

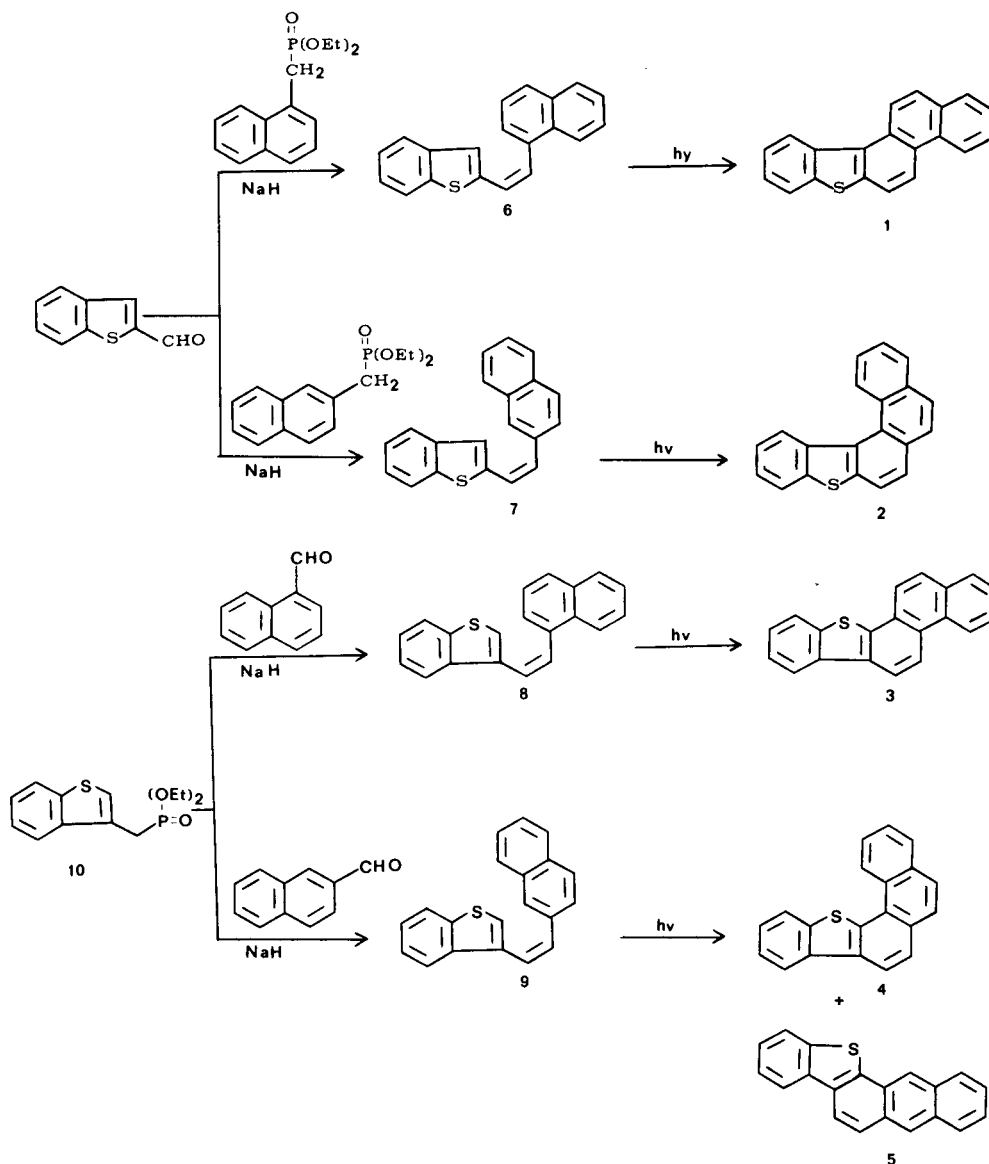
Department of Chemistry, Brigham Young University,
 Provo, Utah 84602
 Received April 23, 1981

The synthesis of benzo[*b*]phenanthro[1,2-*d*]thiophene (**1**), benzo[*b*]phenanthro[4,3-*d*]thiophene (**2**), benzo[*b*]phenanthro[2,1-*d*]thiophene (**3**) and benzo[*b*]phenanthro[3,4-*d*]thiophene (**4**) from appropriately substituted olefins by photochemical cyclodehydrogenation is described. The photolysis of olefin **9** gave a mixture of **4** and anthra[1,2-*b*]benzo[*d*]thiophene (**5**).

