SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF ISOMERIC NAPHTHO[b]THIOPHENES

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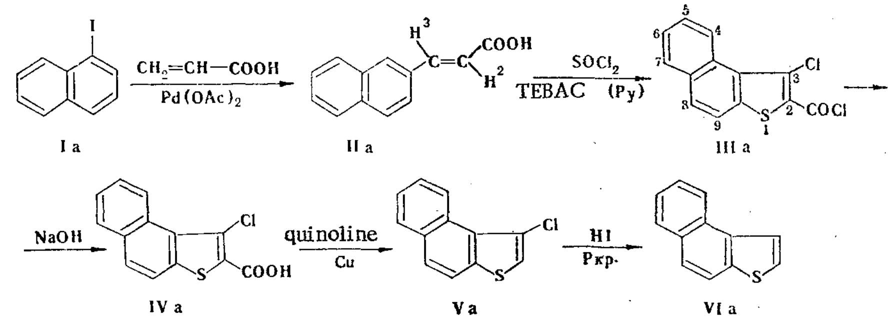
A new method for the preparation of naphtho[1,2-b]- and naphtho [2,1-b]thiophene structures by arylation of acrylic acid with α- and β-iodonaphthalene and subsequent oxidation of the resulting trans-naphthylacrylic acids with thionyl chloride in the presence of triethylbenzylammonium chloride is proposed.

Research on polycondensed heterocyclic compounds that contain a thiophene ring, particularly naphtho[b]thiophenes, as components of the heavy fractions of petroleum and petroleum residues has made it necessary to develop a convenient preparative method for their synthesis. Of the known methods for the preparation of isomeric naphtho[b]thiophenes, the reduction of the corresponding 3-hydroxy derivatives [1] and the cyclization of naphthylthioacetaldehyde dialkylacetals [2] are noteworthy; however, both methods entail the use of starting reagents that are difficult to obtain. We recently [3] proposed a new method for the synthesis of benzo[b]thiophene derivatives on the basis of accessible aromatic iodo derivatives; this method consists in arylation of acrylic acid under the influence of catalytic amounts of palladium acetate and subsequent oxidation of the resulting β-substituted acrylic acids with thionyl chloride.

The aim of the present research was to study the applicability of this method for the synthesis of naphtho[b]thiophene structures.

Arylation of acrylic acid with α- and β-iodonaphthalene (Ia, b) in the presence of catalytic amounts of palladium acetate gave the corresponding β-naphthylacrylic acids (IIa, b) in high yields (Table 1). The absorption bands in the IR spectra of acids IIa, b at 930-960 cm^{-1}, which correspond to C-H vibrations in trans-arylethylenes, and the spin-spin coupling constants (SSCC) of the olefinic protons (J_{23} = 16 Hz) [4] confirm the trans configuration of the acids obtained.



Studies of the oxidation of acid IIa with thionyl chloride with the use of pyridine as a catalyst showed that a significant part of acid IIa is converted to the acid chloride (Table 2). The percentage of 3-chlorocarbonylnaphtho[2,1-b]thiophene (IIIa) in the reaction mixture increased when the amount of pyridine was increased from catalytic quantities to an equimolar amount with respect to acid IIa, and the chloride of the starting acid was not detected; however, the preparative yield of IIIa did not exceed 32%. An increase in the reaction temperature of 180°C was accompanied by a sharp decrease in the yield of desired product IIIa.

In [3] we showed that replacement of pyridine by triethylbenzylammonium chloride (TEBAC) in the oxidation of arylacrylic acids led to a significant increase in the yields of benzo[b]thiophene derivatives. The use of catalytic amounts of TEBAC in the cyclization of acid IIa also proved to be ineffective, since a significant amount of the starting acid remains in the

