# Synthesis of Benzo[3,2]phenanthro[4,5-*bcd*]thiophene and Chryseno[4,5-*bcd*]thiophene

*Robert Douglas Thompson, Masatomo Iwao, Milton L. Lee and Raymond N. Castle* (1)*

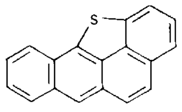
Department of Chemistry, Brigham Young University, Provo, Utah 84602

Received April 21, 1981

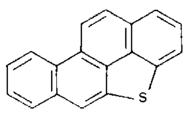
Benzo[2,3]phenanthro[4,5-*bcd*]thiophene and chryseno[4,5-*bcd*]thiophene were synthesized, so that their mutagenic and carcinogenic activity can be determined.

*J. Heterocyclic Chem.*, **18**, 981 (1981).

Previously, we have reported the synthesis of the phenanthro[*b*]thiophenes (2). To further our investigation of polycyclic thiophenes, the study of benzo[2,3]phenanthro[4,5-*bcd*]thiophene (**1**) and chryseno[4,5-*bcd*]thiophene (**2**) was desired. Karcher, *et.al.,* have shown that compounds **1** and **2** are present in polynuclear aromatic hydrocarbons derived from coal tar and that compound **1** possessed high mutagenic acitivity (3). Therefore, in order to assign the absolute structure *via* synthetic routes and to obtain a sufficient sample for carcinogenic and mutagenic testing, it was desired to synthesize compounds **1** and **2**.



1



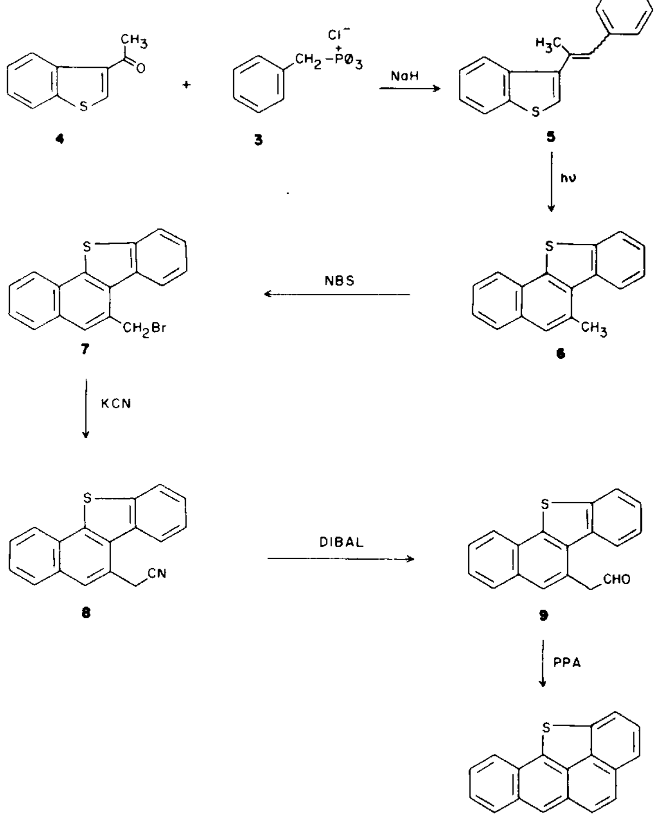
2

Newman and Kannan (4) have reported the synthesis of benzo[*a*]pyrenes form methylbenz[*a*]anthracenes in four steps. Thus, it appeared that compounds **1** and **2** could be obtained from 6-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**7**) (Scheme I) and 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**18**) (Scheme III). The 6-methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**6**) was readily obtained from the Wittig reaction of benzyltriphenylphosphonium chloride (**3**) (5) and 3-acetylbenzo[*b*]thiophene (**4**) followed by photocyclization of the alkene **5**. This method has been shown to be an effective route to polycyclic thiophenes (2).

The methyl compound **6** was brominated with *N*-bromosuccinimide to yield 6-bromomethylbenzo[*b*]naphtho[2,1-*d*]thiophene (**7**). This bromomethyl compound **7** was converted to 6-cyanomethylbenzo[*b*]naphtho[2,1-*d*]thiophene (**8**) with potassium cyanide and Aliquat-336 in good yield. Reduction of the cyano compound **8** with diisobutylaluminum hydride afforded the aldehyde **9**, which was not purified, but allowed to react directly with polyphosphoric acid to give the desired polycyclic thiophene **1**.

