The Insertion and Extrusion of Heterosulfur Bridges. XV. *S*-Bridging of 2,2′-Binaphthyl and 1-(2-Naphthyl)cyclohexene. Studies on Hydrodehalogenation During the Reaction [1]

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Regioselectivity occurs in the sulfur-bridging reactions of 2,2′-binaphthyl (**1**) and 1-(2-naphthyl)cyclohexene (**7**) by means of hydrogen sulfide and a chromia-alumina-magnesia catalyst (designated **I**) in a flow apparatus at 550°. Thus, **1** gives a higher yield (6.1%) of dinaphtho[1,2-*b*:2′,1′-*d*]thiophene from 1,1′-bridging than of dinaphtho[1,2-*b*:2′,3′-*d*]thiophene (3.4%) from 1,3′-bridging. No product expected from 3,3′-bridging was identified. Substrate **7** undergoes both dehydrogenation and bridging to yield 2-phenylnaphthalene (8%), benzo[*b*]naphtho[2,1-*d*]thiophene (9%) from *alpha* bridging, and benzo[*b*]naphtho[2,3-*d*]thiophene (3%) from *beta* bridging into the naphthalene ring.

Exploratory studies showed that either sulfided catalyst **I** or a sulfided molybdenum(VI) oxide-alumina-cobalt(II) oxide catalyst (**II**) effects hydrodehalogenation of various monohalo- and polyhaloarenes (where halo, X, is chloro or bromo) at 450-550°. In the biphenyl, phenanthrene, naphthalene, and pyrene systems, halogen was lost either under sulfur-bridging conditions or under hydrogenolysis conditions, *i.e.* with methanol as a reactant. For every substrate the parent arene was isolated or identified as a reaction product. In selected experiments, acid HX was also identified in the effluent. Use of hydrogen sulfide as a reactant led to formation of dibenzothiophene and phenanthro[4,5-*bcd*]thiophene as main products in the biphenyl and phenanthrene systems, respectively; while use of methanol as a reactant gave small amounts of methyl bromide (for X = Br) and methylarenes.

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In a continuation of investigations [1] on the characteristics of the heterogeneously catalyzed sulfur-bridging reaction using hydrogen sulfide in a flow system we now report results from use of 2,2′-binaphthyl (**1**) and 1-(2-naphthyl)cyclohexene (**7**) as substrates at 550° without added solvent. Barring molecular rearrangement, there are three possible dinaphthothiophene isomers **2**, **3**, and **4** which one might expect to result from 1,1′-, 1,3′-, and 3,3′-bridging, respectively, of substrate **1**. While isolated yields of bridging products were low, it was found that regioselectivity occurs to give more **2** (6.1%) than **3** (3.4%) and no observed **4**, *i.e.* a preference of *alpha* to *beta* substitution into the naphthalene ring of 4.6:1. Substrate **7** yielded three isolated products, namely 2-phenylnaphthalene (**8**) (8%) from dehydrogenation of the cyclohexene ring plus preferential *alpha* to *beta* substitution into the naphthalene ring of 3.3:1 to form **9** (9.2%) and **10** (2.8%). Dehydrogenation of cyclohexene rings under the conditions of the sulfur-bridging reaction was reported previously in the triphenylene system [1]. Moreover, regioselectivity in direct reaction of **8** as substrate to give **9** (24%) and **10** (1.4%) was also found [5]. In addition, several examples of regioselectivity such that *alpha* substitution > *gamma* substitution into a pyridine ring during sulfur bridging have likewise been noted [6]. From the low yields of products obtained and the difficulty of separation of isomers formed it is clear that sulfur bridging is not a suitable preparative pathway from either 2,2′-binaphthyl to **2** and **3** or of 1-(2-naphthyl)cyclohexene to **9** and **10**. Better synthetic routes to **2**, **3**, **4**, **9**, and **10** have been reported [7,8].

Identifications of **9** and **10** were established by direct comparison with authentic samples [5]. However, identifications of **2** and **3** were based largely on ^{1}H nmr, uv, and ms spectra, as well as on comparison with reported melting points. The mass spectra of **2** and **3** were closely similar. They included a molecular ion at m/e 284 as the largest peak and a significant peak at 142 for M^{++}. Symmetric compound **2** (mp 256°) was easily recognized by the presence in its ^{1}H nmr spectrum of four doublets of 2 protons each for the pairs H-1 and H-12, H-4 and H-9, H-5 and H-8, and H-6 and H-7 and of two triplets of 2 protons each for the pairs H-2 and H-11, and H-3 and H-10. While potential product **4** is also symmetrical, its ^{1}H nmr spectrum should show two singlets for pairs H-12 and H-13, and H-5 and H-7; two doublets for pairs H-1 and H-11, and H-4 and H-8; and two triplets (*i.e.* two overlapped doublets of doublets with identical vicinal J values) for pairs H-2 and H-10, and H-3 and H-9. Moreover, the ultraviolet absorption spectrum of **2** (Figure 1a) is closely similar in shape to that of its benzolog picene (Figure 1b) [9,10,11], but with corresponding maxima for the former compound shifted hyposchromically by 2-19 nm in the region 270-380 nm and bathochromically by *ca.* 2-9 nm in the region 220-270 nm [12]. Contrariwise, the uv spectrum of **2** is markedly different from that of **6** (Figure 1d) or of diben-

