Naphtho[1,2-*b*]thiophen. Part I. Preparation and Electrophilic Substitution

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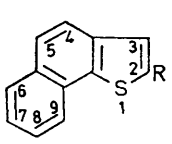
Naphtho[1,2-*b*]thiophen was prepared from 3,4-dihydronaphthalen-1(2*H*)-one by a five-stage process. Bromination, formylation, acetylation, and lithiation of naphtho[1,2-*b*]thiophen occurred at the 2-position. Nitration gave a mixture of the 2- and 5-nitro-derivatives; the structure of the latter was confirmed by transforming it into the 5-bromo-compound, which could be prepared unambiguously. Bromination and nitration of ethyl naphtho-[1,2-*b*]thiophen-2-carboxylate gave mainly the 5-substituted compound in each case.

In 1965 Zahradník and Párkányi [1] used the results of Hückel molecular orbital calculations to predict that the reactivity of the various positions in naphtho[1,2-*b*]-thiophen (1) towards electrophilic attack should be in the order $3 > 2 > 5$, but little experimental confirmation has been forthcoming. Ried and Gross [2] obtained 2,3-bis(chloromethyl)naphtho[1,2-*b*]thiophen by treat-

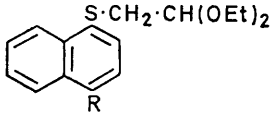
[1] R. Zahradník and C. Párkányi, *Coll. Czech. Chem. Comm.*, 1965, **30**, 195.

[2] W. Ried and R. M. Gross, *Chem. Ber.*, 1957, **90**, 2646.

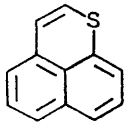
ment of the heterocycle with paraformaldehyde in glacial acetic acid saturated with hydrogen chloride.



(1) R = H
(2) R = CO_2Et
(3) R = CO_2H



(4) R = H
(5) R = Br



(6)

Our studies show that the 2-position is the most reactive towards electrophiles, and that the 5-position is the next to be attacked. We have found no evidence for substitution in the 3-position.

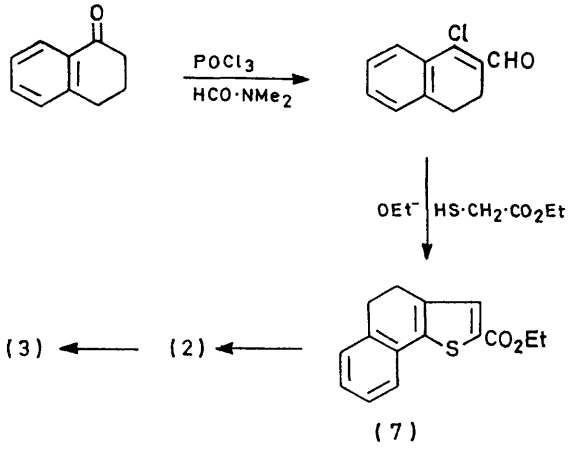
Both Tilak [3] and Campaigne [4] have described syntheses of naphtho[1,2-*b*]thiophen. We repeated Tilak's cyclisation of (1-naphthylthio)acetaldehyde diethyl acetal (4) with hot polyphosphoric acid and obtained a mixture of naphtho[1,2-*b*]thiophen (1) (80%) and naphtho[1,8-*bc*]thiopyran (6) (20%), which proved difficult to separate. The route was not used, therefore, for preparative purposes. Previous workers [3] had obtained only 8% of the thiopyran (6) from this cyclisation. We found that a similar cyclisation of (4-bromo-1-naphthylthio)acetaldehyde diethyl acetal (5) gave a mixture of two components, from which 5-bromonaphtho[1,2-*b*]thiophen could be obtained in low yield by fractional crystallisation.

