

Masatomo Iwao, Milton L. Lee and Raymond N. Castle*

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

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All isomers of the parent phenanthro[*b*]thiophenes, namely, phenanthro[1,2-*b*]thiophene, phenanthro[2,1-*b*]thiophene, phenanthro[2,3-*b*]thiophene, phenanthro[3,2-*b*]thiophene, phenanthro[3,4-*b*]thiophene, phenanthro[4,3-*b*]thiophene and phenanthro[9,10-*b*]thiophene have been synthesized.

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Polycyclic aromatic hydrocarbons have been studied extensively because of their carcinogenic activity and their character as major environmental pollutants (1a,b). Recently, we have separated various polycyclic thiophenes (thiophene isomers of polycyclic hydrocarbons) from coal derived products by glass capillary-column gas chromatography and have postulated their structures by mass spectrometry (2). However, because of the many isomeric structures possible, it was difficult to assign the absolute structure of each polycyclic thiophene based only on mass spectrometry. Therefore, we have decided to synthesize a series of authentic compounds for positive identification of the proposed structures. Furthermore, determination of the carcinogenic and mutagenic activities of the synthetic compounds is also of interest. In this paper, the synthesis of all isomers of the parent phenanthro[*b*]thiophenes will

be described.

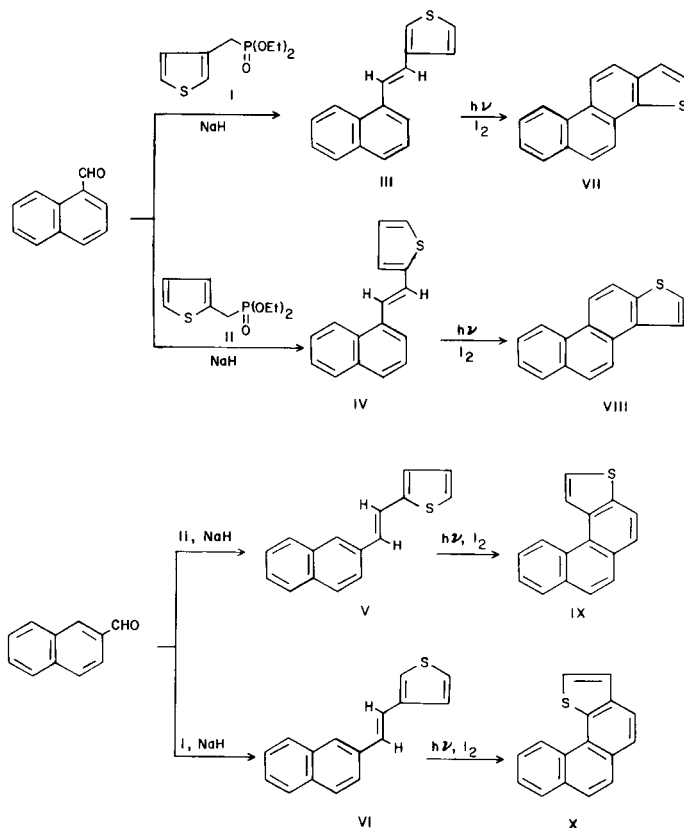
It is well known that chrysene and benzo[*c*]phenanthrene derivatives are conveniently available by the oxidative photocyclization of 1-styryl- and 2-styrylnaphthalenes, respectively (3a-d, 4a-c). By analogy with the above reactions, it was expected that phenanthro[1,2-*b*]thiophene (VII), phenanthro[2,1-*b*]thiophene (VIII), phenanthro[3,4-*b*]thiophene (IX) and phenanthro[4,3-*b*]thiophene (X) should be available from the corresponding naphthylvinylthiophenes by photolysis (Scheme I).

