Synthesis of Anthra[*b*]thiophenes and Benzo[*b*]naphtho[*d*]thiophenes

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Received April 27, 1981

All isomers of the parent anthra[*b*]thiophenes and benzo[*b*]naphtho[*d*]thiophenes, namely anthra[2,3-*b*]thiophene, anthra[2,1-*b*]thiophene, anthra[1,2-*b*]thiophene, benzo[*b*]naphtho[2,3-*d*]thiophene, benzo[*b*]naphtho[2,1-*d*]thiophene and benzo[*b*]naphtho[1,2-*d*]thiophene were synthesized using a new procedure.

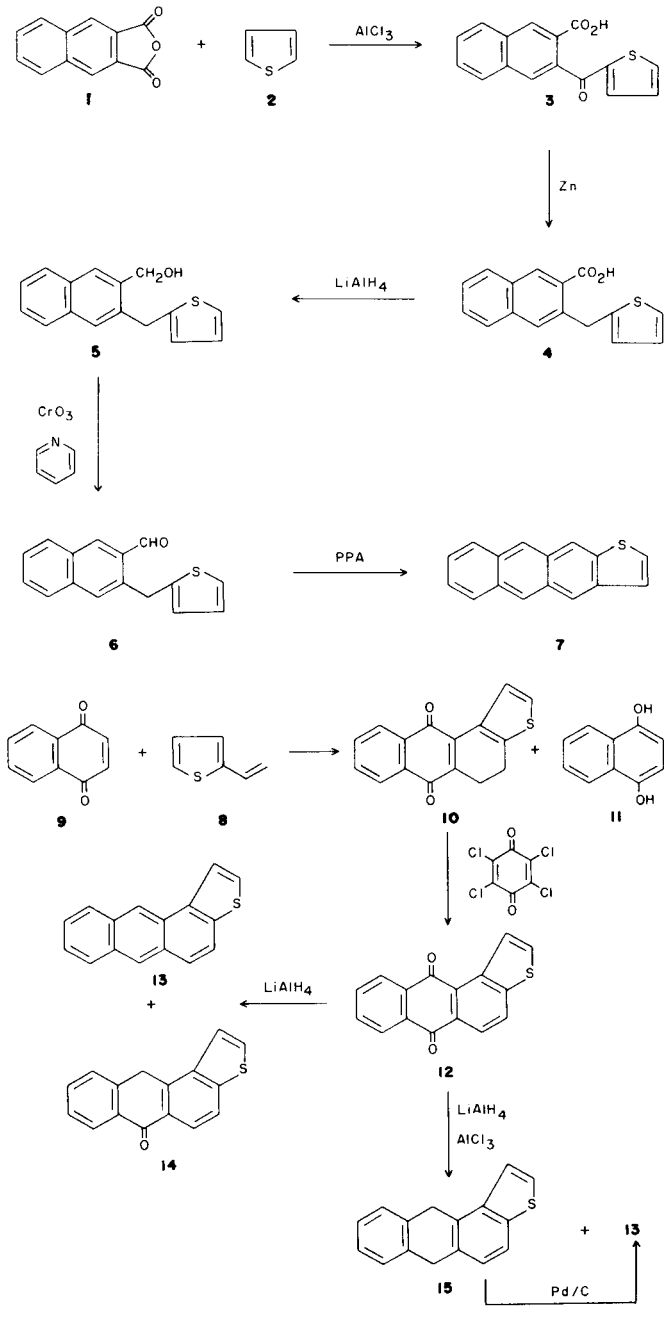
J. Heterocyclic Chem., **18**, 967 (1981).

Recently, using glass capillary gas chromatography/mass spectrometry, a great many heterocyclic sulfur compounds have been separated and identified from coal gasification tar, coal liquids and shale oils (2). It is well known that several unsubstituted tetracyclic thiophene derivatives are contained within these polycyclic thiophene fractions. Iwao, *et.al.*, have reported the synthesis of all isomers of the parent phenanthro[*b*]thiophene ring systems in order to provide samples for the measurement of retention data for programmed temperature capillary column gas chromatography, and have examined the carcinogenic and mutagenic activities of these compounds (3). As a continuation of this research plan to synthesize all of the remaining tetracyclic poly-condensed thiophene derivatives, the present paper describes a new route for the preparation of all isomers of the anthra[*b*]thiophene and benzo[*b*]naphtho[*d*]thiophene ring systems.

The synthesis of anthra[2,3-*b*]thiophene was first reported by Faller, *et.al.*, in 1968 (4), using the Elbs reaction. The Elbs reaction is a useful method for the preparation of polycyclic aromatic compounds. Although the yields of products obtained *via* this procedure are usually quite low, the Elbs procedure is still quite valuable since it can be used to synthesize compounds which are difficult to prepare *via* other methods.