We prepared an authentic sample of naphtho[1,2-*b*]thiophen-2-carboxylic acid (3) by cyclisation of α-mercapto-β-(2-naphthyl)acrylic acid with iodine.[4] This could then be decarboxylated to naphtho[1,2-*b*]thiophen. However, we preferred to employ a five-stage synthesis (see Scheme) starting from 3,4-dihydronaphthalen-1(2*H*)-one, which gave naphtho[1,2-*b*]thiophen in 35% overall yield. The synthesis is a modification and extension of the method outlined by Hauptmann and his co-workers [5] in a preliminary communication. 3,4-Dihydronaphthalen-1(2*H*)-one was treated with phosphoryl chloride and dimethylformamide at 0° to give 1-chloro-3,4-dihydronaphthalene-2-carbaldehyde (78%), which cyclised to ethyl 4,5-dihydronaphtho[1,2-*b*]thiophen-2-carboxylate (7) (68%) when treated with ethyl mercaptoacetate and sodium ethoxide. Using triethylamine as the basic catalyst, Hauptmann [5] claimed an 85% yield. However, he gave no experimental details, and we were unaware of his prior publication at this stage of our investigation.

[3] L. J. Pandya and B. D. Tilak, *J. Sci. Ind. Res., India*, 1959, **18B**, 371.
[4] E. Campaigne and R. E. Cline, *J. Org. Chem.*, 1956, **21**, 39.
[5] S. Hauptmann, M. Weissenfels, M. Scholz, E.-M. Werner, H.-J. Köhler, and J. Weisflog, *Tetrahedron Letters*, 1968, 1317.

Dehydrogenation of the ester (7) was achieved in 86% yield by using 10% palladised charcoal in boiling *p*-cymene, but the reaction was time consuming. A quicker and equally efficient (88%) dehydrogenation was achieved by using *N*-bromosuccinimide in boiling carbon tetrachloride. It seems likely that this reaction involves bromination in the 4- or 5-position, and spontaneous dehydrobromination. Other workers [6] have observed that certain substituted 4,5-dihydronaphtho[1,2-*b*]thiophens react with *N*-bromosuccinimide to give the 4- and/or 5-bromo-compounds, which do not, however, eliminate hydrogen bromide spontaneously. Naphtho[1,2-*b*]thiophen was obtained in high yield from the ester (2) by standard procedures (see Experimental section).

Nitration of naphtho[1,2-*b*]thiophen in glacial acetic acid gave a mixture of 2- and 5-nitronaphtho[1,2-*b*]thiophen (1 : 7). The minor component was not obtained pure and proof of identity rests upon a comparison of its i.r. spectrum, obtained from the mixture by the wedge technique,[7] with that of authentic 2-nitronaphtho[1,2-*b*]thiophen.[8] The major component was isolated by fractional crystallisation and reduced with hydrazine hydrate and Raney nickel to the corresponding amine. Treatment of the diazonium salt with copper(I) bromide in hydrobromic acid gave the corresponding bromo-derivative, which was identical with authentic 5-bromonaphtho[1,2-*b*]thiophen.



SCHEME

Formylation of naphtho[1,2-*b*]thiophen with phosphoryl chloride and *N*-methylformanilide gave the 2-carbaldehyde (69%), which was oxidised by moist silver oxide or by chromic acid to the known 2-carboxylic acid (3) (79 and 65%, respectively). The high yield of aldehyde illustrates that naphtho[1,2-*b*]thiophen is more reactive in electrophilic substitution reactions than benzo[*b*]thiophen; the latter is difficult to formylate by this method. Friedel–Crafts acetylation also occurred at the 2-position (73%). The location of the

[6] E. C. Taylor and J. G. Berger, *J. Org. Chem.*, 1967, **32**, 2376.
[7] H. McCormick, E. L. Deeley, and J. Tadayon, *Nature*, 1965, **207**, 474.
[8] D. N. Gregory, Ph.D. Thesis, Hull, 1973.

acetyl group was confirmed by oxidation with sodium hypobromite to the 2-carboxylic acid (67%).

Huang-Minlon reduction of the 2-formyl and 2-acetyl derivatives gave 2-methyl- (78%) and 2-ethyl-naphtho-[1,2-*b*]thiophen (75%), respectively.