The starting olefins III, IV, V and VI were readily prepared by the Wadsworth-Emmons reaction (5) between diethyl 2- (or 3-)thienylphosphonate (II or I) and 1- (or 2-)naphthaldehyde in good yields (72-90%). The photocyclization of these olefins was carried out in cyclohexane or benzene in the presence of iodine. As expected, the photocyclization of 2-naphthylvinylthiophenes IV and V proceeded smoothly and gave the desired phenanthro[2,1-*b*]thiophene (VIII) and phenanthro[3,4-*b*]thiophene (IX) in 88% and 75% yield, respectively. However, in the photolysis of 3-naphthylvinylthiophenes III and VI, a large amount of tarry material was formed and the yields of the phenanthro[*b*]thiophenes were poor (VII, 32%; X, 17%). A similar tendency of the reaction was observed in the photolysis of a series of thienylvinylthiophenes and the poor results obtained in the photolysis of 3-substituted thiophenes were attributed to the expulsion of the thienyl radicals during the oxidative process of the dihydro intermediates (6).

In these reactions, it is possible that 3-naphthylvinylthiophenes cyclize at the 4-position of the thiophene ring and give phenanthro[*c*]thiophenes. However, this orientation for the cyclization seems to be unlikely, because 3-styrylthiophenes and 3-thienylvinylthiophene are known to cyclize exclusively at the 2-position (6,7).

In fact, the phenanthro[3,4-*c*]thiophene structure for compound X was easily excluded by the agreement of the melting point of X with the reported melting points of phenanthro[4,3-*b*]thiophene (8,9). In addition, the nmr data also supported this exclusion. Namely, in compound IX, two protons at the 1- and 11-positions absorb in the very low aromatic region, apart from the complex multiplet of the other aromatic protons, due to the deshielding effect of the opposite aromatic ring [H_1 : (δ

SCHEME I



8.62, d), H_{11} : (δ 9.12, near dd)]. However, in compound X, only one proton at the 11-position appeared at low field (δ 9.20), because the 1-position of the ring is sulfur. If X were phenanthro[3,4-*c*]thiophene, a proton at the 1-position should also absorb at low field.

In the case of the photolysis of III, however, it is difficult to exclude a phenanthro[1,2-*c*]thiophene structure for the product VII based only on nmr data, because the peaks of the protons around the thiophene ring overlap with other aromatic protons and it is almost impossible to assign these complex multiplets. However, since benzo[*c*]thiophene and its higher benzologs are known to react with dienophiles at the *ortho*-quinodimethane part of the molecule (10-12), it is possible to exclude a phenanthro[1,2-*c*]thiophene structure if VII does not react with a dienophile. In fact, when VII was reacted with maleic anhydride in refluxing xylene for 24 hours, the starting

material was quantitatively recovered. This is support for the phenanthro[1,2-*b*]thiophene structure of VII.

Next, our attention was turned to the synthesis of phenanthro[2,3-*b*]thiophene (XVIII) and phenanthro[3,2-*b*]thiophene (XXIII). The synthesis of the 7,11-dimethyl derivatives of these ring systems has been reported by Sandin, *et al.* (13,14). The parent compounds could be available by a modification of their synthesis. However, the key step of this synthesis, condensation of thienylmagnesium iodide and 1,2-naphthoic anhydride, requires the tedious separation of two isomeric products by fractional crystallization and the yields are poor.

Recently, Newman and Kannan reported the regioselective synthesis of some fluorobenzo[*a*]pyrenes and fluorobenz[*a*]anthracenes (15). The crucial step in these syntheses is the *ortho*-directed lithiation of fluorophenyl-oxazoline followed by condensation with 1- or 2-naphthaldehyde. We applied this procedure for the synthesis of XIV and XX (Scheme II).

