

Ram Pratap, Milton L. Lee, and Raymond N. Castle* (1)

Department of Chemistry, Brigham Young University, Provo, Utah 84602
Received June 22, 1981

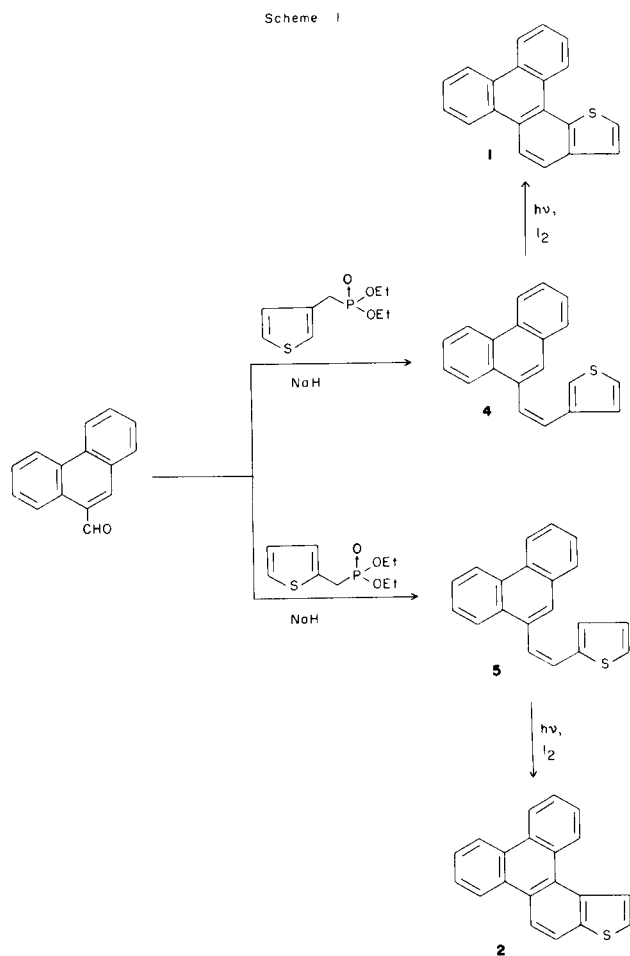
The synthesis of all the isomers of triphenyleno[b]thiophenes namely, triphenyleno[1,2-*b*]thiophene, triphenyleno[2,1-*b*]thiophene and triphenyleno[2,3-*b*]thiophene is described.

J. Heterocyclic Chem., **18**, 1457 (1981).

Recently, attention has been focused on the search for sulfur analogs of the polycyclic aromatic hydrocarbons (PAH) in coal and coal-derived products (2) along with PAH. The mutagenicity of PAH has been extensively studied (3a,b) whereas that of the polycyclic thiophenes is rarely reported. Because of the difficulty encountered in their isolation from coal products, a synthetic effort was initiated to obtain various classes of polycyclic thiophenes. Thus, the availability of the polycyclic thiophenes will allow their positive identification in coal-derived products. It will also provide samples for mutagenic testing. In PAH, it has been observed that the presence of a bay region and the lack of substitution in one of the bay regions is necessary for their carcinogenicity (4). Based on this idea, we report the synthesis of triphenyleno[b]thiophenes which have three unsubstituted bay regions, namely triphenyleno[1,2-*b*]thiophene (1), triphenyleno[2,1-*b*]thiophene (2) and triphenyleno[2,3-*b*]thiophene (3).

The synthesis of angularly fused thiophenes by the oxidative photocyclization of styrylthiophenes has been reported from this laboratory (5). Therefore, angularly fused triphenyleno[b]thiophenes 1 and 2 were synthesized by the photocyclization of styrenes 4 and 5. The styrenes 4 and 5 were prepared by the Wadsworth-Emmons reaction (6) between diethyl 3-thenylphosphonate and phenanthrene-9-carboxaldehyde and between diethyl 2-thenylphosphonate and phenanthrene-9-carboxaldehyde, respectively.

