Substitution Reactions of Benzo[*b*]thiophen Derivatives. Part VI.[1] Reactions of 4-Methoxybenzo[*b*]thiophen and its 3-Methyl Derivative

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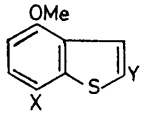
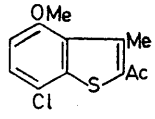
The bromination, nitration, Vilsmeier–Haack formylation, and Friedel–Crafts acetylation reactions of 4-methoxybenzo[*b*]thiophen and its 3-methyl derivative have beeen investigated. For 4-methoxybenzo[*b*]thiophen, these reactions gave the 7-substituted product, whereas for the 3-methyl derivative a mixture of the 2- (*ca.* 40%) and 7-substituted compounds (*ca.* 60%) was obtained in each case. For both compounds, dibromination and dinitration gave the 2,7-disubstituted derivative. The structures of the substitution products were determined by n.m.r. spectroscopy.

THE substitution reactions of 4-hydroxy- and 4-methoxy-benzo[*b*]thiophen,[2-4] unlike those of the corresponding 5-substituted compounds,[5] have not been investigated extensively. We describe here some reactions of 4-methoxybenzo[*b*]thiophen and its 3-methyl derivative, and compare the results where possible with those obtained previously for the analogous benzofuran and naphthalene derivatives. During our work on the 4-methoxy-compound, some parallel observations were published by Campaigne and his co-workers.[2] Despite our use of different reaction conditions, we support Campaigne's finding [2] that monobromination, mononitration, Vilsmeier–Haack formylation, and Friedel–Crafts acetylation gives mainly the 7-substituted product in each case. However, we could not obtain the pure 7-bromo-compound by brominating 4-methoxybenzo[*b*]thiophen at room temperature in carbon tetrachloride (*cf.* ref. 2), because it formed an inseparable mixture with the 2,7-dibromo-derivative (30%) (see later) and a further component (10%; probably the 2-bromo-derivative). However, the 7-bromo-compound could be obtained readily (88%) by carrying out the bromination at 0°. We then dibrominated (bromine in carbon tetrachloride under reflux) and dinitrated (nitric and sulphuric acids in acetic acid under reflux) 4-methoxybenzo[*b*]thiophen, and obtained the 2,7-disubstituted product [(2) or (3)] in each case (79 and 95%, respectively).





(1) Y = H
(2) X = Y = Br
(3) X = Y = NO_2

(4)

Our products were readily identified by n.m.r. spectroscopy. The spectrum of a 7-substituted 4-methoxybenzo[*b*]thiophen (1) showed two distinct AB quartets due to 5-H, 6-H, 2-H, and 3-H; these were easily distinguished because the coupling between two adjacent benzenoid protons ($J_{5,6}$ *ca.* 8 Hz) is greater than that

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[2] E. Campaigne, A. Dinner, and M. Haseman, *J. Heterocyclic Chem.*, 1971, **8**, 755.
[3] P. Demerseman, J.-P. Lechartier, C. Pène, A. Cheutin, and R. Royer, *Bull. Soc. chim. France*, 1965, 1473.
[4] A. Ricci, D. Balucani, and N. P. Buu-Hoï, *J. Chem. Soc.* (*C*), 1967, 779.
[5] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 177.

between two adjacent thiophen protons ($J_{2,3}$ *ca.* 5·7 Hz). Long-range coupling [6] (*ca.* 0·5 Hz) between 2-H and 6-H then enabled the signals due to 2-H and 6-H to be assigned unambiguously. The absence of such coupling in the spectra of compounds (2) and (3) confirmed the presence of a 2-substituent. Because of the presence of the 4-methoxy-group, the 3-H signal appeared in all cases at lower field than the 2-H signal; the opposite is observed for most benzo[*b*]thiophen derivatives.[6] The 5-proton was strongly shielded by the 4-methoxy-group, so that its signal could be readily assigned in all cases.

