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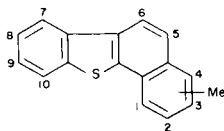
All isomers of the monomethylbenzo[*b*]naphtho[2,1-*d*]thiophenes were synthesized using photocyclization of 3-styrylbenzo[*b*]thiophenes.

The 1-, 3-, 4-, and 5-methylbenzo[*b*]naphtho[2,1-*d*]thiophenes were synthesized by irradiation of the corresponding methylated 3-styrylbenzo[*b*]thiophenes which were prepared by the Wadsworth-Emmons reaction of diethyl benzo[*b*]thienylphosphonate with *o*-, *m*-, *p*-tolualdehyde and acetophenone. The 7-, 8-, 9- and 10-methylbenzo[*b*]naphtho[2,1-*d*]thiophenes were synthesized by decarboxylation of 7-, 8-, 9- and 10-methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acid with copper in quinoline. These carboxylic acids were prepared by photocyclization of the corresponding 2-(benzo[*b*]thiophen-3-yl)-3-phenylpropenoic acids which were prepared by the condensation of the methylated benzo[*b*]thiophene-3-ylacetic acids with benzaldehyde in the presence of triethylamine in acetic anhydride.

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The detailed characterization of polycyclic aromatic compounds in such complex mixtures as coal liquids and shale oils by capillary column gas chromatography-mass spectrometry has been reported (2,3). Recently, using these methods, a great many polycyclic aromatic sulfur heterocycles have been separated and identified from coal gasification tar, coal liquids and shale oils (3,4,5). It is well known that several monomethyl thiophene derivatives occur in the sulfur fraction (2-7). We have reported the synthesis of all of the isomers of the parent condensed thiophene compounds, namely, naphtho[*b*]thiophene, phenanthro[*b*]thiophene (8), anthra[*b*]thiophene (9), benzo[*b*]naphtho[*d*]thiophene (9), phenaleno[1,9-*bc*]thiophene (10) and some pentacyclic thiophene ring systems (11-13) in order to provide samples for the measurement of retention data for temperature programmed capillary column gas chromatography. These compounds have also been examined for mutagenic activity (14).

The present paper describes the synthesis of all possible monomethylbenzo[*b*]naphtho[2,1-*d*]thiophenes (1-10) except the 6-methyl compound 6 which had already been prepared by photocyclization of 3-(α -methylstyryl)benzo[*b*]thiophene (12).

