

FUNCTIONAL DERIVATIVES OF THIOPHENE

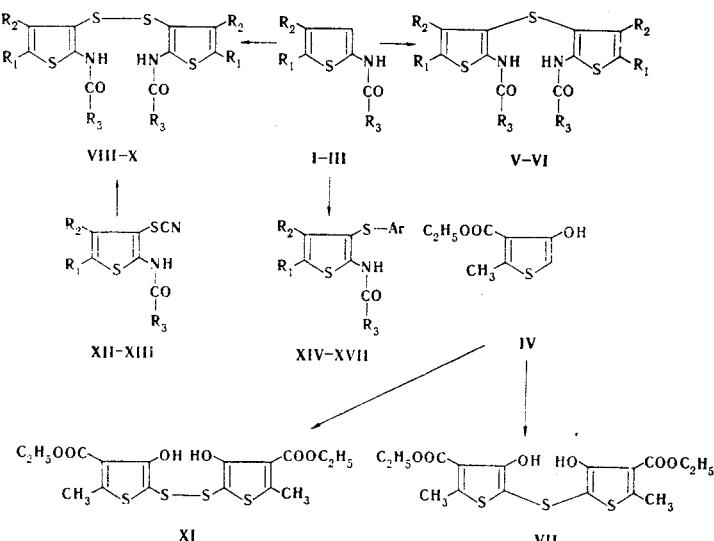
XII.* SYNTHESIS OF DITHIENYL SULFIDES, DITHIENYL DISULFIDES, AND ARYL THIENYL SULFIDES

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A method is proposed for the synthesis of dithienyl sulfides and dithienyl disulfides containing functional substituents in the ortho position with respect to the sulfide sulfur atom. Aryl 3-thienyl sulfides were obtained by reaction of α -acylaminothiophene derivatives with arenesulfenyl chlorides.

Dithienyl sulfides and dithienyl disulfides containing functional substituents in the ortho position with respect to the sulfide sulfur atom were previously unknown. We were able to obtain some of them by reaction of α -acylaminothiophenes (I-III) [2] and 2-methyl-3-carbethoxy-4-hydroxythiophene (IV) [3] with sulfur monochloride or dichloride. The reaction is carried out by heating in inert solvents without any catalyst. Dithienyl sulfides and dithienyl disulfides (V-XI) were obtained in 63-96% yields [4, 5]. It is known that thiocyanato derivatives of the aromatic series are easily converted to diaryl disulfides by the action of bases. We have found that substituted 3-thiocyanatothiophenes (XII, XIII) [6] also readily form dithienyl disulfides VIII-IX on heating in alcohol in the presence of piperidine.



I, V, VIII, XII, XIV, $R_1=R_2=CH_3$, $R_3=C_6H_5$; II, VI, IX, XIII, XVI, XVII, $R_1R_2=(CH_2)_4$, $R_3=C_6H_5$; III, X, XV, $R_1R_2=(CH_2)_4$, $R_3=CH_3$; XIV, XV, $Ar=2-NO_2-4-BrC_6H_5$; XVI, $Ar=2,4-(NO_2)_2C_6H_3$; XVII, $Ar=p-CH_3C_6H_4$

