Addition Reactions of Benzo[*b*]thiophen. Part 4.[1] Reactions of Some Acetoxy- and Hydroxy-benzo[*b*]thiophens with Benzene or Toluene

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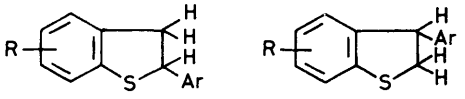
Heating acetoxybenzo[*b*]thiophens with $AlCl_3$–benzene can give the normal Fries-rearranged products (for the 4-OAc and 7-OAc isomers); these sometimes react further to give their 2,3-dihydro- (for 4-OAc and 7-OAc) or 2-phenyl derivatives (for 6-OAc). Alternatively, benzene can add across the 2,3-double bond of the acetoxy-compound, to give the 2- (for 6-OAc) or 3-phenyl-2,3-dihydrobenzo[*b*]thiophens (for 7-OAc). With $AlCl_3$ in dichloromethane, 6-acetoxybenzo[*b*]thiophen undergoes intermolecular transfer of an acetyl group to give a mixture of 6-acetoxy-2- and 3-acetylbenzo[*b*]thiophens and 6-hydroxybenzo[*b*]thiophen. With $AlCl_3$ in benzene at room temperature, 4-acetoxybenzo[*b*]thiophen gives a rearranged product, 4,5-dihydro-2,4-diphenylbenzo-[*b*]thiophen-7(6*H*)-one (3a) (17%).

In the presence of $AlCl_3$ for 0.5 h, 4-, 5-, 6-, and 7-hydroxybenzo[*b*]thiophens undergo addition of benzene or toluene, to give the appropriate 2-aryl-2,3-dihydrohydroxybenzo[*b*]thiophens (1). Yields are high for the 4- and 6-hydroxy-isomers (80—85%), but lower for the 5- (55%) and 7-isomers (10%). In each of these reactions the starting hydroxybenzo[*b*]thiophen is partly converted into its 2,3-dihydro-derivative. 5- and 7-Hydroxybenzo-[*b*]thiophen also each give the *same* 4,5-dihydro-2,4-diarylbenzo[*b*]thiophen-7(6*H*)-one (3) (25%) in this reaction. When the reaction period with benzene or toluene is extended to 5 days, the amount of solvent addition product (1) decreases, but all four hydroxy-isomers now give the same rearranged product (3). The mechanism of of this unusual rearrangement is discussed in terms of a spiro-intermediate.

EARLIER work has established that benzo[*b*]thiophen and many of its ring-substituted derivatives react with aromatic compounds (ArH) in the presence of aluminium chloride.[1-3] The overall picture is complex, but addition generally occurs across the 2,3-double bond to give a mixture of the 2- and 3-aryl-2,3-dihydrobenzo[*b*]thiophen derivatives (1) and (2). The 3-substituted-DHBT † derivatives (2) usually predominate when ArH = benzene, toluene, or ethylbenzene and when the 4-, 5-, or 6-position in the benzo[*b*]thiophen nucleus is either unsubstituted, or contains a bromo- or methyl substituent.[2,3] However, with a phenolic ether, the 2-aryl-DHBT derivative (1) is obtained preferentially and a



(1) (2)

a; R = 4-OMe, Ar = 4-OMe-2- or 3-benzo[*b*]thienyl
b; R = 6-OAc, Ar = Ph
c; R = 7-OH, Ar = Ph
d; R = 7-OAc, Ar = Ph
e; R = 4-OH, Ar = Ph
f; R = 4-OH, Ar = *p*-MeC_6H_4

ring-opened product is also formed in the reaction with anisole.[1] The isomeric methoxybenzo[*b*]thiophens react unusually with benzene or toluene and $AlCl_3$. Reaction is slow (*e.g.* 7-methoxybenzo[*b*]thiophen fails to react at room temperature) and dimeric products, *e.g.* (1a) and (2a), are formed in considerable yield, especially with 4-methoxybenzo[*b*]thiophen (60%).[1]

We have now continued this work by examining the reactions of isomeric hydroxy- and acetoxy-benzo[*b*]-thiophens with benzene or toluene and $AlCl_3$. Fries rearrangements of 4- and 5-acetoxybenzo[*b*]thiophen and their 3-methyl derivatives and of 7-acetoxy-3-methylbenzo[*b*]thiophen have previously been carried out with $AlCl_3$ in boiling benzene, but no evidence for the incorporation of the solvent has been reported. Thus, for 4-,[4] 5-,[5] and 7-acetoxy-3-methylbenzo[*b*]thiophen,[6] the acetyl group migrates preferentially into the 2-position; for 4-[4] and 5-acetoxybenzo[*b*]thiophen [7] it migrates into the 7- and 4-positions, respectively. We have earlier established beyond doubt that the 7-acetyl-4-hydroxy-compound, which is formed in the rearrangement of 4-acetoxybenzo[*b*]thiophen, is converted into its 2,3-dihydro-derivative by continued heating with benzene and $AlCl_3$.[4] The last reaction is evidently dependent on the sample of aluminium chloride used, because when we repeated the Fries rearrangement of 4-acetoxybenzo[*b*]-thiophen, we consistently obtained a mixture of 5- (70%) and 7-acetyl-4-hydroxybenzo[*b*]thiophen (25%) and none of the 2,3-dihydro-compound [*cf.* the work of Lechartier, who has obtained the 7-acetyl compound (1%) from this reaction, together with an isomer (3%), which he described first [8] as the 5-acetyl, and later [9] as the 2-acetyl derivative. Our work confirms that this is the 5-substituted derivative]. These results illustrate clearly that reactions in this area are very sensitive to small changes in reaction conditions.