Naphtho[1,2-*b*]thiophen reacted with bromine in carbon tetrachloride at 10° to give the 2-bromo-derivative (70%). *N*-Bromosuccinimide in boiling carbon tetrachloride gave a mixture (7 : 2 : 1) of products which was not resolved, but in which the 2-bromo-derivative again predominated. The location of the 2-bromo-substituent was confirmed by (*a*) carboxylation of the derived Grignard reagent to give the 2-carboxylic acid (3) and (*b*) treatment with copper(I) cyanide in quinoline to give the corresponding nitrile, which was then hydrolysed to the acid (3).

n-Butyl-lithium reacted with naphtho[1,2-*b*]thiophen to give the 2-lithio-derivative, which reacted with an excess of dimethyl sulphate to give the known 2-methyl-naphtho[1,2-*b*]thiophen (74%).

When the 2-position was occupied by the electron-withdrawing ethoxycarbonyl group, electrophilic substitution occurred in the 5-position. Treatment of ethyl naphtho[1,2-*b*]thiophen-2-carboxylate with bromine in glacial acetic acid gave the 5-bromo-derivative, its structure being established by successive hydrolysis and decarboxylation to give 5-bromonaphtho[1,2-*b*]-thiophen. Nitration of ethyl naphtho[1,2-*b*]thiophen-2-carboxylate with nitric acid in glacial acetic acid containing a little concentrated sulphuric acid also gave the 5-substituted derivative; removal of the ethoxycarbonyl group gave material identical with the major product from the nitration of naphtho[1,2-*b*]thiophen.

The orientation of substituents in benzo[*b*]thiophen derivatives [9] and in other sulphur heterocyclic compounds is often determined readily by n.m.r. spectroscopy. However, this method was of limited use in the present work because the signals due to 4-H and 5-H, except for those in the parent compound (1),[10] were usually unresolved. There was a slight separation of the 4-H and 5-H signals in the case of the 2-ethoxycarbonyl derivative (2), but it was difficult to assign the two signals unambiguously. Equally important, the absence of long-range coupling made it virtually impossible to assign accurately the 3-H and 4-H signals in the 2- and 5-substituted derivatives, respectively. The only long-range coupling observed was between 5-H and 9-H in the parent compound (1).

We carried out LCAO-MO Hückel calculations on naphtho[1,2-*b*]thiophen, similar to those reported by the Czech workers,[1] using the model (*p*-model) in which the 3*d*-orbitals of the sulphur atom are not involved. Our values for electron densities, free valencies, and superdelocalisabilities were of the same order as those reported earlier,[1] and indicated that the reactivity of the various positions towards electrophiles should be in the order **3** > **2** > **5**. We also calculated localisation energies, which indicated the same order of reactivity. Although recent studies [11] have shown that *d*-orbitals are involved to only a minor extent in bonding in the thiophen molecule, we repeated our calculations on naphtho[1,2-*b*]thiophen using the model in which the 3*d*-orbitals are involved in bonding. Even by varying the parameters we obtained results of the same order as before. Calculations [1] similar to those just described (*p*-model) indicate that the isomeric naphtho[2,1-*b*]-thiophen should undergo electrophilic monosubstitution in the 1-position (corresponding to the 3-position in the [1,2-*b*]-isomer), but experiment has shown [12] that the 2-position is again the most reactive. We have suggested [13] that the lack of reactivity of the 1-position in naphtho[2,1-*b*]thiophen may be due to steric interaction between the 1- and 9-positions. Such a steric effect clearly is not possible in naphtho[1,2-*b*]thiophen (1). It must be concluded, therefore, that the simple HMO treatment contains too many approximations to give reliable information on the naphthothiophens; nevertheless it has produced useful guidelines for the study of some of the more simple sulphur heterocyclic compounds.

