

Marvin L. Tedjamulia, Yoshinori Tominaga [1] and Raymond N. Castle* [2]

Department of Chemistry, University of South Florida,
Tampa, Florida 33620

Milton L. Lee

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

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The synthesis of phenanthro[4,5-*bcd*]thiophene and the four monomethylphenanthro[4,5-*bcd*]thiophenes is described.

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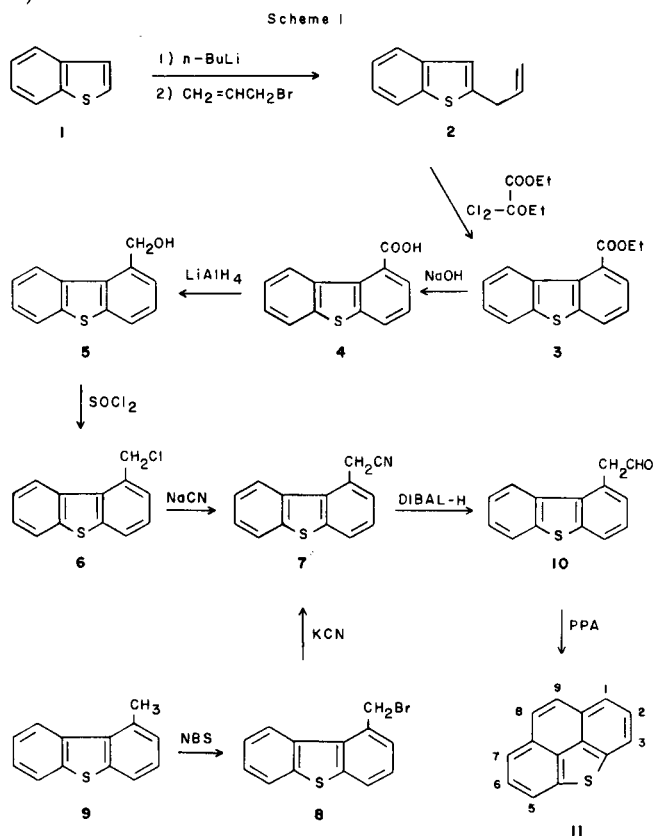
Willey, Iwao, Castle and Lee [3] observed a peak of molecular weight 208 *via* gas chromatography/mass spectrometry (*gc/ms*) in two different coal liquids (SRC-I and SRC-II) and also in both Paraho and Livermore shale oils. The peak was assigned to the parent phenanthro[4,5-*bcd*]thiophene (**11**) thus it was necessary to synthesize an authentic specimen. Willey *et al.* [3] also reported *via gc/ms* the presence of two peaks of molecular weight 222 corresponding to the monomethylphenanthro[4,5-*bcd*]thiophenes, thus it was also necessary to prepare all four of the monomethylphenanthro[4,5-*bcd*]thiophenes in order to ascertain which of the four isomers were present in the coal derived products and shale oils. Thus we now report a continuation of our previous studies on the synthesis of polycyclic thiophenes [4-19] suspected of occurring in coal-derived products and shale oils.

Klemm and Hsin [20] have previously prepared phenanthro[4,5-*bcd*]thiophene (**11**), however, the four monomethylphenanthro[4,5-*bcd*]thiophenes have not been reported in the literature.

We have selected a different synthetic route for the preparation of phenanthro[4,5-*bcd*]thiophene (**11**) from that reported by Klemm and Hsin [20].