The general reactivity and properties of benzo[*b*]-thiophen are often compared loosely with those of naphthalene because the replacement of CH=CH by a divalent sulphur atom is said to produce a sterically and electronically similar system.[7] 1-Methoxynaphthalene behaves like its sulphur analogue, 4-methoxybenzo[*b*]thiophen, in undergoing electrophilic substitution preferentially in the 4-position.[8–10] However, in the nitration reaction,[8] some substitution (14%) takes place in the 2-position. In the case of 4-methoxybenzo[*b*]-thiophen it might be expected that the reactive thiophen ring would compete with the activated benzene ring in substitution reactions, but it is nevertheless surprising that there is no evidence for any substitution in the 5-position, either in the mono- or in the di-nitration reaction. The behaviour of 4-methoxybenzo[*b*]thiophen might correspond more closely to that of the oxygen isostere, but no comparable data are available for 4-methoxybenzofuran.

We examined next the electrophilic substitution reactions of 4-methoxy-3-methylbenzo[*b*]thiophen in order to observe how the relative reactivities of the 2- and 7-positions are altered by the presence of the electron-donating 3-methyl group. The monobromination (bromine in carbon tetrachloride at 0°), mononitration (nitric acid in acetic acid at 5°), and formylation (dimethylformamide and phosphoryl chloride at 100°) reactions gave in each case a mixture of the 2- (*ca.* 40%) and 7-substituted products (*ca.* 60%), which were separated with some difficulty (see Experimental section). A mixture of the 2- (25—40%) and 7-bromo-compounds (60—75%) was also obtained when 4-methoxy-3-methylbenzo[*b*]thiophen was treated with *N*-bromosuccinimide in carbon tetrachloride, provided that the reagents and solvents were not especially pure. Side-chain substitution was not observed under these conditions, but 3-bromomethyl-4-methoxybenzo[*b*]thiophen was obtained almost quantitatively when carefully purified materials were used.[11] Dibromination and dinitration, under the conditions already described, gave the 2,7-disubstituted compound in each case.

Friedel–Crafts acetylation [acetyl chloride and tin(IV) chloride in methylene chloride at 0°] gave the 2- (20%) and 7-acetyl derivatives (58%), together with the 2,7-diacetyl compound (19%) and 2-acetyl-7-chloro-4-methoxy-3-methylbenzo[*b*]thiophen (4) (2%). Because the introduction of a chloro-substituent during Friedel–Crafts acetylation seemed unlikely, it appeared that the chloro-compound (4) was an artefact. In order to prepare our starting material we had cyclised β-(*o*-methoxyphenyl)-β-methyl-α-mercaptoacrylic acid with chlorine in carbon tetrachloride.[12] Evidently the resulting 4-methoxy-3-methylbenzo[*b*]thiophen-2-carboxylic acid was contaminated with a small amount of the corresponding 7-chloro-compound, so that decarboxylation of the mixture of 2-carboxylic acids then gave 4-methoxy-3-methylbenzo[*b*]thiophen, together with some of the corresponding 7-chloro-derivative. The presence of the latter was confirmed by mass spectrometry. It was difficult to obtain pure 4-methoxy-3-methylbenzo[*b*]thiophen, but for most purposes the presence of this minor chloro-contaminant was not detrimental since it was removed by crystallisation at a subsequent stage. 7-Chloro-4-methoxy-3-methylbenzo-[*b*]thiophen was evidently substituted in the 2-position during the acylation reaction, and the product (4) was then isolated when the total product from the reaction was separated by preparative layer chromatography. We wish to stress, therefore, that the cyclisation of β-aryl-α-mercaptoacrylic acids to benzo[*b*]thiophen derivatives by chlorine,[12] excellent though it is, may give rise to chlorinated side products when the aryl ring contains a strongly electron-donating substituent.

The structures of the compounds just described were established as before by n.m.r. spectroscopy (see Experimental section); that of 2-acetyl-4-methoxy-3-methylbenzo[*b*]thiophen was confirmed by hypohalite oxidation to 4-methoxy-3-methylbenzo[*b*]thiophen-2-carboxylic acid. The n.m.r. spectra of the 2,3,4-trisubstituted compounds were simplified by the considerable shielding of 5-H, so that the three benzenoid proton signals could be analysed as an ABX, rather than as an ABC system. We noted that the 3-methyl group in the 2-acetyl-3-methylbenzo[*b*]thiophen derivatives absorbs characteristically at δ 2·90—2·95 p.p.m.; this observation confirmed that the chloro-compound has structure (4).

The substitution reactions of 4-methoxy-3-methylbenzofuran have not been studied extensively. However, its behaviour on formylation [13] and Friedel–Crafts acetylation [3] suggests that, in contrast to the sulphur isostere, it undergoes substitution almost entirely in the 2-position. A comparison of the reactions of 4-methoxy-3-methylbenzo[*b*]thiophen and 1-methoxy-8-methylnaphthalene is not possible owing to lack of data for the naphthalene derivative.

