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SOME REACTIONS OF 2,3,4,5,6,7-HEXACHLOROBENZO [b]THIOPHEN

G. M. Brooke* and R. King
Chemistry Department, Science Laboratories, South Road, Durham, DH1 3LE

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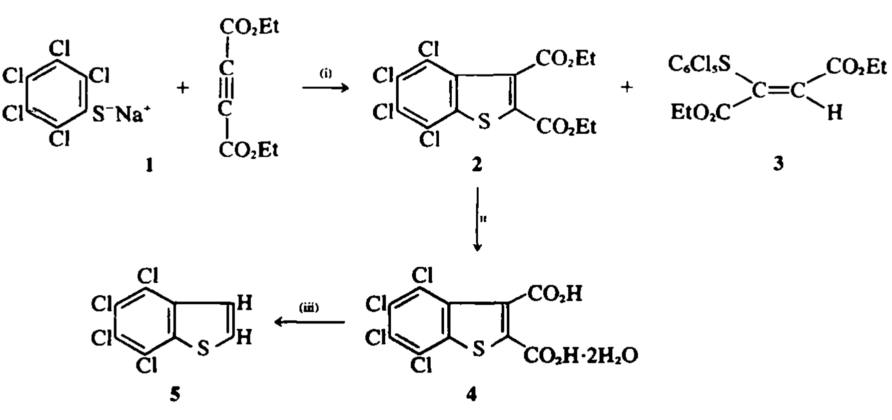
Abstract—2,3,4,5,6,7-Hexachlorobenzo[b]thiophen (**1**) reacts with n-butyl-lithium to give either the 2-lithio derivative or the 2,6-dilithio derivative depending on the reaction conditions; a mixture of mono (2-) and di (2, 6-) Grignard reagents is formed from **1** and magnesium. Nucleophilic replacement of the 2-chlorine atom in **1** has been established for reaction with LAH; sodium benzenethiolate replaces a chlorine in the 5-membered ring, while a monosubstitution product is formed with sodium isopropoxide. 4,5,6,7-Tetrachlorobenzo[b]thiopen (**5**) was synthesised unambiguously and served as a model for ^{1}H NMR spectroscopy experiments. Catalytic hydrogenation of **1** [Pd-C] gives **5**, (99% yield). Compound **1** forms the 1,1-dioxide (**12**) with peroxytrifluoroacetic acid, the vacuum pyrolysis of which gives hexachlorophenyl-acetylene.

Current interest in the chemistry of highly chlorinated heteroaromatic compounds is centred mainly around the nitrogen-containing 6-membered ring systems related to benzene (pentachloropyridine,[1] tetrachloro-pyridazine,[2] -pyrimidine[3,4] and pyrazine[4]) and 10-membered ring systems related to naphthalene (heptachloro-quinoline[5] and -isoquinoline,[5] and hexachloro-cinnoline,[6] -phthalazine,[7] -quinazoline[8] and -quinoxaline[9]) especially with regard to their conversion to the corresponding fluoro-analogues. However, some of the wider aspects of chloroheteroaromatic compounds are now being examined.[10]

Apart from the recently reported fluorination of tetrachlorothiophen,[11] the chemistry of highly chlorinated heteroaromatic compounds containing heteroatoms other than nitrogen has been pursued less vigorously. In this paper we report some of our studies into the chemistry of 2,3,4,5,6,7-hexachlorobenzo[b]thiophen (**1**) a compound which was first prepared by Barger and Ewins in 1908.[12]

In choosing the reactions for investigation we have borne in mind the necessity to relate the products directly or indirectly to compounds containing H atoms directly attached to the aromatic ring system which would be amenable to examination by ^{1}H NMR spectroscopy. As a model for these spectroscopy experiments we synthesised 4,5,6,7-



SCHEME 1

Reagents and conditions. (i) reflux then H_3O^+; (ii) 50% v/v H_2SO_4, reflux; (iii) Cu-quinoline, reflux.

tetrachlorobenzo [b] thiophen unambiguously by a method which has been used to prepare fluorine-containing benzo[b]thiophen derivatives[13] (Scheme 1). Compound **5** has been identified by mass spectroscopy as a main product obtained from the pyrolysis of tetrachlorophthalic anhydride and thiophen, but no physical data were given.[14]