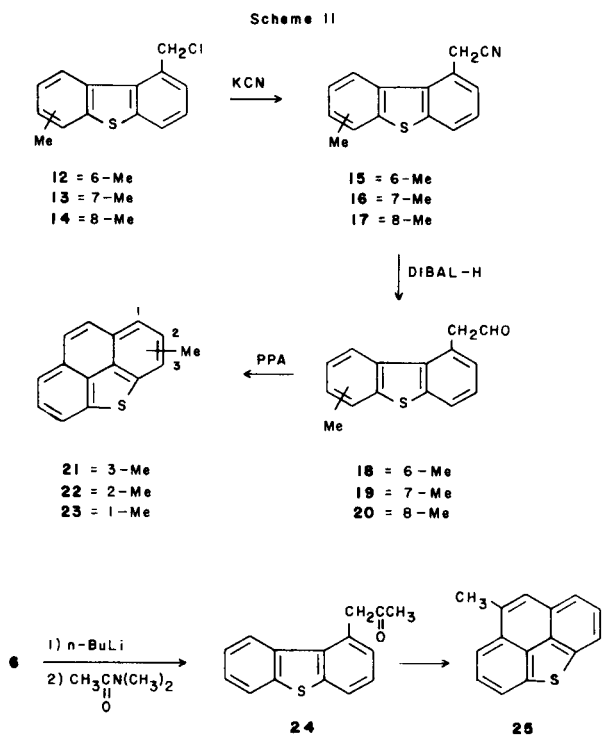
Benzo[*b*]thiophene (**1**) was lithiated in the 2-position [22]. The 2-lithiobenzo[*b*]thiophene was allowed to react with allyl bromide to give 2-allylbenzo[*b*]thiophene (**2**) [21] which upon treatment with ethyl dichloroethoxyacetate gave ethyl dibenzothiophene-1-carboxylate (**3**) [21]. Alkaline hydrolysis of **3** gave dibenzothiophene-1-carboxylic acid (**4**) [22] in 94% yield. Reduction of **4** with lithium aluminum hydride (LAH) gave 1-hydroxymethyldibenzothiophene [21] in 90% yield. When **5** was allowed to react with thionyl chloride, 1-chloromethyldibenzothiophene (**6**) [21] was obtained in 77% yield. 1-Cyanomethyldibenzothiophene (**7**) was prepared from **6** and sodium cyanide in 75% yield and also prepared from **8** upon treatment with potassium cyanide in 85% yield. Compound **8** was obtained from 1-methyldibenzothiophene (**9**) [21] *via* the Wohl-Ziegler reaction in 79% yield. When **7** was

allowed to react with diisobutylaluminum hydride (DIBAL-H), the aldehyde **10** was obtained as an oil and cyclized with polyphosphoric (PPA) into phenanthro[4,5-*bcd*]thiophene (**11**) [20] in 33% yield from **7** (Scheme I).



The preparation of 1-chloromethyl-6-methyl- (**12**), 1-chloromethyl-7-methyl- (**13**) and 1-chloromethyl-8-methyldibenzothiophene (**14**) has been reported by Castle, *et al.* [19]. Reaction of **12**, **13** or **14** with potassium cyanide gave 1-cyanomethyl-6-methyldibenzothiophene (**15**) in 75% yield; 1-cyanomethyl-7-methyldibenzothiophene (**16**) in 78% yield; and 1-cyanomethyl-8-methyldibenzothiophene

phene (**17**) in 78% yield respectively. When **15**, **16** or **17** was allowed to react with DIBAL-H, the aldehydes **18**, **19** or **20** were obtained as oils and used in the next step without purification. Cyclization of the aldehydes **18**, **19** or **20** with PPA gave 3-methylphenanthro[4,5-*bcd*]thiophene (**21**) in 51% yield; 2-methylphenanthro[4,5-*bcd*]thiophene (**22**) in 46% yield; and 1-methylphenanthro[4,5-*bcd*]thiophene (**23**) in 53% yield respectively. When compound **6** was allowed to react with *n*-butyllithium followed by treatment of the lithio derivative with *N,N*-dimethylacetamide, 1-(1-dibenzothiényl)-2-propanone (**24**) was obtained in 70% yield. Cyclization of **24** via PPA gave 8-methylphenanthro[4,5-*bcd*]thiophene in 62% yield (Scheme II).



EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The ¹H-nmr spectra were obtained on a Varian EM 360A spectrometer and on a JEOL FX-90Q spectrometer in deuteriochloroform. Chemical shifts are reported in δ units. The ir spectra were obtained on a Beckman Acculab 2 spectrometer. Mass spectra were obtained on a Hewlett-Packard model 4980A mass spectrometer. Elemental analysis were performed by MHW Laboratories, Phoenix, Arizona.

Ethyl Dibenzo[thiophene-1-carboxylate (**3**).

