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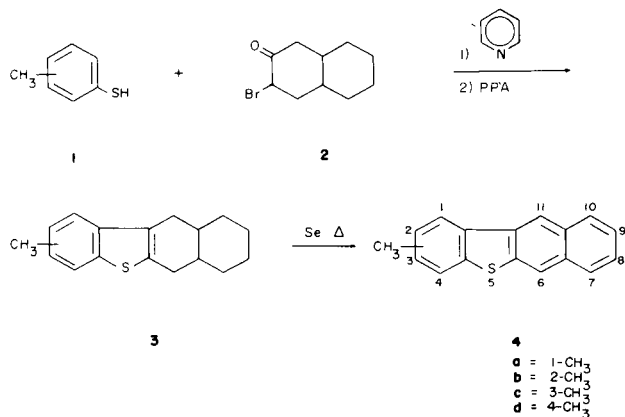
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The synthesis of all the monomethyl derivatives of benzo[*b*]naphtho[2,3-*d*]thiophene is described.*J. Heterocyclic Chem.*, **19**, 865 (1982).

In a recent paper from this laboratory, three tetracyclic ring systems, namely, benzo[*b*]naphtho[1,2-*d*]thiophene, benzo[*b*]naphtho[2,1-*d*]thiophene and benzo[*b*]naphtho[2,3-*d*]thiophene have been identified in coal gasification tar, coal liquids and shale oils (2,3). The presence of all of their methyl derivatives has also been suspected. Therefore, all of the monomethyl derivatives were required for their positive identification in coal products. Therefore we now report the synthesis of all the monomethyl derivatives of benzo[*b*]naphtho[2,3-*d*]thiophene.

The synthesis of the 1-, 2-, 3- and 4-methylbenzo[*b*]naphtho[2,3-*d*]thiophenes has been accomplished by a common procedure and is depicted in Scheme 1. The reaction of *o*-, *m*- and *p*-methylbenzenethiol with 3-bromo-2-

Scheme 1



decalone (2) in pyridine as the base gave the corresponding ketosulfides which were cyclodehydrated in the presence of polyphosphoric acid to yield the octahydrobenzo[*b*]naphtho[2,3-*d*]thiophenes **3a,b,c,d**. As expected, the reaction with *m*-methylbenzenethiol gave two products. Dehydrogenation of **3a,b,c,d** by heating with selenium at $\sim 300^\circ$ gave excellent yields of the corresponding methylbenzo[*b*]naphtho[2,3-*d*]thiophenes **4a,b,c,d**. The two products derived from *m*-methylbenzenethiol were separated on a basic alumina column.