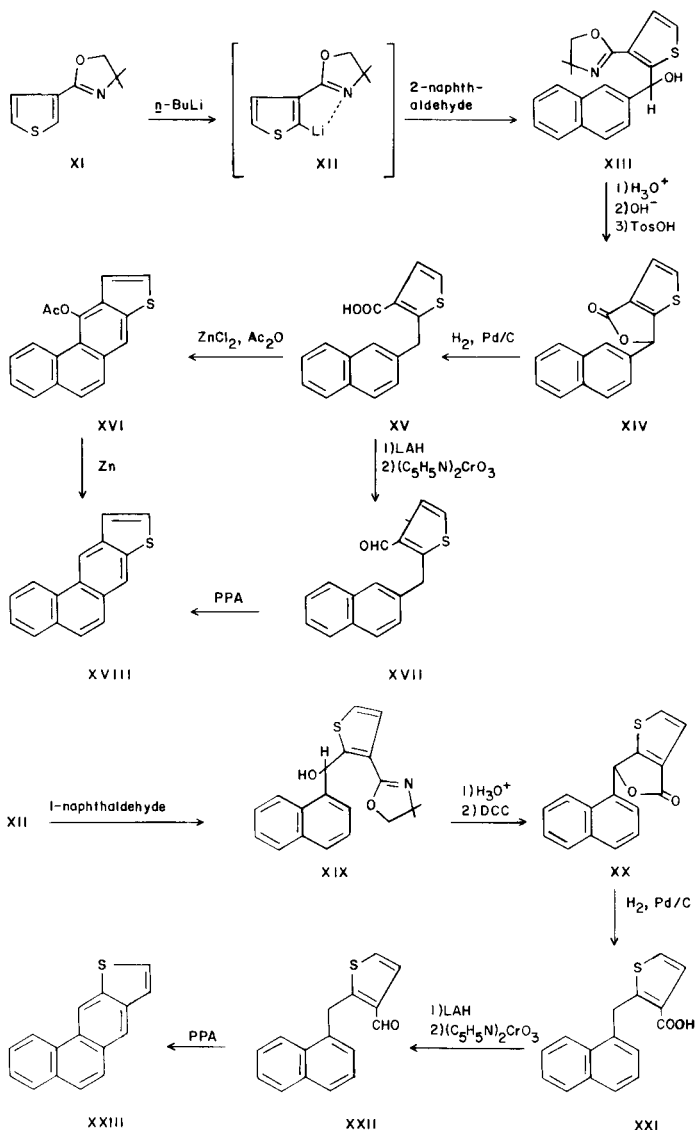
The thienyloxazoline XI was prepared from thiophene-3-carboxoyl chloride and 2-amino-2-methyl-1-propanol. Slocum and Gierer studied the directed metalation of 3-substituted thiophenes and reported that selective metalation occurred at the 2-position (16). On the basis of this report, it was expected that the metalation of XI should occur exclusively at the 2-position.

Compound XI was lithiated with *n*-butyllithium in dry ether at -45° and the resulting lithium compound XII was condensed with 2-naphthaldehyde giving XIII as an oil. The oxazoline ring of XIII was hydrolysed with a combination of acid and alkali. The resulting acid was cyclized to the lactone XIV by heating in toluene with a catalytic amount of *p*-toluenesulfonic acid. The overall yield of XIV from XI is 58%. The lactone XIV was hydrogenolysed to the acid XV over palladium on charcoal in warm acetic acid in 72% yield. Cyclization of XV with zinc chloride in acetic anhydride gave 11-acetoxyphenanthro[2,3-*b*]thiophene (XVI) in 81% yield. Although the yield is quite poor (3%), the parent phenanthro[2,3-*b*]thiophene (XVIII) was obtained by the reductive cleavage of the acetoxy group in XVI with zinc in alkali. A much better yield of XVIII was obtained by using an alternative route *via* the aldehyde XVII (17,18).

Namely, the acid XV was converted to the aldehyde XVII by reduction with lithium aluminum hydride to give the primary alcohol followed by oxidation with the chromium trioxide-pyridine complex. Cyclization of the crude aldehyde XVII by heating with polyphosphoric acid gave XVIII in 56% overall yield from XV.

Using the same rational, phenanthro[3,2-*b*]thiophene (XXIII) was prepared. Condensation of lithiothiophene X with 1-naphthaldehyde gave XIX as colorless crystals in 84% yield. This compound was converted to the lactone

SCHEME II



ms: m/e 234 (M⁺); FT nmr (deuteriochloroform): δ 7.5-7.7 (m, 3H, H₂, H₃ and H₄), 7.8-8.1 (m, 4H, H₅, H₆, H₇ and H₁₁), 8.32 (d, 1H, H₄), 8.65 (d, 1H, H₁₀), 8.73 (near dd, 1H, H₉), J_{4,5} = 9, J_{10,11} = 9 Hz; uv: λ max (log ϵ) 207 (4.48), 232.5 (4.53) 254 (sh) (4.72), 261 (4.82), 289.5 (4.34), 302 (4.22) and 315.5 nm (4.27).

