AN INVESTIGATION OF CONDENSED HETEROAROMATIC SYSTEMS INCLUDING A THIOPHENE RING

XXV.* CATALYTIC LIQUID-PHASE OXIDATION OF SOME SUBSTITUTED BENZO[b]THIOPHENES

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The influence of the temperature, of the natures of the initiator and of the initial compound, and of the concentrations of the reactants on the process and nature of the transformations of 2- and 3-alkyl-, 2- and 3-formyl-, and 2- and 3-hydroxymethylbenzo[b]thiophenes under conditions of liquid-phase oxidation with oxygen in the presence of cobalt acetate in acetic acid has been studied. According to their relative ease of oxidation, the homologs and derivatives of benzo[b]thiophene, thiophene, and benzene can be arranged in the following sequence: 3-methylbenzo[b]thiophene > 2-methylbenzo[b]thiophene > 2-methylthiophene > toluene > 3-methylbenzo[b]thiophene dioxide > 2-methylbenzo[b]thiophene dioxide; benzaldehyde > benzo[b]thiophene-3-carbaldehyde > thiophene-2-carbaldehyde > benzo[b]thiophene-2-carbaldehyde; 3-hydroxymethylbenzo[b]thiophene > 2-hydroxymethylbenzo[b]thiophene > benzyl alcohol > 2-hydroxymethylthiophene. The liquid-phase oxidation of alkyl-substituted benzo[b]thiophenes can be used to obtain aldehydes, ketones, and acids of the benzo[b]thiophene series.

In recent years, the liquid-phase oxidation of benzene homologs as a method of obtaining oxygen-containing compounds has attracted the attention of many workers. The use as catalysts of salts of bivalent cobalt, especially cobalt acetate, with additions of initiators – bromine-containing compounds – in acetic acid permits the process to be carried out fairly intensively and, which is particularly important, in one stage [2].

The liquid-phase catalytic oxidation of some alkyl-substituted thiophenes and selenophenes has been investigated previously [3-5], and the possibility has been shown of obtaining from them by this method acids, aldehydes, ketones, and alcohols. Developing these investigations and ones which we have performed in the field of condensed heteroaromatic compounds including a thiophene ring, it appeared of interest to study the catalytic oxidation of some substituted benzo[b]thiophenes. We many note that the liquid-phase oxidation of compounds of the benzo[b]thiophene series has been studied little hitherto. Only the possibility of oxidizing 3-methylbenzo[b]thiophene (I) to benzo[b]thiophene-3-carboxylic acid (II) in the presence of bromine ions has been shown [6], and the thermal-oxidative transformation of (I) in n-hexadecane has also been studied [7]. In the oxidation of benzo[b]thiophene homologs in the presence of vanadium pentoxide, the cleavage of the thiophene ring was found [8]. Other methods of obtaining oxygen-containing compounds of the benzo[b]thiophene series are also known (see, for example, [9] and the references therein).

The present work was devoted to a study of the influence of a condensed benzene ring on the reactivity and nature of the transformations under liquid-phase oxidation conditions of alkyl, formyl, and hydroxyalkyl groups present in the thiophene moiety of the benzo[b]thiophene molecule, and the dependence

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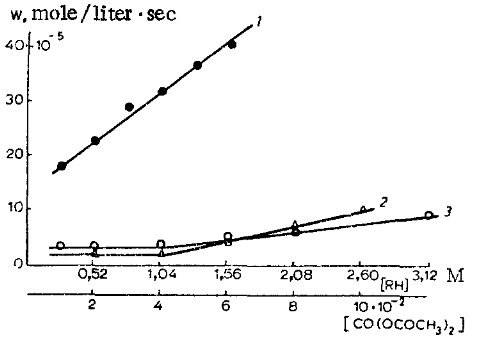


Fig. 1. Dependence of the rate of oxidation on the concentration of (I) and of the catalyst $Co(OCOCH_3)_2$ at 95°C: 1) $[Co(OCOCH_3)_2] = 0.05$ M, $[NaBr] = 0.015$ M; 2) $[I] = 0.752$ M, in the absence of an initiator; 3) $[Co(OCOCH_3)_2] = 0.05$ M, in the absence of an initiator.