Synthesis of 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**18**) was first attempted by the cyclization of the methyl ketone **10** (6) (Scheme II). However, instead of producing the desired methyl compound **18**, deacetylation occurred to afford 2-benzylbenzo[*b*]thiophene (**11**) in low yield. Since cyclization onto the benzene ring proved to be unsuccessful, it was presumed that the 3-position of the thiophene ring should be more suitable for cyclization.

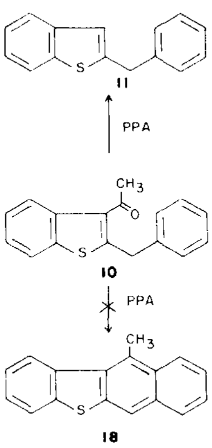
Scheme I



Newman and Kannan (4) have reported the synthesis of 9-fluoro-12-methylbenz[*a*]anthracene, where the methyl ketone was cyclized onto the naphthalene ring. This method also proved to be successful in our case. Therefore, reaction of the oxazoline **12** (7) with *sec*-butyllithium followed by condensation with benzo[*b*]thiophene-2-carbaldehyde (**13**) (8) afforded compound **14**. Hydrolysis of compound **14** with hydrochloric acid in dioxane yielded the lactone **15**. Reduction to **15** with hydrogen and palladium

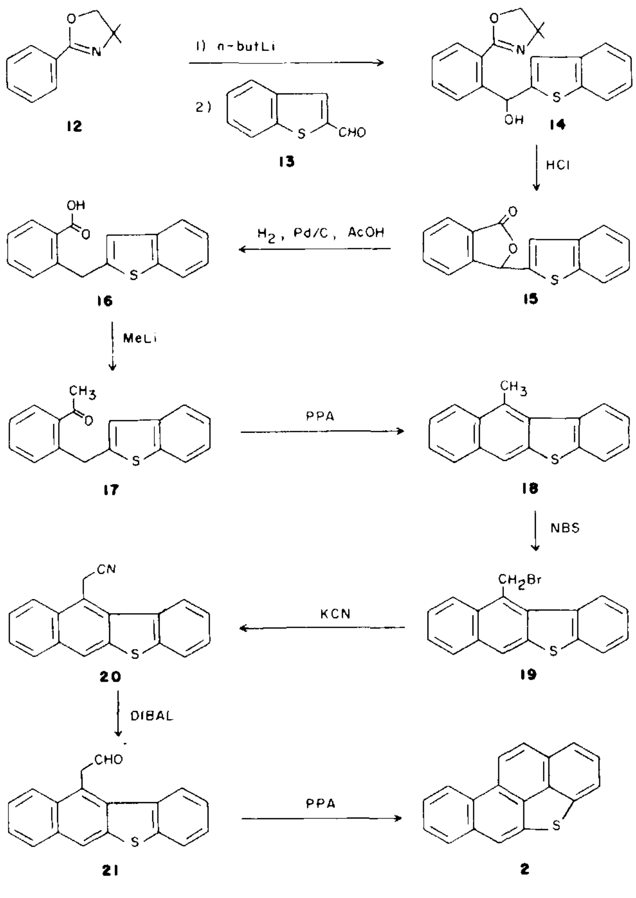
*0022-152X/81/050981-04$02.25*

Scheme II



on carbon in acetic acid gave the acid **16**. When **16** was allowed to react with methyllithium at room temperature the methyl ketone **17** and a small amount of the cyclized methyl compound **18** was obtained. Separation of this mixture was easily achieved by chromatography. The methyl ketone **17** was allowed to react with polyphosphoric acid to give 11-methylbenzo[*b*]napththo[2,3-*d*]thiophene (**18**). The same sequence of reactions which converted the methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**6**) to benzo[2,3]phenanthro[4,5-*bcd*]thiophene (**1**), also proved to be successful in the conversion of 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**18**) to the desired chryseno[4,5-*bcd*]thiophene (**2**).

Scheme III



It should be noted that tlc (cyclohexane as eluent) of compound **2** showed a small impurity of lower Rf value. This small impurity was removed by recrystallization to give pure compound **2**.