Reaction of sodium pentachlorobenzenethiolate with diethyl acetylene-dicarboxylate in tetrahydrofuran (THF) at reflux temperature for 3 h gave the cyclised product **2** (8%) and the olefin **3** (42%). The stereochemistry of **3** is the result of the overall *trans*-addition of C_6Cl_5S-H to the acetylene and was deduced from the chemical shift of the olefinic proton at 6·62δ. This lies within the range (6·15–6·9δ) found for the olefinic proton for the products of overall *trans*-addition of a wide number of nucleophiles to diethyl acetylene-dicarboxylate;[15] for the corresponding geometrical isomers formed by overall *cis*-addition, the olefinic proton lies within the range 5·05–5·57δ. Under more vigorous conditions (18 h reflux) no olefinic material could be isolated and the major product was **2** (76%). Hydrolysis of the diester with 50% sulphuric acid gave the hydrated dicarboxylic acid **4** (86%) which in turn was decarboxylated by copper in quinoline to give 4,5,6,7 - tetrachlorobenzo[b]-thiophen **5** (52%).

The ^{1}H NMR spectrum of **5** gave the coupling constant $J_{2,3} = 5{\cdot}4$ Hz which is typical for this substitution pattern,[16] while the actual identity of the protons was determined from the relative shifts in the absorptions on changing solvents. It has recently been shown for benzo[b]thiophen that while an overall deshielding of protons occurs in acetone relative to carbon tetrachloride, the effect is particularly marked at position 2[solvent shift $\Delta = \delta_{\text{acetone}} - \delta_{CCl_4} = 0{\cdot}27$ ppm *cf* 0·15 ppm at position 3].[17] On this basis, the absorption centred at 7·61δ (CCl_4) and 8·07δ (acetone) having a large solvent shift [$\Delta = 0{\cdot}46$ ppm] was assigned to position 2, and that centred at 7·54δ (CCl_4) and 7·65δ (acetone) [$\Delta = 0{\cdot}11$ ppm] to position 3. A similar large solvent shift ($\delta_{\text{acetone}} - \delta_{CCl_4}$) for 2-H relative to 3-H has been observed in 4,5,6,7 - tetrafluorobenzo[b]thiophen (0·5; *cf* 0·1 ppm][18].

Benzo[b]thiophen is metallated by n-butyllithium in the 2-position.[19] Treatment of 2,3,4,5,6,7 - hexachlorobenzo[b]thiophen (**1**) in THF with one equivalent of n - butyl - lithium followed by hydrolysis gave a pentachlorobenzo[b]thiophen (**6**, 56%), accompanied by unchanged starting material (**1**, 39%). Catalytic (Pd/C) hydrogenation of **6** gave 4,5,6,7 - tetrachlorobenzo[b]thiophen (**5**, 59%) which showed that a chlorine in the 5-membered ring of **1** had been replaced upon metallation. Compound **6** was assigned the structure 3,4,5,6,7 - pentachlorobenzo[b]thiophen on the basis of the following evidence. A large downfield solvent shift ($\delta_{\text{acetone}} - \delta_{CCl_4} = 0{\cdot}55$ ppm) was observed in the position of the absorption in the ^{1}H NMR spectrum. The *difference* between the solvent shift of **6** and the solvent shifts of each of the protons in **5** give the contribution of the chlorine to the overall shift at the adjacent positions. Thus if **6** was a 2-Cl, 3-H compound, the presence of the 2-chlorine would be to increase the solvent shift of 3-H in **5** by 0·44 ppm (0·55–0·11 ppm), whereas if **6** was a 2-H, 3-Cl compound, the presence of the 3-chlorine would be to increase the solvent shift of 2-H in **5** by 0·09 ppm (0·55–0·46 ppm). We have measured the solvent shifts ($\delta_{\text{acetone}} - \delta_{CCl_4}$) of 2-chloro- and 3 - chloro - benzo[b]thiophen and have compared the results with those of benzo[b]thiophen at the same mole fraction.[17] The 2 - chlorine increases the solvent shift at 3-H by 0·10 ppm 0·25–0·15 ppm), and the 3-chlorine increases the solvent shift at 2-H by 0·13 ppm (0·40–0·27 ppm). These results show that chlorine as a substituent in the 5-membered ring of benzo[b]thiophen compounds causes only a slight increase in the overall solvent shifts of protons attached to adjacent C atoms. Consequently the very large solvent shift of the proton in **6** must be due to it being at the 2-position, the 3-chlorine being responsible only for a small increase of 0·09 ppm in the solvent shift of the proton at position 2. Furthermore, in acetone in which the biggest differences in chemical shifts of 2- and 3-protons are found, the 2-H proton in 2-H, 3-Cl benzo[b]thiophen at 7·63δ and the 3-H proton in 2-Cl, 3-H benzo[b]thiophen at 7·39δ have virtually the same chemical shifts as the corresponding protons in benzo[b]thiophen (2-H, 7·61δ; 3-H, 7·41δ); in **6**, the proton at 8·04δ has an almost identical chemical shift with the 2-H proton in 4,5,6,7 - tetrachlorobenzo[b]thiophen **5** (8·07δ; *cf* 7·65δ for 3-H) and is further evidence for assigning the 2-H structure to **6**.

