

Hirotaka Kudo and Raymond N. Castle\* [1]

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

Milton L. Lee

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

Received April 3, 1984

The synthesis of the novel naphtho[2',1':4,5]thieno[2,3-c]quinoline (**11**) ring system and four of the isomeric monomethyl derivatives is described.

*J. Heterocyclic Chem.*, **22**, 211 (1985).

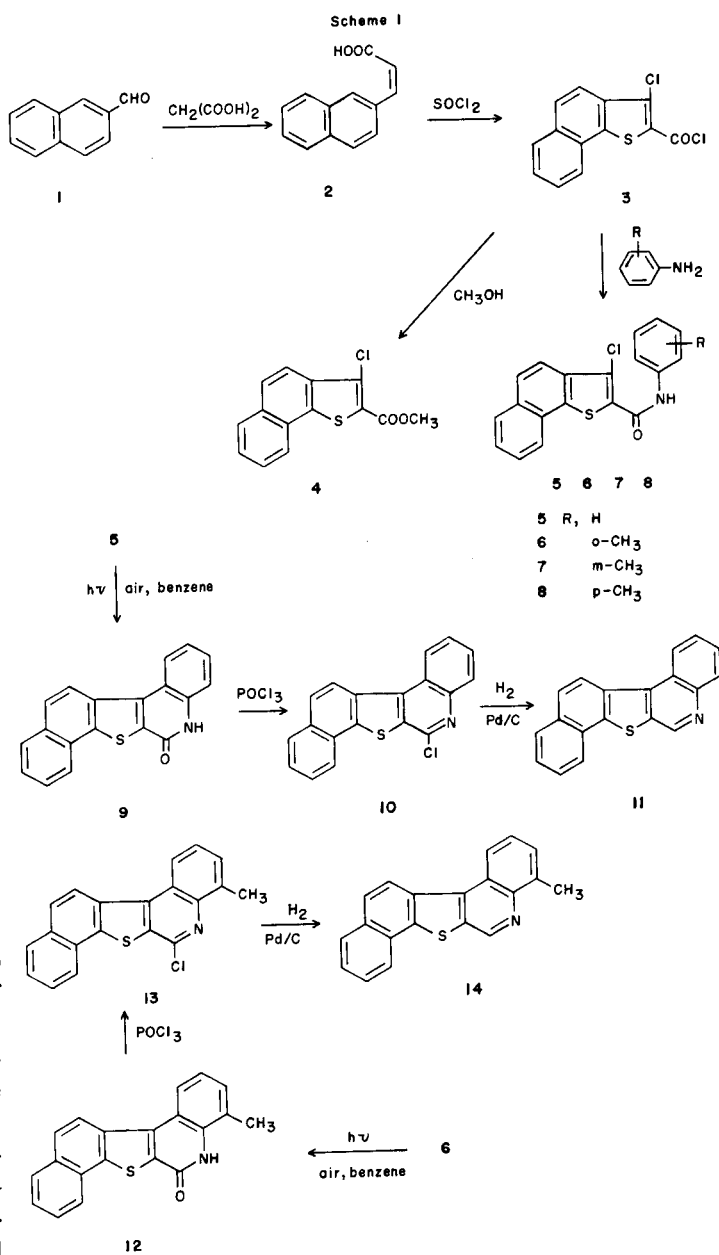
A number of polycyclic thiophenes which occur or are suspected of occurring in coal liquids, coal-derived products and shale oils have been synthesized [2-25]. We now have preliminary evidence by gcms [26] that polycyclic thiophenes in which a pyridine ring and one or more benzene rings are fused together occur in coal-derived products.

