Addition Reactions of Benzo[*b*]thiophen. Part 3.[1] Addition and Ring-opening Reactions with Phenolic Ethers

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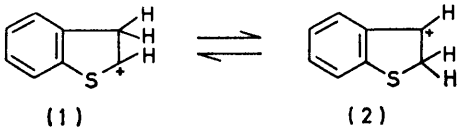
In the presence of aluminium chloride, anisole, phenetole, diphenyl ether, and (methylthio)benzene are added rapidly across the 2,3-bond in benzo[*b*]thiophen to give, *inter alia*, a mixture of 2- and 3-(*p*-substituted aryl)-2,3-dihydrobenzo[*b*]thiophens (3) and (4). Contrary to expectation, the 2-isomer predominates in all cases, and the addition is irreversible. Reaction with anisole also leads to a novel ring-opened product, *viz.* (*E*)-4-methoxy-2′-methylthiostilbene (9a), which was synthesised unambiguously. It is believed that benzo[*b*]thiophen is *S*-methylated by PhOMe–$AlCl_3$ in a ' push–pull ' reaction, and that the resulting positive charge is delocalised into the ring, thus allowing the 2-position to participate in electrophilic attack on a second molecule of anisole. The resulting quadrivalent sulphur intermediate achieves stabilisation by means of a rapid ring-opening reaction. Other aromatic methyl ethers give analogous products, but phenetole, diphenyl ether, and (methylthio)benzene do not promote ring-opening. The ring-opening reaction is aided by the addition of MeBr– or EtBr–$AlCl_3$; even phenetole will then undergo ring-opening. Under these conditions the *S*-alkyl group in the ring-opened product comes from the starting ether, and not from the added MeBr or EtBr.

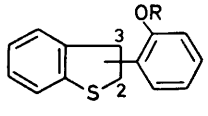
EARLIER we have shown that benzo[*b*]thiophen [2] and some of its ring-substituted derivatives [1] readily undergo addition reactions across the 2,3-double bond when treated with an aromatic solvent at room temperature or below in the presence of $AlCl_3$ or other Lewis acids. We postulated that benzo[*b*]thiophen is protonated by moist $AlCl_3$, and that the resulting carbocations (1) and (2) then react as electrophiles towards a second aromatic molecule (ArH) (which may be either the solvent or a second molecule of benzo[*b*]thiophen), to give the addition products (3) or (4). With benzene and with solvents less reactive than benzene towards electrophiles (*e.g.* PhCl), the dimers (3a), (3b), (4a), and (4b) are formed preferentially; with the more reactive solvents (*e.g.* PhMe and PhEt), only the solvent addition compounds (3c), (3d), (4c), and (4d) are formed. Surprisingly, possibly for steric reasons, 1,3,5-trimethylbenzene does not add to benzo[*b*]thiophen: the reaction gives only the dimeric products (3a), (3b), (4a), and (4b). In all the cases just mentioned, the 3-substituted DHBT † derivatives predominate.



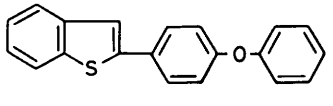
(1) (2)

(3) (4)

a ; Ar = 2 - benzo [*b*] thienyl
b ; Ar = 3 - benzo [*b*] thienyl
c ; Ar = *p* - MeC_6H_4
d ; Ar = *p* - EtC_6H_4
e ; Ar = *p* - $MeOC_6H_4$
f ; Ar = *p* - $EtOC_6H_4$
g ; Ar = *p* - $PhOC_6H_4$
h ; Ar = *p* - $MeSC_6H_4$



(5) a ; 2 - isomer
b ; 3 - isomer



(6)

We now describe reactions of benzo[*b*]thiophen with aromatic ethers, since these represent solvents which are the most reactive towards electrophiles. Even though their reactivity is lowered by complex formation with $AlCl_3$ or other Lewis acids, aromatic ethers rapidly undergo Friedel–Crafts alkylation.[3]

Addition Reactions.—Products obtained from the reaction of benzo[*b*]thiophen with various ethers are listed in the Table. Several interesting points are apparent: (*a*) in all the addition reactions the 2-aryl-DHBT derivative (3) predominated, although considerable amounts of the 3-aryl isomer (4) were also formed; (*b*) in most reactions, small amounts of the *ortho*-substituted products (5a) and (5b) were detected; (*c*) dimers [one or more of (3a), (3b), (4a), and (4b)] were formed in only low yield; and (*d*) some reactions gave ring-opened products (see later). Although $AlCl_3$ can be used to dealkylate ethers, the addition products [*e.g.* (3e) and (4e)] remained intact under the conditions used.

It was not always possible to separate the mixtures of 2- and 3-aryl-DHBT derivatives, but structures were readily assigned by making use of the observation [2] that the characteristic triplet due to 2-H in the ^1H n.m.r. spectrum of a 2-aryl compound (3) is invariably *ca.* 0.4 p.p.m. to low field of that for 3-H in the 3-aryl isomer (4). The other spectroscopic criteria [2] for confirming the structures of the two isomers were applied wherever

† As before,[1,2] 2,3-dihydrobenzo[*b*]thiophen is referred to as DHBT.