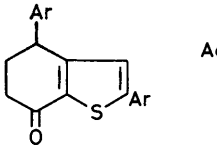
We next attempted the Fries rearrangement of 6-acetoxybenzo[*b*]thiophen with $AlCl_3$ in boiling benzene. After 0.5 h the acetoxy-group was still intact but benzene had added across the 2,3-bond, to give 6-acetoxy-2-phenyl-DHBT (1b) (24%) as the only isolable product. Structures of this and of other 2- and 3-aryl-DHBT derivatives (1) and (2) were determined by ^1H n.m.r. spectroscopy (for details see ref. 3), especially by observ-

† As before,[1-3] DHBT = 2,3-dihydrobenzo[*b*]thiophen.

ing the shift to low field of the characteristic triplet due to 2-H in a 2-aryl-DHBT derivative (1), relative to that of 3-H in the 3-aryl isomer (2). This reaction was unusual because none of the 3-isomer (2b) was detected and because initially formed DHBT derivatives are usually [3] dehydrogenated to the 2-arylbenzo[*b*]thiophen in boiling benzene. After 4 h, dehydrogenation had occurred and an acetyl group had also migrated to the 3-position, to give 3-acetyl-6-hydroxy-2-phenylbenzo[*b*]thiophen (57%). The marked deshielding of 4-H by the strongly anisotropic acetyl group confirmed that the latter was in the 3-position.[10] In an attempt to obtain a normal Fries rearrangement of 6-acetoxybenzo[*b*]thiophen, the reaction was repeated with $AlCl_3$ in dichloromethane at room temperature. Unexpectedly, 2- and 3-acetyl-6-acetoxybenzo[*b*]thiophens (16 and 38%) were formed, and must have arisen from an intermolecular transfer of an acetyl group from a second molecule of 6-acetoxybenzo[*b*]thiophen. Such a transfer has not previously been reported in the benzo[*b*]thiophen field, but in agreement with this suggested mechanism, 6-hydroxybenzo[*b*]thiophen (39%) was also isolated from the reaction.

The attempted Fries rearrangement of 7-acetoxybenzo[*b*]thiophen took yet another course: heating it with $AlCl_3$ in benzene (4 h) gave mainly 7-hydroxy-3-phenyl-DHBT (2c) (51%). The reason for the reversal in the regioselectivity of the addition of benzene to the 2,3-bond in passing from 6-acetoxy- to 7-acetoxy-benzo(*b*)thiophen is not understood. Other products from the reaction with 7-acetoxybenzo[*b*]thiophen were not obtained pure, but were identified spectroscopically as (*a*) 7-acetoxy-3-phenyl-DHBT (2d) (*ca.* 10%), (*b*) the 'normal' Fries-rearranged product, 4-acetyl-7-hydroxybenzo[*b*]thiophen (*ca.* 10%), and (*c*) the 2,3-dihydro-derivative of the foregoing compound (*ca.* 10%) (*cf.* the behaviour of 4-acetoxybenzo[*b*]thiophen [4]).

We next treated 4-acetoxybenzo[*b*]thiophen with $AlCl_3$ in benzene at room temperature. Reaction was slow and intractable products were formed, but it was possible to isolate the ketone (3a) (17%) (see later) and, on occasions, a 3-phenyl-DHBT derivative (8%), which contained in the benzenoid ring an acetyl, an acetoxy-, and a phenyl group. Spectral data are consistent with structure (4), but the position of the acetoxy-group must remain in doubt in the light of the rearrangement reactions which will be reported below.



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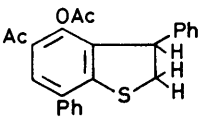


(4)

a; Ar = Ph

b; Ar = *p*-MeC_6H_4

In view of the obvious complexity of this type of reaction, the results of which we were unable to rationalise satisfactorily, we turned our attention to the reactions of 4-, 5-, 6-, and 7-hydroxybenzo[*b*]thiophen with benzene or toluene and $AlCl_3$. Results are summarised in the Table. Each of the four hydroxy-compounds gave the addition compounds (1) and (2) after 0.5 h. These were major products for the 4-, 5-, and 6-hydroxy-compounds, but were minor products for the 7-hydroxy-isomer. The unusual feature of the addition reaction is the formation of the 2-aryl-DHBT (1), with the almost total exclusion of the 3-aryl isomer (2). Benzo[*b*]thiophen [3] and its simple derivatives (including the 5-methoxy-compound) [2] give mainly the 3-aryl-DHBT isomer (2) with benzene or toluene under similar conditions. We have shown previously [3] that the orientation of the addition reaction is subject to a delicate balance of energetic and structural factors. Two factors which we shall discuss below, *viz.* protonation at the ring junction and ring opening, may further influence the regiocontrol of addition in the case of the hydroxybenzo[*b*]thiophens.