In an attempt to drive the halogen - metal exchange to completion, compound **1** was treated with excess n - butyl - lithium (6 eq.) and hydrolysed. Thin layer chromatography showed the absence of both **1** and **6** and the presence of two new components. The major component **7** (89%) was a tetrachlorobenzo[b]thiophen, while the minor component, an oil, was not examined. Compound **7** was assigned the structure 3,4,5,7 - tetrachlorobenzo[b]-thiophen on the basis of the following evidence. The two protons were coupled (J, 0·6 Hz) in the ^{1}H NMR spectrum. One proton was assigned to position 2 by virtue of having identical chemical shifts as the 2-proton in **6** in both carbon tetrachloride and in acetone, while the second proton was assigned to position 6 since it is known that a 2-proton only couples with a 6-proton in the benzo part of benzol[b]thiophen compounds ($J_{2,6} = 0{\cdot}5$—$0{\cdot}6$ Hz).[16]

Reaction of **1** in THF with excess magnesium at room temperature followed by hydrolysis gave an equimolar mixture of **6** (29%) and **7** (29%), deduced by ^{1}H NMR spectroscopy, together with unchanged starting material **1** (29%). Under more forcing conditions, the only product isolated after hydrolysis was compound **7** (9%).

Treatment of **1** with an equimolar amount of LAH in THF at room temperature gave 3,4,5,6,7-pentachlorobenzo[b]thiophen **6** (42%) and unreacted starting material **1** (42%). More vigorous reaction conditions reduced both the amount of **1** (16%) and **6** (32%).

The catalytic replacement of the chlorine by hydrogen at position 3 in 3,4,5,6,7-pentachlorobenzo[b]thiophen **6** to give **5** is a reaction type which has not been reported previously.[16] Furthermore, when the same reaction was performed with 2,3,4,5,6,7-hexachlorobenzo[b]thiophen (**1**), compound **5** was formed in 99% yield. In an attempt to exploit this hydrogenolysis reaction, we reacted **1** with other nucleophiles and subjected the product to hydrogenolysis, in the expectation that ^1H NMR solvent shift experiments on the hydrogen-containing benzo[b]thiophen compounds would permit structure assignments to be made.

Sodium benzenethiolate (1·1 eq.) reacted with 2,3,4,5,6,7-hexachlorobenzo[b]thiophen in pyridine at reflux temperature to give a monothiophenoxy-pentachlorobenzo[b]thiophen **8** (41%) and unchanged starting material (5%). Catalytic hydrogenolysis of the thioether gave 4,5,6,7-tetrachlorobenzo[b]thiophen **5** (78%) by removal of chlorine *and* a thiophenoxy group, and unreacted starting material **8**; no other material retaining the thiophenoxy group was detected in the product. Consequently, although the thiophenoxy group had replaced a chlorine in the 5-membered ring of compound **1**, the orientation can only be inferred as the 2-thiophenoxy derivative by analogy with the product obtained from **1** and LAH.

