Substitution Reactions of Benzo[*b*]thiophen Derivatives. Part V.[1] t-Butylation of Benzo[*b*]thiophen and Nitration of 3-t-Butylbenzo[*b*]-thiophen-2-carboxylic Acid

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Contrary to previous reports, alkylation of benzo[*b*]thiophen with 2-methylpropene in the presence of polyphosphoric acid does not give entirely 3-t-butylbenzo[*b*]thiophen; instead, a mixture containing the 2- (22%) and 3-t-butyl isomers (71%) and an unidentified component (7%) is obtained. Similarly, alkylation with t-butyl alcohol and concentrated sulphuric acid gives mainly 2- (6%) and 3-t-butylbenzo[*b*]thiophen (89%). The mixtures are best separated by successive treatment with n-butyl-lithium and carbon dioxide. 2-t-Butylbenzo[*b*]thiophen is then recovered unchanged, but the 3-t-butyl isomer is converted into the 2-carboxylic acid, from which it can be obtained pure by decarboxylation.

Nitration of 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid in sulphuric acid and acetic acid at 60° or in acetic anhydride and acetic acid at 0° gives differing proportions of the following acidic products in each case: benzo[*b*]-thiophen-2-carboxylic acid, 3-, 4-, 6-, and 7-nitrobenzo[*b*]thiophen-2-carboxylic acid, and 3-t-butyl-4-, 3-t-butyl-6-, and 3-t-butyl-7-nitrobenzo[*b*]thiophen-2-carboxylic acid. The products are identified mainly by n.m.r. spectroscopy; mention is made of the effect of the 3-t-butyl group on the n.m.r. spectra of some benzo[*b*]thiophen derivatives. Mechanisms are proposed to explain the formation of those of the above products which lack a t-butyl group. Neutral material from the nitration reaction contains, *inter alia*, 3-t-butyl-2-nitrobenzo[*b*]thiophen and 2-nitrobenzo[*b*]thiophen.

EARLIER workers who investigated the reaction of benzo[*b*]thiophen with 2-methylpropene in the presence of 80% sulphuric acid [2] or 100% phosphoric acid [3] found that the product in each case was 3-t-butylbenzo[*b*]thiophen. It seemed unusual to us that none of the 2-isomer had been formed, because electrophilic substitution reactions of benzo[*b*]thiophen invariably take place in the 2- and 3-positions [4] and, in particular, alkylation with isopropyl chloride, propan-2-ol, or propene in the presence of various acid catalysts gives a mixture of the 2- and 3-isopropyl compounds, in which the 2-isomer predominates (78—92%).[5] We repeated the alkylation reaction with 2-methylpropene at 125° in the presence of polyphosphoric acid and obtained a mixture which contained (g.l.c.) the 2- (22%) and 3-t-butyl isomers (71%) and an unidentified compound (7%). Treatment of benzo[*b*]thiophen with t-butyl alcohol and concentrated sulphuric acid at 55° gave the same three components, but now the 2- and 3-t-butyl isomers were formed in 6 and 89% yield, respectively. The two t-butyl compounds from each reaction could be obtained in >99% purity by spinning-band fractionation, followed by preparative g.l.c., but the third component had a retention time similar to that of 3-t-butylbenzo[*b*]thiophen and could not be obtained pure by this method. On a preparative scale it was more convenient to treat the crude alkylation mixture successively with n-butyl-lithium and carbon dioxide. This procedure removed the 2-t-butyl isomer, which was not metalated under these conditions, and yielded crystalline 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid, which was readily decarboxylated to give pure 3-t-butylbenzo[*b*]thiophen.

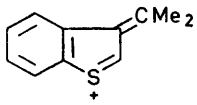
The 2- and 3-t-butyl compounds were readily identified from their n.m.r. spectra, each of which showed the presence of one thiophen proton. The spectrum of the 2-isomer was very similar to that of 2-methylbenzo[*b*]thiophen and, in particular, showed long-range coupling [6] between 3-H and 7-H (*J* 0·5 Hz). The expected [6] long-range coupling between 2-H and 6-H was not resolved in the spectrum of the 3-isomer. An interesting feature of the n.m.r. spectrum of the 3-isomer was the deshielding of 4-H (0·23 p.p.m. relative to benzo[*b*]thiophen) by the 3-t-butyl group. This contrasts with the *shielding* of 4-H (0·12 p.p.m.) in 3-methylbenzo[*b*]thiophen,[6] and reflects the fact that the *peri*-substituents are now in close promixity because of the larger size of the 3-t-butyl group. A similar shielding of 8-H is observed for derivatives of 1-methylnaphthalene,[7] where the *peri*-substituents are closer than in 3-methylbenzo[*b*]thiophen.