EXPERIMENTAL

I.r. spectra were determined for potassium chloride discs with a Perkin-Elmer 457 spectrophotometer. Unless stated otherwise, n.m.r. spectra were obtained at 100 MHz with a JNM-4H-100 spectrometer for solutions in deuteriochloroform, with tetramethylsilane as internal standard. Molecular weights were obtained with an A.E.I. MS902 mass spectrometer. Products were analysed by t.l.c. on plates coated with Silica Gel G (Merck). Identity of compounds with authentic materials was established by mixed m.p. determination and by comparison of i.r. spectra and R_F values (t.l.c.).

4-Bromonaphthalene-1-thiol (75%) was obtained by reduction of the corresponding sulphonyl chloride with tin(II) chloride in glacial acetic acid.[14]

5-Bromonaphtho[1,2-b]*thiophen.*—(*a*) (4-Bromo-1-naphthylthio)acetaldehyde diethyl acetal (54%), obtained by treatment of 4-bromonaphthalene-1-thiol with bromoacetaldehyde diethyl acetal in the presence of sodium ethoxide (*cf.* ref. 15), had b.p. 176—178° at 0·1 mmHg (Found: M^+, 354/356. $C_{16}H_{19}BrO_2S$ requires M^+, 354/356).

(*b*) A mixture of the diethyl acetal (9·5 g) and polyphosphoric acid (50 g) was kept at 80° for 4 h, then cooled and diluted with ice–water. Extraction with ether and short-path distillation of the product gave a yellow solid (3·75 g, 48%), b.p. 235—250° at 0·2 mmHg, which con-

[9] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 177.
[10] D. F. Ewing and R. M. Scrowston, *Org. Magnetic Resonance*, 1971, **3**, 405.
[11] D. T. Clark, in ' Organic Compounds of Sulphur, Selenium, and Tellurium,' Specialist Periodical Reports, The Chemical Society, London, 1970, vol. 1, ch. 1.
[12] K. Clarke, G. Rawson, and R. M. Scrowston, *J. Chem. Soc.* (*C*), 1969, 537.
[13] K. Clarke, G. Rawson, and R. M. Scrowston, *J. Chem. Soc.* (*C*), 1969, 1274.
[14] M. Janczewski, L. Bilczuk, T. Bartnik, and H. Szczeklik, *Roczniki Chem.*, 1964, **38**, 399.
[15] J. E. Banfield, W. Davies, B. C. Ennis, S. Middleton, and Q. N. Porter, *J. Chem. Soc.*, 1956, 2603.

tained (g.l.c.) two components (87 : 13). Four recrystallisations from ethanol gave 5-*bromonaphtho*[1,2-b]*thiophen* (1·0 g, 13%), m.p. 81—83° (Found: C, 54·7; H, 2·55. $C_{12}H_7BrS$ requires C, 54·75; H, 2·7%), δ 7·32 (d, 3-H), 7·45 (d, 2-H), 7·55 (m, 7- and 8-H), 8·05 (m, 6-H), 8·08 (s, 4-H), and 8·29 (m, 9-H) ($J_{2,3}$ 5·1 Hz).

A similar cyclisation of (1-naphthylthio)acetaldehyde diethyl acetal [15] at 200° gave a mixture of products (see text), which was not easily separated.

1-*Chloro*-3,4-*dihydronaphthalene*-2-*carbaldehyde*.— Phosphoryl chloride (265 g, 1·75 mol) was added dropwise with stirring and cooling to dry dimethylformamide (500 ml), at such a rate that the temperature did not exceed 5°. 3,4-Dihydronaphthalen-1(2*H*)-one (250 g, 1·71 mol) was added dropwise to the resulting solution at 0—5° and the mixture was stirred for 0·5 h at 0° and for 1·5 h at 80°, then poured into cold aqueous sodium acetate (25% w/v; 2 l). Extraction with ether and distillation of the product under nitrogen gave an unstable pale green oil (258 g, 78%), which later solidified. It had b.p. 135—140° at 0·7 mmHg (lit.,[16] 145—153° at 5 mmHg) (Found: M^+, 192/194. Calc. for $C_{11}H_9ClO$: M^+, 192/194), $\nu_{max.}$ 1665 cm^{-1} (C=O), δ 2·54—2·96 (m, 3- and 4-H_2), 7·15—7·95 (m, 5-, 6-, 7-, and 8-H), and 10·35 (s, CHO).

