SYNTHESIS OF DERIVATIVES OF FLUORENOTHIOPHENES

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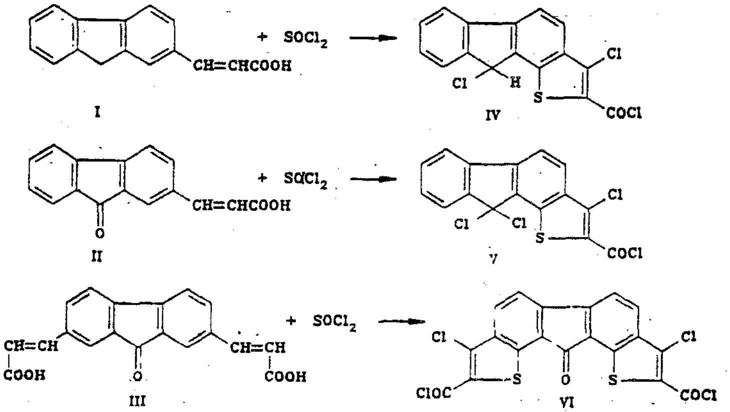
The synthesis of difficult-to-obtain derivatives of fluorenothiophenes was accomplished by cyclocondensation of substituted acrylic acids with thionyl chloride in the presence of triethylbenzylammonium chloride.

The cyclocondensation of substituted acrylic acids with thionyl chloride under the influence of triethylbenzylammonium chloride (TEBAC) leads to derivatives of benzo[b]-, naphtho[b]-, and phenanthro[b]thiophenes [1-3].

The aim of the present research was to investigate the applicability of this method for the synthesis of difficult-to-obtain arenothiophenes containing a naphthene ring. Such compounds have been detected in the high-boiling fractions of petroleum and petroleum residues [4]; in addition, they display high biological activity [5].

The known method for obtaining a derivative of 6-oxo-fluoreno[4,3-b]thiophene by condensation of p-tolyl 2-thienyl ketone with dimethyl succinate with subsequent two-step cyclization [5] is a multistep process and consists of the building of a condensed system onto the available thiophene ring, while the proposed method consists in the formation of a thiophene ring with the use of a prepared fluorene fragment.

3,10-Dichloro-2-chlorocarbonylfluoreno[1,2-b]thiophene (IV), 3,10,10-trichloro-2-chlorocarbonylfluoreno[1,2-b]thiophene (V), and 3,8-dichloro-2,9-dichlorocarbonyl-11-oxofluoreno-[1,2-b][8,7-b]dithiophene (VI) were obtained in reactions involving the cyclocondensation of β-substituted acrylic acids with the general formula R—CH=CH—COOH [I R = 2-fluorenyl-, II R = 9-oxo-2-fluorenyl-, III R = β,β'-(9-oxo-2,7-fluorenylene)] with thionyl chloride in the presence of equimolar amounts of TEBAC.



Cyclization in the 1 position of the fluorene and fluorenone structures is confirmed by data from the IR spectra: the bands of deformation vibrations of the isolated proton of an aromatic ring at 870 cm^{-1} vanish in the spectra of cyclization products IV-VI. The presence of absorption bands at 700-730 cm^{-1} constitutes evidence for the formation of a thiophene fragment. Transformation of the carbonyl absorption bands occurred: bands at 1740-1770 cm^{-1} (C=O in cyclic acid chlorides) appeared in place of bands at 1700-1725 cm^{-1} (C=O in acids). In addition to the general properties of the cyclocondensation presented above, distinctive features are characteristic for each of the cited reactions. Thus, in addition to the formation of a thiophene ring, chlorination of the active methylene group of fluorene occurs in the reaction of acid I with thionyl chloride. An analysis of the PMR spectra of

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	IR spectrum, ν, cm^{-1}	Found, %				Empirical formula	Yield, %				Yield, %
			C	H	Cl	S		C	H	Cl	S	
IV	174—175	1760, 810, 780, 720, 700	53,9	1,9	31,0	9,7	$C_{16}H_7Cl_3OS$	54,3	2,0	30,1	9,1	83
V	185—186	1770, 820, 780, 730, 710	49,0	1,5	36,4	8,8	$C_{16}H_6Cl_4OS$	49,5	1,6	36,0	8,3	68
VI	187—188	1740, 1700, 800, 730, 710	46,8	1,1	30,0	14,1	$C_{19}H_4Cl_4O_3S_2$	46,9	0,8	29,2	13,9	93

the starting compounds and the final products of the reactions shows that the singlet of methylene protons at 3.65 ppm is shifted to 4.02 ppm. The ratio of the integral intensities of the methylene protons of I and IV and the protons of the aromatic ring $H(CH_2)/H(Ar)$ changes from 2:7 to 1:6. These data constitute evidence that cyclization is accompanied by substitutive monochlorination of the methylene link.