zo[*b*,*g*]phenanthrene, the benzolog of **4** [11]. Compound **3** was characterized by its unusually high melting point (322°) [13], as well as the presence of two downfield singlets for H-7 and H-12, a doublet of doublets for H-5 and H-6, and two strongly overlapped multiplets of four protons each in its ^{1}H nmr spectrum. While the ultraviolet absorption spectrum of **3** (Figure 1c) bears similarities to that of its benzolog **6**, the differences in the two spectra seem too great to use the spectra as corroborating evidence for the structural formula of **3**. It should be noted that our mass spectrum of **2** and ^{1}H nmr spectra of **2** and **3** differ considerably from those previously reported [8].

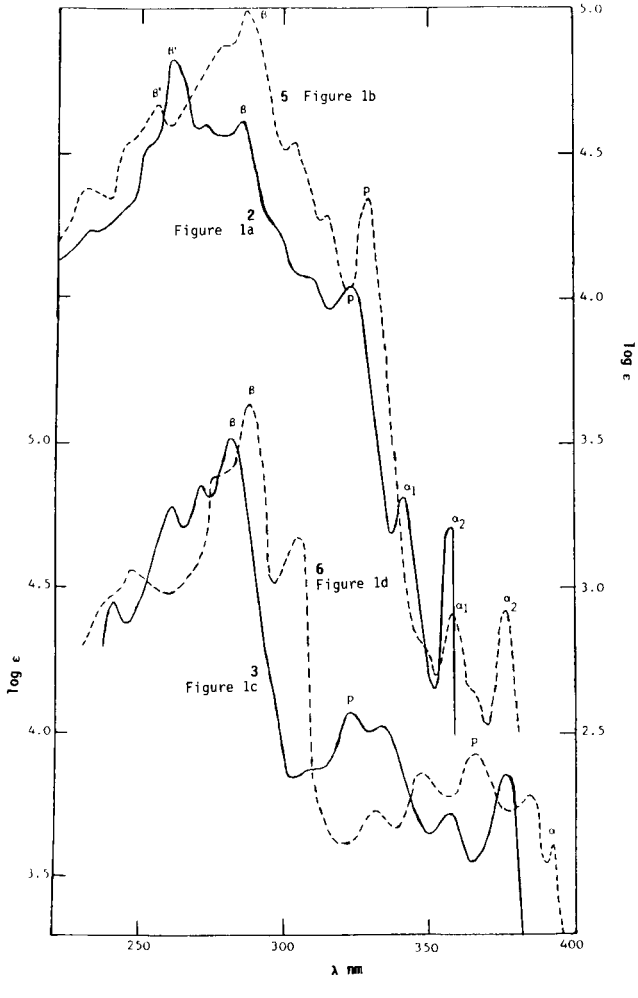
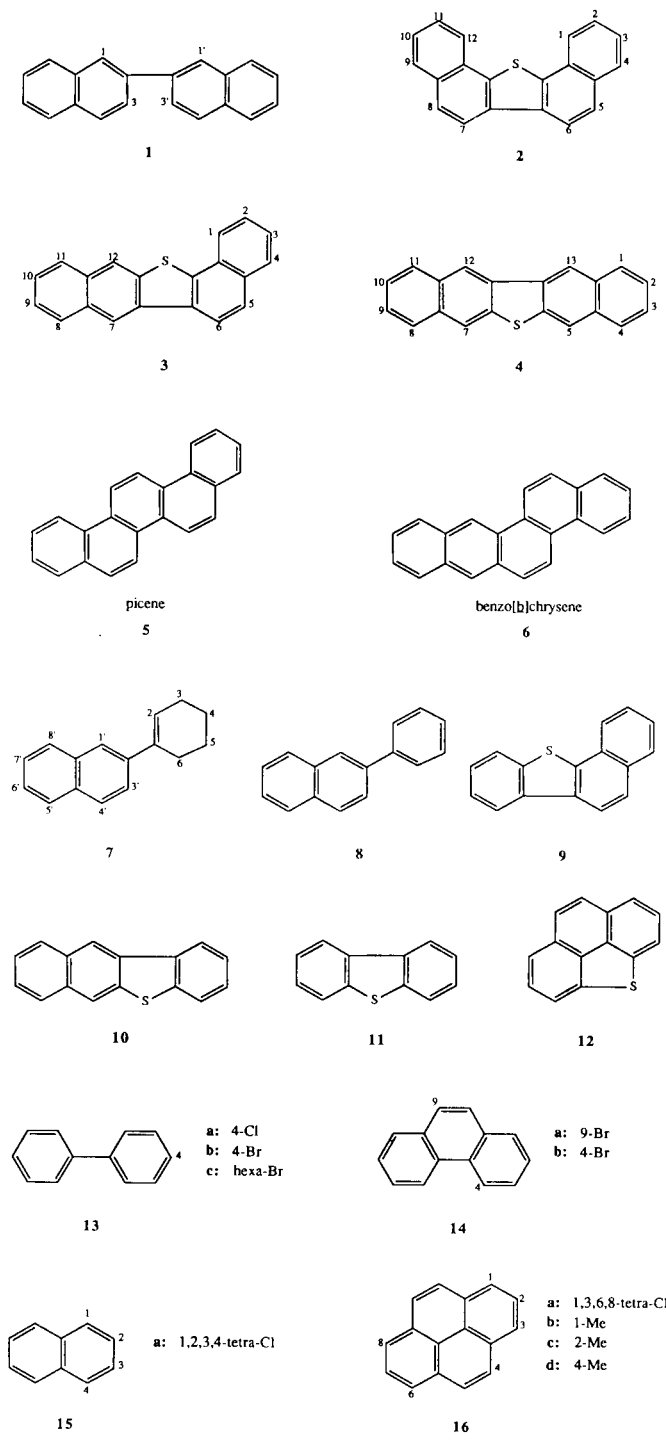