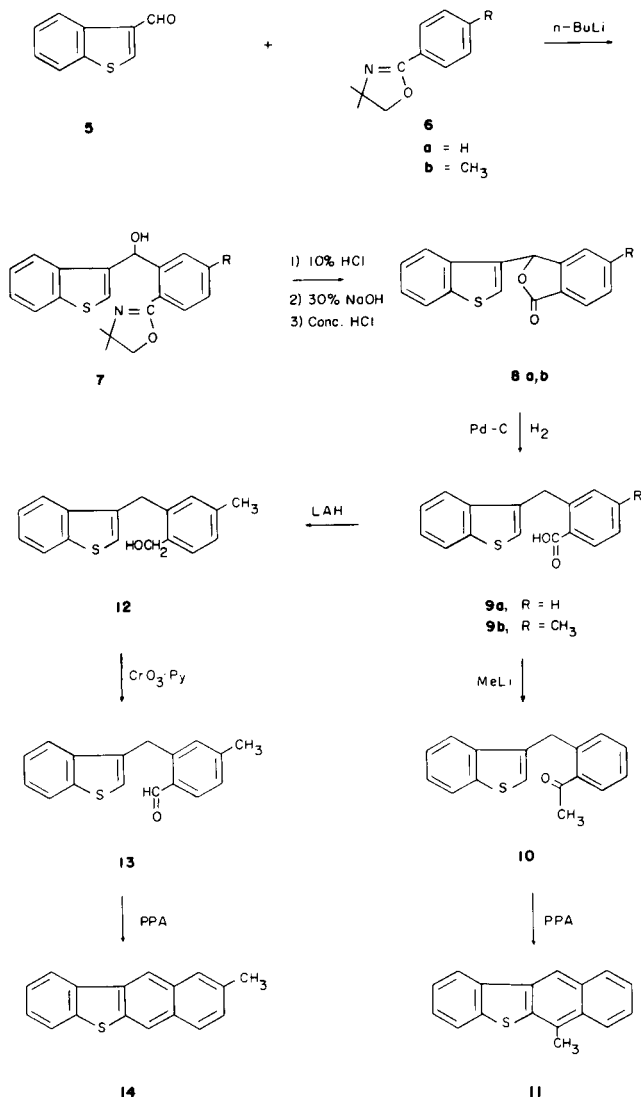
The structural assignments between the 1-methyl and the 3-methyl derivatives are based upon the nmr spectra. In the nmr spectrum of the parent benzo[*b*]naphtho[2,3-*d*]thiophene, the proton at H-11 is more deshielded than that at H-6 due to the ring current effect (4). The methyl derivatives also show the same effect (see Table). Thus, in compound **24** the methyl signal is more deshielded than the methyl signal in compound **21**. Also the methyl signal of the 6-methyl compound **11** appears further downfield than the methyl signal of 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**25**) (7) (see Table). By analogy to the above effect

Table

4a	1-CH ₃ = 2.90 H ₆ = 8.17 H ₁₁ = 8.66
4b	2-CH ₃ = 2.50 H ₆ = 8.15 H ₁₁ = 8.49
4c	3-CH ₃ = 2.49 H ₆ = 8.21 H ₁₁ = 8.51
4d	4-CH ₃ = 2.54 H ₆ = 8.24 H ₁₁ = 8.54
11	6-CH ₃ = 2.83 H ₁₁ = 8.33
21	7-CH ₃ = 2.73 H ₆ = 8.35 H ₁₁ = 8.53
18	8-CH ₃ = 2.54 H ₆ = 8.12 H ₁₁ = 8.51
14	9-CH ₃ = 2.51 H ₆ = 8.15 H ₁₁ = 8.45
24	10-CH ₃ = 2.81 H ₆ = 8.23 H ₁₁ = 8.74
25	11-CH ₃ = 3.15 H ₆ = 8.09

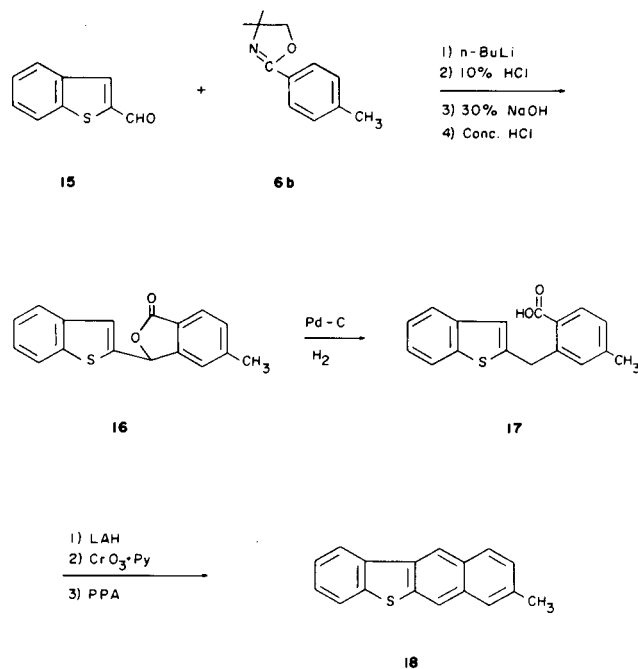
the C-1 methyl should be more deshielded than the C-3 methyl. Therefore, the compound with a methyl signal at δ 2.90 is 1-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**4a**) whereas the compound having a methyl signal at δ 2.49 was assigned as 3-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**4c**). The above assignment is also confirmed by the disappearance of a multiplet centered at δ 8.1 for H-1 assigned by Campaigne, *et al.* (4).