Products [a] from the reaction of benzo[*b*]thiophen with phenolic ethers

Reaction	Reagents	Catalyst	Time (h)	DHBT derivatives (% yield) *p*-Substituted aryl 2-	*p*-Substituted aryl 3-	*o*-Substituted aryl 2- (5a)	*o*-Substituted aryl 3- (5b)	Ring-opened products (% yield)	Dimers [b] (3a), (3b), (4a), (4b) (%)
1	PhOMe	$AlCl_3$	0.5	(3e) (37)	(4e) (23)			(9a) (40)	
2	PhOMe (−20 °C)	$AlCl_3$	1	(3e) (55)	(4e) (43)	0.7	0.7		Trace
3	PhOMe	$SnCl_4$	18	(3e) (41)	(4e) (35)	4	3		
4	PhOMe	BF_3	18	(3e) (54)	(4e) (37)	2	3	(9a) (trace)	3
5	PhOEt	$AlCl_3$	2	(3f) (42)	(4f) (29)	9	7	(9b) (1)	10
6	PhOEt	BF_3	24	(3f) (57)	(4f) (34)	4	2	(9b) (2)	Trace
7	PhOPh	$AlCl_3$	0.5	(3g) (27)	(4g) (20)	4	8		*c*
8	PhSMe	$AlCl_3$	2	(3h) (47)	(4h) (38)	4	4		6
9	PhOMe–MeBr	$AlCl_3$	2	(3e) (20)	(4e) (14)	2	1	(9a) (53)	6
10	PhOMe–EtBr	$AlCl_3$	2	(3e) (14)	(4e) (9)	2	0.7	(9a) (67)	5
11	PhOEt–EtBr	$AlCl_3$	2	(3f) (16)	(4f) (17)	5	2.5	(9b) (54)	3
12	PhOEt–MeBr	$AlCl_3$	2	(3f) (15)	(4f) (8)	7	1	(9b) (62)	5
13	PhOEt–MeBr	BF_3	24	(3f) (47)	(4f) (30)	4	2	(9b) (11)	4
14	PhOEt–MeF	BF_3	24	(3f) (40)	(4f) (25)	3	3	(9b) (13) [d] (9c) (9)	5

[a] Data were obtained (g.l.c.) for the total product after the completion (t.l.c.) of the reaction. [b] The mixture was not further investigated. [c] The 2-aryl product (6) (37%) and its 3-isomer (2.5%) were also formed. [d] Percentages estimated from n.m.r. spectrum.

possible. In some cases (see Experimental section), oily products could be characterised as their crystalline *S,S*-dioxides. Authentic samples of 2- and 3-(*p*-methoxyphenyl)-DHBT (3e) and (4e) were prepared for comparison by converting the appropriate *p*-methoxyphenylbenzo[*b*]thiophen into the *S,S*-dioxide, reducing catalytically, and treating the resulting DHBT 1,1-dioxide with $LiAlH_4$.

As before,[1,2] the reactions were affected by changes in temperature, and depended on the batch of catalyst used. Reactions were taken to completion (t.l.c.), then the total product was analysed by g.l.c. If the reaction was stopped after 0.5 h and due allowance was made for recovered starting material, the relative proportions of products were roughly similar to those quoted in the Table. Reactions 1 and 2 (Table) show the effect of temperature change on the PhOMe–$AlCl_3$ reaction: although the relative proportions of the 2- and 3-aryl-DHBT isomers (3e) and (4e) remain almost the same, the reaction at 20 °C gives a considerable amount of ring-opened product.

Tin(IV) chloride and boron trifluoride both catalyse the addition of ethers (but not of less reactive aromatic solvents [2]) to benzo[*b*]thiophen (Reactions 3, 4, and 6; Table). Reaction is slower than for $AlCl_3$, but the ratio of 2- to 3-substituted addition products is about the same.

In the addition reactions with ethers, benzo[*b*]thiophen showed little tendency to undergo self-condensation to the dimers (3a), (3b), (4a), or (4b). This is in keeping with our earlier proposal [2] that dimer formation becomes significant only when the aromatic solvent is less reactive than benzo[*b*]thiophen towards electrophiles.

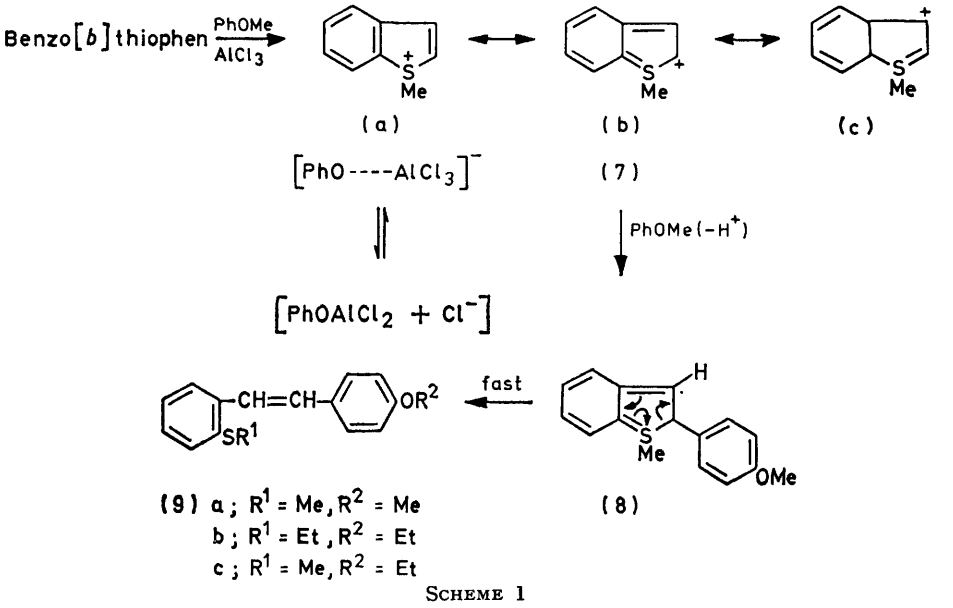
The reaction with diphenyl ether was unusual in that the addition products were accompanied by the substitution product 2-(*p*-phenoxyphenyl)benzo[*b*]thiophen (6) (37%). The structure (6) was confirmed by reductive hydrodesulphurisation to 1-(*p*-phenoxyphenyl)-2-phenylethane. Mixtures of 2- and 3-aryl-DHBT derivatives will give the 2-arylbenzo[*b*]thiophen in the $AlCl_3$ reaction,[1,2] but the aromatisation process usually requires elevated temperatures.