An attempt was made to distinguish between 2- and 3-t-butylbenzo[*b*]thiophen by mass spectrometry, by making use of the observation [8] that 2-alkylbenzo[*b*]-thiophens often show a fragment ion composed of the alkyl group, C-2, and the sulphur atom. In the present case, the 2-isomer showed a peak at *m/e* 101 ($BuCS^+$), but this was too weak to be of real value for diagnostic purposes. The mass spectra of the two isomers were remarkably similar; the base peaks had the probable structures (1) and (2), formed by the loss of a methyl radical from the corresponding molecular ion.

We attempted to prepare 2- and 3-t-butylbenzo[*b*]-thiophen by treatment of t-butylmagnesium chloride with benzo[*b*]thiophen-2(3*H*)-one and benzo[*b*]thiophen-3(2*H*)-one, respectively. An analogous method has

[1] Part IV, J. Cooper and R. M. Scrowston, *J. C. S. Perkin I*, 1972, 265.
[2] U.S.P. 2,652,405/1953 (*Chem. Abs.*, 1954, **48**, 12,178).
[3] B. B. Corson, H. E. Tiefenthal, G. R. Atwood, W. J. Heintzelman, and W. L. Reilly, *J. Org. Chem.*, 1956, **21**, 584.
[4] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 244.
[5] S. F. Bedell, E. C. Spaeth, and J. M. Bobbitt, *J. Org. Chem.*, 1962, **27**, 2026.
[6] N. B. Chapman, D. F. Ewing, R. M. Scrowston, and R. Westwood, *J. Chem. Soc.* (*C*), 1968, 764.
[7] P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.*, 1963, **16**, 1108.
[8] Q. N. Porter, *Austral. J. Chem.*, 1967, **20**, 103.

been used previously to prepare 3-methylbenzo[*b*]-thiophen in low yield.[9] An exothermic reaction was observed when the reactants were mixed, but only starting material was recovered on the addition of mineral acid. It was concluded that in each case an acid–base reaction had taken place between the acidic



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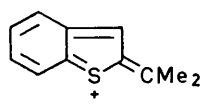


(2)

methylene group and the Grignard reagent to give a resonance-stabilised carbanion. In confirmation of this suggestion, addition of dimethyl sulphate to the reaction product of benzo[*b*]thiophen-2(3*H*)-one and t-butylmagnesium chloride gave a mixture which was shown by the n.m.r. spectrum to contain 3-methylbenzo[*b*]thiophen-2(3*H*)-one and the corresponding 3,3-dimethyl compound.

We next nitrated 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid under conditions (*viz.* fuming nitric acid in sulphuric acid and acetic acid at 60° and in acetic acid and acetic anhydride at 0°) identical to those which we had used [1] to nitrate 3-methylbenzo[*b*]thiophen-2-carboxylic acid, in order to observe how the change from a 3-methyl group to a large 3-t-butyl group affects the position of substitution and the distribution of isomers. Acidic material was separated from neutral material and was esterified with ethereal diazomethane, to give the methyl ester of the starting material and seven other products (A—G). The components were separated by a combination of column chromatography and fractional crystallisation, but separation was impeded by the close similarity in behaviour of the isomers, and by their resistance to crystallisation. Moreover, several of the products had identical R_F values on t.l.c.