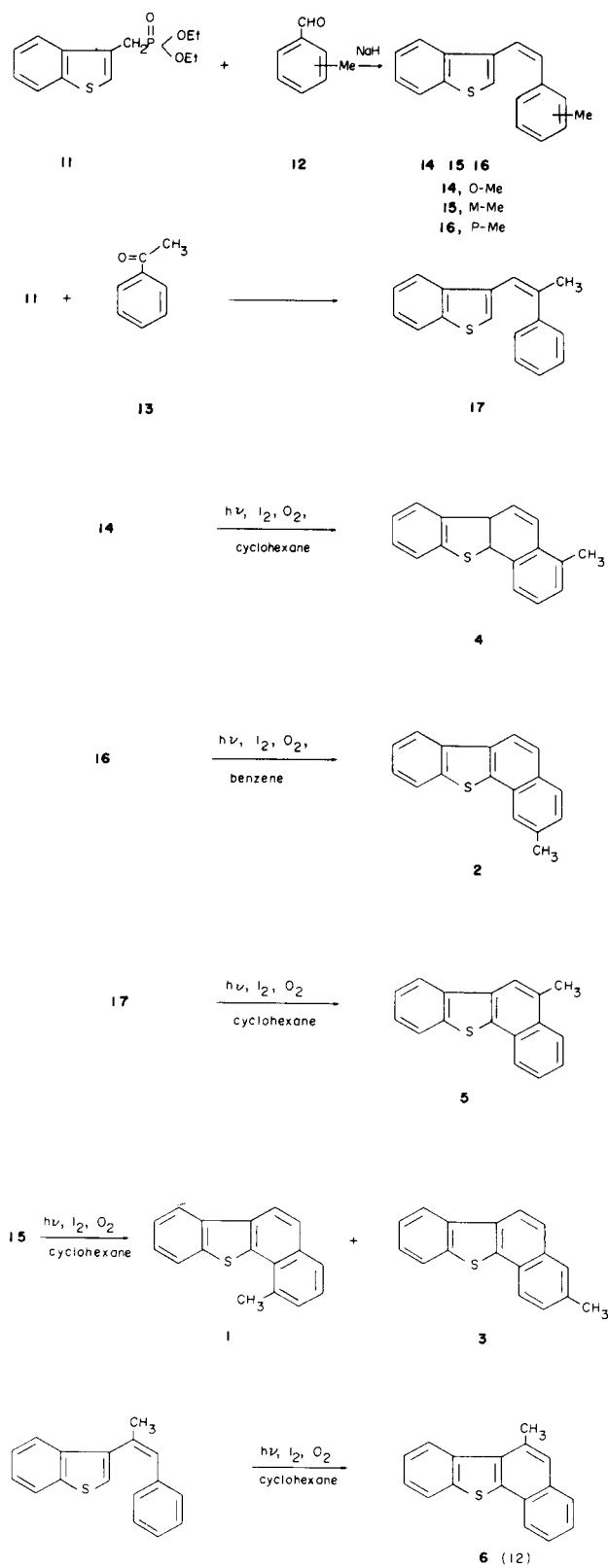


- | | |
|----------|------------|
| 1 = 1-Me | 6 = 6-Me |
| 2 = 2-Me | 7 = 7-Me |
| 3 = 3-Me | 8 = 8-Me |
| 4 = 4-Me | 9 = 9-Me |
| 5 = 5-Me | 10 = 10-Me |

Recently, we have reported the synthesis of benzo[*b*]naphtho[2,1-*d*]thiophene by using the Wadsworth-Emmons reaction followed by photocyclization (9). The corresponding methylated olefins were prepared using the Wadsworth-Emmons reaction (15,16). The reaction of diethyl benzo[*b*]thienylphosphonate (11) (9) with *o*-, *m*-, and *p*-tolualdehyde (12a, b and c) in the presence of sodium hydride in 1,2-dimethoxyethane gave the corresponding 3-(substituted methylstyryl)benzo[*b*]thiophenes (14, 15 and 16) in good yield. Similarly, compound 11 was allowed to react with acetophenone to give 3-(β -methylstyryl)benzo[*b*]thiophene (17) in 15% yield. Generally, the Wadsworth-Emmons reaction with acetophenone (13) affords the desired olefin in quite poor yield (15). The photocyclization of these styryl derivatives was carried out in cyclohexane or benzene in the presence of iodine and air. As expected, the photocyclization of 14, 15 and 17 proceeded smoothly and gave the desired 4-, 2-, and 5-methylbenzo[*b*]naphtho[2,1-*d*]thiophenes (4, 2 and 5) in 52%, 60% and 50% yield, respectively. The photocyclized products were accompanied by black solids which could not be removed from the chromatographic columns. The photocyclization of 3-(*m*-methylstyryl)benzyl[*b*]thiophene (15) afforded a mixture of 1-methyl- and 3-methylbenzo[*b*]naphtho[2,1-*d*]thiophenes (1 and 3) which was easily separated by a combination of column chromatography on silica gel and on basic alumina followed by fractional crystallization. The structural assignments between the 1-methyl and the 3-methyl derivatives are based upon the nmr spectra. In 1 the methyl signal (δ 3.10) is more deshielded than the methyl signal in 3 (δ 2.54) due to the ring current effect.

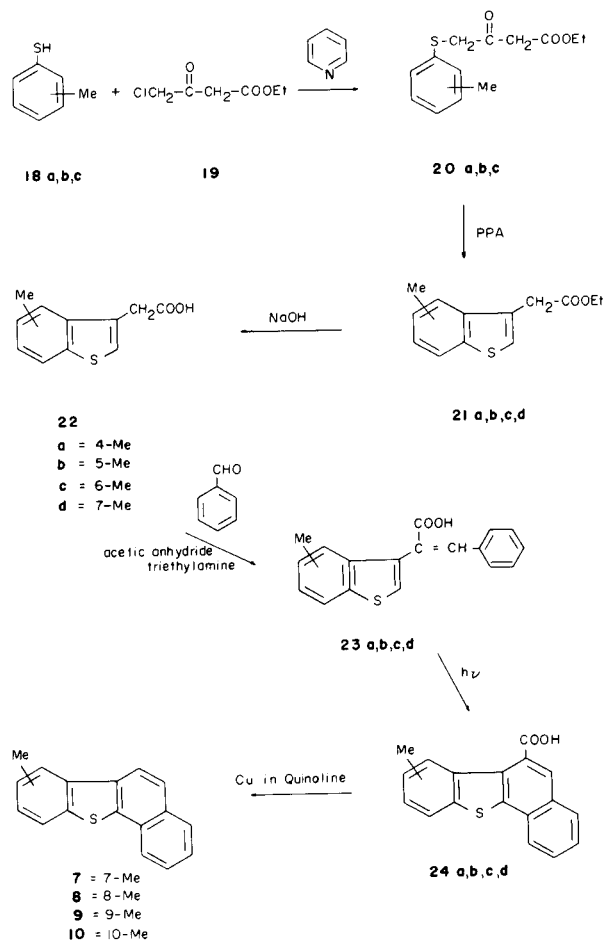
We next turned our attention to the synthesis of 7-, 8-, 9- and 10-methyl[*b*]naphtho[2,1-*d*]thiophenes (7, 8, 9 and