No tractable product could be isolated from the reaction of **1** with sodium methoxide in a variety of solvents (methanol, N,N-dimethylformamide, pyridine, THF, DMSO); a complex mixture of highly coloured materials was always obtained which presumably involves demethylation of initially formed methoxy derivatives. However with sodium isopropoxide (5 eq.) in pyridine, compound **1** gave a monoisopropoxypentachlorobenzo[b]thiophen **9** (64%) and unchanged starting meterial **1** (23%). Attempted catalytic hydrogenolysis of **9**, however, was completely unsuccessful: starting material **1** was recovered unchanged. We tentatively assign the structure of **9** as a 2-isopropoxy derivative only by analogy with the course of reaction of **1** and LAH though the *failure* to effect chlorine hydrogenolysis is entirely in keeping with the absence of a reactive replaceable halogen at position 2.

The hydrodesulphurisation experiments using Raney nickel in ethanol which were so successful with derivatives of 4,5,6,7-tetrafluorobenzo[b]thiophen[20] were of no use with all the highly chlorinated benzo[b]thiophen compounds which we prepared; no readily identifiable products were formed.

Currently, there is little published work concerning nucleophilic replacement reactions in benzo[b]thiophen systems. Nucleophilic replacement of fluorine in 4,5,6,7-tetrafluorobenzo[b]thiophen occurs predominantly by replacement of the 6-F atom.[21] Tetrafluorothiophen has been prepared and substitution of the 2-fluorine by methoxide ion demonstrated.[22] This present study reveals that in the case of reaction between 2,3,4,5,6,7-hexachlorobenzo[b]thiophen **1** and LAH, the Cl atom at position 2 is the most readily replaced. It is interesting, however, that the second site of lithiation of **1**, after position 2, is at position 6. The close connection between the sites of metallation and nucleophilic substitution has already been noted in the case of pentachloropyridine.[23]

It has been reported that the failure to form a 1,1-dioxide from benzo[b]thiophen compounds bearing chlorine substituents simultaneously at positions 2- and 7- is due to steric overcrowding.[24] However, we had no difficulty in converting **1** into 2,3,4,5,6,7-hexachlorobenzo[b]thiophen-1,1-dioxide **12** (85%) using peroxytrifluoroacetic acid.

Pyrolysis of **12** by sublimation through a quartz tube packed with silica fibre at 840° *in vacuo* gave hexachlorophenylacetylene[25] quantitatively by extrusion of SO_2 and migration of chlorine. It is interesting to compare this reaction with the pyrolysis of octafluorodibenzothiophen-1,1-dioxide which formed octafluorodibenzofuran by extrusion of SO.[26]

EXPERIMENTAL

2,3,4,5,6,7-*Hexachlorobenzo*[b]*thiophen* (1)

This material was prepared according to the method of Barger and Ewins.[12]

3,4,5,6,7-*Pentachlorobenzo*[b]*thiophen* (6)

(a) *From the 2-lithio derivatives.* Compound **1** (1·04g) in dry THF (100 ml) was treated at −70° with n-BuLi in hexane (1·6 ml, 2·0N) and the mixture stirred for 1 h. The temp was allowed to rise to 0° and aqueous THF (20 ml, 50% v/v) added. The mixture was acidified with 2N HCl (100 ml), extracted with ether and the dried ($MgSO_4$) extracts evaporated. Two components were present which were separated by chromatography on silica [light petroleum (b.p. 60–80°) as eluant]. The first component (0·40g) was unreacted starting material **1**, identified by IR spectroscopy. The second component (0·52g) was 3,4,5,6,7-*pentachlorobenzo*[b]*thiophen* **6**, m.p. 212–213° (from MeoH) (Found: C, 31·2; H, 0·5; C_8HCl_5S requires; C, 31·4; H, 0·3%). The ^1H NMR spectrum showed a sharp singlet at 7·49δ (mole fraction $3{\cdot}11 \times 10^{-3}$ in CCl_4) and at 8·04δ (mole fraction $3{\cdot}10 \times 10^{-3}$ in acetone).

(b) *From compound* **1** *and lithium aluminum hydride.* Compound **1** (0·5g) and LAH in THF (20 ml, 0·076M) were stirred under N_2 at room temp for 48 h. The mixture was treated with water (50 ml), extracted with ether and the dried ($MgSO_4$) extracts evaporated. Two components were presented which were separated by chromatography on silica [light petroleum (b.p. 60–80°) as eluant]. The first component (0·212g) was unreacted starting material **1**, identified by IR spectroscopy. The second component (0·189g) was **6** m.p. 212–213° identified by IR spectroscopy.