Anal. Calcd. for C₁₆H₁₀S: C, 82.02; H, 4.30; S, 13.68. Found: C, 82.19; H, 4.25; S, 13.67.

Phenanthro[3,4-*b*]thiophene (IX).

The crude product obtained from V was passed through a column of alumina using benzene as eluent to give 1.72 g. of slightly brown solid. Refiltration of this solid through a short column of alumina (cyclohexane) gave 1.31 g. (75%) of colorless crystals of IX, m.p. 82-83°. An analytical sample was recrystallized from methanol, colorless plates, m.p. 82.5-83.5°; ms: m/e 234 (M⁺); nmr (deuteriochloroform): δ 7.5-8.1 (m, 8H, ArH except H₁ and H₁₁), 8.62 (d, 1H, H₁), 9.12 (near dd, 1H, H₁₁), J_{1,2} = 5, J_{10,11} = 9 Hz; uv: λ max (log ϵ) 229 (4.35), 268.5 (4.65), 278 (4.78), 298 (sh) (4.15) and 310 nm (sh) (3.88).

Anal. Calcd. for C₁₆H₁₀S: C, 82.02; H, 4.30; S, 13.68. Found: C, 82.10; H, 4.22; S, 13.48.

Phenanthro[4,3-*b*]thiophene (X).

Crude material obtained from VI was passed through a column of alumina using benzene as the eluent. The eluate was evaporated giving a colorless oil which was passed again through a short column of alumina using initially cyclohexane and then a mixture of cyclohexane and benzene (5:1) as eluents to give 0.30 g. (17%) of colorless crystals of X, m.p. 87-93°. An analytical sample was prepared by recrystallization from methanol/water, colorless prisms or plates, m.p. 94-95° (lit. (8) gives m.p. 91.5-92°; lit (9) gives m.p. 95°); ms: m/e 234 (M⁺); nmr (deuteriochloroform): δ 7.3-8.1 (m, 9H, ArH except H₁₁), 9.20 (d, 1H, H₁₁), J_{10,11} = 8 Hz; uv: λ max (log ϵ) 211 (4.56), 234 (sh) (4.26), 272 (4.76) 291 (sh) (4.13), 304 (4.02) and 317 nm (4.06).

Anal. Calcd. for C₁₆H₁₀S: C, 82.02; H, 4.30; S, 13.68. Found: C, 82.29; H, 4.14; S, 13.58.

Reaction of the VII with Maleic Anhydride.

The mixture of 100 mg. (0.43 mmole) of VII, 42 mg. (0.43 mmole) of maleic anhydride and 10 ml. of *m*-xylene was refluxed for 24 hours. Xylene was evaporated and the residue was passed through a column of silica gel using cyclohexane as the eluent to recover VII in quantitative yield, m.p. 162-165°. Recrystallization from cyclohexane raised the melting point to 165-167.5°, which was not depressed by admixing with an authentic sample of VII.

4,4-Dimethyl-2-(3-thienyl)-2-oxazoline (XI).

