The Insertion and Extrusion of Heterosulfur Bridges. X. Conversions in the Triphenylene-Triphenylo[4,5-*bcd*]thiophene System (1)

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Sulfur bridging of triphenylene (**3**) to form triphenylo[4,5-*bcd*]thiophene (**4**) is effected in 18% yield by means of hydrogen sulfide and a molybdena catalyst (CMA-1) at 500°. Compound **4** is purified through its sulfoxide, converted into its sulfone (**6**), and desulfurized (by means of CMA-1 plus methanol-benzene) back to **3**. The ultraviolet absorption spectrum of **4** resembles closely that of benzo[*e*]pyrene. On electron impact **4** shows little skeletal fragmentation, while **6** readily evolves sulfur monoxide and the formyl group.

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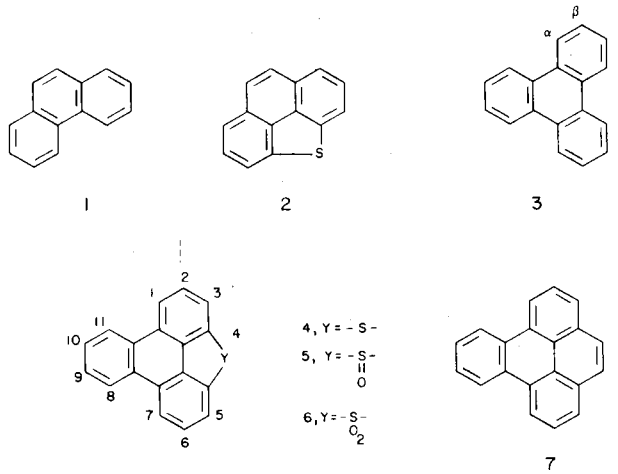
The reaction of a biaryl substrate (biphenyl or 2-phenylnaphthalene, as well as various phenylpyridines, bipyridines, and phenylquinolines) with hydrogen sulfide in the presence of alumina or a mixed metallic oxide catalyst at 350-630° effects the insertion of a heterosulfur bridging atom to produce a tri- or tetracyclic *kata*-condensed thiophene (3-6). In a single instance this method has been extended to use of an *ortho*-condensed (phene-type) arene substrate, whereby phenanthrene (**1**) is converted into the *peri*-condensed product phenanthro[4,5-*bcd*]thiophene (**2**) (3,7,8). We now report that analogously the phene-type compound triphenylene (**3**) is transformed into triphenylo[4,5-*bcd*]thiophene (**4**) in 18% yield by the same procedure, in particular by use of CMA-1 catalyst (9) and hydrogen sulfide at 500°.



Since efforts (crystallization and chromatography) to isolate pure **4** from the crude reaction mixture were of only limited success, **4** was oxidized *in situ* to sulfoxide **5**, a compound readily separable by chromatography on silica gel from accompanying sulfur and unreacted **3** (10). Reduction of **5** by means of sodium bis(2-methoxyethoxy)-aluminum hydride (11) then regenerated **4** (m.p. 190-191°), free from contamination by these other materials. This purification method followed closely that used in the synthesis of **2** (7).

Elemental analyses and determination of the exact mass established the molecular formula of **4** as $C_{18}H_{10}S$. Treatment of **4** with CMA-1 plus methanol-benzene at 450° reconverted **4** into **3**, as the dominant product, and indicated that the carbon skeleton of triphenylene was retained in **4**. Thus, the transformation of **3**→**4** involves the loss of two hydrogen atoms from the triphenylene molecule, plus the addition of a sulfur atom. Comparison of the pmr spectra of **3** and **4** shows that the hydrogen atoms lost are of the α-type. Whereas the spectrum of **3** exhibits two well-separated multiplets of equal areas (6H) at 7.4-7.8 (β-protons) and 8.4-8.7 ppm (α-protons) (12), the spectrum of **4** has three separate signals at 7.6-8.2 (still 6H), 8.47 (2H, tentatively assigned to H-8 and H-11), and 8.5-8.9 (2H, tentatively assigned to H-1 and H-7). Finally, the ultraviolet spectrum of **4** is closely similar in shape and intensity to that reported for benzo[*e*]pyrene (**7**) (13) (*vide infra*), as is expected for two aromatic molecules wherein a sulfur atom replaces a vinylene group (3,14). The aromatic character of **4** (as evidenced by its pmr and ultraviolet spectra) is further corroborated by the occurrence of limited fragmentation of **4** under electron-impact mass spectrometry, whereby the singly charged molecular ion is the most abundant ion in the spectrum and the intensity of the doubly charged molecular ion exceeds that of any ion fragment.