3,4,5,7-*Tetrachlorobenzo*[b]*thiophen* (**7**)

(a) *From a dilithio derivative.* Compound **1** (1·0g) in dry THF (150 ml) was treated at −70° with n-BuLi in hexane (10 m., 2·0N). The mixture was stirred at − 15 to − 20° for 1 h, water (50 ml) was added and the mixture extracted with ether and worked up as before. Two components were present which were separated by chromatography on silica [light petroleum (b.p. 60–80°) as eluant]. The first component was 3,4,5,7 - *tetrachlorobenzo*[b]*thiophen* **7** (0·713g), m.p. 146–147° [from light petroleum (b.p. 60–80°)]. (Found: C, 35·2; h, 1·0; $C_8H_2Cl_4S$ requires C, 35·3; H, 0·7%). The ^{1}H NMR showed two doublets $J_{2,6}$ 0·6 Hz) at 7·49δ (due to H-2) and at 7·56δ (due to H-6) (mole fraction $3{\cdot}15 \times 10^{-3}$ in CCl_4); and at 8·04δ (due to H-2) and at 7·81δ (due to H-6) (mole fraction $3{\cdot}11 \times 10^{-3}$ in acetone). The second component, a yellow oil, was not identified.

(b) *From a Grignard reagent.* Compound **1** (0·55g) and Mg (0·6g) in dry THF (20 ml) were treated with ethylene dibromide (0·25 ml). After the initial reaction had subsided, the mixture was stirred at room temp for 3 h and then heated under reflux for a further 1 h during which time ethylene dibromide (10 ml) was added. The mixture was treated with water (50 ml), extracted with ether, and the dried ($MgSO_4$) extracts evaporated to give a brown oil which crystallised on standing. Recrystallisation of the crude product from light petroleum (b.p. 40–60°) gave **7** (0·04g) identified by IR spectroscopy.

Reaction of **1** (0·98g) with Mg (0·45g) in dry THF (40 ml) at room temp for 0·5 h with activation of the metal by ethylene dibromide (0·2 ml), followed by hydrolysis gave a product containing three components which were partially separated by chromatography on silica [light petroleum (b.p. 60–80°) as eluant]. The first component was unreacted starting material **1** (0·283g), identified by IR spectroscopy, while the second and third components could not be separated on the preparative scale. This material (0·48g) was shown by ^{1}H NMR spectroscopy to be an equimolar mixture of **6** and **7**. [In CCl_4, the absorptions at 7·40δ and 7·46δ were in the ratio 2 : 1; in acetone, and the absorptions at 7·71δ and 7·96δ were in the ratio 1 : 2].

A monochloro monothiophenoxy - 4, 5, 6, 7 - *tetrachlorobenzene*[b]*thiophen* (**8**)

Thiophenol (0·39g) in dry pyridine (20 ml) was treated with sodium hydride (0·1g) and the filtered soln was added dropwise to a soln of **1** (1·01g) in dry pyridine (50 ml). The mixture was heated under reflux for 48 h, and worked up as in the previous experiment. Two components were present which were separated by chromatography on silica. The first component was unreacted starting material **1** (0·05g) identified by IR spectroscopy and the second component (0·50g) was a *monochloro - monthiophenoxy* - 4, 5, 6, 7 - *tetrachlorobenzo*[b]*thiophen* **8** m.p. 146–147° [from light petroleum (b.p. 60–80°)] (Found: C, 40·3; H, 1·2; Cl, 43·3; $C_{14}H_5Cl_5S_2$ requires; C, 40·6; H, 1·2; Cl, 42·8%).

A mono-isopropoxy-pentachlorobenzo[b]*thiophen* (**9**)

A mixture of **1** (0·51g), sodium isopropoxide (0·6g) and dry pyridine (100 ml) was heated under reflux under N_2 for 3 h. The mixture was diluted with water, extracted with ether and the extracts washed with excess 5N HCl. The extracts were dried ($MgSO_4$) and evaporated, and the two components present were separated by chromatography on silica [light petroleum (b.p. 60–80°) as eluant]. The first component (0·155g) was identified as unreacted starting material **1** by IR spectroscopy. The second component (0·35g) was a *mono - isopropoxypentachlorobenzo*[b]-*thiophen* **9**, m.p. 100–100·5° [from light petroleum (b.p. 40–60°)] (Found: C, 36·1; H, 2·3; $C_{11}H_7Cl_5OS$ requires; C, 36·3; H, 1·9%).