This compound was synthesized according to the method of Meth-Cohn *et al.* [21] and colorless needles were obtained, mp 64° (lit mp 62.5° [21]); nmr (deuteriochloroform): δ 1.47 (t, J = 8 Hz, -CH₂-CH₃, 3H), 4.51 (q, J = 8 Hz, -CH₂-CH₃, 2H), 7.11-8.02 (m, H-2, H-3, H-4, H-6, H-7, H-8, 6H, ArH), 8.27 (m, H-9, 1H, ArH); ms: m/e 257 (M⁺ + 1, 15), 256 (M⁺, 100).

Dibenzo[thiophene-1-carboxylic Acid (**4**).

A mixture of ethyl dibenzo[thiophene-1-carboxylate (**3**) (10.0 g, 39.01 mmoles) (**3**) and 10% sodium hydroxide in methanol (200 ml) was refluxed for 2.5 hours. The mixture was poured into 200 ml of ice-water and the undissolved compound was filtered off. The filtrate was acidified with 10% hydrochloric acid solution and a tan solid was collected by filtration. This product was recrystallized from cyclohexane to give 8.37 g (94%) of colorless crystals, mp 177° (lit mp 176-177° [22]); nmr (deuteriochloroform): δ 7.21-8.02 (m, H-2, H-3, H-4, H-6, H-7, H-8, 6H, ArH), 8.40-8.72 (m, H-9, 1H, ArH); ms: m/e 230 (M⁺ + 2, 6), 229 (M⁺ + 1, 15), 228 (M⁺, 100), 211 (23), 183 (25).

1-Hydroxymethyl-dibenzo[thiophene (**5**).

A solution of dibenzo[thiophene-1-carboxylic acid (**4**) (5.0 g, 21.90 mmoles) (**4**) in 200 ml of dry ether was added dropwise to a suspension of lithium aluminum hydride (2.0 g) in 150 ml of dry ether. After refluxing for 3 hours, the reaction mixture was carefully quenched by cautiously adding 80 ml of water and enough 10% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice-water and extracted twice with 150 ml of ether. The ether solution was dried over anhydrous magnesium sulfate and the solvent evaporated to give 4.2 g (90%) of colorless crystals. This product was recrystallized from hexane:benzene (1:1), mp 108° (lit mp 105-107° [21]); nmr (deuteriochloroform): δ 1.89 (bs, OH, 1H), 5.11 (s, CH₂-OH, 2H), 7.12-7.50 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.60-7.89 (m, H-4, H-6, 2H, ArH), 8.23 (dd, J = 1, 8 Hz, H-9, 1H, ArH); ms: m/e 216 (M⁺ + 2, 5), 215 (M⁺ + 1, 15), 214 (M⁺, 100), 197 (32), 185 (83), 184 (43).

1-Chloromethyl-dibenzo[thiophene (**6**).

A mixture of 1-hydroxymethyl-dibenzo[thiophene (**5**) (3.0 g, 14.0 mmoles) (**5**), thionyl chloride (5.0 ml) and dry benzene (60 ml) was refluxed for one hour. After removal of benzene and excess thionyl chloride, the residue was recrystallized from ethanol to give colorless crystals (2.51 g, 77%), mp 99° (lit 99-100° [21]); nmr (deuteriochloroform): δ 5.02 (s, CH₂Cl, 2H), 7.10-7.51 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.53-7.88 (m, H-4, H-6, 2H, ArH), 8.23 (dd, J = 1, 8 Hz, H-9, 1H, ArH); ms: m/e 234 (M⁺ + 2, 16), 233 (M⁺ + 1, 7), 232 (M⁺, 42), 197 (100).

1-Bromomethyl-dibenzo[thiophene (**8**).

A mixture of *N*-bromosuccinimide (0.95 g, 5.3 mmoles), 1-methyl-dibenzo[thiophene (**9**) (1.0 g, 5.0 mmoles) [21], benzoyl peroxide (0.01 g) and dry carbon tetrachloride (50 ml) was refluxed for 3.5 hours. After cooling, the reaction mixture was poured into ice-water and the succinimide crystals were removed by filtration. The filtrate was washed with 10% sodium hydroxide solution and then with water. The organic layer was dried with sodium sulfate and evaporated to give a tan solid. The crude product was recrystallized from hexane to give colorless needles (79%), mp 118°; nmr (deuteriochloroform): δ 5.06 (s, CH₂-Br, 2H), 7.37-7.63 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.74-7.95 (m, H-4, H-6, 2H, ArH), 8.35-8.48 (m, H-9, 1H, ArH); ms: m/e 278 (M⁺ + 2, 10), 276 (M⁺, 10), 197 (M⁺ - 79, 100).