The cyclization of compounds which have an aldehyde group at the *ortho*-position with polyphosphoric acid to give polycyclic aromatic compounds is well known (5,6). Anthra[2,3-*b*]thiophene was prepared according to this method. The key intermediate for the synthesis of **7**, 3-(2-thenyl)-2-naphthalenecarboxaldehyde (**6**), was prepared by the oxidation of 3-(2-thenyl)-2-naphthalenemethanol with chromium trioxide-pyridine complex in pyridine at room temperature. Compound **5** was obtained by the reduction of 3-(2-thenyl)naphthalenecarboxylic acid (**4**) with lithium aluminum hydride. Compound **4** was synthesized by the reduction of 3-(2-thenoyl)naphthalenecarboxylic acid (**3**) which was prepared from 2,3-naphthalenedicarboxylic acid anhydride and thiophene using the Friedel-Crafts condensation reaction. Cyclization of the crude aldehyde **6** by heating with polyphosphoric acid gave anthra[2,3-*b*]thiophene (**7**) (4) as yellow crystals in 51% overall yield from **4**.

Scheme I



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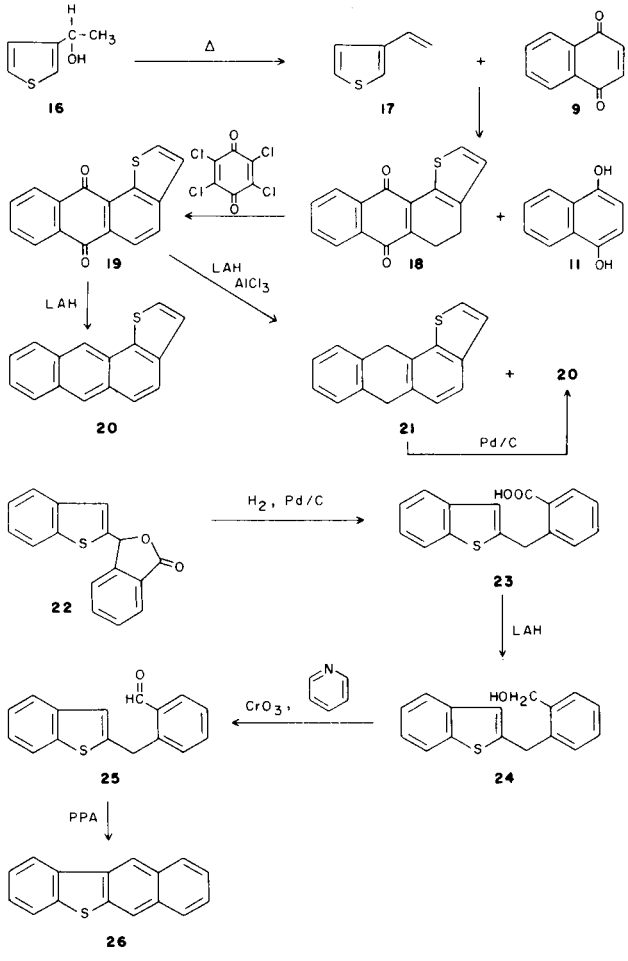
Next, the synthesis of anthra[2,1-*b*]thiophene (**13**) and anthra[1,2-*b*]thiophene (**20**) is described using the Diels-Alder cycloaddition reaction of 1,4-naphthoquinone (**9**) with 2- or 3-vinylthiophene (**8**,**17**). In general, cycloaddition reactions of 1,4-naphthoquinone with various dienophiles is very useful; consequently, variations of this procedure have been frequently reported (7,8). It is well known that 2-vinylthiophene (**8**) reacts with dienophiles such as benzoquinone and anhydrous maleic acid to yield naphthothiophene and benzo[*b*]thiophene derivatives (9,10). However, the reaction of vinylthiophenes (**8**,**17**) with 1,4-benzoquinone (**9**) has not been reported.

