4c, which would not crystallize: ir (neat) 3300 (NH_2), 3400 (NH_2), 1650 (C=O), and 1630 cm^{-1} (C=C); nmr ($CDCl_3$) τ 1.4–3.6 (m, 17, aromatic and olefinic), 2.52 (s, 2, NH_2, exchanges with D_2O); mass spectrum *m/e* 349. The oil was dissolved in ether and treated with hydrogen chloride gas to prepare the hydrochloride salt, mp 182° dec (depends upon rate of heating).

Anal. Calcd for $C_{25}H_{20}ClNO$: C, 77.8; H, 5.2; N, 3.6; Cl, 9.2. Found: C, 77.5; H, 5.3; N, 3.7; Cl, 8.9.

Reduction of 6-Phenyldibenz[*b,f*]azocine. A.—To 50 ml of liquid ammonia at −78° under nitrogen was added 2.0 g (0.0071 mol) of azocine **3a**. The mixture was stirred while 0.78 g (0.020 g-atom) of potassium was added in small pieces over a 15-min period. The dark suspension was stirred 15 min longer and the solvent was distilled using a water bath at room temperature. The residue was suspended in 100 ml of ether and water was added dropwise. The ether layer was washed well with water and concentrated, and the resulting oil was chromatographed on Florisil. Benzene eluted three solids and ethyl acetate, a residual oil.

The first solid was recrystallized from ethanol and gave 0.90 g (45%) of amine **6**: mp 116–117°; ir (KBr) 3400 cm^{-1} (NH); nmr ($CDCl_3$) τ 2.7–3.5 (m, 13, aromatic), 5.6 (broad s, 1, exchangeable with D_2O, NH), 6.48 H_A, 6.82 H_B, 6.10 H_X (3, aliphatic H, ABX system, J_{AB} = 15.9, J_{AX} = 8.0, J_{BX} = 1.5 Hz, actually on the border between ABX and ABC); mass spectrum *m/e* 283.

Anal. Calcd for $C_{21}H_{17}N$: C, 89.0; H, 6.1; N, 4.9. Found: C, 89.2; H, 6.1; N, 4.7.

The second solid was recrystallized from ethanol and gave 0.20 g (10%) of tetrahydroazocine **8**: mp 105–106°; ir (KBr) 3400 cm^{-1} (NH); nmr ($CDCl_3$) τ 6.2–7.0 (m, 5, NH and ethane protons; one is exchangeable with D_2O), 4.18 (s, 1, methine), 2.4–3.0 (m, 14, aromatic); mass spectrum *m/e* 385.

Anal. Calcd for $C_{21}H_{19}N$: C, 88.4; H, 6.7; N, 4.9. Found: C, 88.4; H, 6.7; N, 4.7.

The third solid was recrystallized from ethanol and afforded 0.15 g (8%) of dihydroazocine **7**: mp 94–95°; ir (KBr) 1620 cm^{-1} (C=N); nmr ($CDCl_3$) τ 6.5–7.5 (m, 4, aliphatic methylenes), 2.1–3.3 (m, 13, aromatic); mass spectrum *m/e* 283.

Anal. Calcd for $C_{21}H_{17}N$: C, 89.0; H, 6.1; N, 4.9. Found: C, 89.0; H, 6.3; N, 4.8.

B.—To 50 ml of liquid ammonia at −78° under nitrogen was added 0.70 g (0.0025 mol) of azocine **3a** followed by 0.196 g (0.0050 g-atom) of potassium in small pieces over 10 min with stirring. After stirring had been continued for 15 min, the solvent was removed by a water bath. The solid was treated with 50 ml of ether, and water was carefully added dropwise. The ether layer was separated, washed well with water, and concentrated. The oil was dissolved in benzene and chromatographed on Florisil. The first fraction contained 0.32 g (45%) of amine **6**, mp 115–116°, after recrystallization from ethanol. The second fraction gave 0.15 g (14%) of starting material, mp 116–118°. The nmr spectra of the crude materials showed no trace of either the dihydroazocine **7** or the tetrahydro compound **8**.

Hydrolysis of 11,12-Dihydro-6-phenyldibenz[*b,f*]azocine (7).—A solution of 0.10 g (0.00035 mol) of imine **7** in 20 ml of 1,2-dimethoxyethane was treated with 1 ml of water and 1 ml of concentrated hydrochloric acid and heated at reflux for 30 min. The solvent was removed in a stream of nitrogen and the residue treated with benzene and aqueous sodium bicarbonate solution. The organic layer was chromatographed on Florisil. The amino ketone **9** was eluted with 10% ethyl acetate-benzene and obtained as a noncrystallizable oil: ir (KBr) 3400 and 3500 (NH_2) and 1660 cm^{-1} (C=O); nmr ($CDCl_3$) τ 7.06 (s, 4, aliphatic), 6.09 (s, 2, NH_2, exchanges with D_2O), 2.0–3.4 (m, 13, aromatic); mass spectrum *m/e* 301.

The oil was dissolved in ether, and hydrogen chloride was passed in until separation of the hydrochloride was complete. The oil crystallized and was collected: 0.080 g (68%); mp 165° dec; ir (KBr) 2850 (NH_3^+) and 1660 cm^{-1} (C=O).

Anal. Calcd for $C_{21}H_{20}ClNO$: C, 74.6; H, 6.0; Cl, 10.5; N, 4.1. Found: C, 74.3; H, 6.0; Cl, 10.2; N, 4.0.

Registry No.—**2a**, 27971-66-0; **2c**, 30319-08-5; **3a**, 30319-09-6; **3c**, 30319-10-9; **4a**, 30319-11-0; **4c**, 30319-12-1; **4c** HCl, 30319-13-2; **6**, 30319-14-3; **7**, 30319-15-4; **8**, 30319-16-5; **9**, 19947-17-2; **9** HCl, 19947-18-3.

Acknowledgment.—The author wishes to express thanks to Dr. T. H. Regan for the nmr spectra and their interpretation and to Mr. D. P. Maier for the mass spectra.

The Synthesis and Metalation of Some Phenalenothiophenes and a Fused Benzo Derivative

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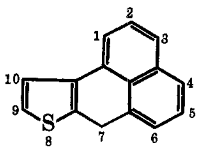
Received February 17, 1971

Three phenalenothiophenes (**1**, **2**, and **3**) have been synthesized by unambiguous methods from the corresponding phenalenothiophenones **4**, **5**, and **6**. Reaction of 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene with glycerol, sulfuric acid, and iron leads to the formation of a mixture of **4** and **5** in contrast to the claim in the literature[4] that only **4** was produced in this reaction. Fusion of 2-(1-naphthoyl)thiophene with an aluminum chloride–sodium chloride–potassium chloride mixture has been shown to produce **4** together with a very small amount of a high-melting dimeric product in contrast to the claim[4] that **5** was the product of this reaction. Metalation of **2** and **3** was shown to occur exclusively at the methylene bridge, the site of metalation being identified by methylation or by deuterium exchange. A benzo derivative of **3**, namely 4*H*-benzo[1,10]phenanthro[3,4-*c*]thiophene, was synthesized and likewise shown to undergo metalation exclusively at the methylene bridge.

Three isomeric 7*H*-phenalenothiophenes[2] are possible, *viz.* 7*H*-phenaleno[2,1-*b*]thiophene (**1**), 7*H*-phenaleno[1,2-*b*]thiophene (**2**), and 7*H*-phenaleno[1,2-*c*]thiophene (**3**). The existence of any of these has not been reported in the literature. This paper describes the synthesis of these compounds and discusses their metalative reactions with *n*-butyllithium.



