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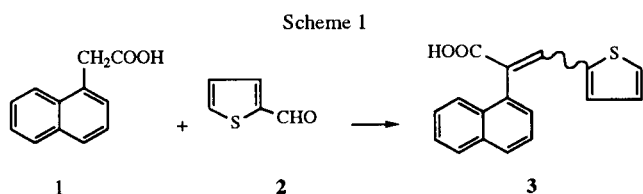
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Received September 16, 1995

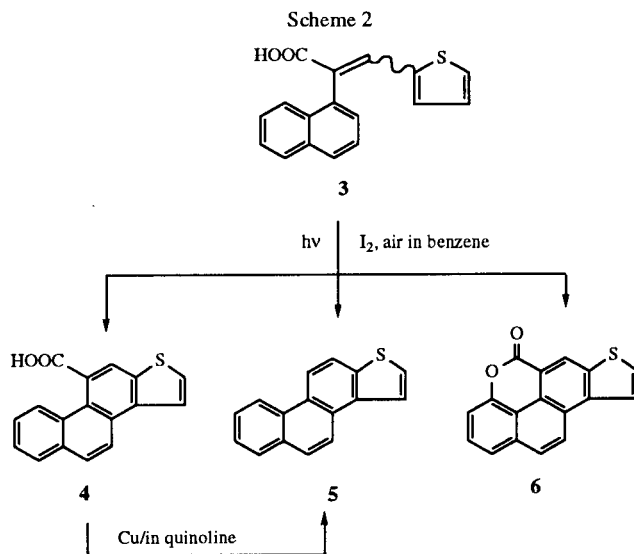
Photocyclization of the substituted 2-(naphth-1-yl)-3-(thien-2-yl)propenoic acid (**3**) in the presence of iodine and air in a benzene-cyclohexane mixture afforded a separable mixture of three compounds, phenanthro[2,1-*b*]thiophene-10-carboxylic acid (**4**), phenanthro[2,1-*b*]thiothene (**5**), and naphtho[1,8-*cde*]-thieno[3,2-*g*][2]benzopyran (**6**)

J. Heterocyclic Chem., **33**, 1017 (1996).

We previously have prepared a large number of polycyclic thiophenes in order to ascertain those present in coal-derived products and shale oils [1]. In the earlier work we did not investigate the nature of the byproducts present in low percentages occurring upon photocyclization. We now report photocyclization studies of 2-(naphth-1-yl)-3-(thien-2-yl)propenoic acid (**3**) [2-5].



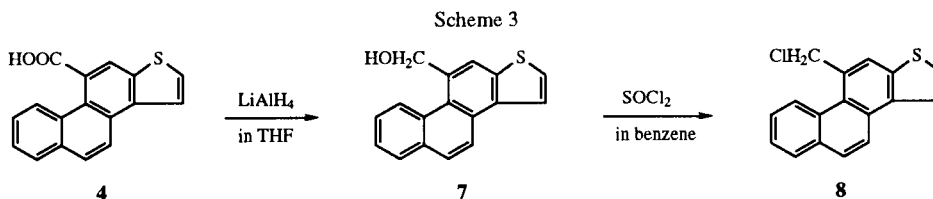
Compound **3** was prepared from the condensation of 1-naphthylethanoic acid (**1**) with thiophene-2-carbaldehyde (**2**) in 62% yield. Photocyclization of **3** in benzene solution in the presence of iodine and air afforded a separable mixture of three products. These are phenanthro[2,1-*b*]thiophene-10-carboxylic acid (**4**) (49% yield), phenanthro[2,1-*b*]thiothene (**5**) (1% yield), and naphtho[1,8-*cde*]thieno[3,2-*g*][2]benzopyran (**6**) (2% yield). Compound **6** bears a formal resemblance to benzo[*a*]pyrene wherein one benzene ring has been replaced by a thiophene ring and a second benzene ring has been replaced by a pyran ring. Neidlein and Schaefer [6] have reported another isomeric ring system of **6**, namely 1*H*-[1]benzothieno[2,3,4-*mna*]xanthene. Compound **4** was also converted into **5** by heating **4** with copper powder in quinoline in 80% yield. Compound **4** was reduced with lithium aluminum hydride in THF to give crude 10-hydroxymethylphenanthro[2,1-*b*]thiophene (**7**) which



upon reaction with thionyl chloride in benzene provided 10-chloromethylphenanthro[2,1-*b*]thiophene (**8**). Reaction of **8** with sodium cyanide in DMSO gave 10-cyanomethylphenanthro[2,1-*b*]thiophene (**9**) in 62% yield. We have previously reported the conversion of **9** into **10** in two steps [7,8]

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The IR spectra were recorded on a Beckman FT100 spectrometer as potassium bromide pellets and frequencies are expressed in cm^{-1} . The ^1H -NMR spectra were obtained on a JEOL FX90Q and a Bruker AMX 360 spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and



J values are in Hz. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. The electron impact and high resolution ionization mass spectra were acquired by the Midwest Center for Mass spectroscopy.

2-(Naphth-1-yl)-3-(thien-2-yl)propenoic Acid (3)

A mixture of 18.6 g (100 mmoles) of 1-naphthylethanoic acid, 17.0 g (150 mmoles) of 2-thiophenecarbaldehyde, 40 ml of acetic anhydride, and 20 ml of triethylamine was refluxed for 6 hours. The reaction mixture was then poured into 300 ml of 10% hydrochloric acid and stirred at room temperature for 1 hour. The product was extracted with 300 ml of benzene. The benzene layer was extracted with 200 ml of a solution of 5% sodium hydroxide. The aqueous solution was separated and acidified with 10% hydrochloric acid. The mixture was stirred for 1 hour. The crystallized product was collected by filtration. After drying in air, the product was recrystallized from benzene to give 17.43 g (62.2 mmoles, 62%) of colorless prisms. An analytical sample was recrystallized from benzene to give colorless prisms, mp 220-222°; ir (potassium bromide): ν 3100-2400 (br, OH), 1661, 1653 (CO), 1601, 1270, 1211, 779, 720, 679 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 6.72-8.00 (m, 10H, aromatic-H), 8.32 (s, 1H, C=CH).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{S}$: C, 72.83; H, 4.31; N, 11.44. Found: C, 72.81; H, 4.32; S, 11.41.