Ethyl 4,5-*Dihydronaphtho*[1,2-b]*thiophen*-2-*carboxylate* (7).—Ethyl mercaptoacetate (162 g, 1·35 mol) was added to a cooled, stirred solution of sodium (39 g, 1·7 g atom) in dry ethanol (600 ml). A solution of 1-chloro-3,4-dihydronaphthalene-2-carbaldehyde (258 g, 1·34 mol) in ethanol (100 ml) was then added dropwise during 0·5 h at 0—5°, and the mixture was stirred overnight at room temperature, boiled for 0·5 h, cooled, and poured into water. The ester (7) was filtered off and obtained as off-white prisms (238 g, 68%), m.p. 81—82° [from light petroleum (b.p. 60—80°)] (lit.,[5] 83°), $\nu_{max.}$ 1695 cm^{-1} (C=O), δ 7·66 (s, 3-H).

Ethyl Naphtho[1,2-b]*thiophen*-2-*carboxylate* (2).—(*a*) A stirred suspension of the ester (7) (52·9 g) and 10% palladised charcoal (5 g) in *p*-cymene (300 ml) was boiled under nitrogen until the reaction was complete [*ca.* 10 days (t.l.c.)]. Filtration and evaporation gave a residue which crystallised from ethanol as cream *prisms* (45 g, 86%), m.p. 87—88° (Found: C, 70·0; H, 4·95%; *M*, 256. $C_{15}H_{12}O_2S$ requires C, 70·3; H, 4·7%; *M*, 256), $\nu_{max.}$ 1695 cm^{-1} (C=O), δ 7·50—8·00 (arom. H) and 8·10 (3-H).

(*b*) *N*-Bromosuccinimide (69 g) was added in portions with stirring to a boiling, irradiated (200 W) solution of the ester (7) (100 g) and dibenzoyl peroxide (0·1 g) in dry carbon tetrachloride (500 ml). The hydrogen bromide which was formed was removed in a stream of nitrogen. When the addition was complete the mixture was boiled for a further 15 min, then cooled and filtered. Evaporation of the filtrate gave a product (87·5 g, 88%), m.p. 86—87°, identical with that just described.

Naphtho[1,2-b]*thiophen*-2-*carboxylic Acid* (3).—Sulphuric acid (50% v/v; 120 ml) was added dropwise to a boiling, stirred solution of the ethyl ester (2) (30 g) in acetic acid (300 ml), then the mixture was boiled for 3 h and cooled. The acid was filtered off and gave needles (20·7 g, 78%), m.p. 248—250° (lit.,[4] 257—258°), $\nu_{max.}$ 1670 cm^{-1} (C=O).

The same product was obtained by hydrolysis of the ester (2) with boiling ethanolic sodium hydroxide (81%) and by cyclisation of α-mercapto-β-(2-naphthyl)acrylic acid with iodine in dioxan [4] (57%).

Naphtho[1,2-b]*thiophen*.—A stirred mixture of naphtho[1,2-*b*]thiophen-2-carboxylic acid (51·9 g), powdered copper bronze (20 g), and dry quinoline (500 ml) was heated slowly (2 h) under nitrogen to 210°, and then kept at this temperature for 2 h. The cooled, filtered mixture was poured into an excess of hydrochloric acid (50% v/v) and the product (40·3 g, 96%) was isolated by extraction with ether. It had b.p. 138—142° at 2·0 mmHg (lit.,[17] 120° at 0·2 mmHg), and formed low melting crystals; the picrate had m.p. 143—145° (lit.,[17] 143—144°) (brown needles from ethanol).