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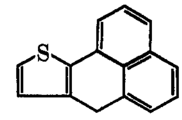

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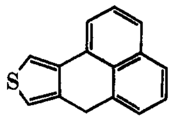

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A logical synthetic route to **1**, **2**, and **3** appeared to lie in reducing the corresponding 7*H*-phenalenothiophenones **4**, **5**, and **6**. The literature contains a few references to the preparation of **4** and **5**. Scholl[3] reported the synthesis of a phenalenothiophenone, mp 210°, in low yield, formulated as **4**, by dehydrogenation of

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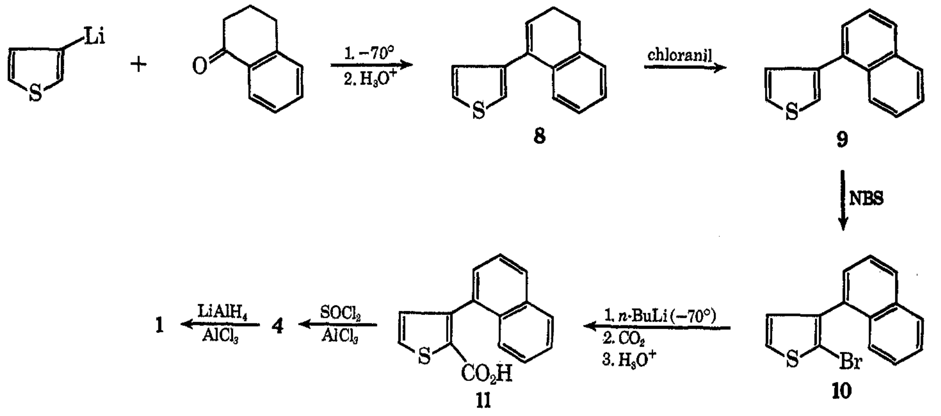
[1] Abstracted from the M.S. Thesis of G. E. Paulovicks, West Virginia University, 1970.

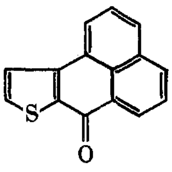
[2] We are indebted to Dr. Kurt L. Loening of Chemical Abstracts Service for information pertaining to the naming of this system.

[3] R. Scholl and C. Seer, *Justus Liebigs Ann. Chem.*, **394**, 111 (1912).

Scheme I



2-(1-naphthoyl)thiophene with aluminum chloride. Weinmayr and coworkers[4] modified Scholl's work by fusing the 2-(1-naphthoyl)thiophene with a mixture of aluminum chloride, sodium chloride, and potassium chloride and obtained a ketone, mp 215–217°, in 6% yield which they formulated as **5**. Inadequate elemental analytical data together with a reconsideration of the mechanism of this reaction led to the suspicion that this ketone is not correctly formulated as **5**.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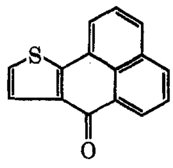
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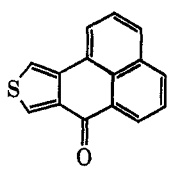
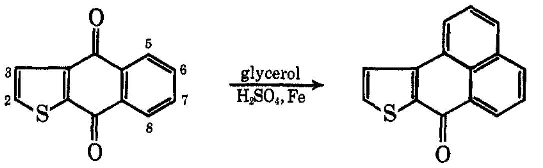

6

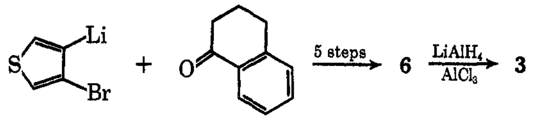
Weinmayr reported that interaction of 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene with glycerol, iron, and sulfuric acid according to the well-known benzanthrone synthesis led exclusively to the formation of **4**, a ketone which they considered to be isomeric with that obtained from the 2-(1-naphthoyl)thiophene. On the basis of the oxidation of this product to give 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene-5-carboxylic acid, the structure was considered confirmed and thus the isomeric phenalenothiophenone obtained by Scholl's method was formulated as **5**. We have reinvestigated this work and have synthesized **4**, **5**, and **6** by unambiguous syntheses.



7*H*-Phenaleno[2,1-*b*]thiophen-7-one (**4**).—Reaction of 1-tetralone with 3-thienyllithium at −70° afforded the crude alcohol which was dehydrated to give the corresponding alkene **8** in 83% yield, which was then dehydrogenated to 3-(1-naphthyl)thiophene (**9**) in 85% yield. Bromination with NBS[5] gave exclusively the 2-bromo-3-(1-naphthyl)thiophene (**10**) which was transformed *via* the corresponding lithio derivative to the acid **11** and hence to the ketone by way of treatment of the acid chloride with aluminum chloride. The ketone **4** had mp 154–155° in contrast to the value reported by Weinmayr[4] for the substance he claimed as **4** (mp 139–140°) (Scheme I).

7*H*-Phenaleno[1,2-*b*]thiophen-7-one (**5**).—The synthetic scheme by which **5** was obtained is similar to that used in the synthesis of **4** and is outlined in Scheme II. In this case the available 3-bromo-2-thienyllithium was the starting heterocyclic moiety. Ketone **5** was an orange solid, mp 154.5–155° (lit.[4] 215–217°).

7*H*-Phenaleno[1,2-*c*]thiophen-7-one (**6**).—Use of 3-bromo-4-thienyllithium instead of 3-bromo-2-thienyllithium in an analogous, synthetic sequence to that used in the preparation of **5** afforded the ketone **6** as an bright yellow solid, mp 165–166°, differing from both **4** and **5** in spectra. The possibility of formation of five-membered ring ketones on cyclization of **11**, **15**, and the corresponding acid precursor of **6** was eliminated by observing that the infrared carbonyl frequencies of **4**, **5**, **6**, and **23** all lay in the range of 1645–1628 cm^{-1}. The infrared carbonyl frequencies of the known indenothiophenones[6a,b] all occurred in the region above 1700 cm^{-1}.



In each case the ketone (**4**, **5**, or **6**) was reduced to the corresponding 7*H*-phenalenothiophene (**1**, **2**, or **3**) by means of mixture of lithium aluminum hydride and aluminum chloride.

Reconsideration of the work of Weinmayr in his claim to have obtained only **4** from 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene led us to suspect that, because of the possibility of reaction at either of the two carbonyl groups, a mixture of **4** and **5** might have been obtained instead of only **4**. Repetition of Weinmayr's work afforded a 51% yield of a bright yellow solid, mp 139–140°, in agreement with Weinmayr's findings. This product exhibited a fairly broad carbonyl absorption in the infrared spectrum. Attempts to separate the components using column chromatography or tlc were unfruitful. Reduction of the product with lithium aluminum hydride–aluminum chloride gave a

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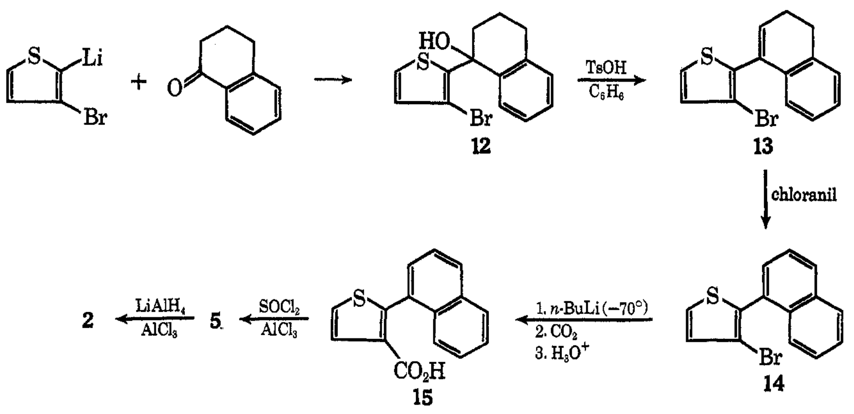
[4] V. Weinmayr, F. S. Palmer, and A. A. Ebert, *J. Amer. Chem. Soc.*, **74**, 4361 (1952).