The most interesting aspect of these addition reactions is the formation of mixtures of 2- and 3-aryl-DHBT derivatives in the ratio of 1 : 1.2 to 1.6 in favour of the 2-isomer, irrespective of the ether (or thioether) used. By extrapolation of our earlier [2] results, the highly reactive ethers were expected to give predominantly the 3-aryl isomer. A further observation also needs to be accounted for: the addition of phenolic ethers is seemingly an irreversible reaction, since the 2- and 3-aryl-DHBT derivatives were both unchanged by further treatment with $AlCl_3$ at room temperature. The addition of aromatic hydrocarbons, however, is a reversible reaction, and the mechanism for the reversal is similar to that observed for the disproportionation of alkylbenzenes.[2] In this mechanism, the 2- or 3-aryl-DHBT is protonated, then ArH separates, to give the relatively stable ion (1) or (2). For the alkoxy-substituted aryl-DHBT derivatives, it seems that the dissociation step leading to these ions has a higher activation energy than that for the corresponding alkyl-substituted compound. This suggestion is supported by the finding that, in general, phenolic ethers containing an alkyl group in the ring do not undergo rearrangement of the ring alkyl group; instead, in the presence of $AlCl_3$, the alkyl group of the *O*-alkyl substituent prefers to migrate into the ring, especially if it can form a stable carbocation.[4]

The irreversibility of the reaction will mean that the formation of the products is subject to kinetic control only, and this factor alone may account for the low regiospecificity. However, the selectivity factor should also be considered. In the case of benzene and the alkylbenzenes, the preferred formation of the 3-aryl-DHBT derivative (4) was consistent with the expectation that the aromatic substrate would show selectivity towards ion (2)—the more reactive [2] of the two electrophiles (1) and (2). It seems likely that the high reacti-

vity of aromatic ethers will result in a much reduced selectivity for ion (2), with a concomitant increase in the amount of the 2-aryl-DHBT isomers (3) formed.

A suggested mechanism for the Friedel–Crafts alkylation of anisole involves initial attack of the electrophile on the oxygen atom of the ether to give an *n*-complex, from which the complexed alkyl group may be transferred to the nucleus.[5] The formation of a high proportion of *ortho*-alkylated product is said to indicate the participation of a non-bonding electron pair on the oxygen atom. This mechanism is therefore not likely to be of major significance in the present case. Nevertheless, it may explain why *ortho*-isomers * are formed, albeit in low yield, in this reaction, but not in reactions involving the addition of aromatic hydrocarbons.[2]



SCHEME 1

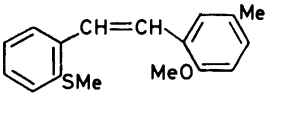
2- and 3-Bromobenzo[*b*]thiophen react with benzene or toluene–$AlCl_3$ at room temperature in an addition–elimination reaction, to give mainly the fully aromatic 2-arylbenzo[*b*]thiophen.[1] These bromo-derivatives undergo a similar reaction with anisole, to give 2-(*p*-methoxyphenyl)benzo[*b*]thiophen (62 and 66%, respectively). This reaction, particularly with the readily available 3-bromobenzo[*b*]thiophen, provides a convenient alternative to the usual lengthy cyclisation procedure (44% yield) [6] for preparing 2-(*p*-methoxyphenyl)benzo[*b*]thiophen. It is not catalysed by $SnCl_4$. 2,3-Dibromobenzo[*b*]thiophen reacts very slowly with anisole–$AlCl_3$ (*cf.* its lack of reactivity with benzene or toluene).[1]

* Pure *ortho*-isomers (5a) and (5b) have not been isolated. Structural assignments are based on the n.m.r. and mass spectra of the mixture of *o*- and *p*-isomers. Since *p*-alkylbenzenes can rearrange to the *meta*-isomers in the presence of $AlCl_3$, the similar formation of a *meta*-isomer in this case cannot be excluded. However, no *meta*-substituted products were identified in the reactions of benzo[*b*]thiophen with alkylbenzenes [2] and the retention times on g.l.c. relative to the *para*-derivative are more indicative of an *ortho* than of a *meta*-isomer.

Ring-opening Reactions.—The reaction of benzo[*b*]thiophen with PhOMe–$AlCl_3$ gave, in addition to the aforementioned products, a crystalline compound (40%), which contained an *S*-Me group (δ 2.44) and an *O*-Me group (δ 3.78). It was identified as the stilbene (9a) by catalytic reduction of the double bond and by hydrodesulphurisation with Raney nickel to 4-methoxybibenzyl. It was a single stereoisomer, but since the signals from the olefinic protons merged with those from the aromatic protons, it was not possible to establish the configuration from the ^1H n.m.r. spectrum. However, its synthesis from *o*-(methylthio)benzyl chloride and *p*-methoxybenzaldehyde by the Horner–Emmons reaction, which invariably proceeds stereospecifically for stilbenes,[6] showed it to be the *E*-isomer.