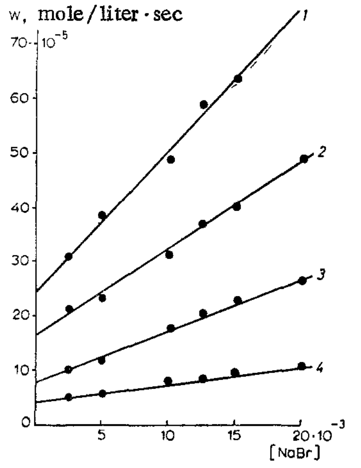
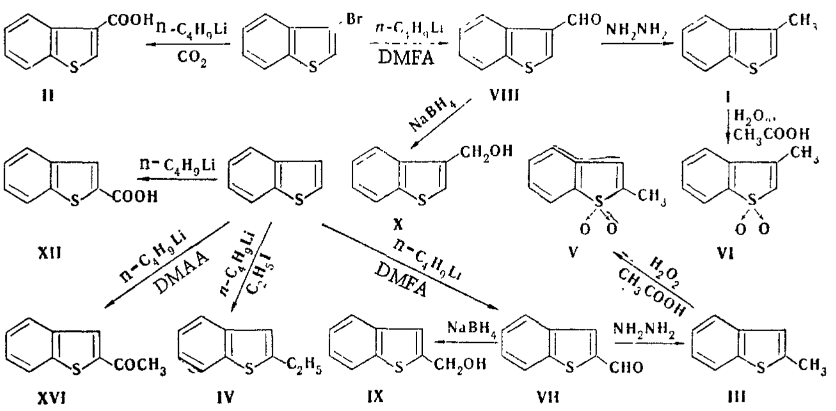


Fig. 2. Dependence of the rate of oxidation of (I) (0.752 M) on the concentration of NaBr at 95°C and the following concentrations of $Co(OCOCH_3)_2$ (M): 1) 0.08; 2) 0.06; 3) 0.04; 4) 0.02.

of the rates of their oxidation on the temperature and on the concentrations of the catalyst, the initiator, and the compound undergoing oxidation, and also an investigation of the influence of a series of organic bromides as oxidation initiators.

We have studied the oxidation of compound (I), of 2-methylbenzo[b]thiophene (III), of 2-ethylbenzo[b]-thiophene (IV), of 2-methyl- and 3-methylbenzo[b]thiophene dioxides (V) and (VI), of benzo[b]thiophene-2-carbaldehyde (VII) and benzo[b]thiophene-3-carbaldehyde (VIII), and of 2- and 3-hydroxymethylbenzo[b]-thiophenes (IX and X) at concentrations of these compounds from 1 to 10 vol.% in glacial acetic acid solution at 65-95°C and at concentrations of the catalyst $[Co(OCOCH_3)_2]$ of $2 \cdot 10^{-2}$ to 10^{-1} M and of initiator [bromide] of $2.5 \cdot 10^{-3}$ to $2 \cdot 10^{-4}$ M. In individual cases, as oxidation initiator, in addition to NaBr and 9, 10-dibromoanthracene (DBA) we used 2- and 3-bromothiophenes, 2,3- and 3,4-dibromothiophenes, 2,3,4, 5-tetrabromothiophene, 2- and 3-bromobenzo[b]thiophenes, bromobenzene, n-butyl bromide, and dibromoethane.

The initial compounds, and also authentic samples to prove the structure of the oxidation products, were synthesized by the following schemes:



DMAA - dimethylacetamide

It must be mentioned that while benzo[b]thiophene derivatives with substituents in position 2 are obtained in the pure state, the corresponding 3-substituted derivatives are contaminated with about 5-7% of the 2-substituted derivatives. This is due to the fact that in the bromination of benzo[b]thiophene to obtain 3-bromobenzo[b]thiophene as an initial compound, as in the case of other electrophilic substitution reactions, in addition to the predominating attack of position 3 of the benzo[b]thiophene system position 2 is attacked as well [9].