## EXPERIMENTAL

All melting points are uncorrected. Ir spectra were obtained on a Beckman Acculab-2 spectrometer. Nmr spectra were obtained on a Varian EM 390 spectrometer or a JEOL FX 90 Q spectrometer. Mass spectra were obtained on a Hewlett-Packard model 5890A mass spectrometer. Uv spectra were recorded for solutions in 95% ethanol with a Perkin Elmer 320 spectrometer.

### 3-Acetylbenzo[*b*]thiophene (**4**).

The synthesis of compound **4** from 3-lithiobenzo[*b*]thiophene and acetonitrile has been reported by Dickinson and Iddon (9). However, reaction of the lithio compound with *N,N*-dimethylacetamide gave a much better yield. Thus, a solution of 3-bromobenzo[*b*]thiophene (21.3 g, 0.10 mole) in 150 ml of absolute ether was added to a mixture of 63 ml (0.10 mole) of 1.6 *M n*-butyllithium solution in hexane and 250 ml of absolute ether keeping the temperature below −70°. A white suspension of 3-lithiobenzo[*b*]thiophene was obtained after 30 minutes. A solution of *N,N*-dimethylacetamide (10.5 g, 0.12 mole) in 10 ml of absolute ether was added. The mixture was stirred at −78° for 4 hours and allowed to warm up to room temperature. Hydrochloric acid (2*N*) was added and the ether layer was separated, followed by extraction of the aqueous layer with ether. The combined extracts were washed with water, dried and evaporated. The residue was distilled *in vacuo* to give 10.4 g (59%) of **4** as a pale yellow liquid, bp 104-107°/0.1 mm. Recrystallization from ether/hexane gave colorless prisms, mp 64° (lit mp 64-65°); $^1$H-nmr (deuteriochloroform): $\delta$ 2.52 (s, 3H, CH$_3$), 7.35 (m, 2H, H5 and H6), 7.75 (m, 1H, H7), 8.10 (s, 1H, H2) and 8.75 (m, 1H, H4).

### 3-(1-Phenyl-1-propen-2-yl)benzo[*b*]thiophene (**5**).

Carruthers and Stewart (10) have reported the formation of compound **5** *via* the Grignard reaction followed by dehydration. However, the Wittig reaction gave a much better yield.

A solution of 38.9 g (0.10 mole) of **3** in 100 ml of absolute ethanol was added to a solution of sodium (2.4 g, 0.105 mole) in 400 ml of absolute ethanol. After 10 minutes of stirring, a solution of 17.6 g (0.10 mole) of **4** in 50 ml of absolute ethanol was added. The mixture was refluxed for 5 hours. The ethanol was removed *in vacuo* and water was added to the residue. The product was extracted with ethyl ether and dried with anhydrous sodium sulfate. The ether was removed and the residue was dissolved in cyclohexane after which the insoluble triphenylphosphine oxide was filtered off. After removal of the cyclohexane, the product was chromatographed on a column of silica gel using cyclohexane as eluent to yield 20.1 g (80%) of a *trans-cis* mixture of **5** as colorless crystals. Recrystallization from hexane gave colorless plates, mp 67-68°; ir (potassium bromide): 1600 and 3090 cm$^{-1}$ (C=C), 680, 780, 900 and 3000 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): $\delta$ 2.24 (3H, *cis* CH$_3$), 2.31 (s, 3H *trans* CH$_3$), 6.68 (d, J = 1.5 Hz, 1H *cis* C=C−H), 6.78 (d, J = 1.5 Hz, 1H, *trans* C=C−H), 6.90-8.07 (m, 10H, aromatic); ms: 250 (M$^+$, 48.5), 235 (M−CH$_3$, 100).

*Anal.* Calcd. for $C_{17}H_{14}S$ (250.37): C, 81.32; H, 5.12; S, 13.57. Found: C, 81.51; H, 5.24; S, 13.34.

### 6-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**6**).

A solution of **5** (2.0 g, 0.008 mole) and 0.10 g of iodine in 750 ml of cyclohexane was irradiated for four hours with a 450 Watt Hanovia medium pressure mercury lamp through a corex filter. During the course of the reaction a slow stream of air was passed through the solution. The cyclohexane was removed *in vacuo* and the residue was passed through a column of silica gel (60-200 mesh) using cyclohexane as eluent to yield 1.97 g of **6** as colorless needles, mp 95.5-96° [lit mp 96° (11)]; ir: 1385 cm$^{-1}$ ($CH_3$), 740, 795 and 3060 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 3.00 (s, 3H, $CH_3$), 7.32-8.52 (m, 9H, aromatic); ms: 248 ($M^+$, 100).