[5] R. M. Kellogg, A. P. Schaap, E. T. Harper, and H. Wynberg, *J. Org. Chem.*, **33**, 2902 (1968).

[6] (a) D. W. H. MacDowell and T. B. Patrick, *ibid.*, **32**, 2441 (1967); (b) D. W. H. MacDowell and A. T. Jeffries, *ibid.*, **35**, 871 (1970); (c) D. W. H. MacDowell and M. H. Maxwell, *Proc. W. Va. Acad. Sci.*, in press.

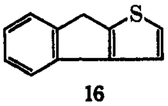
SCHEME II



white solid, the nmr spectrum of which indicated the presence of the two methylene peaks to be expected if the material reduced had consisted of a mixture of the two ketones **4** and **5**. The individual assignments of these two methylene peaks were obtained by comparison with the nmr spectra of authentic **1** and **2** prepared from **4** and **5**. A synthetic (1:1) mixture of **1** and **2** exhibited an nmr spectrum identical with that of the product obtained by reduction of the ketone mixture. Furthermore, a synthetic mixture of ketones **4** and **5** melted at 135–137° and had an ir spectrum identical with that of the product obtained from 4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene by reaction with glycerol.

Careful repetition of the fusion of 2-(1-naphthoyl)-thiophene following the procedures of both Scholl[3] and Weinmayr[4] gave dark resinous material, which upon chromatography over activated alumina in hexane–benzene afforded the ketone **4** rather than **5** as postulated by Weinmayr. Further elution of the column after removal of **4** afforded a yellow solid, mp 235–250°. This solid which was obtained in very small amounts possessed a molecular weight of 470 (mass spectrum) suggesting the formation of a bimolecular product of **4**. It was not investigated further. The literature contains examples of such dimerizations occurring during the reaction of aromatic ketones with fused salts.[3]

Metalation of the Isomeric Phenalenothiophenes.—It has been shown previously that metalation of compounds containing methylene groups attached to thiophene rings depends upon the mode of fusion of the thiophene rings.[6] In the case of the isomeric indenothiophenes **16**, **17**, and **18** below, metalation was shown to occur exclusively at the methylene bridge in



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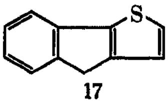

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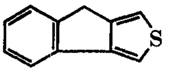

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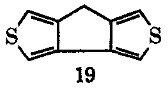

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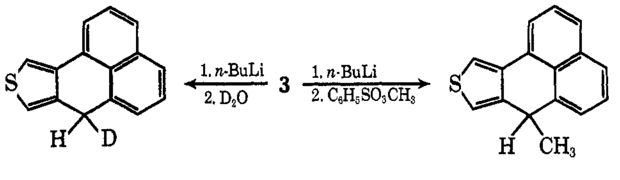
16[6a] and **17**,[6b] while, in the case of **18**,[6b] metalation occurred at the methylene group and at both of the thiophene positions in addition. In the case of **19**[6c] no metalation occurred at the methylene group, substitution occurring only at the two thiophene positions in a 40:60 ratio. The partially or totally diminished methylene metalation was explained on the basis of diminished anionic electron delocalization across the 3,4 bonds of those compounds containing *c*-fused thiophene nuclei in the resulting cyclopentadienoid-like systems.

The metalation of phenalene has been reported by Boekelheide and Larrabee[7] who showed that when phenalene was treated with phenyllithium, followed by the addition of an excess of methyl iodide, methylation occurred. These workers placed the acidity of phenalene intermediate between that of cyclopentadiene and triphenylmethane. They found that attempts to carbonate metalated phenalene yielded base-soluble material from which no carboxylic acid could be obtained.

Reaction of **3** with ethereal *n*-butyllithium at 20° immediately produced a deep blue colored solution. Addition of Dry Ice or DMF yielded solid material in each case which could not be purified due to facile decomposition. Treatment of the deep blue solution with excess methyl benzenesulfonate afforded a methyl derivative which was readily identified as the 7-methyl-7*H*-phenaleno[1,2-*c*]thiophene on the basis of the presence of a clear-cut doublet and quartet in the aliphatic region of the nmr spectrum of the unpurified product. The absence of any signal due to a methyl group attached to an aromatic nucleus and any methylene peaks further confirmed that metalation had occurred exclusively at the methylene group.



Treatment of the metalated **3** with D_2O afforded a white solid product whose nmr spectrum showed a reduction of the signal due to the methylene protons to one-half its original value with the aromatic region remaining unchanged.

Similar treatment of **2** with *n*-butyllithium followed by reaction with Dry Ice or dimethyl sulfate also yielded unstable products which could not be characterized. Treatment of metalated **2** with D_2O, however, led to the isolation of a solid product in whose nmr spectrum the methylene absorption was reduced to

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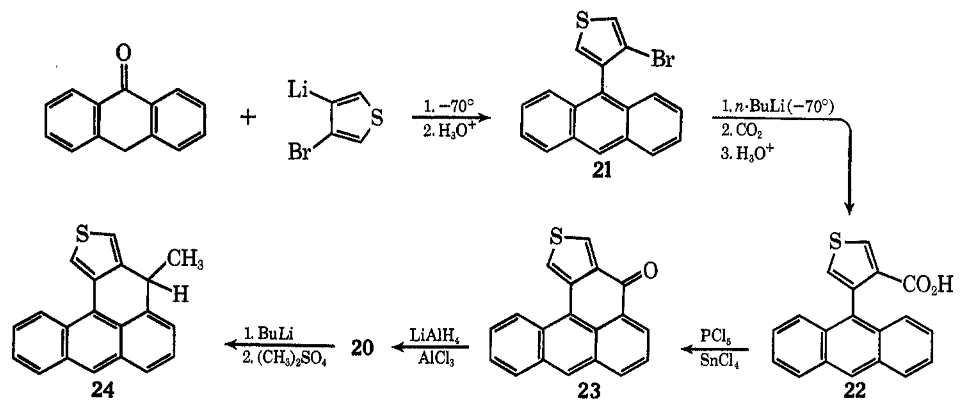
[7] V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.*, **72**, 1245 (1950).

Scheme III

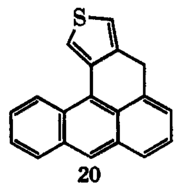


one-half its original value with the aromatic region remaining unchanged.

In view of the exclusive metalation of **2** and **3** at the respective methylene positions, metalation of **1** was not undertaken.

The orientations of metalation, at least in the case of **3**, differ from what might have been expected on the basis of a comparison with the corresponding *c*-fused indenothiophenes and the di-*c*-fused cyclopentadithiophene and probably resides in the increased possibility for delocalization of anionic charge over the naphthalene system.

The fusion of a benzene ring across the 1,2 bond in **3** gives rise to 4*H*-benzo[1,10]phenanthro[3,4-*c*]thiophene[2] (**20**).



20

In work undertaken to ascertain whether the presence of the additional benzene ring might change the metalative properties of **20** compared to **3**, the synthesis of **20** was carried out according to Scheme III.