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	IR spectrum, ν, cm⁻¹	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Cl	S		C	H	Cl	S	
IIa	211—212[a]	1680 (C=O), 1600 (C=C), 960 (trans-arylethylene C—H) 750 (four adj. H)					$C_{13}H_{10}O_2$					92
IIIa	147—149	1750 (C=O), 808 (two adj. H), 745 (four adj. H) 740 (C—S)	55,4	2,4	25,0	11,4	$C_{13}H_6Cl_2OS$	55,5	2,1	25,3	11,4	51
IVa	243—245	1675 (C=O), 800 (two adj. H), 770 (two adj. H), 730 (thiophene C—S)					$C_{13}H_7ClO_2S$					98
IVa[b]	148—150	1730 (C=O), 1250 (COC), 800 (two adj. H), 770 (four adj. H), 730 (thiophene C—S)	60,7	3,5	12,6	11,5	$C_{14}H_9ClO_2S$	60,7	3,2	12,8	11,6	
Va	63—64	810 (two adj. H), 765 (four adj. H), 725 (thiophene C—S)	66,1	3,5	16,2	15,0	$C_{13}H_7ClS$	65,9	3,2	16,2	14,6	54
VIa	108—110[c]	810 (two adj. H), 765 (four adj. H), 720 (thiophene C—S)					$C_{12}H_8S$					50
VIII	111—112	970 (trans-arylethylene C—H), 760, 710 (five adj. H)	77,8	5,5		17,3	$C_{12}H_{10}S$	77,4	5,4		17,2	20
IIb	203—205[d]	1680 (C=O), 1620 (C=C), 930 (trans-arylethylene C—H), 870 (one isolated H)					$C_{13}H_{10}O_2$					80
IIIb	168—169	1770 (C=O), 815 (two adj. H), 760 (four adj. H), 720 (thiophene C—S)	54,9	2,1	25,2	10,9	$C_{13}H_6Cl_2OS$	55,5	2,1	25,3	11,4	62
IVb	296—298	1680 (C=O), 813 (two adj. H), 750 (four adj. H), 720 (thiophene C—S)	59,2	2,4	13,5	11,9	$C_{13}H_7ClO_2S$	59,4	2,7	13,5	12,2	98
Vb	82—84	820 (two adj. H), 750 (four adj. H)	66,1	3,5	16,0	14,6	$C_{13}H_7ClS$	65,9	3,2	16,2	14,6	90
VIb	26—27[e]	820 (two adj. H), 760 (four adj. H), 720 (thiophene C—S)					$C_{12}H_8S$					70

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[a] This compound had mp 211-212°C [5]. [b] The methyl ester of acid IVa; the ester was obtained by esterification with methanol. [c] This compound had mp 108-109°C [1]. [d] This compound had mp 203°C [5]. [e] This compound had mp 27-28°C [1].

TABLE 2. Compositions of the Reaction Mixtures in the Oxidation of Isomeric Naphthylacrylic Acids IIa, b with Thionyl Chloride (140°C, 2 H)

Starting acid	Pyridine: starting acid, mole/mole	TEBAC: starting acid, mole/mole	Amounts in the reaction mixture,[a] %			Yield of desired product,[b] %
			starting acid	sum of the side product	desired product	
IIa	0,125 : 1		80	12	8	
IIa	1 : 1		0	60	40	32
IIa		0,125 : 1	30	45	25	
IIa		1 : 1	0	45	55	51
IIa		1 : 1[c]	0	12	88	17
IIb	1 : 1		0	48	52	
IIb		1 : 1	0	11	89	62

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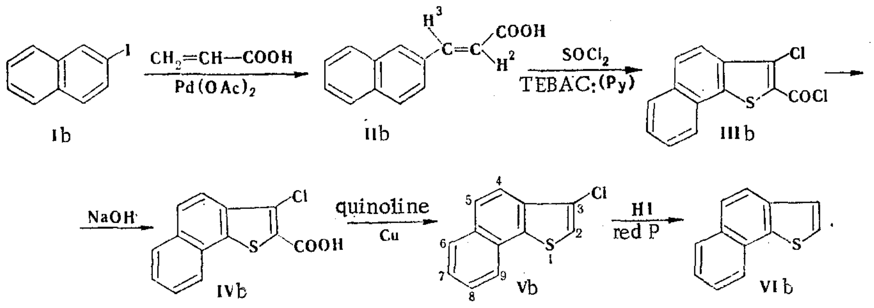
[a] The composition of the reaction mixture was analyzed by GLC after esterification with methanol. [b] The preparative yields are given. [c] At 180°C.

reaction mixture in the form of the acid chloride, side products predominate, and the amount of the desired naphthothiophene IIIa does not exceed 25% (Table 2). Acid chloride IIIa predominates in the reaction products when the reaction is carried out in the presence of equimolar amounts of TEBAC with respect to starting acid IIa. The percentage of IIIa increases markedly when the reaction temperature is increased from 140°C to 180°C; however, the preparative yield is only 17%, and the formation of a coal-like reaction product is observed in this case. An increase in the amount of TEBAC to 3 moles per mole of acid IIa does not lead to an improvement in the results. Thus the optimum conditions for the oxidation of acid IIa are equimolar ratios of acid IIa and TEBAC, a reaction temperature of 140°C, and a reaction time of 2 h. The composition and structure of naphthothiophene IIIa were confirmed by the results of elementary analysis and data from the PMR and IR spectra (Table 1). The PMR spectrum of IIIa contains three groups of signals: a multiplet at 7.57-7.73 ppm (two protons), which should be assigned to the signals of 5-H and 6-H protons, since the latter should show up at strong field as external protons with respect to the fusion nodes in the naphthalene ring [4]; a multplet at 7.79-8.12 ppm (three protons), which corresponds to the 7-H, 8-H, and 9-H protons; a doublet of doublets of the 4-H proton, which is an internal proton with respect to all of the fusion nodes of the rings [4], at very weak field at 9.38 ppm (one proton). Thus the PMR spectral data show that a thiophene ring is formed in the β position of the naphthalene ring.