Figure 1. Ultraviolet absorption spectra of dinaphthothiophenes and their benzologs. Figure 1a--Compound **2** in absolute alcohol. Figure 1b--Picene (**5**), reproduced from Clar [11,12]. Figure 1c--Compound **3** in dioxane. Figure 1d--Benzo[*b*]chrysene (**6**), reproduced from Clar [11]. The vertical scale on the right side of the graph refers to Figures la and 1b; that on the left side, to Figures 1c and 1d.



Development of methods for detoxification of polychloro- and polybromobiphenyls and other haloarenes is an important environmental concern [14,15]. In consideration of the fact that previous studies have shown that methyl, thiol, diethoxymethyl, and deuterio substituents on aromatic rings are lost during sulfur bridging [16,17] we reasoned that chloro and bromo substituents might suffer a similar fate. In fact, sulfur bridging might not be necessary in order to effect hydrodehalogenation. Consequently, we explored the possibility of attaining dehalogenation under (a) conditions used for the catalyzed

Table I

Experimental Results from Heterogeneously Catalyzed Hydrodehalogenation Reactions [a]

Experiment No.	Reactant used Compound	weight used g,	mmoles	Catalyst used (wt, g)	Conditioning of catalyst	Solvent for reactant	Reaction temp, °C & time (hours)	Carrier gas or reagent	Product(s) isolated (mmoles)	Identifications on crude extractable effluent [b]	Other products identified [c]
1	**13a**	1.81	9.60	**I** (150) [d]	H_2S, 2 hours	none	530 (2.8)	H_2S	**11** (4.1), **13** (2), S_8 (0.2) [e]	B, ms, tlc, ^1H nmr: **11:13** = 2.4:1	H^+ (0.04 mequiv, M), Cl^-
2	**13b**	2.23	9.57	**II** (137)	H_2S, MeOH 1 hour	25 ml C_6H_6, 25 ml MeOH	450 (2.5)	N_2	**13** (3.6) [f]	B, ms (**13, 11** trace)	no Br^- (H)
3	**13c**	5.38	8.57	**II** (183)	H_2S, MeOH 1 hour	none	500 (2.2)	N_2, MeOH	**13** (0.5) [g]	B, ms (**13, 11** trace; Me-**13**, trace)	MeBr (crude), no Br^- (H), H^+, (3.46 mequivs, P)
4	**13c**	15.1	24.0	**I** (123)	H_2S, MeOH 0.75 hour	none	500 (2.3)	N_2, MeOH	[h]	[i]	MeBr (0.64 mmoles), Br^- (H, F), H^+ (67.5 mequivs, P)
5	**13c**	7.5	11.9	**I** (120)	H_2S, 2 hours	none	530 (1.8)	H_2S	mixture: **11** & S_8, no **13** [j]	B	[k]
6	**14a**	6.94	27.0	**I** (150) [d]	H_2S, 2 hours	none	550 (2)	H_2S	mixture: **12** (2.7), **14** (2.0), S_8 (0.1)	B, ms, ^1H nmr: **12:14** = 2:1	Br^- (F), no Br^- (H), H^+ (1.4 mequivs, M)
7	**14a**	4.55	17.7	**II** (167)	H_2S, MeOH 1 hour	31 ml C_6H_6, 23 ml MeOH	550 (2)	N_2	**14** (0.5) [l]	B	[k]
8	**15a**	1.92	7.22	**I** (120) [d]	H_2S, 2 hours	none	530 (1.7)	H_2S	mixture: **15** (trace), S_8	B, tlc, ^1H nmr	H^+ (6.8 mequivs, M), Cl^- (5.1 mmoles) [m]
9	**16a**	1.51	4.44	**I** (126)	H_2S, MeOH 1.75 hours	55 ml C_6H_6, 10 ml MeOH	450 (5)	N_2, MeOH	**16** (1.07) **16b** (0.08)	B, ms, ^1H nmr [n]	Cl^-

