amine hydrochloride, 10 ml of ethanol, and two drops of concentrated HCl was refluxed for 8 h, after which it was concentrated to half its original volume, and the product was precipitated by the addition of hot acetone.

The characteristics of the compounds synthesized for the first time are presented in Table 2.

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SYNTHESIS AND SOME TRANSFORMATIONS OF BENZO[b]THIOPHENE DERIVATIVES

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A number of 3-chloro-2-chlorocarbonylbenzo[b]thiophenes with alkyl substituents in various positions of the benzene ring were synthesized by arylation of acrylic acid with the corresponding alkyl-substituted iodobenzenes under the influence of catalytic amounts of palladium acetate and subsequent oxidation of the resulting arylacrylic acids with thionyl chloride. Replacement of the pyridine added in the oxidation reaction by triethylbenzylammonium chloride led to substantial increases in the yields of the desired products. The possibility of conversion of the resulting benzo[b]thiophene derivatives to thiophene ring-unsubstituted benzo[b]thiophenes was shown in the case of 3-chloro-2-chlorocarbonylbenzo[b]thiophene as a result of successive saponification of the 2-chlorocarbonyl group, decarboxylation, and dechlorination.

The research on condensed heteroaromatic compounds that contain a thiophene ring has thus far been quite limited in connection with the synthetic difficulties and the complexity involved in the study of the behavior of such compounds. A knowledge of the principal chemical properties of such structures is necessary for the development of effective methods for the isolation of the sulfur-containing compounds of petroleum and the selection of efficient methods for their chemical refining and skillful utilization. In addition, condensed sulfurous heteroaromatic compounds , particularly benzo[b]thiophenes, may be of practical interest as standard compounds for the study of the composition of the sulfurous components of the heavy fractions of petroleum and petroleum residues.

The known methods for the preparation of benzo[b]thiophenes [1] have a number of disadvantages, the chief of which are the use of difficult-to-obtain starting reagents and the overall low yields of the desired products.

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The aim of the present research was to develop a convenient preparative method for the production of benzo[b]thiophenes with the aid of readily accessible starting substances.

A number of papers dealing with the study of the oxidation with thionyl chloride of phenylpropionic acid and its methyl ester [2], trans-β-arylacrylic and phenylpropionic acids, and phenylpropanones [3, 4], which proceeds with the formation of benzo[b]thiophene derivatives, have been published in recent years. In our opinion, the most promising method for the synthesis of arenothiophenes is oxidation of trans-β-arylacrylic acids with the general formula ArCH=CHCOOH (II).

The possibilities of this method are determined both by the accessibility of starting acids II and by the existence of a convenient preparative method for their production. In this connection, our attention was drawn to the arylation of olefins with aryl halides in the presence of catalytic amounts of compounds of divalent palladium, which is currently being developed by a number of researchers [5-8]. The fundamental possibility of the use of acrylic acid as the starting olefin in this reaction and the preparation from it of trans-β-phenylacrylic acid was demonstrated in [5]. The advantage of the indicated reaction may be its universality for the synthesis of acids II from accessible reagents. The combination of arylation of acrylic acid with aryl halides with subsequent oxidation of the resulting acids II with thionyl chloride opens up extensive synthetic possibilities for the production of derivatives of arenothiophenes and may become a new convenient method for their synthesis.

To verify the possibility of the realization of the proposed method we carried out the arylation of methyl acrylate with various aryl iodides under the influence of catalytic amounts of palladium acetate in conformity with the recommendations presented in [6]. The use of methyl acrylate in place of acrylic acid made it possible to monitor the course of the reaction by gas-liquid chromatography (GLC). At the end of the reaction, the resulting methyl esters of acids IIa-e were converted to the corresponding acids by hydrolysis with 25% aqueous sodium hydroxide solution.

It follows from Table 1 that acids IIa-e are obtained in good yields in all cases. The IR spectra of these compounds contain absorption bands at 960-970 cm^{-1}, which correspond to the out-of-plane C–H deformation vibrations in trans-arylethylenes, at 1680-1690 cm^{-1}, which correspond to C=O stretching vibrations, and at 1600-1635 cm^{-1}, which are characteristic for the stretching vibrations of the C=C bond and the aromatic ring. The positions of the substituents in the benzene ring are confirmed by the presence in the IR spectra of the absorption bands of the corresponding out-of-plane deformation vibrations (Table 1). The spin–spin coupling constants of the olefinic protons (J = 15-16 Hz) confirm the trans configuration of acids IIa-e.

