The Insertion and Extrusion of Heterosulfur Bridges. XIII. Syntheses and Structural Studies of Nitrophenanthro[4,5-*bcd*]thiophenes [1]

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A simplified procedure for sulfur bridging of phenanthrene (**2a**) with hydrogen sulfide and a catalyst, but without solvent, is described. The product, phenanthro[4,5-*bcd*]thiophene (**1a**), undergoes nitration at 25° or 60° in acetic anhydride to give mixtures (56-79%) of 1-nitro-**1a** and 3-nitro-**1a** in varying ratios. Reductive acetylation of these nitro derivatives gives 1- and 3-acetylamino-**1a** (93% and 33%). Hydrodesulfurization of the former amide produces crude 1-acetylamino-**2a**. Positions of substitution are assigned primarily on the basis of nmr chemical shifts of protons *ortho* or *peri* to the nitro substituent, and are consistent with calculations of reactivity indices by simple Hückel molecular orbital theory.

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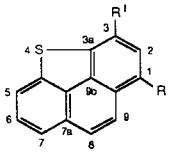
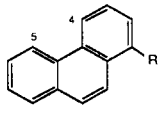
In previous publications we described the synthesis of phenanthro[4,5-*bcd*]thiophene (**1a**) by heterogeneously catalyzed sulfur bridging of phenanthrene (**2a**) [6,7] and the isolation of **1a** from the product mixture by chromatography of its sulfoxide **3** [7]. While this procedure did permit the isolation and study of pure **1a** it was fraught with two main experimental problems. First, use of benzene as a solvent in the sulfur bridging reaction introduced appreciable quantities of biphenyl and dibenzothiophene into the product mixture [1] and these impurities, especially the latter, were hard to remove. Second, conversion of **1a** into **3** (by use of iodobenzene dichloride, acetonitrile, and water)in this product mixture [7] proved to be unreliable in later runs [8]. The second problem has now been solved by effecting *S*-oxidation in a solvent of tetrahydrofuran (THF) and pyridine [10], instead of acetonitrile [11]. Additionally, it was found that isolated **3** can be reconverted to **1a** by means of lithium aluminum hydride in THF as an alternative to the use of sodium bis(2-methoxyethoxy)aluminum hydride in benzene [7], though the latter reagent is still preferred on the basis of mildness of reaction, simplicity of processing, and yield.



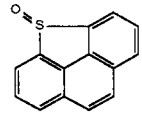
1

	R	R'
a,	H	H
b,	NO_2	H
c,	H	NO_2
d,	NHAc	H
e,	H	NHAc



2

	R
a,	H
b,	NHAc



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Meanwhile, the problem of separating **1a** from the sulfur bridging mixture was greatly simplified by conducting the bridging reaction without solvent, *i.e.* by introducing solid phenanthrene directly into the reactor during the reaction proper. Inasmuch as this procedure avoided cooling of the catalyst due to vaporization of solvent it was possible to select a reaction temperature of 530°, instead of 630° used previously. Moreover, the crude solid mixture was found to contain about 74 mole % of **1a** and only about 11 mole % of **2a** (as analyzed by nmr) and could be readily fractionated into **1a** of high quality (in 30% overall yield from **2a**) merely by recrystallization (without intermediate conversion into a sulfoxide).

As an initial investigation of substitution into the parent phenanthro[4,5-*bcd*]thiophene ring system, **1a** was treated with nitric acid/acetic anhydride either at room temperature or at 60° to give mixtures of 1- and 3-nitrophenanthro[4,5-*bcd*]thiophenes **1b** and **1c** (56-79% yield) in isomeric ratios which varied widely, **1b**/**1c** = (1.2 ± 0.6)/1. We were able to partially separate the mixture by column chromatography on alumina, only when this ratio was large since **1b** has higher solubility than **1c** (melting points 163° and 216°) and slightly higher R_f value (ΔR_f = 0.1 for alumina/petroleum ether-ether, 2:1). Thus, when the ratio was large some **1b** outdistanced the mainly unseparated components on the column, but outdistancing did not occur for most of our mixtures (ratios ≤ 1) under a variety of chromatographic conditions. Since efforts at separation by recrystallization on all mixtures were also unsuccessful [12], many investigations were made directly on the purified, unseparated mononitro isomeric mixtures.