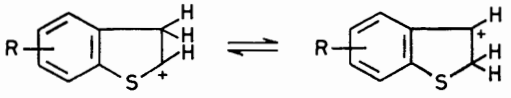
TABLE

Reactions of 4-, 5-, 6-, and 7-hydroxybenzo[*b*]thiophens with $AlCl_3$ and benzene or toluene [a]

Substituent	Solvent [b]	Time	2-Aryl-DHBT (1) (%)	3-Aryl-DHBT (2) (%)	2,3-Dihydro-derivative (7) (%)	Ketone (3) (%)		Other products (%)
4-OH	PhH	0.5 h	80	<5	10 [c]			
4-OH	PhMe	0.5 h	85	<5	10			
5-OH	PhH	0.5 h	55	<5	*ca.* 5	(3a)	25	7-Hydroxy-2-phenyl-DHBT (1c) (10)
6-OH	PhH or PhMe	0.5 h	85	Traces	*ca.* 5			
7-OH	PhH	0.5 h	10	Traces	60	(3a)	25	
7-OH	PhMe	0.5 h	10	Traces	65	(3b)	25	
4-OH	PhH	5 days	10	Traces	40	(3a)	45	
4-OH	PhMe	5 days	10	Traces	35	(3b)	50	
5-OH	PhH	5 days	Traces		5	(3a)	45	Polymeric material (50)
6-OH	PhH or PhMe	5 days	15	Traces	Traces	(3a) or (3b)	30	Polymeric material (45)
7-OH	PhH or PhMe	5 days	Traces		25	(3a) or (3b)	30	Polymeric material (40)

[a] Percentages relate to g.l.c. or h.p.l.c. analyses of the total product from the reaction. Yields of isolated products are given in the Experimental section. In some cases the yields for a given reaction vary from experiment to experiment: the average results (to the nearest 5%) of a typical series of experiments are quoted. [b] All reactions were carried out at room temperature. [c] In some experiments, up to a 40% yield of the 2,3-dihydro-compound (7a) could be obtained, at the expense of the 2-aryl-DHBT derivative (1e).

The reactions shown in the Table display two more unusual features: saturation of the 2,3-double bond to produce the appropriate 2,3-dihydrohydroxybenzo[*b*]-thiophen (7), and the formation of the ketone (3). Hydrogenation of the double bond has previously been observed when benzo[*b*]thiophen reacts with $AlCl_3$ in 1,2-dimethylbenzene,[3] in which case there is evidence for the extraction of a hydride ion from the solvent, and when 4-methylbenzo[*b*]thiophen reacts with benzene, for which it is suggested that a hydride ion might be removed from the 4-methyl group.[2] In the present case, if hydrogenation proceeds by the logical route, *i.e.* by the addition of H^- to the carbocation (5) or (6), it is difficult



(5) (6)

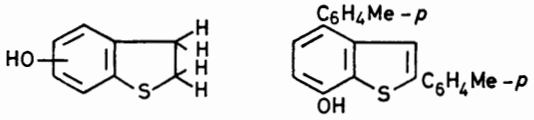
a ; R = 4-OMe
b ; R = 4-OH (or its $AlCl_3$ complex)

to suggest a source of hydride ions. Other workers,[11] in discussing the saturation of certain αβ-unsaturated carbonyl compounds by $AlCl_3$ in benzene, believed that the hydrogen atoms ' are made available by the solvent present in large excess.'

It can be seen (Table) that the amounts of 2,3-dihydro-derivative (7a) and ketone (3) from 4-hydroxybenzo[*b*]-thiophen increase as the reaction time is increased to 5 days; the 2,3-dihydro-derivative (7b) from 7-hydroxy-benzo[*b*]thiophen decomposes as the reaction time is increased. For 4-hydroxybenzo[*b*]thiophen, the initially formed 2-aryl-DHBT derivative (1e) or (1f) could be converted into a mixture of the 2,3-dihydro-compound (7a) and the ketone (3a) or (3b) by treating it with $AlCl_3$ in benzene or toluene. In some experiments, up to 40% of the 2,3-dihydro-product (7a) could be obtained at the expense of the benzene addition product (1e) when 4-hydroxybenzo[*b*]thiophen was treated with $AlCl_3$ in benzene for only 0.5 h. In these reactions it seems that the carbocation (5b) and/or (6b), which is the proposed intermediate in the formation of the 2,3-dihydro-compounds (7), may be formed directly by protonation of the hydroxybenzo[*b*]thiophen or, as shown earlier [3] for benzo[*b*]thiophen itself, could arise by reversal of the benzene addition reaction. It will be shown that the formation of the ketone (3) involves aromatisation of a 2-aryl-DHBT derivative, and it is tempting to speculate that this process may provide the hydride ion necessary to convert the carbocation (5) and/or (6) into the hydrogenated product (7). However, this explanation is not entirely satisfactory, since in one case (Table) the amount of the 2,3-dihydro-derivative (7b) is far in excess of that of the ketone (3).

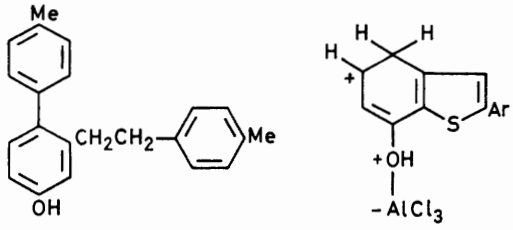
Undoubtedly the most interesting feature of the reactions of toluene or benzene and $AlCl_3$ with the hydroxybenzo[*b*]thiophens is the formation of the *same* ketone (3), irrespective of the position of the hydroxy-group in the benzenoid ring of the starting phenol. With 5- and 7-hydroxybenzo[*b*]thiophens it is obtained (25%) in admixture with the 2,3-dihydro-derivatives (7) after 0.5 h at room temperature; with the 4- and 6-hydroxy-isomers a longer time (5 days) is required in order to obtain the optimum yield (30—50%; Table). Prolonged treatment of 4- or 7-hydroxy-DHBT (7a) or (7b) with $AlCl_3$ in benzene gave intractable material which, in each case, contained at least two ketones (i.r.), neither of which was identical with the ketone (3a).