The position of the substituent in the starting aryl iodide has a substantial effect on the yields of the reaction products: The yields of IIb, c decrease when the substituent is present in the ortho and meta positions. The yields can be increased when the reaction time is increased. Thus the yield of acid IIb reaches 72% when the process is carried out for 14 h (as compared with 66% after 8 h).

The oxidation of the resulting trans-β-acrylic acids with thionyl chloride was carried out in the presence of catalytic amounts of pyridine under the conditions presented in [3]. A study of the composition of the reaction mixture in the oxidation of phenylacrylic acid (IIa) showed that a significant amount of starting acid (up to 34%) does not undergo cyclization but remains in the reaction mixture in the form of the acid chloride. Analytical monitoring of the course of the reaction was accomplished by GLC of the reaction mixture after its esterification. An increase in the amount of thionyl chloride from 3.5 moles to 8 moles per mole of acid IIa increased the fraction of desired product IIIa and decreased the fraction of the chloride of the starting acid in the reaction mixture. Both increasing and decreasing the reaction temperature were found to be undesirable, since the yield of benzothiophene IIIa decreased. The oxidation of acids IIa-e was therefore carried out with an eightfold excess of thionyl chloride at 140°C. It follows from Table 1 that benzo[b]thiophene derivatives IIIb-e, which have alkyl substituents in the benzene ring, were obtained in low yields.

In this connection, we investigated replacement of pyridine in the oxidation reaction by other additives. Better results were obtained with triethylbenzylammonium chloride (TEBAC) in amounts ranging from 0.5 to 1 mole per mole of acid. The results presented in Table 1 show that replacement of pyridine by TEBAC increases the yields of desired products IIIa-e significantly. The lower yield of IIIb as compared with the remaining compounds (both in the

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	mp, °C (lit.)	IR spectrum, ν, cm^{-1}				Yield, %
			C=O	C=C	C–H in the trans-arylethylenes	C–H deformation vibrations of the substituted benzene ring	
IIa	133	133 [9]	1690	1635	960	1080, 720, 690	92
IIb	150		1680	1610	965	740	66
IIc	115–116	115–117 [9]	1680	1620	950	780	54
IId	196	198 [9]	1690	1610	970	1175, 810	90
IIe	125–126		1680	1620	970	810	85
IIIa	114–115	114,5–115 [10]	1760			1060, 750	89 (74)[a]
IIIb	129–130		1750			755	59 (28)
IIIc	118–119		1752			1160, 860, 800	61 (48)
IIId	125–125,5	124,7–125,7 [3]	1745			1175, 860, 810	72 (43)
IIIe	197 (2)[b]		1760			1178, 860, 828	80 (45)
IV	264–266	269–271 [11]	1670			1080, 750	98
V	96–98[b]	111–113/10 [12]				1070, 760	95
VI	31–32	31,4 [13]				1070, 770	75

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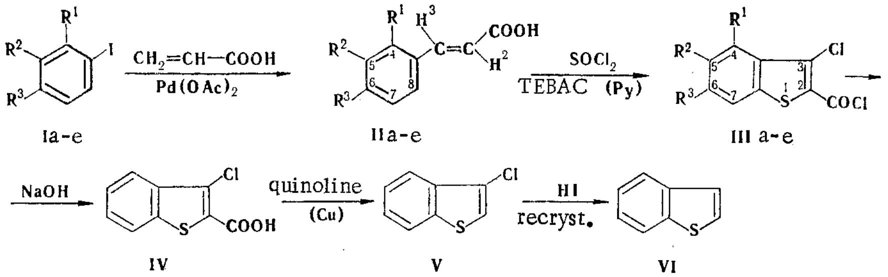
[a] The yields of the products when pyridine was used are indicated in parentheses, while the yields without parentheses are those obtained when triethylbenzylammonium chloride was used. [b] These are the boiling points in degrees Celsius (with the pressures in millimeters of mercury).