Nitration of Naphtho[1,2-b]*thiophen*.—A solution of concentrated nitric acid in glacial acetic acid (10% w/v; 13·7 ml) was added dropwise during 20 min to a stirred solution of naphtho[1,2-*b*]thiophen (4 g) in glacial acetic acid (40 ml). The mixture was boiled for 2 h, then cooled and poured into water. The resulting precipitate (4·3 g) contained two components (12 : 88) (g.l.c.). Crystallisation (×2) from light petroleum (b.p. 60—80°) gave the 5-*nitro-compound* as yellow feathery needles (0·21 g), m.p. 131·5—133° (Found: C, 62·7; H, 3·2; N, 6·2%; *M*, 229. $C_{12}H_7NO_2S$ requires C, 62·85; H, 3·1; N, 6·1%; *M*, 229), t_R 24·16 min, δ 7·52 (d, 3-H), 7·60 (d, 2-H), and 8·56 (s, 4-H or 5-H) ($J_{2,3}$ 5·5 Hz).

The minor component was not purified, but it was identified as 2-nitronaphtho[1,2-*b*]thiophen by a comparison of its i.r. spectrum, obtained by the 'wedge' technique,[7] with that of authentic material.[8]

Identification of 5-*Nitronaphtho*[1,2-b]*thiophen*.—(a) 5-*Aminonaphtho*[1,2-b]*thiophen*. Hydrazine hydrate (98% w/v; 1·0 ml) was added dropwise to a warm, stirred solution of the nitro-compound (0·2 g) in ethanol (10 ml). The vigorous reaction was allowed to proceed for 0·5 h, then more hydrazine hydrate (0·2 ml) was added, and the mixture was kept at just below the b.p. for 0·5 h. The amine, obtained as an oil after filtration and evaporation, was converted into the *hydrochloride* (0·11 g, 52%), which formed white needles, m.p. 243—245·5° (decomp.) (from ethanol) (Found: C, 60·9; H, 4·6; N, 6·2. $C_{12}H_{10}ClNS$ requires C, 61·15; H, 4·3; N, 5·95%).

(b) 5-*Bromonaphtho*[1,2-b]*thiophen*. A suspension of the amine hydrochloride (0·1 g) in hydrobromic acid (1·0 ml) at 0° was diazotised with sodium nitrite (0·03 g) in water (8 ml). The resulting suspension was added to a stirred solution of copper(I) bromide (0·8 g) in hydrobromic acid (48% w/v; 5 ml) at 0—5°, then the mixture was heated slowly to 80° and kept at this temperature for 1 h. Water was added and the 5-bromo-compound (51%), m.p. 81—83° (needles from ethanol), was isolated with ether. It was identical with authentic material.

Formylation of Naphtho[1,2-b]*thiophen* (*with* G. Rawson).—A mixture of naphtho[1,2-*b*]thiophen (1·0 g, 0·005 mol), *N*-methylformanilide (0·7 g, 0·005 mol), and phosphoryl chloride (0·8 g, 0·005 mol) was kept at 80° for 4 h, then cooled. Addition of concentrated aqueous sodium acetate precipitated the 2-*carbaldehyde*, which formed cream needles (0·8 g, 69%), m.p. 98·5—100° (from ethanol) (Found: C, 73·6; H, 3·8%; *M*, 212. $C_{13}H_8OS$ requires C, 73·55; H, 3·8%; *M*, 212), $\nu_{max.}$ 1655 and 1670 cm^{-1} (C=O), δ 8·03 (s, 3-H) and 10·06 (s, CHO).

A stirred mixture of the aldehyde (0·2 g) and silver oxide [from silver nitrate (1·5 g), sodium hydroxide (1 g), and water (50 ml)] was kept at 80° for 1 h, then cooled and

[16] W. Ziegenbein and W. Lang, *Chem. Ber.*, 1960. **93**. 2743.
[17] W. Carruthers, *J. Chem. Soc.*, 1953, 4186.

filtered (Hyflo). Acidification of the filtrate with concentrated hydrochloric acid gave naphtho[1,2-*b*]thiophen-2-carboxylic acid (0·17 g, 79%), m.p. 249—250°, identical with authentic material. The same acid was obtained (65%) by oxidation of the aldehyde with Jones reagent.

