

Sulfur Bridging in 2-Phenylnaphthalene (1)

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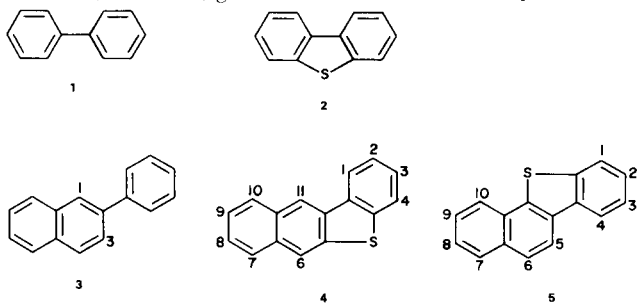
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Sulfur bridging of 2-phenylnaphthalene (**3**) to form benzo[*b*]naphtho[2,1-*d*]thiophene (**5**) (main product) and the isomeric benzo[*b*]naphtho[2,3-*d*]thiophene (**4**) is effected by means of hydrogen sulfide, benzene (solvent), and a sulfided cobaltous oxide-molybdc oxide-alumina (CMA-1) catalyst at 450-630° in a flow system (maximum yield 33% at 500°). The low yield is ascribed to decompositions of both **4** and **5** under reaction conditions.

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In a previous publication (4) we summarized reported methods for the direct insertion of a heterosulfur bridging atom into a biaryl substrate molecule to form an internal, catenated thiophene ring. In the simplest case, biphenyl (**1**) is converted into dibenzothiophene (**2**) in 60-80% yield by means of sulfur and aluminum chloride or in 20-60% yield by means of hydrogen sulfide plus alumina or an alumina-based metallic oxide catalyst (4,5). In contrast, by the former method, 2-phenylnaphthalene (**3**) was converted into a mixture which failed to yield either of the expected sulfur-bridged compounds, benzo[*b*]naphtho[2,3-*d*]thiophene (**4**) or benzo[*b*]naphtho[2,1-*d*]thiophene (**5**), as an isolable product (6). Oxidation of this mixture, however, gave an isolable sulfone, m.p. 231°, to



which Kruber and Rappen (6), apparently erroneously, assigned the structure of 4-sulfone, rather than of 5-sulfone, which we believe is correct (7). Thus, it seems that **5** was formed in very low yield. We now report the successful synthesis of a mixture of **4** and **5** (major isomer) from **3** by means of the hydrogen sulfide method in the presence of a catalyst of sulfided cobaltous oxide-molybdc oxide-alumina (designated CMA-1) and the separation of these isomers. Compound **3** is only the second biaryl hydrocarbon which has been investigated systematically in the sulfur-bridging reaction with hydrogen sulfide.

To ascertain the reaction temperature for maximum yield of bridged products from **3**, exploratory runs 1-4 (Table I) were conducted over the range of 350-630° in the same manner as previously used for substrate **1** (5). It is apparent that the optimal temperature is 500 ± 50° and that isomer **5**, formed from bridging into the 1-position of the naphthalene ring, is obtained preferentially. Yields are lower than for sulfur-bridging in biphenyl. In

particular, biphenyl gives a significant quantity of dibenzothiophene even at 350°, while **3** yields no sulfur-bridged product at this temperature. Comparison of runs 3 and 5 shows that throughput of substrate can be varied without significant change in the activity of the catalyst. Moreover, runs 6 and 7 indicate that decreasing the amount of catalyst traversed by the substrate molecules increases the yield considerably (10).

Yields and isomeric ratios shown in Table I were determined by gas chromatography. Isolation of pure samples of **4** and **5** was accomplished by column chromatography, either on alumina alone (order of adsorbability 4 > 5 > 3) (11), or more efficiently on silica gel and alumina in succession, plus recrystallization. In preparative run 7, yields were 1.4% and 24%, respectively. Unfortunately, this isolation method is tedious and time-consuming, albeit effective.