The ketones (3a) and (3b) ($\nu_{max.}$ 1 676 and 1 673 cm^{-1}, respectively) possessed a fully aromatic thiophen ring (n.m.r. spectrum) and, since 2-phenyl- (1e) or 2-*p*-tolyl-4-hydroxy-DHBT (1f) gave the ketones (3a) and (3b) on prolonged treatment with $AlCl_3$ in benzene or toluene respectively, it was assumed that the thiophen ring contained a 2-aryl substituent. A molecule of solvent had also undergone overall addition to the benzenoid ring. A signal at δ *ca.* 4.3 (1H) in the n.m.r. spectrum indicated a methine group flanked by two aromatic residues, thus locating the second aryl substituent in either the 4- or the 7-position. Aromatisation of the ketone (3b) gave the corresponding phenol (8), the n.m.r. spectrum of which showed an *ortho*-coupled proton signal upfield from the remaining complex group of aromatic proton signals. Such a signal (due to 5-H or 6-H, respectively) would



(7) (8)

a; 4-OH
b; 7-OH



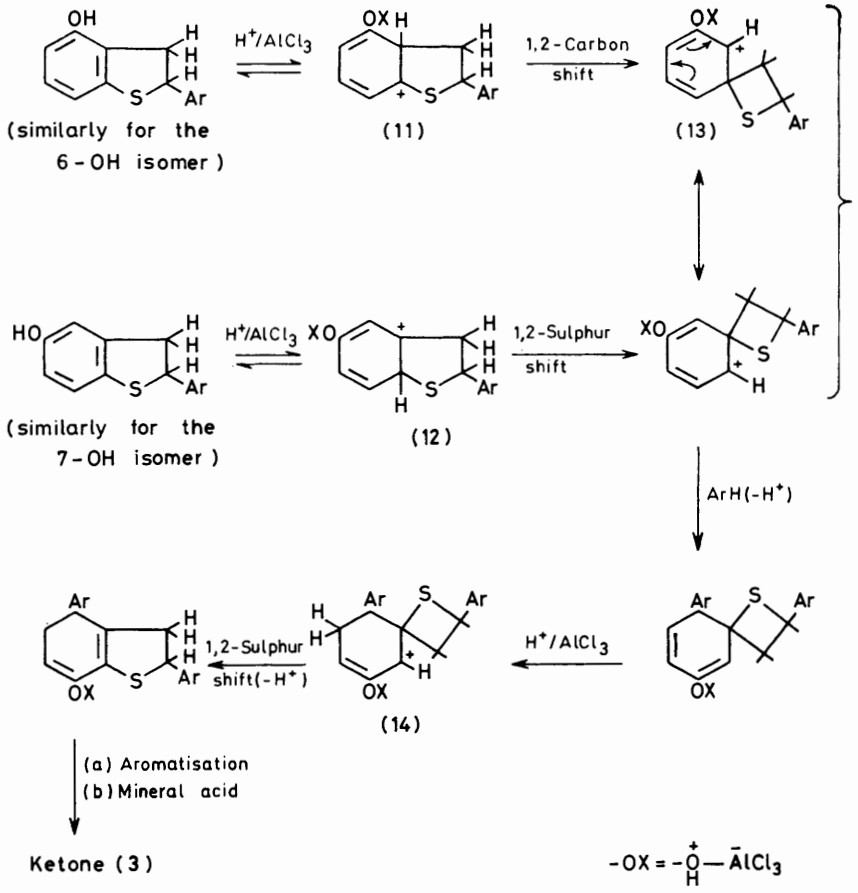
(9) (10)

appear in the spectrum of both 4- and 7-hydroxybenzo-[*b*]thiophen. In a further attempt to locate the position of the hydroxy-group, the phenol (8) was subjected to hydrodesulphurisation with Raney nickel. The product (9) showed no additional methyl signal in the n.m.r. spectrum, thus confirming that one of the aryl groups is in the 2-, and not in the 3-position. It showed two protons *ortho*- to the OH group (n.m.r. spectrum), and it reacted rapidly with bromine in chloroform, to give a dibromo-derivative (mass spectrum), in which the two *p*-tolyl residues were intact. The phenol (9) must, there-

fore, have been derived from a 7-hydroxybenzo[*b*]-thiophen.

Since a further simple method for distinguishing between 4- and 7-hydroxybenzo[*b*]thiophens would be desirable, we investigated the reactions of each with some transition metal ions, in the belief that the 7-hydroxy-group might form a coloured complex involving the participation of a non-bonding electron pair on the sulphur atom (*cf.* 8-hydroxyquinoline), whereas the 4-hydroxy-isomer could not. We found that 7-hydroxybenzo[*b*]-thiophen and a range of its simple derivatives (but not the DHBT derivative) gave an intense green colour with the hexammine Ni(II) ion and a blue colour with the Fe(III) ion, where 4-hydroxybenzothiophen did not. The phenol (8) gave a positive result in each of these tests, thus confirming the proposed structure.