Components A and B were readily identified as methyl benzo[*b*]thiophen-2-carboxylate and methyl 3-nitrobenzo[*b*]thiophen-2-carboxylate, respectively, by comparison with authentic materials (*cf.* ref. 1). Components C, D, and E were isomeric methyl 3-t-butylnitrobenzo-[*b*]thiophen-2-carboxylates (n.m.r. and mass spectra); that C and E were the 4- and 7-nitro-isomers, respectively, followed from the coupling patterns of the benzenoid proton signals in their n.m.r. spectra, and from the observation that the proton signals for E were at lower field than those for C. For reasons given earlier,[1,10] the twisting of a 4-nitro-group out of coplanarity with the benzene ring by *peri*-interaction with a 3-substituent causes the benzenoid protons of a 4-nitro-compound to resonate at higher fields than those of its 7-nitro-isomer. The n.m.r. spectrum of D showed a coupling pattern typical of a 5- or 6-nitro-compound. Usually it is difficult to distinguish spectroscopically between two such isomers because the 4-H and 7-H signals are almost indistinguishable, but in the present case 4-H was deshielded by the 3-t-butyl group and its signal was easily assigned. The values of the coupling constants associated with it then showed the presence of a 6-substituent. Further, apart from the deshielding of 4-H (0·31 p.p.m.) by the t-butyl group, the chemical shifts of D were almost identical with those of the corresponding protons in methyl 3-methyl-6-nitrobenzo[*b*]thiophen-2-carboxylate.[1] The non-formation of the 5-nitro-isomer in the nitration reactions was not unexpected in view of the fact that neither benzo[*b*]-thiophen-2-carboxylic acid nor its 3-methyl derivative [1] undergo substitution in the 5-position.

Components F, G, and H were identified, respectively, as methyl 4-, 6-, and 7-nitrobenzo[*b*]thiophen-2-carboxylate by comparison with the methyl esters of the known [1] nitration products of benzo[*b*]thiophen-2-carboxylic acid.

Quantitative analysis (g.l.c.) of the mixture of methyl esters gave the results shown in the Table. The percentages of methyl 7-nitrobenzo[*b*]thiophen-2-carboxylate and methyl 3-t-butyl-4-nitrobenzo[*b*]thiophen-2-carboxylate are shown as a combined figure because the small percentage of the former (<4%) could not be measured accurately in the presence of larger quantities

Acidic [a] products from the nitration of 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid

Benzo[*b*]thiophen derivative		R_t/min	Nitration procedure: HNO_3–H_2SO_4–AcOH at 60° (%)	Nitration procedure: HNO_3–Ac_2O–AcOH at 0° (%)
2-CO_2Me	(A)	6·95	10	0·3
2-CO_2Me, 3-Bu^t		11·25	10	4
2-CO_2Me, 3-NO_2	(B)	30·8	13	25
2-CO_2Me, 4-NO_2	(F)	57·2	0·5	3
2-CO_2Me, 6-NO_2	(G)	69·1	4	9
2-CO_2Me, 3-Bu^t, 4-NO_2	(C)	76·0	30 [b]	16 [b]
2-CO_2Me, 7-NO_2	(H)	74·4		
2-CO_2Me, 3-Bu^t, 6-NO_2	(D)	95·2	18	23
2-CO_2Me, 3-Bu^t, 7-NO_2	(E)	102·4	7	26

[a] Analysis by g.l.c. on the methyl esters. [b] The small percentage of compound H could not be determined accurately (see text).

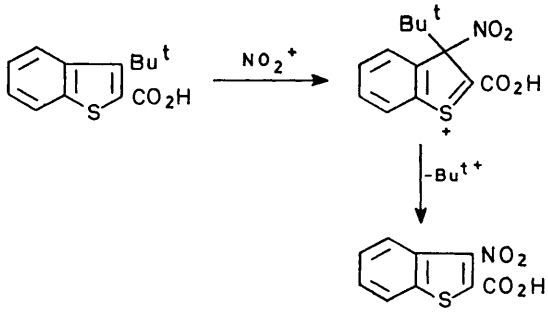
of the latter compound, in view of a similarity in retention times (74·4 and 76·0 min). The retention time recorded for methyl 6-nitrobenzo[*b*]thiophen-2-carboxylate (69·1 min) is intermediate between the value quoted previously [1] for this compound and that for its 5-nitro-isomer. However, this value was assigned unambiguously to the 6-nitro-compound, by observing an increase in peak size when authentic material was added to the mixture.

