The Insertion and Extrusion of Heterosulfur Bridges. XII.
Selectivity and Side Reactions in the Bridging Process

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1-Phenylnaphthalene undergoes sulfur bridging at 500° in the presence of hydrogen sulfide and a heterogeneous catalyst to produce benzo[b]naphtho[1,2-d]thiophene (13%). 3-Methylphenanthrene and 9-formylphenanthrene diethyl acetal (7b) give sulfur bridging to produce phenanthro[4,5-bcd]thiophene, i.e. with loss of the ring substituent. Additionally, 7b hydrogenolyzes to 9-methylphenanthrene. With decadeuteriobiphenyl as a substrate, the dibenzothiophene formed, as well as the biphenyl recovered, is largely devoid of deuterium label. Confirmation that benzene and toluene react under sulfur-bridging conditions is presented.

Previous studies have shown that (a) regioselectivity and (b) loss of ring substituents (retrosubstitution) characterize the process of heterogeneously-catalyzed sulfur bridging in aromatic substrates [5]. Thus, 2-phenylnaphthalene undergoes sulfur bridging principally at C-1 [6], 3-vinylpyridine, 3-phenylpyridine, and 3-phenylquinoline bridge preferentially *alpha* to the heteronitrogen atom [7,8], and 3,3'-bipyridine shows the sequence $\alpha,\alpha' > \alpha,\gamma' > \gamma,\gamma'$ in regioselectivity for bridging [8]. In the biphenyl system, a methyl group at C-4 or a thiol group at either C-3 or C-4 is replaced by hydrogen (presumably from the hydrogen sulfide reagent) as a side reaction to the bridging process [9]. The present research was conducted in order to gain further insight into aspects (a) and (b). Additionally, we report observations on the side reactions of benzene and toluene, used as reaction solvents.

1-Phenylnaphthalene (1) represents another case where sulfur bridging may be expected to occur selectively at C-2 (to form condensed thiophene 2) or at C-8 (to give thiaxanthene 4) [10]. When 1 (either neat or in toluene solution) was subjected to sulfur bridging in the presence of a chromia-alumina catalyst at 500° (the lowest temperature at which bridging proceeded well) it was found that 2 was obtained in a yield of at least 13%. This product was identified both as 2 itself (tlc and vpc) and as its sulfone 3 (mp, tlc, ir) by comparison with authentic samples. We expected that any 4 which might be present would be difficult to separate from 2 by chromatography. Therefore, the mother liquors from purification of sulfone 3 (obtained from oxidation of partially purified 2) were carefully examined for the possible presence of 4-sulfone [11]. There was no clear indication that 4 was produced in the bridging process. In previous sulfur-bridging studies substrates were reacted neat or in benzene solution [5]. Unfortunately, both benzene (*vide infra*) and toluene undergo reactions themselves. From control runs it was ascertained that toluene gives at least two vpc-separable byproducts *per se*

and may interact chemically with 1 besides. For reaction at 500°, product 2 constitutes the major portion of the vpc peak of longest retention time. Exploratory runs, however, show that two other significant, unidentified peaks of still longer retention times occur for reaction temperatures of 630° and 680°.