A solution of 52 g. (0.355 mole) of thiophene-3-carboxyl chloride in 200 ml. of dry dichloromethane was added dropwise to an ice-cooled, stirred solution of 63.2 g. (0.71 mole) of 2-amino-2-methyl-1-propanol in 200 ml. of dry dichloromethane keeping the temperature below 10°. After stirring at room temperature for 2 hours, the reaction mixture was washed with water, dried over sodium sulfate and evaporated. The residual solid of the intermediate amide was dried and finely powdered. To a suspension of this powder in 300 ml. of dry benzene, thionyl chloride (92 ml., 1.17 moles) was added dropwise with mechanical stirring. The suspension became pasty and then clear. After allowing the reaction mixture to stand overnight, excess thionyl chloride and benzene was removed under reduced pressure. The residue was poured into ice water and made basic with sodium hydroxide. The product was extracted with benzene, washed with water and dried over sodium sulfate. Benzene was evaporated and the residue was distilled *in vacuo* to give 54.7 g. (85%) of XI as a colorless solid, b.p. 68-70°/0.4 mm. An analytical sample was recrystallized from petroleum ether, colorless prisms, m.p. 59.5-60.5°; ir (potassium bromide): 1640 cm⁻¹ (C=N); nmr (carbon tetrachloride): δ 1.27 (s, 6H, CH₃), 3.86 (s, 2H, CH₂), 7.12 (dd, 1H, H₃), 7.35 (dd, 1H, H₄), 7.65 (dd, 1H, H₂), J_{2,4} = 1.2, J_{1,5} = 3, J_{4,5} = 5.5 Hz.

Anal. Calcd. for C₈H₁₁NOS: C, 59.64; H, 6.12; N, 7.73; S, 17.69. Found: C, 59.42; H, 6.12; N, 7.69; S, 17.81.

6-(2-Naphthyl)thieno[2,3-*c*]furan-4(6*H*)one (XIV).

Under a nitrogen atmosphere, 34 ml. (0.05 mole) of 1.5 *M* *n*-butyllithium solution in hexane was added dropwise to a solution of 9.06 g. (0.05 mole) of XI in 100 ml. of dry ether keeping the temperature between -35 and -45° (dry ice-chlorobenzene bath). After stirring for one hour, a solution of 7.81 g. (0.05 mole) of 2-naphthaldehyde in 50 ml. of dry ether was added. The reaction mixture was then allowed to warm gradually to room temperature and to stand overnight. Water was added to the mixture, the ether layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with water, dried over sodium sulfate and evaporated. The residual oil of crude XIII was heated with stirring under reflux in 300 ml. of 10% hydrochloric acid for 5 hours. After cooling, the orange solid was collected and heated again under reflux in a mixture of 200 ml. of methanol and 100 ml. of 30% sodium hydroxide. The reaction mixture was poured into ca. 1.5 l. of water and acidified with hydrochloric acid. The precipitated pink solid was collected, washed with water and dried. A solution of this solid and 0.5 g. of *p*-toluenesulfonic acid in 300 ml. of toluene was refluxed for 2 hours with removal of the water formed. The mixture was evaporated to about half amount and passed through a column of silica gel (benzene) to give 7.50 g. (56%) of XIV as colorless solid, m.p. 173-175°. Recrystallization from ethanol gave colorless needles, m.p. 176.5-177.5°; ir (potassium bromide): 1750 cm⁻¹ (C=O); nmr (deuteriochloroform): δ 6.60 (s, 1H, methyne H), 7.2-7.7 (m, 5H, ArH), 7.7-8.0 (m, 4H, ArH).

Anal. Calcd. for C₁₆H₁₀O₂S: C, 72.16; H, 3.78; S, 12.04. Found: C, 72.34; H, 3.86; S, 11.87.

2-(2-Naphthylmethyl)-3-thiophenecarboxylic Acid (XV).

A mixture of 5.00 g. of XIV and 1.0 g. of 5% palladium on charcoal in 300 ml. of acetic acid was stirred under a hydrogen atmosphere at 75° overnight. The mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from methanol (charcoal) to give 3.67 g. (72%) of XV as colorless needles, m.p. 168-170°. An analytical sample had m.p. 171-172°; ir (potassium bromide): 2500-3300 (OH) and 1665 cm⁻¹ (C=O); nmr (DMSO-*d*₆): δ 4.70 (s, 2H, CH₂), 7.3-7.6 (m, 5H, ArH), 7.7-8.0 (m, 4H, ArH), 12.8 (br s, 1H, COOH).

Anal. Calcd. for C₁₆H₁₂SO₂: C, 71.62; H, 4.51; S, 11.95. Found: C, 71.61; H, 4.49; S, 12.00.

11-Acetoxyphenanthro[2,3-*b*]thiophene (XVI).