Scheme 2



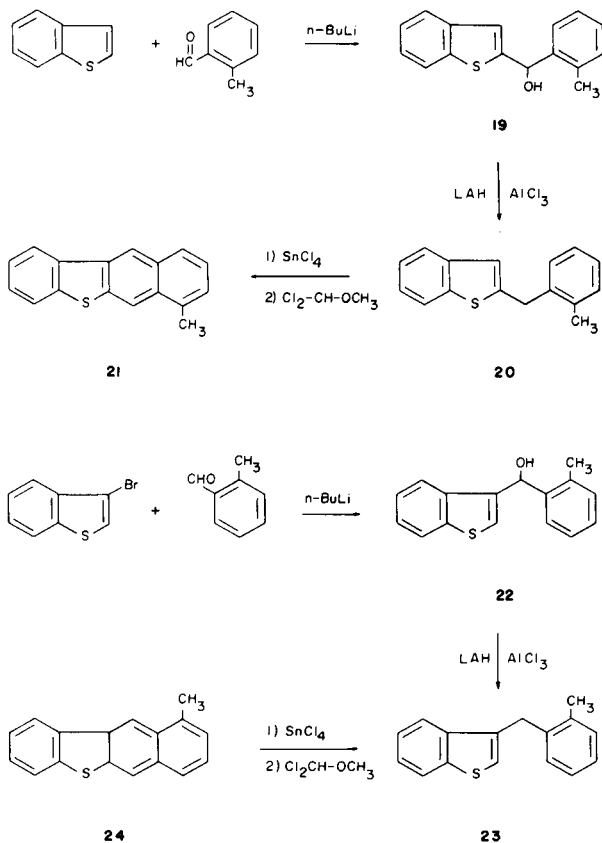
lithium at room temperature followed by cyclodehydration with polyphosphoric acid to yield the required compound **11**. Campaigne, *et al.*, (4) reported the synthesis of **11** by acylation of 4-methyldibenzothiophene with succinic anhydride in several steps. From *p*-methylphenyloxazoline **6b** and benzo[*b*]thiophene-3-carboxaldehyde (**5**) we obtained the acid **9b**, which was converted into the corresponding aldehyde (**13**) by reduction with lithium aluminium hydride followed by oxidation with chromium trioxide-pyridine complex. The cyclization of the crude aldehyde by heating with polyphosphoric acid in *m*-xylene gave the desired 9-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**14**). Ahmed, *et al.*, have synthesized **14** by a different route (6). The synthesis of 8-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**18**) was accomplished by the method outlined in Scheme 2 except that benzo[*b*]thiophene-2-carboxaldehyde (**15**) was the starting material. The synthesis of the 7- and 11-methyl

