Addition Reactions of Benzo[*b*]thiophen. Part 1.† Self-addition and Addition of Simple Aromatic Hydrocarbons

By **Peter David Clark, Kenneth Clarke, David F. Ewing,** and **Richard M. Scrowston,*** Department of Chemistry, The University, Hull HU6 7RX

Benzo[*b*]thiophen undergoes facile addition reactions across the 2,3-bond when treated with aluminium chloride in an appropriate solvent at 0 or 20 °C. In carbon disulphide or dichloromethane, it undergoes self-addition to give two or more of the four possible 2- or 3-(2- or 3-benzo[*b*]thienyl)2,3-dihydrobenzo[*b*]thiophens (3)—(6). In the presence of an aromatic solvent, the dimerisation reaction just mentioned predominates at low temperatures (0 °C or below), or at room temperature if the solvent is benzene, chlorobenzene, t-butylbenzene, isopropylbenzene, or 1,3,5-trimethylbenzene. At room temperature, in toluene, ethylbenzene, and 1,2- or 1,4-dimethylbenzene, solvent addition occurs to give a mixture of the corresponding 2- and 3-aryl-2,3-dihydrobenzene[*b*]thiophens. At 80 °C, benzene and toluene give the fully aromatic 2-arylbenzo[*b*]thiophen. The reactions are discussed in terms of an ionic mechanism involving protonation of benzo[*b*]thiophen by moist aluminium chloride and reaction of the resulting electrophile with benzo[*b*]thiophen or with an aromatic substrate.

ALUMINIUM CHLORIDE promotes a wide range of reactions between homocyclic aromatic hydrocarbons and benzene.[1-3] Commonly, the initial reaction is phenylation;[4] this may be followed by phenyl migration,[5] cyclodehydrogenation,[6-8] or skeletal rearrangements.[4,9] Products arising from the addition of benzene across an aromatic double bond have been postulated as intermediates in the phenylation reaction.[10]

Polycyclic benzo-derivatives of carbazole,[11,12] dibenzofuran, and dibenzothiophen [13] undergo rearrangement reactions in the presence of $AlCl_3$–benzene. Knowledge of the reactions of simpler heterocycles with $AlCl_3$–benzene is extremely limited. Benzo[*b*]furan-2-carboxylic acid is reported [14] to give 2,3-dihydro-2-phenylbenzo[*b*]furan-2-carboxylic acid. $AlCl_3$ removes thiophen from benzene as a complex mixture of products, containing, *inter alia*, tetrahydrothiophen and its 3-phenyl derivative.[15]

Our interest in this area was stimulated by our observation that the cyclisation of (*p*-chlorophenylthio)acetone with $AlCl_3$ in boiling benzene by an established [16] general procedure gave, not only the expected 5-chloro-3-methylbenzo[*b*]thiophen (36%), but also the corresponding 2-phenyl derivative (52%). The latter was also obtained (55%) by heating 5-chloro-3-methylbenzo[*b*]thiophen with $AlCl_3$–benzene. We then showed that benzo[*b*]thiophen gave the 2-phenyl- (76%) and 2-*p*-tolyl-derivatives (76%), when treated respectively with benzene and toluene in the presence of $AlCl_3$ at 80 °C.

TABLE 1

Products [a] from the $AlCl_3$-catalysed addition reactions of benzo[*b*]thiophen

Reaction	Solvent	Temp. (°C)	DHBT derivatives (%) 2-Ar	DHBT derivatives (%) 3-Ar	Dimers (%) (3)	Dimers (%) (5)	Dimers (%) (4)	Dimers (%) (6)	Aromatic products [b] (%)	2,2′-bis-DHBT (%)
1	CH_2Cl_2	0			49	33	9	9		
2	CH_2Cl_2	20			64	21				15
3	CS_2	20			36	19	20	25		
4	PhH	0		2	58	39				
5	PhH	20	8	18	32	16	8			15
6	PhH [c]	20			40	46			14	
7	PhH	80							100	
8	PhMe	−15	3	10	62	25				
9	PhMe	0	11	49	27	13				
10	PhMe	20	18	82						
11	PhMe	80							100	
12	PhEt	20	10	90						
13	$PhPr^i$	20			45	35	13	7		
14	$PhBu^t$	20	2	13	41	19	19	6		
15	$1,4\text{-}Me_2C_6H_4$	20	46	54						
16	$1,2\text{-}Me_2C_6H_4$ [d]	20		74						
17	$1,3,5\text{-}Me_3C_6H_3$	20			36	34	23			5
18	PhCl	0			58	27	7	7		
19	PhCl	20			40	21	15	9	*e*	15

[a] Product distributions (mol %) are normalised to 100% over indicated products. This does not imply 100% yields. Any unchanged benzo[*b*] thiophen is always discounted. The percentage of dimers (4) and (6) is based on the tentative n.m.r. assignments noted in the text. [b] For the structures of these products, see discussion in the text. [c] With $TiCl_4$ as catalyst. [d] 2,3-Dihydrobenzo[*b*]thiophen (25%) was also formed. [e] 2-(2-Benzo[*b*]thienyl)benzo[*b*]thiophen was formed, but not quantified.

RESULTS

In order to investigate this interesting reaction more fully, we treated benzo[*b*]thiophen with $AlCl_3$ in a range of solvents and at various temperatures (Table 1). The results of the reaction with benzene at 20 °C are typical: an

† Part of this work was reported at a meeting of the Heterocyclic Group of the Chemical Society, at Queen Elizabeth College, London, January 1976.

intense red colour developed immediately, which was destroyed after 0.5 h by the addition of dilute acid, to give an oil containing *ca.* six major components (g.l.c. or h.p.l.c.). A preliminary n.m.r. spectroscopic examination indicated the addition of benzene across the 2,3-bond of benzo[*b*]thiophen, to give 2- and 3-phenyl-2,3-dihydrobenzo[*b*]thiophen (2- and 3-phenyl-DHBT *) (1) and (2), together with completely resolved by g.l.c., and fully aromatic compounds of high b.p. were retained by the column. Aryl derivatives of DHBT [types (1) and (2)] were usually obtained by column chromatography as oils, which could be characterised as the crystalline *SS*-dioxides.