Structures of the nitro products were established by means of 300 MHz pmr spectra, which showed two down-

field doublets at 8.92 and 8.82 ppm (in hexadeuterioacetone) for the *peri* (H-9) and *ortho* (H-2) hydrogen atoms in the 1-isomer (**1b**). The 3-isomer (**1c**) showed only one downfield doublet at 8.76 ppm for the *ortho* (H-2) hydrogen atom. Because of the symmetry of **1a** there are only four possible mononitro derivatives, with the substituent located at positions 1, 2, 3, or 8. Not only were the pmr spectral patterns of our products totally consistent with the structural assignments indicated, but they were inconsistent with location of a nitro group at C-2 or C-8, for which one would expect to observe two singlets (or, alternatively, two very close doublets from *meta* coupling) or one singlet in the spectrum, respectively. No singlets or close doublets were found. Electrophilic substitution at positions 1 and 3 is qualitatively expected on the basis of *ortho,para* orientation by a ring-activating sulfur atom. Quantitatively, molecular orbital calculations (Table I) show nearly idential reactivity indices for the 1 and 3 positions and are consistent with the observed variable ratios of isomers produced in the nitration reaction.

Table I

Calculated Reactivity Indices for Compound **1a** (a)

Position r	S_r^{elec}	S_r^{nucl}
1	2.63	0.83
2	0.98	0.78
3	2.65	0.85
3a	0.68	0.88
4 (S)	6.60	0.42
7a	0.92	0.72
8	1.19	0.99
9b	1.44	0.64

(a) S_r is given in units of β_C^{-1} and represents superdelocalizability toward *elec*trophilic or *nucl*eophilic attack, as based on simple HMO theory with $\alpha_S = \alpha_C$ and $\beta_{C\text{-}S} = 0.9\ \beta_{C\text{-}C}$ [13,14].

The downfield shift of aromatic hydrogen atoms *peri* and *ortho* to a nitro group has been reported by Emsley *et al.* [15] who obtained 100 and 220 MHz pmr spectra for 1-nitronaphthalene. Their spectrum at the higher external field was nearly first order and showed a marked downfield shift of the doublet for H-8 (*peri*, δ 8.52 in cyclohexane) and a smaller shift of the doublet for H-2 (*ortho*, 8.05). All other proton signals fell in the range of 7.35 to 7.90 [*cf.* 16,17]. In the spectra of our mononitro compounds (run at 300 MHz) the gap between *peri* and *ortho* proton signals was smaller (0.10 in **1b**), while the gap between *ortho* and other proton signals was larger (0.36 in **1b**, 0.30 in **1c**).

Initially, verification that nitration of phenanthrothiophene **1a** had produced a mixture of two mononitro isomers was obtained by reductive acetylation [18] of this isomeric mixture to yield two chromatographically separable acetylaminophenanthro[4,5-*bcd*]thiophenes, **1d** (R_f 0.22 for silica gel/ethyl acetate-carbon tetrachloride, 1:1) and **1e** (R_f 0.34). Structures of these individual amides were then assigned by direct comparison of samples with the single amides produced by reductive acetylation (in yields of 93% and 33%, respectively) of the separated isomeric nitro compounds **1b** and **1c**.

Further corroboration of the structure of **1d** was obtained by its hydrodesulfurization with Raney nickel/ethanol to a mixture ostensibly containing 1-acetylaminophenanthrene (**2b**) and its partially ring-hydrogenated derivatives, as indicated by mass spectral and 360 MHz pmr analysis. An attempt to follow the progress of the reaction by tlc was unsuccessful since both **1d** and product mixture showed spots at R_f 0.22. As a consequence, the reaction was continued for two days without noticeable change in this spot. The presence of a large amount of acetylaminophenanthrene in the product mixture was apparent from high resolution of the mass spectral peak at m/e 235. Moreover, hydrogenolysis of the C-S bonds was established by the appearance of two downfield doublets (J = 9 Hz) for the bay-region protons (H-4 and H-5) at δ 8.64 and 8.52 (other aromatic proton signals at 7.95-7.55) of a phenanthrene nucleus in the product mixture [19].

EXPERIMENTAL [20]

Phenanthro[4,5-*bcd*]thiophene (**1a**).

(a) Run with Solvent.

Sulfur bridging of phenanthrene was conducted with benzene as a solvent and catalyst Cr-0101 T at 630° [7]. A solution of two g of the crude product mixture [containing 1.2 g (5.8 mmoles) of **1a**] in 20 ml of tetrahydrofuran was treated with 1.5 g (5.5 mmoles) of iodobenzene dichloride, 10 ml of water, and 10 ml of pyridine. The yellow solution was stirred for 2 hours at room temperature and then treated with 300 ml (excess) of 10% aqueous hydrochloric acid and extracted with chloroform. Rotoevaporation of the extract gave an orange solid which was chromatographed on a column of silica gel [7] to give 1.2 g (98%, based on iodobenzene dichloride used) of crude sulfoxide **3**, mp 175-182°.