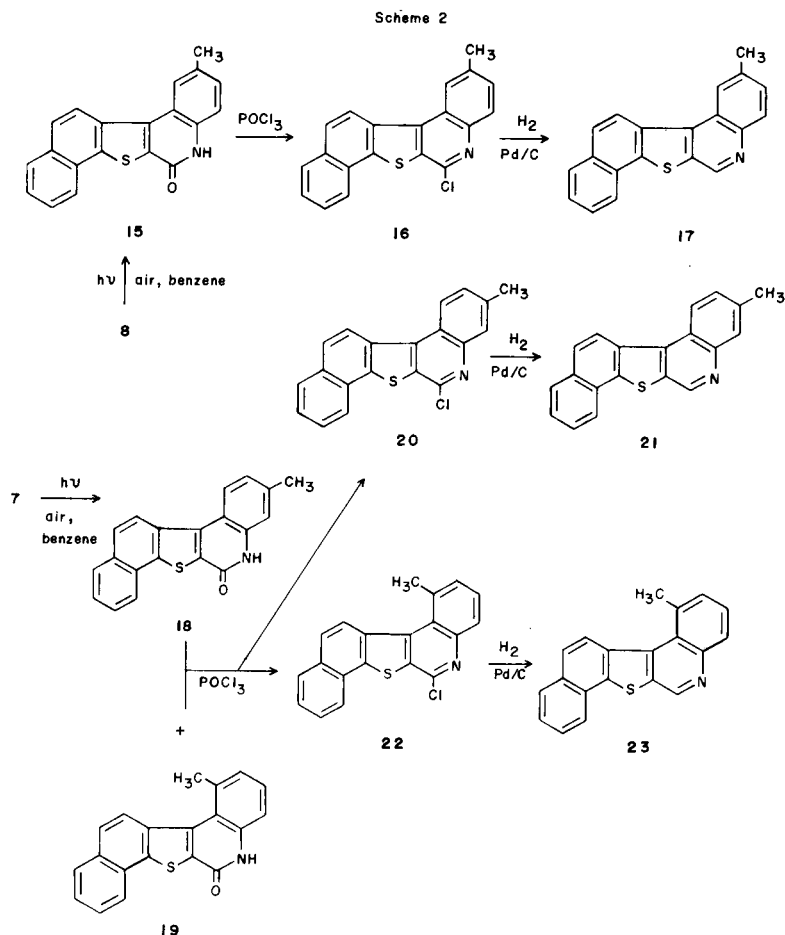
We now describe the synthesis of the novel naphtho[2',1':4,5]thieno[2,3-c]quinoline (**11**) ring system and four of the monomethyl isomers of this ring system.

The reaction of naphthalene-2-carboxaldehyde (**1**) with malonic acid gave 3-(2-naphthyl)propenoic acid (**2**) [27] (93% yield) which when allowed to react with thionyl chloride gave 3-chloronaphtho[1,2-*b*]thiophene-2-carboxoyl chloride (**3**) [28] in 73% yield [29]. Treatment of **3** with methanol produced methyl 3-chloronaphtho[1,2-*b*]thiophene-2-carboxylate (**4**) in 82% yield. The reaction of **3** with aniline, *o*-toluidine, *m*-toluidine or *p*-toluidine gave the corresponding carboxamides, namely: 3-chloro-*N*-phenylnaphtho[1,2-*b*]thiophene-2-carboxamide (**5**) (93% yield); 3-chloro-*N*-(2-methylphenyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**6**) (97% yield); 3-chloro-*N*-(3-methylphenyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**7**) (97% yield); and 3-chloro-*N*-(4-methylphenyl)naphtho[1,2-*b*]thiophene-2-carboxamide (**8**) (94% yield) respectively.

Photocyclization (benzene, triethylamine) of **5**, **6**, or **8** gave respectively: naphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**9**) (93% yield); 4-methylnaphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**12**) (93% yield); and 2-methylnaphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**15**) (90% yield). Photocyclization of **7** gave a mixture of 3-methylnaphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**18**) and 1-methylnaphtho[2',1':4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (**19**) in a combined yield of 89%. This mixture was not readily separated at this stage.