TABLE 1. Concentrations of the Products of the Oxidation of (I) as Functions of the Time

Time, min	Concentration, %			Conversion of (I), %
	I	VIII	X	
5	4,27	0,83	0,002	14,6
10	4,02	0,91	0,168	19,6
20	3,28	1,68	0,240	34,4
30	2,26	1,79	0,251	54,9
40	2,09	2,57	0,171	58,2
50	1,77	2,32	0,089	64,8
60	1,62	1,82	0,079	68,3

TABLE 2. Concentrations of the Products of the Oxidation of (XIII) as Functions of the Time

Time, min	Concentration,* %			Conversion of (XIII), %
	XIII	XIV	XV	
5	2,50	0,029	0,040	—
10	1,65	0,270	0,172	34
20	1,34	0,700	0,442	46,6
30	0,62	1,173	0,311	75,2
40	0,33	0,364	0,160	87,1
50	—	0,039	—	100

* (XIV) – thiophene-2-carbaldehyde; (XV) – 2-hydroxymethylthiophene.

TABLE 3. Concentrations of the Products of the Oxidation of (I) and (XIII) as Functions of the Temperature

Temp., °C	Concentration, %			Concentration, %		
	I	VIII	X	XIII	XIV	XV
75	1,66	1,40	0,179	—	—	—
85	1,17	1,41	0,085	—	0,36	0,160
95	1,92	1,79	0,006	—	0,48	—

In 1949 [10], a method was proposed for synthesizing 3-alkylbenzo[b]thiophenes by the cyclization of (arylthio)acetones with phosphorus pentoxide or zinc chloride. However, as was found later [11], on cyclization with phosphorus pentoxide or polyphosphoric acid at 160-180°C (phenylthio)acetone (XI) forms a mixture of (I) and (III) in a ratio of about 5 : 1. On being heated with polyphosphoric acid at 100-150°C, 3-alkylbenzo[b]thiophenes are converted into the corresponding 2-alkyl isomers, which is due to the preliminary protonation of the heterocycle with the subsequent intramolecular migration of the substituent [12].

In order to obtain compound (I), we decided to use a method of cyclizing (arylthio)acetones in the presence of aluminum chloride under milder conditions – in benzene at room temperature – that we had developed previously [13]. However, as an analysis by the GLC method showed, in this case, again, in addition to (I) compound (III) is formed, although in much smaller amounts (about 2%). Consequently, to prepare compounds (I, VI, VIII, and X) we started from 3-bromobenzo[b]thiophene prepared by the method of Dickinson and Iddon [11].

It was shown by special experiments that under the conditions selected for liquid-phase oxidation, no migration of an alkyl or a formyl group from position 3 to position 2 of benzo[b]thiophene takes place.

The depth of oxidation of the benzo[b]thiophene homologs depends on their nature. Under identical conditions – concentration of initial compound 0.518 M, of catalyst [$Co(OCOCH_3)_2$] 0.05 M, of initiator [NaBr or DBA] 0.015 M, temperature 95°C – compound (I) oxidizes to the acid (II), and compound (III) to the aldehyde (VII). The concentration of the initial compound substantially affects the depth of oxidation. Thus, at concentrations less than 0.1 M under otherwise similar conditions compound (III) is oxidized not to the aldehyde (VII) but to benzo[b]thiophene-2-carboxylic acid (XII).

As was to be expected, in the absence of an initiator the rate of oxidation of (I) is proportional to the square of the concentration of the compound being oxidized and does not depend on the concentration of catalyst (up to 0.04 M; Fig. 1, curves 2 and 3). The addition of an initiator strongly affects both the rate and the degree of oxidation. For example, with a decrease in the concentration of (I) the rate of oxidation tends to a value determined by the concentrations of the initiator and the catalyst (Fig. 1, curve 1). At low concentrations of initiator, the rate of oxidation rises linearly with an increase in the concentration of