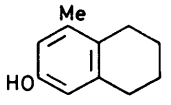
The introduction of the aryl group into the thiophen ring of ketone (3) may be regarded as a dehydrogenation of the first-formed 2-aryl-DHBT derivative (1). Such aromatisation reactions normally require higher temperatures,[2,3] but occasionally they occur at room temperature.[1] In considering the mechanism for the introduction of the aryl group into the benzenoid ring, we propose that the ring is protonated by moist $AlCl_3$ *ortho* or ***para*** to the strongly electron-donating hydroxy-group. Although phenols form complexes with $AlCl_3$, they are nevertheless highly activated towards Friedel–Crafts reagents. The precise nature of the complex is not known in the present case. It could be (*a*) a binary complex in which the phenol is structurally unchanged;[12] or (*b*) a complex of $AlCl_3$ with the tautomeric oxo-form of the phenol.[13] We shall represent it (ArOX in the Scheme) as alternative (*a*).



SCHEME

In the case of 7-hydroxybenzo[*b*]thiophen, for which the reaction with benzene or toluene apparently proceeds without rearrangement, we initially considered protonation in the 4-position. However, the resulting carbocation (10) would then produce a 5-aryl derivative, rather than the observed 4-aryl isomer. The ion (10) would need to undergo a 1,2-hydride ion shift (*cf.* 1-naphthol [14]) in order to explain the experimental observations. However, a similar mechanism could not explain the rearrangement reactions which were observed for the isomeric hydroxy-compounds. We therefore propose that the initial protonation occurs at a ring junction position (Scheme), and that the resulting carbocations (11) and (12) rearrange to give the same spiro-intermediate (13), which can then react as an electrophile towards benzene or toluene. We do not know whether the re-aromatisation of the thiophen ring takes place before or

after the formation of the spiro-intermediate. The former process is shown in the Scheme, since the ensuing thietan ring (13) will be less strained than the alternative thiet structure would be. There is a precedent for rearrangement reactions proceeding *via* spirocyclic intermediates, both in preparative benzo[*b*]thiophen chemistry [15] and in the acid-catalysed isomerisation of the reduced naphthol (15).[16] 1,2-Sulphur shifts take place more readily than the corresponding carbon shifts;



(15)

hence a possible reason for the relative ease of the reactions involving 5- and 7-hydroxybenzo[*b*]thiophen. Further, since none of the 4-oxo-isomer of the ketone (3) has been isolated, it seems that the recyclisation step involving the protonated intermediate (14) proceeds entirely *via* a 1,2-sulphur shift.

From the addition reaction of 5-hydroxybenzo[*b*]-thiophen with benzene, we obtained some 7-hydroxy-2-phenyl-DHBT (1c) (10%), which no doubt arose by direct recyclisation of the ion (13) (1,2-sulphur shift). Otherwise we know of no other reactions of benzo[*b*]-thiophen or its derivatives which involve this novel rearrangement. We are satisfied that the addition of benzene or toluene (0.5 h) to the isomeric hydroxybenzo-[*b*]thiophens proceeded without rearrangement. Clearly, however, it is important to realise that, under acidic conditions, benzo[*b*]thiophens containing strongly electron-donating substituents may be susceptible to this type of behaviour.

EXPERIMENTAL

General details have been described before.[1-3] Discussion will be restricted in the main to those reactions from which pure products have been isolated.

Fries Rearrangement of 4-Acetoxybenzo[b]*thiophen.*—Heating 4-acetoxybenzo[*b*]thiophen for 24 h with aluminium chloride in benzene as described before [4] gave a semi-solid product which was triturated with light petroleum–ether (10 : 1). The resulting solid was filtered off, to give 7-acetyl-4-hydroxybenzo[*b*]thiophen as needles (25%), m.p. 259—260 °C (lit.,[4] 254—256 °C) (from light petroleum–chloroform).

Concentration of the mother-liquors gave 5-acetyl-4-hydroxybenzo[*b*]thiophen (70%) as *needles*, m.p. 96—98 °C (from ether–light petroleum) (Found: C, 62.3; H, 4.25%; M^+, 192. $C_{10}H_8O_2S$ requires C, 62.5; H, 4.2%; *M*, 192); $\nu_{max.}$ 1 620 cm^{-1} (C=O); δ 2.65 (s, Me), 10.75 (s, OH), 7.23 (d, 7-H), 7.31 (d, 2-H), 7.51 (d, 6-H), and 7.60 (d, 3-H) ($J_{2.3}$ 5.5, $J_{6.7}$ 8.5, $J_{3.7}$ 0.7, and $J_{2.6}$ 0.5 Hz).

6-Acetoxybenzo[b]*thiophen.*—A mixture of 6-hydroxybenzo[*b*]thiophen [17] (2 g), acetic anhydride (10 ml), and acetic acid (4 ml) was heated under reflux for 0.5 h, then cooled and poured into water. An excess of sodium hydrogencarbonate was added and then the product was filtered off, and washed well. It gave long *needles* (2.3 g, 90%), m.p. 71—72 °C (from light petroleum) (Found: C, 62.35; H, 4.2%; M^+, 192); $\nu_{max.}$ 1 755 cm^{-1} (C=O); δ 2.25 (s, Me).

Formed similarly from 7-hydroxybenzo[*b*]thiophen,[18] 7-acetoxybenzo[*b*]thiophen (91%) was isolated by extraction with ether. It formed an *oil*, b.p. 118 °C (bath) at 0.4 mmHg (Found: C, 62.45; H, 4.2%; M^+, 192); $\nu_{max.}$ 1 775 cm^{-1} (C=O); δ 2.40 (s, Me).