We established first that the addition compounds (3e) and (4e) (which are formed at −20 °C) and 2- or 3-(*p*-methoxyphenyl)benzo[*b*]thiophen are all unchanged when treated with PhOMe–$AlCl_3$ at 20 °C; none of these is therefore a precursor of the ring-opened product (9a).

Benzo[*b*]thiophen also underwent ring opening with *p*-methoxytoluene–$AlCl_3$; a higher temperature (60 °C) was required and the product (10) was obtained in only 13% yield, probably because of steric hindrance to *ortho*-attack. 2-Methylbenzo[*b*]thiophen gave the ring-opened



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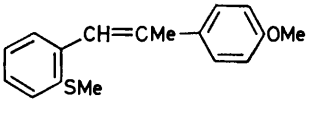
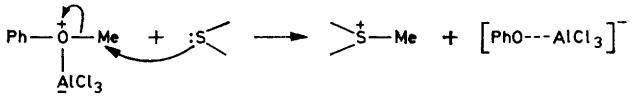


(11)

product (11) (12%) with PhOMe–$AlCl_3$ at 100 °C. 3-Methylbenzo[*b*]thiophen did not undergo ring opening, but gave the addition product, 2-(*p*-methoxyphenyl)-3-methyl-DHBT, with difficulty (100 °C) and in low yield (9%) (*cf.* its reaction with benzene or toluene).[1]

It seems likely that methylation of the sulphur atom by PhOMe–$AlCl_3$ is the first step in the ring-opening reaction, but we have no definite evidence to preclude methylation at a later stage. To our knowledge, the PhOMe–$AlCl_3$ system has not been used previously as a methylating agent. We tried unsuccessfully to methylate a variety of sulphur-containing compounds (*e.g.* thiols, sulphides, disulphides, and heterocyclic compounds) with the reagent. Only thiophen and benzo[*b*]thiophen gave *S*-methylated products and the stoicheiometric amount of phenol; dibenzothiophen was unchanged. The reaction with thiophen is being further investigated.

It is well known that anisole is cleaved by $AlCl_3$ to give phenol and MeCl; the latter might act as an *S*-alkylating agent as its Friedel–Crafts complex with $AlCl_3$. We dismissed this suggestion for two reasons: (*a*) the reaction takes place at a temperature far below that (100 °C) normally used to cleave ethers: indeed, the methoxy-group in (9a) remains intact during the reaction; (*b*) a Friedel–Crafts alkylating agent would undoubtedly also give *C*-alkylated products (*cf.* thiophen [7]), but none was observed. We therefore suggest that the electron-deficient methyl group (a soft acid) in the PhOMe–$AlCl_3$ complex (hard base–hard acid) is transferred to sulphur (a soft base) in an S_N2 reaction (Scheme 2). Such a process would satisfy Saville's



SCHEME 2

criteria [8] for a ' push–pull ' mechanism, and should be favoured. Aluminium bromide (hard acid) also gives the ring-opened product (9a) (21%). The PhSMe–$AlCl_3$ (soft base–hard acid) and the PhOMe–$SnCl_4$ (hard base–softer acid) systems should be less effective in the methylation process, and indeed give no ring-opened products with benzo[*b*]thiophen. Likewise, benzo[*b*]furan undergoes only addition of PhOMe because the oxygen atom (hard base) is not readily methylated.

The resulting sulphonium salt (7) can behave as an electrophile since the positive charge may be delocalised into both positions in the thiophen ring. Attack of anisole in the 2-position of ion (7) would give the quadrivalent sulphur intermediate (8), which might undergo electrocyclic ring fission stereospecifically to give the *E*-alkene (9a). Fission of the strained intermediate (8) to restore aromatic stability to the carbocycle and provide extended conjugation in the stilbene (9a) must provide the driving force for the reaction, and will be the fast step in the mechanistic sequence. Attack of anisole in the 3-position of (7) will not be favoured because the product, unlike its isomer (8), cannot achieve stability by ring fission.

We next treated benzo[*b*]thiophen with PhOEt–$AlCl_3$ at 20 °C, but obtained only a trace of the ring-opened compound (9b) (Table). We believe that this result reflects the difficulty of transferring an ethyl group to sulphur in the first step of the reaction. Phenetole is said to be cleaved more readily (S_N1) than anisole (S_N2) by $AlCl_3$.[9] However, in this case, the ethyl group should be transferred to sulphur less readily than the methyl group, partly because it is a harder acid,[10] and partly because in an S_N2 reaction (*cf.* Scheme 2) an ethyl group is much less reactive than a methyl group.

In order to test the mechanism (Scheme 1), benzo[*b*]-thiophen was treated with $AlCl_3$ in an excess of PhOMe–PhOEt (1 : 1) at 20 °C. It was expected that anisole would provide the carbocation (7), which would then attack both anisole and phenetole, to give the *two* ring-opened products (9a) and (9c), respectively. This was found to be the case, and the latter (41%) predominated [*cf.* (9a) (10%)], in keeping with the established fact [11] that PhOEt is more reactive than PhOMe towards electrophiles. Likewise, of the four addition products (3e), (3f), (4e), and (4f) (45%) which accompanied the ring-opened products in the competitive reaction, those [(3f) and (4f)] from the addition of PhOEt (26%) were in excess. The stilbene (9c) was prepared unambiguously by the Horner–Emmons reaction.