5a, R = H
b, R = CH₃

a, X = Br
b, X = CH(OEt)₂
c, X = CH₃

10, Y = H
11, Y = NO₂
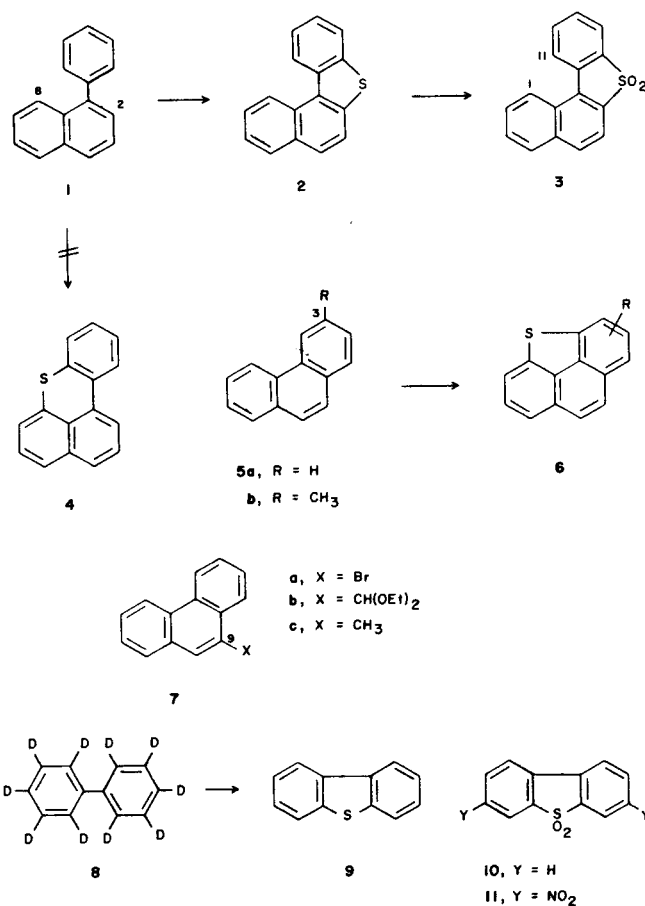
In reported runs on phenanthrene (**5a**) the substrate was dissolved in hot benzene (3.7 ml/g) for addition to the reactor [12]; and the crude product was treated with iodobenzene dichloride-water to form **6a**-sulfoxide [13], separable from unreacted **5a** by means of column chromatography [14]. No problem was encountered by the presence of dibenzothiophene (**9**) in the crude product. In a recent modification of this procedure we added a solution of **5a** in benzene at room temperature (10 ml/g) to the reactor and refluxed the crude product with hydrogen peroxide-acetic acid to produce a mixture of sulfones (presumed to contain **6a**-sulfone and **10**), separable from unreacted **5a** by crystallization. However, when the sulfone mixture was nitrated (in an effort to prepare a nitro derivative of **6a**-sulfone) only 3,7-dinitrodibenzothiophene 5,5-dioxide (**11**) was isolated. This product was identified by direct comparison (mp, mixture mp, tlc, ir) with an authentic sample of **11**, synthesized by nitration of commercial dibenzothiophene 5,5-dioxide under the same conditions [15,16].

In further study of the possible retention of ring substituents during sulfur bridging 3-methylphenanthrene (**5b**) was subjected to the reaction at 550°. Extensive demethylation occurred and the yield of phenanthrothiophene **6a** was comparable to that from phenanthrene itself [12]. However, mass spectral investigation of the crude product mixture indicated that only a trace (if any) of desired **6b** was formed. Similarly, 9-formylphenanthrene diethyl acetal (**7b**) failed to yield evidence for formation of a substituted phenanthrothiophene, though hydrogenolysis of the acetal group to yield 9-methylphenanthrene (**7c**) was apparent and **6a** was also produced.

Last of all decadeuteriobiphenyl (**8**) was sulfur-bridged at 500° and the resultant dibenzothiophene plus recovered biphenyl were analyzed by gc-ms for the possible presence of deuterated components. Nearly all of the deuterium was exchanged with protium in both products. Thus, 61% of the recovered biphenyl molecules were devoid of deuterium, while 18% retained only one deuterium atom. Correspondingly, 83% of the dibenzothiophene molecules lacked deuterium and 10% bore only one such atom. In summary, the action of sulfided Cr-0101 T catalyst in effecting loss of deuterium atoms and methyl groups from aromatic rings and that of sulfided CoMo-0603 T catalyst in effecting loss of methyl and thiol groups are consistent with our previously proposed ECEC mechanism for the sulfur-bridging reaction [5], wherein electron-transfer from an adsorbed aromatic ring to the catalyst occurs in an initial equilibrium step. The substituent can then be lost as either a cation or a free radical, irrespective of whether or not sulfur bridging occurs. Only in the case of the thiol group does the substituent foster the bridging process [9]--perhaps by anchoring the ring to the catalyst surface.