We will now consider possible mechanisms for the formation of some of the compounds present in the nitration mixture. Benzo[*b*]thiophen-2-carboxylic acid evidently results from the protode-t-butylation of 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid. It was

[9] F. Krollpfeiffer, H. Hartmann, and F. Schmidt, *Annalen*, 1949, **563**, 15.

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

present to a greater extent when the nitration was carried out in acetic acid and sulphuric acid (10%) than when it was carried out in acetic anhydride (0·3%). which is consistent with the fact that a solution of nitric acid in sulphuric acid will result in strong proton donation, whereas a solution in acetic anhydride will



not. Similarly, 3-nitrobenzo[*b*]thiophen-2-carboxylic acid almost certainly arises by the illustrated mechanism from the nitrode-t-butylation of 3-t-butylbenzo[*b*]-thiophen-2-carboxylic acid. A similar replacement of the alkyl group was not observed in the nitration of 3-methylbenzo[*b*]thiophen-2-carboxylic acid.[1] It is favoured for the 3-t-butyl compound because the t-butyl carbonium ion is more stable than the methyl carbonium ion, and hence will be displaced more readily. Also, in the transition state C-3 will be sp^3 hybridised, which means that the t-butyl group will no longer be coplanar with the ring, and that its steric interaction with 4-H will be decreased relatively more than for the 3-methyl compound. Hence the activation energy for electrophilic attack on the 3-position of the 3-t-butyl compound should be less than that for attack on the corresponding position of the 3-methyl compound.

As the 3-position in 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid is adjacent to the electron-withdrawing carboxy-group, it might be expected that the activation energy for nitration in this position would be rather higher than for nitration in the benzene ring, and that a rise in temperature should favour the displacement of the t-butyl group. In practice, the opposite effect was observed: 3-nitrobenzo[*b*]thiophen-2-carboxylic acid was obtained in 13% yield (as the methyl ester) at 60° and in 25% yield at 0°. Protode-t-butylation (10%) occurred as a competing reaction at 60°, but not to a sufficient extent to account for this anomalous result. In accordance with the above predictions, the 3-position in benzo[*b*]thiophen-2-carboxylic acid is more readily substituted at 60° than at 0°;[1] this suggests that the activation energy for electrophilic attack in the 3-position of the 3-t-butyl compound might be reduced by steric factors.

Benzo[*b*]thiophen-4-, 6-, and 7-carboxylic acids could be formed by three possible routes (*a*)—(*c*). (*a*) 3-t-Butylbenzo[*b*]thiophen-2-carboxylic acid might undergo protode-t-butylation to give benzo[*b*]thiophen-2-carboxylic acid, which could then be nitrated. If this were the case, the ratios of the 4-, 6-, and 7-nitro-compounds should be the same as those reported[1] for the nitration of benzo[*b*]thiophen-2-carboxylic acid. However, in view of the difficulties already mentioned it was not possible to measure these ratios accurately by g.l.c. (*b*) The nitration products of 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid could undergo protode-t-butylation. However, protonation of highly deactivated systems such as nitrocarboxylic acids seems unlikely, except possibly in concentrated acid. (*c*) Nitration may proceed with the concomitant expulsion of a t-butyl carbonium ion from the positively charged intermediate. We do not wish to express a preference for any of these routes.

The neutral material from the nitration of 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid was obtained as an orange oil, from which we were unable to isolate any pure materials. However, the mass spectrum showed significant peaks at *m/e* 235 and 179, corresponding to the molecular ions of 3-t-butyl-2-nitrobenzo[*b*]thiophen and 2-nitrobenzo[*b*]thiophen, respectively, present in the relative proportions of 4 : 1. We obtained t.l.c. and g.l.c. evidence for the latter compound. The n.m.r. spectrum of the mixture showed a t-butyl signal at δ 1·57 p.p.m. [*i.e.* at lower field than that of the corresponding signal for 3-t-butylbenzo[*b*]thiophen (δ 1·46 p.p.m.)], which confirmed the presence of the former compound. At least one other unidentified t-butyl compound was present: the n.m.r. spectrum showed a t-butyl signal at δ 1·49 p.p.m.