If the proposed mechanism (Scheme 1) is correct, a pre-formed *S*-methylbenzo[*b*]thiophenium salt [12] might be expected to undergo the ring-opening reaction. However, the tetrafluoroborate salt [(7); counter anion BF_4^-] was recovered unchanged (or gave only small amounts of benzo[*b*]thiophen in some cases) when treated with anisole at various temperatures, in the presence or in the absence of $AlCl_3$. The failure to react does not necessarily mean that the mechanism (Scheme 1) is incorrect. The importance of the role of the counter ion in governing the reactivity of sulphonium salts has recently been stressed.[13] Because the BF^-_4 ion is small, hard, and not easily polarised, it is likely to form a tight ion-pair with the positive sulphur atom (especially in a solvent of low dielectric constant, such as PhOMe), and thus reduce the electrophilic reactivity of the carbocation (7). There is an analogy in the chemistry of the tropylium ion, the ability of which to undergo electrophilic reaction with anisole depends markedly on the nature of the counter anion.[14] In an effort to provide a source of the $[PhO{-}{-}{-}{-}AlCl_3]^-$ ion (*cf.* Scheme 1), we carried out the reaction of *S*-methylbenzo[*b*]thiophenium tetrafluoroborate with PhOMe–$AlCl_3$ in the presence of phenol, but again no reaction was observed.

We still favour broadly the proposed mechanism, but feel that Scheme 1 may be an oversimplification. We therefore suggest a concerted mechanism, in which the anisole molecule attacks the 2-position as soon as a positive charge begins to develop on the sulphur atom.

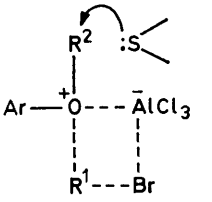
When benzo[*b*]thiophen was treated with other *S*-methylating agents (MeI–$AgPF_6$, methyl fluorosulphonate, or methyl toluene-*p*-sulphonate) in the presence of phenetole, there was again no reaction.

Finally, we treated benzo[*b*]thiophen with phenetole in the presence of Friedel–Crafts alkylating agents. These

normally give *C*-alkylated products, but some (*e.g.* MeF–$SbCl_5$) [15] are known to alkylate sulphur. In an initial experiment with PhOEt–EtBr–$AlCl_3$ (Reaction 11; Table), an *S*-ethylated product (9b) was obtained for the first time in a significant amount (54%). However, it seems that the *S*-Et group does *not* originate from the added alkyl halide because a similar reaction with PhOEt–MeBr–$AlCl_3$ (Reaction 12) also gave the same *S*-ethyl product (9b) (62%). Similarly with PhOMe–$AlCl_3$, the addition of MeBr increased the amount of the *S*-Me compound (9a) to 53%; addition of EtBr gave (9a) (67%) and no *S*-Et compound.

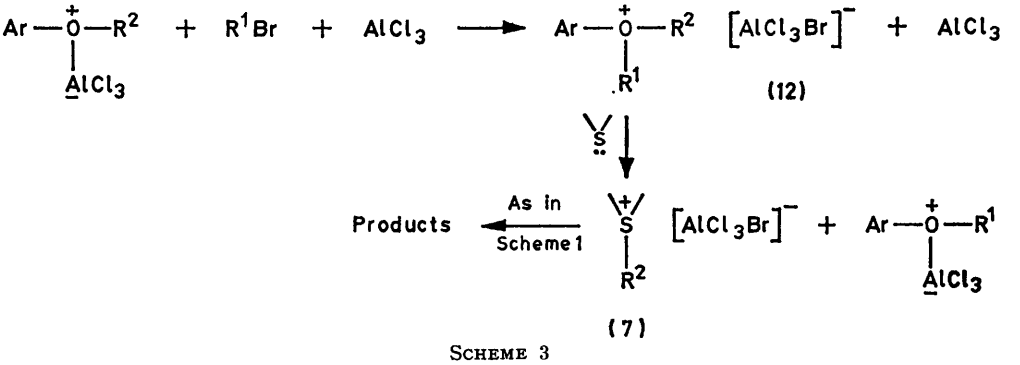
Little ring fission was noted for boron trifluoride and PhOMe or PhOEt (Reactions 4 and 6; Table). However, with MeBr–BF_3 or MeF–BF_3 and PhOEt (Reactions 13 and 14), the *S*-Et compound (9b) was obtained, albeit in low yield (11 and 13%, respectively). Interestingly, in the latter reaction the MeF gave rise to a small amount (9%) of the *S*-Me compound (9c). This is the only reaction in the present work in which *S*-alkylation was brought about by a Friedel–Crafts alkylation catalyst. There is other evidence that BF_3–alkyl fluoride is a significantly more powerful alkylating agent than BF_3–alkyl chloride or bromide.[16]

It must therefore be assumed that Scheme 3 represents an ' extreme ' mechanism, and that the added R^1Br–$AlCl_3$ aids the breaking of the O–R^2 bond (*cf.* Scheme 2). Perhaps the added R^1Br might interact with the $ArOR^2$,-$AlCl_3$ complex in a four-centre reaction (13), thus localising the positive charge on oxygen and aiding the transfer



(13)

of R^2 to sulphur. Whatever the mechanism, it seems that the group R^2 is transferred to sulphur so rapidly that the intermediate oxonium ion (12) is not actually formed. A similar argument will explain the role of MeBr or MeF in aiding the formation of ring-opened compounds with BF_3–PhOEt. The mixture $AlCl_3$–MeBr–toluene did not give a ring-opened product, thus highlighting the need for a phenolic ether to act as a source of the *S*-alkylating species.