Authentic samples of 2- and 3-phenyl-DHBT (2) and (1) for spectroscopic examination were conveniently prepared

TABLE 2

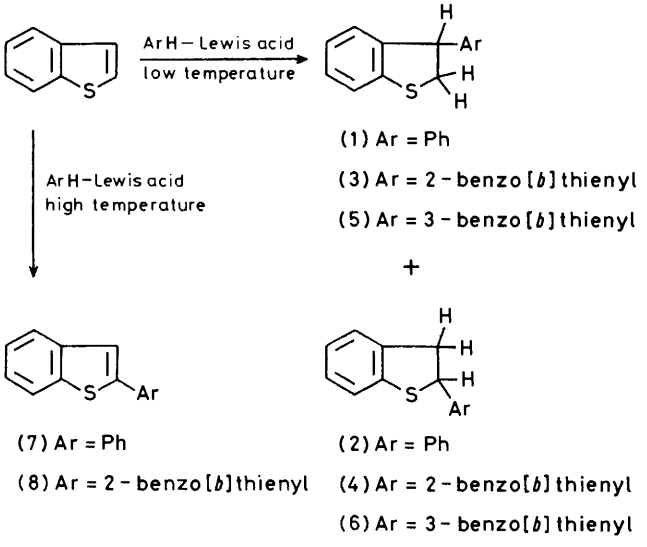
N.m.r. parameters [a] for 2,3-dihydrobenzo[*b*]thiophen and its 2- and 3-phenyl derivatives, and their 1,1-dioxides

Compound	δ H_A	δ H_B	δ H_X	$^3J_{AX}$	$^3J_{BX}$	$^2J_{AB}$
DHBT	3.23	3.23	3.23	*b*	*b*	*b*
DHBT 1,1-dioxide [c]	3.45 (2.70)	3.45 (2.70)	3.40 (2.42) [d]	*e*	*e*	*e*
(2)	3.59 (3.14)	3.39 (3.14)	5.00 (4.71)	7.3 (*b*)	8.9 (*b*)	−15.0 [b]
(9)	3.60 (3.05)	3.60 (2.79)	4.64 (4.17)	*b* (6.5)	*b* (8.3)	*b* (−15.6)
(1)	3.60 (3.22)	3.36 (3.06)	4.62 (4.29)	7.8 (7.3)	9.8 (10.0)	−11.0 (−11.1)
(10)	3.88 (3.35)	3.46 (3.07)	4.77 (4.24)	6.9 (7.5)	7.2 (7.9)	−13.6 (−13.3)

[a] Data refer to solutions in $CDCl_3$; values in C_6D_6 are given in parentheses. Chemical shifts are in p.p.m. from $SiMe_4$; coupling constants are in Hz. [b] Unobtainable from degenerate spectrum. [c] F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, 1950, **72**, 1985. [d] Value refers to a proton in the 3-position. [e] Not evaluated.

analogous self-addition of benzo[*b*]thiophen to give the four possible isomers of benzo[*b*]thienyl-DHBT (3)—(6).

Similar behaviour was observed in the presence of other Lewis acid catalysts, *e.g.* Magic Acid (SbF_5 in FSO_3H) and $TiCl_4$, but only polymeric products were obtained with



SCHEME 1

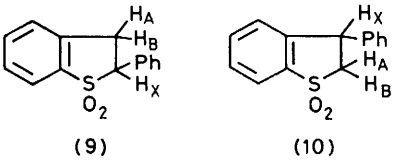
$FeCl_3$ and $SbCl_5$. There was no reaction in the presence of $SnCl_4$ at room temperature, but under reflux we were able on occasions to isolate the fully aromatic 2-(2-benzo[*b*]-thienyl)benzo[*b*]thiophen (8) (up to 80% yield). It should be stressed that all the reactions which we describe are affected by small changes in temperature and time, and also depend on the batch of catalyst used. However, all our results have been reproduced at least three times. The development of a deep red colour is an indication that the reaction is proceeding; benzo[*b*]thiophen 1,1-dioxide, for example, fails to react with $AlCl_3$–benzene, and does not give this colour. The above reactions are summarised in Scheme 1.

Product Analysis.—The complex mixtures were in-

* For simplicity, we shall refer to 2,3-dihydrobenzo[*b*]thiophen as DHBT.

by reduction of the appropriate phenylbenzo[*b*]thiophen 1,1-dioxide, first with H_2–Pd to give the 2,3-dihydro-derivative, then with $LiAlH_4$ to remove the *SS*-dioxide group.

Their ^1H n.m.r. spectra were very similar: in neither case was the complex aromatic region capable of analysis, but the aliphatic proton pattern (AMX, becoming A_2X in cases of accidental equivalence) could be analysed fully (Table 2). It was not possible to assign specifically the geminal protons (H_A and H_B), and the data are given in terms of the spin labels, A to low field of B, in the usual way. Inspection of the shifts in Table 2 indicated the following spectral differences between isomers (1) and (2) and their 1,1-dioxides, which could be generally diagnostic: (*a*) the chemical shift of H_X (δ_X) in (2) is 0.4 p.p.m. to lower field of that in (1) in both solvents; (*b*) although there is no clear distinction between (1) and (2) on the basis of the individual shifts of H_A and H_B, the separation Δ_{AB} in $CDCl_3$ is 0 in 2-phenyl-DHBT 1,1-dioxide (9) and 0.4 p.p.m. in the corresponding 3-isomer (10); (*c*) the mean shift (δ_{AB}) in C_6D_6 for (9) is 0.3 p.p.m. to lower field than that for (10); (*d*) although the vicinal coupling constants are of little diagnostic value, the geminal coupling (J_{AB}) in (2) (−15.0 Hz) is considerably larger than that in (1) (−11.0 Hz); and (*e*) oxidation of the 2-isomer (2) to its dioxide (9) produces a change in J_{AB} of −0.6 Hz, whereas the 3-isomer (1) on similar oxidation gives a much bigger corresponding change of −2.6 Hz. Although none of these five diagnostic



changes is itself very reliable, a structural assignment based on all of them (or fewer in unfavourable cases) was taken as acceptable, and in practice this appeared to give reliable results. Some assignments made on this basis are shown in Table 3; in every case where all five parameters could be obtained, there is excellent agreement. Only δ_X could be determined for isomers which were present as minor components.

Assignments for the dimeric compounds (3)—(6) were more difficult, since only 3-(2-benzo[*b*]thienyl)-DHBT (3) could be obtained pure (most easily from the reaction of benzo[*b*]thiophen in toluene at −15 °C). Reductive hydrodesulphurisation * to $PhCH(Me)CH_2CH_2Ph$ established its

TABLE 3

N.m.r. parameters [a] for the structural assignment of 2- and 3-substituted 2,3-dihydrobenzo[*b*]thiophens

Substituted	δ_X	Δ_{AB}	δ_{AB}	J_{AB}	ΔJ_{AB}
2-Ph	5.00	0.0	2.9	−15.0	0.6
3-Ph	4.62	0.4	3.2	−11.1	2.5
2-(4-MeC_6H_4) [b]	5.03				
3-(4-MeC_6H_4)	4.61	0.4	3.3	−10.9	2.6
2-(4-EtC_6H_4) [b]	5.00				
3-(4-EtC_6H_4)	4.58	0.4	3.2	−10.6	2.3
2-(2,5-$Me_2C_6H_3$)	5.26	0.0	2.9	−16.1	
3-(2,5-$Me_2C_6H_3$)	4.89	0.4	3.2	−11.1	2.3
3-(3,4-$Me_2C_6H_3$)	4.56	0.2		−10.8	
2-(4-$Bu^tC_6H_4$) [b]	4.91				
3-(4-$Bu^tC_6H_4$) [b]	4.57				
3-(3-benzo[*b*]thienyl)	5.02			−11.0	
3-(2-benzo[*b*]thienyl) [b]	4.93	0.2	3.8	−10.6	2.9
2-(3-benzo[*b*]thienyl) [b]	5.26				
2-(2-benzo[*b*]thienyl) [b]	5.33				