EXPERIMENTAL

General experimental details are described in Parts I[10] and II.[11] Preparative g.l.c. was carried out on a Varian Aerograph Autoprep machine equipped with a 16 ft × $\frac{3}{8}$ in (o.d.) copper column packed with 20% (w/w) polypropylene glycol sebacate on Chromosorb W (30—60 mesh). The temperature was 195° and the nitrogen flow rate was 150 ml min^{-1}. Analytical g.l.c. was carried out on a similar column and under similar conditions, on a Perkin-Elmer F11 instrument.

t-Butylation of Benzo[b]*thiophen.—Method A.* Benzo[*b*]-thiophen was treated with 2-methylpropene at 125° in the presence of polyphosphoric acid, using the method of Corson *et al.*[3] Distillation of the product gave an oil (64%), b.p. 152—154° at 25 mmHg, which contained (g.l.c.) 2-t-butylbenzo[*b*]thiophen (22%), R_t 11·8 min, 3-t-butylbenzo[*b*]thiophen (71%), R_t 19·0 min, and an unidentified component (7%), R_t 20·2 min. Spinning-band fractionation followed by preparative g.l.c. gave a low recovery of *2-t-butylbenzo*[b]*thiophen*, b.p. 118—119° at 3 mmHg (Found: C, 75·8; H, 7·3; S, 16·7%; *M*, 190. $C_{12}H_{14}S$ requires C, 75·75; H, 7·4; S, 16·85%; *M*, 190), $\nu_{max.}$ 1395 and 1365 (Bu^t) cm^{-1}, δ 1·43 (s, Bu^t) p.p.m.; and the *3-t-butyl isomer*, b.p. 115—117° at 3 mmHg (Found: C, 75·6; H, 7·2; S, 16·8%; *M*, 190), $\nu_{max.}$ 1395 and 1365 cm^{-1}, δ 1·46 p.p.m. Each isomer was obtained in >99% purity; the minor component could not be obtained pure.

Method B. Concentrated sulphuric acid (10 ml) was added dropwise to a stirred mixture of benzo[*b*]thiophen

[11] J. Cooper and R. M. Scrowston, *J. Chem. Soc.* (*C*), 1971, 3052.

(33·5 g) and t-butyl alcohol (37 g), whereupon the temperature rose to 50°. Stirring was continued for 48 h at 25° and for 6 h at 60°, then the mixture was cooled, poured into water, and extracted with ether. The dried extracts were evaporated, unchanged benzo[*b*]thiophen and excess of t-butyl alcohol were distilled off, and the resulting mixture of 2- and 3-t-butylbenzo[*b*]thiophen [6 and 89%, respectively (g.l.c.)] was subjected to spinning-band fractionation. By this means, the 3-t-butyl isomer (11 g) was obtained sufficiently pure (*ca.* 95%) for most purposes.

3-t-Butylbenzo[b]*thiophen-2-carboxylic Acid.*—The crude alkylation product (19 g) from method B was added to a solution of n-butyl-lithium [from lithium (0·3 g atom) and n-butyl bromide (0·15 mol)] in ether (250 ml) at −40° under an atmosphere of nitrogen. The resulting green solution was stirred for 15 h at room temperature, then added to an excess of solid carbon dioxide. Acidic material was extracted from the ethereal solution with aqueous 5% potassium hydroxide and crystallised from ethyl acetate–light petroleum, to give *prisms* (12·4 g), m.p. 127—128° (Found: C, 66·8; H, 6·0. $C_{13}H_{14}O_2S$ requires C, 66·65; H, 6·0%), $\nu_{max.}$ 1680 (C=O) cm^{-1}, δ [$(CD_3)_2CO$] 1·59 (s, Bu^t) p.p.m. Addition of an excess of ethereal diazomethane gave the *methyl ester* (95%) as a viscous oil, b.p. 134—136° at 0·4 mmHg (Found: *M*, 248. $C_{14}H_{16}O_2S$ requires *M*, 248), $\nu_{max.}$ 1725 (C=O) cm^{-1}, R_t 11·24 min.

Decarboxylation of 3-t-butylbenzo[*b*]thiophen-2-carboxylic acid with copper bronze and quinoline under the usual conditions [12] gave almost pure 3-t-butylbenzo[*b*]-thiophen (90%), b.p. 140—142° at 20 mmHg, identical with that already described.