Despite the fact that sulfoxide **5** is a crucial intermediate in the purification of **4**, compound **5** was not obtained analytically pure itself. Elemental analyses and mass spectra of our best samples of this intermediate indicated the presence of minor components bearing more than one oxygen atom or more than one sulfur atom per molecule (15). These impurities must be lost during subsequent steps in the isolation of **4**.

No difficulty was encountered in the oxidation of purified **4** to sulfone **6** (m.p. 325-327°) by means of

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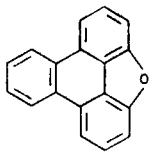
hydrogen peroxide in glacial acetic acid. The mass spectrum of **6** shows extensive fragmentation, particularly with loss of sulfur monoxide and the formyl radical from the molecular ion. In fact, the most abundant peak occurs at m/e 242 and corresponds to the singly charged ion of proposed skeletal structure **8**. There is also



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a peak at 121 for doubly charged **8**. Thus, the fragmentation pattern of **6** resembles closely that of dibenzothiophene sulfone (16a) and of **2**-sulfone (3). These similarities again serve to corroborate the structural assignment of **4**. It is interesting that the spectrum of **6** shows only a minor peak (<4%) at 258 (probably corresponding to singly charged **4**) while this is the most abundant peak in the spectrum of crude **5**.

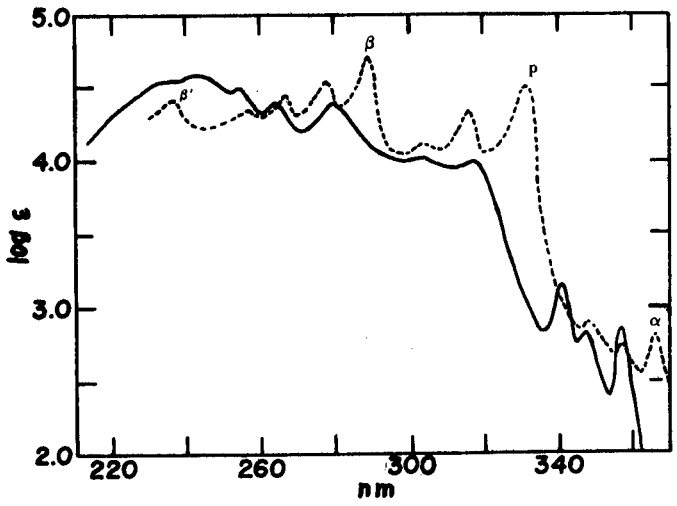

Figure 1. Ultraviolet absorption spectra for triphenylo[4,5-*bcd*]thiophene (**4**) (solid line) and benzo[*e*]pyrene (**7**) (13) (broken line) in 95% ethanol.

In Figure 1 are compared the ultraviolet spectra of **4** and **7** in the same solvent, 95% ethanol. In the wavelength range of 230-370 nm there are eleven distinct peaks recorded for the hydrocarbon **7**. These have been classified into four different sets, α, p, β, and β', by Clar (13). The same four sets are noted in the spectrum of **4**. However, one principal peak, believed to be the counterpart of the prominent p-band of longest wavelength (at 332 nm) in **7**, is either completely absent in **4** or markedly weakened and shifted bathochromically into the α-region. Otherwise, both the α- and β-bands of **4** are displaced hypsochromically by 7-9 and 9-14 nm, respectively, in comparison to those of **7**, and there is little or no shift in the β'-band and the two observed p-bands.

While specific reference to **4** has not been found in the literature, Lee and Hites (22) identified (by combined gas chromatography-mass spectrometry plus high resolution mass spectrometry) a "benzo[*def*]naphthobenzothiophene" in carbon black. This component should either be **4** or a structural isomer of **4**.