Material balance in runs 1-7 is poor. For example, in preparative run 7 the total yield of crude, non-volatile effused product is only 46 weight % of the 2-phenylnaphthalene used, and benzonaphthothiophenes (**4** + **5**) constitute 83% of this weight. Very little unreacted **3** appears in the effluent. Additionally, only a small quantity of sulfur is obtained from extraction of the spent catalyst with chloroform. In control runs it was found that compound **5** is unstable (33% recovery) under the conditions of run 6, *i.e.* in the presence of the CMA-1 catalyst, or even at 500° in the absence of catalyst (69% recovery, for the reactor packed with glass beads). Moreover, **4** appears to be less stable than **5**, since a standard mixture containing a molar ratio of 5:4 = 3.2:1.0 likewise gave a recovery of 35% under the conditions of run 6, but the effluent was richer in **5** (molar ratio 5.9:1.0) than was the influent. On the basis of these control runs it seems likely that the variable yields and isomeric ratios found in runs 1-6 result from a high conversion of **3** into a mixture of **4** and **5** (preferentially the latter) combined with extensive decomposition of these products (preferentially **4**) before effusion from the catalyst bed (10,15).

Campaigne and Osborn (8) noted significant differences in the ultraviolet absorption spectra of **4** and **5**. These isomers are also distinguishable by their pmr spectra. In particular, **4** is easily identified in mixtures by the presence

Table I

Various Runs on Sulfur Bridging of 2-Phenylnaphthalene (**3**) with Hydrogen Sulfide and CMA-1 Catalyst (a)

Run No.	Wt. of 3 Used, g.	Wt. of CMA-1 Used, g. (b)	Reaction Temp., °C	Yield of Products (c)	
				Mole % (4 + 5)	Isomeric Ratio 5 : 4
1	1	75	350	none	----
2	1	75	450	21	9:1
3	1	75	550	18	6:1
4	1	75	630	10	10:1
5	2	75	550	19	5:1
6	1	25 (d)	500	32	4:1
7	5 (e)	125 (f)	500	33	(g)

(a) In runs 1-6 a solution of **3** in 50 ml. of benzene was added to the reactor over a period of 2 hours. Then, 25 ml. of plain benzene was added during one hour. (b) In runs 1-6, the packing formed a column 42 cm long. (c) Determined by gas chromatography (see Experimental). (d) Admixed with 5-mm pyrex glass beads. (e) Preparative run made in a larger reactor. (f) Admixed with glass beads and rods to give a column packing 33 cm long. (g) Not determined by VPC (see Experimental for isolation of isomers).

of a singlet at low field (δ 8.57), ascribed to the presence of the angular proton at C-11. Contrariwise, the mass spectra of **4** and **5** are quantitatively identical (16). Notable peaks occur at m/e 232 (M-2), 189 (M-CHS, corroborated by high resolution matching), and 117 (doubly charged molecular ion).

EXPERIMENTAL (18)

Runs 1-6 were conducted in the manner described in previous publications (5,19). Control runs on 0.5 g. of pure **5** and of a standard mixture of **4** and **5** (in 30 ml. of benzene) were made under the conditions of run 6. A control run was likewise made on **5** with a packing of glass beads only. The combined yield of benzonaphthothiophenes **4** and **5** was determined by gas chromatographic analysis at 260° of the crude, dried reactor effluent by means of a 1.2-m column packed with 10% Apiezon L on Chromosorb P. 1,1'-Binaphthyl was used as an internal standard. For isomeric analysis, a 2.4-m column of mixed nitrate salts at 185° was used (19).

Preparative Scale Sulfur Bridging of **3**.

In run 7, a Vycor reactor tube (3.5 cm in diameter) was packed to a height of 33 cm with an admixture of 125 g. of cobaltous oxide-molybdc oxide-alumina catalyst (Harshaw Co-Mo-0603, T 1/8"), pyrex glass beads, and pyrex glass rods. The packing was heated to 100° and conditioned by passing both methanol (1 ml. per minute) and hydrogen sulfide (60-100 ml. per minute) through the tube for a period of two hours, while the temperature was raised to 500°. Addition of methanol was then stopped. The reaction temperature was maintained at 500 ± 20° for 4.5 hours while addition of hydrogen sulfide, along with a solution of 5 g. of 2-phenylnaphthalene (**3**) (Fluka, *purum* grade) in 75 ml. of benzene (added over four hours), followed by a wash of 20 ml. of benzene (added over 30 minutes), was continued. The reaction was stopped and the collected liquid effluent was dried (sodium sulfate), evaporated (2.3 g. crude weight), and analyzed by gas chromatography (*vide supra*) for combined yield (1.9 g., 33%) of mixed **4** and **5**.