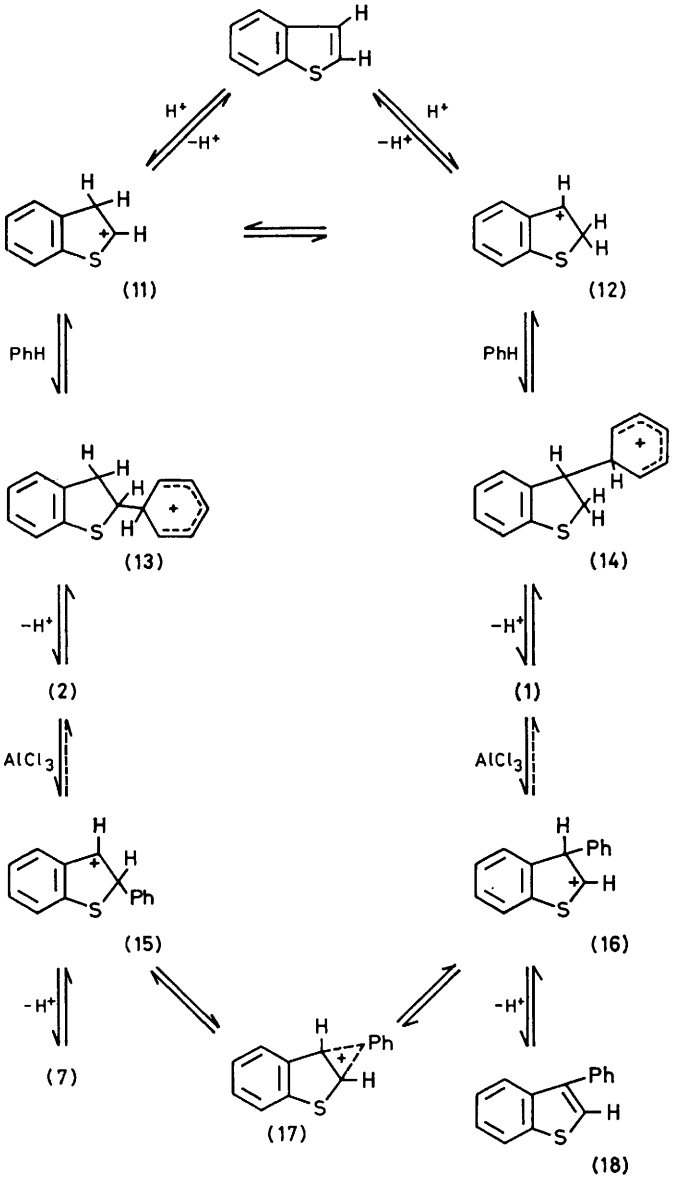
[a] These parameters are defined in the text. [b] This compound could only be detected in admixture with other products; analysis of the AB spectrum was impossible.

structure unambiguously. Dimer (3) was the predominant isomer in most cases, but varying amounts of the other three isomers could usually also be detected. The methine proton (H_X) in (3) was at δ 4.93, and the corresponding signals for isomers (4)—(6) were tentatively assigned as 5.33, 5.04, and 5.26, respectively; these assignments were consistent with subsequent chemical observations.

DISCUSSION

A mechanism for the addition of benzene across the 2,3-bond of benzo[*b*]thiophen is shown in Scheme 2; this requires initial protonation of the molecule, to give the carbonium ions (11) and (12). It is well known [17] that hypothetical species such as $[H^+][AlCl_4^-]$ or $[H^+][AlCl_3OH^-]$ act as indirect proton sources in reactions involving $AlCl_3$ which has not been rigorously dried. When we used carefully dried $AlCl_3$, the reaction took place at a much slower rate. Under these conditions, once a small amount of a DHBT derivative had been formed, it could provide a proton (*cf.* the final stages of Scheme 2) to promote further reaction. There is ample evidence for the formation of σ-complexes analogous to (11) and (12) from polyalkylbenzenes [18] and from thiophen derivatives,[19,20] in which cases the ^1H n.m.r. spectra of the protonated species have been observed. We failed to observe such spectra of intermediates (11) and (12); with $AlCl_3$–CD_2Cl_2 at −80 °C no reaction occurred, but at −30 °C only the signals due to the products were observed. An equally fast reaction was observed with Magic Acid in liquid SO_2 at −70 °C. Proton acids such as concentrated sulphuric acid or perchloric acid failed to promote the reaction at room temperature, but it is accepted [21] that they have lower catalytic activity than $AlCl_3$. Heating benzo[*b*]thiophen with perchloric acid in acetic acid at 160 °C gave significant amounts of 2-(2-benzo[*b*]thienyl)benzo[*b*]thiophen (8).[22]

The initially formed electrophiles (11) and (12) can attack either an aromatic substrate, to give the ions (13) and (14) respectively, or another molecule of benzo[*b*]thiophen, to give analogous species. Proton elimination



SCHEME 2

then affords the appropriate arylated DHBT. Formation of the fully aromatic derivatives (7) and (18) at higher temperatures may be achieved *via* hydride abstraction by $AlCl_3$ to give the carbonium ions (15) and (16), followed by elimination of a proton. There is abundant evidence that carbonium ions of the types (15) and (16) can interconvert *via* the synartetic ion (17), hence the ratio of 2- and 3-arylbenzo[δ]thiophen should reflect their relative thermodynamic stabilities. In

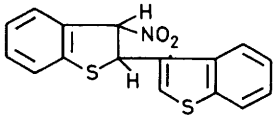
* The structures of two other products from the reaction with toluene were confirmed by this technique (see Experimental section).

practice, only the former is found (Table 1; Reactions 7 and 11), suggesting that the 2-isomer is generally the more stable, in agreement with other observations.[23]

In one case where only self-addition of benzo[*b*]thiophen occurred (*cf.* Table 1; Reaction 19), a small amount of 2-(2-benzo[*b*]thienyl)benzo[*b*]thiophen (8) was formed, confirming that all products analogous to (1) and (2) dehydrogenate to a single isomer. The 2-aryl product (8) was also formed in high yield when the mixture of dimers (3)—(6) was kept at 80 °C with $AlCl_3$–chlorobenzene. Further, in the absence of $AlCl_3$, 3-(*p*-tolyl)-DHBT was recovered unchanged from boiling toluene, but in the presence of $AlCl_3$ it underwent isomerisation and dehydrogenation, to give 2-(*p*-tolyl)benzo[*b*]thiophen.

The data in Table 1 offer firm evidence of regiocontrol in the formation of an aryl-DHBT: the 3-aryl isomer is favoured in every case, irrespective of whether the aryl group is derived from the solvent (*e.g.* Reactions 10 and 12), from benzo[*b*]thiophen (*e.g.* Reactions 1 and 18), or from both (*e.g.* Reactions 5 and 9). If the formation of these addition products is irreversible, then the observed regiocontrol requires ion (12) to be more stable than ion (11).