Scheme II



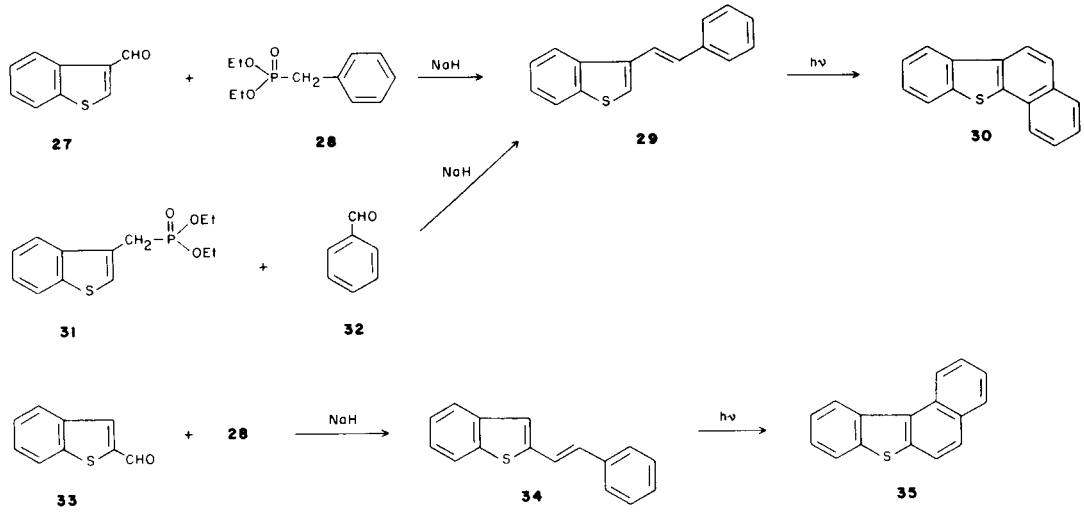
Scheme II outlines a new procedure for the preparation of anthra[2,1-*b*]- and anthra[1,2-*b*]thiophene (**13**,**20**) by an application of the Diels-Alder reaction, significantly enhancing the overall synthetic utility of the Diels-Alder approach to anthra[*b*]thiophenes. 2-Vinylthiophene (**8**) and 1,4-naphthoquinone (**9**) were refluxed in dry toluene for 24 hours giving the adduct **10** as red needles in 22% yield. The structure of this compound **10** was implied from the nmr data; namely, **10** has lost two protons relative to the first theoretical adduct, and the four protons due to an ethylene group at 2.98 ppm are apparent. The mass spectrum and the elemental analysis also agree with this structure. Compound **10** was readily dehydrogenated by chloranil to the quinone **12** in 81% yield (yellow needles). Compound **12** has been previously prepared by other less convenient routes.

Reduction of **12** with lithium aluminum hydride in tetrahydrofuran gave two products, anthra[2,1-*b*]thiophene (**13**) and 6,11-dihydro-6-oxoanthra[2,1-*b*]thiophene (**14**) in 19% and 11% yield, respectively. The ir spectrum of **14** showed a peak at 1660 cm^{-1} due to the carbonyl group. The nmr spectrum of **14** indicated a methylene proton at 5.51 ppm, showing no low field shift for the deshielding effect of the carbonyl group. The nmr spectrum of **10** showed one hydrogen atom at the 1-position, which was deshielded by the carbonyl group at the 11-position, appearing as a doublet at 8.77 ppm (J = 6 Hz). When the reduction with lithium aluminum hydride was carried out in the presence of aluminum chloride, a mixture of **13** and 6,11-dihydroanthra[2,1-*b*]thiophene (**15**) was obtained. This mixture could not be separated by fractional crystallization or column chromatography. This mixture, on treatment with 10% palladium on charcoal, gave a single product, **13**, in 41% yield from **12**.

Anthra[1,2-*b*]thiophene (**20**) was synthesized from **9** and 3-vinylthiophene (**17**), which was prepared by thermolysis of 1-(3-thienyl)ethanol (**16**) in a manner similar to the preparation of **13**. Reaction of **17** with **9** gave the dihydro product **18** in 44% yield, which was converted to 6,11-dihydro-6,11-dioxoanthra[1,2-*b*]thiophene (**19**) by treatment with chloranil. Compound **19** reacted with lithium aluminum hydride in tetrahydrofuran and zinc dust in ammonium hydroxide to give **20** in 6% and 7% yield, respectively. When **19** was treated with lithium aluminum hydride in the presence of aluminum chloride, a mixture of **20** and 6,11-dihydroanthra[1,2-*b*]thiophene (**21**) was obtained. This mixture was also reacted with 10% palladium on charcoal to give only one product, the desired compound **20** in 37% yield.