### 6-Bromomethylbenzo[*b*]naphtho[2,1-*d*]thiophene (**7**).

A mixture of **6** (0.5 g, 2.0 mmoles), *N*-bromosuccinimide (0.38 g, 2.1 mmoles), 15 ml of carbon tetrachloride and 10 mg of benzoyl peroxide was refluxed for two hours (tlc showed a small amount of starting material). The succinimide was filtered off and washed with carbon tetrachloride. The filtrate was concentrated and cooled to give 0.3 g of light yellow needles. Further concentration of the mother liquor gave an additional 0.2 g, to give a total yield of 0.5 g (77.5%), mp 169-170°. Recrystallization of a small amount gave colorless needles, mp 176°; ir (potassium bromide): 690 cm$^{-1}$ (Br), 720, 750 and 3020 cm$^{-1}$(m, 9H, aromatic); $^1$H-nmr (deuteriochloroform): δ 5.08 (s, 2H, $CH_2$), 7.35-8.52 (aromatic); ms: 328 ($M^+$, $^{81}$Br, 14.0), 326 ($M^+$, $^{79}$Br, 13.2), 247 (M-Br, 100).

*Anal.* Calcd. for $C_{17}H_{11}BrS$: (327.25): C, 62.40; H, 3.39; Br, 24.42; S, 9.80. Found: C, 62.56; H, 3.48; Br, 24.50; S, 9.65.

### 6-Cyanomethylbenzo[*b*]naphtho[2,1-*d*]thiophene (**8**).

A stirred mixture of **7** (5.0 g, 15.3 mmoles), potassium cyanide (2.0 g, 30.8 mmoles), 10 drops of Aliquat-336, 200 ml of benzene and 100 ml of water was refluxed for 3 hours. The benzene layer was separated and the aqueous layer was extracted with benzene. The combined benzene extracts were washed with water, dilute hydrochloric acid and again with water. The benzene extracts were dried with anhydrous sodium sulfate and removed *in vacuo* to give a light brown solid. Recrystallization from benzene/cyclohexane (charcoal) gave 3.55 g (85%) of colorless needles, mp 162-164°. An analytical sample was obtained by two recrystallizations from benzene/cyclohexane, mp 165.5-166°; ir (potassium bromide): 2125 cm$^{-1}$ (CN), 730, 760 and 3030 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 4.32 (s, 2H, $CH_2$), 7.45-8.17 (m, 9H, aromatic); ms: 273 ($M^+$, 100).

*Anal.* Calcd. for $C_{18}H_{11}NS$ (273.36): C, 79.09; H, 4.06; N, 5.12; S, 11.73. Found: C, 78.88; H, 4.03; N, 4.92; S, 11.36.

### Benzo[2,3]phenanthro[4,5-*bcd*]thiophene (**1**).

A solution of diisobutylaluminum hydride (2.0 ml, Ventron, 25%) in toluene was added **via** a syringe into a dry stirred solution of **8** (0.5 g, 1.83 mmoles) in 30 ml of benzene under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Dilute hydrochloric acid was added to the mixture, followed by extraction with chloroform. The chloroform extracts were dried with anhydrous sodium sulfate followed by removal of the chloroform *in vacuo* to give the aldehyde as a solid (ir, 1720 cm$^{-1}$, aldehyde). Polyphosphoric acid (6 g) was added to the crude aldehyde dissolved in 10 ml of *m*-xylene. The mixture was heated at 100° for 2 hours with vigorous stirring. Ice was added to decompose the acid, after which the aqueous mixture was extracted with chloroform, dried with anhydrous sodium sulfate and evaporated *in vacuo* to dryness. The residue was chromatographed on a column of alumina using cyclohexane:benzene (3:1) as eluent to give 0.2 g (42%) of **1** as a pale yellow solid, mp 151-152°. An analytical sample was recrystallized from cyclohexane to give pale yellow needles, mp 152-153°; ir (potassium bromide): 730, 750, 800, 840, 860 and 3020 cm$^{-1}$(aromatic); $^1$H-nmr (deuteriochloroform): δ 7.53-8.33 (m, 9H, aromatic), 8.28 (s, 1H, H6); uv: λ max (log ε) 208 (3.94), 221, (2.93), 262 (4.02), 277 (3.93), 288 (4.00), 298 (3.98), 331 (3.09), 347 (3.38), 364 (3.62) 385 nm (3.56); ms: 258 ($M^+$, 100).

