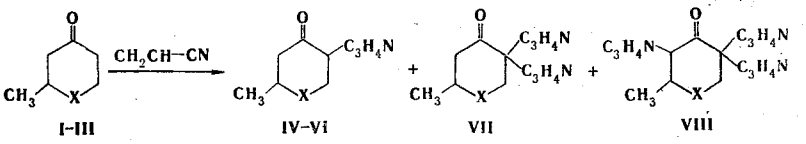
Only a mono(cyanoethyl) compound is formed from thiopyranone in the cyanoethylation of six-membered heterocyclic ketones that contain a methyl group attached to the C_2 atom of the heteroring, whereas primarily bis- and tris(cyanoethyl) derivatives are obtained from pyranone due to the effect of the heteroatom.

We have previously studied [1, 2] the cyanoethylation of some N-substituted 2,5-dimethyl-4-piperidones and 2,5-dimethyltetrahydro-4-thiopyranone. Continuing these studies, we have carried out the cyanoethylation of 1,2-dimethyl-4-piperidone (I), 2-methyltetrahydro-4-pyranone (II), and 2-methyltetrahydro-4-thiopyranone (III) with acrylonitrile in equimolar ratios in the presence of potassium hydroxide.



I, IV, VIII X=N–CH_3; II, V, VII X=O; III, VI X=S

From piperidone I we obtained 1,2-dimethyl-5-(β-cyanoethyl)-4-piperidone (IV) and 1,2-dimethyl-3,5,5-tris(β-cyanoethyl)-4-piperidone (VIII) in 1 and 84% yields, respectively, from tetrahydropyranone II we obtained 2-methyl-5-(β-cyanoethyl)tetrahydro-4-pyranone (V) and 2-methyl-5,5-bis(β-cyanoethyl)tetrahydro-4-pyranone (VII) in 2 and 73% yields, respectively, whereas from tetrahydrothiopyranone III we obtained only 2-methyl-5-(β-cyanoethyl)tetrahydro-4-pyranone (VI) in 20% yield.

Thus tris(cyanoethylation) product VIII is primarily formed from piperidone I, bis(cyanoethyl) derivative VII is primarily formed from pyranone II, and only mono(cyanoethylated) compound VI is obtained from thiopyranone III. This difference in the behavior of heterocyclic ketones in cyanoethylation is apparently explained by the different effects of the hetero-

Institute of the Chemistry of Petroleum and Natural Salts, Academy of Sciences of the Kazakh SSR, Gurev 465050.

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