Photocyclization of 3.

A solution of 1.0 g, 83.0 mmoles) of 3, 100 mg of iodine in a mixture of 200 ml of benzene and 300 ml of cyclohexane was irradiated for 6 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 precipitate that appeared was collected by filtration to give 0.28 g (1.01 mmoles, 28%) of tan crystals of 4. An analytical sample was recrystallized from benzene to give tan needles, mp 226-228°; ir (potassium bromide): ν 3100-2600 (br, OH), 1687 (CO), 1278, 1191, 820, 756 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.52-8.40 (m, 8H, aromatic-H), 8.52 (s, 1H, 11-H)

Anal. Calcd. for $\text{C}_{17}\text{H}_{10}\text{O}_2\text{S}$: C, 73.36; H, 3.62; S, 11.52. Found: C, 73.38; H, 3.72; S, 11.45.

The solvent of the above filtrate was evaporated and the residue was washed with 50 ml of benzene to give 0.175 g (0.63 mmole, 21%) of tan crystals of 4. The solvent of the above benzene solution was evaporated and the residue was chromatographed on a silica gel column (20 g) using a mixture of benzene and hexane (1:4) as the eluent to give colorless crystals, which were recrystallized from hexane to give 12 mg (0.05 mmole, 1%) of colorless leaflets of 5, mp 235-236° (lit [8], mp 236°); ir (potassium bromide): ν 2916, 2849, 1257, 813, 751, 690 cm^{-1} .

Subsequent elution using a mixture of benzene and hexane (1:1) as the eluent afforded colorless crystals which were recrystallized from methanol to give 21 mg (0.076 mmole, 2%) of colorless needles of 6, mp 237-239°; ir (potassium bromide): ν 2918, 2849, 1725 (CO), 1587, 1396, 1237, 820, 741 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.55-8.19 (m, 5H, aromatic-H), 8.07 (d, J = 8.9 Hz, 10-H), 8.42 (d, J = 8.9 Hz, 11-H), 9.17 (s, 1H, 4-H).

Anal. Calcd. for $\text{C}_{17}\text{H}_8\text{O}_2\text{S}$: C, 73.90; H, 2.92; S, 11.60. Found: C, 74.07; H, 3.14; S, 11.46.

Phenanthro[2,1-b]thiophene (5).

A mixture of 0.278 g (1.0 mmole) of 4, 0.3 g of powdered

copper and 5 ml of quinoline was refluxed for 1 hour. The reaction mixture was poured into 100 ml of ice-water and acidified with 10% hydrochloric acid solution. The mixture was extracted with 100 ml of benzene. The benzene layer was washed successively with saturated sodium bicarbonate solution and water, dried over sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on a silica gel column using hexane as an eluent to give a white solid, which was recrystallized from hexane to give 0.187 g (0.799 mmole, 80%) of colorless prisms, of 5, mp 235-236° (lit [7] mp 236°).

10-Cyanomethylphenanthro[2,1-b]thiophene (9).

A solution of 2.0 g (7.19 mmoles) of 4 in 50 ml of dry tetrahydrofuran was added to a suspension of 0.7 g of lithium aluminum hydride in 50 ml of dry tetrahydrofuran. After refluxing 3 hours, the reaction mixture was poured into 300 ml of ice-water and acidified with 10% hydrochloric acid. The mixture was extracted with benzene. The benzene layer was dried with sodium sulfate and evaporated to give 1.51 g (5.68 mmoles, 79%) of a brown caramel oil, 7. This compound was 10-hydroxymethylphenanthro[2,1-b]thiophene (7); $^1\text{H-nmr}$ (deuteriochloroform): δ 5.17 (s, 2H, $\text{CH}_2\text{-O}$), 7.15-8.25 (m, 8H, aromatic-H), 8.45-8.85 (m, 1H, 9-H). This compound was used in the next step without the purification. A mixture of the above product (1.50 g, 5.68 mmoles) of 7, 2 ml of thionyl chloride, and 20 ml of dry benzene was refluxed for 2 hours. After removal of the benzene and excess thionyl chloride, the residue was recrystallized from hexane to give 1.1 g (3.9 mmoles, 69%) of white crystals, 8, mp 140-144°. This compound is 10-chloromethylphenanthro[2,1-b]thiophene; $^1\text{H-nmr}$ (deuteriochloroform): δ 5.29 (s, 2H, $\text{CH}_2\text{-Cl}$), 7.50-8.30 (m, 8H, aromatic-H), 8.82-9.00 (m, 1H, 9-H). A mixture of 1.0 g (3.55 mmoles) of 8, 1.0 g of sodium cyanide, 3 ml of water, and 20 ml of dimethyl sulfoxide was stirred at 40° for 2 hours. The reaction mixture was poured into 200 ml of ice-water and extracted with chloroform. The chloroform layer was dried over sodium sulfate and evaporated. The residue was chromatographed on an alumina column using a mixture of cyclohexane and benzene (1:1) to give 0.61 g (2.23 mmoles, 63%) of tan crystals. The product was recrystallized from methanol to give colorless needles of 9, mp 155-157° (lit [8] mp 157°); ir (potassium bromide): ν 2242 (CN), 1425, 867, 828, 756.

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