[a] For general details on the reactants, catalysts, processing, and analysis of products see the Experimental section. [b] B indicates negative Beilstein test; ms, tlc, and ^1H nmr are the usual analytical methods. [c] Except for methyl bromide these were determined in the total aqueous effluent. Hydrogen ion was determined by titration with standard sodium hydroxide solution using either methyl orange (M) or phenolphthalein (P) as an indicator. Chloride ion was determined, in the presence of sulfide ion and reducing agents, as silver chloride [20]. Bromide ion was determined by means of hypochlorite and carbon tetrachloride (H) [21]; or, with more sensitivity, by means of fluorescein (F) [21]. Methyl bromide was determined as the quinoline salt. [d] About 2.5 cm of glass beads was placed atop the column of catalyst. [e] Separated by chromatography using alumina/petroleum ether (30-60°). [f] Scraped directly from the effluent end of the reactor tube, mp 65.5-68°, undepressed on admixture with an authentic sample. [g] Obtained by recrystallization of solid effluent from ethanol, mp 60-62°, identified by ^1H nmr. [h] Not identified. [i] The effluent gave a positive Beilstein test. [j] Analyzed by tlc. [k] Not investigated. [l] Identified by mp and mixture mp. [m] Weighed as silver chloride. [n] Both ms and ^1H nmr indicated that the product contained small amounts of monomethylpyrenes, with the 1-isomer predominant; observed ^1H nmr signals for the methyl groups of reference samples (Aldrich): δ 3.03 for **16b**, 2.84 for **16c**, and 2.91 for **16d**.

sulfur-bridging reaction where the substrate molecule would be susceptible to attendant sulfur bridging (biphenyl and phenanthrene systems), (b) the conditions of (a), but where the substrate molecule could not undergo sulfur bridging (naphthalene system), and (c) conditions used in our hydrodesulfurization reactions, *i.e.* with methanol as an *in situ* source of hydrogen plus a sulfided catalyst [18,19], but on molecules which contain no sulfur (biphenyl, phenanthrene, and pyrene systems). A summary of the results from nine representative experiments is presented in Table I, where experiments 1, 5, and 6 fall in category (a), experiment 8 comes in (b), and experiments 2-4, 7, and 9 fall in (c). In general, both the solid organic and the water-soluble effluents were examined, but no attempt was made to investigate products retained on the catalyst. Thus, an attempt to react tetrachloropyrene **16a** by procedure (b) is not included in the table since it gave no organic effluent.

In every experiment except 4, the crude solid from the effluent was free of halogen, as determined by a Beilstein test and confirmed by mass spectral analysis in five cases, and contained either an amount of the parent arene (from hydrodehalogenation) or its sulfur-bridged derivative, or both. In most cases the isolated yields of dehalogenated organic substrates were small. However, in experiment 1 (on 4-chlorobiphenyl) a combined yield of biphenyl and dibenzothiophene of 64 mole % was obtained. Also notable are combined yields of 17% (phenanthrene plus phenanthrothiophene) from 9-bromophenanthrene (experiment 6) and 26% (pyrene plus 1-methylpyrene) from 1,3,6,8-tetrachloropyrene (experiment 9). Very little naphthalene was obtained from 1,2,3,4-tetrachloronaphthalene, however (experiment 8), despite the fact that 18% of the chlorine in the substrate was set free as chloride ion. The yield of biphenyl from 4-bromobiphenyl (experiment 2) may be unrealistically high due to the use of benzene (a precursor of biphenyl [17]) as a solvent in the reaction. However, no biphenyl was detected in experiments 7 and 9, where it also is expected. Experiment 4 with hexabromobiphenyl as substrate was used largely to identify the nature of the bromine atoms which were lost from the substrate. One sees that both hydrogen bromide (aqueous solution $p\mathrm{H} < 2$, positive test for bromide ion by means of hypochlorite oxidation to free bromine) and methyl bromide (trapped with quinoline) were produced. Bromide ion was not observed by the hypochlorite test in experiments 2, 3, and 6, but it was detected by the more sensitive fluorescein test in 6. The acidity to methyl orange in experiment 6 then corroborates the formation of hydrogen bromide there. Chloride ion was produced in the three experiments (1, 8, and 9) where chlorinated substrates were used. Especially informative are the results from experiment 8 where at least an 18% yield of hydrogen chloride was produced. No test for the formation of methyl chloride was made.