However, quantitative studies [24] of tritium exchange in 2- or 3-tritiobenzo[*b*]thiophen suggest that the order of stabilities is (11) > (12). The results of numerous other electrophilic substitution reactions of benzo[*b*]thiophen,[25] which yield preferentially the 3-isomer, have confirmed this conclusion. It is interesting to note that an addition product (19),[26] analogous to dimer (6), is



(19)

formed *via* the ' more stable ' ion (*cf.* 11) when benzo[*b*]-thiophen is nitrated at low temperatures; no isomeric product derived from the ' less stable ' ion (*cf.* 12) has been observed. Thiophen forms a trimer under acidic conditions, again *via* the ' more stable ' protonated intermediate.[27] In contrast, pyrrole forms a trimer *via* the 3*H*-pyrrolium ion,[28] which is said to be more electrophilic than the more stable and more abundant 2*H*-pyrrolium ion.

We used a CNDO/2 MO method to calculate the energies of ions (11) and (12) (Table 4), and thereby confirm the experimental prediction that the major product from the $AlCl_3$-catalysed addition of benzene to benzo[*b*]thiophen should be 2-phenyl-DHBT, formed *via* ions (11) and (13). Substitution in the 3-position might be favoured by co-ordination of $AlCl_3$ with the sulphur atom in ions (11) and (12) since, of the two resulting species (20) and (21), the latter will be the more stable in view of the greater charge separation. Even so, this is unlikely to be more than a minor contributing factor. At first sight, co-ordination of the sulphur atom of benzo[*b*]thiophen itself, either with H^+ or with $AlCl_3$, would seem to offer a more attractive explanation for the extent of 3-substitution: by classical arguments, the positive charge on the resulting ion (22) would be preferentially localised in the 3-position. However, MO calculations (Table 5) show that protonation of the

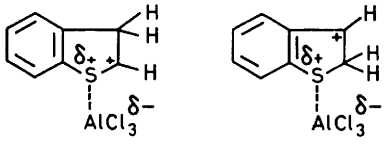
TABLE 4

Energy * of protonated benzo[*b*]thiophen

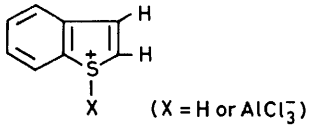
Position of protonation	Un-protonated	1-	2-	3-
Molecular energy	−72.116	−72.458	−72.619	−72.593

* In atomic units.

sulphur atom does not produce significant delocalisation of positive charge into the π-molecular orbitals. On the contrary, C-2 shows a small increase in π-electron population. By comparison, protonation at C-2 or C-3 produces a much larger perturbation at the adjacent carbon atom: a decrease of about 0.4 π-electrons in each



(20) (21)



(22)

case. These results are not surprising, since protonation of the sulphur atom would involve the non-bonding electrons and would not significantly perturb the π-framework. The total net π-positive charge is only 0.19, the remaining charge appearing in the σ-orbitals.

The preferential formation of 3-phenyl-DHBT (1) can be accounted for if there exists some mechanism for the interconversion of (1) and its 2-isomer (2), whereby the equilibrium distribution would reflect the relative

TABLE 5

Electron populations in protonated benzo[*b*]thiophen *

Position of protonation	C-2 σ	C-2 π	C-3 σ	C-3 π	S σ	S π	S *d*
On sulphur	2.89	1.08	3.03	0.89	3.48	1.91	0.55
C-2	4.10		3.18	0.56	3.66	1.88	0.42
C-3	3.21	0.64	4.03		3.85	1.49	0.49

* Calculated by CNDO/2 method. The π-populations on sulphur correspond to p_π electrons only. The small, relatively constant, total populations for the *d*-orbitals means that d_π contributions can be neglected.

stabilities of (1) and (2), rather than those of the precursors (11) and (12). Two possibilities are evident from Scheme 2: (*a*) isomerisation *via* ions (15)—(17) and (*b*) isomerisation *via* ions (11) and (12). The first possibility is not very likely, since the activation energy of the hydride abstraction step leading to ions (15)—(17) must be higher than that for the subsequent step leading

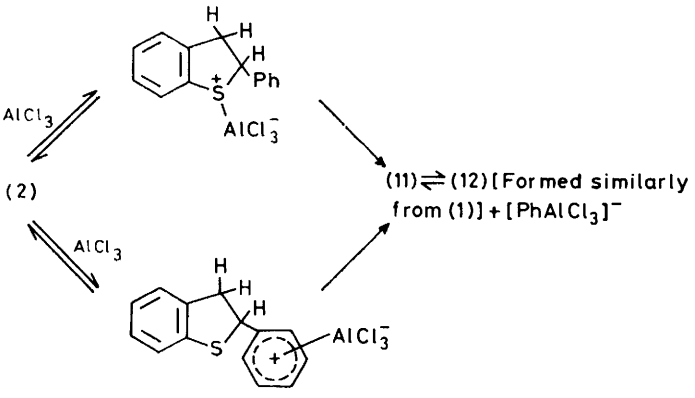
to the aromatic compounds (7) or (18). This final step, like the first step in Scheme 2, involves protonation/deprotonation of aromatic species: a process widely recognised as having a low activation energy. A high barrier to the formation of ions (15) or (16) is indicated by the high temperatures required for the formation of fully aromatic compounds (Table 1). Hence it seems that the conversion of a phenyl-DHBT (1) or (2) into ions (15) or (16) is an essentially irreversible process, which always proceeds to the aromatic compounds (7) or (18).

However, we have evidence for isomerisation *via* ions (11) and (12). First, the reaction between benzo[*b*]thiophen and toluene in the presence of $AlCl_3$ was carried out at 0 °C, then the products were maintained at 20 °C for a few minutes in the presence of $AlCl_3$. The resulting product distribution was identical with that for a reaction carried out entirely at 20 °C. Secondly, when the mixture of dimers (3)—(6) was treated with toluene–$AlCl_3$ at 20 °C, toluene was incorporated to give 3-(*p*-tolyl)-DHBT, together with a trace of the corresponding 2-isomer. The only product from a similar reaction at 80 °C was 2-(*p*-tolyl)benzo[*b*]thiophen. These results indicate the reversibility of the reaction leading to DHBT derivatives, such that exposure to $AlCl_3$ leads to the appropriate products irrespective of whether the starting material is benzo[*b*]thiophen, a mixture of the 2- and 3-aryl-DHBT derivatives, or a mixture of dimeric benzo[*b*]thiophens. In the last case, the solvent (toluene) is preferentially incorporated with the elimination of benzo[*b*]thiophen, and eventually, at higher temperatures, the appropriate fully aromatic species is formed as described above.

The above evidence clearly confirms that the addition reactions shown in Scheme 2 are reversible, but it does not necessarily imply that the steps are themselves reversible as indicated. The reverse reactions [(2)→(13)→(11)] are analogous to those which are widely believed to promote the isomerisation of alkylbenzenes in the presence of $AlCl_3$;[29] they may, therefore, be significant in the present case. However, our reactions take place under much milder conditions than those normally employed for the isomerisation of alkylbenzenes.[29] We suggest, therefore, that co-ordination of the Lewis acid to the non-bonding electrons of the sulphur atom or to the π-electrons of the substituent aryl group may assist the regeneration of the carbonium ions (11) and (12) (Scheme 3).

