

REACTIONS OF HETEROAROMATIC THIOLS
WITH 1,3-BUTADIENE AND CYCLOPENTADIENE

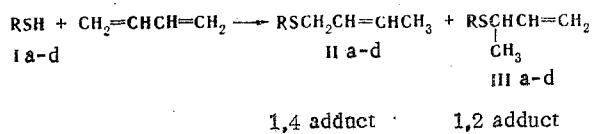
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The formation of 1,2 and 1,4 adducts in the reaction of 5-chloro-2-thiophenethiol, 2-benzofuranthiol, 2-benzothiophenethiol, and 3-methyl-2-benzothiophenethiol with conjugated dienes in the presence of various amounts of ethylsulfuric acid and also without a catalyst was studied. Catalytic acceleration of the reaction with ethylsulfuric acid indicates the heterolytic character of the addition.

A number of studies have been devoted to the reaction of aliphatic and aromatic thiols with 1,3-butadiene [1] and cyclopentadiene; however, the literature contains no data on such reactions for heteroaromatic thiols. In the present research we investigated the addition of four heteroaromatic thiols, viz., 5-chloro-2-thiophenethiol (Ia), 2-benzofuranthiol (Ib), 2-benzothiophenethiol (Ic), and 3-methyl-2-benzothiophenethiol (Id) to 1,3-butadiene and cyclopentadiene in the presence of various amounts of ethylsulfuric acid and also without a catalyst.

The products of the reaction of thiols Ia-d with 1,3-butadiene, viz., sulfides IIa-d and IIIa-d, are formed in high yields (up to 93%) when the mixture of reagents is maintained at 5°C for 10 h.



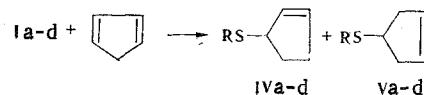
a R = 5-chloro-2-thienyl; b R = 2-benzofuryl; c R = 2-benzothienyl; d R = 3-methyl-2-benzothienyl

According to the PMR spectroscopic data, the selectivity of 1,4 addition is 95%; 1,2 adducts IIIa-d (up to 5%), respectively, are present as impurities in IIa-d.

The acidity of the thiol used and the addition of an acidic catalyst have a decisive effect on the rate of the process and the yields of the final products. The introduction of ethylsulfuric acid, which has been previously used in similar reactions of thiophenol [3], into the reaction mixture, while it does not change the ratios of the isomers, increases the reaction rate (Fig. 1) and the overall yields of the sulfides by 10–20%, depending on the acidity of the starting thiol (Table 1).

The effect of the catalyst is manifested to a greater degree for thiols Ib-Id, which have relatively low acidities, whereas this effect is minimal for 5-chloro-2-thiophenethiol.

In contrast to 1,3-butadiene, a mixture of 1,2 (IVa-d) and 1,4 adducts (Va-d) in approximately equal amounts is formed in up to 79% yield with cyclopentadiene (Table 2), regardless of the experimental conditions:



The character of the effect of the acidities of the starting thiols on the rates of addition and the yields of the sulfides and the increase in the yields when ethylsulfuric acid is added make it possible to assume that the process takes place as heterolytic addition of

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TABLE 1. Results of Experiments on the Addition of Heteroaromatic Thiols to 1,3-Butadiene (-5°C , 10 h)

Thiol	pK_a [4]	Amt. of ethylsulfuric acid, %	Yields of II and III, %
Ia	5,74	—	93
Ib	6,60	20	95
Ic	6,70	—	66
Ic	6,70	20	74
Id	6,90	—	77
Id	6,90	20	87
Id	6,90	—	70
Id	6,90	20	83

*The amount of III in the reaction products does not exceed 5%, according to the PMR spectroscopic data.