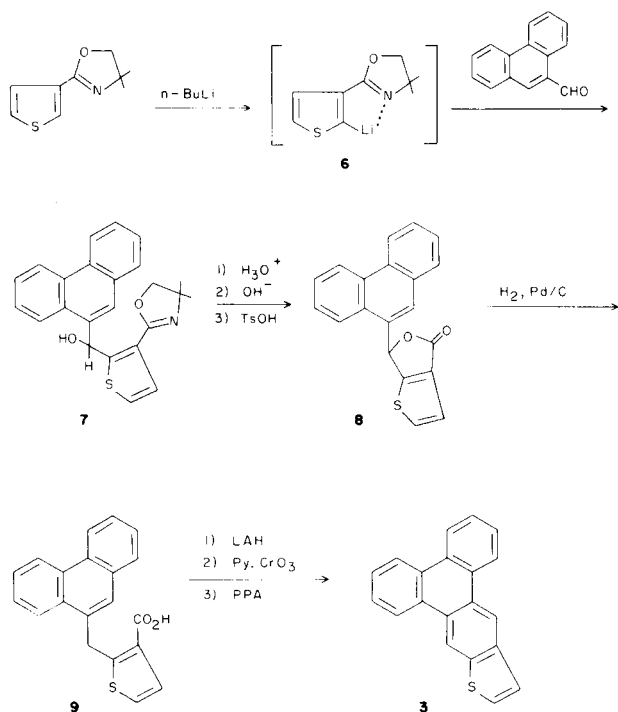
The synthesis of linearly fused triphenyleno[2,3-*b*]thiophene (3) was reported by Nicolaides (7) from thiophene-2,3-dicarboxaldehyde. Here we report another synthesis of 3 depicted in Scheme II. Iwao, *et al* have reported the synthesis of some linearly fused thiophenes by the metalation of thenyloxazoline (5). Compound 3 has also been synthesized by the above route. Thus the 4,4-dimethyl-2-(3-thenyl)-2-oxazoline was lithiated with *n*-butyllithium in dry ether at -45° and the resulting lithium compound 6 was condensed with phenanthrene-9-carboxaldehyde giving 7 as an oil. The oxazoline ring of 7 was hydrolysed with and the resulting acid was cyclized to the lactone 8 by heating in toluene with a catalytic amount of *p*-toluenesulfonic acid. The lactone 8 was hydrogenated to the acid 9 over palladium on charcoal in warm acetic



acid. The acid 9 was converted to the corresponding aldehyde by reduction with lithium aluminium hydride followed by oxidation with chromium trioxide-pyridine complex. The cyclization of the crude aldehyde by heating with polyphosphoric acid in *m*-xylene gave the desired thiophene 3.

In the nmr spectrum of 1, H-11 appeared as doublet ($J = 8$ Hz) at δ 8.23 and in the compound 2, H-13 appeared as doublet ($J = 8$ Hz) at δ 8.21 and protons H-9 and H-10 in 2 showed doublets ($J = 4$ Hz) at δ 8.52 and 7.90 respectively. In the spectrum of 3, H-9 and H-13 appeared as two singlets at δ 9.28 and 9.37, respectively.

Scheme 11



EXPERIMENTAL

The ir spectra were recorded on a Beckmann Acculab-2 spectrometer. The ^1H nmr spectra were obtained on a Varian EM 390 spectrometer and a JEOL FX 90Q spectrometer in the solvents indicated. Chemical shifts are reported in ppm from TMS as an internal reference and are given in δ units. Mass spectra were recorded on a Hewlett-Packard model 5980A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

Diethyl 2-Thenylphosphonate and Diethyl 3-Thenyl Phosphonate.

These were prepared following the procedure of Iwao, *et al* (5) by the reaction of 2-chloromethylthiophene and 3-bromomethylthiophene with triethyl phosphite, respectively.

3-[β -(9-Phenanthryl)vinyl]thiophene (4).

Sodium hydride (50% oil suspension, 0.23 g, 9.58 mmoles) was placed in 1,2-dimethoxyethane after washing with hexane. To the above slurry, diethyl 3-thenylphosphonate (0.89 g, 4.8 mmoles) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for about one half hour. To the light yellow solution was added dropwise a solution of phenanthrene-9-carboxaldehyde (1.0 g, 4.8 mmoles) in dimethoxyethane. The reaction mixture was stirred at room temperature for one hour and then at 50° for one half hour. After cooling, the reaction mixture was decomposed with a large excess of water and the product was collected by filtration. The solid was crystallized from hexane to give **4** (1 g, 72%) as light yellow crystals, mp 102° .