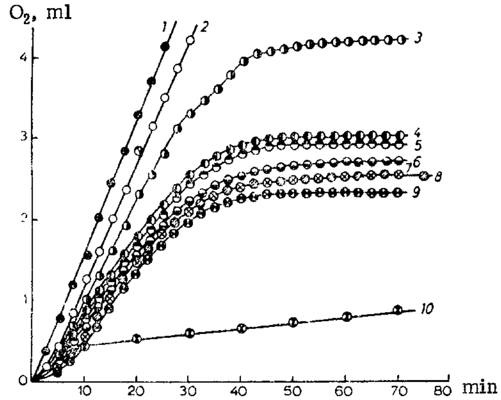


Fig. 3. Kinetics of the absorption of oxygen in the oxidation of (I) (0.518 M), [$Co(OCOCH_3)_2$] = 0.05 M at 95°C in the presence of the following bromides (0.0155 M): 1) 2-bromobenzo[b]thiophene; 2) 2,3,4,5-tetrabromothiophene; 3) 3-bromobenzo[b]thiophene; 4) 2,3-dibromothiophene; 5) 2-bromothiophene; 6) 3-bromothiophene; 7) 3,4-dibromothiophene; 8) dibromoethane; 9) n-butyl bromide; 10) bromobenzene.

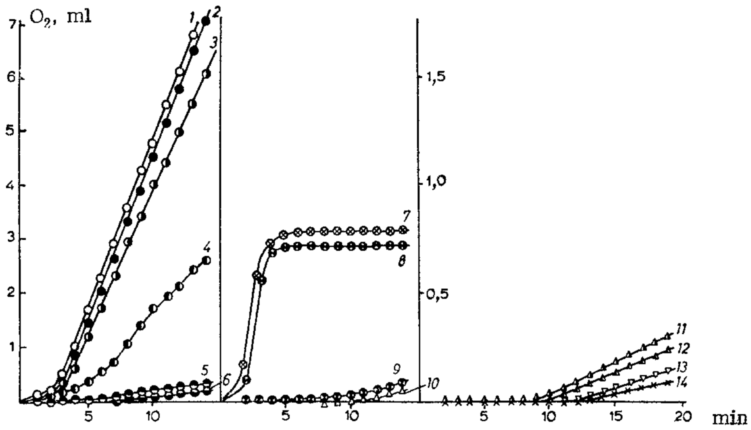


Fig. 4. Kinetics of the absorption of oxygen at a concentration of the initial compound of 0.518 M, [$Co(OCOCH_3)_2$] = 0.05 M, [NaBr] = 0.0155 M at 95°C: 1) (I); 2) (III); 3) (XIII); 4) toluene; 5) (VI); 6) (V); 7) benzaldehyde; 8) (VIII); 9) (XIV); 10) (VII); 11) (X); 12) (XI); 13) benzyl alcohol; 14) (XV).

initiator (Fig. 2). An increase in the concentration of initiator (NaBr) from 0.0155 to 0.1 M leads to the complete oxidation to the corresponding acids of both (I) and (III), compound (I) being oxidized approximately 1.5 times faster than (III). From the dependence of the rate of oxidation on the concentration of the catalyst [$Co(OCOCH_3)_2$] and of the initiator (NaBr) (Fig. 2) it may be concluded that in the presence of an initiator both cobalt ions and bromide ions take part in the chain-propagating reactions. We may note that both in the presence of an initiator and in its absence the induction period in the oxidation of benzo[b]thiophene homologs does not exceed 5 min.

It has been shown previously [3] that the oxidation of thiophene homologs takes place faster when DBA, rather than NaBr, is used as initiator. However, in the case of compound (I) a different picture is found – the oxidation takes place faster when NaBr is used – and in the case of (III) DBA and NaBr behave almost identically. In the oxidation of the benzo[b]thiophene homologs we investigated a number of other initiators, as well (Fig. 3). In this case, the most active, together with NaBr and DBA, are bromine-substituted heteroaromatic compounds. The bromides investigated as initiators of the oxidation of benzo[b]thiophene homologs can be arranged in the following sequence according to their activities: NaBr > DBA > 2-bromobenzo[b]thiophene > 2,3,4,5-tetrabromothiophene > 3-bromobenzo[b]thiophene > 2,3-dibromothiophene ≃ 2-bromothiophene > 3-bromothiophene > 3,4-dibromothiophene ≃ dibromoethane ≃ n-butyl bromide > bromobenzene.