In our proposed mechanism for the sulfur-bridging reaction the substrate is adsorbed onto the catalyst surface where it initially loses an electron to form a cation radical [6]. As a model for rationalizing the fate of the halo substituent on the substrate we consider known transformations of cation radicals in electron-impact mass spectrometry. It is reported that halobiphenyls **13a** and **13b** eject either a halogen atom or a hydrogen halide molecule in mass spectrometry, while hydrogen atoms on the carbon skeleton are scrambled at the same time [22]. Tetrachloropyrene **16a** readily loses hydrogen chloride from its molecular ion (see Experimental). Analogously, 4-bromophenanthrene shows loss of a bromine atom or of hydrogen bromide [23], while various di- and polychlorobiphenyls and dichloronaphthalenes lose chlorine atoms, chlorine molecules, and hydrogen chloride [24]. In our experiments where hydrogen sulfide is used as a reactive carrier gas, one would then expect to observe the effluence of halogen *only* in the form of hydrogen halide (see experiments 1, 6, and 8) due to reduction by hydrogen sulfide of any free elemental halogen.

In the experiments with methanol, as an *in situ* hydrogen source, on a pre-sulfided catalyst we have proposed that one has effectively the reverse of the sulfur-bridging process [6]. Thus, one can visualize an initial step of electron transfer from the catalyst to the adsorbed substrate molecule to form an anion radical. A model for rationalization of our results is drawn from the studies of Freeman *et al.* on negative chemical ionization mass spectroscopy of chlorobenzenes [25], where both chlorine atoms and chloride ions are produced from dissociation of the anion radical. Likewise, in electrochemical reductions, albeit run on a surface in a liquid medium as a different hydrogen source, **13a** is converted into chloride ion and biphenyl while polychlorobiphenyls sometimes give simultaneous replacement of two chloro substituents by hydrogen (*via* a benzyne intermediate?) [26,27]. Again the free elemental halogen should be converted into hydrogen halide in our studies (see experiments 4 and 9).

The availability of hydrogen sources in all of our dehalogenation experiments, easily accounts for the formation of the parent hydrocarbon (biphenyl, phenanthrene, or pyrene) in appreciable yield in experiments 1, 2, 6, and 9, where the halogen atom is flanked by one or two hydrogen atoms in the substrate. With 1,2,3,4-tetrachloronaphthalene (**15a**) and hexabromobiphenyl (**13c**), where halogen atoms are grouped together, the carbon skeleton of the substrate may decompose extensively on the catalyst due to various side reactions. Reaction of methanol with hydrogen bromide is the likely source of the methyl bromide found. The preferential formation of the 1-isomer amongst the methylpyrene byproducts (experiment 9) is consistent with the substitution pattern in pyrene itself [28].

EXPERIMENTAL [29]

Sulfur Bridging of 2,2'-Binaphthyl.

The general procedure was the same as used previously for sulfur bridging of phenanthrene without solvent [30]. Conditioning of the catalyst and the reaction proper were conducted at 550°. The substrate used, 2,2'-binaphthyl (**1**), 2.78 g (10.9 mmoles) (Aldrich), had these physical properties: mp 182-188°; ^{1}H nmr: δ 8.18 and 7.88 (2m, 1H each, H-1 and H-1'), 7.63 (d, J = 7.4 Hz, 3H), 7.42-7.58 (m, 6H), 7.28-7.42 (m, 3H). The solid isolated from the effluent (0.8 g) was separated into elemental sulfur (0.71 g) and dinaphtho[1,2-*b*:2',3'-*d*]thiophene (**3**) (14 mg) by chromatography on alumina with an eluent of petroleum ether (35-60°)/ether (4:1). Extraction of the catalyst with benzene gave 0.9 g of solid, mp 165-310°, which showed the presence of sulfur (R_f 0.8), unreacted **1** (R_f 0.58), and sulfur-bridged products (R_f 0.47) by tlc on alumina with the foregoing eluent. Column chromatography produced 396 mg of sulfur, 5 mg of **1**, and 294 mg (10% combined yield) of a mixture of dinaphtho[1,2-*b*:2',1'-*d*]thiophene (**2**) and **3**. The ^{1}H nmr analysis of successive fractions of effluent indicated a higher yield (189 mg, 6.1%) of **2** (slightly less strongly adsorbed) than of **3** (90 mg, 3.4% combined) [31].