TABLE 2. Results of Experiments on the Addition of Heteroaromatic Thiols to Cyclopentadiene (-5°C , 2 h, 20% ethylsulfuric acid)

Thiol	Yields of the sulfides, %			
	IV		V	
	without a cata- lyst	in the presence of a catalyst	without a cata- lyst	in the presence of a catalyst
Ia	33	39	33	40
Ib	29	38	29	37
Ic	27	36	26	37
Id	22	34	23	34

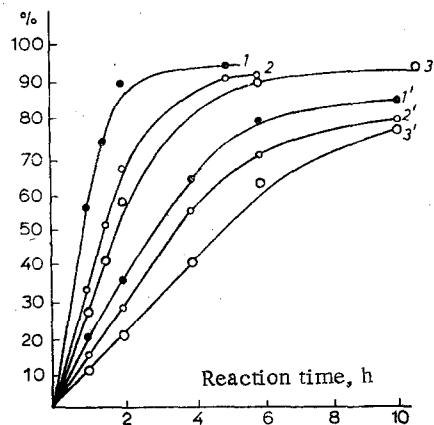


Fig. 1. Change in the rates of the reaction of thiols with 1,3-butadiene in the presence of ethylsulfuric acid: 1), 2), and 3) 5-chloro-2-thiophenethiol; 1'), 2'), and 3') 3-methyl-2-benzothiophenethiol; 1) and 1') in the presence of 20% ethylsulfuric acid; 2) and 2') in the presence of 10% ethylsulfuric acid; 3) and 3') without a catalyst.

thiols Ia-d to the dienes, which is undoubtedly promoted by the high polarity of the medium created by the thiols themselves. In this case one may assume the intermediate formation of protonated forms of the diene hydrocarbons with subsequent attack on them at the nucleophilic center by the sulfur atom.

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.

5-Chloro2-thiophenethiol (Ia). This compound was obtained by the method in [5] by the action of n-butyllithium and sulfur in absolute ether on 2-chlorothiophene with subsequent acidification [6]; the product had bp 54°C (2 mm) and n_D^{25} 1.6131.

2-Benzofuranthiol (Ib). This compound, with mp 95-96°C, was obtained in 93% yield by a method similar to that used to prepare thiol Ia. PMR spectrum: 3.57 (1H, s, SH), 6.66 (1H, s, benzofuran β -H), and 7.3 ppm (4H, m, aromatic). Found: C 64.5; H 3.9; S 21.4%. C_8H_6OS . Calculated: C 64.0; H 4.0; S 21.3%.

2-Benzothiophenethiol (Ic) [7]. This compound, with mp 45-46°C and bp 106-110°C (2 mm), was obtained in 81% yield by a method similar to that used to prepare thiol Ia.

3-Methyl-2-benzothiophenethiol (Id). This compound was obtained in 77% yield by a method similar to that used to prepare thiol Ia. PMR spectrum: 2.3 (3H, s, CH_3), 3.2 (1H, s, SH), and 7.0-7.8 ppm (4H, m, aromatic).

Reaction of Thiols with Dienes. A mixture of 40 mmole of the thiol, 9.8 mmole of ethylsulfuric acid (prepared by mixing 9.8 mmole of concentrated H_2SO_4 and 38 mmole of absolute ethanol) was cooled to 2-5°C in a stream of argon, and 5 ml (0.12 mole) of previously liquefied 1,3-butadiene (or 0.12 mole of cyclopentadiene) was added dropwise with stirring. After the mixture had been stirred in a weak stream of argon at -5° (at 0°C for cyclopentadiene) for the necessary time, it was dissolved in ether (50 ml), and the ether solution was washed with aqueous KOH solution and water and dried with $MgSO_4$. The ether was removed, and the residue was distilled and chromatographed with a column filled with silica gel (100/250 μ) ($d = 1$ cm, $l = 15$ cm) by elution with hexane.

2-Butenyl 2-Benzothienyl Sulfide (IIc). This compound 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 7.40 ppm (5H, m, aromatic). Found: C 63.8; H 5.2; S 30.0%. $C_{12}H_{12}S_2$. Calculated: C 65.4; H 5.4; S 29.1%.

2-Butenyl 2-Benzofuryl Sulfide (IId). This compound 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, m, benzofuran β -H), and 7.30 ppm (4H, m, aromatic). Found: C 71.4; H 6.0; S 15.6%. $C_{12}H_{12}OS$. Calculated: C 70.6; H 5.9; S 15.7%.

2-Butenyl 3-Methyl-2-benzothienyl Sulfide (IIe). This compound had bp 131-132°C (1 mm), n_D^{20} 1.6465, and d_4^{20} 1.1765. PMR spectrum: 1.55 (3H, d, allyl CH_3), 2.28 (3H, s, CH_3), 3.32 (2H, 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%. $C_{14}H_{14}S_2$. Calculated: C 66.7; H 6.0; S 27.4%.