Phosphorus oxychloride chlorination of **9**, **12** or **15** produced respectively: 6-chloronaphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**10**) (75% yield); 6-chloro-4-methylnaphtho[2',1':4,5]thieno[2,3-*c*]quinoline (**13**) (75% yield); and





6-chloro-2-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**16**) (68% yield). Chlorination (phosphorus oxychloride) of the mixture of **18** and **19** afforded a mixture of 6-chloro-3-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**20**) and 6-chloro-1-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**22**) in a combined yield of 84%. Crystallization of the mixture of **20** and **22** from benzene gave pure **20** in 52% yield. The residue was contaminated with **20** (ratio of **20** to **22** was 2:1, nmr analysis).

Catalytic dechlorination (Pd-C) of **10**, **13**, **16** or **20** produced respectively: naphtho[2',1':4,5]thieno[2,3-c]quinoline (**11**) (74% yield), 4-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**14**) (61% yield); 2-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**17**) (83% yield); and 3-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**21**) (52% yield). Catalytic dechlorination of **22** contaminated with **20** was accomplished (Pd-C) and the product, 1-methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**23**) was obtained after purification.

Compounds **11**, **14**, **17**, **21** and **23** are being screened for mutagenic activity against TA-98 and TA-100 in the Ames test (S9 liver homogenate activation) and these results will be published elsewhere.

## EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The <sup>1</sup>H nmr spectra were obtained on a Varin EM 360 spectrometer in the solvents indicated with TMS as the internal standard. The ir spectra were obtained on a Perkin Elmer 337 spectrometer. Mass spectra were obtained on a Hewlett Packard model 5980A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

### 3-Chloronaphtho[1,2-*b*]thiophene-2-carbonyl Chloride (**3**).

A mixture of **2** (9.9 g, 0.05 mole), dry pyridine (0.8 ml, 0.01 mole), thionyl chloride (18.2 ml, 0.25 mole) and chlorobenzene (50 ml) was heated at reflux temperature for 72 hours. After cooling, the precipitate was collected by filtration to give 8.5 g of yellow needles. The filtrate was concentrated and the residue was triturated with hexane (50 ml) and filtered giving 1.6 g (75% yield). An analytical sample was recrystallized from benzene to give yellow needles, mp 191-192°; nmr (deuteriochloroform): δ 7.19-8.21 (m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 6H, ArH); ms: m/e 282 (M<sup>+</sup>, 22), 247 (M<sup>+</sup>, -Cl, 37), 245 (100), 182 (27), 91 (32).

Anal. Calcd. for C<sub>13</sub>H<sub>6</sub>Cl<sub>2</sub>OS: C, 55.54; H, 2.15; S, 11.40. Found: C, 55.48; H, 2.36; S, 11.37.

### Methyl 3-Chloronaphtho[1,2-*b*]thiophene-2-carboxylate (**4**).

A mixture of **3** (1 g, 0.0036 mole) and methanol (50 ml) was refluxed for one hour. After evaporation of the methanol, the residue was recrystallized from methanol to give 0.81 g (82%) of colorless needles, mp

145-146°; nmr (deuteriochloroform):  $\delta$  3.97 (s, CH<sub>3</sub>, 3H), 7.3-7.8 (m, 6-H, 7-H, 8-H, 9-H, 4H, ArH), 7.82-8.12 (m, 4-H, 5-H, 2H, ArH); ms: m/e 278 (M<sup>+</sup> + 2, 38), 276 (M<sup>+</sup>, 100), 245 (99), 182 (36).

Anal. Calcd. for C<sub>14</sub>H<sub>9</sub>ClO<sub>2</sub>S: C, 60.76; H, 3.28; S, 11.59. Found: C, 60.52; H, 3.48; S, 11.36.