Anal. Calcd. for C₁₃H₉BrS: C, 56.33; H, 3.27; S, 11.57. Found: C, 56.42; H, 3.47; S, 11.67.

1-Cyanomethyl-dibenzo[thiophene (**7**).

Method A.

A mixture of 1-bromomethyl-dibenzo[thiophene (**8**) (1.0 g, 3.6 mmoles), potassium cyanide (1.5 g), 50 ml of benzene, 8 ml of water and 5 drops of Aliquat 336 was refluxed for 2.5 hours. After addition of 50 ml of benzene, the benzene was washed successively with water and 10% hydrochloric acid, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was recrystallized from methanol giving 0.68 g (85%) of colorless needles, mp 87°.

Method B.

A mixture of 1-chloromethyl-dibenzo[thiophene (**6**) (1.0 g, 4.3 mmoles), sodium cyanide (1.0 g), 3 ml of water and 20 ml of dimethyl sulfoxide was heated at 40-50° for 2 hours. The reaction mixture was poured into 100

ml of ice-water and then extracted twice with 100 ml of benzene. The combined extracts were washed successively with water and 10% hydrochloric acid, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a neutral alumina column using cyclohexane:benzene (1:1) as the eluent giving colorless needles (75%), mp 87°; ir (potassium bromide): 2240 cm^{-1} (CN); nmr (deuteriochloroform): δ 4.21 (s, CH_2 , 2H), 7.32-7.54 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.71-8.12 (m, H-4, H-6, H-9, 3H, *ArH*); ms: *m/e* 224 ($M^+ + 1$, 16), 223 (M^+ , 100), 222 (30), 195 (11).

Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{NS}$: C, 75.30; H, 4.06; N, 6.27; S, 14.35. Found: C, 75.21; H, 4.33; N, 6.22; S, 14.21.

Phenanthro[4,5-*bcd*]thiophene (11).

Diisobutylaluminum hydride (25% solution in toluene, 3.75 ml, 5 mmoles) was added with a syringe to a solution of 1-cyanomethyl-dibenzothiophene (7) (1.0 g, 4.5 mmoles) in 60 ml of dry benzene under a nitrogen atmosphere. The mixture was stirred at room temperature for three hours. Dilute hydrochloric acid was added and the mixture was stirred at the same temperature for another 1.5 hours. The reaction mixture was evaporated *in vacuo* affording the aldehyde 10 as an oil.

The crude aldehyde 10 and polyphosphoric acid (10 g) were heated with continuous stirring at 130-140° for two hours. The reaction mixture was poured into ice-water and extracted with benzene. The organic layer was washed with water, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using hexane as the eluent giving colorless crystals (0.31 g, 33%), mp 118-122°. This product was recrystallized from hexane to give colorless needles, mp 138° (lit mp 134-135° [20], 139-140° [23]); nmr lit [23]; ms: *m/e* 210 ($M^+ + 2$, 5), 209 ($M^+ + 1$, 16), 208 (M^+ , 100), 184 (14), 163 (14).

The second eluted product from hexane:benzene (1:1) was pale yellow crystals, mp 170°, which were recrystallized from hexane; ms: *m/e* 223 ($M^+ + 2$, 6), 222 ($M^+ + 1$, 18), 221 (M^+ , 100), 220 (15), 219 (12), 207 (10), 197 (19), 194 (11), 189 (10), 176 (10). We could not identify the structure of this second product.

1-Cyanomethyl-6-methyldibenzothiophene (15).