To a stirred solution of 0.5 g of lithium aluminum hydride in 20 ml of purified tetrahydrofuran [21] in an atmosphere of nitrogen was added, in small portions, 1 g of preceding **3** at room temperature. A vigorous reaction occurred. Two hours later the mixture was treated with ethyl acetate, added dropwise until bubbling subsided. The mixture was filtered to remove inorganic salts and rotoevaporated to leave crude **1a**, mp 126-130° (lit [6] 139-140°) after crystallization from methanol-water (9:1), yield 0.4 g (43%) of yellow needles.

(b) Run without Solvent.

The general procedure was the same as reported previously, but with the following modifications. The dropping funnel was replaced by a stopper and the reactor tube was packed with a column (21 cm long) of 150 g of Harshaw Cr-0101T catalyst and then (on top of it) a zone of impregnated alumina, made by rotoevaporating to dryness a mixture of 35 g of Houdry hard alumina grade HA 100S with a solution of 4.82 g of phenanthrene in benzene. Conditioning of the Harshaw catalyst was conducted at 530° in a stream of hydrogen sulfide gas while the zone of impregnated alumina was positioned just above the furnace. The reaction pro-

per (at 530°) was then conducted in the same way, but by introducing the phenanthrene into the heated region by incremental lowering of the reactor tube until, finally, all of the column packing was inside the furnace. After the reaction was complete the effluent and the solid which collected near the bottom of the reactor tube were combined and extracted with methylene chloride. The organic layer was separated from the aqueous phase, washed with excess 5% aqueous sodium hydroxide solution and then with water, dried (magnesium sulfate), and evaporated to leave 3.37 g of yellow solid, mp 62-108°, containing *ca.* 74 mole % of **1a**, 11 mole % of phenanthrene, plus impurities by nmr analysis. Three successive steps of recrystallization, using the residue from evaporation of the mother liquor each time, gave 1.8 g (32% overall yield) of **1a** (yellow needles from acetone, mp 127-132°, > 96% pure by NMR analysis) from steps 1 and 3, 0.19 g of elemental sulfur from methanol/acetone (1:1) from step 2, plus a remaining low-melting, unidentified mixture.

Nitration of **1a**.

(a) Reaction at 60°.

A stirred solution of 200 mg (0.96 mmole) of **1a** in 20 ml of acetic anhydride at room temperature was treated dropwise with 0.06 ml (0.96 mmole) of 71% nitric acid (density 1.42 g/ml). The mixture was then maintained at 60° for 4 hours, allowed to stir at room temperature overnight, and poured into ice and water. The resultant precipitate was collected by suction filtration, washed with water to remove acids, and dried in air. Tlc (carbon tetrachloride/silica gel F-254) of this crude product showed three spots at R_f values 0.90 (recovered **1a**), 0.51 (mixed mononitro products), and 0.30 (not investigated). The mononitro mixture was isolated by thick-layer chromatography and recrystallized from methanol-water (8:1) to give 160 mg (66%) of orange crystals, mp 160-165°. Futher recrystallizations from the same solvent gave an analytically pure sample, mp 181-186°; ir: 1570, 1510, 1320, 1305 cm^{-1} (nitro groups); pmr (deuteriochloroform): δ 8.92 (d, J = 8-9 Hz, 1 H, H-9 in **1b**), overlapping doublets at 8.73 and 8.66 (J = 8-9 Hz, 2.6 H, H-2 in **1b** and H-2 in **1c**), 8.3 -7.8 (m, 14.4 H, *i.e.* 5 H in **1b** plus 6 x 1.6 H in **1c**) - corresponding to a ratio of **1c**/**1b** of 1.6; ms (160°): m/e 254 (20), 253 (M^+, 100), 223 (M^+ - NO, 32), 207 (M^+ - NO_2, 78), 206 (21), 163 (M^+ - [NO_2 + CS], 26), 128* (207 → 163).

Anal. Calcd. for $C_{14}H_7NO_2S$: C, 66.39; H, 2.79; N, 5.53; exact mass, 253.020. Found: C, 66.13; H, 2.72; N, 5.40; exact mass, 253.020.

(b) Reaction at Room Temperature.