Finally, the synthesis of benzo[*b*]naphtho[2,3-*d*]thiophene (**26**), benzo[*b*]naphtho[2,1-*d*]thiophene (**30**) and benzo[*b*]naphtho[1,2-*d*]thiophene (**35**) are described. Compound **26** was synthesized from **23** in a manner similar to the preparation of **7**. Reduction of 2-(2-benzo[*b*]thenyl)-benzenecarboxylic acid (**23**) to the corresponding primary alcohol (not purified) followed by oxidation with chromic oxide-pyridine reagent afforded the aldehyde **25** which was readily cyclized with polyphosphoric acid to the desired compound **26** in an overall yield of 58% from the acid **23**. Recently, the required acid **23** was efficiently prepared in two steps from benzo[*b*]thiophene-2-carboxaldehyde **33** by condensation with phenyloxazoline using *n*-butyllithi-

Scheme III



um, followed by reduction with hydrogen in the presence of palladium on charcoal (11). Various syntheses of compound **26** have been reported (12-18). Of these procedures, Mayer's method was the most convenient and useful preparation due to its simplicity and wide range of applicability. Carruthers, *et.al.*, (14), reported the simple and convenient synthesis of **30** by irradiation of 3-styrylbenzo[*b*]-thiophene (**29**), which was readily prepared using the Wittig reaction of 3-benzo[*b*]thienyltriphenylphosphonium chloride with benzaldehyde (**32**). The styryl derivative **29** is the key intermediate in this reaction. We attempted the synthesis of **29** using the Wadsworth-Emmons reaction (20-22).

Thus, the reaction of benzo[*b*]thiophene-3-carboxaldehyde (**27**) with diethyl benzylphosphonate (**28**) gave **29** in good yield. Alternatively, compound **29** was obtained by the reaction of diethyl 3-benzo[*b*]thenylphosphonate (**31**) with benzaldehyde (**32**) in 76% yield. Similarly, benzo[*b*]thiophene-2-carboxaldehyde (**33**) reacted with **28** to give 2-styrylbenzo[*b*]thiophene (**34**) in 72% yield. The photocyclization of these styryl derivatives was carried out in cyclohexane in the presence of iodine and air. As expected, the photocyclization of 2- or 3-styrylbenzo[*b*]thiophene (**29**,**34**) proceeded smoothly and gave the desired benzo[*b*]naphtho[2,3-*d*]thiophene (**30**) and benzo[*b*]naphtho[1,2-*d*]thiophene (**35**) in 68% and 51% yield, respectively.

EXPERIMENTAL

Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Acculab-2 spectrometer. Nmr spectra were recorded on a Varian EM 390 spectrometer or a JEOL FX 90 Q spectrometer. The chemical shift values are expressed as δ values relative to tetramethylsilane as an internal standard. Mass spectra were obtained on a Hewlett-Packard model 5980 A mass spectrometer. Uv spectra were recorded for solutions in cyclohexane with a Perkin Elmer 320 spectrometer.

3-(2-Thenoyl)-2-naphthalenecarboxylic Acid (**3**).

A solution of 2.7 g of anhydrous aluminum chloride and 1 g (5 mmoles) of 2,3-naphthalenedicarboxylic acid anhydride in 10 ml of dry nitrobenzene was prepared at 50°. To this solution, 0.5 g (5.9 mmoles) of thiophene was added uniformly over a period of 20 minutes while maintaining the reaction temperature at 40-50°. One hour later, the reaction temperature was raised to 50-55° and this temperature was maintained for one hour, after which time hydrochloric acid evolution had practically ceased. The dark red colored reaction mass was poured into ice-water and the nitrobenzene layer was washed nearly acid free. The crude 2-(2-thenoyl)-3-naphthalenecarboxylic acid, obtained after steam distillation of the nitrobenzene, was washed acid free and dissolved at 90° in water containing an excess of sodium carbonate. The filtered solution was carefully acidified with hydrochloric acid. The product was recrystallized from methanol-benzene giving 0.45 g (32%) of pale brown prisms, mp 212°; ir (potassium bromide): 3050-2400 (OH), 1670, 1635 (C=O); ms: m/e 282 (M^+, 55), 238 (M - 44), 237 (M - 45, 48), 111 (100).

Anal. Calcd. for $C_{16}H_{10}OS$: C, 68.07; H, 3.57; S, 11.36. Found: C, 68.02; H, 3.82; S, 10.91.

3-(2-Thenyl)-2-naphthalenecarboxylic Acid (**4**).

3-(2-Thenoyl)-2-naphthalenecarboxylic acid (1.4 g, 5 mmoles) was dissolved in 20 ml of concentrated ammonium hydroxide and 12 ml of water. The resulting solution was heated at 90-95° in an oil bath for 4 hours with 3 g of zinc dust (activated with copper sulfate). During the reduction, the solution changed color from reddish-orange to pale yellow. The cooled reaction mixture was filtered to remove excess zinc and the filtrate was extracted once with ether. The aqueous layer was acidified with hydrochloric acid and a tan oil separated which solidified on standing. The solid was filtered, washed with water, dried and recrystallized from benzene giving 1.1 g (82%) of colorless needles, mp 188°; ir (potassium bromide): 3100-2700 (OH, broad), 1690 (C=O); nmr (deuteriochloroform + trifluoroacetic acid, 1:1): 4.69 (s, CH_2, 2H), 6.75 (dd, J = 1, 5 Hz, H-3', 1H), 6.83 (dd, J = 5, 6 Hz, H-4, 1H), 7.13 (dd, J = 1, 6 Hz, H-5', 1H), 7.48-7.98 (m, H-5, H-6, H-7, H-8, 4H), 7.77 (s, H-4, 1H), 8.68 (s, H-1, 1H); ms: m/e 268 (M^+, 50) 250 (M - 18, 100), 221 (M - 47, 56).