I, II, III a $R^1=R^2=R^3=H$; b $R^1=CH_3$, $R^2=R^3=H$; c $R^2=CH_3$, $R^1=R^3=H$; d $R^3=CH_3$, $R^1=R^2=H$; e $R^3=C_5H_{11}$, $R^1=R^2=H$

presence of pyridine and under the influence of TEBAC) may be associated with the fact that one of the two possible cyclization pathways is occupied by a methyl group. The structures of the products IIIa-e are in good agreement with the data from the IR and PMR spectra; the compositions of IIIb-e, which were synthesized for the first time, were confirmed by the results of elementary analysis. In the PMR spectra of IIIa-e (Table 2) the assignment of the signals was made with allowance for the fact that the signals of the 4-H and 7-H protons, which are located in the α position relative to the node of fusion of two rings, appear at weaker field than the signals of the 5-H and 6-H β protons [14], as well as with allowance for the effect of the alkyl substituents and the sulfur atom of the thiophene ring on the chemical shifts of the ring protons. The position of the signal of the methyl group in the spectrum of product IIIc at stronger field as compared with IIIb confirms the structure of isomer IIIc. The second possible isomer with a methyl group in the 7 position is not detected, probably because its formation entails greater steric hindrance.

Further transformations of the benzo[b]thiophene derivatives in order to develop a method for the preparation of thiophene ring-unsubstituted benzo[b]thiophenes were studied in the case of IIIa. Saponification of IIIa with 20% aqueous sodium hydroxide solution and subsequent decarboxylation of resulting acid IV in refluxing quinoline in the presence of copper led to chloro derivative V. Dehalogenation of the latter with 57% hydriodic acid by the method in [15] was accompanied by intensive desulfuration of the thiophene ring, and the yield of unsubstituted benzo[b]thiophene VI was insignificant. The use in this reaction of red phosphorus, which has been previously used for dehalogenation in the indole series [16], made it possible to obtain VI in 75% yield. The formation of very small amounts of 2,3-dihydrobenzo[b]thiophene, which, according to the GLC data, was identical to the authentic preparation, was observed as a side process.

TABLE 2. Parameters of the PMR Spectra of the Synthesized Compounds

Compound	Chemical shifts, δ, ppm								SSCC, J, Hz
	CH_3	2-H	3-H	4-H	5-H	6-H	7-H	8-H	
IIa	—	7,90 d	6,70 d	7,52 s	7,52 s	7,52 s	7,52 s	7,52 s	$J_{23}=15$
IId	2,10 s	7,90 d	6,60 d	7,58 d	7,33 d	—	7,33 d	7,58 d	$J_{23}=16$; $J_{45}=J_{78}=8$
IIe[a]	—[b]	7,50 d	6,20 d	7,77 d	7,00 d	—	7,00 d	7,77 d	$J_{23}=15$; $J_{45}=J_{78}=8$
IIIa	—	—	—	7,85 m	7,40 m	7,40 m	7,85 m	—	
IIIb	2,85 s	—	—	—	7,08 br. d	7,30 m	7,53 br. d	—	$J_{56}\approx 8$; $J_{67}\approx 7{,}5$; $J_{57}\approx 1$
IIIc	2,45 s	—	—	7,52 br. s	—	7,30 br. d	7,80 d	—	$J_{67}=8{,}5$, $J_{46}=1$
IIId	2,45 s	—	—	7,70 d	7,23 br. d	—	7,48 br. s	—	$J_{45}=8$, $J_{57}=1$
IIIe	—[b]	—	—	7,60 d	7,12 br. d	—	7,35 br. s	—	$J_{45}=8{,}5$; $J_{57}=1{,}5$
V	—	7,08 s	—	7,65 m	7,20 m	7,20 m	7,65 m	—	
VI	—	7,15 m	7,15 m	7,60 m	7,15 m	7,15 m	7,60 m	—	

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[a] The parameters of the spectrum of the methyl ester of acid IIe are presented. [b] The C_5H_{11} grouping shows up in the form of the following three multiplets: 0.82 (CH_3), 1.3 (CH_2), and 2.65 ppm (benzyl CH_2).

