

The Insertion and Extrusion of Heterosulfur Bridges. III.  
A Useful Chemical-Chromatographic Separation Procedure (1)

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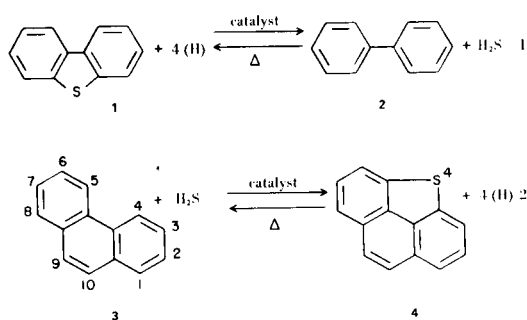
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A method is described for the isolation of pure phenanthro[4,5-*bcd*]thiophene (**4**) from a sulfur-bridging reaction mixture, also containing phenanthrene (**3**) and elemental sulfur, by selective oxidation of **4** to the sulfoxide (**5**) by means of iodobenzene dichloride, chromatographic separation of **5** on silica gel, and finally reduction of **5** back to **4** by means of sodium bis(methoxyethoxy)aluminum hydride in 25% overall yield from **3**.

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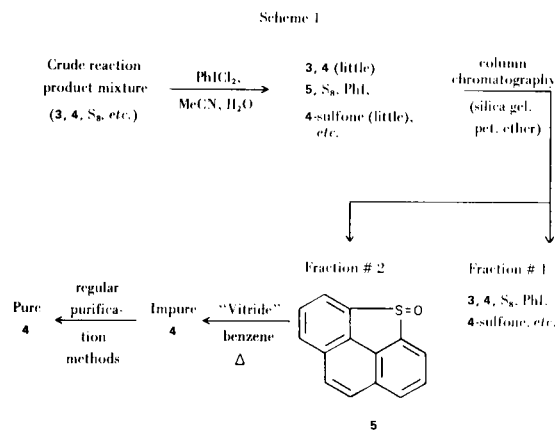
The insertion of sulfur bridging atoms into biaryls and angularly annellated (phene-type) arenes to form polycyclic condensed thiophenes, and the extrusion of sulfur bridging atoms from condensed thiophenes, may be considered to be reversible processes (as illustrated in equations 1 and 2). Currently there is a great amount of



interest in the extrusion process (hydrodesulfurization) as a means of removing thiophene-type sulfur atoms from compounds present in petroleum, coal, and oils resulting from hydrogenation of coal (3,4). Dibenzothiophene (**1**), the first member of the thia-bridged biaryl series, is the only polycyclic condensed thiophene which is commercially available for use in desulfurization studies. Use of the sulfur-bridging reaction to synthesize other desired, condensed thiophenes is an attractive pathway because of its apparent generality and simplicity, as well as the ready availability of the requisite aromatic hydrocarbon starting materials (5).

Both insertion and extrusion on a preparative scale are beset with the experimental problem of successfully sepa-

rating unreacted starting material, product(s), and byproducts (including elemental sulfur). *Prima facie*, the report of Badger, *et al.*, (6) on the use of Raney cobalt (plus sand) for separation of **1** and **2** by column chromatography would seem to represent an ideal solution to this problem. However, repeated efforts by several workers in our laboratory to reproduce this separation both with synthetic mixtures of **1** and **2** and with the crude mixture from reaction 2 have been of no avail. While the latter mixture can be separated by crystallization (5), the method is tedious. Moreover, column chromatography on alumina (5) or silica gel, as well as fractional sublimation, are unsuccessful. We now report the successful isolation of pure phenanthro[4,5-*bcd*]thiophene (**4**) from the reaction mixture by means of a chemical-chromatographic sequence which involves the sulfoxide of **4** as a key intermediate.