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[8] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.*, 1965, **18**, 1391.
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[12] P. M. Chakrabarti, N. B. Chapman, and K. Clarke, *Tetrahedron*, 1969, **25**, 2781.
[13] R. Royer, P. Demerseman, J.-F. Rossignol, and A. Cheutin, *Bull. Soc. chim. France*, 1971, 2072.

EXPERIMENTAL

General experimental directions are given in Part I.[14] Molecular weights of bromine-containing compounds relate to the ^{79}Br isotope. Preparative g.l.c. was carried out manually on a Pye 104 instrument equipped with a flame-ionisation detector and 6 ft × ¼ in (o.d.) glass column packed with 5% (w/w) ECNSS-M on acid- and base-washed 60—80 mesh Celite. The temperature was 165° and the nitrogen flow rate 60 ml min^{-1}. Preparative t.l.c. was carried out on glass plates coated with silica gel G (Merck) (0·5 mm layer). The descriptions of n.m.r. spectra are simplified by the omission of details of long-range couplings.

4-Methoxybenzo[*b*]thiophen (84%), prepared by treatment of 4-hydroxybenzo[*b*]thiophen with methyl iodide and potassium hydroxide,[3] had b.p. 136—137° at 15 mmHg (lit.,[3] 141° at 17 mmHg).

Monobromination Reactions.—A solution of bromine (0·98 g, 0·0061 mol) in dry carbon tetrachloride (10 ml) was added dropwise during 3 h to a stirred solution of 4-methoxybenzo[*b*]thiophen (1·0 g, 0·0061 mol) in carbon tetrachloride (30 ml) at 0°. Stirring was continued at 0° for 1·5 h, chloroform was added, then the solution was shaken with aqueous sodium hydrogen carbonate and water, dried, and evaporated. 7-Bromo-4-methoxybenzo-[*b*]thiophen (1·32 g, 88%) formed white needles, m.p. 66—67° (lit.,[2] 63—64°) (from ethanol). When the reaction was repeated at room temperature a brown oil was obtained, the three components of which (see text) could not be separated by preparative g.l.c. or by t.l.c. The mass spectrum of the mixture showed the presence of a dibromo-compound (M^+, 320/322/324; *ca.* 30%), which was identified by g.l.c. as the 2,7-disubstituted compound.

Bromination of 4-methoxy-3-methylbenzo[*b*]thiophen [11] at 0° by the method just described gave a pale yellow solid (93%), which was resolved by preparative g.l.c. into (a) 7-*bromo*-4-*methoxy*-3-*methylbenzo*[b]*thiophen* (60% of the mixture), m.p. 67—68° [needles from light petroleum (b.p. 40—60°)] (Found: C, 46·5; H, 3·5; Br, 31·15; S, 12·65%; M^+, 256. $C_{10}H_9BrOS$ requires C, 46·7; H, 3·5; Br, 31·1; S, 12·45%; *M*, 256), δ 2·55 (d, 3-Me), 3·85 (s, OMe), 6·55 (d, 5-H), 6·9 (q, 2-H), and 7·3 (d, 6-H) p.p.m. ($J_{2,3\text{-Me}}$ 0·8, $J_{5,6}$ 8·0 Hz), and (b) 2-*bromo*-4-*methoxy*-3-*methylbenzo*-[b]*thiophen* (40% of the mixture), m.p. 79—80° [white needles from light petroleum (b.p. 40—60°)] (Found: C, 46·45; H, 3·55; Br, 31·15; S, 12·55%; M^+, 256), δ 2·6 (s, 3-Me), 3·95 (s, OMe), 6·75 (dd, 5-H), 7·26 (t, 6-H), and 7·36 (dd, 7-H) p.p.m. ($J_{5,6} = J_{6,7}$ = 8·0, $J_{5,7}$ 2·0 Hz). Treatment of 4-methoxy-3-methylbenzo[*b*]thiophen with *N*-bromosuccinimide (1 mol. equiv.) in boiling carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide, with or without irradiation, for times ranging from 15 min to 2 h, gave mixtures of the 2- (25—40%) and 7-bromo-compounds (60—75%) just described. When the solvent and reactants were purified carefully 3-bromomethyl-4-methoxybenzo[*b*]thiophen (98%) was the only product.[11]