EXPERIMENTAL (16b)

Triphenylo[4,5-*bcd*]thiophene (**4**).

In the manner previously described (9), a bed (3.5 cm in diameter and 16 cm in length) of 150 g. of Harshaw pelletized Co-Mo-0603T catalyst (containing 3% cobaltous oxide, 12% molybdic oxide, and 85% aluminum oxide) was conditioned with methanol and hydrogen sulfide in a vycor reactor tube to form CMA-1 catalyst *in situ* at 500°. This temperature and the flow (at 125 ml./minute, as measured at room temperature) of hydrogen sulfide were maintained constant for a period of 2 hours while a solution of 5 g. of triphenylene (**3**) in 250 ml. of benzene was added dropwise to the tube, plus an additional 30 minutes while 50 ml. of benzene was added for washing. The cooled catalyst was refluxed with chloroform (Soxhlet apparatus) for 4 hours. This extract (shown to contain about 60% of the total **4** formed) was combined with the dried (sodium sulfate), collected reactor effluent and analyzed quantitatively by means of gas chromatography on a stationary phase of 10% Apiezon L on Diatoport-S at 260° with 1,1'-binaphthyl as a standard of reference, yields: **4**, 1.0 g. (18%); recovered **3**, 1.0 g.; relative retention times: standard, 1.0; **3**, 2.0; **4**, 5.8.

The residue from evaporation of the preceding mixed solvent was dissolved in a mixture of 20 ml. of tetrahydrofuran, 10 ml. of pyridine, and 10 ml. of water. To this stirred solution was added at 15-minute intervals, 0.5 g. portions (2.4 g. total used) (17) of iodobenzene dichloride (18) while the reaction mixture was monitored for the disappearance of **4** by means of thin layer chromatography on silica gel F-254 plates with carbon tetrachloride as eluent and detection of spots in 254 nm light; R_f values: iodobenzene, 1; sulfur, 0.9; **4**, 0.77; **3**, 0.67; **5** and **6**, 0 (19). When all of the **4** had reacted, the mixture was treated with 70 ml. of 10% sulfuric acid (20) and extracted with chloroform.

An admixture of the dried (sodium sulfate) chloroform layer and 4 g. of silica gel (Baker 60-200 mesh) was rotoevaporated to dryness. The residue, placed atop a column of 60 g. of plain silica gel, was eluted, in succession, with petroleum ether (30-60°) to remove sulfur, 15% chloroform-petroleum ether to recover **3**, chloroform, and acetone to collect **5** (observed as a blue-violet band in 366 nm light); crude yield of sulfoxide **5**, 1.3 g.

A mixture of this crude sulfoxide, 20 ml. of benzene, and 3.3 ml. (excess) of 70% solution of sodium bis(2-methoxyethoxy)-aluminum hydride in benzene (21) was refluxed for one hour and processed in the manner used on an analog (7). Regenerated **4** was purified further by column chromatography in the foregoing manner. Product collected from the first two eluates was recrystallized from 600 ml. of 9:1 methanol-benzene; yield 996 mg. of **4** as fine needles, m.p. 190-191°, soluble in carbon tetra-

chloride, chloroform, and acetone; insoluble in 30-60° petroleum ether; uv (ethanol): λ max (log ε) 233 nm, shoulder (4.53), 243 (4.58), 254 (4.49), 264 (4.41), 280 (4.40), 304 (4.02), 317 (4.01), 341 (3.15), 348 (2.82), 357 (2.85); pmr: δ 7.6-8.2 (m, 6H), 8.47 (d, J = 7.5 Hz, 2H), 8.5-8.9 ppm (m, 2H); ms: m/e (% relative abundance) 260 (7), 259 (21), 258 (M^+, 100), 257 (5), 256 (11), 213 ([M-CHS]$^+$, 5), 129 (M^{++}, 12), 128 (6); exact mass: Calcd. for $C_{18}H_{10}S$, 258.050; found, 258.051.

Anal. Calcd. for $C_{18}H_{10}S$: C, 83.69; H, 3.90. Found: C, 83.57; H, 3.75.