Anal. Calcd. for $C_{16}H_{12}O_2S$: C, 71.06; H, 4.47; S, 11.86. Found: C, 71.33; H, 4.46; S, 11.59.

Anthra[2,3-*b*]thiophene (**7**).

A solution of 0.73 g (3.17 mmoles) of 3-(2-thenyl)-2-naphthalenecarboxylic acid in 20 ml of dry ether was added dropwise to a suspension of 0.14 g of lithium hydride in 30 ml of dry ether. After refluxing for 3 hours, 10% sodium hydroxide was added dropwise and the precipitated aluminum hydroxide was filtered. The dried filtrate (sodium sulfate) was evaporated to give the crude alcohol as a colorless oil; ir (neat): 3370 (OH, broad).

The solution of the above alcohol in 8 ml of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine. After stirring for 2 hours at room temperature, the reaction mixture was filtered and washed with chloroform. The filtrate was washed with 10% hydrochloric acid and then 10% sodium carbonate. After drying over sodium sulfate, chloroform was evaporated to leave the crude aldehyde as a dark oil; ir (neat): 1690 (C=O).

A mixture of the crude aldehyde and 7 ml of polyphosphoric acid was heated at 100° for 15 minutes. After cooling, ice water was added to the mixture and the resulting precipitated yellow solid was collected by filtration. After drying, the product was recrystallized from benzene giving 0.32 g (51%) of yellow cotton needles, mp 320° dec [lit (4) mp 330° dec]; ms: 234 (M^+, 100).

4,5,6,11-Tetrahydro-6,11-dioxoanthra[2,1-*b*]thiophene (**10**).

A solution of 6.2 g (40 mmoles) of 1,4-naphthoquinone and 4.4 g (40 mmoles) of 2-vinylthiophene (23,24) in 200 ml of toluene was refluxed for 2 days. After cooling, the precipitate which formed was removed by filtration. The product gave colorless needles, mp 187° and was identified as 1,4-dihydroxynaphthalene (**24**). The toluene layer was washed with 200 ml of 10% sodium hydroxide solution and dried with sodium sulfate. The toluene was removed at reduced pressure. The residue was chromatographed on silica gel using hexane followed by benzene-hexane (1:1) as the eluents giving 2.30 g (22%) of a red oil which slowly crystallized. This crude product was used without purification in the subsequent reaction step. The analytical sample was recrystallized from benzene to give red needles, mp 188°; ir (potassium bromide): 1660, 1645 (C=O); nmr (deuteriochloroform): 2.98 (s, $-CH_2-CH_2-$, 4H), 7.09 (d, J = 5.5 Hz, H-2, 1H), 7.63-7.75 (m, H-8, H-9, 2H), 7.96 (d, J = 5.5 Hz, H-1, 1H), 8.00-8.30 (m, H-7, H-10, 2H); ms: m/e 266 (M^+, 30), 264 (M - 2, 100).

Anal. Calcd. for $C_{16}H_{10}OS$: C, 72.16; H, 3.78; S, 12.04. Found: C, 72.39; H, 3.58; S, 12.09.

6,11-Dihydro-6,11-dioxoanthra[2,1-*b*]thiophene (**12**).

A solution of 2.67 g (10 mmoles) of 4,5,6,11-tetrahydro-6,11-dioxoanthra[2,1-*b*]thiophene and 2.46 g (10 mmoles) of chloranil in 100 ml of toluene was refluxed for 15 hours. After cooling, the precipitate was removed by filtration and the toluene solution was poured into 300 ml of ice water and added to 50 ml of 10% sodium hydroxide solution. This mixture was then extracted with 200 ml of benzene and the organic layer was dried over sodium sulfate. The benzene and toluene were removed by evaporation to yield a dark yellow oil which was chromatographed on silica gel using benzene-hexane as the eluent giving 2.1 g (81%) of yellow needles, mp 196° [lit. (4) mp 196°]; ir (potassium bromide): 1660 (C=O); nmr (deuteriochloroform): 7.71-7.82 (m, aromatic H, 3H), 8.12-8.38 (m, aromatic H, 4H), 8.77 (d, J = 6 Hz, H-1, 1H); ms: m/e 264 (M^+, 100).