Table 1

Distribution of Deuterium Labels Amongst Reaction Products from S-Bridging of Decadeuteriobiphenyl [a]

Product (gc peak)	Observed m/e	D atoms per molecule	Mole % of product
benzenethiol	110	0	91
	111	1	6
	112	2	2
benzothiophene	134	0	80
	135	1	14
	136	2	6
biphenyl	154	0	61
	155	1	18
	156	2	9
	157	3	5
	158	4	3
	159	5	2
	160	6	2
dibenzothiophene	184	0	83
	185	1	10
	186	2	6
	187	3	1

[a] Control runs with benzene alone [9] indicate that none of the biphenyl and < 30% of the dibenzothiophene produced may arise from the solvent under the reaction conditions used.

EXPERIMENTAL [17]

Sulfur Bridging in 1-Phenylnaphthalene (**1**).

A. Preparative Reaction, Run No. 1.

In a modification of previously described procedures [14] a solution of 5 g of 1-phenylnaphthalene (**1**) [18] in 50 ml of toluene was added to a pyrex reactor tube containing 80 g of pre-sulfided (*in situ*) Harshaw Cr-0101 T catalyst intermixed with pyrex beads (total height of catalyst bed 16 cm) maintained at 500° in a stream of hydrogen sulfide to yield 5.6 g of crude solid product in the effluent [19]. Tlc (alumina/30-60° petroleum ether) of this product showed four spots of R_f values 1.0 (sulfur), 0.80 (unreacted **1**), 0.72 (same as the reaction product from toluene, *vide infra*), and 0.51 (identical with that of authentic benzo[*b*]naphtho[1,2-*d*]thiophene (**2**) [20]). Column chromatography of the crude product on 335 g of alumina (monitored by tlc) caused elution of the first three substances in 1 ℓ of petroleum ether and of **2** only (yield 1.05 g of oily yellow solid [21], mp 82-96°, reported, mp 101.5-102° [20]) in the next 1.2 ℓ.

A sample of the oily solid was refluxed with 30% hydrogen peroxide in glacial acetic acid [20] to give benzo[*b*]naphtho[1,2-*d*]thiophene 7,7-dioxide (**3**), obtained as yellow crystals (from acetone), mp 228-230°, identical with an authentic sample [22] as based on direct comparison, mixture mp undepressed; tlc (silica gel/ether) R_f 0.68; ir (potassium bromide): 1280 and 1140 (SO_2), 1170, 1110, 780, 710 cm⁻¹; pmr (deuteriochloroform): δ 8.67 (split d, 1 H) and 8.41 (d, 1 H, J = 7 Hz, H-1 and H-11), 8.2-7.6 (m, 8 H). Tlc, ir, and pmr examination of the residue (mp 198-208°) from the acetone mother liquor showed no clear evidence for the presence of a second component [11].

B. Runs at Other Temperatures, and Control Runs.

Four other runs on sulfur bridging were made in the preceding manner but with these variations: run No. 2, made without solvent; run No. 3, 630°; run No. 4, 630°, run without substrate **1**, *i.e.* on solvent only; run No. 5, 680°.