*Anal.* Calcd. for $C_{18}H_{10}S$ (258.34): C, 83.69; H, 3.90; S, 12.41. Found: C, 83.80; H, 3.80; S, 12.14.

### 2-Benzylbenzo[*b*]thiophene (**11**).

Compound **10** (1.0 g, 3.75 mmoles) was heated with 10 g of polyphosphoric acid at 150° for 20 minutes. Ice was added to decompose the acid. The aqueous mixture was extracted with ether, washed with aqueous sodium bicarbonate, water and then dried with anhydrous sodium sulfate. The ether was removed *in vacuo* to give an oily solid (tlc in cyclohexane showed one spot, however in benzene many spots were present). Chromatography on silica gel with cyclohexane as eluent gave 0.08 g (9.5%) of a white solid (mixed melting point and nmr showed this compound to be identical with **11**), mp 84-85° [lit mp 86-87° (11)]; $^1$H-nmr (deuteriochloroform): δ 4.20 (s, 2H, $CH_2$), 6.96 (s, 1H, H3), 7.20-7.45 (m, 7H, H5, H6, and phenyl), 7.56-7.83 (q, 2H, H4 and H7).

### 2-[2-(1-Benzo[*b*]thiophen-2-yl-1-hydroxymethyl)phenyl]-4,4-dimethyl-2-oxazoline (**14**).

*sec*-Butyllithium (48.3 ml of 1.3 *M* solution in hexane, 0.063 moles) was added *via* a syringe over a period of 30 minutes to a dry solution of **12** (10 g, 0.057 mole) and 600 ml of ethyl ether under nitrogen at −78°. The solution turned yellow followed by a yellow precipitate. The mixture was allowed to warm slowly to −15° and then cooled back to −78°, after which **13** (9.3 g, 0.057 mole) dissolved in 200 ml of dry ethyl ether was added dropwise. The mixture was allowed to slowly warm to room temperature and then stirred overnight. The mixture was then poured into 400 ml of ice water and the layers separated. The aqueous layer was extracted with ethyl ether and the combined extracts were dried with anhydrous sodium sulfate. The ether was removed *in vacuo* to give a yellow solid. The solid was filtered and washed with ether to give a white solid. The mother liquor was concentrated to give more product, total yield, 6 g (62%), mp 134-135°. An analytical sample was recrystallized from benzene/hexane to give colorless prisms, mp 135-136°; ir (potassium bromide): 700, 760 and 2990 cm$^{-1}$ (aromatic), 3090 cm$^{-1}$ (OH), 1640 cm$^{-1}$ (C=N); $^1$H-nmr (deuteriochloroform): δ 0.87 (s, 3H, $CH_3$), 1.29 (s, 3H, $CH_3$), 3.88 (q, 2H, $CH_2$), 6.08 (d, J = 9 Hz, 1H, C−H), 6.74 (s, 1H, H3), 7.15-7.98 (m, 8H, aromatic), 8.65 (d, J = 9 Hz, 1H, OH); ms: 337 ($M^+$, 100).

*Anal.* Calcd. for $C_{20}H_{19}NO_2S$ (337.44): C, 71.12; H, 5.68; N, 4.15; S, 9.50. Found: C, 71.33; H, 5.74; N, 4.13; S, 9.61.

### 5-Benzo[*b*]thiophen-2-yl-2,5-dihydrobenzo[*c*]furan-2-one (**15**).

A solution of **14** (1.7 g, 5.04 mmoles), 40 ml of 10% hydrochloric acid and 50 ml of 1,4-dioxane was refluxed for 18 hours. The solution was allowed to cool slowly to give light brown needles. Filtration and recrystallization from benzene/methanol (charcoal) gave 1.2 g (89%) of **15**, mp 171-172°; ir (potassium bromide): 1750 cm$^{-1}$ (C=O), 1050 and 1280 cm$^{-1}$ (C−O), 690, 745 and 3030 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 6.72 (s, 1H, CH), 7.26-8.13 (m, 9H, aromatic); ms: 266 ($M^+$, 100).