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{S}$: C, 83.87; H, 4.92; S, 11.19. Found: C, 83.64; H, 4.89; S, 11.37.

2-[β -(9-Phenanthryl)vinyl]thiophene (5).

This compound was also prepared by the Wadsworth-Emmons reaction between diethyl 2-thenylphosphonate and phenanthrene-9-

carboxaldehyde, m.p. 109° .

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{S}$: C, 83.87; H, 4.92; S, 11.19. Found: C, 83.88; H, 4.90; S, 11.17.

Triphenyleno[1,2-*b*]thiophene (1).

A solution of **4** (1.0 g, 3.49 mmoles) and iodine (0.05 g) in 500 ml of cyclohexane 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 also passed through the solution. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column using hexane as the eluant to give **1** as white crystals which were recrystallized from hexane, yield 0.20 g, (20%), mp 135° ; ms: m/e 284 (M^+ , 100%); nmr (deuterioacetone): 7.59-8.03 (m, 6H, H-2, H-3, H-6, H-7, H-10, H-12); 8.23 (d, 1H, J = 8 Hz, H-11); 8.70-9.37 (m, 5H, H-1, H-4, H-5, H-8, H-9).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{S}$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.67; H, 4.50; S, 11.06.

Triphenyleno[2,1-*b*]thiophene (2).

This compound was also prepared by the oxidative photocyclization of **5** (1.0 g, 3.49 mmoles) following the above procedure, yield 0.7 g, (70%); mp 97° ; ms: m/e 284 (M^+ , 100%); nmr (deuterioacetone): 7.58-7.81 (m, 5H, H-2, H-3, H-6, H-7, H-12); 7.90 (d, 1H, J = 6 Hz, H-10); 8.21 (d, 1H, J = 8 Hz, H-13); 8.52 (d, 1H, J = 6 Hz, H-9); 8.61-9.06 (m, 4H, H-1, H-4, H-5, H-8).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{S}$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.60; H, 4.42; S, 11.20.

6-(9'-Phenanthryl)thieno[2,3-*c*]furan-4-(6*H*)one (8).

Under a nitrogen atmosphere, 20 ml (0.03 mole) of 1.5 *M* *n*-butyllithium solution in hexane was added dropwise to a solution of 5.43 g (0.03 mole) of 4,4-dimethyl-2-(3-thenyl)-2-oxazoline in 100 ml of dry ether keeping the temperature between -35 and -45° (dry ice-chlorobenzene bath). After stirring for one hour, a solution of phenanthrene-9-carboxaldehyde (6.18 g, 0.03 moles) in 75 ml of dry tetrahydrofuran was added dropwise. The reaction mixture was allowed to warm gradually to room temperature and to stand overnight. Water was added to the reaction mixture, the ether layer was separated and the aqueous layer was extracted with ether. The combined extracts after drying over sodium sulfate were evaporated. The residual crude oil **7** was refluxed with 250 ml of 10% hydrochloric acid for five hours with stirring. After cooling, a brown solid was collected by filtration and refluxed again with a mixture of 250 ml of methanol and 100 ml of 30% of sodium hydroxide. The reaction mixture was poured into *ca* 1 ℓ of water and acidified with hydrochloric acid. The precipitated solid was collected by filtration, washed with water and dried. A solution of this solid in 300 ml of toluene and 0.5 g of *p*-toluenesulfonic acid was refluxed for two hours with removal of water using a Dean-Stark water separator. The reaction mixture was passed through a silica gel column and eluted with benzene to give 2.0 g (21%) of **8** as a brown solid, mp 163° ; ir (potassium bromide): 1750 cm^{-1} (C=O); nmr (deuteriochloroform): 7.12 (s, 1H methine proton), 7.23 (d, 1H, J = 5 Hz, H-2 in thiophene ring), 7.34 (d, 1H, J = 5 Hz, H-3 in thiophene ring), 7.45-7.92 (m, 6H, H-2, H-3, H-6, H-7, H-8, H-9 in phenanthrene ring), 8.08 (m, 1H, H-1 in the phenanthrene ring), 8.48-8.83 (m, 2H, H-4, H-5 in the phenanthrene ring).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_2\text{S}$: C, 75.93; H, 3.82; S, 10.13. Found: C, 76.06; H, 3.57; S, 9.84.

2-(9-Phenanthrylmethyl)-3-thiophenecarboxylic Acid (9).