The synthesis of the isomeric naphtho[1,2-b]thiophene structure was realized by a similar method, viz., by oxidation of trans-β-(β-naphthyl)acrylic acid IIb with thionyl chloride under the influence of TEBAC. For comparison, we carried out the oxidation of acid IIb in the presence of pyridine. It follows from the data in Table 2 that the percentage of the desired product in the reaction mixture when TEBAC is used considerably exceeds the percentage obtained in the case of pyridine.



The direction of cyclization (in the α position of the naphthalene ring) is confirmed by the disappearance in the IR spectrum of acid chloride IIIb of the band of the vibrations of an isolated α proton of the naphthalene ring at 870 cm^{-1}. In addition, the physical constants of naphthothiophene VIb obtained from IIIb by successive transformations are in agreement with the data for naphtho[1,2-b]thiophene [1].

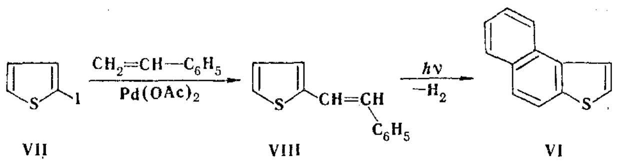
The results obtained in the oxidation of isomeric acids IIa, b showed that acid IIa has lower activity: This may be associated with the participation of the less reactive β position of the naphthalene ring in the reaction.

The chemical properties of the derivatives of the isomeric naphtho[b]thiophenes obtained were studied in accordance with the scheme presented above. The saponification of acid chlorides IIIa, b to give the corresponding 3-chloro-2-carboxy derivatives IVa, b proceeds smoothly in the case of treatment with alcoholic alkali.

The decarboxylation of acid IVb in refluxing quinoline in the presence of copper leads to 3-chloronaphtho[1,2-b]thiophene (Vb), the subsequent dechlorination of which to give naphtho[1,2-b]thiophene (VIb) by means of constantly boiling hydriodic acid with the addition of red phosphorus is accompanied by slight desulfuration of the thiophene ring.

Considerable desulfuration of the thiophene ring is observed in the decarboxylation of acid IVa to give 3-chloronaphtho[2,1-b]thiophene (Va) under the same conditions; this may explain the relatively low yield of chloride Va (Table 1). Similar desulfuration, but to a smaller extent, occurs in the dehalogenation of chloride Va to give unsubstituted naphtho[2,1-b]thiophene (VIa).

The compositions and structures of IIIa,b-VIa,b were confirmed by the results of elementary analysis and IR spectroscopic data (Table 1). The naphtho[2,1-b]thiophene structure was additionally confirmed by alternative synthesis:



The photochemical cyclization of 2-α-styrylthiophene (VIII) was carried out by the method in [6]. The IR spectra of the product of photochemical cyclization and the product obtained by dechlorination of Va are identical, and the melting points of both samples are in agreement with the literature value for naphtho[2,1-b]thiophene.

Thus the method of synthesis based on the successive arylation of acrylic acids in the presence of catalytic amounts of palladium acetate and oxidation of the resulting substituted acrylic acids with thionyl chloride is applicable to the preparation of isomeric naphtho[b]thiophenes. By replacing pyridine by TEBAC in the oxidation reaction we were able to substantially increase the yields of the desired products.

A study of the chemical properties in series of isomeric naphtho[b]thiophenes and benzo[b]thiophenes [3] showed that the reactivities and thermal stabilities of arenothiophene derivatives depend both on the number of condensed rings and on their type of fusion.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 were recorded with a Tesla BS 487 spectrometer with hexamethyldisiloxane as the internal standard. Analysis of the reaction mixtures by gas–liquid chromatography (GLC) was carried out with an LKhM-8MD chromatograph with a thermal conductivity conductor; the carrier gas was helium, the column (2 m × 3 mm) was packed with 5% SE-30 on Chromaton N-AW as the stationary phase, and the analysis was performed under isothermal conditions.