J. Heterocyclic Chem., **19**, 219 (1982).

As part of a program to identify the mutagenic and/or carcinogenic components of coal derived products, we have initiated in this laboratory a synthetic method of obtaining the sulfur analogs of a variety of polycyclic aromatic hydrocarbons. Here we report the synthesis of some benzo[*b*]phenanthro[*d*]thiophenes such as benzo[*b*]phenanthro[1,2-*d*]thiophene (**1**), benzo[*b*]phenanthro-

[4,3-*d*]thiophene (**2**), benzo[*b*]phenanthro[2,1-*d*]thiophene (**3**) and benzo[*b*]phenanthro[3,4-*d*]thiophene (**4**) which are the sulfur-containing isosteres of certain pentacyclic hydrocarbons. These compounds were synthesized by photochemical cyclodehydrogenation of appropriately substituted olefins (**6**, **7**, **8** and **9**) as depicted in the scheme below.



The Wadsworth-Emmons reaction between 2-benzo[*b*]thiophenecarboxaldehyde and diethyl 1-naphthylmethylphosphonate and diethyl 2-naphthylmethylphosphonate gave olefins **6** and **7**, respectively. Photocyclization of stilbenes **6** and **7** with a 450 Watt Hanovia medium pressure mercury lamp gave 41% of benzo[*b*]phenanthro[1,2-*d*]thiophene (**1**) and 25% of benzo[*b*]phenanthro[4,3-*d*]thiophene (**2**), respectively. Davis, *et al.*, prepared **1** in 50% yield by a multistep synthesis starting from 3-vinylthiophene and naphthoquinone (**2**). The compounds **3** and **4** were also prepared by photochemical cyclodehydrogenation of olefins **8** and **9**, respectively. This reaction was studied earlier by Croisy, *et al.*, (3). In the photolysis of **9**, we isolated both benzo[*b*]phenanthro[3,4-*d*]thiophene (**4**) and anthra[1,2-*b*]benzo[*d*]thiophene (**5**) in the ratio of 1:3, whereas Croisy, *et al.*, obtained **5** as the sole product. We prepared olefins **8** and **9** by the Wadsworth-Emmons reaction in higher yields than those reported previously (3).

EXPERIMENTAL

The ¹H-nmr were recorded on a Varian EM-390 spectrometer and a JEOL FX 90 spectrometer in the solvents indicated. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. Mass spectra were recorded on a Hewlett-Packard model 5980A mass spectrometer. The uv spectra were recorded on a Hitachi spectrophotometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

1-(Benzo[*b*]thiophen-2-yl)-2-(1'-naphthyl)ethene (**6**).

Sodium hydride (50% oil suspension, 0.6 g, 12 mmoles) was suspended in 1,2-dimethoxyethane and diethyl 1-naphthylmethylphosphonate (2.62 g, 10 mmoles) was added dropwise to the suspension. The resulting solution was stirred at room temperature for about one hour. To the yellow solution was added dropwise 2-benzo[*b*]thiophenecarboxaldehyde and the reaction mixture was stirred at room temperature for one additional hour. The reaction mixture was decomposed with water and the solid collected by suction filtration, yield 2.5 g (87%), mp 152-153°; ms: 286 (M⁺, 100).

Anal. Calcd. for C₂₀H₁₄S: C, 83.87; H, 4.92; S, 11.19. Found: C, 83.67; H, 5.12; S, 11.32.

1-(Benzo[*b*]thiophen-2-yl)-2-(2'-naphthyl)ethene (**7**).

This compound was prepared according to the above procedure except that diethyl 2-naphthylmethylphosphonate was used, yield 80%, mp 253-255°; ms: 286 (M⁺, 100).

Anal. Calcd. for C₂₀H₁₄S: C, 83.87; H, 4.92; S, 11.19. Found: C, 84.05; H, 4.73; S, 10.91.

Benzo[*b*]phenanthro[1,2-*d*]thiophene (**1**).

A solution of 1-(benzo[*b*]thiophen-2-yl)-2-(1'-naphthyl)ethene (0.5 g, 17 mmoles) and iodine (0.5 g) in cyclohexane (500 ml) was irradiated for four hours with a 450 Watt Hanovia medium pressure mercury lamp through a Corex filter. During the course of the reaction a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue was chromatographed on a silica gel column using hexane as the eluant to give, after crystallization from hexane, 0.2 g (41%) of **1** as white crystals, mp 162-164° (lit (2) 168.5°); ms: 284 (M⁺, 100); nmr (deuteriochloroform): 7.36-8.20 (m, H-2, H-3, H-6, H-8, H-9, H-10, H-11, H-12, 8H), 8.76 (d, J = 10 Hz, H-1, H-13, 2H), 8.98 (d, J = 10 Hz, H-4, H-5, 2H); uv (cyclohexane): λ max (log ε) 215 (4.73), 239 (4.50), 256 (4.60), 266 (4.73),

275 (4.92), 284 (4.63), 299 (4.37), 314 (4.42), 327 (4.48), 350 (3.60), 367 (3.60).