C. VPC Analysis of Products.

VPC analysis was conducted with a Beckman Model GC 4 dual column

analytical instrument [23] and a stainless steel column (0.32 cm i.d. × 1 m) containing 5% N,N'-bis(p-methoxybenzylidene)-α,α'-bi-p-toluidine (Eastman Kodak BMBT, nematic liquid crystals) on Chromosorb W (HP, 100-120 mesh) at 210° with a helium flow rate of 30 ml/sec. Under these conditions retention times (t_R in minutes) were as follows: starting material **1**, 0.5: recrystallized solid (mp 143-159°) from control run (No. 4) on toluene alone, 0.8 and 1.3 (two peaks); oily solid from run No. 1 (part A.), analogous product from control run (No. 2) without toluene, and authentic **2**--all 6.2 ± 0.3. All of these peaks were symmetrical except that from run No. 1, which tailed toward greater t_R. On the assumption that the skewing of this peak is caused by impurities in **2** one can estimate that the oily solid from part A. is 70% pure, *i.e.* that the yield of **2** in run No. 1 is *ca.* 0.74 g (13%).

For run No. 3 at 630° the fraction which contained the component of R_f 0.72 was collected from the alumina column, yield 0.77 g of needles, mp 137-150° after recrystallization from ethanol; vpc: t_R 0.8, 1.0, and 1.3 (3 peaks). The fraction which contained the component of R_f 0.51 gave a mixture of white and yellow solids (0.95 g); vpc: t_R 5.9, 7.3, and 8.5 (shoulder) of relative areas 1.0:0.52:0.15. For run no. 5 at 680° this corresponding fraction (0.14 g) contained very little of the component of t_R 5.9. Instead, the main component had t_R 7.3 and the shoulder at 8.5 was readily apparent in the chromatogram. No effort was made to identify peaks at $t_R > 6.2$.

Sulfur Bridging in Decadeuteriobiphenyl (8).

A solution of 0.5 g of decadeuteriobiphenyl (**8**) (99 atom % D, Merck, Sharp, and Dohme, Montreal, Canada) in 25 ml of benzene was subjected to sulfur-bridging with CMA-1 catalyst at 500° [24]. Evaporation of the effluent organic layer and gc-ms investigation of the crude residue, as previously desribed [25], showed four chromatographic peaks identified as benzenethiol, benzothiophene [26], biphenyl, and dibenzothiophene (in order of increasing t_R). The mass spectrum for each chromatographic peak was measured in order to determine the relative abundances of the undeuteriated parent compound (100%) and the array of isotopically labelled modifications of this parent (*i.e.* of associated mass spectral peaks). Percentages in the array were corrected for the presence of ^{13}C, ^{33}S, and ^{34}S in natural abundance [27]. Data for each product were then converted to mole % and are presented in Table I to show the distribution of deuterium labels in the four products.

3,7-Dinitrodibenzothiophene 5,5-Dioxide (11).

A. From Commercial Sulfone **10** [28].

To a cold (5°), well-stirred [29] mixture of 37 g (0.17 mole) of dibenzothiophene 5,5-dioxide (**10**) (Aldrich) and 150 ml of concentrated sulfuric acid was added (without additional cooling) dropwise over a period of 45-60 minutes 108 ml (2.3 moles) of fuming nitric acid (white, 90%, density 1.48 g/ml). If the mixture became a thick paste it was warmed gently and/or treated with 25 ml more of concentrated sulfuric acid to decrease the viscosity. The reaction mixture (at 50-55°) was heated to 98° over a period of 75 minutes and maintained at this temperature for 10-15 minutes longer and then poured into a stirred mixture of crushed ice (1.2 kg) and water. The resultant precipitate was collected by filtration, washed repeatedly until the filtrate attained pH 6, and dried in air to give 50 g (96%) of yellow powder, mp 250-270°. Recrystallization from acetone (3.8 ℓ) produced prisms (39 g, mp 262-270°). Further recrystallization plus sublimation at 210° (0.6 mm) raised the melting point to 276-278°, lit [15], 290°; ir: 1600, 1540 (nitro), 1360 and 1340 (nitro and sulfone), 1180 (sulfone), 890 (lone aromatic H), 850 (2 vicinal aromatic H), 740 cm^{-1}; pmr (hexadeuteriodimethyl sulfoxide): δ 8.30 (broad s, 4 H, H-1, H-2, H-8, H-9), 8.60 (broad s, 2 H, H-4 and H-6); ms: m/e 307 (15), 306 (M⁺, 100), 276 (M⁺ - NO, 10), 232 (M⁺ - [NO₂ + CO], 27), 186 (24), 158 (19), 150 (34), 138 (14), 74 (11), 176* (306 → 232); exact mass: Calcd. for $C_{12}H_6N_2O_6S$: 305.995. Found: 305.996.