Attempted Fries Reactions.—(a) *With 6-acetoxybenzo*[b]*thiophen.* (i) *In benzene.* A mixture of 6-acetoxybenzo[*b*]-thiophen (1 g, 0.0052 mol), anhydrous aluminium chloride (1.6 g, 0.0104 mol), and benzene (30 ml) was stirred under reflux for 4 h, then aqueous 10% hydrochloric acid (30 ml) was added to the cooled mixture. Extraction with ether gave 3-acetyl-6-hydroxy-2-phenylbenzo[*b*]thiophen as *needles* (0.8 g, 57%) [from chloroform–light petroleum (charcoal)] (Found: C, 71.3; H, 4.6%; M^+, 268. $C_{16}H_{12}O_2S$ requires C, 71.6; H, 4.5%; *M*, 268); $\nu_{max.}$ 1 660 cm^{-1} (C=O); δ 2.40 (s, Ac), 7.01 (dd, 5-H), 7.24 (d, 7-H), 7.43 (s, Ph), and 8.09 (d, 4-H) ($J_{4.5}$ 8.2 and $J_{5.7}$ 1.8 Hz).

When the reaction was repeated for 0.5 h, a yellow gum was obtained, which slowly solidified. Recrystallisation from light petroleum (charcoal) gave 6-acetoxy-2,3-dihydro-2-phenylbenzo[*b*]thiophen (1b) as *plates* (24%), m.p. 130—131 °C (Found: C, 71.35; H, 5.25%; M^+, 270. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.2%; *M*, 270); $\nu_{max.}$ 1 730 cm^{-1} (C=O); δ 2.26 (s, Me) and 5.15 (t, 2-H).

(ii) *In dichloromethane.* The reaction was also carried out at room temperature for 4 h in dichloromethane (40 ml). The mixture was treated as usual with hydrochloric acid, then organic material was extracted into chloroform. The extracts were washed (NaOH, then H_2O), dried, and evaporated, then the residue was chromatographed on silica. Elution with light petroleum–ethyl acetate (4 : 1) gave first 6-acetoxy-3-acetylbenzo[*b*]thiophen (0.45 g, 38%) as *needles*, m.p. 138—139 °C (from chloroform–light petroleum) (Found: C, 61.55; H, 4.0%; M^+, 234. $C_{12}H_{10}O_3S$ requires C, 61.5; H, 4.3%; *M*, 234); $\nu_{max.}$ 1 760 and 1 660 cm^{-1} (C=O); δ 2.31 (s, OAc), 2.62 (s, Ac), 7.21 (dd, 5-H), 7.61 (d, 7-H), 8.22 (s, 2-H), and 8.75 (d, 4-H) ($J_{4.5}$ 8.7 and $J_{5.7}$ 2.2 Hz).

The second fraction gave 6-acetoxy-2-acetylbenzo[*b*]-thiophen (0.17 g, 16%) as *microneedles*, m.p. 144—145 °C (from chloroform–light petroleum) (Found: C, 61.5; H, 4.1%; M^+, 234); $\nu_{max.}$ 1 760 and 1 655 cm^{-1} (C=O); δ 2.32 (s, OAc), 2.62 (s, Ac), 7.10 (dd, 5-H), 7.55 (dd, 7-H), 7.86 (d, 4-H), and 7.92 (d, 3-H) ($J_{4.5}$ 8.5, $J_{5.7}$ 1.9, and $J_{3.7}$ 0.6 Hz).

Acidification and extraction of the alkaline washings with ether gave 6-hydroxybenzo[*b*]thiophen (0.3 g, 39%).

(b) *With 7-acetoxybenzo*[b]*thiophen.* The reaction was carried out in boiling benzene (4 h) as in method (a). Neutral and phenolic materials were isolated with ether in the usual way. The phenolic fraction crystallised from light petroleum (b.p. 40—60 °C) to give 2,3-dihydro-7-hydroxy-3-phenylbenzo[*b*]thiophen (2c) as *plates* (51%), m.p. 43—43.5 °C (Found: C, 73.4; H, 5.1%; M^+, 228. $C_{14}H_{12}OS$ requires C, 73.65; H, 5.3%; *M*, 228); no C=O absorption in the i.r.; δ 3.26 (d, 2-CH_2), 4.23 (t, 3-H), and 6.30 (s, OH). The mother-liquors were separated by preparative t.l.c. ($CHCl_3$) into two components, neither of which could be obtained quite pure. The slower running component was 4-acetyl-7-hydroxybenzo[*b*]thiophen (*ca.* 10%) (Found: M^+, 160. $C_{10}H_8O_2$ requires *M*, 160); $\nu_{max.}$ 1 635 cm^{-1} (C=O); δ [$(CD_3)_2SO$] 2.55 (s, Ac), 6.85 (d, 6-H), 7.35 (d, 2-H), 7.80 (d, 5-H), and 7.97 (d, 3-H) ($J_{5.6}$ 7.9 and $J_{2.3}$ 5.8 Hz). The other product was 4-acetyl-2,3-dihydro-7-hydroxybenzo[*b*]-

thiophen (*ca.* 10%) (Found: M^+, 162. $C_{10}H_{10}O_2$ requires M, 162); $\nu_{max.}$ 1 635 cm^{-1} (C=O); δ [$(CD_3)_2SO$] 2.52 (s, Ac), 3.28 (m, $CH_2{\cdot}CH_2$), 6.82 (d, 6-H), and 7.80 (d, 5-H) ($J_{5,6}$ 8.0 Hz).