### 3-Chloro-*N*-phenylnaphtho[1,2-*b*]thiophene-2-carboxamide (5).

A mixture of **3** (5.6 g, 0.02 mole), aniline (3.7 g, 0.04 mole) and benzene (100 ml) was heated for an hour on a steam bath. After cooling, the resulting precipitate was collected by filtration and washed with water and recrystallized from ethanol, giving colorless prisms, 6.2 g (93%), mp 214-215°; nmr (deuteriochloroform):  $\delta$  7.1-7.4 (m, 3'-H, 4'-H, 5'-H, 3H, ArH), 7.25-7.55 (m, 2'-H, 6'-H, 6-H, 7-H, 8-H, 9-H, 6H, ArH), 8.01-8.21 (m, 4-H, 5-H, 2H, ArH), 8.9 (bs, NH, 1H); ms: m/e 337 (M<sup>+</sup>, 21), 247 (37), 245 (M<sup>+</sup> -NHC<sub>6</sub>H<sub>5</sub>, 100), 217 (M<sup>+</sup> -OCNHC<sub>6</sub>H<sub>5</sub>, 21), 182 (M<sup>+</sup> -Cl + OCNHC<sub>6</sub>H<sub>5</sub>), 30).

Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>ClNOS: C, 67.55; H, 3.58; N, 4.15; S, 9.49. Found: C, 67.41; H, 3.64; N, 4.12; S, 9.35.

### 3-Chloro-*N*-(2-methylphenyl)naphtho[1,2-*b*]thiophene-2-carboxamide (6).

This compound was prepared from **3** (5.6 g, 0.02 mole), *o*-toluidine (4.2 g, 0.04 mole) and benzene (100 ml) in a manner similar to the preparation of **5** and was obtained as colorless prisms, 6.5 g (97%), mp 205-206°; nmr (deuteriochloroform):  $\delta$  2.4 (s, CH<sub>3</sub>, 3H), 7.05-7.43 (m, 3'-H, 4'-H, 5'-H, 3H, ArH), 7.45-8.1 (m, 6'-H, 6-H, 7-H, 8-H, 9-H, 5H, ArH), 8.02-8.45 (m, 4-H, 5-H, 2H, ArH), 8.8 (bs, NH, 1H); ms: m/e 245 (M<sup>+</sup> -NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 100), 217 (M<sup>+</sup> -OCNHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 49), 182 (M<sup>+</sup> -Cl + OCNHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 70), 173 (39).

Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>ClNOS: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 68.09; H, 4.10; N, 3.97; S, 9.12.

### 3-Chloro-*N*-(2-methylphenyl)naphtho[1,2-*b*]thiophene-2-carboxamide (7).

This compound was prepared from **3** (11.2 g, 0.04 mole), *m*-toluidine (8.4 g, 0.08 mole) and benzene (200 ml) in a manner similar to the preparation of **7** and was obtained as colorless prisms, 12.8 g (96%), mp 168-169°; nmr (deuteriochloroform):  $\delta$  2.4 (s, CH<sub>3</sub>, 3H), 6.81-7.31 (m, 4'-H, 5'-H, 2H, ArH), 7.32-7.72 (m, 2'-H, 6'-H, 2H, ArH), 7.7-8.1 (m, 6-H, 7-H, 8-H, 9-H, 4H, ArH), 8.13-8.31 (m, 4-H, 5-H, 2H, ArH), 8.9 (bs, NH, 1H); ms: m/e 351 (M<sup>+</sup>, 15), 247 (37), 245 (M<sup>+</sup> -NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 100), 217 (M<sup>+</sup> -OCNHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 19), 182 (M<sup>+</sup> -Cl + OCNHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 25).

Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>ClNOS: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 68.32; H, 4.14; N, 4.07; S, 9.12.