Dehydration of the tertiary alcohol formed in the first step occurred very readily in the usual work-up. Considerable difficulty was encountered in the cyclization of the acid **22** to product 4*H*-benzo[1,10]phenanthro[3,4-*c*]thiophen-4-one (**23**). Treatment of **22** with thionyl chloride followed by aluminum chloride in carbon disulfide, or benzene or 1,2-dichloroethane or treatment with thionyl chloride followed by stannic chloride in benzene, gave unreacted starting material upon work-up. The ring closure was accomplished in 56% yield by means of phosphorus pentachloride followed by stannic chloride in benzene. Reduction of **23** to **20** in the usual manner proceeded normally in 82% yield.

Treatment of **20** with *n*-butyllithium followed by dimethyl sulfate gave only one product, 4-methyl-4*H*-benzo[1,10]phenanthro[3,4-*c*]thiophene (**24**), with the anticipated quartet and doublet in the nmr spectrum of the unpurified product and shown to be homogeneous by tlc. It is thus seen that fusion of an additional benzene ring into the *c*-fused phenalenothiophene does not cause any change in the site of metalation.

Experimental Section[8]

Synthesis of 3-[1-(3,4-Dihydronaphthyl)]thiophene (**8**).—To a stirred solution of ethereal *n*-butyllithium (87 ml, 1.27 *M*, 0.11 equiv) at −70° under dry nitrogen was added a solution of 16.3 g (0.10 mol) of 3-bromothiophene in 25 ml of dry ether. To the resulting solution, maintained at −70°, was added a solution of 1-tetralone (12.1 g, 0.083 mol) in 25 ml of dry ether. The mixture was stirred at −70° for about 1 hr and then at room temperature for 2.5 hr. The mixture was then hydrolyzed and worked up to give 20 g of crude alcohol, which was dehydrated by refluxing a benzene solution with *p*-toluenesulfonic acid using a Dean–Stark trap. Evaporation of the solvent after removal of traces of acid by means of sodium bicarbonate solution gave a brown-orange oil, 18.5 g (88%). The oil was purified by distillation under reduced pressure: bp 112–113° (0.05 mm); $n^{20}{}_D$ 1.6550; 13.5 g (63%); ir (neat) 3100, 3070, 3030, 2950, 2880, 2840 cm^{-1}; nmr (CCl_4) τ 2.75–3.05 (7 H, m, aromatic), 3.95 (1 H, t, vinyl), 7.25 (2 H, m, CH_2), 7.7 (2 H, m, CH_2). *Anal.* Calcd for $C_{14}H_{12}S$: C, 79.19; H, 5.70; S, 15.11. Found: C, 79.20; H, 5.51; S, 14.83.

3-(1-Naphthyl)thiophene (**9**).—To a stirred refluxing solution of chloranil (27.0 g, 0.11 mol) in 125 ml of xylene was added dropwise a solution of olefin (21.1 g, 0.1 mol) in 50 ml of xylene. The mixture was refluxed with stirring for 20 hr. The xylene was removed, and the resulting red oil was passed through a column of alumina using hexane as an eluent. The yellow-orange oil resulting from evaporation of the hexane was distilled and the fraction, bp 115–116° (0.05 mm), was collected as a colorless oil: 18.5 g (88%); $n^{20}{}_D$ 1.6892, (lit.[9] $n^{20}{}_D$ 1.6892); ir (neat) no aliphatic absorption; nmr (CCl_4) τ 1.95–2.40 (3 H, m, arom), 2.55–2.6 (3 H, d, arom), 2.7–2.9 (4 H, m, arom). *Anal.* Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.88; H, 4.75; S, 15.42.

2-Bromo-3-(1-naphthyl)thiophene (**10**).—A mixture of **9** (12.6 g, 0.06 mol) and NBS (10.8 g, 0.06 mol) dissolved in 300 ml of a 1:1 chloroform–acetic acid solution was heated under gentle reflux for 0.5 hr. By this time all the NBS had dissolved to give an orange colored solution. The reaction mixture was then diluted with an equal volume of water, and the chloroform layer was separated, washed with sodium hydroxide and water, and then dried ($MgSO_4$). The resulting oil was chromatographed in hexane over alumina to give 13.5 g (78%) of white solid, mp 80–82°. Recrystallization from hexane gave 11.7 g (67%) of **10**: mp 82–83°; nmr (CCl_4) τ 2.05–2.25 (2 H, m, arom), 2.50–2.75 (6 H, m, arom), 3.05 (1 H, d, J = 5.5 Hz, H_4 on thiophene). *Anal.* Calcd for $C_{14}H_9BrS$: C, 58.14; H, 3.14; Br, 27.63; S, 11.09. Found: C, 58.35; H, 3.02; Br, 27.49; S, 10.87.

3-(1-Naphthyl)thiophene-2-carboxylic Acid (**11**).—To a stirred solution of 47 ml of 1.2 *M* *n*-butyllithium maintained under dry nitrogen at −70° was added dropwise a solution of the bromide

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[8] All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nuclear magnetic resonance spectra were recorded on a Varian HA-60 spectrometer using tetramethylsilane as an internal standard (τ 10) and solvents as specified. Infrared spectra were recorded on a Perkin-Elmer Model 127 and Beckman IR-8 spectrophotometer. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 spectrophotometer.

[9] H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *J. Amer. Chem. Soc.*, **89**, 3487 (1967).

10 (14.9 g, 0.051 mol) dissolved in dry ether (25 ml). The mixture was stirred at −70° for 0.5 hr after the addition was complete. The resulting solution of the lithium salt was then added to a large excess of Dry Ice suspended in anhydrous ether. After standing for 1 hr, the mixture was allowed to warm to room temperature and was decomposed with ice and water. The ether layer was separated and extracted with sodium bicarbonate, and the basic extracts were added to the water layer. Acidification of the water layer afforded the desired acid, 12.4 g, mp 170–175°. Recrystallization from benzene–hexane (1:1) gave 11.0 g (84%) of acid, mp 181–183°; an analytical sample melted at 187.5–188°: ir (KBr) 3000–2500 (broad, OH), 1660 cm^{-1} (CO_2H); nmr (d_6-DMSO) τ 2.6 (1 H, hump, CO_2H), 1.90–2.15 (3 H, m, arom), 2.30–2.70 (5 H, m, arom), 2.85 (1 H, d, J = 5 Hz, H_4 on thiophene). *Anal.* Calcd for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.96; S, 12.61. Found: C, 70.80; H, 3.89; S, 12.90.

7*H*-Phenaleno[2,1-*b*]thiophen-7-one (4).—A mixture of acid **11** (5.0 g, 0.0195 mol) and thionyl chloride (25 ml) was heated under reflux for 1 hr. Excess thionyl chloride was removed by codistillation with benzene and the solid acid chloride remaining was dissolved in carbon disulfide (50 ml) and added to a suspension of aluminum chloride (5 g) in carbon disulfide (50 ml) at room temperature. The resulting deep red mixture was stirred for 2 hr and was then decomposed with ice and water. Removal of the CS_2 gave a yellow solid which was dissolved in chloroform and the solution extracted with sodium bicarbonate solution. Evaporation gave a yellow solid which was chromatographed over alumina with benzene as eluent to yield 4.0 g (87%) of 7*H*-phenaleno[2,1-*b*]thiophen-7-one (**4**), mp 153–154°. An analytical sample (benzene) had mp 154.5–155°: ir (KBr) 3080, 1628 cm^{-1} (CO); nmr ($CDCl_3$) τ 1.35 (1 H, m, H_6), 1.82–2.7 (7 H, m, arom); uv λ_{max} (95% C_2H_5OH) 245 nm (ϵ 20,500), 256 (16,800), 336 (8280), 370 (8280). *Anal.* Calcd for $C_{15}H_8OS$: C, 76.24; H, 3.41; S, 13.57. Found: C, 76.23; H, 3.51; S, 13.71.