For isolation of pure **2** an effluent fraction containing a ratio of **2:3** of 3.4:1 was re-chromatographed with an eluent of 24:1 petroleum ether/ether and the light yellow solid (27 mg) from the first 1.2 l of effluent was recrystallized from chloroform, mp 255-257° (lit 255° [8]); ^{1}H nmr: δ *ca.* 8.26 and 8.24 (2 overlapping d, 4H, H-1, H-6, H-7, H-12), 8.02 (d, J = 7.5 Hz, 2H, H-4 and H-9), 7.92 (d, J = 8.2 Hz, 2H, H-5 and H-8), 7.67 and 7.58 (2t, J = 7.2-7.5 Hz, 2H each, H-2, H-3, H-10, H-11); uv (absolute ethanol): λ max 232 nm (log ε 4.23), 244 shoulder (4.31), 254 shoulder (4.54), 262 (4.82), 273 (4.60), 285 (4.60), 297 shoulder (4.23), 307 shoulder (4.08), 323 (4.05), 341 (3.32), 357 (3.21); ms: (5.2 V) m/e 285 (29), 284 (M^+, 100), 282 (21), 142 (M^{++}, 26), 141 (14).

Pure **3** was obtained from a separate sulfur-bridging reaction conducted at 530°, wherein 1 g of crystalline 2,2'-binaphthyl was shaken onto heated glass beads atop the conditioned catalyst over a 20 minute period. Then 150 ml of ethyl acetate was added dropwise over 60 minutes to assist in moving the products through the reactor. This addition sequence was repeated a second time. Workup of the effluent gave a black solid, which left 1.03 g of beige residue on trituration with acetone. Column chromatography of the residue, as with the preceding effluent, gave a final fraction of 87 mg of sulfur-bridged products rich in **3** (72 mole %). This fraction was deposited on a 25 x 25-cm reversed phase thin-layer plate (E. Merck RP-18 F_{254_m}, 0.25 mm) and eluted eight consecutive times with acetonitrile-water (5.7:1). Extraction of the band remaining at R_f 0 and recrystallization of this product from chloroform gave **3** as a beige solid, mp 321-322.5° (lit 321° [8]); ^{1}H nmr: δ 8.70 and 8.43 (2s, 1H each, H-7 and H-12), 8.32 (d, J = 8.5 Hz, H-6), 8.17-7.94 (m, 4H, H-11, H-8, H-4, H-1), 7.93 (d, 1H, H-5), 7.7-7.5 (m, 4H, H-10, H-9, H-3, H-2); uv (dioxane): λ max 241 nm (log ε 4.45), 261 (4.78), 272 (4.86), 282 (5.02), 312 shoulder (3.88), 323 (4.08), 334 (4.02), 357 (3.73), 376 (3.86); ms (8.9 V): m/e 285 (31), (M^+, 100), 282 (19), 142 (M^{++}, 35), 141 (15).

Sulfur Bridging of 1-(2-Naphthyl)cyclohexene.

This reaction was conducted in the manner used with 2,2'-binaphthyl. The substrate used, 1-(2-naphthyl)cyclohexene (**7**), 5.35 g (25.7 mmoles), mp 59-60°, was available from previous research [32]; ^{1}H nmr: δ 7.93-7.73 (m, 4H, H-1', H-4', H-5', H-8'), 7.62 (dd, J = 8.5, 1.5 Hz, 1H, H-3'), 7.52-7.37 (m, 2H, H-6' and H-7'), 6.33 (split s, H-2), 2.57 and 2.29 (2m, 2H each, 2 H-3, 2 H-6), 1.87 and 1.73 (2m, 2H each, 2 H-4, 2 H-5). The total reaction time (after conditioning of the catalyst) was 4.5 hours. Extraction of the effluent with benzene gave 1.67 g of yellow solid, mp 100-135°. Tlc (alumina/petroleum ether, 30-60°) of this solid showed three spots: R_f 0.14 (mixture of benzonaphthothiophenes **9** and **10**), 0.22 (2-phenylnaphthalene, **8**), and 0.70 (elemental sulfur). Eluting this plate four consecutive times with the same solvent caused separation of the spot at R_f 0.14 into its components, benzo[*b*]naphtho[2,1-*d*]thiophene (**9**) (R_f on fourth elution 0.72) and benzo[*b*]naphtho[2,3-*d*]thiophene (**10**) (R_f 0.68). Reference compounds were available from a previous study [5].

For isolation of the four products formed, 9 g of alumina was impregnated with 0.6 g of crude product and placed atop a column (2.5 cm by 90 cm) of 400 g of chromatographic alumina (Merck, neutral grade). Elution with petroleum ether (8.5 l) and then benzene (1.5 l, last fraction) gave this succession of products and bands (as viewed with ultraviolet light): sulfur, 76 mg; **8**, purple, 150 mg; **9**, white fluorescence, 183 mg; mixed **9** and **10** (ratio 0.67:1 by ^{1}H nmr analysis), light purple, 37 mg; and **10** only, diffuse purple, 38 mg. The corresponding percentage yields from substrate **7** are 8 for **8**, 9.2 for **9**, and 2.8 for **10**. Purified samples of these three products were obtained by recrystallizations from petroleum ether and identifications were established by direct comparison with authentic samples - melting point, mixture mp, tlc, and ^{1}H nmr spectra [5].

Catalyzed Hydrodehalogenation Reactions.

(a) Starting Materials and Catalysts.