1-(3-Thienyl)ethanol (**16**).

Into a stirred solution of 5.2 g of lithium aluminum hydride in 50 ml of dry ether was slowly dropped 12.6 g (100 mmoles) of 3-acetylthiophene. When the addition was complete (5 hours), the reaction mixture was quenched with the cautious addition of 50 ml of water and enough 10% hydrochloric acid to dissolve the inorganic salts. The ether phase was evaporated and the aqueous phase was extracted with 3 × 100 ml of ether. The dried (sodium sulfate) ether extracts were evaporated yielding a pale yellow oil which was distilled at 105-110°/20 mm [lit (26) bp 98°/12 mm] to give 11.0 g (86%) of a colorless oil.

3-Vinylthiophene (**17**).

1-(3-Thienyl)ethanol (10 g) was heated at reflux temperature. In order to prevent possible loss of the monomeric 3-vinylthiophene through polymerization in the dehydrating flask, 0.1% hydroquinone was added to the alcohol before dehydration. The temperature of the vapor rose rapidly to 100° and then gradually rose to 130-150°, remaining at this latter temperature until the dehydration was complete. The mixture of the product and water was extracted with ether. After drying the ether solution with anhydrous sodium sulfate, the ether was removed on a steam bath and the residue was distilled under reduced pressure at 55-59°/20 mm [lit (27) bp 156-158°] to give 4.6 g (54%) of a colorless liquid; ir (neat): 1790, 1630; nmr (deuteriochloroform): 5.13 (dd, J = 1, 11 Hz, *cis* H, 1H), 5.50 (dd, J = 1, 18 Hz, *trans* H, 1H), 6.57 (q, J = 11, 18 Hz, -CH=C-, 1H), 7.00-7.23 (m, H-2, H-4, H-5, 3H).

4,5,6,11-Tetrahydro-6,11-dioxoanthra[1,2-*b*]thiophene (**18**).

This compound was synthesized from 1,4-naphthoquinone and 3-vinylthiophene in 44% yield in a manner similar to the preparation of 4,5,6,11-tetrahydro-6,11-dioxoanthra[2,1-*b*]thiophene, and was obtained as red needles after recrystallization from benzene/hexane (1:1), mp 176-177°; ir (potassium bromide): 1655, 1635 (C=O); nmr (deuteriochloroform): 2.92 (s, $-CH_2-CH_2-$, 4H), 6.90 (d, J = 5 Hz, H-3, 1H), 7.56 (d, J = 5 Hz, H-2, 1H), 7.59-7.81 (m, H-8, H-9, 2H), 7.99-8.73 (m, H-7, H-10, 2H); ms: m/e 266 (M^+, 100).

Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 72.16; H, 3.78; S, 12.04. Found: C, 72.43; H, 3.70, S, 11.73.

6,11-Dihydro-6,11-dioxoanthra[1,2-*b*]thiophene(**19**).

This compound was synthesized from 4,5,6,11-tetrahydro-6,11-dioxoanthra[1,2-*b*]thiophene in 85% yield in a manner similar to the preparation of 6,11-dihydro-6,11-dioxoanthra[2,1-*b*]thiophene and was obtained as red needles after recrystallization from benzene, mp 219-220° [lit (28) mp 221°]; ir (potassium bromide): 1665 (C=O); ms: m/e 264 (M^+, 100); nmr (deuteriochloroform): 7.46 (d, J = 5 Hz, H-3, 1H), 7.89 (d, J = 5 Hz, H-2, 1H), 7.72-7.88 (m, H-8, H-9, 2H), 8.09-8.40 (m, H-4, H-5, H-7, H-9, 4H).

Anthra[2,1-*b*]thiophene (**13**).

a) Into a stirred solution of 0.86 g of lithium aluminum hydride in 50 ml of tetrahydrofuran, 1 g (3.79 mmoles) of 6,11-dihydro-6,11-dioxoanthra[2,1-*b*]thiophene was slowly added dropwise. When the addition was complete, the tetrahydrofuran was brought to reflux for 48 hours after which time it was quenched by cautiously adding 10 ml of water, and enough 10% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice water and extracted with 100 ml of benzene. The extract was washed successively with water and saturated sodium bicarbonate solution, and was then dried (sodium sulfate) and evaporated. The residue was chromatographed on a column of silica gel using hexane as an eluent giving pale yellow crystals which were recrystallized from ethanol giving 0.17 g (19%) of white leaflets, mp 196° [lit (4) mp 196°]; ms: m/e 234 M^+, 100).