Scheme 3

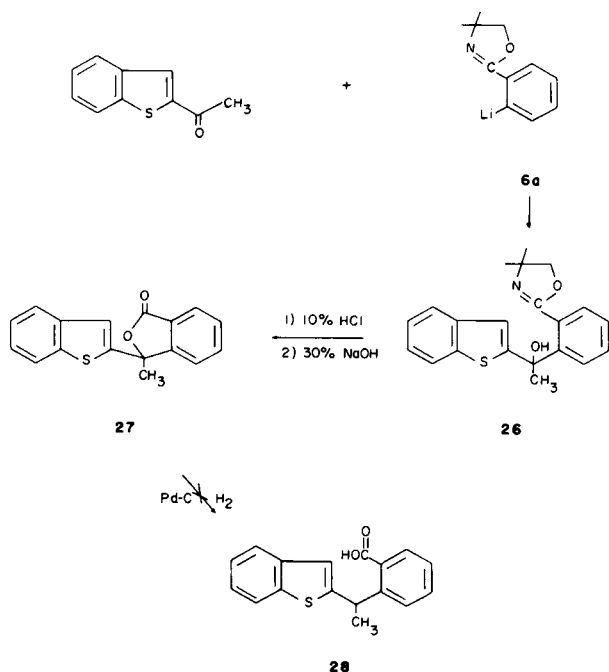


derivatives was achieved by the Bradsher reaction (6) and illustrated in Scheme 4. The reaction of 2-lithio- and 3-lithiobenzo[*b*]naphtho[2,3-*d*]thiophene (derived from the reaction of *n*-butyllithium on 3-bromobenzo[*b*]thiophene) with *o*-tolualdehyde gave the alcohols **19** and **22**, respectively. These alcohols were converted to the corresponding diarylmethanes **20** and **23** by reacting with a mixture of lithium aluminium hydride and aluminium chloride. The reaction of diarylmethane **20** with α,α -dichloromethyl ether in the presence of tin(IV) chloride gave **21** in good yield while the reaction with **23** gave the desired compound **24** in a somewhat smaller yield.

Scheme 4



Scheme 5



The synthesis of 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**25**) has already been described in a published paper from this laboratory (7).

An attempt to prepare 6-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**11**) from the reaction of **25** with **6a** gave **26** as an unisolated intermediate which was converted into lactone **27** which, however, could not be converted into **28** as indicated in Scheme 5.

EXPERIMENTAL

The ir spectra were recorded on a Beckmann Acculab-2 spectrometer. The ^1H nmr spectra were obtained on a Varian EM 360 spectrometer in the solvents indicated. Chemical shifts are reported in ppm from TMS as an internal reference and are given in δ units. Mass spectra were recorded on a Hewlett-Packard model 5980A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Melting points were determined on a Thomas-Hoover melting points apparatus and are uncorrected.

3-Methyl-3-(benzo[*b*]thiophen-2-yl)-1*H*,3*H*-benzo[*c*]furan-1-one (**27**).

Under a nitrogen atmosphere, *n*-butyllithium (20 ml, 0.03 mole, 1.6 *M* solution in hexane) was added dropwise to a solution of 4,4-dimethyl-2-phenyl-2-oxazoline (5.1 g, 0.03 mole) in 100 ml of dry ether, keeping the temperature between -35 to -45° (dry ice-chlorobenzene bath). After stirring for one hour, a solution of 2-acetylbenzo[*b*]thiophene (5.1 g, 0.03 mole) in 75 ml of dry ether was added dropwise. The reaction mixture was allowed to warm gradually to room temperature and to stand overnight. Water was added to the reaction mixture, the ether layer was separated and the aqueous layer was extracted with ether. The combined extracts were evaporated after drying over sodium sulfate. The residual oil **26** was refluxed with 200 ml of 10% hydrochloric acid for five hours with stirring. After cooling, the aqueous layer was decanted, washed with water and the residual oil was again refluxed with a mixture of 250 ml of methanol and 60 ml of 30% sodium hydroxide solution. The reaction mixture was poured into *ca* 1 *l* of water and acidified with hydrochloric acid. The precipitated solid was collected by filtration, washed with water, dried and recrystallized from methanol to afford 7.5 g (93%), mp $110\text{--}112^\circ$; ms: m/e 280 (M^+ , 32.6%), 265 ($M^+ - 15$, 100%); ir (potassium bromide): 1770 cm^{-1} ; nmr (deuteriochloroform): 7.0-8.0 (m, 9H, ArH), 2.0 (s, 3H CH_3).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{S}$: C, 72.83; H, 4.31; S, 11.44. Found: C, 72.66; H, 4.55; S, 11.60.

3-(Benzo[*b*]thiophen-3-yl)-1*H*,3*H*-benzo[*c*]furan-1-one (**8a**).