Distillation of the non-acidic material from the metalation reaction gave 2-t-butylbenzo[*b*]thiophen in >95% purity.

Reaction of Benzo[b]*thiophen-3*(2H)*-one and Benzo*[b]*-thiophen-2*(3H)*-one with t-Butylmagnesium Chloride.*—A solution of t-butylmagnesium chloride [13] [from magnesium (0·5 g atom) and t-butyl chloride (0·5 mol)] in ether (200 ml) was added under nitrogen to a stirred solution of benzo[*b*]thiophen-3(2*H*)-one [14] (45 g) in ether (300 ml). The solution became warm during the addition and a white solid separated out. When the addition was complete the mixture was heated under reflux for 8 h, then a solution of ammonium chloride (40 g) in dilute sulphuric acid (300 ml) was added slowly with stirring. Evaporation and distillation of the dried ethereal layer gave benzo[*b*]-thiophen-3(2*H*)-one (24 g, 53% recovery), b.p. 118—120° at 2·5 mmHg, m.p. 68—69° (lit.,[14] 71°), and an involatile purple residue, believed to be thioindigo. No 3-t-butylbenzo[*b*]thiophen was detected by g.l.c.

The reaction was then repeated with benzo[*b*]thiophen-2(3*H*)-one,[15] and an excess of dimethyl sulphate was added prior to the addition of ammonium chloride and sulphuric acid. The mixture was heated under reflux for 3 h and the product, b.p. 90—94° at 0·6 mmHg, was isolated as before. It contained (n.m.r. spectrum) mainly 3-methylbenzo[*b*]thiophen-2(3*H*)-one, together with some 3,3-didimethylbenzo[*b*]thiophen-2(3*H*)-one and some starting material. When the reaction was carried out without the addition of dimethyl sulphate, benzo[*b*]thiophen-2(3*H*)-one was recovered in 80% yield.

Nitration of 3-t-Butylbenzo[b]*thiophen-2-carboxylic Acid.*—*Method A.* The acid (11·7 g, 0·05 mol) was treated with fuming nitric acid in glacial acetic acid and concentrated sulphuric acid under conditions described in Part III.[1] Organic material was extracted with ether, and then separated into neutral and acidic fractions by treatment with aqueous 5% sodium hydroxide. The neutral material (2·5 g) was obtained as a viscous orange oil containing several components (see Text), from which no crystalline material could be isolated. The acidic material (10·0 g) was treated with ethereal diazomethane to give an oily mixture of methyl esters, the composition of which is shown in the Table.

Method B. Nitration with fuming nitric acid, acetic anhydride, and acetic acid (*cf.* Part III [1]) gave a mixture, which was separated as before into acidic and neutral fractions.

The mixtures of esters obtained by methods A and B were chromatographed separately on silica gel. Elution with light petroleum–chloroform (95 : 5) gave, in the following order: methyl 3-t-butylbenzo[*b*]thiophen-2-carboxylate, compound A, a mixture of compounds B and C, a mixture of compounds D and E, and compounds F, G, and H. Crystallisation of the mixture of B and C from ethanol (×3) gave pure compound B. The filtrate from the first crystallisation was evaporated to dryness and crystallised from light petroleum to give C. The mixture of D and E obtained from reaction A was crystallised from light petroleum to give compound D, but E could not be obtained pure. The mixture of D and E from reaction B contained a larger proportion of E; this was obtained pure by crystallisation of the mixture from light petroleum–ethanol (3 : 1) and then from light petroleum (×3). The filtrate from the first crystallisation was evaporated to half volume and allowed to crystallise. The resulting crystals were recrystallised from light petroleum (×3) to give pure compound D.

The following details refer to the pure compounds obtained by separation of the mixture of esters (5 g) from method A.

Compound A (methyl benzo[*b*]thiophen-2-carboxylate) crystallised from light petroleum as needles (0·1 g), m.p. 71—72° (lit.,[16] 72—73°), identical with authentic material.

Compound B formed pale yellow needles (0·3 g), m.p. 104—105°, identical with authentic methyl 3-nitrobenzo-[*b*]thiophen-2-carboxylate (lit.,[1] m.p. 104—105°).