7*H*-Phenaleno[2,1-*b*]thiophene (1).—To a solution of aluminum chloride (3.4 g, 0.025 mol) and lithium aluminum hydride (0.96 g, 0.025 mol) in 50 ml of ether was added, in small portions with stirring, ketone **4** (3.0 g, 0.0126 mol). The mixture was refluxed with stirring for 17 hr. After hydrolysis with dilute sulfuric acid, the ether layer was extracted with sodium bicarbonate solution and dried ($MgSO_4$). The red solid that remained upon removal of the ether was dissolved in hexane and the solution chromatographed over alumina to give a pale yellow solid, 1.7 g (64%), mp 55–57°. Rechromatography in hexane over alumina give 1.5 g of white solid, mp 62–64°. Recrystallization from hexane raises the melting point to 63–64°. The reduced compound is moderately stable but yellows upon standing at room temperature. An analytical sample melted at 64–65°: ir (KBr) 3050, 2950, 2850 cm^{-1}; nmr (CCl_4) τ 2.5–3.0 (8 H, m, arom), 5.5 (2 H, singlet, CH_2); uv λ_{max} (95% C_2H_5OH) 232 nm (ϵ 32,400), 322 (5330), 334 (6770), 352 (4900). *Anal.* Calcd for $C_{15}H_{10}S$: C, 81.04; H, 4.53; S, 14.43. Found: C, 80.87; H, 4.52; S, 14.60.

3-Bromo-2-[1-hydroxy-1-(1,2,3,4-tetrahydronaphthyl)]thiophene (12).—To a solution of 3-bromo-2-thienyllithium prepared from 2,3-dibromothiophene (19.8 g, 0.082 mol) and ethereal *n*-butyllithium at −70° was added an ethereal solution of 1-tetralone (11.9 g, 0.082 mol). The reaction temperature was maintained at −70° until the addition was completed. The mixture was then stirred for 2 hr at room temperature and decomposed by pouring into an ice-water solution containing 0.6 equiv of HCl, and the ether layer separated. The water layer was saturated with NaCl and extracted with ether. The ether portions were combined and washed successively with water, saturated $NaHCO_3$, water, and brine and then dried ($MgSO_4$). Evaporation of the ether gave 25.7 g of crude alcohol **12**. Recrystallization from hexane gave 15.4 g (60.6%) of white crystals: mp 85–86°; ir (KBr) 3600–3400 cm^{-1} (OH); nmr (CCl_4) τ 2.9–3.3 (6 H, arom), 7.0–8.2 (7 H, aliphatic and OH). *Anal.* Calcd for $C_{14}H_{13}BrOS$: C, 54.34; H, 4.23; Br, 25.83; S, 10.37. Found: C, 54.54; H, 4.34; Br, 26.02; S, 10.37.

3-Bromo-2-[1-(3,4-dihydronaphthyl)]thiophene (13).—The alcohol **12** (5.0 g, 0.016 mol) was dissolved in benzene. A catalytic amount of *p*-toluenesulfonic acid was added and the solution was refluxed until water was no longer collected. Crude olefin **13** (4.8 g) which could not be crystallized was obtained. Distillation gave a light yellow oil, bp 154° (1.1 mm). Chromatography over alumina (hexane) failed to provide any additional purification: ir (neat) 3120–3000, 2940 cm^{-1}; nmr (CCl_4) τ 2.8–3.3 (6, H, arom), 3.75–3.95 (1 H, olefinic), 7.0–7.9 (6 H, aliphatic).

3-Bromo-2-(1-naphthyl)thiophene (14).—A solution of the olefin **13** (4.95 g, 0.017 mol) in 20 ml of xylene was added dropwise to a stirred solution of chloranil (4.65 g, 0.019 mol) in anhydrous xylene (30 ml) at reflux. After the addition was completed the mixture was refluxed for 11 hr, cooled, and allowed to stand overnight. The solution was washed with 2 *M* NaOH solution until the alkaline solution was colorless and then washed with water and dried ($MgSO_4$). The mixture was concentrated and chromatographed over Al_2O_3 (1:1 hexane–benzene). Recrystallization (hexane) gave 3.85 g (78%) as clusters of colorless needles, analytical sample, mp 83–84° (sublimation). *Anal.* Calcd for $C_{14}H_9BrS$: C, 58.14; H, 3.14; Br, 27.64; S, 11.05. Found: C, 58.08; H, 3.11; Br, 27.70; S, 10.85.

2-(1-Naphthyl)thiophene-3-carboxylic Acid (15).—A 1.08 *M* *n*-butyllithium solution (34.5 ml, 37.2 mequiv) in 100 ml of dry ether was added to a special reaction flask which had been previously flame-dried and flushed with N_2. The solution was cooled to −70° and kept under a N_2 atmosphere. To the above stirred solution was added dropwise a solution of 10.0 g (34.6 mmol) of **14** in dry ether. After addition, the reaction mixture was stirred for 0.5 hr at −70° and was then added dropwise to a stirred ether–Dry Ice slurry. The mixture was allowed to warm to room temperature and was poured onto cracked ice and HCl. The white precipitate which formed was extracted with ether. The ether solution was extracted with aqueous NaOH, and the product precipitated by addition of HCl and again extracted into ether. The ether was evaporated and left 7.3 g of a white powder. Recrystallization from acetonitrile gave 6.5 g (74%) of colorless needles: mp 223–225°; ir (KBr) 3500–2100, (OH), 1660 cm^{-1} (C=O); nmr (DMSO) τ −2.4 (1 H, OH), 1.8–2.5 (9 H, arom). *Anal.* Calcd for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.96; S, 12.61. Found: C, 71.02; H, 3.99; S, 12.83.

7*H*-Phenaleno[1,2-*b*]thiophen-7-one (5).—The acid chloride of **15** (ir 1750–1720 cm^{-1}) was prepared by addition of 7.0 g (0.028 mol) of the acid **15** to 35 ml of freshly distilled thionyl chloride with refluxing for 1 hr. Excess $SOCl_2$ was removed by repeated codistillation with benzene. The remaining dark oil was not purified but was dissolved in 50 ml of CS_2 and added dropwise at room temperature to a stirred mixture of $AlCl_3$ (7.0 g, 0.05 mol) in 250 ml of CS_2. The reaction mixture was stirred for 3 hr after addition of the acid chloride was complete and was then poured into an ice–water mixture. The CS_2 was removed by distillation and the aqueous portion was extracted with $CHCl_3$. The organic portions were combined, washed with $NaHCO_3$ and water, and dried ($MgSO_4$). The $CHCl_3$ was evaporated and left a solid orange material which was sublimed: yield of pure ketone 4.4 g (68%); mp 153–154°; ir (KBr) 1645 cm^{-1}; uv (cyclohexane) λ_{max} 238.8 nm (ϵ 20,000), 254 (17,000), 260.4 (19,000), 354 (5700); nmr ($CDCl_3$) τ 1.2–2.8 (arom); analytical sample, mp 154–155° sublimed. *Anal.* Calcd for $C_{15}H_8OS$: C, 76.25; H, 3.41; S, 13.57. Found: C, 76.11; H, 3.43; S, 13.37.