B. From Transformation of Benzene.

A solution of 15 g of phenanthrene in 150 ml of benzene was added to a reactor containing 150 g of Harshaw Cr-0101 T catalyst at 500-550°

under sulfur-bridging conditions. The hot column was then washed with 75 ml of benzene. Crude product from the effluent was oxidized with refluxing 30% hydrogen peroxide in glacial acetic acid and the purified sulfone (mp 246-250°) was nitrated as in part A. Thick layer chromatography (silica gel/ benzene-ether, 2:3) gave three zones (R_f 0, 0.35, 0.65). The fastest moving zone yielded nitrosulfone **11** (identified by direct comparison with compound from A.), while only tarry products were isolated from the other zones.

Sulfur Bridging in Phenanthrene Derivatives.

A. 3-Methylphenanthrene (5b) as Substrate.

The bridging reaction was conducted with 3 g of 3-methylphenanthrene (**5b**) (Aldrich), 30 ml of benzene as solvent, 80 g of catalyst, and a reaction temperature of 550°. Tlc on the crude product (2.1 g) showed two spots for **5b** (R_f 0.60) and bridged demethylated **5** (*i.e.* **6a**, R_f 0.49); pmr (deuteriochloroform): δ 8.8-8.5 (m, relative area 2, H-4 and H-5), 8.2-7.3 (m, 12.9, other aromatic H), 2.54 (s, 0.9, CH₃ at C-3)--corresponding to 82% demethylation and 39% S-bridging [30]; ms: (60°), 222 (<0.1, **6b⁺**), 208 (5, **6a⁺**), 192 (25, **5b⁺**), 184 (11, **9⁺**), 178 (100, **5a⁺**), 154 (13, biphenyl⁺).

B. 9-Formylphenanthrene Diethyl Acetal (7b) as Substrate.

Following a published procedure [31] 9-bromophenanthrene (**7a**) was converted into acetal **7b**, purified by evaporative distillation at 110° (0.25 mm) and then column chromatography (silica gel/benzene), obtained as a brown-yellow liquid [32,33]; ir (neat): 1125, 1065, 1050 (acetal C-O), 1105 cm^{-1} (C-H) [34]; pmr (deuteriochloroform): aliphatic protons at δ 6.02 (s, 1 H, CH), 3.65 (q, J$_{Et}$ = 7 Hz, 4 H, 2 OCH_2CH₃), 1.25 (t, 6 H, 2 OCH₂CH_3); ms (90°): 280 (**7b⁺**). The bridging reaction was conducted as with **5b**, but on only 0.9 g of substrate in 10 ml of benzene. Spectral examination of the crude product indicated the presence of **5a**, **6a**, and 9-methylphenanthrene (**7c**) (pmr singlet at δ 2.73 [35], ms peak at m/e 178), but showed no evidence for the formation of **6b**.

REFERENCES AND NOTES

[1] Exchange student from École Nationale Superieure de Chimie, Academie de Montpellier, France, 1981-1982.

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[3] Undergraduate Teaching and Research Assistant, 1982-1983.

[4] Research Assistant, 1977-1978.

[5] L. H. Klemm, J. J. Karchesy, and D. R. McCoy, *Phosphorus Sulfur*, **7**, 9 (1979).

[6] L. H. Klemm, J. J. Karchesy, and R. F. Lawrence, *J. Heterocyclic Chem.*, **15**, 773 (1978).

[7] L. H. Klemm and D. R. McCoy, *ibid.*, **6**, 73 (1969).