A mixture of 2.00 g. of XV, 0.10 g. of fused zinc chloride, 10 ml. of acetic anhydride and 15 ml. of acetic acid was refluxed for 1 hour. Water (8.5 ml.) was added to the hot solution. After cooling, the precipitated yellow needles were collected by filtration giving 1.76 g. (81%) of XVI, m.p. 156-158°. An analytical sample was recrystallized from ethanol, m.p. 159-160°; ir (potassium bromide): 1760 cm⁻¹ (C=O); nmr (deuteriochloroform): 2.53 (s, 3H, CH₃), 7.25 (d, 1H, H₂), 7.4-7.9 (m, 6H, ArH except H₁, H₇ and H₉), 8.16 (s, 1H, H₇), 9.08 (m, 1H, H₁), J_{9,10} = 5.5 Hz.

Anal. Calcd. for C₁₈H₁₂SO₂: C, 73.95; H, 4.14; S, 10.97. Found: C, 74.07; H, 4.17; S, 10.93.

Phenanthro[2,3-*b*]thiophene (XVIII).

Method A.

A solution of 1.46 g. (5.4 mmoles) of XV in 20 ml. of dry tetrahydrofuran was added dropwise to a suspension of 0.23 g. (6.1 mmoles) of lithium aluminum hydride in 50 ml. of dry ether. After reflux for 3 hours, 10% sodium hydroxide was added dropwise and the precipitated aluminum hydroxide was filtered off. The dried filtrate (sodium sulfate) was evaporated to give the crude alcohol as a pale yellow oil which on standing solidified; ir (neat): 3330 and 3230 cm⁻¹ (OH).

The solution of this crude alcohol in 11 ml. of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine complex made from 1.1 g. of chromium trioxide and 11 ml. of dry pyridine. After stirring for 2 hours at room temperature, the reaction mixture was filtered through celite 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 XVII as a dark oil; ir (neat): 1670 cm^{-1} ($\text{C}=\text{O}$).

A mixture of the crude XVII and 10 ml. of polyphosphoric acid was heated over a steam bath for 15 minutes. After cooling, ice water was added to the mixture and the precipitated gray solid was collected by filtration. After drying, this solid was passed through a column of alumina using benzene as the eluent giving 0.72 g. (56%) of XVIII, m.p. 160-161°. An analytical sample was recrystallized from cyclohexane, colorless fine plates, m.p. 161-161.5° (lit. (24) gives m.p. 81-82° (25)); ms: *m/e* 234 (M^+); nmr (deuteriochloroform): δ 7.4-8.0 (m, 7H, ArH except H₁, H₇, and H₁₁), 8.30 (s, 1H, H₇), 8.71 (m, 1H, H₁), 9.10 (s, 1H, H₁₁); uv: λ max (log ϵ) 222 (4.50), 254 (sh) (4.43), 275 (4.86), 283.5 (4.74), 309 (sh) (3.93), 319.5 (4.06) 334 (4.10), 347 (3.15) and 366 nm (2.65).

Anal. Calcd. for C₁₆H₁₀S: C, 82.02; H, 4.30; S, 13.68. Found: C, 82.29; H, 4.34; S, 13.29.

Method B.

A mixture of 0.50 g. of acetate XVI, 2.5 g. of zinc dust which was activated by washing with an aqueous solution of copper sulfate, 5 ml. of toluene and 25 ml. of 10% sodium hydroxide was refluxed for 24 hours. After cooling, the organic layer was separated and the aqueous layer was extracted with benzene. The combined extracts were washed with water, dried and evaporated. The residue was chromatographed on a column of silica gel using a mixture of cyclohexane and benzene (2:1) as the eluent. From the first fraction, 13 mg. (3%) of XVIII was obtained. The FT nmr spectrum of this compound was identical with that of XVIII obtained by method A. From the next fraction, 0.32 g. of the starting material was recovered.

4,4-Dimethyl-2-[2-(1-naphthylhydroxymethyl)-3-thienyl]-2-oxazoline (XIX).