### 3-Chloro-*N*-(4-methylphenyl)naphtho[1,2-*b*]thiophene-2-carboxamide (8).

This compound was prepared from **3** (5.6 g, 0.02 mole), *p*-toluidine (4.2 g, 0.04 mole) and benzene (100 ml) in a manner similar to the preparation of **7** and was obtained as colorless prisms, 6.3 g (94%), mp 208-209°; nmr (deuteriochloroform):  $\delta$  2.4 (s, 4'-CH<sub>3</sub>, 3H), 7.02-7.31 (m, 3'-H, 5'-H, 2H, ArH), 7.41-7.61 (m, 2'-H, 6'-H, 2H, ArH), 7.62-8.31 (m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 6H, ArH), 8.84 (bs, NH, 1H); ms: m/e 247 (37), 245 (M<sup>+</sup> -NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 100), 217 (M<sup>+</sup> -OCNHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 16), 182 (M<sup>+</sup> -Cl + OCNHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 19).

Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>ClNOS: C, 68.27; H, 4.01; N, 3.98; S, 9.11. Found: C, 68.04; H, 3.93; N, 3.94; S, 9.16.

### Naphtho[2',1':4,5]thieno[2,3-c]quinolin-6(5H)-one (9).

A solution of **5** (0.5 g, 0.0015 mole), triethylamine (0.16 g, 0.0015 mole) in dry benzene (500 ml) was irradiated for 3.5 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 resulting precipitate was collected by filtration and used in the next reaction without further purification, giving pale yellow prisms 0.4 g (93%), mp >300°; ir (nujol): 1655 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid):  $\delta$  6.91-7.61 (m, 1-H, 2-H, 3-H, 4-H, 4H, ArH), 7.63-7.92 (m, 8-H, 9-H, 10-H, 11-H, 4H ArH), 7.93-8.23 (m, 12-H, 13-H, 2H, ArH); ms: m/e 273 (M<sup>+</sup> -CO + H<sup>+</sup>), 53), 272 (100), 245 (21), 151 (17).

### 6-Chloronaphtho[2',1':4,5]thieno[2,3-c]quinoline (10).

A mixture of **9** (1.5 g, 0.005 mole) and phosphorus oxychloride (40 ml) was gently refluxed for 3.5 hours in an oil bath. The residue obtained upon removal of the excess of phosphorus oxychloride was poured into ice water (200 ml). The solid which separated was collected by filtration and washed with water, recrystallized from benzene giving colorless prisms, 1.2 g (75%), mp 226-227°; nmr (deuteriochloroform + deuteriotrifluoroacetic acid):  $\delta$  7.71-8.54 (m, 2-H, 3-H, 4-H, 8-H, 9-H, 10-H, 11-H, 7H, ArH), 8.72-9.05 (m, 12-H, 13-H, 2H, ArH), 9.3 (s, 1-H, 1H, ArH); ms: m/e 321 (M<sup>+</sup> + 2, 38), 319 (M<sup>+</sup>, 100), 283 (M<sup>+</sup> -HCl, 37), 245 (50).

Anal. Calcd. for C<sub>19</sub>H<sub>10</sub>ClNS: C, 71.36; H, 3.15; N, 4.38; S, 10.02. Found: C, 71.28; H, 3.25; N, 4.18; S, 9.93.

### Naphtho[2',1':4,5]thieno[2,3-c]quinoline (11).

A solution of **10** (0.64 g, 0.002 mole) and potassium hydroxide (0.11 g, 0.002 mole) in methanol (80 ml) and benzene (80 ml) was reduced catalytically using a palladium catalyst (5% palladium on carbon, 0.5 g) at atmospheric pressure and room temperature. After the uptake of an equimolar amount of hydrogen, the catalyst was filtered off and the solvent was removed under reduced pressure. The product was treated with water and extracted with benzene. The benzene solution was dried over anhydrous sodium sulfate and evaporated. The residue was recrystallized from benzene to give colorless prisms, 0.42 g (74%), mp 226-227°; nmr (deuteriochloroform):  $\delta$  7.41-7.97 (m, 2-H, 3-H, 4-H, 3H, ArH), 7.98-8.42 (m, 9-H, 10-H, 11-H, 3H, ArH), 8.47-8.81 (m, 1-H, 8-H, 12-H, 13-H, 4H, ArH), 9.3 (s, 6-H, 1H, ArH); ms: m/e 286 (M<sup>+</sup> + 1, 22), 285 (M<sup>+</sup>, 100), 284 (M<sup>+</sup> - 1, 10).