Triphenylo[4,5-*bcd*]thiophene 4-Oxide (**5**).

A sample of crude, preceding sulfoxide was sublimed at 170° (0.5 mm) and recrystallized from methanol to give needles, m.p. 223-225°; ir (chloroform): 1020 cm^{-1}; ir (potassium bromide): 1035 cm^{-1}; pmr: δ 7.6-8.0 (m, 4, H-2, H-6, H-9, and H-10), 8.1-8.3 (partially split d, J = 7.5 Hz, 2, H-8 and H-11), 8.4-8.7 ppm (m, 4, H-1, H-3, H-5, and H-7); exact mass: calcd for $C_{18}H_{10}OS$, 274.045; found, 274.043. Compound **5** was not obtained analytically pure.

Triphenylo[4,5-*bcd*]thiophene 4,4-Dioxide (**6**).

A mixture of 100 mg. of pure **4**, 10 ml. of glacial acetic acid, and 1 ml. of 30% hydrogen peroxide was refluxed for 30 minutes, cooled, and treated with 15 ml. of water. The yellow precipitate was collected, dried, decolorized by percolation of a chloroform solution through a short column of silica gel, and recrystallized from 9:1 methanol-chloroform to give white platelets, yield 54 mg. (48%), m.p. 325-327°; ir (chloroform): 1160 and 1310 cm^{-1}; ir (potassium bromide): 1170 and 1300 cm^{-1}; uv (ether): λ max (log ε) 252 nm, shoulder (4.84), 257 (4.94), 284 (4.31); pmr: δ 7.7-8.2 (m, 6H), 8.5-8.8 ppm (m, 4H); ms: m/e (% relative abundance) 291 (14), 290 (M^+, 74), 261 ([M-CHO]$^+$, 13), 243 (25), 242 ([M-SO]$^+$, 100), 224 ([M-H_2SO_2]$^+$, 12), 213 ([M-$CHSO_2$]$^+$, 29), 121 ([M-SO]$^{++}$, 13), 106.5 ([M-$CHSO_2$]$^{++}$, 11); exact mass: calcd for $C_{18}H_{10}O_2S$, 290.040; found, 290.040.

Anal. Calcd. for $C_{18}H_{10}O_2S$: C, 74.46; H, 3.47. Found: C, 74.45; H, 3.17.

Desulfurization of **4**.

In an exploratory run a solution of 0.24 g. of **4** in 80 ml. of 1:1 benzene-methanol was passed through a column of 30 g. of CMA-1 catalyst at 450° over a period of 5 hours with nitrogen as a carrier gas (9). Gas chromatographic and pmr analyses of the effluent showed the presence of triphenylene as the predominant product plus a small amount of an unidentified by-product but no evidence for recovered **4**.

REFERENCES AND NOTES

(1) This investigation was supported by research grant MPS 75-04116 from the National Science Foundation. For paper IX in this series see reference 6.

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(15) The mass spectrum of this sample provides indirect evidence that triphenylene will undergo the insertion of more than one sulfur atom. However, at this time no compound bearing more than one inserted heterosulfur bridge has been isolated from the reaction mixture of any substrate used in our studies.

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(16b) Pmr spectra were obtained on deuteriochloroform solutions by means of a Varian Associates HA-100 or XL-100 instrument. Infrared spectra were determined by means of a Beckman IR-7 or IR-10 spectrometer; ultraviolet absorption spectra, by means of a Cary model 15 spectrophotometer. Dr. Richard Wielesek obtained low and high resolution mass spectra by means of a CEC model 21-110 double focusing instrument, operated at 70 eV. He also carried out the elemental analyses.

(17) This amount represents 130 mole % excess of iodobenzene dichloride over that calculated for the conversion **4**→**5**. The fate of this excess was not ascertained.

(18) H. J. Lucas and E. R. Kennedy, *Org. Syn.*, Coll. Vol. III, 482 (1955).

(19) The R_f value of zero was confirmed for isolated samples of crude **5** and pure **6**.

(20) This represents 23% excess of acid, as based on protonation of the pyridine present.

(21) E. K. Co. Vitride was used.

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