Sources and properties of the starting materials are as follows: 4-chlorobiphenyl (**13a**), K and K Labs., mp 76-78°, 4-bromobiphenyl (**13b**), Fluka, mp 89-90°; hexabromobiphenyl (**13c**), ICN Biochemicals, technical grade, mp 132-138°; ^{1}H nmr: δ 7.94 (s, 2H), 7.47 (s, 2H); 9-bromophenanthrene (**14a**), Aldrich, mp 60-62°; 1,2,3,4-tetrachloronaphthalene (**15a**), K and K Labs., mp 193-196°; ^{1}H nmr: δ 8.28 (dd, 2 *alpha* H), 7.68 (dd, 2 *beta* H); 1,3,6,8-tetrachloropyrene (**16a**), K and K Labs., recrystallized from toluene, mp 373-377°; ms: (quadrapole): m/e 342 (47), 340 ($C_{16}H_6{}^{35}Cl_3{}^{37}Cl^+$, 98), 338 (77), 306 ($C_{16}H_5{}^{35}Cl^{37}Cl_2{}^+$, 92), 304 ($C_{16}H_5{}^{35}Cl_2{}^{37}Cl^+$, 100). Catalyst **I** is Harshaw Cr-0101T, 1/8-inch pellets, consisting of 12% Cr_2O_3/86% Al_2O_3/2% MgO [33]. Catalyst **II** is Harshaw Co-Mo-0603T, 1/8-inch pellets, consisting of 12% MoO_3/85% Al_2O_3/3% CoO. This sulfided catalyst was designated as CMA-1 in a previous paper [18]. Generally the catalyst was conditioned at the reaction temperature either with hydrogen sulfide alone or with hydrogen sulfide plus methanol.

(b) The Reaction Proper and Processing.

The reaction proper was conducted under conditions used for sulfur-bridging (with hydrogen sulfide alone) or for desulfurization (with nitrogen alone or with nitrogen plus methanol). The reactant was added to the reactor tube either as a solution or an emulsion in the solvent (in a dropwise manner) or as increments of fine crystals without solvent [1,18]. The total liquid-solid effluent was extracted with a suitable water-immiscible organic solvent. Aqueous and organic phases were separated. The aqueous phase was tested qualitatively or quantitatively for the presence of acid, chloride ion, or bromide ion. The organic phase was washed with aqueous sodium hydroxide and then with water, dried, and evaporated to give a crude, water-insoluble product. Components of this crude product were established qualitatively by such methods as the Beilstein test, thin-layer chromatography with accompanying authentic reference compounds, and mass spectrometry. Quantitative correlations of products formed were obtained by ^{1}H nmr spectra (including spectra of authentic reference compounds) and/or chromatographic separation on alumina and/or direct recrystallization. In two cases (experiments 3 and 4) the gaseous effluent from the reactor tube was passed successively through traps of aqueous sodium bicarbonate (to remove volatile acid), solid potassium hydroxide plus anhydrous calcium sulfate, a solution of quinoline in dry benzene, solid calcium sulfate, and then aqueous potassium hydroxide (to remove hydrogen sulfide). Precipitate which formed in the quinoline trap was collected by suction filtration, washed with fresh benzene, dried *in vacuo*, weighed, and identified as *N*-methylquinolinium bromide by comparison of its ^{1}H nmr spectrum with that of a synthetic sample, mp 97.5-98° lit. 96-97° [34], positive Beilstein test; ^{1}H nmr (hexadeuterioacetone): δ 9.18 (d, J = 5 Hz, 1H, H-2), 8.97 d, J = 8 Hz, 1H, H-8), 8.3-7.8 (m, other aromatic protons), 4.78 (s, 1H, 0.5 H_2O), 4.58 (s, 3H, MeN^+).

REFERENCES AND NOTES

[1] For the preceding paper in this series see L. H. Klemm, E. Hall, L. Cousins, and C. E. Klopfenstein, *J. Heterocyclic Chem.*, **24**, 1749 (1987).

[2] Postbaccalaureate research assistant, 1986-1987.

[3] Undergraduate research assistant, 1986-1987.

[4] Undergraduate research assistant, 1985-1987.

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

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

[7] R. Wilputte and R. H. Martin, *Bull. Soc. Chim. Belg.*, **65**, 874 (1956); E. Campaigne and S. W. Osborn, *J. Heterocyclic Chem.*, **5**, 655 (1968).

[8] M. L. Tedjamulia, Y. Tominaga, R. N. Castle, and M. L. Lee, *J. Heterocyclic Chem.*, **20**, 1143 (1983).

[9] For the concept that isosteric pairs of condensed thiophenes and their benzologs [10] should show similarity of patterns in their ultraviolet absorption spectra see G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 3438 (1956). Also see R. Zahradnik, in "Advances in Heterocyclic Chemistry", Vol **5**, A. R. Katritzky, ed, Academic Press, New York, NY, 1965, p 42.