Diethyl 4,5,6,7-*tetrachlorobenzo*[b]*thiophen* - 2, 3 - *dicarboxylate* **2**

Pentachlorothiophenol (6·3g) in dry THF (200 ml) was treated with sodium hydride (0·55g) and after the initial reaction had ceased, diethyl acetylenedicarboxylate (4·5g) in dry THF (40 ml) was added and the mixture was heated under reflux for 18 h. The soln was treated with 4N HCl (100 ml), extracted with ether and the dried ($MgSO_4$) extracts evaporated. The major component in the product separated by chromatography on silica (CCl_4 followed by $CHCl_3$ as eluants) was *diethyl*-4,5,6,7-*tetrachlorobenzo*[b]*thiophen* - 2, 3 - *dicarboxylate* **2** (7·1g) m.p. 119–120° [from light petroleum (b.p. 60–80°)] (Found: C, 40·6; H, 2·4: Cl, 34·6; $C_{14}H_{10}Cl_4O_4S$ requires; C, 40·3; H, 2·5; Cl, 34·9%).

Treatment of pentachlorothiophenol (10·0g) in dry THF (300 ml) with sodium hydride (0·8g) followed by reaction with diethyl acetylenedicarboxylate (6·4g) in THF (20 ml) at reflux temp for 3 h gave, after working the mixture up as before, a crude product (9·3g) which was separated by chromatography on silica (benzene as eluant) into two components. The first component was **2** (1·2g), identified by IR spectroscopy, and the second component was a *diethyl - cis* - 1 - *pentachlorothiophenoxybutenedioic acid* **3** (6·7g), m.p. 125–127° [from light petroleum (b.p. 60–80°)] (Found: C, 36·9; H, 2·4; Cl, 38·8; S, 7·4; $C_{14}H_{11}Cl_5O_4S$ requires; C, 37·1; H, 2·5; Cl, 39·2; S, 7·1%).

4,5,6,7 - *Tetrachlorobenzo*[b]*thiophen* - 2, 3 - *dicarboxylic acid dihydrate* **4**

The diester **3** (0·5g) was heated under reflux with H_2SO_4 (40 ml, 50% v/v) for 7·5 h. The mixture was diluted with water, extracted with ether, and the dried ($MgSO_4$) extracts evaporated. The crude residue (0·41g) was leeched with boiling benzene, and the impure adduct which did not dissolve was recrystallised from water to give 4,5,6,7 - *tetrachlorobenzo*[b]*thiophen* - 2, 3 - *dicarboxylic acid dihydrate* **4**, m.p. 280° with dec (found: C, 30·2; H, 1·2; $C_{10}H_6Cl_4O_6S$ requires; C, 30·3; H, 1·5%).

4,5,6,7-*Tetrachlorobenzo*[b]*thiophen* **5**

(a) *From* 4,5,6,7 - *tetrachlorobenzo*[b]*thiophen* - 2, 3 - *dicarboxylic acid dihydrate* **4**. Compound **4** (0·9g), Cu powder (1·0g) and quinoline (60 ml) were heated under reflux for 1 h. The mixture was acidified with H_2SO_4 (200 ml, 50% v/v) extracted with ether and the extracts washed with further H_2SO_4 (50%v/v), dried ($MgSO_4$) and evaporated. The crude red oil which remained (0·79g) was chromatographed on silica [light petroleum (b.p. 60–80°) as eluant] to give 4,5,6,7 - *tetrachlorobenzo*[b]*thiophen* **5** (0·32g) m.p. 209–211° [from light petroleum, (b.p. 60–80°)] (Found: C, 35·1; H, 0·7; $C_8H_2Cl_4S$ requires; C, 35·3; H, 0·77%). The ^{1}H NMR spectrum of **5**, mole fraction $3{\cdot}11 \times 10^{-3}$ in CCl_4 was a distorted AB spectrum with H-2 at 7·61δ and H-3 at 7·54δ ($J_{2,3}$ 5·4 Hz). In acetone, (mole fraction solute $3{\cdot}11 \times 10^{-3}$) the chemical shifts were: H-2, 8·07δ; H-3, 7·65δ ($J_{2,3}$ 5·4 Hz).