This reaction was conducted in a manner similar to that in part (a) but with 2.4 g (11.5 mmoles) of **1a**, 230 ml of acetic anhydride, and 0.58 ml (11.9 mmoles) of 90% nitric acid (density 1.44 g/ml added at room temperature over a period of 15 minutes). The mixture was stirred overnight (without heating) until tlc showed that all **1a** had reacted. Nmr analysis of the washed and dried mixture of isomers (2.61 g, mp 155-165°) from workup of the reaction mixture showed a ratio of **1b**/**1c** of 1.7 [22]. One g of this mixture was deposited onto 12 g of Baker neutral alumina which was placed atop a chromatographic coumn of 110 g of the plain alumina and eluted with petroleum ether (bp 35-60°)/ether (2:1) to yield (in order of elution) 292 mg of 1-nitrophenanthro[4,5-*bcd*]-thiophene (**1b**) (mp 152-159°), 388 mg of unseparated **1b** and **1c**, 200 mg of 3-nitrophenanthro[4,5-*bcd*]thiophene (**1c**) (mp 212-215°), and 75 mg of unidentified products: yield, 79% of **1b** plus **1c** from **2a**. Each of the isomers was recrystallized from methanol/dioxane (4:1). This gave bright yellow, matted needles (mp 160-163°) for **1b**; R_f (alumina/petroleum ether-ether, 2:1) 0.55; ir: (FT [23]) 1510, 1329, 1303, 1200 cm^{-1}; pmr (hexadeuterioacetone): 300 MHz [24], δ 8.92 (d, $J_{8,9}$ = 8.9 Hz, H-9), 8.82 (d, $J_{2,3}$ = 8.5 Hz, H-2), 8.46 (d, H-8), 8.42 (d, $J_{6,7}$ = 7.6 Hz, H-7), 8.41 (d, H-3), 8.26 (d, $J_{5,7}$ = 7.6 Hz, H-5), 8.10 (t, J = 7.6 Hz, H-6); ms: (140°) m/e 253 (M^+, 100), 252 (33), 223 (69), 207 (75), 195 (M^+ - [NO + CO], 35), 163 (51).

Anal. Found: C, 66.37; H, 2.57.

Compound **1c** was obtained as dark yellow needles, mp 215-216°; R_f (alumina/petroleum ether-ether, 2:1) 0.45; ir: (FT [23]) 1576, 1523, 1321, 1303 cm^{-1}; pmr (hexadeuterioacetone): 300 MHz [24], δ 8.76 (d, $J_{1,2}$ = 8.7 Hz, H-2), 8.46 (d, $J_{6,7}$ = 7.7 Hz, H-7), 8.39 (d, $J_{8,9}$ = 9.1 Hz, H-8 or H-9), 8.26 (d, 2H) which overlaps 8.25 (d, 1 H), 8.08 (t, J = 7.7 Hz, H-6); ms: (250°) m/e 253 (M^+, 28), 224 (18), 223 (100), 222 (21), 207 (39), 195 (15), 163 (16), 111.5 (16).

Anal. Found: H, 2.53; N, 5.15.

Reductive Acetylation of Nitrophenanthro[4,5-*bcd*]thiophenes.

(a) Using an Isomeric Mixture.

An isomeric mixture of **1b** and **1c** (0.5 g, mp 174-178°; isomeric ratio 1:1) was stirred with 14 ml of glacial acetic acid, 1.5 ml of acetic anhydride, and 0.67 g of iron powder (Mallinckrodt electrolytically reduced) and warmed to 80-90°, whereupon bubbling and a yellow, creamy texture were noted [18]. This temperature was maintained for 30 minutes, *i.e.* until tlc indicated that all starting material had reacted. The residue from filtration plus rotoevaporation of the mixture was chromatographed repeatedly on silica gel (60-200 mesh) with ethyl acetate/carbon tetrachloride (1:1) as eluent to give 0.16 g (31%) of 3-acetylaminophenanthro-[4,5-*bcd*]thiophene (**1e**), R_f 0.34, mp 220-230°; 0.16 g (31%) of 1-acetylaminophenanthro[4,5-*bcd*]thiophene (**1d**), R_f 0.22, mp 214-222°; and 0.03 g (6%) of unresolved mixture of **1d** and **1e**.

A sample of **1d** was rechromatographed and recrystallized from methanol/water (1:1) to give fine needles, mp 241-242° dec; ir: 3265 (NH), 1645 and 1520 (amide I and II), 815 cm^{-1}; pmr (hexadeuteriodimethyl sulfoxide): δ 10.1 (s, NH), 8.3-7.8 (m, aromatic protons), 2.22 (s, Ac) ms: (200°) m/e 266 (12), 265 (M^+, 61), 224 (18), 223 (M^+ - CH_2=C=O, 100), 222 (33), 195 (22), 43 (Ac^+, 8).