To a suspension of the lithio derivative of XI (0.05 mole) in dry ether, prepared in the same manner as described above, a solution of 7.81 g. (0.05 mole) of 1-naphthaldehyde in 15 ml. of dry ether was added. After stirring at room temperature for 3 hours, water was added to the mixture. The ether layer was separated and the aqueous layer was extracted with dichloromethane. The combined extracts were dried over sodium sulfate and evaporated. The residual colorless solid was washed with ether and filtered giving 14.16 g. (84%) of XIX, m.p. 131.5-133°. An analytical sample was recrystallized from dichloromethane/ether, colorless prisms, m.p. 133.5-134.5°; ir (potassium bromide): 3100 (OH) and 1640 cm^{-1} ($\text{C}=\text{N}$); nmr (deuteriochloroform): δ 1.39 (s, 3H, CH₃), 1.41 (s, 3H, CH₃), 4.15 (s, 2H, CH₂), 6.86 (s, 1H, methyne H) 6.94 (d, 1H, H₅ of thiophene ring), 7.2-7.6 (m, 4H, ArH), 7.75-8.1 (m, 4H, ArH), J_{4,5} = 6 Hz.

Anal. Calcd. for C₂₀H₁₅NO₂S: C, 71.19; H, 5.68; N, 4.15; S, 9.50. Found: C, 71.09; H, 5.45; N, 3.96; S, 9.39.

6-(1-Naphthyl)thieno[2,3-*c*]furan-4(6H)one (XX).

A solution of 9.00 g. (0.027 mole) of XIX in a mixture of 180 ml. of dioxane and 180 ml. of 10% hydrochloric acid was refluxed for 21 hours. After evaporation of the solvent, water was added to the residue and the product was extracted with chloroform. The residue obtained by the evaporation of chloroform was dissolved in 100 ml. of benzene and 5.6 g. (0.027 mole) of dicyclohexylcarbodiimide was added to this solution. After allowing it to stand at room temperature for 3 hours, the mixture was concentrated and passed through a column of silica gel using benzene as the eluent. The colorless solid obtained by the evaporation of the eluate was washed with ether and filtered to give 2.72 g. (38%) of XX, m.p. 135.5-137°. An analytical sample was prepared by recrystallization from dichloromethane/ether, colorless prisms, m.p. 137-137.5°; ir (potassium bromide): 1750 cm^{-1} ($\text{C}=\text{O}$); nmr (deuteriochloroform): 7.2-8.2 (m, methyne H and ArH).

Anal. Calcd. for C₁₄H₁₀O₂S: C, 72.16; H, 3.78; S, 12.04. Found: C, 72.29; H, 3.87; S, 11.87.

2-(1-Naphthylmethyl)-3-thiophenecarboxylic Acid (XXI).

A mixture of 3.00 g. of XX and 0.6 g. of 5% palladium on charcoal in 150 ml. of acetic acid was stirred under a hydrogen atmosphere at 70° overnight. The mixture was filtered and the filtrate was evaporated. The

residue was recrystallized from benzene/hexane to give 1.86 g. (62%) of colorless needles of XXI, 157-157.5°; ir (potassium bromide): 2500-3300 (OH) and 1675 cm^{-1} ($\text{C}=\text{O}$); nmr (DMSO-*d*₆): δ 5.00 (s, 2H, CH₂), 7.2-7.7 (m, 6H, ArH), 7.7-8.2 (m, 3H, ArH), 11.8 (br s, 1H, COOH).

Anal. Calcd. for C₁₆H₁₂O₂S: C, 71.62; H, 4.51; S, 11.95. Found: C, 71.35; H, 4.48; S, 12.14.

Phenanthro[3,2-*b*]thiophene (XXIII).