Scheme 1



10) by photocyclization of the corresponding methyl-substituted 3-styrylbenzo[b]thiophenes. Campbell, *et al.* (17), described the synthesis of these methyl compounds using the Pschorr cyclization procedure, however, the overall yields of the products obtained are inadequate for our program. Wood and Mallory (18) have reported the synthesis of 9-phenanthrenecarboxylic acid from α -stilbene-carboxylic acid by irradiation in the presence of iodine in good yield. The corresponding stilbenes were readily obtained (19-21). The 3-styryl compounds (23a, b, c and d) were readily prepared by the condensation between acetic acid derivatives (22a, b, c and d) and benzaldehyde in the presence of triethylamine in acetic anhydride solution. The photocyclization of 23a, b, c and d was carried out in dry benzene in the presence of iodine and air. Decarboxylation of 24a, b, c and d with copper in quinoline proceeded smoothly to give the required compounds 7, 8, 9 and 10 in 36%, 52%, 48% and 60% yield, respectively from 23. The preparation of 22a, b, c and d is described in the experimental.

Scheme 2



EXPERIMENTAL

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

3-(*o*-Methylstyryl)benzo[b]thiophene (14).

Sodium hydride (50%, 0.96 g, 20 mmoles) in 200 ml of 1,2-dimethoxyethane was cooled to 25°. Diethyl 3-benzo[b]thienylphosphonate (11) (2.84 g, 10 mmoles) 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 20°, *o*-tolualdehyde (1.2 g, 10 mmoles), was added dropwise. The solution was stirred at room temperature for 2 hours and heated at 50° for 20 minutes. After cooling a large excess of water was added to decompose the reaction mixture and the resulting precipitate was collected by filtration. The crude product was purified by chromatography on a silica gel column using hexane as the eluent giving 1.52 g (61%) of product as pale yellow crystals, mp 85° (lit (22) mp 85°); ms: m/e 250 (M⁺, 100).

3-(*m*-Methylstyryl)benzo[b]thiophene (15).

This compound was prepared from 11 (2.84 g, 10 mmoles) and *m*-tolualdehyde (1.2 g, 10 mmoles) in a manner similar to the preparation of 14 and was obtained as a pale yellow oil in 60% yield, (lit (22) bp 260°/0.4 mm Hg).

3-(*p*-Methylstyryl)benzo[b]thiophene (16).

This compound was synthesized from 11 (2.84 g, 10 mmoles) and *p*-tolualdehyde (1.2 g, 10 mmoles) in a manner similar to the preparation of 14 and was obtained as colorless crystals, mp 109° (lit mp 110° (22)), in 64% yield.

3-(β -Methylstyryl)benzo[b]thiophene (17).

This compound was synthesized from 11 (2.84 g, 10 mmoles) and acetophenone (13) (1.2 g, 10 mmoles) in a manner similar to the preparation of 14 and was obtained as a pale tan oil (lit 240°/0.4 mm Hg (22)) in 15% yield.

4-Methylbenzo[b]naphtho[2,1-d]thiophene (4).