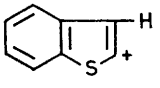
So far, we have pursued a protonation mechanism, for which there is ample precedent (*cf.* ref. 17). We excluded the possibility of the abstraction of a hydride ion from benzo[*b*]thiophen since the resulting vinylic cation, *e.g.* (23), would be highly unstable (*cf.* ref. 30), and would undoubtedly lead directly to a fully aromatic product. We also considered the possibility of a mechanism involving radical ions (*cf.* refs. 31 and 32), but the only e.s.r. signals * which we obtained were poorly resolved and were probably due to cation radicals, on the surface only, of the red complex formed from benzo[*b*]thiophen, benzene, and $AlCl_3$.

Detailed examination of Table 1 reveals several interesting results. The distribution of isomeric DHBT derivatives is basically the same for all reactions: the aryl substituent appears preferentially at C-3, as already



SCHEME 3

accounted for in the proposed mechanism. In cases where the aryl substrate is benzo[*b*]thiophen, the major component is 3-(2-benzo[*b*]thienyl)-DHBT (3). This structure is in agreement with the regiocontrol normally observed for the addition reaction, but substitution in the 2-position of benzo[*b*]thiophen is unexpected. Normally, benzo[*b*]thiophen undergoes electrophilic substitution in the 3-position. However, because of a *peri*-steric effect involving 4-H, bulky substituents sometimes appear in the 2-position, either because of initial attack of the electrophile in this position, or as a consequence of isomerisation of the initially formed



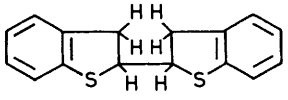
(23)

3-substituted derivative.[23] Certainly, in these experiments, 3-substituted benzo[*b*]thiophens always isomerised to the fully aromatic 2-substituted compounds under conditions which force the addition products to dehydrogenate. The three remaining dimers (4)—(6) could not be obtained pure; of these, 3-(3-benzo[*b*]thienyl)-DHBT (5) was the only one obtained in significant amounts. Its structure was indicated by the close similarity of its n.m.r. spectra (in $CDCl_3$ and C_6D_6) with those of isomer (3); it was confirmed by dehydrogenating the mixture of dimers from Reaction 4 (Table 1) with DDQ to give, *inter alia*, 3-(3-benzo[*b*]thienyl)benzo[*b*]thiophen. Generally, the ratio dimer (3) : dimer (5) is *ca.* 2 : 1.

In addition to the dimers (3)—(6), small amounts of a symmetrical bis-DHBT (24) were also formed in Reactions 2, 5, 17, and 19 (Table 1). Its n.m.r. spectrum showed methine absorption consistent with the $[A_2X]_2$ system expected for both (24) and the 3,3′-isomer. However, the proposed structure (24) was confirmed by

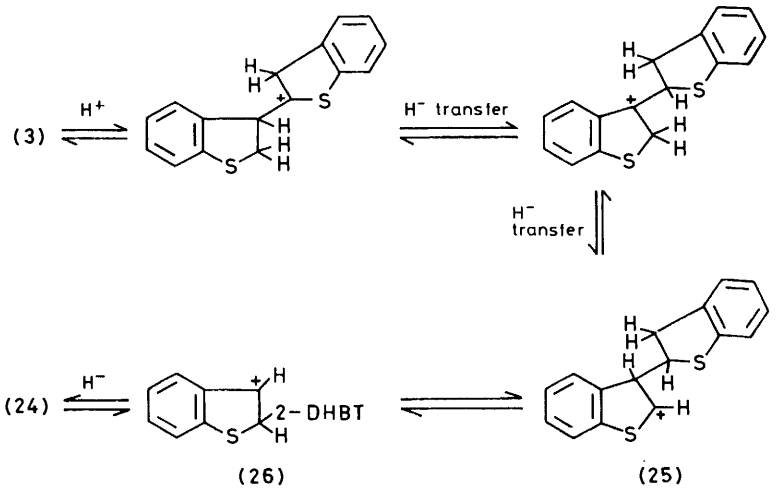
* We thank Dr. B. C. Gilbert, University of York, for the e.s.r. results.

dehydrogenating the total product from Reaction 2 (Table 1) and observing the formation of 2-(2-benzo[*b*]-thienyl)benzo[*b*]thiophen (8). Dimer (4), the other precursor of (8), was known to be absent from the starting mixture, and the possibility of (8) having arisen following an isomerisation reaction during the dehydrogenation



(24)

process was excluded because the dehydrogenation of the products from Reaction 4 (Table 1) gave no compound (8). A possible mechanism for the formation of the bis-DHBT (24) is shown in Scheme 4, in which protonation of the predominant dimer (3), followed by two consecutive 1,2-hydride ion shifts, leads to the ion (25), dimeric benzo[*b*]thiophens. Reactions in isopropylbenzene or t-butylbenzene appear to be anomalous, in that self-addition of benzo[*b*]thiophen becomes the major reaction. Some solvent addition might be expected, because isopropylbenzene and t-butylbenzene are generally more reactive towards electrophiles than is benzene itself, but less reactive than toluene.[33,34] However, the relative reactivities of alkylbenzenes in electrophilic substitution are usually evaluated from a study of the reactions of small electrophiles. If electrophilic attack is considered to involve the formation of a π-complex as a precursor to the formation of a σ-complex, then the reduced reactivity of isopropyl- and t-butyl-benzene can be attributed to the increased difficulty of forming a π-complex with the large electrophile (11) or (12) involved in the present case. The rate of the $AlCl_3$-catalysed benzylation of various alkylbenzenes correlates [34] well with the relative stability of the appropriate



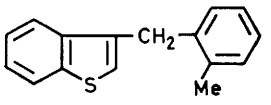
SCHEME 4

which can isomerise to the more stable 2-substituted species (26) as described already. It seems that hydride ion addition to (26) may be preferred to proton loss because, in contrast to the reactions previously described (*cf.* Scheme 2), the latter process would not lead to a fully aromatic product.

The results for the addition of benzene (Reactions 4 and 5; Table 1) to benzo[*b*]thiophen can be rationalised on the basis of the relative reactivities of benzene and benzo[*b*]thiophen with respect to electrophiles. At 0 °C, the more reactive benzo[*b*]thiophen adds mainly to itself, whereas at 20 °C the slower addition of benzene to benzo[*b*]thiophen becomes significant, probably largely because of the considerable excess of benzene (the solvent) relative to benzo[*b*]thiophen. With toluene, solvent addition takes place more rapidly, and is the sole reaction at 20 °C. Not surprisingly, Reactions 12 and 15 (Table 1), involving the reactive aromatic substrates, ethylbenzene and 1,4-dimethylbenzene, give solvent addition products almost exclusively, whereas the less reactive chlorobenzene (Reactions 18 and 19) gives only π-complex, but not with the basicity of the σ-complex. Further, as the number of alkyl groups attached to the benzene ring increases, steric effects play a major role; in a mixture of toluene and 1,3,5-trimethylbenzene, for example, the former is benzylated exclusively.[35] Moreover, in the presence of $AlCl_3$–HCl, 1,3,5-trimethylbenzene is completely protonated, thus reducing further its reactivity towards electrophiles.[36] The last two factors would contribute towards the failure of 1,3,5-trimethylbenzene to undergo addition to benzo[*b*]thiophen (Reaction 17; Table 1).