SCHEME 3

It is easy to envisage that a phenolic ether will react with R^1Br–$AlCl_3$, to give a tertiary oxonium salt (12) (Scheme 3). Oxonium salts with the $[AlCl_4]^-$ anion are less stable than those with the $[SbCl_6]^-$ or $[BF_4]^-$ anion.[17] However, they are postulated as intermediates in the *C*-methylation of anisole,[5] in which case the R^1 group is transferred to the ring. In our experiments, *C*-alkylated products were not detected. However, oxonium salts, especially those derived from aliphatic ethers (Meerwein's salts) are well-known *O*- and *S*-alkylating agents.[12,17] Hence it should be possible for the salt (12) to alkylate benzo[*b*]thiophen (Scheme 3). This mechanism does not, however, explain why group R^2, rather than the added group R^1, is always transferred to sulphur. Other workers have shown that $Me_3O^+BF_4^-$, but not $Et_3O^+BF_4^-$, will *S*-alkylate benzo[*b*]thiophen,[12] and that $EtMe_2O^+$ BF_4^- is a methylating, rather than an ethylating agent.[17] Hence, salt (12; R^1 = Me, R^2 = Et) would be expected to give an *S*-Me, and not the observed *S*-Et compound.

EXPERIMENTAL *

General experimental details are given in refs. 1 and 2.

G.l.c. Separations.—These were carried out as before,[2] but with a column temperature of 230 °C and a flow rate of 60 ml min^{-1}. Components were always eluted in the following order: 3-(*o*-substituted)aryl-DHBT (5; 3-isomer) (t_R typically 8—10 min); 2-(*o*-substituted)aryl-DHBT (5; 2-isomer); 3-(*p*-substituted)aryl-DHBT (4); 2-(*p*-substituted)aryl-DHBT (3); dimers (3a), (3b), (4a), and (4b); ring-opened products (t_R typically 25—33 min).

Addition Reactions.—The general procedure given in Part 1 [2] was followed, except that 2.0 mol equiv. of aluminium chloride were used. Reactions were carried out at the temperature shown in the Table, and were continued until no benzo[*b*]thiophen remained (t.l.c.).

(a) *With anisole at* −20 °C. The oily mixture of 2-(*p*-methoxyphenyl)-DHBT (3e) [δ 5.02 ($CDCl_3$), 4.75 (C_6D_6) (t, 2-H)] and 3-(*p*-methoxyphenyl)-DHBT (4e) [δ 4.73

* Discussion will be restricted in the main to those reactions from which pure products were obtained. Details of other reactions and products are given in the text and in the Table.

($CDCl_3$), 4.42 (C_6D_6) (t, 3-H)] was oxidised under reflux for 0.5 h with hydrogen peroxide in acetic acid. Dilution with water gave 2-(p-*methoxyphenyl*)-*DHBT* 1,1-*dioxide* as needles (31%), m.p. 153—154 °C (from ethanol) (Found: C, 65.6; H, 5.0%; M^+, 274. $C_{15}H_{14}O_3S$ requires C, 65.7; H, 5.1%; *M*, 274); δ 3.75 (s, OMe) and 4.61 ($CDCl_3$), 4.13 (C_6D_6) (t, 2-H). The mother-liquors were kept at 0 °C for 24 h, and the resulting solid was crystallised from ethanol, to give 3-(p-*methoxyphenyl*)-*DHBT* 1,1-*dioxide* as prisms (23%), m.p. 163—164 °C (Found: C, 65.8; H, 4.85%; M^+, 274); δ 3.74 (s, OMe) and 4.55 ($CDCl_3$), 4.13 (C_6D_6) (t, 3-H).

(b) *With phenetole*. A solution of the oily product in light petroleum (100 ml) was kept at 0 °C for 24 h. 2-(*p*-Ethoxyphenyl)-DHBT (3f) (28%) separated as *plates*, m.p. 91—92 °C (from light petroleum) (Found: C, 75.25; H, 6.3%; M^+, 256. $C_{16}H_{16}OS$ requires C, 75.0; H, 6.25%; *M*, 256); δ 1.34 (t, CH_2Me), 3.94 (q, $O.CH_2Me$), and 5.07 (t, 2-H).

The mother-liquors were evaporated, to give an oil which consisted mainly (97%) of 3-(*p*-ethoxyphenyl)-DHBT (4f) (Found: M^+, 256); δ 1.45 (t, CH_2Me), 3.85 (q, $O.CH_2Me$), and 4.65 (t, 3-H).

(c) *With diphenyl ether*. Elution of a benzene solution of the oily product from alumina [with light petroleum–ether (10 : 1)] gave 2-(*p*-phenoxyphenyl)benzo[*b*]thiophen (6) as *plates* (20%), m.p. 164—165 °C (from light petroleum–chloroform) (Found: C, 79.4; H, 4.4%; M^+, 302. $C_{20}H_{14}OS$ requires C, 79.5; H, 4.6%; *M*, 302); δ 6.8—7.8 (m, arom. H).

Refluxing the ether (6) with ethanolic Raney nickel for 0.5 h gave 1-(*p*-phenoxyphenyl)-2-phenylethane as an oil (95% pure; g.l.c.). This slowly solidified to give needles, m.p. 71—72 °C (from ethanol); identical with authentic material.