The neutral product (*ca.* 10%) consisted mainly of 7-acetoxy-2,3-dihydro-3-phenylbenzo[*b*]thiophen (2d) (Found: M^+, 270. $C_{16}H_{14}O_2S$ requires M, 270); $\nu_{max.}$ 1 735 cm^{-1} (C=O); δ 2.37 (s, OAc), 3.25 (m, 2-CH_2), and 4.56 (t, 3-H).

(c) *With 4-acetoxybenzo*[b]*thiophen.* The oily product obtained in the usual way from the reaction with benzene–$AlCl_3$ (48 h) at room temperature was chromatographed on alumina. Elution with light petroleum–ether (1 : 1) gave 4,5-dihydro-2,4-diphenylbenzo[*b*]thiophen-7(6*H*)-one (3a) (17%) as *needles*, m.p. 107—108 °C (from chloroform–light petroleum) (Found: C, 78.85; H, 5.4; S, 10.5%; M^+, 304. $C_{20}H_{16}OS$ requires C, 78.9; H, 5.3; S, 10.5%; M, 304); $\nu_{max.}$ 1 676 cm^{-1} (C=O); δ 2.25—2.6 (m, $CH_2{\cdot}CH_2$), and 4.38 (m, ArC*H*Ar').

Continued elution gave material from which 4-acetoxy-5-acetyl-2,3-dihydro-3,7-diphenylbenzo[*b*]thiophen (4) (tentative structure) could sometimes be crystallised. It formed needles (8%), m.p. 96—97 °C (from ether–light petroleum) (Found: M^+, 388.118. $C_{24}H_{20}O_3S$ requires M^+, 388.113); $\nu_{max.}$ 1 755 and 1 700 cm^{-1} (C=O); δ 2.24 (s, OAc), 2.50 (s, Ac), and 4.08 (t, 3-H).

Reactions of Hydroxybenzo[b]*thiophens with Benzene or Toluene.*—(a) *General procedure.* A mixture of the appropriate hydroxybenzo[*b*]thiophen (2.0 g, 0.0013 mol), freshly powdered aluminium chloride (3.54 g, 0.0026 mol), and benzene or toluene (20 ml) was stirred at room temperature either for 0.5 h or for 5 days. The resulting deep red mixture was then poured into an excess of aqueous 20% hydrochloric acid and phenolic and neutral fractions were isolated in the usual way with ether. Most of the oily 2-aryl-DHBT derivatives (1) could be characterised as their crystalline *S,S*-dioxides, but the oxidation (H_2O_2–AcOH) was often sluggish, and the products (*ca.* 50%) had usually to be isolated by dilution of the reaction mixture with water, followed by the addition of an excess of sodium hydrogen carbonate, and extraction with ether. Traces of the 3-aryl-DHBT derivatives (2) in the total phenolic product before oxidation could be detected by means of the characteristic triplet in the n.m.r. spectrum at δ 4.3—4.5 (3-H) (in $CDCl_3$); traces of the DHBT derivatives (7) showed a broad signal at δ *ca.* 3.3 ($CH_2{\cdot}CH_2$).

(b) *4-Hydroxybenzo*[b]*thiophen.* (i) *For 0.5 h.* The ethereal solution of phenolic material from the reaction with toluene was filtered through alumina, to give 4-hydroxy-2-*p*-tolyl-DHBT (1f) as a clear oil (67%), which was purified by short-path distillation at 175 °C (bath) and 0.2 mmHg (Found: M^+, 242. $C_{15}H_{14}OS$ requires M, 242); δ 4.97 ($CDCl_3$), 4.60 (C_6D_6) (t, 2-H). The 1,1-*dioxide* crystallised from ethanol as needles, m.p. 210—212 °C (Found: C, 65.7; H, 5.0%; M^+, 274. $C_{15}H_{14}O_3S$ requires C, 65.7; H, 5.1%; M, 274); δ 4.76 (t, 2-H).

Obtained similarly from the reaction with benzene, 4-hydroxy-2-phenyl-DHBT (1e) (60%) (Found: M^+, 228. $C_{14}H_{12}OS$ requires M, 228) showed δ 4.99 ($CDCl_3$), 4.67 (C_6D_6) (t, 2-H). The 1,1-dioxide formed *needles*, m.p. 202—203 °C (Found: C, 64.5; H, 4.6%; M^+, 260. $C_{14}H_{12}O_3S$ requires C, 64.6; H, 4.6%; M, 260); δ 4.68 (t, 2-H).

In some experiments, 4-hydroxy-DHBT (7a) was obtained (up to 40%), and could be isolated as described below.

(ii) *For 5 days.* Short-path distillation [140 °C (bath) at 0.2 mmHg] of the phenolic fraction from either the benzene or the toluene reaction gave 4-hydroxy-DHBT (7a) as long *needles* (31 and 33%, respectively), m.p. 51—52 °C (Found: C, 63.35; H, 5.3%; M^+, 152. C_8H_8OS requires C, 63.1; H, 5.3%; M, 152); δ 3.31 (m, $CH_2{\cdot}CH_2$). The 1,1-dioxide formed *cubes*, m.p. 226—227 °C (from ethanol) (Found: C, 52.45; H, 4.5%; M^+, 184. $C_8H_8O_3S$ requires C, 52.15; H, 4.4%; M, 184); δ 3.48 (m, $CH_2{\cdot}CH_2$).