A solution of 1.5 g (6 mmoles) of 14 and 0.1 g of iodine in 750 ml of cyclohexane was irradiated for 4 hours with a 450 Watt Hanovia medium pressure mercury lamp. 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 purified by chromatography on a silica gel column using hexane as the eluent giving 1.2 g (80%) of white crystals, mp 206° (lit (22) mp 206°); ms: m/e 249 (M⁺ + 1, 20), 248 (M⁺, 100), 247 (40), 250 (12); nmr (deuteriochloroform): 280 (s, 4-CH₃, 3H), 7.39-7.66 (m, aromatic H, 4H), 7.95-8.30 (m, aromatic H, 5H).

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

A solution of 1 g (4 mmoles) of 16 and 0.125 g of iodine in 360 ml of dry benzene was irradiated for 4 hours with a 450 Watt Hanovia medium pressure mercury lamp. 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 purified by chromatography on a silica gel column using hexane as the eluent giving 0.6 g (60%) of colorless needles, mp 145° (lit (22) mp 143°); ms: m/e 249 (M⁺ + 1, 20), 248 (M⁺, 100), 247 (38), 245 (12), nmr (deuteriochloroform): 2.51 (s, 2-CH₃, 3H), 7.17-8.17 (m, aromatic H, 9H).

5-Methylbenzo[b]naphtho[2,1-d]thiophene (5).

This compound was synthesized from 17 (0.2 g, 0.8 mmole) in a manner similar to the preparation of 4 and was obtained as colorless needles, mp 96° (lit (22) mp 97°) in 50% yield; ms: m/e 249 (M⁺ + 1, 21), 248 (M⁺,

100), 247 (52), 245 (13); nmr (deuteriochloroform): 2.77 (s, 5-CH₃, 3H), 7.37-7.70 (m, 2-H, 3-H, 8-H, 9-H, 4H, ArH), 7.92 (s, 6-H, 1H, ArH), 7.85-7.99 (m, 1-H, 4-H, 7-H, 10-H, 4H, ArH).

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

A solution of 1.5 g (6 mmoles) of 15 and 0.1 g of iodine in 750 ml of cyclohexane was irradiated for 4 hours with a 450 Watt Hanovia medium pressure mercury lamp. 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 chromatographed on a silica gel column using hexane as the eluent giving 0.95 g of white crystals, mp 80 ~ 90°. This product was recrystallized from ethanol to give 0.35 g (24%) of colorless needles of 3, mp 160° (lit (21) mp 161°); ms: m/e 249 (M⁺ + 1, 20), 248 (M⁺, 100), 247 (39), 245 (13); nmr (deuteriochloroform): 2.54 (s, 3-CH₃, 3H), 7.33-7.53 (m, 2-H, 8-H, 9-H, 3H, ArH), 7.65-8.23 (m, 1-H, 5-H, 6-H, 7-H, 10-H, 5H, ArH), 8.03 (s, 4-H, 1H, ArH).

The mother liquor of the above recrystallization was evaporated at reduced pressure and the residue was chromatographed on a basic aluminum oxide column (Aldrich Chemical Company) using hexane as the eluent to give colorless crystals which were recrystallized from methanol to give 0.25 g (17%) of 1 as colorless needles, mp 108° (lit (22) mp 108°); ms: m/e 249 (M⁺ + 1, 20), 248 (M⁺, 100), 247 (45), 245 (14); nmr (deuteriochloroform): 3.10 (s, 1-CH₃, 3H), 7.38-7.56 (m, 2-H, 3-H, 8-H, 9-H, 4H, ArH), 7.81-8.04 (m, 4-H, 10-H, 2H, ArH), 7.81 (d, J = 8 Hz, 5-H, 1H, ArH), 8.17 (d, J = 8 Hz, 6-H, 1H, ArH), 8.17-8.32 (m, 7-H, 1H). Subsequent elution with hexane/benzene (1:3) afforded colorless crystals which were recrystallized from ethanol to give 0.1 g (7%) of colorless needles of 3, mp 160°.

5-Methylbenzo[b]thiophen-3-ylacetic Acid (22b).

Ethyl 4-chloro-3-oxobutanoate (8.3 g, 50 mmoles) was added dropwise to a stirred solution of 6.2 g (50 mmoles) of *p*-methylbenzenethiol in 50 ml of dry pyridine maintained at 25-30°. After 15 minutes, the mixture was heated on a steam bath for 2 hours. The pyridine was dissolved by the slow addition of 10% hydrochloric acid solution and then the reaction mixture was extracted with chloroform (30 × 2 ml). The chloroform extracts were washed with water and dried over sodium sulfate. After removal of the solvent, 20c was obtained as a brown oil; ir (neat): 1750 (C=O); nmr (deuteriochloroform): 1.22 (t, J = 7 Hz, -OCH₂-CH₃, 3H), 2.27 (s, 4-CH₃, 3H), 3.57 (s, -CH₂, 2H), 3.68 (s, -CH₂, 2H), 4.12 (q, J = 7 Hz, O-CH₂, 2H), 7.16 (d, J = 5 Hz, phenyl-H, 2H), 7.32 (d, J = 5 Hz, phenyl-H, 2H); ms: m/e 252 (M⁺, 38), 164 (38), 137 (100).