The addition of 1,4-dimethylbenzene to benzo[*b*]thiophen (Reaction 15) was unusual in that the proportion of the 2-isomer was much greater than that observed for other aromatic substrates. Examination of models shows that the 2-isomer may be preferred in view of the considerable steric interaction that exists between the 3-(2,5-dimethylphenyl) substituent and the 4-(*peri*) position. The reaction of benzo[*b*]thiophen with 1,2-dimethylbenzene was exceptional in that solvent addition was confined to the 3-position (74%); the only

other product was 2,3-dihydrobenzo[*b*]thiophen (25%). The latter presumably arose *via* abstraction of a hydride ion from 1,2-dimethylbenzene by the ions (11) and (12). The resulting 2-methylbenzyl carbonium ion might then be expected to undergo electrophilic substitution in the 2- and/or 3-position of a benzo[*b*]thiophen molecule. In support of this mechanism, we confirmed the presence of 3-(*o*-tolylmethyl)benzo[*b*]thiophen (27) (8%) in the reac-



(27)

tion product; we were unable to detect any of the corresponding 2-isomer. An authentic sample of compound (27) was prepared by Huang-Minlon reduction of 3-(*o*-toluoyl)benzo[*b*]thiophen, which was obtained by Friedel–Crafts aroylation of benzo[*b*]thiophen. In contrast to the observations of earlier workers [37] we also obtained the corresponding 2-(*o*-toluoyl) isomer (32%) from this aroylation reaction. Hydride abstraction from 1,4-dimethylbenzene has previously been observed; [38] however, we were unable to detect any 2,3-dihydrobenzo[*b*]-thiophen in the reaction involving 1,4-dimethylbenzene.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained at 100 MHz with a JNM-4H-100 spectrometer, for 5—10% solutions in $CDCl_3$ and/or C_6D_6 with tetramethylsilane as internal standard. G.l.c. separations were carried out on a 2.5 m × 2 mm column of OV-225 (3% w/w) on 100—120 mesh Gaschrome-Q with column temperatures of up to 240 °C and a flow rate of up to 60 m min^{-1}. Light petroleum had b.p. 60—80 °C.

5-Chloro-3-methyl-2-phenylbenzo[b]*thiophen* (*with* A. J. Humphries).—Powdered anhydrous aluminium chloride (60 g) was added portionwise to a vigorously stirred solution of (*p*-chlorophenylthio)acetone (36.1 g) in dry benzene (100 ml) at 0 °C. The mixture was kept at this temperature for 0.5 h, then stirred under reflux for 3 h, cooled, and treated with dilute hydrochloric acid. Distillation of the washed and dried benzene solution gave 5-chloro-3-methylbenzo[*b*]thiophen (11.8 g, 36%), b.p. 107—110 °C at 3 mmHg (lit.,[23] 92—93 °C at 0.3 mmHg) and 5-chloro-3-methyl-2-phenylbenzo[*b*]thiophen (24 g, 52%), b.p. 162—165 °C at 0.1 mmHg, which formed *needles*, m.p. 106—107 °C (from light petroleum) (Found: C, 69.5; H, 4.1; Cl, 13.75; S, 12.4%; M^+, 258/260. $C_{15}H_{11}ClS$ requires C, 69.6; H, 4.3; Cl, 13.7; S, 12.4%; M^+, 258/260); no 2-H signal in the n.m.r. spectrum.

Authentic 5-chloro-3-methyl-2-phenylbenzo[*b*]thiophen, m.p. and mixed m.p. 107—108 °C, was obtained (82%) by cyclodehydration of 2-(*p*-chlorophenylthio)-2-phenylpropanone with polyphosphoric acid (*cf.* ref. 23).

2-Arylbenzo[b]*thiophens*.—A mixture of benzo[*b*]thiophen (2.0 g) and finely powdered aluminium chloride (2.0 g; 1 mol equiv.) was stirred in boiling benzene (50 ml) for 1 h, then cooled and poured into aqueous 20% hydrochloric acid. A small amount of 2-(2-benzo[*b*]thienyl)-benzo[*b*]thiophen (8) was filtered off (Hyflo), then neutral organic material was recovered in the usual way. This gave 2-phenylbenzo[*b*]thiophen (2.4 g, 76%) as white feathers, m.p. 175—176 °C (lit.,[39] 175—176 °C) (from aqueous ethanol).

Obtained similarly, in toluene at 80 °C, 2-*p*-tolylbenzo[*b*]-thiophen (76%) formed platelets, m.p. 169—170 °C (lit.,[40] 169—169.5 °C) (from ethanol). Hydrodesulphurisation [41] with Raney nickel gave 1-phenyl-2-*p*-tolylethane as an oil, b.p. 140—145 °C at 0.1 mmHg (Found: M^+, 196. $C_{15}H_{16}$ requires M, 196); δ 1.6—3.1 (m, CH_2CH_2).

5-Chloro-3-methylbenzo[*b*]thiophen gave the 2-phenyl derivative (55%), m.p. 106—107 °C, identical with that just described.

Addition Reactions of Benzo[b]*thiophen*.*—(a) *General procedure*. Freshly powdered aluminium chloride (2.0 g; 1 mol equiv.) was added to a solution of benzo[*b*]thiophen (2.0 g) in the appropriate solvent (50 ml), then the resulting deep red mixture was stirred at the required temperature for 0.5 h and poured into ice-cold aqueous 20% hydrochloric acid (100 ml). If necessary, the mixture was filtered (Hyflo) to remove 2-(2-benzo[*b*]thienyl)benzo[*b*]thiophen, then oily organic material was isolated with ether in the usual way. Chromatography on alumina and elution, unless stated otherwise, with light petroleum–ether (20 : 1) gave first a mixture of 2- and 3-aryl DHBT derivatives, then a mixture of two or more of the dimers (3)—(6).

(b) *With benzene at* 0 °C. The semi-solid mixture of dimers (3) and (5) (1.75 g) crystallised from ethanol, to give 3-(2-*benzo*[b]*thienyl*)-*DHBT* (3) (0.5g) as prisms, m.p. 88—90 °C (Found: C, 71.7; H, 4.35%; M^+, 268. $C_{16}H_{12}S_2$ requires C, 71.6; H, 4.5%; M, 268). It was heated with Raney nickel in boiling ethanol for 2 h, to give 2,4-diphenylbutane as an oil, b.p. 110—120 °C at 0.1 mmHg (lit.,[42] 155—160 °C at 2.0 mmHg) (Found: M^+, 210. Calc. for $C_{16}H_{18}$: M, 210); δ 1.33 (d, Me). Dimer (3) was oxidised in the usual way (*cf.* ref. 23) with hydrogen peroxide in glacial acetic acid, to give the bis-SS-*dioxide* (95%) as prisms, m.p. 194—195 °C (from ethanol) (Found: C, 57.8; H, 3.55%; M^+, 332. $C_{16}H_{12}S_2O_4$ requires C, 57.8; H, 3.65%; M, 332).