(b) *From* 2,3,4,5,6,7 - *hexachlorobenzo* [b]*thiophen* **1**. A mixture of **1** (0·2g), the catalyst (0·15g, 10% Pd on charcoal), KOH (0·2g) and MeOH (40 ml) was shaken in an atmosphere of H_2 at room temp and atmospheric pressure until 30 ml of H_2 had been absorbed. The soln was filtered, diluted with water, extracted with ether and the dried ($MgSO_4$) extracts evaporated to give **5**, (0·157g) m.p. 210–211°, identified by IR spectroscopy.

(c) *From* 3,4,5,6,7 - *pentachlorobenzo* [b]*thiophen* **6**. A mixture of **6** (0·12g), the catalyst (0·1g, 10% Pd on C), KOH (0·2g) and MeOH (20 ml) was shaken with H_2 at room temp and atmospheric pressure until 8 ml of H_2 had been absorbed. The mixture was worked up as before to give **5** (0·105g) m.p. 210–211°, identified by IR spectroscopy.

(d) *From the monochloro monothiophenoxy* - 4, 5, 6, 7 - *tetrachlorobenzo* [b]*thiophen* **8**. A mixture of **8** (0·46g), the catalyst (0·9g, 10% Pd-C), KOH (0·3g) and MeOH(40 ml) was shaken with H_2 at room temperature and atmospheric pressure for 8 h and the soln was worked up as before. Two components were present which were separated by chromatography on silica [light petroleum (b.p. 40–60°) as eluant]. The first component was unreacted starting material **8** (0·146g), identified by IR spectroscopy and the second component was **5** (0·236g) m.p. 210–211° identified by IR spectroscopy.

2,3,4,5,6,7 - *Hexachlorobenzo* [b]*thiophen* - 1,1 - *dioxide* (**12**)

Compound **1** (0·86g) in CCl_4 (50 ml) was added to a stirred soln of trifluoroacetic anhydride (10 ml) and H_2O_2 (5 ml, 90%) in CCl_4 (50 ml) at room temp. The mixture was heated under reflux for 5 hr, diluted with water and the organic layer separated, dried ($MgSO_4$) and evaporated to give 2,3,4,5,6,7 - *hexachlorobenzo* [b]*thiophen* - 1,1 - *dioxide* **12** (0·8g) m.p. 166–167° [from light petroleum (b.p. 60–80°)] (Found: C, 25·7; Cl, 56·7; S, 8·6; $C_8Cl_6SO_2$ requires: C, 25·8; Cl, 57·0; S, 8·6%).

Pyrolysis of **12**

The dioxide **12** (0·035g) was slowly sublimed at 10^{-2} mm into a quartz pyrolysis tube packed with silica wool and heated to 840°. Volatile material from the tube was collected in a liquid N_2 trap and chromatographed on silica [light petroleum (b.p. 60–80°) as eluant] to give hexachlorophenylacetylene (0·033g) m.p. 137–138°, identified by IR spectroscopy.

2-*Chlorobenzo* [b]*thiophen*

This was prepared from benzo[b]thiophen.[27] The 3-H proton was readily identified in the ^1H NMR spectrum by its high intensity, due to the absence of $J_{2,3}$. In CCl_4, at mole fraction $3{\cdot}3 \times 10^{-2}$, the 3-H absorption occurred at 7·14δ; in acetone, at mole fraction $3{\cdot}3 \times 10^{-2}$, the 3-H absorption was at 7·39δ.

3-*Chlorobenzo* [b]*thiophen*

This was prepared from benzo[b]thiophen.[28] The 2-H proton was readily identified in the ^1H NMR spectrum by its high intensity, due to the absence of $J_{2,3}$. In CCl_4, at mole fraction $3{\cdot}3 \times 10^{-2}$ the 2-H absorption occurred at 7·23δ; in acetone, at mole fraction $3{\cdot}3 \times 10^{-2}$, the 2-H absorption was at 7·63δ.

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