5-Phenyl-3,6-dihydro-1,4-diazepino[6,5-b]benzofuran-2(1H)-one (XII). A mixture of 3 g (0.01 mole) of benzofuran XI and 1.4 g (0.01 mole) of urotropin in 50 ml of absolute alcohol was refluxed for 10 h, after which it was cooled and the resulting precipitate was removed by filtration to give 1.5 g of XII. The solvent was removed from the mother liquor by distillation to give another 0.5 g of product with mp 255° (dec., from alcohol). Found: C 73.8; H 4.7%. $C_{17}H_{12}N_2O_2$. Calculated: C 73.9; H 4.3%. IR spectrum, cm^{-1}: 1685 (C=O) and 3080 (N–H). PMR spectrum, ppm: 4.83 (doublet, CH_2) and 7.6-8.0 (aromatic H).

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ARYL 2-THIENYL SULFIDES AND ARYL 2-THIENYL SULFONES

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UDC 547.569.2+547.544.3+547.732

A method was developed for the synthesis of the previously unknown aryl 2-thienyl sulfides; the method is based on the reaction of 2-chlorothiophene and its derivatives with thiophenols in the gas phase at 450-500°C. The synthesized sulfides were oxidized to the corresponding aryl 2-thienyl sulfones, which were also previously unknown. 2,5-Dichlorothiophene reacts with excess thiophenol to give 2,5-bis(phenylthio)thiophene, which is oxidized to the corresponding disulfone.

Up until now, aryl thienyl sulfides have been unknown. We have developed a simple method for the synthesis of aryl 2-thienyl sulfides based on the reaction of thiophenols with 2-chlorothiophene and its derivatives at 450-500°C in an inert gas atmosphere.

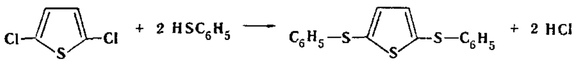
2-Chlorothiophene and its derivatives (I) react with thiophenols in a flow system (in an empty quartz tube) to give the corresponding aryl 2-thienyl sulfides (II) in 30-50% yields.

(1)

I II

$X = H, C_2H_5, Cl, C_6H_5S;\ R = C_6H_5, 4\text{-}CH_3C_6H_4, 1\text{-}C_{10}H_7$

2,5-Bis(phenylthio)thiophene (III) is simultaneously formed from 2,5-dichlorothiophene and thiophenol.



(2)

III

The yield of III increases as the ratio of RSH to RCl is raised (Table 1).

4-Thiocresol does not undergo reaction (2), and 1-thionaphthol does not react at all with 2,5-dichlorothiophene.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1322-1323, October, 1975. Original article submitted November 4, 1974.

TABLE 1. Aryl 2-Thienyl Sulfides (II and III)

X	R	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %		Calc., %		Yield, %
					found	calc.		S	Cl	S	Cl	
H	C_6H_5	123(3)	1,6250	1,2100	56,20	56,15	$C_{10}H_8S_2$	33,3	—	33,3	—	50,5
C_2H_5	C_6H_5	146(4)	1,6380	1,2149	65,08	65,32	$C_{12}H_{11}S_2$	29,1	—	29,4	—	43,0
Cl	C_6H_5	128(2)	1,6425	1,2890	63,50	62,96	$C_{10}H_7ClS_2$	28,0	13,5	28,0	13,4	44,0
H	4-$CH_3C_6H_4$	123(3)	—	—	—	—	$C_{11}H_{10}S_2$	31,0	—	31,1	—	35,0
Cl	4-$CH_3C_6H_4$	143(3)	—	—	—	—	$C_{11}H_9ClS_2$	26,3	14,6	26,2	14,7	38,1
H	1-$C_{10}H_7$	180(3)	—	—	—	—	$C_{14}H_{10}S_2$	26,2	—	26,3	—	42,5
C_6H_5S	C_6H_5	mp 48—49	—	—	—	—	$C_{16}H_{12}S_3$	32,0	—	32,0	—	20,4
C_6H_5S*	C_6H_5	mp 48—49	—	—	—	—		—	—	—	—	32,0

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* For an RCl to RSH ratio of 1 : 2.

TABLE 2. Aryl 2-Thienyl Sulfones (IV) .

X	R	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	S	C	H	S	
H	C_6H_5	119—120	$C_{10}H_8O_2S_2$	53,6	3,5	28,5	53,8	3,6	28.5	78,5
H	4-$CH_3C_6H_4$	113—114	$C_{11}H_{10}O_2S_2$	55,4	4,2	27,2	55,5	4,2	27,0	83,4
Cl	4-$CH_3C_6H_4$	81—82	$C_{11}H_9ClO_2S_2$*	—	—	23,7	—	—	23,5	80,5
H	1-$C_{10}H_8$	107—108	$C_{14}H_{11}O_2S_2$	61,4	4,2	23,1	61,2	4,0	23,3	82,0
$C_6H_5SO_2$	C_6H_5	129—130	$C_{16}H_{12}O_4S_3$	52,6	3,2	26,7	52,7	3,3	26,6	90,0

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* Found: Cl 12.9%. Calculated: Cl 12.9%.

Aryl 2-thienyl sulfides II and III are readily oxidized to the corresponding sulfones (IV) by refluxing with a sixfold excess of hydrogen peroxide in glacial acetic acid (Table 2).

The IR spectra of aryl 2-thienyl sulfides II and III contain the frequencies of deformation vibrations of the C—H bonds of benzene and thiophene rings (680-700 and 870 cm^{-1}), of stretching vibrations of aromatic-ring double bonds (1580 cm^{-1}), and of stretching vibrations of C—H bonds of benzene and thiophene rings (3050-3080 cm^{-1}). The band at 730 cm^{-1} can be ascribed to vibrations of the C—S bond. The IR spectra of sulfones IV contain two broad, intense bands at 1160 and 1320 cm^{-1}, which are absent in the spectra of II and III and correspond to stretching vibrations of S=O bonds.

EXPERIMENTAL

Sulfides II were formed in 30-50% yields based on converted I when an equimolar mixture of I and the appropriate thiol were passed through a heated (to 450-550°) empty quartz tube (655 mm long and 30 mm in diameter) in a stream of dry nitrogen (V = 3 liter/h) at 10 ml/h.

The physicochemical constants, results of analysis, and yields of the synthesized II and III, which were isolated by means of vacuum distillation, are presented in Table 1. Compound III was purified by recrystallization from ethanol—benzene (3 : 1). The sulfones were purified by recrystallization from ethanol. The physicochemical constants, results of microanalysis, and yields of sulfones IV are presented in Table 2.