A solution of the above crude product (ethyl 4-(4-methylphenylthio)-3-oxobutanoate) 20c in 200 ml of chlorobenzene was heated at the reflux temperature for three hours with 100 g of polyphosphoric acid. The chlorobenzene was decanted and the remaining semisolid was heated at the reflux temperature for 3 hours with 200 ml of benzene. The benzene was decanted and the combined organic solutions were washed with aqueous sodium bicarbonate followed by saturated sodium chloride solution. The solvents were removed under reduced pressure to give a brown oil. A mixture of the above crude product 21b and 200 ml of 10% sodium hydroxide solution was refluxed for 1.5 hours. After cooling, 200 ml of water was added to the reaction mixture and extracted with 200 ml of benzene. The aqueous layer was acidified with concentrated hydrochloric acid solution. The mixture was cooled and the solid material was collected by filtration. The product was recrystallized from benzene/cyclohexane to give 3.1 g (30%) of tan prisms, mp 153°; ir (potassium bromide): 3300 2500 (broad), 1720 (C=O); nmr (deuteriochloroform): 2.46 (s, 5-CH₃, 3H), 3.83 (s, -CH₂-COOH, 2H), 7.05 (d, J = 8 Hz, 6-H, 1H, ArH), 7.32 (s, 2-H, 1H, ArH), 7.53 (s, 4-H, 1H, ArH), 7.73 (d, J = 8 Hz, 7-H, 1H, ArH); ms: m/e 206 (M⁺, 43), 161 (100).

Anal. Calcd. for C₁₁H₁₀O₂S: C, 64.05; H, 4.89; S, 15.55. Found: C, 63.57; H, 5.07; S, 15.12.

7-Methylbenzo[b]thiophen-3-ylacetic Acid (22d).

This compound was synthesized *via* 20a and 21d from *o*-methylbenzenethiol (6.2 g, 50 mmoles) and ethyl 4-chloro-3-oxobutanoate (8.3 g,

50 mmoles) in a manner similar to the preparation of **22b**. Tan needles, mp 138° were obtained in 45% yield. An analytical sample was recrystallized from cyclohexane, mp 132°; ir (potassium bromide): 1700 (C=O) 3500 2200 (broad); nmr (deuteriochloroform): 2.55 (s, 7-CH₃, 3H), 3.87 (s, CH₂-COOH, 2H), 7.13-7.47 (m, 4-H, 5-H, 2H, ArH), 7.34 (s, 2-H, 1H, ArH), 7.62 (bd, J = 7 Hz, 4-H, 1H, ArH); ms: m/e 206 (M⁺, 44), 161 (100).

Anal. Calcd. for C₁₁H₁₀O₂S: C, 64.05; H, 4.89; S, 15.55. Found: C, 64.01; H, 5.04; S, 15.40.

Ethyl 4-(2-Methylphenylthio)-3-oxobutanoate (**20a**).

This compound was obtained as a light brown oil; ir (neat): 1700, 1725 (C=O); nmr (deuteriochloroform): 1.21 (t, J = 7 Hz, O-CH₂-CH₃, 3H), 2.37 (s, 2-CH₃, 3H), 3.48 (s, -CH₂-, 2H), 3.69 (s, -CH₂-, 2H), 4.10 (q, J = 7 Hz, -CH₂-CH₃, 2H), 7.00-7.35 (m, 3-H, 4-H, 5-H, 6-H, 4H, ArH); ms: m/e 252 (M⁺, 45), 164 (44), 137 (100).

4-Methylbenzo[*b*]thiophen-3-ylacetic Acid (**22a**) and 6-Methylbenzo[*b*]thiophen-3-ylacetic Acid (**22c**).