Compound C (methyl 3-t-butyl-4-nitrobenzo[*b*]thiophen-2-carboxylate) formed yellow *plates* (0·3 g), m.p. 90—91·5° (Found: C, 57·4; H, 5·2; N, 4·8%; *M*, 293. $C_{14}H_{15}NO_4S$ requires C, 57·3; H, 5·15; N, 4·75%; *M*, 293), $\nu_{max.}$ 1729 (C=O), 1520, and 1355 (NO_2) cm^{-1}, δ 7·79 (dd, 5-H), 7·41 (dd, 6-H), 7·95 (dd, 7-H), and 1·54 (s, Bu^t) p.p.m. ($J_{5,7}$ 1·3 and $J_{5,6} = J_{6,7}$ 7·9 Hz), R_t 76·0 min.

Compound D (methyl 3-t-butyl-6-nitrobenzo[*b*]thiophen-2-carboxylate) was obtained as pale yellow *needles* (0·1 g), m.p. 103—105° (Found: C, 57·1; H, 5·3; N, 4·9%; *M*, 293), $\nu_{max.}$ 1724 (C=O), 1525, and 1345 (NO_2) cm^{-1}, δ 8·26 (dd, 4-H), 8·20 (dd, 5-H), 8·71 (dd, 7-H), and 1·57 (s, Bu^t) p.p.m. ($J_{4,5}$ 9·0, $J_{4,7}$ 0·4, and $J_{5,7}$ 1·8 Hz), R_t 95·2 min. The ester was hydrolysed with aqueous ethanolic sodium hydroxide and the resulting acid was decarboxylated

[12] *Cf.* N. B. Chapman, K. Clarke, and S. N. Sawhney, *J. Chem. Soc.* (*C*), 1968, 518.
[13] F. C. Whitmore and D. E. Badertscher, *J. Amer. Chem. Soc.*, 1933, **55**, 1559.
[14] P. Friedländer, *Annalen*, 1907, **351**, 390.
[15] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1970, 1926.
[16] R. Weissgerber and O. Kruber, *Ber.*, 1920, **53**, 1551.

with copper bronze and quinoline [12] to give 3-t-butyl-6-nitrobenzo[*b*]thiophen (85%), which crystallised from light petroleum as pale yellow *needles*, m.p. 125—126° (Found: C, 61·3; H, 5·5; N, 5·6%; *M*, 235. $C_{12}H_{13}NO_2S$ requires C, 61·25; H, 5·55; N, 5·95%; *M*, 235), $\nu_{max.}$ 1515 and 1335 (NO_2) cm^{-1}, δ 7·46 (s, 2-H), 8·13 (dd, 4-H), 8·20 (dd, 5-H), 8·76 (dd, 7-H), and 1·51 (s, Bu^t) p.p.m. ($J_{4,5}$ 9·2, $J_{4,7}$ 0·4, and $J_{5,7}$ 2·2 Hz).

Compound E (methyl 3-t-butyl-7-nitrobenzo[*b*]thiophen-2-carboxylate) formed pale yellow *needles* (0·2 g from reaction B), m.p. 117—118° (Found: C, 57·3; H, 4·9; N, 4·7%; *M*, 293), $\nu_{max.}$ 1730 (C=O), 1515, and 1343 (NO_2) cm^{-1}, δ 8·42 (dd, 4-H), 7·56 (dd, 5-H), 8·51 (dd, 6-H), and 1·57 (s, Bu^t) p.p.m. ($J_{4,5}$ 8·0 $J_{4,6}$ 1·3, and $J_{5,6}$ 8·2 Hz), R_t 102·4 min.

Compounds F, G, and H could be isolated in only small amounts (*ca.* 40 mg) and they could not be obtained pure. However, they were sufficiently pure (>90%) to enable them to be identified by comparison (i.r. and n.m.r. spectra, g.l.c. retention times, and mixed m.p.) with authentic materials. Compound F was methyl 4-nitrobenzo[*b*]-thiophen-2-carboxylate, m.p. 140—143° (lit.,[1] 147—149°) (from ethanol); G was the 6-nitro-isomer, m.p. 198—200° (lit.,[1] 204—205°) (from ethyl acetate); H was the 7-nitro-isomer, m.p. 161—163° (lit.,[1] 170—171°) (from ethanol).

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