Dibromination Reactions.—4-Methoxybenzo[*b*]thiophen was treated with bromine (2 mol. equiv.) in boiling carbon tetrachloride for 48 h, then the product was isolated as before. 2,7-*Dibromo*-4-*methoxybenzo*[b]*thiophen* (79%) crystallised from light petroleum (b.p. 60—80°) (charcoal) as white needles, m.p. 98—100° (Found: C, 33·4; H, 2·0; Br, 49·35%; M^+, 320. $C_9H_6Br_2OS$ requires C, 33·55; H, 1·85; Br, 49·65%; *M*, 320), δ 3·8 (s, OMe), 6·5 (d, 5-H), 7·25 (d, 6-H), and 7·46 (s, 3-H) p.p.m. ($J_{5,6}$ 8·0 Hz).

4-Methoxy-3-methylbenzo[*b*]thiophen was stirred at room temperature for 15 h with bromine (2 mol. equiv.) in carbon tetrachloride, to give the 2,7-*dibromo-derivative* (95%) as fluffy needles, m.p. 97—98° [from light petroleum (b.p. 60—80°)] (Found: C, 35·45; H, 2·4; Br, 47·7; S, 9·75%; M^+, 334. $C_{10}H_8Br_2OS$ requires C, 35·75; H, 2·4; Br, 47·55; S, 9·55%; *M*, 334), δ 2·65 (s, 3-Me), 4·0 (s, OMe), 6·6 (d, 5-H), and 7·3 (d, 6-H) p.p.m. ($J_{5,6}$ 8·0 Hz).

Mononitration Reactions.—A solution of concentrated nitric acid (0·39 g, 0·0061 mol) in glacial acetic acid (10 ml) was added dropwise during 3·5 h to a stirred solution of 4-methoxybenzo[*b*]thiophen (1 g, 0·0061 mol) in glacial acetic acid (20 ml) at 0°. The mixture was stirred at 0° for a further 45 min, then poured into water. The precipitate was filtered off and crystallised from ethanol, to give 4-methoxy-7-nitrobenzo[*b*]thiophen (1·1 g, 88%) as pale yellow needles, m.p. 133—134° (lit.,[2] 135—136°).

A similar nitration of 4-methoxy-3-methylbenzo[*b*]thiophen (1·0 g) at 5°, followed by stirring overnight at room temperature, gave a yellow solid, which was resolved into two components by preparative t.l.c. in benzene–light petroleum (b.p. 60—80°) (9 : 1). 4-Methoxy-3-methyl-2-nitrobenzo[*b*]thiophen (0·5 g, 40%), R_F 0·71, formed pale orange *needles*, m.p. 136—138° (from ethanol) (Found: C, 53·65; H, 3·9; N, 5·95; S, 14·6%; M^+, 223. $C_{10}H_9NO_3S$ requires C, 53·8; H, 4·05; N, 6·25; S, 14·35%; *M*, 223), δ 3·05 (s, 3-Me), 3·95 (s, OMe), 6·8 (dd, 5-H), 7·32 (t, 6-H), and 7·49 (dd, 7-H) p.p.m. ($J_{5,6} = J_{6,7}$ = 8·0, $J_{5,7}$ 1·8 Hz). 4-Methoxy-3-methyl-7-nitrobenzo[*b*]thiophen (0·75 g, 60%), R_F 0·59, formed pale yellow *needles*, m.p. 123—125° (from ethanol) (Found: C, 53·8; H, 4·0; N, 5·95; S, 14·4%; M^+, 223), δ 2·56 (d, 3-Me), 4·0 (s, OMe), 6·77 (d, 5-H), 7·05 (q, 2-H), and 8·33 (d, 6-H) p.p.m. ($J_{2,3\text{-Me}}$ 0·8, $J_{5,6}$ 8·0 Hz).