The neutral material from the reaction with toluene crystallised from light petroleum, to give 4,5-dihydro-2,4-di-*p*-tolybenzo[*b*]thiophen-7(6*H*)-one (3b) as long *needles* (43%), m.p. 123—124 °C (Found: C, 79.5; H, 6.1; S, 9.7%; M^+, 332. $C_{22}H_{20}OS$ requires C, 79.5; H, 6.0; S, 9.65%; M, 332); $\nu_{max.}$ 1 673 cm^{-1} (C=O); δ 2.29, 2.31 (s, Me), 2.55 (m, $CH_2{\cdot}CH_2$), and 4.29 (m, ArC*H*Ar').

The ketone (3a), m.p. and mixed m.p. 106—107 °C, was obtained similarly (39%) from the reaction with benzene.

(c) *5-Hydroxybenzo*[b]*thiophen.* Neutral material from the reaction with benzene (0.5 h or 5 days) was dissolved in benzene and filtered through alumina. Evaporation gave the ketone (3a) (16 and 38%, respectively), identical with that already described.

Phenolic material from the reaction with benzene (0.5 h) was chromatographed on alumina. Elution with light petroleum–ether (1 : 1) gave a fraction (40%) enriched with 5-hydroxy-2-phenyl-DHBT (Found: M^+, 228); δ 5.12 (t, 2-H), 6.91 (dd, 6-H), 7.20 (d, 4-H), and 7.59 (d, 7-H) ($J_{6,7}$ 8.5 and $J_{4,6}$ 2.5 Hz). The 1,1-*dioxide* formed needles, m.p. 218—219 °C (from ethanol) (Found: C, 64.4; H, 4.7%; M^+, 260); δ 4.71 (t, 2-H). The second fraction was impure and was subjected to preparative t.l.c. [in light petroleum–ethyl acetate (1 : 1)]. The major component was 7-hydroxy-2-phenyl-DHBT (1c) (5%), identical with that described below.

(d) *6-Hydroxybenzo*[b]*thiophen.* The reaction with benzene (0.5 h) gave 6-hydroxy-2-phenyl-DHBT (78%) as an oil (Found: M^+, 228); δ 5.23 (t, 2-H). Acetylation in the usual way gave 6-acetoxy-2-phenyl-DHBT (1b), identical with the product obtained from the attempted Fries reaction on 6-acetoxybenzo[*b*]thiophen.

Similar reaction with toluene gave 6-hydroxy-2-*p*-tolyl-DHBT (75%) as an oil (Found: M, 242); δ 5.00 (t, 2-H), 7.11 (dd, 5-H), 7.25 (d, 7-H), and 7.98 (d, 4-H) ($J_{4,5}$ 8.0 and $J_{5,7}$ 2.0 Hz). The 1,1-*dioxide* formed needles (from ethyl acetate–light petroleum), m.p. 218—219 °C (Found: C, 65.8; H, 4.85%; M^+, 274); δ 4.84 (t, 2-H).

The ketones (3a) and (3b) were isolated in *ca.* 15% yield from the reactions (5 days) with benzene and toluene respectively.

(e) *7-Hydroxybenzo*[b]*thiophen.* The reaction with benzene (0.5 h) gave mainly 2,3-dihydro-7-hydroxybenzo[*b*]-thiophen (7b) (Found: M^+, 152); δ 3.26 (br, $CH_2{\cdot}CH_2$). The phenolic fraction also contained 7-hydroxy-2-phenyl-DHBT (1c) (Found: M^+, 228); δ 5.16 (t, 2-H) and 6.66 (d, 6-H) (signals for the other aromatic protons were unresolved). It showed chromatographic characteristics similar to those of the minor product from the reaction of 5-hydroxybenzo[*b*]-thiophen with benzene. Analogous results were obtained with toluene (0.5 h) (see Table).

Neutral material from the reaction with benzene or toluene (5 days) was dissolved in ether and passed through alumina in order to remove polymeric material. Evaporation gave the ketones (3a) and (3b) (23 and 18%), respectively. The same ketones were isolated in lower yields from the

neutral extract from the reaction (0.5 h) with benzene or toluene.

Identification of 2,4-*Di*-(p-*tolyl*)*benzo*[b]*thiophen*-7(6H)-*one* (3b). A mixture of the ketone (3b) (0.4 g) and sulphur (1.5 g) was heated under reflux in *p*-cymene (50 ml) for 20 h. The cooled and filtered solution was then evaporated and the residue was triturated with light petroleum, to give 7-hydroxy-2,4-di-(*p*-tolyl)benzo[*b*]thiophen (8) (0.2 g, 50%) as pale yellow *feathers*, m.p. 114—116 °C [from chloroform–light petroleum (charcoal)] (Found: C, 79.75; H, 5.5%; M^+, 330. $C_{22}H_{18}OS$ requires C, 79.95; H, 5.5%; *M*, 330); $\nu_{max.}$ 3 250 cm^{-1} (OH) (no C=O absorption); δ 2.35 (s, Me), 2.40 (s, Me), 6.77 (d, 6-H), and 7.1—7.9 (remainder of arom. H) ($J_{5,6}$ 8.4 Hz).

Refluxing the phenol with ethanolic Raney nickel for 0.5 h gave solid material (Found: M^+, 302. $C_{22}H_{22}O$ requires *M*, 302); δ 6.75 (m, 2 H, protons *ortho* to OH). Its solution in chloroform was treated with an excess of bromine in chloroform for 10 min. The product showed M^+, 458 ($C_{22}H_{20}$-$^{79}Br_2O$ requires M^+, 458) and gave no signal at δ 6.75 in the n.m.r. spectrum; with neutral aqueous iron(III) chloride or ammoniacal nickel(II) chloride, it gave the colour reactions described in the text.

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