As mentioned above, the rate of oxidation of (I) substantially exceeds that of (III). In view of this, it appeared of interest to compare the reactivities of (III) and 2-methylthiophene (XIII) in liquid-phase oxidation. The results of the competing oxidation of a mixture of (III) and (XIII) (1 : 1, with a concentration of them in the mixture of 2 vol.%) showed that only (III) underwent oxidation with the formation of the aldehyde (VII) and the alcohol (IX) which was then oxidized to the acid (XII).

Intermediate products of the oxidation both of benzo[b]thiophene homologs and of thiophene are aldehydes and alcohols. Tables 1 and 2 give the results on the accumulation and consumption of the intermediate products of the oxidation of (I) and (XIII) with time (according to GLC).

The temperature also has a substantial influence on the oxidation of benzo[b]thiophene homologs and thiophene, this being reflected not only in the rate but also in the ratio of intermediate reaction products. With a rise in the temperature, the amount of aldehyde increases and the amount of alcohol decreases, as is illustrated by the figures of Table 3.

The difference in the reactivities of substituted benzo[b]thiophenes with methyl groups in positions 2 and 3, respectively, that has been mentioned is also observed in the case of the corresponding formyl and hydroxymethyl derivatives: (VII and VIII) and (IX and X). Thus, at a concentration of 0.518 M in the absence of an initiator, compound (VIII) is far more readily oxidized to the acid (II), which we have isolated and characterized, than its isomer (VII) is oxidized to the acid (XII). The addition of an initiator (NaBr, DBA) substantially raises the rate of oxidation of (VIII) and shortens the reaction time from 60 to 6 min. At the same concentration, (VII) is not oxidized either in the absence or in the presence of an initiator, and only at a concentration below 0.1 M and with an induction period of 90 min does its oxidation to the acid (XII) take place. Under the same conditions and at a concentration of 0.518 M, the corresponding alcohols are oxidized somewhat more slowly than the aldehydes, the 2-isomer (IX) far more slowly than the 3-isomer (X).

It is interesting to note the observed correlation between the ease of oxidation of 2- and 3-substituted benzo[b]thiophenes and thiophenes and the distribution of the electron density in the molecules of benzo[b]thiophene [14] and of thiophene [15].

On passing from the benzo[b]thiophene homologs to the corresponding dioxides, the capacity of the methyl group for undergoing oxidation falls sharply. In the case of (V and VI), a slow and slight absorption of oxygen is observed (conversion does not exceed 8-10%). The reaction products were found by the GLC method to contain, in addition to the initial dioxides (V and VI) two unidentified substances with retention times considerably smaller than those of the initial dioxides. It is possible that under the conditions of oxidation the splitting of the thiophene ring of the dioxides takes place to some extent with the formation of products which inhibit oxidation, which is responsible for the low conversion.

The results obtained in a study of the reactivity of methyl-, formyl-, and hydroxymethyl-substituted benzo[b]thiophenes at equal concentrations in the initial stage of oxidation and a comparison of these with data on the oxidation of homologs of thiophene and of benzene (Fig. 4) permit the following sequence to be drawn up with respect to ease of oxidation: (I) > (III) > (XIII) > toluene > (VI) > (V); benzaldehyde > (VIII) > (XIV) > (VII); (X) > (IX) > benzyl alcohol > (XV).

In conclusion, let us consider the results obtained in the oxidation of 2-ethylbenzo[b]thiophene (IV). Under the conditions that were found to be the optimum for the oxidation of the benzo[b]thiophene homologs – temperature 95°C, concentration of $Co(OCOCH_3)_2$ 0.05 M and of NaBr 0.0155 M – a solution of (IV) (5 vol.%) absorbs oxygen almost quantitatively as calculated for 2-acetylbenzo[b]thiophene (XVI) in 2 h to 2 h 30 min. Compound (XVI) was isolated from the reaction products with a yield of 44%. In contrast to the reactions of 2-ethylthiophene, forming a considerable amount of the corresponding alcohol in addition to 2-acetothienone [4], the oxidation of (XVI) forms almost no alcohol.