In order to confirm the structure of dimer (5), the mixture of dimers (3) and (5) (0.5 g) was heated under reflux in benzene (30 ml) for 2 h with dichlorodicyano-*p*-benzoquinone (DDQ) (2.0 g). The resulting neutral material was filtered through alumina, to give a mixture of two major components [*ca.* 3 : 2 (g.l.c.)], from which 3-(3-benzo[*b*]-thienyl)benzo[*b*]thiophen, m.p. 82 °C (lit.,[43] 83 °C), was isolated by preparative t.l.c.

(c) *With toluene*. The chromatographed product from the reactions at 0 °C and −15 °C gave 3-(2-benzo[*b*]thienyl)-DHBT (3) (0.25 g and 0.9 g, respectively), m.p. 89—90 °C (from ethanol), identical with that already described.

Distillation of the total product from the reaction at 20 °C gave 3-p-*tolyl-DHBT* (2.6 g, 78%) as an oil, b.p. 165—170 °C (bath) at 0.1 mmHg (Found: M^+, 226. $C_{15}H_{14}S$ requires M, 226); δ 2.32 (s, Me). It was characterised as the 1,1-*dioxide*, which formed needles (100%), m.p. 139—140 °C (from ethanol) (Found: C, 70.1; H, 5.35%; M^+, 258. $C_{15}H_{14}O_2S$ requires C, 69.75; H, 5.45%; M, 258).

The structure of 3-*p*-tolyl-DHBT was confirmed by hydrodesulphurisation, to give 1-phenyl-1-*p*-tolylethane, b.p. 150—152 °C at 10 mmHg (lit.,[44] 151—156 °C at 10

* For the sake of brevity, discussion will be restricted in the main to those reactions from which pure products were isolated. Details of other reactions and products are given in the text and in Table 1.

mmHg) (Found: M^+, 196. Calc. for $C_{15}H_{16}$: M, 196); δ 1.6 (d, Me) and 4.1 (q, C*H*Me).

(d) *With ethylbenzene.* Chromatography of the crude product and elution with light petroleum–ethyl acetate (40 : 1) gave 3-(*p*-ethylphenyl)-DHBT as a pale yellow oil (3.17 g, 88%) (Found: M^+, 240. $C_{16}H_{16}S$ requires M, 240). The 1,1-*dioxide* crystallised from chloroform–light petroleum as needles, m.p. 85—86 °C (Found: C, 70.5; H, 5.85%; M^+, 272. $C_{16}H_{16}O_2S$ requires C, 70.55; H, 5.9%; M, 272).

(e) *With* 1,2-*dimethylbenzene.* The two products were separated by chromatography. Elution with light petroleum gave successively 2,3-dihydrobenzo[*b*]thiophen (0.45 g, 21%), b.p. 105—110 °C at 20 mmHg (lit.,[45] 108—110 °C at 20 mmHg) and 3-(3,4-*dimethylphenyl*)-*DHBT* (2.6 g, 72%), which was obtained as a pale yellow oil (Found: M^+, 240. $C_{16}H_{16}S$ requires M, 240). The 1,1-*dioxide* of the latter compound had m.p. 101—102 °C (Found: C, 70.35; H, 5.75%; M^+, 272).

(f) *With* 1,4-*dimethylbenzene.* The two products could not be separated satisfactorily by chromatography, so the mixture was oxidised with hydrogen peroxide in acetic acid. The resulting solid crystallised from light petroleum–chloroform, then from ethanol, to give 3-(2,5-dimethylphenyl)-DHBT 1,1-dioxide as *needles*, m.p. 196—197 °C (Found: C, 70.45; H, 6.05%; M^+, 272); δ 2.24 and 2.38 (s, Me). Concentration and cooling of the mother-liquors gave 2-(2,5-dimethylphenyl)-DHBT 1,1-dioxide as *needles*, m.p. 144—145 °C (from light petroleum–chloroform) (Found: C, 70.7; H, 6.1%; M^+, 272); δ 2.26 and 2.44 (s, Me).

(g) *In dichloromethane.* The crude product from the reaction at 20 °C was shown by mass spectrometry to contain 2,2′-bis-DHBT (24) (Found: M^+, 270.0521. $C_{16}H_{14}S_2$ requires M, 270.0537). To confirm its presence, the crude product was dehydrogenated as before with DDQ in boiling benzene for 4 h. Filtration of the cooled solution gave 2-(2-benzo[*b*]thienyl)benzo[*b*]thiophen (8) (0.05 g), m.p. 259—261 °C (lit.,[46] 262 °C); i.r. spectrum identical with that of authentic material.

2,3-*Dihydro*-2-*phenylbenzo*[b]*thiophen* (2).—2-Phenylbenzo[*b*]thiophen 1,1-dioxide [47] (2.0 g) was hydrogenated in glacial acetic acid (125 ml) at 35 °C for 0.25 h in the presence of 10% Pd–C. Filtration and evaporation gave 2,3-*dihydro*-2-*phenylbenzo*[b]*thiophen* 1,1-*dioxide* (9) as needles (1.95 g, 96%), m.p. 157—158 °C (Found: C, 68.9; H, 5.0%; M^+, 244. $C_{14}H_{12}O_2S$ requires C, 68.8; H, 4.95%; M, 244).

A solution of the foregoing 1,1-dioxide (2.0 g) in dry tetrahydrofuran (100 ml) was added dropwise to a stirred mixture of lithium aluminium hydride (0.62 g) in ether (50 ml) and the mixture was heated under reflux for 8 h. The usual work-up gave the product (2) as platelets (1.1 g, 64%), m.p. 43—44 °C (from aqueous methanol) (lit.,[48] yellow oil) (Found: C, 79.3; H, 5.7%; M^+, 212. Calc. for $C_{14}H_{12}S$: C, 79.2; H, 5.7%; M^+, 212).

2,3-*Dihydro*-3-*phenylbenzo*[b]*thiophen* (1).—Prepared as for the 2-phenyl isomer (reduction time 0.5 h), this formed plates (89%), m.p. 75—77 °C (from aqueous methanol) (lit.,[49] 77—77.5 °C). The intermediate 1,1-dioxide (10) (90%) had m.p. 122—123 °C (from light petroleum–chloroform) (lit.,[50] 119—121 °C).

3-(o-*Tolylmethyl*)*benzo*[b]*thiophen* (27).—Treatment of benzo[*b*]thiophen with *o*-toluoyl chloride in the presence of tin(IV) chloride [37] gave a solid product which contained (g.l.c.) 3-(*o*-toluoyl)benzo[*b*]thiophen (67%) and the corresponding 2-isomer (32%). Recrystallisation (×4) from ethanol gave the 3-isomer (65%), m.p. 90—91 °C (lit.,[37] 94 °C; 90%); $\nu_{max.}$ 1 640 cm^{-1} (C=O).