7*H*-Phenaleno[1,2-*b*]thiophene (2).—To a stirred suspension of $AlCl_3$ (40.25 g, 0.302 mol) and $LiAlH_4$ (5.91 g, 0.156 mol) in a 250 ml of dry ether under N_2 was added *via* Gooch tubing solid ketone **5**, 5.0 g (0.021 mol). On addition of **5** the reaction mixture turned red. The color soon faded and the mixture acquired a light yellow color. After addition was complete the mixture was refluxed for 15 hr and then poured over ice to give a white precipitate. The ether phase was separated, the aqueous portion was extracted with ether, and the ether portions were combined, washed with water, saturated $NaHCO_3$, and brine, and dried ($MgSO_4$). Concentration of the ether solution and chromatography over alumina (hexane) gave 3.9 g (83%) of **2**: analytical sample mp 57.5–59° recrystallized from pentane as colorless plates; ir (KBr) 3040 cm^{-1}; uv (cyclohexane) λ_{max} 247 nm (ϵ 22,000), 330.7 (15,000), 346.4 (20,000), 359.5 (14,000), 364.7 (15,000); nmr (CS_2) τ 2.3–3.3 (8 H, m, arom), 5.6 (2 H, s, aliphatic). *Anal.* Calcd for $C_{15}H_{10}S$: C, 81.04; H, 4.53; S, 14.43. Found: C, 80.85; H, 4.63; S, 14.32.

3-Bromo-4-[1-hydroxy-1-(1,2,3,4-tetrahydronaphthyl)]thiophene.—To a solution of 3-bromo-4-thienyllithium prepared from 3,4-dibromothiophene (40 g, 0.165 mol) and ethereal *n*-butyllithium at −70° was added a solution of 1-tetralone (24.1 g, 0.165 mol) in 40 ml of ether. The reaction temperature was maintained at −70° for 1 hr. The mixture was then stirred at room temperature for 2 hr and was decomposed with 2 *M* HCl. The ether solution was washed with sodium bicarbonate solution and dried ($MgSO_4$). Evaporation left 43.6 g of crude alcohol as a yellow viscous oil which, upon standing in a refrigerator, solidified. Recrystallization of the alcohol from hexane gave white needles (27.0 g, 53%), mp 86–88°. An analytical sample (hexane) melted at 88–90°: ir (KBr) 3600–3400 cm^{-1} (OH); nmr (CCl_4) τ 2.65 (1 H, d, J = 3.5 Hz, H_5), 2.9–3.3 (5 H, m, arom), 7.1–8.3 (7 H, aliphatic and OH). *Anal.* Calcd for $C_{14}H_{13}BrOS$: C, 54.37; H, 4.24; Br, 25.84; S, 10.37. Found: C, 54.50; H, 4.22; Br, 26.03; S, 10.36.

3-Bromo-4-[1-(3,4-dihydronaphthyl)]thiophene.—Dehydration of 20.0 g (0.065 mol) of the above alcohol with *p*-toluenesulfonic acid in refluxing benzene for 3 hr as before gave the corresponding crude olefin (16.1 g). Recrystallization from hexane (Norit) gave solid olefin: 12.4 g (66%); mp 68–70°; ir (neat) 3110, 3070, 3030, 2940, 2890, 2840 cm^{-1}; nmr (CCl_4) τ 2.9–3.4 (6 H, m, arom), 4.1 (1 H, t, vinyl), 7.1–7.9 (4 H, m, aliphatic). *Anal.* Calcd for $C_{14}H_{11}BrS$: C, 57.74; H, 3.81; Br, 27.44; S, 11.01. Found: C, 57.58; H, 3.91; Br, 27.58; S, 11.05.

3-Bromo-4-(1-naphthyl)thiophene.—A solution of chloranil (14 g, 0.056 mol) in 60 ml of xylene was refluxed with stirring under anhydrous conditions while a solution of the above olefin (15 g, 0.052 mol) in 60 ml of xylene was added dropwise. The resulting mixture was refluxed with stirring for 24 hr. Some solid material which had separated upon cooling was removed and the cold solution was extracted with 2 *M* sodium hydroxide. Removal of solvent from the dried ($MgSO_4$) xylene extract gave a red oil which was dissolved in a minimum amount of benzene and chromatographed over alumina using hexane as eluent to give white crystals (8.8 g, 58%), mp 61–63°. An analytical sample (hexaane had mp 62–63°: ir (KBr) 3120, 3060 cm^{-1}, no aliphatic peaks; nmr (CCl_4) τ 2.1–2.9 (m, arom). *Anal.* Calcd for $C_{14}H_9BrS$: C, 58.14; H, 3.14; Br, 27.63; S, 11.09. Found: C, 57.97; H, 3.21; Br, 27.70; S, 10.92.

3-(1-Naphthyl)thiophene-4-carboxylic Acid.—To a stirred solution of 46 ml of 1.5 *M* *n*-butyllithium maintained under dry nitrogen at −70° was added dropwise a solution of the above bromide (20 g, 0.07 mol) dissolved in dry ether (50 ml). The mixture was stirred at −70° for 0.5 hr, after the addition was complete. The resulting solution of the lithium salt was then added to a large excess of Dry Ice suspended in anhydrous ether. After standing for 1 hr, the mixture was allowed to warm to room temperature and was decomposed with ice and water. The ether layer was separated and extracted with $NaHCO_3$, and the basic extracts were added to the water layer. Acidification of the water layer afforded the desired acid, 14.4 g, mp 203–205°. Recrystallization from acetonitrile gave white solid: 13.5 g (76%); mp 210–221°; ir (KBr) 3100–2500 (OH), 1675 cm^{-1} (CO); nmr (DMSO-d_6) τ 1.5 (1 H, d, J = 3.5 Hz, H_5 on thiophene), 1.8–2.1 (2 H, m, arom), 2.3–2.6 (6 H, m, arom). *Anal.* Calcd for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.96; S, 12.61. Found: C, 71.03; H, 4.05; S, 12.59.

***7H*-Phenaleno[1,2-*c*]thiophen-7-one (6).**—A mixture of the above acid (5.0 g, 0.0195 mol) and thionyl chloride (25 ml) was heated under reflux for 1 hr. Excess thionyl chloride was removed by codistillation with benzene and the solid acid chloride remaining was dissolved in carbon disulfide (50 ml) and added to a suspension of aluminum chloride (5 g) in carbon disulfide (50 ml) at room temperature. The resulting deep red mixture was stirred for 2 hr and was then decomposed with ice and water. Removal of CS_2 gave a yellow-brown solid, which was dissolved in chloroform, and the solution extracted with $NaHCO_3$ solution and dried ($MgSO_4$). Evaporation gave a yellow-brown solid (3.8 g) which was sublimed to yield 2.8 g (61%) of bright yellow solid, mp 161–163°. Recrystallization from glacial acetic acid afforded 2.6 g (57%) of ketone **6** as bright yellow needles: mp 165–166°; ir (KBr) no aliphatic peaks, 1645 cm^{-1} (CO); nmr ($CDCl_3$) τ 1.5 (1 H, broad d, H_6), 1.7 (1 H, d, J = 3 Hz, H_8), 2.0–2.6 (6 H, m, arom); uv λ_{max} (95% C_2H_5OH) 234 nm (ϵ 49,300), 264 (8800), 296 (10,600). *Anal.* Calcd for $C_{15}H_8OS$: C, 76.24; H, 3.41; S, 13.41. Found: C, 76.43; H, 3.51; S, 13.47.

***7H*-Phenaleno[1,2-*c*]thiophene (3).**—To a solution of aluminum chloride (3.4 g, 0.025 mol) and lithium aluminum hydride (0.96 g, 0.025 mol) in 50 ml of dry ether was added, in small portions with stirring, ketone **6** (3.0 g, 0.013 mol). The mixture was refluxed for 22 hr. After hydrolysis with dilute sulfuric acid, the ether layer was extracted with $NaHCO_3$ solution and dried ($MgSO_4$). The yellow solid that remained upon removal of the ether was dissolved in hexane and the solution chromatographed over alumina to give a pale yellow solid, mp 83–84°. Rechromatography in hexane over alumina yielded 1.9 g of white solid (70%), mp 84–85°. Recrystallization from hexane gave an analytical sample: mp 85–86°; ir (KBr) 3110, 3060, 2940, 2860 cm^{-1}; nmr (CCl_4) τ 2.4–3.2 (8 H, m, arom), 5.70 (2 H, s, CH_2); uv λ_{max} (95% C_2H_5OH) 228 nm (ϵ 26,700), 314 (5100), 326 (11,000), 343 (10,200). *Anal.* Calcd for $C_{15}NH_{10}S$: C, 81.04; H, 4.53; S, 14.43. Found: C, 80.97; H, 4.71; S, 14.21.