The second fraction from the chromatogram was an oily mixture of the 2-aryl-DHBT derivative (3g) [δ 4.96 (t, 2-H)] and the 3-aryl isomer (4g) [δ 4.57 (t, 3-H)].

(d) *With methylthiobenzene*. A mixture of the 2- and 3-aryl-DHBT derivatives (3h) and (4h) was obtained; δ 5.00 and 4.65 (t, 2-H and 3-H, respectively) and 2.50 (s, SMe).

(e) *Use of other catalysts*. (i) A solution of benzo[*b*]thiophen (1 g) in anisole (25 ml) was stirred for 18 h with tin(IV) chloride (4 g, 2 mol equiv.), then the red mixture was poured into ice-cold aqueous 20% hydrochloric acid. Extraction with ether gave an oily product, the composition of which is shown in the Table.

(ii) A solution of benzo[*b*]thiophen (1 g) in phenetole (25 ml) was saturated with boron trifluoride and the orange mixture was stirred for 24 h. Work-up as just described gave the results shown in the Table (Reaction 6). Reaction 4 was carried out similarly.

1-(p-*Phenoxyphenyl*)-2-*phenylethane*.—A mixture of 1-(*p*-phenoxyphenyl)-2-phenylethanone [18] (14.4 g), hydrazine hydrate (15 ml), and diethylene glycol (70 ml) was heated under reflux for 2 h, then potassium hydroxide (7 g) was added, and the mixture was distilled until the temperature of the distillate reached 145 °C. The mixture was then successively heated under reflux for 2 h, distilled until the temperature of the distillate reached 195 °C, heated under reflux for 2 h, cooled, and poured into water. Extraction with ether gave *needles* (12.2 g, 89%), m.p. 71—72 °C (from ethanol) (Found: C, 87.85; H, 6.65%; M^+, 274. $C_{20}H_{18}O$ requires C, 87.55; H, 7.5%; *M*, 274); δ 3.0 (s, $CH_2{\cdot}CH_2$); identical with the product from the Raney nickel reaction.

2,3-*Dihydro*-2- *and* 3-(p-*methoxyphenyl*)*benzo*[b]*thiophen* (3e) *and* (4e).—(*a*) 2-(*p*-Methoxyphenyl)benzo[*b*]thiophen was prepared by Banfield's method,[19] except that the cyclisation of the intermediate sulphide with polyphosphoric acid was carried out in chlorobenzene at 170 °C for 1 h. The product (40%) crystallised from the cooled mixture as needles, m.p. 193—194 °C (lit.,[19] 193—194 °C).

Oxidation with H_2O_2–AcOH gave the 1,1-dioxide (100%). The crude product, m.p. 139—141 °C, was hydrogenated in glacial acetic acid at 35 °C for 10 min in the presence of 10% Pd–C. Filtration and evaporation gave 2,3-dihydro-2-(*p*-methoxyphenyl)benzo[*b*]thiophen 1,1-dioxide (90%), m.p. 154—155 °C (from ethanol), identical with that obtained before.

The dioxide (1.5 g) was reduced with lithium aluminium hydride (0.5 g) in boiling tetrahydrofuran (50 ml) for 8 h. The usual work-up gave a dark oil which was purified on alumina. Elution with light petroleum–ether (10 : 1) gave (3e) as *plates* (0.12 g, 9%), m.p. 50—51 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 74.25; H, 6.0%; M^+, 242. $C_{15}H_{14}OS$ requires C, 74.4; H, 5.8%; *M*, 242).

(*b*) 3-(*p*-Methoxyphenyl)benzo[*b*]thiophen [20] was oxidised as before, then the crude 1,1-dioxide was reduced catalytically (Adams catalyst in acetic acid) for 1.5 h, to give 2,3-dihydro-3-(*p*-methoxyphenyl)benzo[*b*]thiophen 1,1-dioxide as prisms (79%), m.p. 163—164 °C (from ethanol), identical with the product described before.

The dioxide was reduced (2 h) with lithium aluminium hydride in tetrahydrofuran and the product was purified on alumina [elution with light petroleum–ether (20 : 1)], then by short-path distillation, to give (4e) as *needles* (11%), m.p. 41—42 °C (Found: C, 74.5; H, 6.0%; M^+, 242).

2-(p-*Methoxyphenyl*)*benzo*[b]*thiophen*.—A mixture of 2- or 3-bromobenzo[*b*]thiophen (0.5 g), anisole (5 ml), and aluminium chloride (0.7 g) was stirred vigorously for 0.5 h. The usual work-up gave pale yellow platelets [0.37 g, 66% (from the 3-Br isomer); 0.35 g, 62% (from the 2-Br isomer)], m.p. 192—193 °C (lit.,[19] 193—194 °C) (from ethanol).

Ring-opening Reactions.—(a) *With anisole*. A stirred solution of benzo[*b*]thiophen in anisole was treated with finely powdered aluminium chloride (2 mol equiv.), whereupon the temperature rose by 20 °C. The pale yellow (sometimes deep red) solution was stirred for 0.5 h, treated with hydrochloric acid in the usual way, and extracted with ether. The ethereal extracts were shaken with aqueous sodium hydroxide, then dried and evaporated. The residue was distilled, to give (*E*)-4-methoxy-2′-methylthiostilbene (9a) as a pale yellow oil (34%), b.p. 200—210 °C (bath) at 0.1 mmHg. It slowly solidified, to give *needles*, m.p. 46.5—47.5 °C (from light petroleum) (Found: C, 74.9; H, 6.45%; M^+, 256. $C_{16}H_{16}OS$ requires C, 74.95; H, 6.3%; *M*, 256); spectroscopic data in main text.