In our method (Scheme 1) one first approximates the amount of **4** in the crude mixture from reaction 2 and then adds (as nearly as possible) an equimolar amount of iodobenzene dichloride (plus water) to yield sulfoxide **5**. The sulfoxide is easily separated from other components of the mixture by means of chromatography on silica gel (7,8), to which the sulfoxide is strongly held by means of hydrogen bonding. The other components (including, perhaps, small amounts of **4**-sulfone) are readily eluted from the column. The isolated, relatively pure sulfoxide is then reduced back to **4** by means of "Vitride" (9). To help insure that one has added the optimum quantity of iodobenzene dichloride in the first step [*i.e.* has added the amount which will produce a maximal yield of sulfoxide, with minimal amounts of unreacted **4** (from under-oxidation) and byproduct **4**-sulfone (10) (from overoxidation)] the composition of the sulfoxide mixture is monitored by thin layer chromatography (11).

In previous studies (5) of reaction 2 the best yield of **4** was obtained with a chromia-alumina catalyst (Harshaw Cr-0101T) at 630°. Our present results indicate that a cobalt oxide-molybdena-alumina catalyst (Harshaw Co-Mo-0603T) at 430-600° gives a somewhat higher yield (12) of **4**. While an accurate yield on the sulfur-bridging reaction *per se* was not obtained, the average overall yield of sulfoxide **5** from phenanthrene (**3**) was 29% and that of purified **4** (from **3**) was 25%.

#### EXPERIMENTAL (13)

##### Catalytic Bridging Reaction.

In the previously described manner (5,14), a solution of 15 g. of phenanthrene in 55 ml. of benzene was added to a pyrex reactor tube containing  $180 \pm 10$  g. of pre-sulfided (*in situ*) Harshaw catalyst (1/8" pellets) in a stream of hydrogen sulfide while the temperature was maintained at a constant value. Combined effluents were shaken with a mixture of ether and 2 M aqueous sodium hydroxide solution. Evaporation of the ether solution gave crude product which was weighed and analyzed for apparent mol fraction of **4** by comparing integrations of the pmr spectrum in the region  $\delta$  8.5-9.0 ppm (ascribed to the presence of H-4 and H-5 in **3**) and in the region  $\delta$  7.4-8.2 ppm (ascribed to H-1 to H-3 and H-6 to H-10 in **3** plus all aromatic protons in **4**) (15). Yields of crude product mixture and apparent mol fractions of **4** therein for 3 runs were as follows: (a) for Cr-0101 T catalyst at 630°, 8.9 g., 0.53; (b) for Co-Mo-0603 T catalyst at 430°, 13.3 g., 0.43; (c) for Co-Mo-0603 T catalyst at 600°, 8.6 g., 0.67. These products were mixed together for further processing.

##### Formation of Phenanthro[4,5-*bcd*]thiophene 4-Oxide (**5**).

To a stirred suspension of 20 g. of crude preceding product mixture (containing 0.62 mole fraction of **4**, as estimated by pmr analysis) (15) was added slowly (over a period of 20 minutes) a solution of 15 g. (87% of the estimated theoretical amount) of iodobenzene dichloride (16,17) in 320 ml. of acetonitrile. The mixture was stirred for 30 minutes longer, treated with 100 ml. of water, and extracted with chloroform to give 18.7 g. of yellow

residue.

A solution of 2.64 g. of the residue in chloroform was chromatographed on a column of 108 g. of Baker 60-200 mesh silica gel (predried at 100° for 12 hours) with petroleum ether (30-60°) as eluent and monitoring by means of 366-nm light. A preceding purplish band was eluted (discarded) and the following bluish band was eluted with methanol (air pressure). Evaporation of the latter effluent gave 1.7 g. (quantitative yield as based on the iodobenzene dichloride used; average 29% overall yield from phenanthrene) of sulfoxide **5**, free of other components as based on tlc analysis (11).

##### Isolation of Phenanthro[4,5-*bcd*]thiophene (**4**).

Beneath the surface of a stirred slurry of 2.2 g. (9.8 mmoles) of preceding sulfoxide **5** in 10 ml. of benzene was added (by syringe) 7 ml. of a 70% solution of sodium bis(2-methoxyethoxy)-aluminum hydride (EK Co. Vitride) (18) in benzene (25 mmoles). After the sulfoxide had dissolved, the brown solution was refluxed for 45 minutes, cooled, and poured into 250 ml. of 1 M hydrochloric acid. A benzene extract of the mixture was dried and evaporated to yield impure **4**, which was chromatographed on a column of 108 g. of dried silica gel in the previous manner. The purplish band yielded a white solid which formed needles of **4** (m.p. 126-130°) on recrystallization from chloroform, yield 1.75 g. (86%). The product was purified further by sublimation at 100° (0.06 mm.) (m.p. 132-135°), recrystallization from methanol, and drying over phosphorus pentoxide. On a hot stage these needles melted at 138.5-139° and partially sublimed (starting at 115-120°) to give prisms, m.p. 134-135°.