A solution of the crude mixture in chloroform was rotoevaporated onto 3 g. of silica gel which was added to the top of a column (4 cm x 40 cm) of 240 g. of silica gel (Baker no. 5-3405, 60-200

mesh) and eluted with petroleum ether (30-60°), with monitoring of the column in 366 nm light, to give fractions in the following order: (1) 925 ml., non-fluorescent plus violet, 0.2 g. (largely dibenzothiophene and recovered **3**); (2) 375 ml., light blue, 0.7 g. (largely **4** plus **5**); (3) 850 ml., violet, 1.4 g. (main product); and (4) 750 ml., blue (yellow in white light), <0.1 g. Fraction 3 was recrystallized from 80 ml. of acetone to give 0.52 g. (m.p. 186-188°) and 0.33 g. (second crop, m.p. 180-182°) of **5**; reported m.p. 182-184° (8), 185-186° (20).

Preceding fraction 2 plus residues from recrystallizations of fraction 3 were chromatographed on a column (2.5 x 61 cm) of 250 g. of alumina (Merck, neutral, activity 1) by gradient elution with petroleum ether (decreasing concentration with time) and benzene to give these successive fractions: (a) 1425 ml. (15:1), non-fluorescent plus first violet band and light blue band, 0.2 g. (largely recovered **3**); (b) 4430 ml. (4:1), second violet band, 0.8 g. (mainly **5**); (c) 750 ml. (3:1), overlapping zones, <0.1 g.; (d) 2000 ml. (changed to pure benzene), dark violet band, 0.2 g. (mainly **4**). Recrystallization of fraction b gave 0.57 g. of **5** (plates, m.p. 186-187°). Recrystallization of fraction d from 20 ml. of acetone gave 40 mg. (m.p. 158-159°) of **4**. Rechromatography of the residues (from recrystallization of d) by the petroleum ether-silica gel (5 g.) procedure gave an additional 40 mg. of **4**, m.p. 159-160°, reported m.p. (8) 160.5-161°; combined yields: 1.4% of **4**, 24% of **5**.

Spectral data for benzo[*b*]naphtho[2,3-*d*]thiophene (**4**) is as follows: pmr δ : 7.3-7.7 (m, 4, H-2, H-3, H-8, and H-9), 7.7-8.1 (m, 3, H-4, H-7, and H-10), 8.24 (s) superimposed on 8.1-8.4 (m, 2, H-1 and H-6), 8.57 ppm (s, 1, H-11); ms m/e (relative abundance) (21): 236 (6), 235 (17), 134 (100, M⁺), 232 (6), 189 (5, C₁₅H₉⁺ by high resolution), 117 (12, M⁺⁺). Exact mass: Calcd. for C₁₆H₁₀S, 234.051. Found: 234.050.

Benzo[*b*]naphtho[2,1-*d*]thiophene (**5**) showed a mass spectrum consistent with the literature (17); pmr δ : 7.3-7.7 (m, 4, H-2, H-3, H-8, and H-9), 7.83 (d, J = 9 Hz) which partially overlaps 7.7-8.07 (m, 3, H-1, H-6, and H-7), 8.07-8.3 ppm (m, 3, H-4, H-5, and H-10). Exact mass: Calcd. for C₁₆H₁₀S, 234.051. Found: 234.050.

REFERENCES AND NOTES

- (1) This investigation was supported by research grant no. MPS

75-04116 from the National Science Foundation. For Paper VIII in this series see reference 5.

(2) Research Associate and Visiting Assistant Professor, 1975-1977.

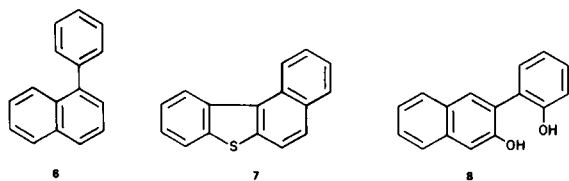
(3) Research Assistant, 1977-

(4) L. H. Klemm, D. R. McCoy, and D. R. Olson, *J. Heterocyclic Chem.*, **7**, 1347 (1970), and references cited therein.

(5) L. H. Klemm and J. J. Karchesy, *ibid.*, in press.