Anal. Calcd. for $C_{16}H_{11}NOS$: C, 72.43; H, 4.18; N, 5.28; exact mass, 265.056. Found: C, 72.07; H, 4.14; N, 5.09; exact mass, 265.056.

A sample of **1e** was sublimed repeatedly at 115-120° (0.005 mm) to give a white powder, mp 256.5-257° dec; ir: 3240 (NH), 1650 and 1530 (amide I and II), 825 cm^{-1}; pmr (hexadeuteriodimethyl sulfoxide): δ 10.4 (s, NH), 8.3-7.7 (m, aromatic protons), 2.19 (s, Ac); pmr (hexadeuterioacetone plus a drop of hexadeuteriodimethyl sulfoxide): δ 8.2-7.8 (m, aromatic H), 2.60 (s, Ac); ms: (200°) m/e 266 (11), 265 (M^+, 62), 224 (20), 223 (M^+ -CH_2=C=O, 100), 222 (27), 195 (18).

Anal. Calcd. for $C_{16}H_{11}NOS$: *vide supra.* Found: C, 72.07; H, 4.11; N, 5.26; exact mass, 265.057.

(b) Using **1b** Only.

In the preceding manner 250 mg of **1b** (mp 152-159°) was reductively acetylated. The residue was dissolved in chloroform and this solution was filtered, washed repeatedly with water (to remove acetic acid), and rotoevaporated to give 244 mg (93%) of **1d** as a brown solid, mp 236-241°, raised to 249-251° on recrystallization from methanol; R_f 0.22; pmr (hexadeuterioacetone): 300 MHz [24], δ 9.55 (s, NH, disappears on addition of deuterium oxide), 8.38 (d, $J_{8,9}$ = 8.6 Hz, H-9), 8.24 (d, H-8), 8.17 and 8.13 (2 d, $J_{2,3}$ = 7.9 Hz, H-2 and H-3), 8.06 and 8.02 (2 d, $J_{5,6}$ = $J_{6,7}$ = 7.7 Hz, H-5 and H-7), 7.90 (t, H-6), 2.30 (s, Ac).

(c) Using **1c** Only.

In the preceding manner 180 mg of **1c** (mp 212-215°) was reductively acetylated and processed further to give crude **1e**, purified by sublimation *in vacuo*, yield 63 mg (33%) of powder (mp 257-258°, raised to 260-261° on recrystallization from methanol); R_f 0.34; pmr (hexadeuterioacetone): 300 MHz [24], δ 9.60 (s, NH), 8.13 (broad d, J = 7.8 Hz, 2 H), 8.06-7.95 (m, 4 H), 7.88 (t, J = 7.6 Hz, H-6), 2.30 (s, Ac).

Desulfurization of **1d**.

Approximately 1 g of W-2 Raney nickel (Aldrich) was washed with distilled water until it was neutral to *p*H paper. A mixture of this nickel, 60 mg of **1d**, and 15 ml of 95% ethanol was refluxed for 2 days while an unsuccessful effort was made to follow the reaction by tlc [R_f = 0.22 for both **1d** and product(s)]. The cooled mixture was filtered and rotoevaporated to give 50 mg of white solid, mp 194-199°, raised to 196-200° on recrystallization from ethanol-water (1:1); pmr (deuteriochloroform): 360 MHz Nicolet instrument, δ 8.64 and 8.52 (2 d, J = 9 Hz, H-4 and

H-5), 7.95-7.55 (m, other aromatic H), 2.31 (s, Ac) for 1-acetylaminophenanthrene (**2b**), plus impurity peaks in the region of 2.25-1.6; ms: strong peak at m/e 235 (exact mass calculated for $C_{16}H_{13}NO$: 235.100; found: 235.100) for the presence of acetylaminophenanthrene, plus other peaks at m/e > 235 for partially hydrogenated acetylaminophenanthrenes (?). Acidification of the spent nickel residue with hydrochloric acid gave evolution of hydrogen sulfide.

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[22] A smaller run at room temperature gave an isomeric ratio of 1:1, mp 174-178°, used in reductive acetylation (*vide infra*).

[23] Determined on a Nicolet 5-DXB FTIR instrument by Eliot Hall.

[24] Determined on a General Electric QE-300 instrument.