*Anal.* Calcd. for $C_{16}H_{10}SO_2$ (266.32): C, 72.16; H, 3.78; S, 12.04. Found: C, 72.13; H, 3.87; S, 11.88.

### 2-(2-Carboxyphenylmethyl)benzo[*b*]thiophene (**16**).

A mixture of **15** (1.6 g, 6.0 mmoles), 0.5 g of 5% palladium on carbon and 200 ml of acetic acid was hydrogenated at 80-90° and atmospheric pressure. The solution was then boiled and filtered to remove the catalyst. The acetic acid was removed *in vacuo* to give a white solid, which was recrystallized from benzene/hexane (charcoal) to give 1.4 g (87%), mp 142-144°; ir (potassium bromide): 2580-3030 cm$^{-1}$ (OH), 1670 cm$^{-1}$ (C=O), 1240 cm$^{-1}$ (C−O); $^1$H-nmr (DMSO-$d_6$): δ 4.64 (s, 2H, $CH_2$), 7.04 (s, 1H, H3), 7.15-7.96 (m, 8H, aromatic), 11.0-13.6 (broad s, 1H, COOH); ms: 268 ($M^+$, 67), 250 ($M$-$H_2O$, 100).

*Anal.* Calcd. for $C_{16}H_{12}SO_2$ (268.34): C, 71.62; H, 4.51; S, 11.95. Found: C, 71.37; H, 4.56; S, 11.81.

### 2-(2-Acetylphenylmethyl)benzo[*b*]thiophene (**17**) and 11-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene (**18**).

Methyllithium (6.9 ml of a 1.4 *M* solution in ethyl ether, 9.7 mmoles) was added rapidly to a stirred solution of **16** (1.0 g, 3.7 mmoles) dissolved in 40 ml of dry ethyl ether. The solution was stirred for an additional hour, followed by decomposition with saturated ammonium chloride. The ether was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried with anhydrous sodium sulfate. The ether was removed *in vacuo* to give an oily solid. Chromatography on silica gel using toluene:hexane (1:1) as eluent gave 0.15 g (14%) of **18** and 0.5 g (50%) of **17** (ir, 1670 cm$^{-1}$, C=O). The crude methyl ketone **17** (0.5 g, 1.9 mmoles) was heated with 6 ml of polyphosphoric acid at 80-90° for 15 minutes. Ice was added to decompose the acid. The aqueous mixture was extracted with benzene, dried with anhydrous sodium sulfate and the benzene removed *in vacuo* to give a dark yellow solid. Chromatography on silica gel using hexane:toluene (5:1) as eluent gave 0.25 g. Total yield of **18** was 0.4 g (43% overall yield from **16**), mp 160-161°. An analytical sample was recrystallized from benzene/cyclohexane to give colorless needles, mp 161-162°; ir (potassium bromide): 1390 cm$^{-1}$ ($CH_3$), 730, 755 and 3030 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 3.15 (s, 3H, $CH_3$), 7.49-8.41 (m, 9H, aromatic); ms: 248 (M$^+$, 100).

*Anal.* Calcd. for $C_{17}H_{12}S$ (248.35): C, 82.22; H, 4.87; S, 12.91. Found: C, 82.10; H, 4.91; S, 12.76.

### 11-Bromomethylbenzo[*b*]naphtho[2,3-*d*]thiophene (**19**).

Bromination was achieved in the same manner as described for compound **6**, thus, 1.33 g (5.36 mmoles) of **18**, 1.24 g (6.97 mmoles) of *N*-bromosuccinimide, 30 mg of benzoyl peroxide and 50 ml of carbon tetrachloride gave 1.33 g (76%) of yellow needles, mp 201-203°; ir (potassium bromide): 695 cm$^{-1}$ (Br), 720, 750 and 2910 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 5.52 (s, 2H, $CH_2$), 7.43-8.62 (m, 9H, aromatic); ms: 328 (M$^+$, $^{81}$Br, 12.3), 326 (M$^+$, $^{79}$Br, 11.7), 247 (M-Br, 100). A satisfactory analysis was not obtainable after repeated recrystallization from benzene/cyclohexane, however the compound is homogeneous by tlc (benzene/cyclohexane).

*Anal.* Calcd. for $C_{17}H_{11}BrS$ (327.25): C, 62.40; H, 3.39; Br, 24.42; S, 9.80. Found: C, 60.61; H, 3.57; Br, 26.00; S, 9.66.