Metalation of *7H*-Phenaleno[1,2-*c*]thiophene (3). A. 7-Methyl-*7H*-phenaleno[1,2-*c*]thiophene.—To a solution of **3** (1.0 g, 0.0046 mol) in dry ether (50 ml) at room temperature was added 2.4 ml of 1.94 *M* *n*-butyllithium (0.0046 equiv) with stirring. The color of the solution changed from yellow to deep blue. After the addition was complete, the blue solution was stirred an additional 15 min before it was added to a solution of methyl benzenesulfate (0.86 g, 0.005 mol) in dry ether (25 ml). The resulting orange solution was hydrolyzed with water and extracted with ether. Evaporation yielded 1.1 g of a red-brown oil. Chromatography in hexane over alumina gave 0.55 g (50%) of a white solid, mp 85–88°. Recrystallization from isopropyl alcohol gave an analytical sample: mp 89–90°; ir (KBr) 3100, 3050, 2970, 2930 cm^{-1}; nmr (CCl_4) τ 2.2–3.0 (8 H, m, arom), 5.55 (1, H q, methine, J = 7.5 Hz), 8.50 (3 H, d, methyl, J = 7.5 Hz); uv λ_{max} (95% C_2H_5OH) 230 nm (ϵ 26,900), 314 (7080), 324 (11,300), 342 (10,000). *Anal.* Calcd for $C_{16}H_{12}S$: C, 81.31; H, 5.12; S, 13.57. Found: C, 81.47; H, 4.96; S, 13.36.

B. 7-Deuterio-*7H*-phenaleno[1,2-*c*]thiophene.—To a solution of **3** (0.5 g, 0.0023 mol) in dry ether (25 ml) at room temperature was added 2.7 ml of 0.84 *M* *n*-butyllithium (0.0023 equiv) with stirring. The deep blue solution was added to D_2O (5 ml) and worked up as above. The resulting yellow-brown solid was purified over Florisil using hexane as the eluent. A peach-colored solid was obtained: mp 84–85°; nmr (CCl_4) 2.2–3.0 (8 H, m, arom), 5.7 (1 H, s, CDH).

Metalation of *7H*-Phenaleno[1,2-*b*]thiophene (2).—To 2.0 g (0.0083 mol) of **2** in 50 ml of dry ether under N_2 in a flame-dried special reaction flask was added 7.3 ml of 1.23 *M* *n*-butyllithium (8.85 mequiv) in 50 ml of dry ether at room temperature. The solution turned red on formation of the anion. After addition of the *n*-butyllithium was complete (about 30 min), the solution was stirred for 15 min and then added dropwise at room temperature to D_2O. Work-up followed the procedure used for **3** and afforded 1.5 g of a white solid: mp 57–58.5°; nmr (CS_2) τ 2.3–3.3 (8, m, arom), 5.6 (1, s, CDH).

Interaction of 4,9-Dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene with Glycerol, Sulfuric Acid, and Iron.—4,9-Dioxo-4,9-dihydronaphtho[2,3-*b*]thiophene (10.7 g, 0.05 mol) was dissolved in 98% sulfuric acid (82.5 g) to give a deep red solution. Water (13 ml) containing copper(II) sulfate (0.2 g) was then added dropwise to the stirred solution and the temperature was allowed to rise to 110°. Glycerol (9.5 g, 0.13 mol) and iron filings (4.9 g, 0.09 g-atom) were added uniformly over a 1-hr period at the reaction temperature, 116–117°. The temperature was maintained for 4 hr before the dark reaction mixture was poured into water and heated to boiling. The mixture was then cooled and filtered. The dark solid mass was air-dried and extracted with benzene in a Soxhlet apparatus. Evaporation of the dark benzene solution yielded 7.2 g of brown solid. Chromatography in benzene over alumina yielded a bright yellow solid, mp 135–137°. Recrystallization from benzene (Norite) gave 6.0 g (51%): mp 139–140°; ir (KBr) 1635 cm^{-1} (C=O); nmr ($CDCl_3$) τ 1.5 (1 H, m, H_6), 2.0–2.9 (7 H, m, arom); uv λ_{max} (95% C_2H_5OH) 240 nm (ϵ 18,600), 258 (15,800), 336 (6150). *Anal.* Calcd for $C_{15}H_8OS$: C, 76.24; H, 3.41; S, 13.57. Found: C, 76.47; H, 3.53; S, 13.37.

Reduction of the Above Ketonic Product.—To a solution of aluminum chloride (2.24 g, 0.016 mol) and lithium aluminum hydride (0.68 g, 0.016 mol) in 25 ml of ether was added, in small portions with stirring, the above ketonic product (1.9 g, 0.008 mol); the mixture was refluxed with stirring for 20 hr. Work-up followed by chromatography in hexane over alumina gave 0.9 g (51%) of a pale yellow solid, mp 43–47°. Sublimation gave 0.75 g (43%) of white solid, mp 44–46°. An additional sublimation gave an analytical sample: mp 45–46°; nmr (CCl_4) τ 2.5–3.1 (15 H, m, arom), 3.3 (1 H, d, J = 5 Hz, H_8 on [1,2-*b*] isomer), 5.6 (2 H, s, CH_2), 5.75 (2 H, s, CH_2); uv λ_{max} (95% C_2H_5OH) 234 nm (ϵ 23,900), 332 (8640), 346 (8400), 364 (3700). *Anal.* Calcd for $C_{15}H_{10}S$: C, 81.04; H, 4.53; S, 14.43. Found: C, 81.16; H, 4.72; S, 14.20.

A mixture of equal amounts (25 mg) of synthetic samples of **1** and **2**, dissolved in CCl_4, gave the following nmr spectrum: τ

2.4–3.0 (15 H, m, arom), 3.3 (1 H, d, $J = 5$ Hz, H_8 on [1,2-*b*]), 5.5 (2 H, s, CH_2), 5.7 (2 H, s, CH_2).

Fusion of 2-(1-Naphthoyl)thiophene with Aluminum Chloride, Sodium Chloride, and Potassium Chloride.—2-(1-Naphthoyl)thiophene, 16.0 g (0.067 mol), was slowly added (0.5 hr) with stirring to a beaker containing NaCl (18.0 g, 0.31 mol), $AlCl_3$ (130.5 g, 0.98 mol), and KCl (15.3 g, 0.15 mol) fused at 120–130°. After the addition was complete the mixture was stirred for 20 min. The temperature was then raised to 150° and allowed to cool immediately to 120°. The mixture, a dark red melt, was poured into cold water. The precipitate, a dark green resinous material (24 g), was filtered off, dried (vacuum desiccator), and extracted in a Soxhlet extractor (benzene) overnight. The benzene solution was concentrated to about 200 ml and was chromatographed on alumina activated at 350°. After 8 hr of eluting with benzene, the alumina was extracted and the middle portion separated; 0.67 g of a bright yellow material was isolated and purified by sublimation 135° (0.075 mm), mp 154°. Mixture melting point with authentic 7*H*-phenaleno[1,2-*b*]thiophen-7-one gave no depression. Mixture melting point with authentic 7*H*-phenaleno[2,1-*b*]thiophen-7-one (mp 154°) gave mp 134°, a depression of 20°; ir and uv identical with **4**.