Thus in the present research we have demonstrated the fundamental possibility of the synthesis of benzo[b]thiphene derivatives and subsequently benzo[b]thiophenes themselves on the basis of accessible iodo-substituted aromatic compounds owing to the successful combination of arylation of acrylic acid with subsequent oxidation of unsaturated acids II with thionyl chloride. The use of a new effective additive, viz., triethylbenzylammonium chloride (TEBAC), in place of pyridine significantly improves the preparative possibilities of the oxidation reaction. The results obtained in this research may serve as a certain prerequisite for the synthesis of polycyclic condensed arenothiophenes, which will be the subject of our future studies.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla BS 487 spectrometer with hexamethyldisiloxane as the internal standard. Analysis by GLC was carried out with an LKhM-8MD chromatograph with a thermal conductivity detector and helium as the carrier gas; the columns (2 m by 3 mm) were packed with stationary phases consisting of 3% Se-30 on Inerton-Super with temperature programming from 50 to 280°C (for monitoring of the arylation reaction) and 5% SE-30 on Chromaton N-AW under isothermal conditions (for monitoring of the oxidation reaction).

Arylation of Methyl Acrylate with Aryl Iodides Ia-e. A mixture of 0.075 mole of methyl acrylate, 0.06 mole of aryl iodide Ia-e, 0.13 g of palladium acetate, and 0.06 mole of tributylamine was heated with stirring on a boiling-water bath for 8 h, after which it was diluted with water, the organic layer was separated, and the aqueous layer was extracted with ether (two 50-ml portions). The solvent was removed, and the organic part was hydrolyzed by refluxing with 200 ml of 20% aqueous sodium hydroxide solution for 2 h. The organic impurities were extracted with ether, and the alkaline solution was refluxed with a small amount of activated charcoal and filtered. The filtrate was neutralized with hydrochloric acid, and the precipitated reaction product was removed by filtration, washed with water, dried, and recrystallized from alcohol or hexane. The yields of acids IIa-e and their characteristics are presented in Table 1.

Trans-β-(n-amyl)acrylic Acid (IIe). Found: C 76.9; H 8.1%. $C_{14}H_{18}O_2$. Calculated: C 77.1; H 8.3%.

Oxidation of Acids IIa-e with Thionyl Chloride. A flask equipped with a stirrer, a reflux condenser, and a dropping funnel was charged with 15 mmole of acid IIa-e, 7.5-15 mmole of TEBAC (or 15 mmole of pyridine), and one third of 9 ml (0.12 mole) of thionyl chloride, and the mixture was heated to 140°C and treated dropwise with the remaining thionyl chloride at this temperature in the course of an hour. The mixture was heated for another 2 h at 140°C. Reaction products IIIa-e were extracted with boiling hexane and recrystallized from hexane.

4-Methyl-3-chloro-2-chlorocarbonylbenzo[b]thiophene (IIIb). Found: C 49.3; H 2.6; Cl 28.6; S 13.1%. $C_{10}H_6Cl_2OS$. Calculated: C 49.0; H 2.4; Cl 29.0; S 13.1%.

5-Methyl-3-chloro-2-chlorocarbonylbenzo[b]thiophene (IIIc). Found: S 13.0%. $C_{10}H_6Cl_2OS$. Calculated: S 13.1%.

6-Amyl-3-chloro-2-chlorocarbonylbenzo[b]thiophene (IIIe). Found: C 55.7; H 4.6; Cl 23.7; S 10.4%. $C_{14}H_{14}Cl_2OS$. Calculated: C 55.8; H 4.6; Cl 23.6; S 10.6%.

3-Chloro-2-carboxybenzo[b]thiophene (IV). A mixture of 23.1 g (0.1 mole) of IIIa with 250 ml of 20% aqueous sodium hydroxide solution was refluxed for 4 h, after which the solution was cooled and acidified with dilute hydrochloric acid. The precipitated IV was removed by filtration, washed with water, dried, and recrystallized from 90% ethanol.

3-Chlorobenzo[b]thiophene (V). A mixture of 21.25 g (0.1 mole) of acid IV, 10 g of copper powder, and 200 ml of quinoline was refluxed for 5 h, after which it was cooled, and the copper was removed by filtration. The filtrate was acidified with hydrochloric acid and extracted with pentane. The extract was washed with water and dried, the solvent was evaporated, and V was distilled at reduced pressure.

Benzo[b]thiophene (VI). A mixture of 16.85 g (0.1 mole) of V, 4.6 g (0.15 mole) of red phosphorus, and 200 ml of 57% hydriodic acid was refluxed for 3 h, after which it was extracted with pentane. The extract was washed successively with water, sodium bisulfite solution, and water, and dried. Product VI was purified by low-temperature crystallization from methanol.

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