The absorption band of the carbonyl group of the fluorene ring at 1690 cm^{-1} that is characteristic for starting acid II is absent in the IR spectrum of cyclization product V. According to the results of elemental analysis, four chlorine atoms are present in the molecule (Table 1). Structure V was assigned to the cyclization product on the basis of the data obtained. Chlorination of the oxo group of fluorenone is not unexpected, since it is known that the reaction of carbonyl compounds with thionyl chloride leads to the formation of gem-dichlorides [6, 7]. However, the keto group remains unchanged when substituted diacrylic acid III is treated with thionyl chloride under the same conditions; this is probably associated with the significant steric hindrance to its chlorination. The IR spectrum of fluorenodithiophene VI contains absorption bands of two types of carbonyl groups: 1740 (C=O in acid chlorides) and 1700 cm^{-1} (fluorenone C=O). The structures of the condensed thiophene derivative obtained (IV-VI) were proved by the IR and PMR spectra, and the compositions were confirmed by the results of elemental analysis (Table 1).

Thus the reaction of fluorenyl- and 9-oxofluorenylacrylic acids with thionyl chloride proceeds with the formation of fluoreno[b]thiophene derivatives in high overall yields and in one step from accessible acids.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 or $CDCl_3$ were recorded with a Tesla BS-487 spectrometer with hexamethyldisiloxane (HMDS) as the internal standard.

The characteristics of IV-VI are presented in Table 1.

3,10-Dichloro-2-chlorocarbonylfluoreno[1,2-b]thiophene (IV). A 15.5-g (0.13 mole) sample of thionyl chloride was added dropwise with stirring in the course of 20-30 min to a mixture of 4.7 g (0.05 mole) of acid I and 13.4 g (0.05 mole) of triethylbenzylammonium chloride (TEBAC), after which the reaction mixture was heated to 140°C and treated dropwise with 32.1 g (0.27 mole) of $SOCl_2$. It was then stirred at 140°C for 2 h, after which it was extracted with hot benzene (three 100-ml portions). The benzene extracts were washed with water, dried with $CaCl_2$, and concentrated to half the original volume. The concentrate was poured into hexane, and the liberated fluorenothiophene IV was removed by filtration.

3,10,10-Trichloro-2-chlorocarbonylfluoreno[1,2-b]thiophene (V). This compound was obtained from 10 g (0.04 mole) of acid II, 9.1 g (0.04 mole) of TEBAC, and 38 g (0.32 mole) of thionyl chloride as in the preparation of IV.

3,8-Dichloro-2,9-dichlorocarbonyl-11-oxofluoreno[1,2-b][8,7-b]-dithiophene (V). A 38-g (0.32 mole) sample of thionyl chloride was added dropwise to a mixture of 19.2 g (0.05 mole) of acid III and 27.3 g (0.12 mole) of TEBAC, and the mixture was heated to 130°C and treated dropwise with 208.4 g (0.64 mole) of $SOCl_2$ in the course of 80-90 min. The resulting mixture was maintained at 130°C for 2 h, after which the product was extracted with hot benzene.

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SULFUR-CONTAINING DERIVATIVES OF FIVE-MEMBERED CYCLIC SULFONES.

1. SYNTHESIS OF SALTS OF ISOTHIOUREIDOTHIOLENE 1,1-DIOXIDES

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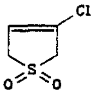
543.422.25

Salts of isothioureidothiolene 1,1-dioxides with different positions of the ring double bond were obtained by the reaction of thiourea with halo derivatives of thiolene 1,1-dioxides.

Sulfur-containing derivatives of five-membered cyclic sulfones are of considerably practical interest: light stabilizers for polymers [1], antioxidants [2], and emulsifiers [3] have been detected among them, and the use of these compounds as biologically active substances has been patented [4-6]. Substituted 3-thiolene 1,1-dioxides are also used to obtain difficult-to-obtain functionally substituted dienes that are used in syntheses of heterocyclic analogs of anthracyclines [7].

We have previously reported the preparation of 3-methyl-5-isothioureido-2-thiolene 1,1-dioxide hydrobromide [8]; however, other salts of isothioureidothiolene 1,1-dioxides were unknown. We studied the possibility of obtaining such salts by the reaction of halo derivatives of thiolene 1,1-dioxides I-V with thiourea.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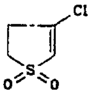
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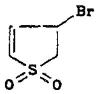
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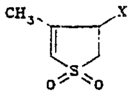
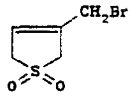

IVa, b


V

IV a X=Br; b X=Cl

It was established that 3-chloro-3-thiolene 1,1-dioxide (I) does not undergo this reaction; this can be explained by the low activity of the vinyl halogen atom in nucleophilic substitution reactions and the impossibility of isomerization of the double bond from the 3 position to the 2 position of the thiolene 1,1-dioxide ring under the influence of the weakly basic thiourea. In contrast to sulfone I, the presence of an electron-acceptor SO_2 group in the α position with respect to the double bond in 3-chloro-2-thiolene 1,1-dioxide (II) increases the activity of the vinyl chlorine atom, as a result of which sulfone II gives 2-isothioureido-2-thiolene 1,1-dioxide hydrochloride (VI) when it is heated with thiourea

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*Deceased.

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