#### REFERENCES AND NOTES

- (1) This investigation was supported by research grant no. MPS 75-04116 from the National Science Foundation. For paper II see L. H. Klemm, D. R. McCoy, and C. E. Klopfenstein, *J. Heterocyclic Chem.*, **8**, 383 (1971).
- (2) Undergraduate research student, 1974-1976.
- (3) S. Akhtar, A. G. Sharkey, J. L. Schultz and P. M. Yavorsky, "Organic Sulfur Compounds in Coal Hydrogenation Products," ERDA report, Pittsburgh Energy Research Center, Pittsburgh, Pa., 1974.
- (4) B. C. Gates, "NSF Workshop on the Fundamental Organic Chemistry of Coal," J. W. Larsen, Ed., U. Tenn., Knoxville, Tenn., July, 1975, pp. 157-169, and references cited therein.
- (5) L. H. Klemm, D. R. McCoy and D. R. Olson, *J. Heterocyclic Chem.*, **7**, 1347 (1970).
- (6) G. M. Badger, N. Kowanko and W. H. F. Sasse, *J. Chromatog.*, **13**, 234 (1964); G. M. Badger, P. Cheuychit and W. H. F. Sasse, *Aust. J. Chem.*, **17**, 366 (1964).
- (7) The isolation of the sulfoxides of sulfur-bearing components in high-boiling petroleum fractions by means of column chromatography on silica gel was described by H. V. Drushel and A. L. Sommers, *Anal. Chem.*, **39**, 1819 (1967).
- (8) The strong retention of sulfoxides on silica gel in tlc has been noted previously [L. Fishbein and J. Fawkes, *J. Chromatog.*, **22**, 323 (1966); F. H. W. Lee, unpublished observations in this laboratory].
- (9) T. L. Ho and C. M. Wong, *Org. Prep. Proced. Int.*, **7**, 163 (1975).
- (10) The sulfone is not reduced by Vitride.
- (11) Thin layer chromatography by means of benzene and Baker silica gel 7G gives the following  $R_f$  values: iodobenzene, 0.89; **4**, 0.86; **3**, 0.74; **4**-sulfone, 0.22; **5**, < 0.1.

(12) It is noteworthy that catalysts of cobalt and molybdenum oxides (after sulfidation) are widely used for desulfurization of thiophene compounds [O. Weisser and S. Landa, "Sulphide Catalysts, Their Properties and Applications," Pergamon Press, New York, N.Y., 1973, pp. 210-244; "Harshaw Catalysts for Industry," Catalog No. 500, Harshaw Chemical Co., Cleveland, Ohio, p. 21]. Catalyst Co-Mo-0603 T contains 3% CoO, 12% MoO<sub>3</sub>, and 85% Al<sub>2</sub>O<sub>3</sub>.

(13) Pmr spectra were determined on deuteriochloroform solutions by means of a Varian Associates T-60 instrument. Sulfoxide **5** and **4**-sulfone were identified by comparison of infrared spectra

with those previously obtained (5).

(14) As in runs 1-14 by L. H. Klemm, D. R. McCoy, J. Shabtai, and W. K. T. Kiang, *J. Heterocyclic Chem.*, **6**, 813 (1969).

(15) Calculation of the apparent mol fraction of **4** is based on the assumption that *only* **3** and **4** (free of sulfur or other impurities) are present in the sample.

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

(17) As indicated by tlc (11) use of a larger ratio of iodobenzene dichloride to product mixture caused formation of some **4**-sulfone.

(18) Aldrich Chemical Co. brand name is Red-al.