Anal. Calcd. for C<sub>19</sub>H<sub>11</sub>NS: C, 79.75; H, 3.89; N, 4.93; S, 11.23. Found: C, 79.95; H, 3.86; N, 4.76; S, 11.40.

### 4-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinolin-6(5H)-one (12).

This compound was prepared from **6** (0.5 g, 0.0014 mole), triethylamine (0.15 g, 0.0014 mole) and dry benzene (500 ml) in a manner similar to the preparation of **9** and was obtained as colorless prisms, which were used in the next step without further purification, yield 93% (0.41 g), mp >280°; ir (nujol): 1665 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid):  $\delta$  2.43 (s, 4-CH<sub>3</sub>, 3H), 7.13-8.03 (m, 2-H, 3-H, 9-H, 10-H, 11-H, 12-H, 6H, ArH), 8.11-8.53 (m, 1-H, 8-H, 13-H, 3H, ArH); ms: m/e 316 (M<sup>+</sup> + 1, 24), 315 (100), 314 (14), 286 (M<sup>+</sup> -CO + H<sup>+</sup>), 13).

### 4-Methyl-5-chloronaphtho[2',1':4,5]thieno[2,3-c]quinoline (13).

This compound was prepared from **12** (1.5 g, 0.0048 mole) and phosphorus oxychloride (40 ml) in a manner similar to the preparation of **10** and was obtained as white prisms, 1.2 g (75%), mp 211-212°; nmr (deuteriochloroform + deuteriotrifluoroacetic acid):  $\delta$  2.9 (s, 4-CH<sub>3</sub>, 3H), 7.64-8.44 (m, 2-H, 3-H, 9-H, 10-H, 11-H, 5H, ArH), 8.45-8.77 (m, 8-H, 12-H, 2H, ArH), 8.88-9.24 (m, 1-H, 13-H, 2H, ArH).

Anal. Calcd. for C<sub>20</sub>H<sub>12</sub>ClNS: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 71.97; H, 3.71; N, 4.17; S, 9.76.

### 4-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (14).

This compound was prepared from **13** (0.4 g, 0.0012 mole), potassium hydroxide (0.1 g, 0.0018 mole) and palladium on carbon (5%, 0.5 g) in methanol (50 ml) and benzene (50 ml) in a manner similar to the preparation of **11** and colorless prisms were obtained 0.22 g (61%), mp 197-198°; nmr (deuteriochloroform):  $\delta$  2.93 (s, CH<sub>3</sub>, 3H), 7.51-8.38 (m, 2-H, 3-H, 9-H, 10-H, 11-H, 12-H, 6H, ArH), 8.63-9.03 (m, 1-H, 8-H, 13-H, 3H, ArH), 9.43 (s, 6-H, 1H, ArH); ms: m/e 300 (M<sup>+</sup> + 1, 24), 299 (M<sup>+</sup>, 100), 298 (M<sup>+</sup> - 1, 23), 148 (39).

Anal. Calcd. for C<sub>20</sub>H<sub>13</sub>NS: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 79.99; H, 4.51; N, 4.58; S, 10.82.

### 2-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinolin-6(5H)-one (15).

This compound was prepared from **8** (0.5 g, 0.0014 mole), triethylamine (0.15 g, 0.0014 mole) and dry benzene (500 ml) in a manner similar to the preparation of **9** and was obtained as colorless prisms, 0.4 g (90%); mp >20°; ir (nujol): 1650 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid):  $\delta$  2.43 (s, CH<sub>3</sub>, 3H), 7.03-7.63 (m, 3-H, 4-H, 9-H, 10-H, 11-H, 5H, ArH), 7.69-8.12 (m, 1-H, 8-H, 12-H, 13-H, 4H, ArH); ms: m/e 316 (M<sup>+</sup> + 1, 24), 315 (M<sup>+</sup>, 100), 314 (M<sup>+</sup> - 1, 21).