Dinitration Reactions.—A solution of concentrated nitric acid (0·78 g, 0·0122 mol) in acetic acid (10 ml) was added during 10 min to a stirred solution of 4-methoxybenzo-[*b*]thiophen (1 g, 0·0061 mol) and concentrated sulphuric acid (2 drops) in acetic acid (20 ml). The mixture was then stirred under reflux for 48 h and poured into water. Crystallisation of the resulting precipitate from benzene gave 4-methoxy-2,7-dinitrobenzo[*b*]thiophen (1·46 g, 94%) as bright yellow *needles*, m.p. 190—192° (Found: C, 42·7; H, 2·4; N, 10·9; S, 12·45%; M^+, 254. $C_9H_6N_2O_5S$ requires C, 42·5; H, 2·35; N, 11·0; S, 12·6%; *M*, 254), δ [$(CD_3)_2SO$] 4·14 (s, OMe), 7·35 (d, 5-H), 8·45 (s, 3-H), and 8·7 (d, 6-H) p.p.m. ($J_{5,6}$ 8·0 Hz).

Similar treatment of 4-methoxy-3-methylbenzo[*b*]thiophen gave the 2,7-*dinitro-compound* (70%), m.p. 209—211° (bright yellow needles from ethanol) (Found: C, 45·1; H, 3·0; N, 10·5; S, 11·9%; M^+, 268. $C_{10}H_8N_2O_5S$ requires C, 44·75; H, 3·0; N, 10·45; S, 11·95%; *M*, 268), δ 3·05 (s, 3-Me), 4·15 (s, OMe), 6·96 (d, 5-H), and 8·55 (d, 6-H) p.p.m. ($J_{5,6}$ 8·0 Hz).

Vilsmeier–Haack Formylations.—Phosphoryl chloride (2·59 g, 0·0177 mol) and 4-methoxybenzo[*b*]thiophen (2·5 g, 0·015 mol) were added successively with stirring, during 15 and 30 min, respectively, to dimethylformamide (5·2 ml). The mixture was stirred at 100—105° for 3·5 h, then cooled and poured into an excess of saturated aqueous sodium carbonate. Extraction with ether gave 4-methoxybenzo-[*b*]thiophen-7-carbaldehyde (2·88 g, 98%), m.p. 109—110°

[14] J. Cooper, D. F. Ewing, R. M. Scrowston, and R. Westwood, *J. Chem. Soc.* (*C*), 1970, 1949.

(lit.,[2] m.p. 108·5—109°, yield 74%) [needles from light petroleum (b.p. 60—80°) (charcoal)], $\nu_{max.}$ 1675 cm^{-1} (C=O).

4-Methoxy-3-methylbenzo[*b*]thiophen was formylated similarly for 4·5 h at 90—100° and the solid residue was separated by preparative t.l.c. [in benzene–light petroleum (1 : 1)] into two components. *4-Methoxy-3-methylbenzo*[b]-*thiophen-2-carbaldehyde* (0·4 g, 35%), R_F 0·25, formed needles, m.p. 119—120° [from light petroleum (b.p. 60—80°)] (Found: C, 63·9; H, 4·8; S, 15·35%; M^+, 206. $C_{11}H_{10}O_2S$ requires C, 64·05; H, 4·9; S, 15·55%; *M*, 206), $\nu_{max.}$ 1665 cm^{-1} (C=O), δ 2·9 (s, 3-Me), 3·9 (s, OMe), 6·9 (diffuse dd, 5-H), 7·35 (m, 6-H and 7-H), and 10·22 (s, CHO) p.p.m. The 5-H signal was resolved when the spectrum was run in C_6D_6 (δ 6·16 p.p.m.) ($J_{5,6}$ 8·0, $J_{5,7}$ 1·9 Hz). *4-Methoxy-3-methylbenzo*[b]*thiophen-7-carbaldehyde* (0·72 g, 62%), R_F 0·13, formed pale yellow needles, m.p. 100—101° [from light petroleum (b.p. 60—80°)] (Found: C, 64·15; H, 4·9; S, 15·65%; M^+, 206), $\nu_{max.}$ 1670 cm^{-1} (C=O), δ 2·55 (d, 3-Me), 3·95 (s, OMe), 6·82 (d, 5-H), 7·0 (q, 2-H), 7·7 (d, 6-H), and 10·01 (s, CHO) p.p.m. ($J_{2,3\text{-Me}}$ 0·8, $J_{5,6}$ 8·0 Hz).