Arylation of Butyl Acrylate with Iodonaphthalenes Ia, b. A mixture of 25.4 g (0.1 mole) of α-iodonaphthalene (or β-iodonaphthalene), 16 g (0.125 mole) of butyl acrylate, 18.8 g (0.1 mole) of tributylamine, and 0.224 g (1 mmole) of palladium acetate was heated with stirring on a boiling-water bath for 16 h, after which it was diluted with water, and the organic layer was separated, and the aqueous layer was extracted with ether. After removal of the solvent, the combined organic layers were hydrolyzed with 200 ml of 20% aqueous sodium hydroxide solution by refluxing for 2 h. The organic mixtures were extracted with ether, and the alkaline solution was treated with dilute hydrochloric acid. The precipitated acid was removed by filtration, washed with water, dried, and recrystallized from benzene. The yields of acids IIa, b and their characteristics are presented in Table 1.

Methyl β-(α-naphthyl)acrylate had mp 147-149°C. PMR spectrum: 3.65 (3H, s, OCH_3), 6.30 (1H, d, 3-H), 8.34 (1H, d, 2-H, J_{23} = 16 Hz), and 7.23-8.10 ppm (7H, m, naphthalene ring protons). Methyl β-(β-naphthyl)acrylate had mp 90-91°C. PMR spectrum: 3.63 (3H, s, OCH_3), 6.33 (1H, d, 3-H), 7.70 (1H, d, 2-H, J_{23} = 16 Hz), and 7.25-7.88 ppm (7H, m, naphthalene ring protons).

Oxidation of Acids IIa, b with Thionyl Chloride. One third of a 96-g (0.8 mole) sample of thionyl chloride was added to a mixture of 19.8 g (0.1 mole) of acid IIa, b and 22.7 g (0.1 mole) of TEBAC, the mixture was heated to 140°C, and the remaining thionyl chloride was added dropwise at such a rate that the temperature of the reaction mixture did not decrease appreciably. Stirring was then continued for 2 h, after which the mixture was cooled, and products IIIa, b were extracted with boiling benzene and reprecipitated with hexane. The characteristics of IIIa, b are given in Table 1.

Hydrolysis of 3-Chloro-2-chlorocarbonylnaphtho[b]thiophenes IIa, b. Mixtures of 14 g (0.05 mole) of IIIa, b, 200 ml of ethanol, and 100 ml of 30% aqueous sodium hydroxide were refluxed for 5-6 h, after which the precipitates were removed by filtration and dissolved in water. The solutions were treated with hydrochloric acid, and the precipitated 3-chloro-2-carboxynaphtho[b]thiophenes IVa, b were removed by filtration, washed with water, and dried (Table 1).

Decarboxylation of 3-Chloro-2-carboxynaphtho[b]thiophenes IVa, b. Mixtures of 13.1 g (0.05 mole) of acids IVa, b, 100 ml of quinoline, and 4 g of powdered copper were refluxed for 5 h, after which the reaction solutions were decanted, acidified with hydrochloric acid, and extracted with pentane. The extracts were washed with water and dried over calcium chloride, and the solvent was removed to give 3-chloronaphtho[b]thiophenes Va, b. PMR spectrum of Va: 7.25 (1H, s, thiophene ring 2-H), 7.32-7.85 (5H, group of multiplets, naphthalene ring protons and 4-H), and 9.26 ppm (1H, dd, 4-H). PMR spectrum of Vb: 7.15 (1H, s, thiophene ring 2-H) and 7.30-8.00 ppm (6H, group of multiplets, naphthalene ring protons).

Reductive Dehalogenation of 3-Chloronaphtho[b]thiophenes. A 50-ml sample of 57% hydriodic acid was added to 4.6 g (0.025 mole) of chloride Va or Vb and 1.18 g (0.038 mole) of red phosphorus, and the mixture was refluxed for 2 h. It was then cooled and diluted with water, and the aqueous mixture was extracted with pentane. The extract was washed successively with water, bisulfite solution, and water and dried over calcium chloride. Naphtho[2,1-b]thiophene (VIa) was recrystallized from cyclohexane, while naphtho[1,2-b]thiophene (VIb) was recrystallized from methanol. Data on VIa, b are presented in Table 1.

2-α-Styrylthiophene (VIII). A 6.5-g (0.063 mole) sample of styrene, 9.25 g (0.05 mole) of tributylamine, 0.11 g (5 mmole) of palladium acetate, and 0.26 g (1 mmole) of triphenylphosphine were added to 10.5 g (0.05 mole) of α-iodothiophene, and the mixture was stirred at 100°C for 6 h. It was then cooled and treated with dilute hydrochloric acid, and the mixture was extracted with ether. Workup gave 1.8 g (20%) of VIII with mp 111-112°C (mp 112-113°c [7]).

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