This compound was prepared from compound 12 (5.0 g, 20.26 mmoles), potassium cyanide (5 g), water (8.0 ml) and dimethyl sulfoxide (50 ml) in a manner similar to the preparation of compound 7 (Method B). An analytical sample was chromatographed on a neutral alumina column using cyclohexane:benzene (1:1) as the eluent giving colorless needles (75%), mp 152°; nmr (deuteriochloroform): δ 2.62 (s, CH_3 , 3H), 4.32 (s, $\text{CH}_2\text{-CN}$, 2H), 7.17-7.58 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.83 (dd, $J = 1, 8$ Hz, H-4, 1H, *ArH*), 7.89 (dd, $J = 1, 8$ Hz, H-9, 1H, *ArH*); ms: *m/e* 239 ($M^+ + 2$, 6), 238 ($M^+ + 1$, 19), 237 (M^+ , 100), 236 (67), 208 (22).

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{NS}$: C, 75.92; H, 4.67; S, 13.51. Found: C, 76.15; H, 4.73; S, 13.41.

1-Cyanomethyl-7-methyldibenzothiophene (16).

This compound was prepared in a manner similar to the preparation of compound 15. An analytical sample was obtained by chromatography on neutral alumina using cyclohexane:benzene (1:1) as the eluent affording colorless needles (78%), mp 128°; nmr (deuteriochloroform): δ 2.43 (s, CH_3 , 3H), 4.25 (s, $\text{CH}_2\text{-CN}$, 2H), 7.10-7.46 (m, H-2, H-3, H-8, 3H, *ArH*), 7.51-7.70 (m, H-4, 1H, *ArH*), 7.79 (s, H-6, 1H, *ArH*), 7.83 (s, H-9, 1H, *ArH*); ms: *m/e* 238 ($M^+ + 1$, 19), 237 (M^+ , 100), 236 (44).

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{NS}$: C, 72.92; H, 4.67; S, 13.51. Found: C, 73.01; H, 4.73; S, 13.68.

1-Cyanomethyl-8-methyldibenzothiophene (17).

This compound was prepared from compound 14 in a similar manner to the preparation of compound 15. An analytical sample was prepared by chromatography on a neutral alumina column using cyclohexane:benzene (1:1) as the eluent affording colorless needles (78%), mp 150-151°; nmr (deuteriochloroform): δ 2.54 (s, CH_3 , 3H), 4.30 (s, $\text{-CH}_2\text{-CN}$, 2H), 7.19-7.56 (m, H-2, H-3, H-7, 3H, *ArH*), 7.62-7.89 (m, H-4, H-6, 2H, *ArH*), 7.85 (s, H-9, 1H, *ArH*); ms: *m/e* 239 ($M^+ + 2$, 5), 238 ($M^+ + 1$, 19), 237 (M^+ , 100), 236 (62).

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{NS}$: C, 75.92; H, 4.67; S, 13.51. Found: C, 75.99; H, 4.77; S, 13.47.

3-Methylphenanthro[4,5-*bcd*]thiophene (21).

Compound 18 was prepared in a similar manner to the preparation of the aldehyde 10 and a tan oil was obtained (65%). The crude aldehyde was used in the next reaction without further purification; ir (neat): 1730 cm^{-1} (C=O); nmr (deuteriochloroform): δ 2.38 (s, CH_3 , 3H), 4.22 (s, CH_2CHO , 2H), 7.08-7.51 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.75 (dd, $J = 1, 8$ Hz, H-4, 1H, *ArH*), 7.80 (dd, $J = 1, 8$ Hz, H-9, 1H, *ArH*).

Compound 21 was prepared from the crude aldehyde 18 in a manner similar to the preparation of compound 11 and colorless crystals were obtained (51%), mp 106-108°. An analytical sample was chromatographed on neutral alumina using hexane as the eluent affording colorless crystals, mp 142°; nmr (deuteriochloroform): δ 2.48 (s, CH_3 , 3H), 7.54-7.92 (m, H-1, H-2, H-5, H-6, H-7, 5H, *ArH*), 8.00 (s, H-8, H-9, 2H, *ArH*); ms: *m/e* 223 ($M^+ + 1$, 20), 222 (M^+ , 100), 221 (95), 111 (18).

Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{S}$: C, 81.04; H, 4.53; S, 14.42. Found: C, 81.36; H, 4.49; S, 14.68.

2-Methylphenanthro[4,5-*bcd*]thiophene (22).