The observed characteristics can be described on the basis of ideas on the oxidation of benzene homologs in the presence of cobalt salts and bromine compounds [16] by a reaction mechanism similar to that for the oxidation of alkylthiophenes and selenophenes [3]. According to this scheme, the main intermediate products in the oxidation of the methyl derivatives are aldehydes and alcohols, as is also observed in the case of the methyl-substituted benzo[b]thiophenes.

EXPERIMENTAL

The experimental procedure has been described elsewhere [2]. The kinetic investigations were performed in a cell fitted with a thermostatted jacket and a sample-taker enabling samples of 0.0005-0.01 ml to be taken with a microsyringe. The total volume of the catalyst solution was 2 ml. The bromides used as initiators were synthesized by known methods.

Analysis by the GLC method was performed on an LKhM-8MD chromatograph (5th model) with a flame-ionization detector under conditions of the programming of the temperature from 70 to 220°C (the rate of change of temperature was 12 deg/min); stainless-steel columns (200 × 0.3 cm) filled with quartz glass (0.25-0.50 mm) upon which 0.64% of SE-30 silicon elastomer had been deposited. The rate of flow of the carrier gas (argon) was 24 ml/min, and acetophenone was used as internal standard.

2-Methylbenzo[b]thiophene (III) was obtained by the Kishner [Wolff–Kishner] reduction of compound (VII) with a yield of 75%, mp 51.5-52°C (from ethanol). According to the literature [17], mp 51-52°C.

Benzo[b]thiophene-2-carboxylic acid (XII) was obtained with a yield of 85% by the metallation and subsequent carbonation of benzo[b]thiophene, mp 237°C (from water). According to the literature [18], mp 236°C.

2-Hydroxymethylbenzo[b]thiophene (IX) was obtained with a yield of 62% by the reduction of (VII) with sodium tetrahydroborate, mp 99-100°C (from petroleum ether) [19].

2-Methylbenzo[b]thiophene dioxide (V) was obtained by the oxidation of (III) with hydrogen peroxide in glacial acetic acid with a yield of 83%, mp 110-111°C (from benzene). According to the literature [20], mp 108.5-110°C.

2-Ethylbenzo[b]thiophene (IV) was obtained with a yield of 30% by the metallation of benzo[b]thiophene followed by the reaction of the 2-benzo[b]thienyllithium with ethyl iodide. bp 88-89°C (3 mm); n_D^{20} 1.5539. According to the literature [17], bp 162-165°C (23 mm); n_D^{22} 1.5544.

Benzo[b]thiophene-3-carbaldehyde (VIII) was obtained by the method of Dickinson and Iddon [11] with a yield of 71%, bp 130-133°C (4 mm); mp 56.5-57°C (from ethanol). According to the literature [11], bp 173-175°C (16 mm); mp 56-57°C.

3-Methylbenzo[b]thiophene (I). A. At 20°C, 32.2 ml of chloroacetone was added to a mixture of 40.8 ml of thiophenol and 53.3 ml of 30% aqueous NaOH, and after 30 min the mixture was treated with ether and the ethereal extract was washed with water and dried. This gave 55.6 g (77%) of (phenylthio)acetone (XI), bp 112-114°C (3.5 mm); according to the literature [21], bp 142°C (17 mm). Under conditions excluding the access of moisture, 30 g of (XI) was added at 20°C to a suspension of 60 g of anhydrous $AlCl_3$ in 100 ml of absolute benzene. After being stirred at 20°C for 14 h, the reaction mixture was hydrolyzed with water, and the aqueous layer was separated off and extracted with benzene. The benzene extracts were combined and were washed with water, with 5% NaOH, and twice more with water, and were dried with $MgSO_4$. This gave 19.3 g (72%) of (I), bp 80-83°C (2-2.5 mm); n_D^{20} 1.6230. Literature data [21]: bp 127-129°C (25 mm); n_D^{20} 1.6232. According to GLC, it contained about 2% of (III).