The reaction of 4,4-dimethyl-2-(2-lithiophenyl)-2-oxazoline [prepared from 4,4-dimethyl-2-phenyl-2-oxazoline (5.1 g, 0.03 mole) and *n*-butyllithium (20 ml, 0.03 mole, 1.6 *M* solution in hexane)] with benzo[*b*]thiophene-3-carboxaldehyde (4.5 g, 0.03 mole) following the above procedure yielded 1.0 g (15%) of **8a**, mp $128\text{--}130^\circ$; ms: m/e 266 (M^+ , 30%); ir (potassium bromide): 1750 cm^{-1} ; nmr (deuteriochloroform): 7.2-8.1 (m, 9H, H-4, H-5, H-6, H-7 of benzothiophene ring, CH, H-3, H-4, H-5, H-6 of benzofuran), 6.7 (s, 1H, H-2 of benzothiophene ring).

Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{O}_2\text{S}$: C, 72.16; H, 3.78; S, 12.03. Found: C, 71.90; H, 3.93; S, 11.97.

3-(Benzo[*b*]thiophen-3-yl)-1*H*,3*H*-5-methylbenzo[*c*]furan-1-one (**8b**).

The reaction of 4,4-dimethyl-2-(2-lithio-4-methylphenyl)-2-oxazoline with benzo[*b*]thiophene-3-carboxaldehyde following the above procedure gave **8b** in 59% yield, mp $157\text{--}158^\circ$; ms: m/e 280 (M^+ , 30%), 118 ($M^+ - 162$, 100%); ir (potassium bromide): 1750 cm^{-1} ; nmr (deuteriochloroform): 7.7-8.0 (m, 9H, ArH, CH), 2.0 (s, 3H, CH_3).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{S}$: C, 72.83; H, 4.37; S, 11.44. Found: C, 73.06; H, 4.44; S, 11.23.

3-(2-Carboxyphenylmethyl)benzo[*b*]thiophene (**9a**).

A mixture of 0.7 g of **8a** and 0.1 g of 5% palladium on carbon in 100 ml of warm acetic acid (95°) was stirred under an atmosphere of hydrogen overnight. The catalyst was filtered and concentrated under vacuum. The residue was crystallized from acetic acid to give 0.5 g (72%) of **9a**, mp 97-100°; ir (potassium bromide): 1680 cm⁻¹; nmr (deuteriochloroform): 6.8-8.2 (m, 8H, H-4, H-5, H-6, H-7 of benzothiophene ring and H-3', H-4', H-5', H-6' of phenyl ring); 6.6 (s, 1H, H-2 of thiophene ring); 4.45 (s, 2H, CH₂).

Anal. Calcd. for C₁₆H₁₂O₂S: C, 71.62; H, 4.51; S, 11.95. Found: C, 71.35; H, 4.61; S, 12.07.

3-(2-Carboxy-5-methylphenylmethyl)benzo[*b*]thiophene (**9b**).

This compound was prepared from **8b** following the same procedure as for **9a**, yield 60%, mp 131-132°; ir (potassium bromide): 1680 cm⁻¹; nmr (deuteriochloroform): 6.6-7.9 (m, 8H, ArH), 4.5 (s, 2H, CH₂), 2.25 (s, 3H, CH₃).

Anal. Calcd. for C₁₇H₁₄O₂S: C, 72.34; H, 5.08; S, 11.44. Found: C, 72.18; H, 4.80; S, 11.52.

3-(2-Acetylphenylmethyl)benzo[*b*]thiophene (**10**) and 6-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**11**).

Methylolithium (3.5 ml of 1.4 M solution in ethyl ether, 5.2 mmoles) was added rapidly to a stirred solution of **9a** (0.5 g, 1.9 mmoles) dissolved in 40 ml of dry ether. The solution was stirred for an additional hour, followed by decomposition with water. The ether phase was separated and the aqueous layer was extracted with ether. The combined extracts were dried with anhydrous sodium sulfate. The ether was removed and the residual oil was heated with 5 ml of polyphosphoric acid on a steam bath for 15 minutes. Ice was added to decompose the acid. The aqueous mixture was extracted with benzene, dried over sodium sulfate and the benzene was removed *in vacuo* to give a dark oil which was chromatographed on a silica gel column using hexane as the eluent, yield 0.2 g (44%), mp 96° [lit mp (4) 96°]; ms: m/e 248 (M⁺, 100%).