Compound 19 was prepared in a similar manner to the preparation of compound 10 and was obtained as a tan oil (62%). The crude aldehyde 19 was used in the next reaction without any further purification; ir (neat): 1745 cm^{-1} (C=O); nmr (deuteriochloroform): δ 2.30 (s, CH_3 , 3H), 4.20 (s, CH_2CHO , 2H), 7.07-7.53 (m, H-2, H-3, H-8, 3H, *ArH*), 7.78 (s, H-6, 1H, *ArH*), 7.88 (dd, $J = 1, 8$ Hz, H-9, 1H, *ArH*).

Compound 22 was prepared from the crude aldehyde 19 in a manner similar to the preparation of compound 11 and colorless crystals were obtained (46%), mp 135°; nmr (deuteriochloroform): δ 2.71 (s, CH_3 , 3H), 7.70 (s, H-3, 1H, *ArH*), 7.82 (s, H-1, H-5, H-6, H-7, 4H, *ArH*), 7.89 (s, H-8, H-9, 2H, *ArH*); ms: *m/e* 223 ($M^+ + 1$, 19), 222 (100), 221 (97).

Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{S}$: C, 81.04; H, 4.53; S, 14.42. Found: C, 81.36; H, 4.40; S, 14.27.

1-Methylphenanthro[4,5-*bcd*]thiophene (23).

Compound 20 was prepared in a similar manner to the preparation of compound 10 and was obtained as a tan oil (65%). The crude aldehyde 20 was used in the next reaction without any further purification; ir (neat): 1740 cm^{-1} (C=O); nmr (deuteriochloroform): δ 2.33 (s, CH_3 , 3H), 4.21 (s, CH_2CHO , 2H), 7.08-7.52 (m, H-2, H-3, H-7, 3H, *ArH*), 7.58-7.80 (m, H-4, H-6, 2H, *ArH*), 8.01 (s, H-9, 1H, *ArH*).

Compound 23 was prepared from the crude aldehyde 20 in a manner similar to the preparation of compound 11 and colorless crystals were obtained (53%), mp 140°; nmr (deuteriochloroform): δ 2.72 (s, CH_3 , 3H), 7.72 (s, H-2, H-3, H-5, H-6, H-7, 5H, *ArH*), 7.82 (s, H-8, H-9, 2H, *ArH*); ms: *m/e* 223 ($M^+ + 1$, 20), 222 (M^+ , 100), 221 (98).

Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{S}$: C, 81.04; H, 4.53; S, 14.42. Found: C, 81.32; H, 4.70; S, 14.63.

8-Methylphenanthro[4,5-*bcd*]thiophene (25).

n-Butyllithium (4.0 ml of 1.6 *M* solution in hexane) was added *via* a syringe over a period of 15 minutes to a dry mixture of 1-chloromethyl-dibenzothiophene (6) (1.0 g, 4.30 mmoles) and 50 ml of dry ether under nitrogen at -78°. The mixture was allowed to warm to -5° and cooled back to -78°, after which *N,N*-dimethylacetamide (0.41 g, 4.70 mmoles) was added slowly *via* a syringe. The mixture was allowed to warm slowly and was then stirred for six hours at room temperature. It was then poured into ice, the layers separated and extracted twice with 30 ml of ether. The ether layer was dried over magnesium sulfate and evaporated giving a pale yellow oil (70%); ir (neat): 1730 cm^{-1} (C=O). The crude ketone was mixed with 10 g of PPA and heated to 100° for 90 minutes with continuous stirring. After cooling the reaction mixture was poured into ice-water, extracted twice with 30 ml of benzene, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on an alumina column using hexane as the eluent affording colorless crystals (62%), mp 145°; nmr (deuteriochloroform): δ

2.72 (s, CH_3 , 3H), 7.73 (s, H-1, H-2, H-3, H-5, H-6, H-7, 6H, ArH), 7.89 (s, H-9, 1H, ArH); ms: m/e 222 (M^+ , 100), 221 (95).

Anal. Calcd. for $C_{15}H_{10}S$: C, 81.04; H, 4.53; S, 14.42. Found: C, 81.26; H, 4.37; S, 14.20.

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- [1] Present address: Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki, 852, Japan.
- [2] To whom correspondence regarding this work should be addressed at the University of South Florida, Department of Chemistry, Tampa, FL 33620 USA.
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