A mixture of 1.8 g of **8** and 0.6 g. of 5% palladium on charcoal in 300 ml of acetic acid was stirred under a hydrogen atmosphere at 95° overnight. The mixture was filtered and the residue was again refluxed in acetic acid and filtered. The combined filtrates were evaporated to dryness. The residue was crystallized from acetic acid to give 1.0 g (33%) of **9** as white crystals, mp $261-262^\circ$; ms: m/e 318 (M^+ , 84.5%) 300 ($\text{M}^+ - 18$, 100%); ir (potassium bromide): 3300 (OH) , 1665 cm^{-1} (C=O); nmr (DMSO- d_6): 5.15 (s, 2H, CH_2), 7.33 (d, 1H, J = 4 Hz, H-2 in the thiophene

ring), 7.46 (d, 1H, $J = 4$ Hz, H-3 in the thiophene ring), 7.56-8.23 (m, 7H, ArH), 8.77-9.00 (m, 2H, H-1, H-8 in the phenanthrene ring).

Anal. Calcd. for $C_{20}H_{12}O_2S$: C, 75.44; H, 4.43; S, 10.07. Found: C, 75.26; H, 4.46; S, 10.00.

Triphenyleno[2,3-*b*]thiophene (**3**).

A solution of 1.0 g (3.1 mmoles) of **9** in 50 ml of dry tetrahydrofuran was added dropwise to a suspension of 0.2 g (5.2 mmoles) of lithium aluminium hydride in 50 ml of dry ether. After refluxing for three hours, 10% sodium hydroxide was added dropwise and the precipitated aluminium hydroxide was filtered. The dried filtrate (sodium sulfate) was evaporated to give the crude alcohol as a pale yellow oil; ir (neat): 3360 cm^{-1} (OH).

The solution of this crude alcohol in 11 ml of dry pyridine was added slowly to a suspension of chromium trioxide-pyridine complex made from 1.1 g of chromium trioxide and 11 ml of pyridine. After stirring for two hours at room temperature, the reaction mixture was filtered through celite and washed with chloroform. The filtrate was washed with 10% hydrochloric acid and then 10% sodium carbonate. After drying over sodium sulfate, chloroform was evaporated to leave the crude aldehyde as an oil; ir (neat): 1660 cm^{-1} (C=O).

A mixture of the above crude aldehyde, 5 ml of polyphosphoric acid and 10 ml of *m*-xylene was heated over a steam bath for seven hours. After cooling, ice-water was added to the mixture and extracted with benzene. The benzene extracts were washed with water, dried over sodium sulfate and evaporated. The residue was chromatographed on a silica gel column using hexane as the eluant. The solid obtained was recrystallized from hexane to give 0.10 g (11%) of **3** as colorless crystals,

mp 141-143°; ms: 284 (M^+ , 100%); nmr (deuterioacetone): 7.54-7.81 (m, 6H, H-2, H-3, H-6, H-7, H-11, H-12); 8.57-8.92 (m, 4H, H-1, H-4, H-5, H-8); 9.28 (s, 1H, H-9); 9.37 (s, 1H, H-13).

Anal. Calcd. for $C_{20}H_{12}S$: C, 84.47; H, 4.25; S, 11.27. Found: C, 84.27; H, 4.28; S, 11.32.

Acknowledgement.

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

REFERENCE AND NOTES

- (1) To whom inquires regarding this work should be directed at the Department of Chemistry, University of South Florida, Tampa, FL 33620 USA.
- (2) C. Willey, M. Iwao, R. N. Castle, and M. L. Lee, *Anal. Chem.*, **53**, 400 (1981).
- (3) For a compilation of recent work, see (a) P. W. Jones and P. Leber, eds., "Polynuclear Aromatic Hydrocarbons", Ann Arbor Science, Ann Arbor, MI, 1979; (b) H. V. Gelbin and P. O. P. Ts'O, eds., Academic Press, New York, San Francisco, London, 1978.
- (4) R. Dagani, *Chem. Eng. News*, March 9, p. 26 (1981).
- (5) M. Iwao, M. L. Lee, and R. N. Castle, *J. Heterocyclic Chem.*, **17**, 1259 (1980).
- (6) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83** 1733 (1961).
- (7) D. N. Nicolaides, *Synthesis*, **10**, 675 (1976).