Anal. Calcd. for C₂₀H₁₂S: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.32; H, 4.41; S, 11.05.

Benzo[*b*]phenanthro[4,3-*d*]thiophene (**2**).

This compound was prepared following the above procedure described for **1**, yield, 25%, mp 132-133°; ms: 284 (M⁺, 100); nmr (deuteriochloroform): 7.25-8.0 (m, H-1, H-2, H-3, H-4, H-7, H-8, H-10, H-11, H-12, H-13, 10H), 8.70 (near dd, J = 10 Hz, H-6, 1H), 9.04 (near dd, J = 10 Hz, H-5, 1H); uv (cyclohexane): λ max (log ε) 212 (4.96), 237 (4.76), 244 (4.65), 250 (4.58), 255 (4.56), 262 (4.57), 282 (4.57), 299 (4.61), 315 (4.42), 335 (3.94), 365 (3.94), 382 (3.46).

Anal. Calcd. for C₂₀H₁₂S: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.46; H, 4.32; S, 11.00.

Diethyl Benzo[*b*]thiophen-3-ylphosphonate (**10**).

The compound **10** (bp 176-182°/1.5 mm Hg) was prepared by the reaction of 3-chloromethylbenzo[*b*]thiophene and triethyl phosphite following the procedure of Tominaga *et al.*, (4).

1-(Benzo[*b*]thiophen-3-yl)-2-(1'-naphthyl)ethene (**8**).

This compound was prepared by the Wadsworth-Emmons reaction between **10** and 1-naphthalenecarboxaldehyde following the method used for **6**, yield 56%, mp 130° (lit (3) 134°).

1-(Benzo[*b*]thiophen-3-yl)-2-(2'-naphthyl)ethene (**9**).

This compound was also prepared in the same manner as **8** by the reaction of **10** and 2-naphthaldehyde, yield 56%, mp 150° (lit (3) 152°).

Benzo[*b*]phenanthro[2,1-*d*]thiophene (**3**).

This compound was prepared by photocyclization of **8** following the method used for **1**, yield 10%, mp 230° (lit (3) 331°); ms: 284 (M⁺, 100); uv (cyclohexane): λ max (log ε) 214 (5.14), 246 (5.06), 253 (5.15), 258 (5.20), 264 (5.21), 280 (5.10), 292 (4.90), 310 (4.75), 350 (4.24), 367 (4.29).

Anal. Calcd. for C₂₀H₁₂S: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.23; H, 4.46; S, 11.14.

Benzo[*b*]phenanthro[3,4-*d*]thiophene (**4**) and Anthra[1,2-*b*]benzo[*d*]thiophene (**5**).

The olefin **9** was irradiated following the procedure used for **1**. The solid obtained (yield 5%) after chromatography on a silica gel column with hexane was crystallized from hexane to give **5**, mp 226-227° (lit (3) 228°), ms: 284 (M⁺, 100); uv (cyclohexane): λ max (log ε) 215 (4.80), 234 (4.75), 243 (4.74), 250 (4.75), 275 (4.77), 283 (4.76), 294 (4.67), 310 (4.52), 324 (4.54), 350 (3.90), 369 (3.90).

Anal. Calcd. for C₂₀H₁₂S: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.43; H, 4.45; S, 11.19.

Concentration of the mother liquor from the above reaction gave **4** in the ratio 3:1, mp 120-122° (lit (3) 127°), ms: 284 (M⁺, 100); uv (cyclohexane): λ max (log ε) 213 (4.57), 230 (4.49), 242 (4.58), 251 (4.57), 266 (4.55), 283 (4.78), 295 (5.00), 310 (4.14), 324 (4.14), 353 (3.82), 372 (3.92), 393 (3.78).

Anal. Calcd. for C₂₀H₁₂S: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.43; H, 4.45; S, 11.19.

Acknowledgement.

This study was supported by the U.S. Department of Energy, Office of Health and Environmental Research, Contract No. DE-AC02-79EV10237.

REFERENCES AND NOTES

- (1) To whom inquiries regarding this work should be directed at: Department of Chemistry, University of South Florida, Tampa, FL 33620 USA.
- (2) W. Davies and Q. N. Porter, *J. Chem. Soc.*, 459 (1957).
- (3) A. Croisy, P. Jacquignon and F. Perin, *J. Chem. Soc., Chem. Commun.*, 106 (1975).
- (4) Y. Tominaga, M. L. Lee and R. N. Castle, *J. Heterocyclic Chem.*, **18**, 967 (1981).