*See [1] for communication XI.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C*	Empirical formula	Found, %				Calc., %				Yield, %
			C	H	N	S	C	H	N	S	
V	251-252	C ₂₄ H ₂₄ N ₂ O ₂ S ₃	63.5	5.1	5.7	19.4	63.4	4.9	5.7	19.5	94
VI	234.5-236	C ₂₅ H ₂₆ N ₂ O ₂ S ₃	66.3	5.1	5.1	17.6	66.1	5.2	5.1	17.6	96
VII	159-161.5	C ₁₆ H ₁₈ O ₄ S ₃	47.7	4.4	—	24.1	47.7	4.5	—	23.9	74.5
VIII	207.5-208.5	C ₂₆ H ₂₄ N ₂ O ₂ S ₄	59.4	4.6	5.3	24.7	59.3	4.6	5.3	24.7	68.5
IX	187.5-188.5	C ₂₆ H ₂₈ N ₂ O ₂ S ₄	62.6	4.9	4.7	22.3	62.5	4.9	4.9	22.3	75
X	200.5-201.5	C ₂₇ H ₂₄ N ₂ O ₂ S ₄	53.4	5.4	6.1	28.3	53.1	5.3	5.8	28.3	85
XI	117-118	C ₁₆ H ₁₈ O ₆ S ₄	44.3	4.1	—	29.6	44.2	4.2	—	29.5	63.6
XIV	218.5-219.5	C ₁₉ H ₁₆ N ₂ O ₂ S ₂ Br	—	—	6.2	13.8	—	—	6.0	13.8	50
XV	186-187	C ₁₆ H ₁₅ N ₂ O ₂ S ₂ Br	45.0	3.6	6.5	15.0	45.0	3.5	6.5	15.0	49.9
XVI	235-236	C ₂₁ H ₁₇ N ₃ O ₅ S ₂	—	—	9.2	14.1	—	—	9.2	14.1	67
XVII	148-149	C ₂₂ H ₂₁ NOS ₂	—	—	3.6	16.9	—	—	3.7	16.9	75

*The compounds were recrystallized: V, VI, VII, XIV, and XVI from dioxane, VIII-XI from acetone, XV from methanol, and XVII from alcohol.

Aryl 2-thienyl sulfides are usually obtained by reaction of 2- and 3-methyl thiophenes with 2,4-dinitrobenzenesulfenyl chloride in the presence of catalysts [7]. In the case of 3-hydroxythiophene derivatives, owing to their high reactivities, the reaction with arenesulfenyl chlorides proceeds under mild conditions without a catalyst [3]. We have found that α -acylaminothiophenes (I-III) also react readily with arenesulfenyl chlorides in the absence of a catalyst to give aryl 3-thienyl sulfides (XIV-XVII) in high yields [8]. The structures of the compounds obtained were confirmed by their PMR spectra. The singlet at 6.38 ppm that corresponds to the β proton of starting thiophenes I-III is absent in the spectra of V, VI, VIII-X, and XIV-XVII, and the spectra of VII-XI do not contain the signal of an α proton at 6.1 ppm that was observed in the spectrum of starting thiophene IV.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a JEOL-4H 100 spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard.

Dithienyl Sulfides (V-VII). A 5-mmole sample of sulfur dichloride was added to a solution of 0.01 mole of I or II in absolute benzene*, and the mixture was refluxed for 1 h, after which the solvent was removed by distillation. Data on V-VII are presented in Table 1.

Dithienyl Sulfides (VIII-XI). A 5-mmole sample of sulfur monochloride was added to a solution of 0.01 mole of I-III in absolute benzene*, and the mixture was refluxed for 30 min, after which the solvent was removed by distillation. Data on VIII-XI are presented in Table 1.

B) A 0.5-ml sample of piperidine was added to a solution of 4.3 mmole of XII or XIII in a mixture of 45 ml of alcohol and 15 ml of acetone, after which the mixture was refluxed for 1.5 h. It was then concentrated to half its original volume, the concentrated solution was cooled, and the resulting crystals were removed by filtration. Dithienyl sulfides VIII and IX were obtained in 40% yields. No melting-point depressions were observed for samples of VIII and IX obtained by methods A and B.

Aryl 3-Thienyl Sulfides (XIV-XVII). A 0.01-mole sample of arenesulfenyl chloride was added to a solution of 0.1 mole of I-III in 30 ml of dry dioxane, after which the mixture was heated at 90-100° for 30 min. It was then cooled, and the resulting precipitate was removed by filtration. Data on XIV-XVII are presented in Table 1.

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*Reaction IV took place in ether.

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