9-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**14**).

A solution of 1.0 g (3.5 mmoles) of 3-(2-carboxy-5-methylphenylmethyl)benzo[*b*]thiophene (**9b**) in 50 ml of dry ether was added dropwise to a suspension of 0.15 g of lithium aluminium hydride in 40 ml of dry ether. After refluxing for three hours, the reaction mixture was carefully quenched by adding water. The ether phase was separated and the aqueous phase was extracted again with ether. The combined ether extracts after drying over sodium sulfate were evaporated to give a colorless oil.

The solution of the above crude alcohol in 15 ml of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine complex made from 1.2 g of chromium trioxide and 12 ml of dry pyridine. After stirring for two hours at room temperature, the reaction mixture was filtered and washed with chloroform. The filtrate was washed with 10% hydrochloric acid and 10% sodium carbonate, successively. After drying over sodium sulfate, the chloroform was evaporated to leave the crude aldehyde as a dark oil.

A mixture of the crude aldehyde and 10 ml of polyphosphoric acid was heated at 100° for 30 minutes. After cooling, ice was added to the reaction mixture and the aqueous phase was extracted with benzene. The benzene phase after drying over sodium sulfate was evaporated and the residual oil was chromatographed on a silica gel column using hexane to give 0.1 g (11%) of **14**, mp 181-182° [lit mp (6) 185°]; ms: m/e 248 (M⁺, 100%).

5-Methyl-3-(benzo[*b*]thiophen-2-yl)-1*H*,3*H*-benzo[*c*]furan-1-one (**16**).

This compound was prepared from benzo[*b*]thiophene-2-carboxaldehyde and 4,4-dimethyl-2-(4-methylphenyl)-2-oxazoline *via* the method used for **8a**, yield 58%, mp 177-178°; ir (potassium bromide): 1750 cm⁻¹; nmr (deuteriochloroform): 7.1-8.0 (m, 8H, H-4, H-5, H-6, H-7 of the benzothiophene ring and H-3, H-4, H-5 of the phenyl ring), 6.95 (s, 1H, H-3 of the thiophene ring) 2.3 (s, 3H, CH₃).

Anal. Calcd. for C₁₇H₁₂O₂S: C, 72.83; H, 4.31; S, 11.44. Found: C, 73.06; H, 4.56; S, 11.51.

2-(2-Carboxy-5-methylphenylmethyl)benzo[*b*]thiophene (**17**).

This compound was prepared from **16** by hydrogenolysis following the procedure used for **9a**, yield 78%, mp 187-189°; ir (potassium bromide): 1660 cm⁻¹; nmr (DMSO-*d*₆): 7.0-7.9 (m, 8H, ArH), 4.6 (s, 2H, CH₂), 2.3 (s, 3H, CH₃).

Anal. Calcd. for C₁₇H₁₆O₂S: C, 72.31; H, 5.00; S, 11.36. Found: C, 72.34; H, 5.08; S, 11.44.

8-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**18**).

This compound was prepared from **16** following the previous procedure, yield 25%, mp 172-174° [lit mp (4) 178°]; ms: m/e 248 (M⁺, 100%).

2-(*o*-Methylbenzyl)benzo[*b*]thiophene (**20**).

Benzo[*b*]thiophene (10 g, 75 mmoles) in dry ether (250 ml) at -40° was treated with *n*-butyllithium (52 ml, 1.6 M solution in hexane). After the addition, the reaction mixture was stirred at room temperature for two hours. The reaction mixture was then cooled to -40° and *o*-tolualdehyde (8.9 g, 75 mmoles) in ether was added dropwise. The reaction mixture was allowed to come to room temperature and then stirred overnight. The reaction mixture was decomposed with water, the ether phase was separated, dried over sodium sulfate and evaporated to give the alcohol **19** as an oil which was used for the next step without further purification.