A mixture of **22a** and **22c** was synthesized from *m*-methylbenzenethiol (6.2 g, 50 mmoles) and ethyl 4-chloro-3-oxobutanoate (8.3 g, 50 mmoles) in a manner similar to the preparation of **22b** and was obtained as tan crystals. The crude acetic acid derivatives (4.8 g) (**22a** and **c**) were recrystallized from cyclohexane to give 2.0 g (19%) of tan prisms of **22a**, mp 150°. An analytical sample was recrystallized from cyclohexane/hexane, mp 157°; ir (potassium bromide): 3200 ~ 2500 (broad), 1700 (C=O); nmr (deuteriochloroform): 2.68 (s, 4-CH₃, 3H), 4.04 (s, -CH₂-COOH, 2H), 7.21 (s, 2-H, 1H, ArH), 7.02-7.26 (m, 5-H, 6-H, 2H, ArH), 7.66 (bd, J = 7 Hz, 7-H, 1H, ArH); ms: m/e 206 (M⁺, 44), 161 (100).

Anal. Calcd. for C₁₁H₁₀O₂S: C, 64.05; H, 4.89; S, 15.55. Found: C, 63.97; H, 4.84; S, 15.43.

The above cyclohexane mother liquor was concentrated after treatment with activated charcoal. The residue was recrystallized from cyclohexane/hexane to give 1.5 g (15%) of **22c** as needles, mp 110°. An analytical sample was recrystallized from cyclohexane/hexane, mp 125°; ir (potassium bromide): 3100 ~ 2500 (broad), 1705 (C=O); nmr (deuteriochloroform): 2.43 (s, 6-CH₃, 3H), 3.82 (s, -CH₂-COOH, 2H), 7.14 (bd, J = 7 Hz, 5-H, 1H, ArH), 7.22 (s, 2-H, 1H, ArH), 7.61 (bs, 7-H, 1H, ArH), 7.60 (d, J = 7 Hz, 4-H, 1H, ArH); ms: m/e 206 (M⁺, 39), 161 (100).

Anal. Calcd. for C₁₁H₁₀O₂S: C, 64.05; H, 4.89; S, 15.55. Found: C, 64.30; H, 4.85; S, 15.37.

Ethyl 4-(3-Methylphenylthio)-3-oxobutanoate (**20b**).

This compound was obtained as a light brown oil, ir (neat): 1710, 1700 (C=O); nmr (deuteriochloroform): 1.22 (t, J = 7 Hz, OCH₂CH₃, 3H), 2.29 (s, 3-CH₃, 3H), 3.59 (s, -CH₂-, 2H), 2.77 (s, -CH₂-, 2H), 4.11 (q, J = 7 Hz, O-CH₂-CH₃, 2H), 7.00-7.27 (m, 2-H, 4-H, 5-H, 6-H, 4H, ArH); ms: m/e 252 (M⁺, 45), 164 (44), 137 (100).

2-(5-Methylbenzo[*b*]thiophen-3-yl)-3-phenylpropenoic Acid (**23b**).

A mixture of 0.8 g (3.9 mmoles) of **22b**, 0.5 g (4.7 mmoles) of benzaldehyde, 1 ml of acetic anhydride and 0.5 ml of triethylamine was refluxed for 5 hours. The reaction mixture was poured into 10% hydrochloric acid solution. The oily product was extracted with benzene (200 ml). The benzene solution was extracted three times with 50 ml portions of 5% sodium hydroxide. The aqueous solution was acidified with 10% hydrochloric acid solution to give an oily product. The oily product was extracted with benzene (200 ml) and the benzene was removed after drying over sodium sulfate. The residue was triturated with cyclohexane and hexane (1:1 mixture) to give 0.6 g (51%) of tan crystals, mp 168°. An analytical sample was recrystallized from cyclohexane, mp 177°; ir (potassium bromide): 3100-2200 (broad), 1660 (C=O); nmr (deuteriochloroform): 2.33 (s, 5-CH₃, 3H), 7.04-7.33 (m, phenyl-H, 4-H, 6-H, 7H), 7.75 (d, J = 8 Hz, 7-H, 1H, ArH), 8.16 (s, ethenyl-H, 1H, ArH), 10.00 (bs, OH, 1H); ms: m/e 294 (M⁺, 87), 249 (100), 234 (83).

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.24; H, 4.89; S, 11.00.

2-(4-Methylbenzo[*b*]thiophen-3-yl)-3-phenylpropenoic Acid (**23a**).