Subsequent elution using hexane-benzene (1:1) gave 0.3 g of the starting material as yellow crystals. Further elution using benzene afforded a brown crystalline substance which was recrystallized from benzene to give 0.1 g of 6,11-dihydro-6-oxoanthra[2,1-*b*]thiophene (**14**) as colorless needles, mp 260°; ir (potassium bromide): 1660 (C=O); nmr (deuteriochloroform): 5.51 (s, CH_2, 2H), 7.25-8.00 (m, aromatic proton, 8H); ms: m/e 250 (M^+, 27), 249 (M - 1, 100); gc-ms retention time: 1.7, this mass showed as a benzene peak at m/e 78.

Anal. Calcd. for $C_{10}H_{10}OS + 0.5\ C_6H_6$: C, 78.86; H, 4.53; S, 11.08. Found: C, 78.90; H, 4.42; S, 10.94.

b) A solution of 1.2 g of aluminum chloride in 50 ml of absolute ether was added to a stirred suspension of 0.4 g of lithium aluminum hydride

in 15 ml of absolute ether. The mixture was stirred for 15 minutes and then 0.5 g of 6,11-dihydro-6,11-dioxoanthra[2,1-*b*]thiophene was added portionwise. The gray ethereal suspension was maintained at reflux for 2 hours. Ethyl acetate (15 ml) was added dropwise in order to decompose the excess hydride reagent. The reaction mixture was poured into ice and 5% hydrochloric acid. The ether layers were separated and the aqueous phase was extracted with 3 × 50 ml portions of ether. The combined ethereal solution was washed successively with saturated sodium bicarbonate solution and water, and was dried with sodium sulfate and concentrated *in vacuo*. The pale yellow gummy solid was chromatographed on a silica gel column using hexane as an eluent to yield a white solid material. The nmr of the product showed two methylene protons at 4.12 and 4.28 ppm, and two singlet peaks at 8.48 and 8.84 ppm, due to the aromatic proton at the 6-and 11-positions. These peaks indicate a mixture of 6,11-dihydroanthra[2,1-*b*]thiophene (**15**) and anthra[2,1-*b*]thiophene (**13**). A mixture of **13** and **15**, 0.05 g of palladium on charcoal and 20 ml of *m*-xylene was refluxed for 30 hours. After removing the palladium on charcoal, *m*-xylene was evaporated at reduced pressure. The residue was recrystallized from ethanol to give 0.18 g (41%) of the product as pale yellow leaflets, mp 196°, [lit (4) mp 196°]; ms: m/e 234 (M^+, 100). The picrate was obtained as dark red needles, mp 157° [lit (4) mp 157°].

Anthra[1,2-*b*]thiophene (**20**).

This compound was synthesized from 6,11-dihydro-6,11-dioxoanthra[1,2-*b*]thiophene by the following three methods. Methods a and b are similar to the methods used for the preparation of anthra[2,1-*b*]thiophene. Method c is described below. The yields by methods a, b and c were 6%, 37% and 7%, respectively. This compound gave colorless leaflets, mp 120° [lit (4) mp 121°] and the picrate gave brown red needles, mp 145°, [lit (4) mp 145°].

c) A mixture of 0.5 g of 6,11-dihydro-6,11-dioxoanthra[1,2-*b*]thiophene, 2 g of zinc dust (treated with 0.1% copper sulfate solution for 5 minutes), 50 ml of 2*N* sodium hydroxide solution and 30 ml of toluene was refluxed for 10 hours. The toluene layer was separated and the aqueous layer was extracted once with 50 ml of benzene. The combined toluene and benzene extracts were washed successively with saturated sodium bicarbonate solution and water, and were evaporated *in vacuo* following drying (sodium sulfate). The residue was chromatographed on a column of silica gel using hexane as the eluent to give pale yellow needles, which were recrystallized from ethanol giving 0.03 g (7%) of colorless crystals, mp 120°; ms: m/e 234 (M^+, 100).

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

A solution of 1.35 g (5 mmoles) of 2-(2-benzo[*b*]thenyl)benzenecarboxylic acid in 50 ml of dry ether was added dropwise to a suspension of 0.2 g of lithium aluminum hydride in 40 ml of dry ether. After refluxing for 3 hours, the reaction mixture was carefully quenched by cautiously adding 6 ml of water and enough 10% hydrochloric acid to dissolve the inorganic salts. The ether phase was separated and the aqueous phase was extracted with 3 × 50 ml portions of ether dried over sodium sulfate. Evaporation of the ether yielded colorless crystals, mp 92°; ir: 3370 (OH, broad).

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 2 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; ir (neat): 1690 (C=O).