To a suspension of lithium aluminium chloride (1.9 g, 0.05 mole) in dry ether (100 ml) was added aluminum chloride (6.7 g, 0.05 mole) in dry ether (50 ml). To this solution was added the alcohol **19** (12.0 g, 0.047 mole) in ether at such a rate that reflux was maintained and then the mixture was refluxed for an additional one hour. The mixture was cooled and treated cautiously with moist ether and then poured into 2*N* sulfuric acid (250 ml). The ether phase was washed with water, dried over sodium sulfate and evaporated. The residue was crystallized from hexane, yield 7.4 g (66%), mp 58-60°; nmr (deuteriochloroform): 6.9-8.0 (m, 9H, ArH), 4.2 (s, 2H, CH₂), 2.3 (s, 3H, CH₃).

Anal. Calcd. for C₁₆H₁₄S: C, 80.62; H, 5.92; S, 13.45. Found: C, 80.71; H, 5.78; S, 13.48.

7-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**21**).

Tin(IV) chloride (2 ml, 17 mmoles) was added to a stirred solution of **20** (4 g, 17 mmoles) in methylene chloride (40 ml) at 0°. To this solution was added dichloromethyl methyl ether (1.2 ml, 17 mmoles) and the mixture was maintained at 0° for 1 hour and then allowed to stand at room temperature overnight. The reaction mixture was poured into water and the organic phase was separated, washed with water, dried over sodium sulfate and concentrated. The residual oil was chromatographed on a neutral alumina column using cyclohexane as the eluent to give 1.4 g, 35%, mp 180° [lit mp (4) 176°]; ms: m/e 248 (M⁺, 100%).

3-(2-Methylbenzyl)benzo[*b*]thiophene (**23**).

This compound was prepared following the procedure used for **20** in 60% yield, bp 165-171° (10 mm); nmr (deuteriochloroform): 6.6-8.0 (m, 9H, ArH), 4.1 (s, 2H, CH₂), 2.3 (s, 3H, CH₃).

Anal. Calcd. For C₁₆H₁₄S: C, 80.62; H, 5.92; S, 13.45. Found: C, 80.48; H, 5.87; S, 13.53.

10-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**24**).

This compound was prepared from **23** in 15% yield, mp 140-141°; nmr (deuteriochloroform): 8.74 (s, 1H, H-11, ArH), 8.23 (s, 1H, H-6, ArH), 8.14-8.35 (m, 1H, H-1, ArH), 7.63-7.90 (m, 2H, H-4, H-7, ArH), 7.23-7.58 (m, 4H, H-2, H-3, H-8, H-9, ArH), 2.8 (s, 3H, CH₃).

Anal. Calcd. for C₁₇H₁₂S: C, 82.21; H, 4.87; S, 12.91; Found: C, 82.39; H, 4.86; S, 12.99.

2-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**4b**).

3-Bromo-2-decalone (4.6 g, 0.02 mole) was added to 4-methylbenzenethiol (2.5 g, 0.02 mole) in 30 ml of dry pyridine maintained at 25-30°. After allowing the reaction mixture to stand for 15 minutes, the mixture was heated on a steam bath for 2 hours and then cooled. The reaction

mixture was acidified by the addition of 200 ml of 10% hydrochloric acid whereupon the reaction mixture separated into two layers. The organic phase was extracted into chloroform (200 ml) and the extract was washed with water and dried over anhydrous sodium sulfate. After removal of the drying agent and evaporation of the solvent, a light brown oil was obtained which was used without further purification in the next step.