2-*Acetylnaphtho*[1,2-b]*thiophen*.—A mixture of naphtho-[1,2-*b*]thiophen (5 g) and acetyl chloride (2·13 g) in methylene chloride (50 ml) was added dropwise to a stirred suspension of aluminium chloride (4 g) in methylene chloride (20 ml) at 0°. The mixture was stirred overnight at room temperature, then heated under reflux for 1 h, cooled, and acidified with dilute sulphuric acid. Extraction with ether gave *needles* (4·5 g, 73%), m.p. 129—130·5° (from ethanol) (charcoal) (Found: C, 74·3; H, 4·4%; *M*, 226. $C_{14}H_{10}OS$ requires C, 74·3; H, 4·45%; *M*, 226), $\nu_{max.}$ 1660 cm^{-1} (C=O), δ 2·63 (s, Ac) and 7·92 (s, 3-H). The *oxime* formed white needles, m.p. 221—223° (from ethanol) (Found: C, 69·53; H, 4·6; N, 5·9. $C_{14}H_{11}NOS$ requires C, 69·7; H, 4·6; N, 5·8%).

Oxidation of the acetyl compound for 2 h at 35—40° with an excess of sodium hypobromite in dioxan gave naphtho[1,2-*b*]thiophen-2-carboxylic acid (67%), m.p. 248—250°, identical with authentic material.

2-*Ethyl- and* 2-*Methyl-naphtho*[1,2-b]*thiophen*.—A mixture of 2-acetylnaphtho[1,2-*b*]thiophen (1 g), hydrazine hydrate (98% w/v; 2 ml), potassium hydroxide (1 g), and diethylene glycol (20 ml) was boiled under reflux for 1 h. Water and the excess of hydrazine hydrate were distilled off and the solution was boiled for a further 4 h. Dilution with water and extraction with ether gave the 2-ethyl compound (0·7 g, 75%) as a pale yellow *oil*, b.p. 135—140° at 0·4 mmHg (Found: C, 79·05; H, 5·6%; *M*, 212. $C_{14}H_{12}S$ requires C, 79·2; H, 5·7%; *M*, 212).

Similar reduction of the 2-carbaldehyde gave the 2-*methyl compound* (78%), b.p. 110—118° at 0·1 mmHg (Found: C, 78·4; H, 4·9%; *M*, 198. $C_{13}H_{10}S$ requires C, 78·75; H, 5·1%; *M*, 198).

Bromination of Naphtho[1,2-b]*thiophen*.—(*a*) A solution of bromine in dry carbon tetrachloride (10% w/v; 8·7 ml) was added dropwise during 0·5 h to a stirred solution of naphtho[1,2-*b*]thiophen (1·0 g) in dry carbon tetrachloride (30 ml) at 10°. The solution was then stirred overnight at room temperature, washed (2M-NaOH and water), dried, and evaporated. 2-Bromonaphtho[1,2-*b*]thiophen (1·0 g; 70%) formed *prisms*, m.p. 57—59° (Found: C, 54·7; H, 2·55%; M^+, 262/264. $C_{12}H_7BrS$ requires C, 54·75; H, 2·7%; M^+, 262/264), δ 2·37 (s, 3-H), t_R 2·85 min.

The bromo-compound was treated with magnesium in dry ether in the presence of ethyl bromide and the resulting Grignard reagent was carboxylated with solid carbon dioxide in the usual way. The resulting naphtho[1,2-*b*]-thiophen-2-carboxylic acid (60%), m.p. 249—251°, was identical with an authentic sample.

(*b*) A mixture of naphtho[1,2-*b*]thiophen (1·0 g), *N*-bromosuccinimide (0·97 g), dibenzoyl peroxide (0·05 g), and carbon tetrachloride (40 ml) was boiled for 20 h, then cooled and filtered. Evaporation of the filtrate gave an oily mixture of three bromo-compounds (7 : 2 : 1) (g.l.c.), which was not separated.