[8] L. H. Klemm, D. R. McCoy, and C. E. Klopfenstein, *ibid.*, **8**, 383 (1971).

[9] L. H. Klemm and J. J. Karchesy, *ibid.*, **15**, 561 (1978).

[10] L. H. Klemm, in "Advances in Heterocyclic Chemistry," Vol 32, A. R. Katritzky, ed, Academic Press, New York, NY, 1982, pp 165-166.

[11] The sulfone of **4**, mp 196°, was reported by W. Davies, Q. N. Porter, and J. R. Wilmshurst [*J. Chem. Soc.*, 3366 (1957)] from oxidation of **4** (mp 80°) with hydrogen peroxide-acetic acid.

[12] L. H. Klemm, D. R. McCoy, and D. R. Olson, *J. Heterocyclic Chem.*, **7**, 1347 (1970).

[13] Recently it was found that this oxidation is more reliable in a solvent of tetrahydrofuran-pyridine-water than with acetonitrile-water [L. H. Klemm and R. Tsuchiya, unpublished results].

[14] L. H. Klemm and W. Hsin, *ibid.*, **13**, 1245 (1976).

[15] N. M. Cullinane, C. G. Davies, and G. I. Davies, *J. Chem. Soc.*, 1435 (1936).

[16] It seems likely that these nitration conditions caused destruction of the **6a**-sulfone ring system.

[17] Infrared spectra were determined on potassium bromide pellets by means of a Beckman IR-10 instrument; and pmr spectra, by means of a Varian T-60 or XL-100 instrument. Dr. Richard Wielesek determined mass spectra by means of a CEC model 21-110 double focusing instru-

ment, operated at 70 eV and also determined gc-ms data (see reference [25]).

[18] L. H. Klemm, D. Reed, and C. D. Lind, *J. Org. Chem.*, **22**, 739 (1957).

[19] Only sulfur was obtained from extraction of the used catalyst.

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

[21] It is believed that this oily solid contains a small amount of non-volatile alkane from the solvent.

[22] F. G. Bordwell, W. H. McKellin, and D. Babcock, *J. Am. Chem. Soc.*, **73**, 5566 (1951).

[23] L. H. Klemm, J. N. Louris, and B. Boettcher, *J. Chromatogr.*, **259**, 453 (1983). We thank J. N. Louris for assistance in this analysis.

[24] Conducted as in run numbers 2 and 3, reference [9].

[25] L. H. Klemm, J. J. Karchesy, R. F. Lawrence, and P. Wang, *J. Heterocyclic Chem.*, **17**, 771 (1980).

[26] It is suggested that benzothiophene may arise from benzene, methanol (used in activation of the catalyst), and hydrogen sulfide.

[27] F. W. McLafferty, "Interpretation of Mass Spectra," 2nd Ed, W.

A. Benjamin, Inc., Reading, Mass., 1974, Tables 2-1 and 2-2.

[28] Modified from the procedure in reference [15], only in that more precise reaction conditions are defined here. A referee has suggested that our product may contain impurities isomeric with **11**.

[29] A motor-driven, mechanical stirrer was used.

[30] Calculations are based on the approximation that the crude product contains only the four components **5a**, **5b**, **6a**, and **6b**. However, see the mass spectral data.

[31] C. A. Dornfeld and G. H. Coleman, *Org. Synth.* Coll Vol **3**, 701 (1955).

[32] Mass spectral analysis indicated the presence of **5a** and **7a** as impurities.

[33] H. F. Miller and G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 766 (1935); C. Weizmann, E. Bergmann, and T. Berlin, *ibid.*, **60**, 1331 (1938).

[34] D. J. Pasto and C. R. Johnson, "Organic Structure Determination", Prentice-Hall, Inc., Englewood Cliffs, NJ, 1969, pp 378-379.

[35] L. H. Klemm, J. J. Karchesy, and R. F. Lawrence, *J. Heterocyclic Chem.*, **15**, 417 (1978).