This compound was synthesized from **22a** (0.8 g, 3.9 mmoles) and benzaldehyde (0.5 g) in a manner similar to the preparation of **23b** and was obtained as tan crystals in 42% yield. An analytical sample was recrystallized from cyclohexane, mp 110°, ir (potassium bromide): 3100-2200 (broad), 1660 (C=O); nmr (deuteriochloroform): 2.51 (s, 4-CH₃, 3H), 7.00-7.55 (m, phenyl-H, 2-H, 5-H, 6-H, 8H), 7.67 (d, J = 7 Hz, 7-H, 1H, ArH), 8.04 (s, ethenyl-H, 1H), 11.44 (s, OH, 1H); ms: m/e 294 (M⁺, 78), 249 (43), 171 (100).

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.21; H, 4.78; S, 11.11.

2-(6-Methylbenzo[*b*]thiophen-3-yl)-3-phenylpropenoic Acid (**23c**).

This compound was synthesized from **22c** (0.8 g, 3.9 mmoles) and benzaldehyde (0.5 g) in a manner similar to the preparation of **23b** and was obtained as tan crystals in a 32% yield, mp 125°; ir (potassium bromide): 3100-2200 (broad), 1665 (C=O); nmr (deuteriochloroform): 2.41 (s, 6-CH₃, 3H), 7.00-7.65 (m, phenyl-H, 2-H, 4-H, 5-H, 8H), 7.88 (s, 4-H, 1H, ArH), 8.14 (s, ethenyl-H, 1H), 9.97 (s, OH, 1H); ms: m/e 294 (M⁺, 71), 249 (95), 234 (100).

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.50; H, 5.01; S, 11.02.

2-(7-Methylbenzo[*b*]thiophen-3-yl)-3-phenylpropenoic Acid (**23d**).

This compound was synthesized from **22d** (0.8 g, 3.9 mmoles) and benzaldehyde (0.5 g) in a manner similar to the preparation of **23b** and was obtained as tan crystals in 67% yield. An analytical sample was recrystallized from cyclohexane/benzene to give tan crystals, mp 201°; ir (potassium bromide): 3100-2200 (broad), 1650 (C=O); nmr (deuteriochloroform + methyl sulfoxide-d₆): 2.56 (s, 7-CH₃, 3H), 6.99-7.25 (m, phenyl-H, 2-H, 4-H, 5-H, 6-H, 9H), 8.02 (s, ethenyl-H, 1H).

Anal. Calcd. for C₁₈H₁₄O₂S: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.52; H, 5.04; S, 11.00.

7-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**7**).

A solution of 0.5 g (1.7 mmoles) of **23a** and 0.10 g of iodine in 100 ml of benzene and 260 ml of cyclohexane was irradiated for 4 hours with a 450 Watt Hanovia medium pressure mercury lamp. 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 washed with hexane to give 7-methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acid (**24a**) as a brown solid, mp 210°; ms: m/e 292 (M⁺, 100), 274 (31), 247 (28), 245 (24); ir (potassium bromide): 3100-2200 (broad), 1670 (C=O).

A mixture of the above crude cyclized product, 1 g of powdered copper and 15 ml of quinoline was refluxed for 1 hour. The reaction mixture was poured into 100 ml of ice-water and acidified with 10% hydrochloric acid solution. The mixture was extracted with 200 ml of benzene. The benzene layer was washed successively with saturated sodium bicarbonate solution, water, dried over sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using hexane as the eluent to give a white solid, which was recrystallized from methanol to give 0.15 g (36%) of colorless needles, mp 162° (lit (17) mp 167°); ms: m/e 249 (M⁺ + 1, 21), 248 (M⁺, 100), 247 (44), 245 (11), 215 (12); nmr (deuteriochloroform): 2.91 (s, 7-CH₃, 3H), 7.17-8.15 (m, aromatic-H, 7H), 7.73 (d, J = 9 Hz, 5-H, 1H, ArH), 8.33 (d, J = 9 Hz, 6-H, 1H, ArH).

8-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**8**).

This compound was synthesized from **23b** (0.5 g, 1.7 mmoles) in a manner similar to the preparation of **7**, and was obtained as colorless needles, mp 168° (lit (17) mp 148°) in 52% yield; ms: m/e 249 (M⁺ + 1, 21), 248 (M⁺, 100), 247 (43), 215 (12); nmr (deuteriochloroform): 2.50 (s, 8-CH₃, 3H), 7.18-8.16 (m aromatic-H, 9H).