B. The Kishner reduction of (VIII) gave an 87% yield of (I), bp 116-117°C (16 mm); n_D^{20} 1.6090, d_4^{20} 1.1096. According to GLC, it was not contaminated with (III).

3-Hydroxymethylbenzo[b]thiophene (X) was obtained with a yield of 85% by the reduction of (VIII) with sodium tetrahydroborate; bp 148-148.5°C (4 mm), mp 42.5-43°C (from ethanol). According to the literature [22], bp 141-144°C (1.5 mm), mp 43-44°C.

3-Methylbenzo[b]thiophene dioxide (VI) was obtained with a yield of 35% by the oxidation of (I) with hydrogen peroxide; mp 141.5-142°C (from dilute ethanol). According to the literature [23], mp 142-143°C.

2-Acetylbenzo[b]thiophene (XVI). A. This was synthesized with a yield of 79% by the metallation of benzo[b]thiophene followed by the reaction of the 2-benzo[b]thienyllithium with DMAA under conditions similar to those for the preparation of (VII), mp 86-87°C (sublimation in vacuum). According to the literature [24], mp 88°C.

B. Oxidation of 2-Ethylbenzo[b]thiophene (IV). The oxidation of (IV) was performed at 95°C with vigorous shaking. The concentration of $Co(OCOCH_3)_2$ was 0.05 M, of NaBr 0.015 M, and of (IV) 0.518 M, and the total volume was 40 ml. After the end of the absorption of oxygen (2 h to 2 h 30 min), 80% of (XVI) had been formed according to GLC. The acetic acid was distilled off in vacuum and the residue was washed with 20 ml of n-hexane and extracted with 20 ml of benzene. The extract was filtered and was treated with 80 ml of n-hexane. The precipitate that deposited after cooling was separated off and washed with n-hexane to give 0.97 g (45%) of (XVI), mp 85.5-86°C (after two recrystallizations from a 1:4 mixture of benzene and n-hexane and vacuum sublimation). A mixture with the (XVI) obtained by method A gave no depression of the melting point; their identity was also confirmed by GLC.

Benzo[b]thiophene-2-carbaldehyde (VII). A. This was obtained by Dickinson and Iddon's method [11] with a yield of 70%, bp 135-136°C (8 mm); mp 33.5-34.5°C. According to the literature [20], mp 34-34.5°C.

B. Oxidation of 2-Methylbenzo[b]thiophene (III). The oxidation of 2.58 g of (III) was performed similarly to that of (IV) for 3 h. The acetic acid was distilled off in vacuum and the residue was subjected to steam distillation. This gave 1.04 g (40%) of the initial (III) with mp 51.5°C (60% conversion), and 0.77 g (30%) of (VII) with bp 136°C (9 mm), mp 33.5-34.5°C; 2,4-dinitrophenylhydrazone, mp 308.5-309°C (from pyridine). A mixture with the (VII) (obtained by method A) gave no depression of the melting point, and their IR spectra were completely identical.

Benzo[b]thiophene-3-carboxylic Acid (II). A. This was obtained with a yield of 85% by the metallation at −70°C and subsequent carbonation of 3-bromobenzene[b]thiophene. mp 178-178.5°C (from dilute ethanol). According to the literature [22], mp 175-176°C.

B. Oxidation of 3-Methylbenzo[b]thiophene (I) and of Benzo[b]thiophene-3-carbaldehyde (VIII). The oxidation of compounds (I) and (VIII) was performed like the oxidation of (III) and (IV). After the end of the process, the reaction mixture was diluted with water, the precipitate that deposited was extracted with benzene, the extract was washed repeatedly with sodium carbonate solution, and the aqueous layer was separated off and was acidified with 5% hydrochloric acid. The precipitate was filtered off and washed with ice water. This gave a 40-63% yield of the acid (II), mp 175-176°C (from dilute ethanol). A mixture with a sample of the (II) obtained by method A gave no depression of the melting point.

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