## 2-Methyl-6-chloronaphtho[2',1':4,5]thieno[2,3-c]quinoline (16).

This compound was prepared from **15** (1.5 g, 0.0048 mole) and phosphorus oxychloride (40 ml) in a manner similar to the preparation of **10** and was obtained as yellow prisms, 1.1 g (68%), mp 227-228°; nmr (deuteriochloroform):  $\delta$  2.6 (s, CH<sub>3</sub>, 3H), 7.18-8.27 (m, 3-H, 4-H, 9-H, 10-H, 11-H, 5H, ArH), 8.3-8.61 (m, 1-H, 8-H, 12-H, 13-H, 4H, ArH); ms: m/e 336 (M<sup>+</sup> + 3, 22), 335 (M<sup>+</sup> + 2, 100), 334 (M<sup>+</sup> + 1, 76), 333 (75), 296 (M<sup>+</sup> - Cl, 41).

Anal. Calcd. for C<sub>20</sub>H<sub>21</sub>NS: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 71.83; H, 3.69; N, 4.09; S, 9.39.

## 2-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (17).

This compound was prepared from **16** (0.67 g, 0.002 mole) and potassium hydroxide (0.16 g, 0.002 mole) in methanol (100 ml) and benzene (100 ml) in a manner similar to the preparation of **11** and was obtained as colorless prisms, 0.5 g (83%), mp 191-192°; nmr (deuteriochloroform):  $\delta$  2.68 (s, CH<sub>3</sub>, 3H), 7.29-8.35 (m, 3-H, 4-H, 9-H, 10-H, 11-H, 5H, ArH), 8.55-8.93 (m, 1-H, 8-H, 12-H, 13-H, 4H, ArH), 9.3 (s, 6-H, 1H, ArH); ms: m/e 300 (M<sup>+</sup> + 1, 24), 299 (M<sup>+</sup>, 100), 298 (M<sup>+</sup> - 1, 24), 297 (M<sup>+</sup> - 2, 14).

Anal. Calcd. for C<sub>20</sub>H<sub>13</sub>NS: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.14; H, 4.35; N, 4.58; S, 10.66.

1-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinolin-6(5H)-one (**18**) and 3-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinolin-6(5H)-one (**19**).

This mixture was prepared from **7** (0.5 g, 0.0014 mole), triethylamine (0.15 g, 0.0014 mole) and dry benzene (500 ml) in a manner similar to the preparation of **9** and was obtained as colorless prisms and was used without further purification in the next step, 0.4 g (89%), mp >280°; ir (nujol): 1660 (NHCO); nmr (deuteriochloroform + deuteriotrifluoroacetic acid):  $\delta$  2.33 (s, 1-CH<sub>3</sub>, 3H), 2.7 (s, 3-CH<sub>3</sub>, 3H), 6.67-8.13 (m, 1-H, 2-H, 4-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 9H, ArH), or (m, 2-H, 3-H, 4-H, 9-H, 10-H, 11-H, 12-H, 13-H, 9H, ArH); ms: m/e 316 (M<sup>+</sup> + 1, 21), 315 (100), 314 (M<sup>+</sup> - 1, 26).

3-Methyl-6-chloronaphtho[2',1':4,5]thieno[2,3-c]quinoline (**20**) and 1-Methyl-6-chloronaphtho[2',1':4,5]thieno[2,3-c]quinoline (**22**).