8-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic Acid (**24b**).

This compound was obtained with mp 240°; ir (potassium bromide): 3200-2200 (broad), 1690 (C=O), ms: m/e 292 (M⁺, 100), 247 (22).

9-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**9**).

This compound was synthesized from **23c** (0.5 g, 1.7 mmoles) in a manner similar to the preparation of **7** and was obtained as colorless needles, mp 184° (lit (17) mp 185-186°) in 48% yield; ms: m/e 249 ($M^+ + 1$, 21), 248 (M^+ , 100), 247 (45), 245 (10); nmr (deuteriochloroform): 2.51 (s, 9-CH₃, 3H), 7.31-8.21 (m, aromatic-H, 9H).

9-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic Acid (**24c**).

This compound had mp 235°; ir (potassium bromide): 3200-2200 (broad), 1695 (C=O), ms: m/e 292 (M^+ , 100), 247 (23), 246 (13).

10-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene (**10**).

This compound was synthesized from **23d** (0.5 g, 1.7 mmoles) in a manner similar to the preparation of **7** and was obtained as colorless needles, mp 148° (lit (17) mp 148°) in 60% yield; ms: m/e 249 ($M^+ + 1$, 20), 248 (M^+ , 100), 247 (39), 245 (10); nmr (deuteriochloroform): 2.62 (s, 10-CH₃, 3H), 7.17-8.22 (m, aromatic-H, 9H).

10-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic Acid (**24d**).

This compound had mp 251°; ir (potassium bromide): 3100-2200 (broad), 1660 (C=O); ms: m/e 292 (M^+ , 100), 247 (22), 245 (14).

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REFERENCES AND NOTES

- (1) To whom correspondence regarding this paper should be addressed.
- (2) K. D. Bartle, M. L. Lee and S. A. Wise, *Chem. Soc. Rev.*, 113 (1981).
- (3) M. L. Lee, C. Willey, R. N. Castle and C. M. White, "Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects", A. Bjørseth and A. J. Dennis, eds, Battelle Press, Columbus, Ohio, 1980, pp 59-73.
- (4) C. Willey, M. Iwao, R. N. Castle and M. L. Lee, *Anal. Chem.*, **53**, 400 (1981).
- (5) R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao, R. N. Castle and S. A. Wise, *J. Chromatogr. Sci.*, accepted for publication.
- (6) W. Carruthers and A. G. Douglas, *J. Chem. Soc.*, 2813 (1959).
- (7) M. Pailer and L. Berner-Fenz, *Monatsh. Chem.*, **104**, 339 (1973); *Chem. Abstr.*, **79**, 81266x (1973).
- (8) M. Iwao, M. L. Lee and R. N. Castle, *J. Heterocyclic Chem.*, **17**, 1259 (1980).
- (9) Y. Tominaga, M. L. Lee and R. N. Castle, *ibid.*, **18**, 967 (1981).
- (10) Y. Tominaga, M. L. Lee and R. N. Castle, *ibid.*, **18**, 977 (1981).
- (11) R. Pratap, Y. Tominaga, M. L. Lee and R. N. Castle, *ibid.*, **18**, 973 (1981).
- (12) R. D. Thompson, M. Iwao, M. L. Lee and R. N. Castle, *ibid.*, **18**, 981 (1981).
- (13) R. Pratap, M. L. Lee and R. N. Castle, *ibid.*, **18**, 1457 (1981).
- (14) R. A. Pelory, Y. Tominaga, M. Iwao, R. N. Castle and M. L. Lee, *Mutat. Res.*, accepted for publication.
- (15) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).
- (16) W. S. Wadsworth, *Org. React.*, **25**, 73 (1977).
- (17) A. D. Campbell and A. R. Keen, *J. Chem. Soc.*, 1637 (1964).
- (18) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).
- (19) R. E. Buckles and K. Bremer, "Organic Synthesis", Coll. Vol. IV, John Wiley and Sons, Inc, New York, NY, 1963, p 777.
- (20) R. E. Buckles and E. A. Hausman, *J. Am. Chem. Soc.*, **70**, 415 (1948).
- (21) R. E. Buckles, M. P. Bellis and W. D. Coder, Jr., *ibid.*, **73**, 4972 (1951).
- (22) W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.*, 6221 (1965).