Friedel–Crafts Acetylations.—A solution of 4-methoxybenzo[*b*]thiophen (1 g, 0·0061 mol) and acetyl chloride (0·5 ml, 0·0062 mol) in dry methylene chloride (50 ml) was added dropwise during 4 h to a stirred solution of tin(IV) chloride (2·19 g, 0·009 mol) in methylene chloride (20 ml) at 0°, then the mixture was stirred overnight at room temperature. Dilute hydrochloric acid (10%; 15 ml) was added cautiously and the mixture was boiled for 10 min. Organic material (1·24 g) was isolated in the usual way with chloroform and crystallised from light petroleum (b.p. 60—80°), to give 7-acetyl-4-methoxybenzo[*b*]thiophen (1·12 g, 90%) as needles, m.p. 115—116° (lit.,[2] 114·5—115·5°), $\nu_{max.}$ 1650 cm^{-1} (C=O). The mother liquor contained a minor component which could not be isolated pure.

Similar treatment of 4-methoxy-3-methylbenzo[*b*]thiophen (contaminated with a small percentage of the corresponding 7-chloro-compound) gave a solid product (81%), which was separated into four components by preparative t.l.c. (in benzene). *2-Acetyl-4-methoxy-3-methylbenzo*[b]-*thiophen* (20·3% of the mixture), R_F 0·75, crystallised from light petroleum (b.p. 60—80°) as pale yellow needles, m.p. 138—139° (Found: C, 65·5; H, 5·5; S, 14·55%; M^+, 220. $C_{12}H_{12}O_2S$ requires C, 65·4; H, 5·5; S, 14·55%; *M*, 220), $\nu_{max.}$ 1665 cm^{-1} (C=O), δ 2·55 (s, Ac), 2·92 (s, 3-Me), 3·88 (s, OMe), 6·69 (diffuse dd, 5-H), and 7·3 (m, 6-H and 7-H). The 5-H signal (δ 6·25 p.p.m.) was resolved when the spectrum was run in C_6D_6 ($J_{5,6}$ 7·8, $J_{5,7}$ 1·8 Hz). Oxidation of the 2-acetyl compound with sodium hypoiodite in dioxan, and acidification of the product, gave 4-methoxy-3-methylbenzo[*b*]thiophen-2-carboxylic acid (65%), m.p. and mixed m.p. 248—249° (lit.,[11] 248—249°), identical with an authentic[11] specimen. *7-Acetyl-4-methoxy-3-methylbenzo*[b]*thiophen* (58·3% of the mixture), R_F 0·62, formed white needles, m.p. 127—128° [from light petroleum (b.p. 40—60°)] (Found: C, 65·4; H, 5·6; S, 14·65%; M^+, 220), $\nu_{max.}$ 1650 cm^{-1} (C=O), δ 2·54 (s, Ac), 2·6 (d, 3-Me), 3·9 (s, OMe), 6·65 (d, 5-H), 6·98 (q, 2-H), and 7·28 (d, 6-H) ($J_{2,3\text{-Me}}$ 0·8, $J_{5,6}$ 8·0 Hz). *2,7-Diacetyl-4-methoxy-3-methylbenzo*[b]*thiophen* (18·8% of the mixture), R_F 0·15, crystallised from light petroleum (b.p. 60—80°) as pale yellow needles, m.p. 149—151° (Found: C, 63·8; H, 5·6; S, 12·25%; M^+, 262. $C_{14}H_{14}O_3S$ requires C, 64·1; H, 5·4; S, 12·2%; *M*, 262), $\nu_{max.}$ 1660br cm^{-1} (C=O), δ 2·64 (s, 6H, 2 × Ac), 2·90 (s, 3-Me), 3·98 (s, OMe), 6·73 (d, 5-H), and 8·03 (d, 6-H) p.p.m. ($J_{5,6}$ 8·0 Hz). *2-Acetyl-7-chloro-4-methoxy-3-methylbenzo*[b]*thiophen* (2·4% of the mixture), R_F 0·91, formed white needles, m.p. 93—95° [from light petroleum (b.p. 40—60°)] (Found: C, 56·65; H, 4·3; Cl, 14·0%; M^+, 254 and 256. $C_{12}H_{11}ClO_2S$ requires C, 56·6; H, 4·35; Cl, 13·9%; *M*, 254 and 256), $\nu_{max.}$ 1670 cm^{-1} (C=O), δ 2·6 (s, Ac), 2·95 (s, 3-Me), 3·90 (s, OMe), 6·72 (d, 5-H), and 7·34 (d, 6-H) p.p.m. ($J_{5,6}$ 8·0 Hz).

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