The crude 3-(*p*-methylphenylthio)-2-decalone [ms: (M^+ , 274)] was heated on a steam bath with 20 g of polyphosphoric acid for 3 hours. The reaction mixture was poured into an ice-water mixture and extracted with benzene. The benzene extract was washed with water, dried (anhydrous sodium sulfate) and the benzene evaporated. The residue was chromatographed on a column of silica gel using hexane as the eluent giving a pale yellow oil, 2-methyl-6,6a,7,8,9,10,10a,11-octahydrobenzo[*b*]naphtho[2,3-*d*]thiophene [ms: (M^+ , 256)].

The crude octahydro compound was aromatized by heating (300°) with 5 g of powdered selenium for 8 hours. At this time the evolution of hydrogen selenide had ceased, whereupon the crude reaction mixture was extracted repeatedly with hot benzene. The benzene extracts were dried (anhydrous sodium sulfate) and the benzene was evaporated to give a crude residue which was chromatographed on a silica gel column using cyclohexane as the eluent. Colorless crystals of **4b** were obtained, mp 160°, yield 0.61 g (12% from 3-bromo-2-decalone); nmr (deuteriochloroform): 8.49 (s, 1H, H-11, *ArH*), 8.15 (s, 1H, H-6, *ArH*), 7.27-8.05 (m, 6H, H-3, H-4, H-7, H-8, H-9, H-10, *ArH*), 2.50 (s, 3H, *CH*₃); ms: (M^+ , 248).

Anal. Calcd. for C₁₇H₁₂S: C, 82.21; H, 4.87; S, 12.91. Found: C, 82.39; H, 5.05; S, 12.70.

4-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**4d**).

3-Bromo-2-decalone (4.6 g, 0.02 mole) and 2-methylbenzenethiol (2.5 g, 0.02 mole) in 30 ml of dry pyridine was treated as described for **4b**. Colorless crystals of **4d**, mp 191° were obtained in a yield of 18% (0.9 g); nmr (deuteriochloroform): 8.54 (s, 1H, H-11, *ArH*), 8.24 (s, 1H, H-6, *ArH*), 7.86-8.17 (m, 3H, H-1, H-7, H-10, *ArH*), 7.22-7.61 (m, 4H, H-2, H-3, H-8, H-9, *ArH*), 2.54 (s, 3H, *CH*₃); ms: (M^+ , 248).

Anal. Calcd. for C₁₇H₁₂S: C, 82.21; H, 4.87; S, 12.91. Found: C, 81.97; H, 4.78; S, 12.81.

1-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**4a**) and 3-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**4c**).

3-Bromo-2-decalone (4.6 g, 0.02 mole) and 3-methylbenzenethiol in 30

ml of dry pyridine was treated as described for **4b**. The crude aromatized mixture of **4a** and **4c** could not be separated satisfactorily on a silica gel column, therefore the mixture was separated on basic alumina (Aldrich 19,944-3) using hexane-benzene mixtures as the eluent.

Compound **4a**.

This compound was eluted first and was obtained in a yield of 7% (0.35 g), mp 99°; nmr (deuteriochloroform): 8.66 (s, 1H, H-11, *ArH*), 8.17 (s, 1H, H-6, *ArH*), 7.16-8.17 (m, 7H, H-2, H-3, H-4, H-7, H-8, H-9, H-10, *ArH*), 2.90 (s, 3H, *CH*₃); ms: (M^+ , 248).

Anal. Calcd. for C₁₇H₁₂S: C, 82.21; H, 4.87; S, 12.91. Found: C, 82.05; H, 5.01; S, 12.90.

Compound **4c**.

This compound eluted last, yield 0.51 g (10%), mp 201°; nmr (deuteriochloroform): 8.51 (s, 1H, H-11, *ArH*), 8.21 (s, 1H, H-6, *ArH*), 7.22-8.10 (m, 7H, H-1, H-2, H-4, H-7, H-8, H-9, H-10, *ArH*), 2.49 (s, 3H, *CH*₃); ms: (M^+ , 248).

Anal. Calcd. for C₁₇H₁₂S: C, 82.21; H, 4.87; S, 12.91. Found: C, 81.72; H, 4.79; S, 12.80.

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