### 11-Cyanomethylbenzo[*b*]naphtho[2,3-*d*]thiophene (**20**).

Conversion of compound **19** to the cyano compound **20** was achieved in the same manner as described for compound **7**. Thus, 1.25 g (3.82 mmoles) of **19**, 0.5 g (77 mmoles) of potassium cyanide, 50 ml of benzene, 25 ml of water and 3 drops of Aliquat-336 gave 0.75 g (72%) of light brown needles, mp 230-230.5°; ir (potassium bromide): 2120 cm$^{-1}$ (C≡N), 700, 730, 760 and 2910 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 4.70 (s, 2H, $CH_2$), 7.47-8.43 (m, 9H, aromatic); ms: 273 (M$^+$, 100).

*Anal.* Calcd. for $C_{18}H_{11}NS$ (273.36): C, 79.09; H, 4.06; N, 5.12; S, 11.73. Found: C, 79.23; H, 4.29; N, 5.13; S, 11.78.

### Chryseno[4,5-*bcd*]thiophene (**2**).

Conversion of compound **20** to compound **2** was achieved in the same manner as described for compound **8**. Thus, 1 g (3.66 mmoles) of **20**, 60 ml of dry benzene and 4 ml of diisobutylaluminum hydride (25% solution in toluene) gave the aldehyde (ir, 1715 cm$^{-1}$, C=O) as a light brown solid. The crude aldehyde, 21 g of polyphosphoric acid and 20 ml of dry xylene gave after chromatography 0.35 g of the crude product **2** (tlc in cyclohexane showed the presence of an impurity). Recrystallization from cyclohexane gave 0.3 g (32%) of colorless needles, mp 172-173°; ir (potassium bromide): 690, 740 and 2960 cm$^{-1}$ (aromatic); $^1$H-nmr (deuteriochloroform): δ 7.60-8.31 (m, 8H, aromatic), 8.70 (d, $J_{10,11}$ = 9 Hz, 1H, H10), 8.77 (near dd, 1H, H9); uv: λ max (log ε) 202 (3.61), 213 (3.48), 246 (3.87), 253 (3.07), 268 (3.75), 278 (3.74), 340 (3.32), 357 (3.40) and 380 nm (2.44); ms: 258 (M$^+$, 100).

*Anal.* Calcd. for $C_{19}H_{10}S$ (258.34): C, 83.69; H, 3.90; S, 12.41. Found: C, 83.46; H, 3.66; S, 12.19.

Acknowledgement.

This study was supported by the U. S. Department of Energy, Office of Health and Environmental Research, Contract No. DE-AC02-79EV10237.

## REFERENCES AND NOTES

(1) To whom correspondence should be addressed at the Department of Chemistry, University of South Florida, Tampa, FL 33620 USA.

(2) M. Iwao, M. L. Lee and R. N. Castle, *J. Heterocyclic Chem.*, **17**, 1259 (1980).

(3a) W. Karcher, R. Depaus, J. Van Eijk and J. Jacob, "Polynuclear Aromatic Hydrocarbons", P. W. Jones and P. Leber, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1979, pp. 348-349; (b) W. Karcher, A. Nelen, R. Depaus, J. van Eijk, P. Glaude and J. Jacob, Proceedings of the 5th International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, October, 1980.

(4) M. S. Newman and R. Kannan, *J. Org. Chem.*, **44**, 3388 (1979).

(5) K. Friedrich and H. Henning, *Chem. Ber.*, **92**, 2756 (1959).

(6) R. Royer, P. Demerseman and A. Cheutin, *Bull. Soc. Chim. France*, 1534 (1961).

(7) A. I. Meyers, D. L. Temple, D. Haldukewych and E. D. Mihelich, *J. Org. Chem.*, **39**, 2787 (1974).

(8) The same procedure of D. A. Shirley and M. J. Danzig, *J. Am. Chem. Soc.*, **74**, 2935 (1952) was employed, except *N,N*-dimethylformamide was used in place of *N*-methylformanilide to give a yield of 81%, mp 33-34° (lit mp 34-34.5°).

(9) R. P. Dickinsen and B. Iddon, *J. Chem. Soc.* (C), 2733 (1968).

(10) W. Caruthers and H. N. M. Stewart, *J. Chem. Soc.*, 6221 (1965).

(11) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1957).