In a similar manner as described for the synthesis of XVIII (Method A), 1.80 g. (6.7 mmoles) of the acid XXI was reduced to the alcohol with 0.30 g. of lithium aluminum hydride and then the alcohol was oxidized to the aldehyde XXII with chromium trioxide-pyridine complex (1.3 g. of chromium trioxide and 13 ml. of pyridine). A mixture of the crude aldehyde and 15 ml. of polyphosphoric acid was heated on a steam bath for 20 minutes. After cooling, ice water was added to the mixture and the precipitated solid was collected by filtration. The crude compound was first purified by passing through a column of alumina (benzene) and then by passing again through a column of silica gel using warmed cyclohexane as the eluent to give 0.90 g. (57%) of XXIII as colorless crystals, m.p. 119-121.5°. An analytical sample was recrystallized from hexane, colorless fine plates, m.p. 121-122°; ms: *m/e* 234 (M^+); nmr (deuteriochloroform): δ 7.3-7.9 (m, 7H, ArH except H₁, H₇, and H₁₁), 8.28 (s, 1H, H₇), 8.69 (m, 1H, H₁), 9.18 (s, 1H, H₁₁); uv: λ max (log ϵ) 210 (4.47), 242.5 (4.45), 272 (4.78), 282 (4.88), 302 (4.03), 314 (4.04), 328 (sh) (3.98), 352 (3.17) and 370 nm (3.17).

Anal. Calcd. for C₁₆H₁₀S: C, 82.02; H, 4.30; S, 13.68. Found: C, 81.79; H, 4.18; S, 13.88.

Phenanthro[9,10-*b*]thiophene (XXV).

Under a nitrogen atmosphere, a solution of 25.71 g. (0.1 mole) of 9-bromophenanthrene (26) in 20 ml. of dry benzene was added slowly to a mixture of 2.43 g. (0.1 g.-atom) of magnesium turnings and 50 ml. of dry ether. The reaction was initiated by the addition of a small amount of iodine and ethyl bromide. After completion of the addition, the reaction mixture was refluxed for one hour. Dry benzene (50 ml.) was added and the reaction mixture was refluxed for an additional 3 hours. After cooling, 29.85 g. of β,β -diethoxyethylsulfide (27) was added. After refluxing for one hour, an aqueous solution of ammonium chloride was added. The product was extracted with ether, washed with aqueous sodium hydroxide and then with water and dried over sodium sulfate. The crude oily product obtained by the evaporation of ether was applied to a column of silica gel. Elution with cyclohexane gave unreacted 9-bromophenanthrene. Further elution with benzene gave 20 g. of the sulfide XXIV as a yellow oil; nmr (deuteriochloroform): δ 1.15 (t, 6H, CH₂CH₂O), 3.21 (d, 2H, -CH₂S), 3.55 (m, 4H, CH₂CH₂O), 4.68 (t, 1H, methyne H), 7.4-8.0 (m, 5H, ArH), 7.82 (s, 1H, H₁₀), 8.4-8.7 (m, 3H, ArH).

A mixture of the crude sulfide and 200 g. of polyphosphoric acid was stirred at 150-160° (external temperature) for 10 minutes. After cooling, the mixture was poured into ca. 1 l. of water and the precipitated brown solid was collected. The dried crude product was dissolved in benzene and applied on a column of silica gel. The solid obtained by the elution with a mixture of cyclohexane and benzene (3:1) was passed again through a column of silica gel using hot cyclohexane as the eluent. The orange needles which precipitated from the eluate were collected by filtration to give 2.95 g. of XXV, m.p. 150-151°. Condensation of the filtrate gave 3.00 g. of additional XXV as orange needles, m.p. 150-151°.

The total yield was 5.95 g. (25% from 9-bromophenanthrene). An analytical sample was prepared by recrystallization from cyclohexane, as colorless needles, m.p. 151-152° (lit. (19) gives m.p. 151-153° and m.p. 153-154°); ms: *m/e* 234 (M^+); nmr (deuteriochloroform): δ 7.3-7.7 (m, 5H, H₂, H₃, H₆, H₉ and H₁₀), 7.88 (near d, 1H, H₃), 8.0-8.3 (m, 2H, H₄ and H₁₁), 8.4-8.8 (m, 2H, H₇ and H₈), uv: λ max (log ϵ) 253.5 (4.76), 258.5 (sh) (4.71), 279 (sh) (4.12), 289 (4.21) and 309 nm (3.92).

Anal. Calcd. for C₁₆H₁₀S: C, 82.02; H, 4.30; S, 13.68. Found: C, 82.19; H, 4.25; S, 13.81.

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