Acidification of the alkaline extracts gave phenol (1 mol. equiv.).

Hydrogenation of the stilbene (9a) (10% Pd–C; 48 h) in acetic acid gave 1-(*p*-methoxyphenyl)-2-(*o*-methylthiophenyl)ethane (95%) as an oil, b.p. (bath) 190—195 °C at 0.01 mmHg (Found: M^+, 258. $C_{16}H_{18}OS$ requires *M*, 258); δ 2.53 (s, SMe), 2.92 (s, $CH_2{\cdot}CH_2$), and 3.8 (s, OMe).

Hydrodesulphurisation of the stilbene (9a) with boiling ethanolic Raney nickel gave 4-methoxybibenzyl (76%) as plates, m.p. 61—62 °C (lit.,[19] 59—61 °C) (from aqueous ethanol).

(b) *With anisole–phenetole*. A solution of benzo[*b*]thiophen (0.5 g) in anisole (6 ml) and phenetole (6 ml) was

treated as just described with aluminium chloride (1.25 g). Crystallisation of the neutral organic product from light petroleum gave (*E*)-4-ethoxy-2′-methylthiostilbene (9c) as *needles* (0.28 g, 28%), m.p. 101—102 °C (Found: C, 75.6; H, 6.7%; M^+, 270. $C_{17}H_{18}OS$ requires C, 75.5; H, 6.7%; *M*, 270); δ 1.40 (t, *Me*CH_2), 2.48 (s, SMe), and 4.08 (q, O.CH_2Me). The mother-liquors contained the products listed in the main text.

(c) *With* p-*methoxytoluene*. The reaction was carried out as in method (a), except that it was necessary to keep the mixture at 50—60 °C for 4 h to complete the reaction. Chromatography of the resulting dark product gave 2-methoxy-5-methyl-2′-methylthiostilbene (10) (13%) as a colourless oil (Found: M^+, 270. $C_{17}H_{18}OS$ requires *M*, 270); δ 2.23 (s, ArMe), 2.35 (s, SMe), and 3.73 (s, OMe).

(d) *With* 2-*methylbenzo*[b]*thiophen*. Treatment with anisole–$AlCl_3$ at 100 °C for 2 h gave a dark brown oil. Elution from alumina with light petroleum–ether (10 : 1) gave the alkene (11) as long *needles* (12%), m.p. 106—107 °C (from ether–light petroleum) (Found: C, 75.5; H, 6.55%; M^+, 270. $C_{17}H_{18}OS$ requires C, 75.55; H, 6.65%; *M*, 270); δ 2.12 (d, Me), 2.40 (s, SMe), and 3.82 (s, OMe) ($J_{allylic}$ 1.2 Hz).

Similar treatment of 3-methylbenzo[*b*]thiophen gave 2-(*p*-methoxyphenyl)-3-methyl-DHBT (9%) as an oil (Found: M^+, 256. $C_{16}H_{16}OS$ requires *M*, 256); δ 1.31 (d, Me), 3.5 (m, 3-H), 3.78 (s, OMe), and 4.55 (d, 2-H) ($J_{3\text{-H,Me}}$ 6.5 and $J_{2,3}$ 10.0 Hz).

(e) *In the presence of an alkyl halide*. A solution of benzo[*b*]thiophen (2 g) in phenetole (50 ml) was saturated with methyl bromide, then aluminium chloride (4 g) was added. The red mixture was stoppered, stirred for 2 h, then worked up as before, to give the results described in the main text.

Reactions with ethyl bromide (10 g) were carried out similarly.

o-*Methylthiobenzyl Chloride*.—A suspension of *o*-methylthiobenzyl alcohol [21] (9.3 g) in concentrated hydrochloric acid (60 ml) was shaken for 1 h at room temperature, then the resulting solution was extracted with ether. The ethereal extracts were washed with aqueous potassium carbonate and water, then dried. Evaporation and distillation gave the product as an oil (8.6 g, 83%), b.p. 72—74 °C at 0.15 mmHg (lit.,[21] 75—76 °C at 10^{-2} mmHg); δ 4.80 (s, CH_2Cl).

Prepared similarly, *o*-ethylthiobenzyl chloride (82%) had b.p. 80—82 °C at 0.2 mmHg (lit.,[22] 79—82 °C at 0.2 mmHg); δ 4.82 (s, CH_2Cl).

This method is more convenient than that used previously.[21,22]

Stilbene Derivatives.—(*a*) A mixture of *o*-methylthiobenzyl chloride (3.75 g) and redistilled triethyl phosphite (3.65 g) was heated under reflux for 20 min, then the cooled solution was added to a solution of dry sodium methoxide [from sodium (1.0 g)] in dimethylformamide (20 ml). Redistilled *p*-methoxybenzaldehyde (2.85 g) was added dropwise to the stirred mixture then, after 10 min, water was added and the product was extracted with ether. Crystallisation from light petroleum gave (*E*)-4-methoxy-2′-methylthiostilbene (9a) (4.1 g, 67%), m.p. 46.5—47.5 °C; identical with that already described.

(*b*) Prepared similarly (86%), except that it crystallised directly from the diluted solution, the 4-ethoxy-analogue (9c) had m.p. 103—104 °C, and was identical with that obtained before.

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