(6) O. Kruber and L. Rappen, *Chem. Ber.*, **73**, 1184 (1940).

(7) Comparison should be made with the paper by Campaigne and Osborn (8), who synthesized all of the three possible isomeric benzonaphthothiophenes and their sulfones, reported melting points: **4**, 160.5-161°; **4**-sulfone, 267-268°; **5**, 182-184°; **5**-sulfone, 232-234°; **7**, 101.5-102°; **7**-sulfone, 228-229°. The melting point of the Kruber and Rappen sulfone (designated A



here) indicates that these workers isolated either **5**-sulfone or (after preliminary rearrangement **3**→**6**) **7**-sulfone. Since some unreacted **3** was recovered, it seems unlikely that skeletal rearrangement occurred in their experiment. In an effort to establish the structure of A, Kruber and Rappen treated **8** with phosphorus pentasulfide to yield **4** (m.p. 160°). Since oxidation of **4** gave sulfone B (m.p. 264°), different from A, these workers surmised, again probably erroneously, that B was a byproduct and that A remained in the mother liquor. The proposal (6) that a chrysene fraction of coal tar was found to contain **4** because it formed sulfone A must be considered incorrect. In a later paper, Kruber and Grigoleit (9) isolated from a coal-tar pyrene fraction a compound melting at 185°, to which they assigned, apparently correctly, structure **5**. This compound was desulfurized to **3**, but, surprisingly, was not converted into its sulfone (See also footnote 22).

(8) E. Campaigne and S. W. Osborn, *J. Heterocyclic Chem.*, **5**, 655 (1968).

(9) O. Kruber and G. Grigoleit, *Chem. Ber.*, **87**, 1895 (1954).

(10) It is clear that an extended study of total yield plus iso-

meric ratio as functions of catalyst/substrate ratio, flow rate, and reaction temperature is desirable.

(11) One can predict with considerable confidence that **3**, non-coplanar in solution (12,13), will be less strongly adsorbed on alumina than **4** or **5**, planar and bearing a thiophene sulfur atom in addition to the biaryl π -electronic system of **3**. Rationalization of the adsorbability order **4**>**5** is more difficult, though the order is consistent with the relative extents of linearity, wavelengths of the longest ultraviolet absorption band (8), and energies of the highest occupied molecular orbitals (13,14). Compound **4** is also retained longer than **5** in gas chromatography on Apiezon L (incomplete separation) and on mixed nitrate salts (baseline separation).

(12) L. H. Klemm, D. Reed, L. A. Miller, and B. T. Ho, *J. Org. Chem.*, **24**, 1468 (1959).

(13) L. R. Snyder, "Principles of Adsorption Chromatography", Marcel Dekker, New York, N.Y., 1968, pp. 321-330.

(14) R. Zahradnik, in "Advances in Heterocyclic Chemistry", Vol. 5, A. R. Katritzky, Ed., Academic Press, New York, N.Y., 1965, pp. 58-59.

(15) A mechanistic rationalization for the formation of more **5** than **4** is planned for a subsequent paper.

(16) When run at 125° and 70 eV, corresponding peaks for **4** and **5** differed by only 0-1.2% in relative abundance. The reported spectrum of **5** (17), at 320° and 70 eV, shows 6% more of the doubly charged ion at m/e 117 than found here, but other peaks agree within 2%.

(17) American Petroleum Institute, Research Project 44, Catalog of Mass Spectra, no. 1376.

(18) Pmr spectra were obtained on deuteriochloroform solutions by means of a Varian XL-100 instrument. Low and high resolution mass spectrometry was performed by Dr. Richard Wielesek on a CEC model 21-110 double focusing instrument, operated at 70 eV.

(19) L. H. Klemm and J. J. Karchesy, *J. Heterocyclic Chem.*, **15**, 65 (1978).

(20) W. Davies, Q. N. Porter, and J. R. Wilmshurst, *J. Chem. Soc.*, 3366 (1957).

(21) For all peaks of relative abundance > 5%.

(22) W. Carruthers and A. G. Douglas, *J. Chem. Soc.*, 2813 (1959), and B. J. Mair and J. L. Martinez-Pico, *Proc. Am. Petrol. Inst., Sect. III*, **42**, 173 (1962), reported the isolation of **5** from high-boiling petroleum fractions.