5-Chloro-2-butenyl 2-Thienyl Sulfide (IIa). This compound had bp 127-128°C (4 mm), n_D^{20} 1.5930, and d_4^{20} 1.5990. PMR spectrum: 1.7 (3H, d, CH_3), 3.3 (2H, d, CH_2), 5.44 (2H, m, $CH = CH$), and 6.82 ppm (2H, m, aromatic). Found: C 47.3; H 4.4; Cl 17.7; S 30.2%. $C_8H_9ClS_2$. Calculated: C 46.9; H 4.4; Cl 17.4; S 31.3%.

Mixture of Cyclopenten-2-yl 2-Benzothienyl Sulfide and Cyclopenten-3-yl 2-Benzothienyl Sulfide. PMR spectrum: 2.0-2.4 (4H, m, CH_2CH_2), 2.4-2.8 (4H, m, CH_2CH_2), 3.5-4.0 (1H, m, CH), 4.0-4.4 (1H, m, CH), 4.6 (2H, s, $CH = CH$), 4.8 (2H, s, $CH = CH$), and 7.0-7.9 ppm (5H, m, aromatic).

Mixture of Cyclopenten-2-yl 2-Benzofuryl Sulfide and Cyclopenten-3-yl 2-Benzofuryl Sulfide. PMR spectrum: 1.8-2.3 (4H, m, CH_2CH_2), 2.3-2.8 (4H, m, CH_2 ; CH_2), 3.6-4.4 (2H, m, CH), 5.5 (2H, s, $CH = CCH$), 5.7 (2H, s, $CH = CH$), 6.6 (1H, s, benzofuran β -H), and 6.9-7.5 ppm (4H, m, aromatic).

Mixture of Cyclopenten-2-yl 5-Chloro-2-thienyl Sulfide and Cyclopenten-3-yl 2-Benzothienyl Sulfide. PMR spectrum: 2.1-2.6 (4H, m, CH_2CH_2), 2.5-3.0 (4H, m, CH_2CH_2), 3.4-3.9 (1H, m, CH), 3.9-4.3 (1H, m, CH), 5.6-6.1 (4H, m, $CH = CH$), and 6.7-7.4 ppm (4H, m, aromatic).

Mixture of Cyclopenten-2-yl 3-Methyl-2-benzothienyl Sulfide and Cyclopenten-3-yl 3-Methyl-2-benzothienyl Sulfide. PMR spectrum: 1.9-2.3 (4H, m, CH_2CH_2), 2.4-3.0 (4H, m, CH_2 ; CH_2), 2.4 (3H, s, CH_3), 3.5-3.9 (1H, m, CH), 3.9-4.3 (1H, m, CH), 5.6-6.1 (2H, m, $CH = CH$), and 7.4 ppm (4H, m, aromatic).

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SIGMATROPIC REARRANGEMENTS OF ALKENYL BENZOFURYL
AND BENZOTHIENYL SULFIDES

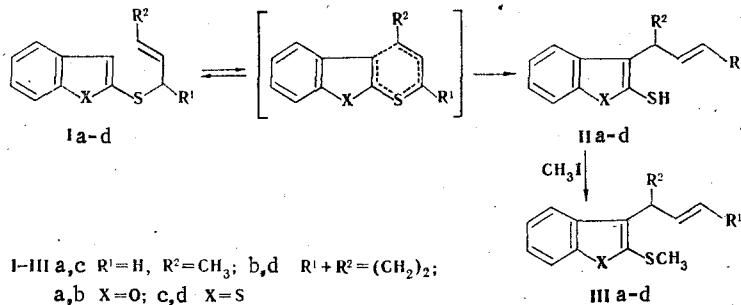
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The thio Claisen rearrangement of 2-butenyl 2-benzofuryl sulfide, cyclopenten-2-yl 2-benzofuryl sulfide, 2-butenyl 2-benzothienyl sulfide, and cyclopenten-2-yl 2-benzothienyl sulfide was investigated. The rates, energies and entropies of activation 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 furanethiols [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 benzothiophene-thiols, 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 and without a solvent, they undergo 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, cc 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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