An orange band near the top of the column was isolated and yielded a small amount of an orange material (0.035 g), mp 235–250° (CH_3CN). No further purification attainable: ir (KBr) 1640 cm^{-1}; nmr unavailable because of insolublility. The mass spectrum showed a parent peak at *m/e* 470.

3-Bromo-4-(9-anthryl)thiophene (21).—An ethereal solution of 4-bromo-3-thienyllithium prepared from 3,4-dibromothiophene (6.17 g, 0.026 mol) was added at −70° to a stirred suspension of anthrone (4.85 g, 0.025 mol) in ether (100 ml) also at −70°. The mixture was allowed to warm to room temperature and hydrolyzed with ice and hydrochloric acid, and the solution washed with sodium bicarbonate and dried. Evaporation of the solvent left a yellow-brown solid (6.3 g) which upon chromatography of its solution in benzene over alumina followed by recrystallization from benzene yielded 5.5 g (65%) of a light yellow solid: mp 123.5–125°; ir (KBr) 3100, 3050, 785, 730 cm^{-1}; nmr (CS_2) τ 1.60 (1 H, s, H_{10} of anthracene), 2.04 (2 H, m, thiophene), 2.64 (8 H, m, anthracene). *Anal.* Calcd for $C_{18}H_{11}BrS$: C, 63.72; H, 3.27; Br, 23.56; S, 9.45. Found: C, 63.94; H, 3.34; Br, 23.38; S, 9.25.

4-(9-Anthryl)thiophene-3-carboxylic Acid (22).—Treatment of 3-bromo-4-(9-anthryl)thiophene (8.4 g, 0.025 mol) in ether (100 ml) at −70° with 25.45 ml of 1.08 *M* *n*-butyllithium (0.028 mol) followed by stirring at −70° for 30 min gave the lithio derivative which was poured onto a suspension of Dry Ice in ether. Work-up in the usual manner gave a light brown solid which upon recrystallization from glacial acetic acid yielded 5.9 g (77%) of white needles: mp 285–287°; ir (KBr) 3650–2400, 1675 cm^{-1}; nmr (polysol-*d*) τ 1.44 (2 H, m, 1 or 8, and 10 proton of anthracene), 1.94 (2 H, m, anthracene), 2.61 (7 H, m, aromatic). *Anal.* Calcd for $C_{19}H_{12}O_2S$: C, 74.97; H, 3.89; S, 10.54. Found: C, 75.07; H, 4.00; S, 10.37.

***4H*-Benzo[1,10]phenanthro[3,4-*c*]thiophen-4-one (23).**—A suspension of the acid **22** (5.02, 0.017 mol) in benzene (50 ml) was treated with phosphorus pentachloride (3.43 g, 0.017 mol) with cooling in ice. The mixture was then allowed to warm to room temperature and stirred under reflux for 1 hr. To the solution (cooled to 0°) was slowly added a solution of anhydrous stannic chloride (8.88 g, 0.034 mol) in benzene (50 ml). The mixture was heated under reflux for 15 hr by which time its color had changed from light green to deep purple. The mixture was then hydrolyzed by adding concentrated HCl and stirring at 0° for 1 hr. Extraction with ether followed by the usual work-up gave crude brown material (3.3 g) which upon chromatography in benzene over alumina gave 2.67 g (56%) of orange fibrous **23**: mp 178.5–179°; ir (KBr) 1645 cm^{-1} (C=O); nmr (TFA) τ 2.10 (1 H, s, H_{10} anthracene), 2.41 (1 H, d, H_1 of anthracene), 3.00 (8 H, m, anthracene). *Anal.* Calcd for $C_{19}H_{10}OS$: C, 79.69; H, 3.52; S, 11.20. Found: C, 79.73; H, 3.32; S, 11.07.

***4H*-Benzo[1,10]phenanthro[3,4-*c*]thiophene (20).**—To a mixture of aluminum chloride (2.35 g, 0.018 mol) and lithium aluminium hydride (0.333 g, 0.0088 mol) in ether (50 ml) under dry nitrogen was slowly added 1.00 g (0.0035 mol) of 4*H*-benzo-[1,10]phenanthro[3,4-*c*]thiophen-4-one (**23**). The mixture was heated under reflux for 20 hr, cooled, and hydrolyzed with ice and 3 *M* sulfuric acid. The usual work-up afforded an amber oil (0.85 g) which was chromatographed in benzene solution over alumina to yield a light yellow solid which was recrystallized from hexane to give pure 4*H*-benzo[1,10]phenanthro[3,4-*c*]thiophene (**20**) as a yellow solid (0.781 g, 82%): mp 135–136.5°; ir (KBr) 3115, 2930 cm^{-1}; nmr (CS_2) τ 1.10 (1 H, m, H_1 of anthracene), 1.79 (1 H, s, H_{10} of anthracene), 2.40 (8 H, m, arom), 5.62 (2 H, s, CH_2). *Anal.* Calcd for $C_{19}H_{12}S$: C, 83.79; H, 4.44; S, 11.77. Found: C, 83.64; H, 4.44; S, 11.82.

Metalation of 20.—To a solution of **20** (1.82 g, 0.0067 mol) in ether (50 ml) at room temperature was added 6.1 ml of 1.1 *M* *n*-butyllithium (0.0067 equiv) with stirring. The solution changed from a yellow to a dark blue-green color. Addition of a solution of dimethyl sulfate (0.92 g, 0.0073 mol) in ether (25 ml) caused the color of the mixture to change to orange. Upon completion of the addition, the mixture was hydrolyzed with ice and extracted with ether. Work-up yielded 1.7 g of a reddish-yellow oil. Chromatography in hexane over alumina gave 1.26 g (66%) of 4-methyl-4*H*-benzo[1,10]phenanthro[3,4-c]thiophene (**24**): mp 158–159°; ir (KBr) 2950 cm^{-1}; nmr (CS_2) τ 1.18 (1 H, m, H_1 of anthracene), 1.86 (1 H, s, H_{10} of anthracene), 2.50 (8 H, m, arom), 5.66 (1 H, 1, CH), 8.56 (3 H, d, CH_3). *Anal.* Calcd for $C_{20}H_{14}S$: C, 83.88; H, 4.92; S, 11.20. Found: C, 83.66; H, 4.85; S, 11.19. Both crude and purified materials indicated the presence of only one substance upon tlc analysis over silica gel using a variety of solvents.

Registry No.—**1**, 212-02-2; **2**, 211-98-3; **3**, 1210-02-2; **4**, 30415-22-6; **5**, 30415-23-7; **6**, 30415-24-8; **8**, 30415-25-9; **9**, 17574-57-1; **10**, 30415-27-1; **11**, 30415-28-2; **12**, 30415-29-3; **13**, 30415-30-6; **14**, 30409-49-5; **15**, 30409-50-8; **20**, 30477-06-6; **21**, 30409-51-9; **22**, 30409-52-0; **23**, 30409-53-1; **24**, 30477-07-7; 3-bromo-4-[1-hydroxy-(1,2,3,4-tetrahydronaphthyl)]thiophene, 30409-54-2; 3-bromo-4-[1-(3,4-dihydronaphthyl)]thiophene, 30409-55-3; 3-bromo-4-(1-naphthyl)thiophene, 30409-56-4; 3-(1-naphthyl)thiophene-4-carboxylic acid, 30409-57-5; 7-methyl-7*H*-phenaleno[1,2-*c*]thiophene, 30409-58-6; 7-deuterio-7*H*-phenaleno[1,2-*c*]thiophene, 30409-59-7.

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