The crude product (1·0 g), copper(I) cyanide (0·34 g), and quinoline (40 ml) were stirred under reflux for 4 h. The mixture was then cooled, and poured into an excess of 2M-hydrochloric acid. Extraction with chloroform gave an oil which was hydrolysed with aqueous ethanolic sodium hydroxide, to give naphtho[1,2-*b*]thiophen-2-carboxylic acid (0·4 g), m.p. 247—249°, identical with an authentic specimen.

Lithiation of Naphtho[1,2-b]*thiophen*.—A solution of naphtho[1,2-*b*]thiophen (5·0 g, 0·0272 mol) in dry ether (40 ml) was added to a stirred solution of n-butyl-lithium (0·058 mol) in dry ether (150 ml) at −40° under nitrogen. The temperature was allowed to rise to 0° during 1·5 h, and then kept at 0° for 1 h. A solution of dimethyl sulphate (3·5 g) in dry ether (20 ml) was added during 10 min, and the mixture was stirred overnight at room temperature. Sodium ethoxide [from sodium (2 g)] in ethanol (30 ml) was added, then the mixture was boiled for 1 h and poured into water. Extraction with ether gave 2-methylnaphtho[1,2-*b*]thiophen (4·0 g, 74%), b.p. 106—110° at 0·1 mmHg, identical with that obtained before.

Ethyl 5-Bromonaphtho[1,2-b]*thiophen-2-carboxylate*.—A solution of bromine in acetic acid (10% w/v; 12·5 ml) was added dropwise during 0·5 h to a boiling, stirred solution of ethyl naphtho[1,2-*b*]thiophen-2-carboxylate (2 g) in acetic acid (50 ml). The solution was stirred and heated for a further 3 h, then diluted with water. The resulting precipitate formed cream *prisms* (1·7 g, 65%), m.p. 129—130° (from ethanol) (Found: C, 53·7; H, 3·4%; M^+, 334/336. $C_{15}H_{11}BrO_2S$ requires C, 53·75; H, 3·3%; M^+, 334/336), $\nu_{max.}$ 1715 cm^{-1} (C=O), δ 7·97 (s, 3-H) and 8·03 (s, 4-H).

Hydrolysis of the ester with ethanolic sodium hydroxide gave the *acid* (90%) as needles, m.p. 294—296° (decomp.) (from ethanol) (Found: C, 50·5; H, 2·5%; M^+, 306/308. $C_{13}H_7BrO_2S$ requires C, 50·8; H, 2·3%; M^+, 306/308), $\nu_{max.}$ 1675 cm^{-1} (C=O). Decarboxylation of the acid by the method already described gave 5-bromonaphtho[1,2-*b*]-thiophen (67%), m.p. 81·5—83°, identical with authentic material.

Ethyl 5-Nitronaphtho[1,2-b]*thiophen-2-carboxylate*.—Ethyl naphtho[1,2-*b*]thiophen-2-carboxylate was nitrated by the method already described in the presence of sulphuric acid (2 drops). The product formed yellow *needles* (68%), m.p. 184—185·5° (from ethanol) (Found: C, 59·8; H, 3·7; N, 4·7%; *M*, 301. $C_{15}H_{11}NO_4S$ requires C, 59·8; H, 3·7; N, 4·65%; *M*, 301), $\nu_{max.}$ 1715 cm^{-1} (C=O), δ 8·14 (s, 3-H) and 8·51 (s, 4-H).

Hydrolysis of the ester with aqueous sulphuric acid (50% v/v) and acetic acid gave the corresponding *acid* (89%) as pale yellow needles, m.p. 287—290° (decomp.) (from ethanol) (Found: C, 57·1; H, 2·6; N, 4·85%; *M*, 273. $C_{13}H_7NO_4S$ requires C, 57·15; H, 2·6; N, 5·1%; *M*, 273), $\nu_{max.}$ 1685 cm^{-1} (C=O).

Decarboxylation of the acid with copper bronze in quinoline gave 5-nitronaphtho[1,2-*b*]thiophen (79%), m.p. 128—130·5°, identical with authentic material.

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