These compounds were prepared from the mixture of **18** and **19** (3 g, 0.0096 mole) and phosphorus oxychloride (60 ml) in a manner similar to the preparation of **10**. Compound **20** was recrystallized from benzene to give 2.2 g (69%) of colorless prisms, mp 236-237°; nmr (deuteriochloroform):  $\delta$  2.57 (s, CH<sub>3</sub>, 3H), 7.3-7.81 (m, 2-H, 4-H, 9-H, 3H, ArH), 7.82-8.32 (m, 10-H, 11-H, 12-H, 3H, ArH), 8.41-8.87 (m, 1-H, 8-H, 13-H, 3H, ArH); ms: m/e 335 (M<sup>+</sup> + 1, 39), 334 (M<sup>+</sup>, 29), 333 (M<sup>+</sup> - 1, 100), 332 (M<sup>+</sup> - 2, 16).

Anal. Calcd. for C<sub>20</sub>H<sub>12</sub>ClNS: C, 71.96; H, 3.62; N, 4.20; S, 9.60. Found: C, 71.85; H, 3.63; N, 4.08; S, 9.44.

The mother liquor from the above recrystallization was evaporated at reduced pressure and the residue was chromatographed on a silica gel column using hexane-benzene as the eluent giving 0.5 g (16%) of yellow prisms of **22**, mp 197-198°. This compound was used in the next reaction without further purification; nmr (deuteriochloroform):  $\delta$  2.93 (s, CH<sub>3</sub>, 3H), 7.05-7.89 (m, 2-H, 3-H, 4-H, 9-H, 10-H, 11-H, 12-H, 7H, ArH), 7.9-8.31 (m, 8-H, 13-H, 2H, ArH).

3-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**21**).

This compound was prepared from **20** (0.67 g, 0.002 mole), potassium hydroxide (0.11 g, 0.002 mole) and palladium on carbon (5%, 0.5 g) in methanol (80 ml) and benzene (80 ml) in a manner similar to the preparation of **11** and was obtained as colorless prisms, 0.3 g (52%), mp 217-218°; nmr (deuteriochloroform):  $\delta$  2.57 (s, CH<sub>3</sub>, 3H), 7.28-8.21 (m, 2-H, 4-H, 11-H, 12-H, 4H, ArH), 8.28-8.73 (m, 1-H, 8-H, 13-H, 3H, ArH), 8.93 (s, 6-H, 1H, ArH); ms: m/e 301 (M<sup>+</sup> + 2, 29), 300 (M<sup>+</sup> + 1, 100), 296 (37), 148 (55).

Anal. Calcd. for C<sub>20</sub>H<sub>13</sub>NS: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.15; H, 4.32; N, 4.66; S, 10.66.

1-Methylnaphtho[2',1':4,5]thieno[2,3-c]quinoline (**23**).

This compound was prepared from **22** (0.4 g, 0.0012 mole), potassium hydroxide (0.0067 g, 0.0012 mole) and palladium on carbon (5%, 0.3 g) in methanol (50 ml) and benzene (50 ml) in a manner similar to the preparation of **11** and was obtained as colorless prisms, 0.3 g (75%), mp

192-193°; nmr (deuteriochloroform):  $\delta$  2.88 (s, CH<sub>3</sub>, 3H), 7.34-8.3 (m, 2-H, 3-H, 4-H, 9-H, 10-H, 11-H, 6H, ArH), 8.10-8.36 (m, 8-H, 12-H, 13-H, 3H, ArH), 9.28 (s, 6-H, 1H, ArH); ms: m/e 299 (M<sup>+</sup>, 100), 298 (M<sup>+</sup> - 1, 51), 297 (M<sup>+</sup> - 2, 31), 266 (34).

Anal. Calcd. for C<sub>20</sub>H<sub>13</sub>NS: C, 80.24; H, 4.38; N, 4.68; S, 10.71. Found: C, 80.09; H, 4.60; N, 4.84; S, 10.49.

Acknowledgement.

This study was supported by the U. S. Department of Energy, Office of Health and Environmental Research, Contract No. DE-AC0279EV10237.

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