[10] For a definition of the term "benzolog" see L. H. Klemm, in "Advances in Heterocyclic Chemistry", Vol **32**, A. R. Katritzky, ed, Academic Press, New York, NY, 1982, p 154.

[11] E. Clar, "Polycyclic Hydrocarbons", Vol **I**, Academic Press, New York, NY, 1964, pp 274, 349, 357.

[12] It should be noted that the uv spectrum of **2** was determined in ethanol from 200-400 nm, while that of picene was determined in ethanol at wavelengths below 280 nm and in benzene at wavelengths above 280 nm.

[13] The total number of dinaphtho[*b,d*]thiophenes, $C_{20}H_{12}S$, possible is six. All are reported (see reference 10, Tables II and IV), but only **3** has a melting point >300° [8].

[14] O. Hutzinger, S. Safe, and V. Zitko, "The Chemistry of PCB's", CRC Press, Cleveland, Ohio, 1974; M. D. Erickson, "Analytical Chemistry of PCB's", Butterworth Publishers, Boston, MA, 1986.

[15] "Polychlorinated Biphenyls and Terphenyls", Environmental Health Criteria 2, World Health Organization, Geneva, Switzerland, 1976; "PCB Poisoning and Pollution", K. Higuchi, ed, Academic Press, New York, NY, 1976; E. Chen, "PBB: An American Tragedy", Prentice-Hall, Inc., Englewood Cliffs, NJ, 1979; J. Egginton, "The Poisoning of Michigan", W. W. Norton and Co, New York, NY, 1980.

[16] L. H. Klemm and J. J. Karchesy, *J. Heterocyclic Chem.*, **15**, 561 (1978).

[17] L. H. Klemm, S. Pou, W. D. Detlefsen, C. Higgins, and R. F. Lawrence, *ibid.*, **21**, 1293 (1984).

[18] L. H. Klemm and J. J. Karchesy, *ibid.*, **15**, 65 (1978).

[19] L. H. Klemm, J. J. Karchesy, and R. F. Lawrence, *ibid.*, **15**, 417 (1978).

[20] R. K. McAlpine and B. A. Soule, "Fundamentals of Qualitative Chemical Analysis", 2nd Ed, van Nostrand Co., New York, NY, 1941, p 287. The method consists of treating the solution with excess silver nitrate to precipitate silver chloride, silver sulfide, and free silver (formed from reducing agents such as formaldehyde), dissolution of only the silver chloride in ammonium hydroxide, and the reprecipitation of white silver chloride with nitric acid.

[21] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th Ed, John Wiley and Sons, New York, NY, 1967, p 65.

[22] S. Safe, *Org. Mass Spectrom.*, **5**, 1221 (1971).

[23] S. R. Heller and G. W. A. Milne, "EPA/NIH Mass Spectral Data Base", Vol **2**, National Bureau of Standards, U. S. Government Printing Office, Washington, DC, 1978, p 1815.

[24] S. Safe and O. Hutzinger, *J. Chem. Soc., Perkin Trans. I*, 686 (1972); *Idem.*, "Mass Spectrometry of Pesticides and Pollutants", CRC Press, Cleveland, Ohio, 1973, Chapter 5.

[25] P. K. Freeman, R. Srinivasa, J.-A. Campbell, and M. L. Deinzer, *J. Am. Chem. Soc.*, **108**, 5531 (1986).

[26] S. O. Farwell, F. A. Beland, and R. D. Geer, *J. Electroanal. Chem. Interfacial Electrochem.*, **61**, 315 (1975).

[27] T. F. Connors and J. F. Rusling, *J. Electrochem. Soc.*, **130**, 1120 (1983).

[28] E. Clar, "Polycyclic Hydrocarbons", Vol **II**, Academic Press, New York, NY, 1964, p 119.

[29] Unless otherwise noted, ^{1}H nmr spectra were obtained by means of a General Electric QE-300 instrument on solutions in deuteriochloroform and ultraviolet absorption spectra, with a Beckman DU-7 spectrophotometer. Mass spectra were obtained by Dr. Richard Wielesek at 70 eV with a CEC 21-110 double-focusing instrument or at variable voltage with a VG 12-250 instrument.

[30] L. H. Klemm, R. Tsuchiya, E. K. L. Wong, M. P. Stevens, J. J. Lu, and C. E. Klopfenstein, *J. Heterocyclic Chem.*, **24**, 357 (1987).

[31] The presence of a minor, unidentified component in the crude mixture was apparent from the presence of a small, sharp singlet at δ 8.62 in the ^{1}H nmr spectrum. This component was lost on chromatography.

[32] L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951). The picrate of **7** was recrystallized (mp 81-83°) and then dissociated by chromatography.

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

[34] R. C. Fuson, G. E. Ullyot, R. F. Stedman, and P. O. Tawney, *J. Am. Chem. Soc.*, **60**, 1447 (1938).