Huang-Minlon reduction (*cf.* refs. cited in ref. 23) of 3-(*o*-toluoyl)benzo[*b*]thiophen at 200 °C for 4 h (shorter times led to the recovery of the intermediate hydrazone in high yield) gave an oil, which was filtered in benzene through alumina in order to remove small amounts of the hydrazone. Removal of the solvent and distillation of the residue at 140 °C (bath) at 0.1 mmHg, gave a solid, which crystallised from ethanol as *needles* (77%), m.p. 45—46 °C (Found: C, 80.4; H, 6.0%; M^+, 238. $C_{16}H_{14}S$ requires C, 80.6; H, 5.9%; M, 238); δ 4.1 (s, CH_2) and 2.18 (s, Me).

G.l.c. of the total product from the reaction of benzo[*b*]-thiophen with 1,2-dimethylbenzene showed a peak (8%) with approximately the same R_t as (27). This evidence was inconclusive because of the proximity of other peaks. The mixture was therefore dehydrogenated as before with DDQ, evaporated under reduced pressure to remove benzo[*b*]thiophen (from 2,3-dihydrobenzo[*b*]thiophen), and subjected to preparative t.l.c. One of the spots has a mass spectrum identical to that of (27).

We thank the S.R.C. for a Studentship (to P. D. C.) and Mrs. M. Vickers for technical assistance.

[9/497 *Received*, 27*th March*, 1979]

REFERENCES

[1] C. A. Thomas, 'Anhydrous Aluminium Chloride in Organic Chemistry,' Reinhold Publishing Corp., New York, 1941, ch. 16.
[2] G. E. Hall and E. A. Johnson, *J. Chem. Soc.* (*C*), 1966, 2043.
[3] P. Kovacic and A. Kyriakis, *J. Amer. Chem. Soc.*, 1963, **85**, 454.
[4] G.-P. Blümer, K.-D. Gundermann, and M. Zander, *Chem. Ber.*, 1976, **109**, 1991, and refs. cited therein.
[5] F. A. Vingiello and C. S. Menon, *Chem. Comm.*, 1968, 326.
[6] E. Clar and D. G. Stewart, *J. Chem. Soc.*, 1951, 687.
[7] A. T. Balaban and C. D. Nenitzescu, in ' Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. II, part 2, ch. XXIII.
[8] N. P. Buu-Hoï, O. Périn-Roussel, and P. Jacquignon, *Bull. Soc. chim. France*, 1970, 1194.
[9] N. P. Buu-Hoï and D. Lavit-Lamy, *Bull. Soc. chim. France*, 1962, 1398.
[10] M. Zander, *Naturwiss.*, 1962, **49**, 300.
[11] M. Zander and W. H. Franke, *Chem. Ber.*, 1967, **100**, 2649.
[12] G.-P. Blümer, K.-D. Gundermann, and M. Zander, *Chem. Ber.*, 1977, **110**, 2005.
[13] G.-P. Blümer, K.-D. Gundermann, and M. Zander, *Chem. Ber.*, 1977, **110**, 269.
[14] E. J. King, *J. Amer. Chem. Soc.*, 1927, **49**, 562.
[15] D. H. Johnson, *J. Chem. Soc.* (*C*), 1967, 2275.
[16] U.S.S.R.P. 157,981/1963 (*Chem. Abs.*, 1964, **60**, 10651).
[17] H.-H. Perkampus and E. Baumgarten, *Angew. Chem. Internat. Edn.*, 1964, **3**, 776.
[18] G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, 1958, **80**, 6535.
[19] L. I. Belen'kii, A. P. Yakubov, and Ya. L. Gol'dfarb, *J. Org. Chem.* (*U.S.S.R.*), 1975, **11**, 412.
[20] H. Hogeveen, *Rec. Trav. chim.*, 1966, **85**, 1072.
[21] S. H. Patinkin and B. S. Friedman, in ref. 7, vol. II, part 1, ch. XIV.
[22] G. Collier, personal communication.
[23] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 177.
[24] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.
[25] *Cf.* S. Clementi, P. Linda, and C. D. Johnson, *J.C.S. Perkin II*, 1973, 1250.
[26] G. Van Zyl, C. J. Bredeweg, R. H. Rynbrandt, and D. C. Neckers, *Canad. J. Chem.*, 1966, **44**, 2283.
[27] R. F. Curtis, D. M. Jones, and W. A. Thomas, *J. Chem. Soc.* (*C*), 1971, 234.
[28] G. F. Smith, *Adv. Heterocyclic Chem.*, 1963, **2**, 287.

[29] D. A. McCaulay, in ref. 7, vol. II, part 2, ch. XXIV.
[30] G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185.
[31] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, 1961, 142.
[32] D. M. Brouwer and J. A. Van Doorn, *Rec. Trav. chim.*, 1972, **91**, 1110.
[33] G. A. Olah and S. J. Kuhn, in ref. 7, vol. III, part 2, ch. XLIII.
[34] G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, 1962, **84**, 1688.
[35] P. Finocchiaro, *Tetrahedron*, 1972, **27**, 581.
[36] G. A. Olah and M. W. Meyer, in ref. 7, vol. I, ch. VIII.
[37] G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 1956, 3435.
[38] B. S. Friedman, F. L. Morritz, C. J. Morrissey, and R. Koncos, *J. Amer. Chem. Soc.*, 1958, **80**, 5867.
[39] J. E. Banfield, W. Davies, N. W. Gamble, and S. Middleton, *J. Chem. Soc.*, 1956, 4791.
[40] A. E. Siegrist and H. R. Meyer, *Helv. Chim. Acta*, 1969, **52**, 1282.
[41] G. M. Badger, H. J. Rodda, and W. H. F. Sasse, *J. Chem. Soc.*, 1954, 4162.
[42] R. M. Lagidze and B. S. Potskhverashvili, *Subshcheniya Akad. Nauk Gruzin. S.S.R.*, 1957, **19**, 429 (*Chem. Abs.*, 1962, **56**, 10003).
[43] H. Wynberg and M. Cabell, *J. Org. Chem.*, 1973, **38**, 2814.
[44] L. N. Petrova and O. V. Shvarts, *Zhur. obshchei Khim.*, 1950, **20**, 2168 (*Chem. Abs.*, 1951, **45**, 7075).
[45] W. Carruthers, A. G. Douglas, and J. Hill, *J. Chem. Soc.*, 1962, 704.
[46] D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, 1952, **74**, 664.
[47] D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res., India*, 1959, **18B**, 77.
[48] T. L. Fletcher, H.-L. Pan, C.-A. Cole, and M. J. Namkung, *J. Heterocyclic Chem.*, 1974, **11**, 815.
[49] I. M. Nasyrov, I. U. Numanov, G. D. Gal'pern, and A. A. Bakaev, *Doklady Akad. Nauk Tadzh. S.S.R.*, 1966, **9**, 23 (*Chem. Abs.*, 1966, **65**, 18549.
[50] S. Dayagi, I. Goldberg, and U. Shmueli, *Tetrahedron*, 1970, **26**, 411.