A mixture of the crude aldehyde and 10 g of polyphosphoric acid was heated at 100° for 30 minutes. After cooling, ice water was added to the reaction mixture and the precipitated brown solid was collected by filtration. After drying, the product was recrystallized from benzene-hexane (1:1) giving 0.68 g (58%) of colorless crystals, mp 158-159° [lit mp (12) 158°, (15) 168°, (13,16) 160°]; ms: m/e 234 (M^+, 100). The picrate gave red needles, mp 130° [lit (16) mp 132°].

Diethyl Benzo[*b*]thenylphosphonate (**31**).

A mixture of 30 g (165 mmoles) of 3-chloromethylbenzo[*b*]thiophene (**28**) and 30 g (180 mmoles) of triethyl phosphite was heated at 160° for 8 hours. The reaction product was distilled to give 42 g (90%) of a colorless oil, bp 176-189°/1.5 mm; nmr (deuteriochloroform): 1.13 (t, J = 7 Hz, $-CH_2-CH_3$, 6H), 3.21 (s, $-CH_a-$ 1H), 3.46 (s, $-CH_b$, 1H), 3.94 (q, O-CH_2-, 4H), 7.89 (s, H-2, 1H), 7.19-7.36 (m, H-5, H-6, 2H), 7.66-7.79 (m, H-4, H-7, 2H).

Anal. Calcd. for $C_{13}H_{17}O_3PS$: C, 55.03; H, 6.03; P, 10.89; S, 11.28. Found: C, 55.11; H, 6.14; P, 10.66; S, 11.13.

a) Under a nitrogen atmosphere, 1.34 g (28 mmoles) of sodium hydride (the mineral oil was removed by washing with dry petroleum ether) was added to an ice cooled stirred solution of 4.06 g (25 mmoles) of benzo[*b*]thiophene-3-carboxaldehyde and 5.71 g (25 mmoles) of diethyl benzylphosphonate (**29**) in 50 ml of 1,2-dimethoxyethane. After stirring for 15 minutes, the ice bath was removed. The mixture was stirred at room temperature for 3 hours and poured into ice water. The precipitate was collected by filtration and recrystallized from ethanol giving 5.11 g (86%) of pale yellow crystals, mp 95-96°.

b) Sodium hydride (50%, 0.98 g, 10 mmoles) was placed in 50 ml of dry 1,2-dimethoxyethane. The slurry was cooled to 20° and 2.84 g (10 mmoles) of diethyl benzo[*b*]thenylphosphonate was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 30 minutes. To the pale yellow solution, maintained below 25°, was added dropwise, 1.06 g (10 mmoles) of benzaldehyde. During the addition, a gummy precipitate appeared. The solution was stirred at room temperature for 1 hour and heated at 50° for thirty minutes. After cooling, a large excess of water was added and the product was collected by filtration. The product was recyrstallized from ethanol giving 1.8 g (76%) of pale yellow crystals, mp 96° [lit (19) mp 97°]; ms: m/e 234 (M^+, 100).

Benzo[*b*]naphtho[2,1-*d*]thiophene (**30**).

A solution of 1.77 g (75 mmoles) of 3-styrylbenzo[*b*]thiophene and 0.10 g of iodine in 750 ml of cyclohexane was irradiated for 4 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 solvent was evaporated *in vacuo* and the residue was effectively purified by silica gel chromatography using benzene as an eluent giving 1.28 g (72%) of fine colorless plates, mp 185-186° [lit (31) mp 185-186°, lit (32) mp 182-184°]; ms: m/e 234 (M^+, 100). The picrate gave orange-red needles, mp 145° [lit (32) mp 142°].

2-Styrylbenzo[*b*]thiophene (34).

This compound was synthesized from 2-benzo[*b*]thiophenecarboxaldehyde and diethyl benzylphosphonate in a manner similar to the preparation of 3-styrylbenzo[*b*]thiophene and was obtained as pale yellow leaflets (ethanol) in 72% yield, mp 196-197°; ms: m/e 236 (M^+, 100), 234 (M - 2, 61).

Anal. Calcd. for $C_{16}H_{12}S$: C, 81.31; H, 5.12; S, 13.57. Found: C, 81.31; H, 5.18; S, 13.41.

Benzo[*b*]naphtho[1,2-*b*]thiophene (**35**).

This compound was synthesized by photocyclization from 2-styrylbenzo[*b*]thiophene in a manner similar to the preparation of benzo[*b*]naphtho[2,1-*d*]thiophene, and was obtained as colorless crystals, mp 103-104° [lit (32,34) mp 102-105°] in 51% yield; ms: m/e 234 (M^+, 100). The picrate was obtained as orange-red needles, mp 149° [lit(34)147-148°].

Acknowledgement.

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

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