Dibenzothiophene from Biphenyl and Derivatives (1)

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Sulfur bridging of biphenyl (4), 4-methylbiphenyl, and the biphenylthiol isomers (7) to yield dibenzothiophene (3) is effected by means of hydrogen sulfide, benzene (solvent), and a sulfided cobaltous oxide-molybdic oxide-alumina (CMA-1) catalyst at 450° in a flow system. Alumina also catalyzes a number of these transformations. The possibility that compounds 7 (especially the 2-isomer) are intermediates in the conversion 4 → 3 is noted.

In previous publications in this series (3,4) we established that phenanthrene (1) and phenanthro[4,5-bcd]-thiophene (2) are interconvertible (equation 1) under the same conditions of temperature (450°), pressure (ca. one atmosphere), and catalyst (sulfided cobaltous oxide-molybdic oxide-alumina; designated CMA-1) in a flow system by selecting the other reactant present. Thus, insertion of a sulfur bridging atom (1→2) is effected in the presence
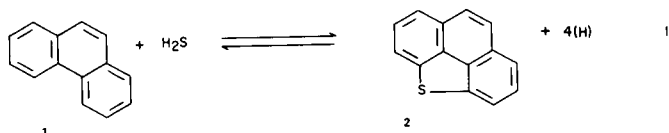
of hydrogen sulfide as a reactant and carrier gas, while extrusion of the sulfur bridging atom (2 → 1) occurs in the presence of methanol, an in situ hydrogen source. Some methylation of the aromatic rings accompanies the latter process of desulfurization. We have also found that dibenzothiophene (3) is desulfurized to biphenyl (4), monomethylbiphenyls (5), and fluorene (6, probably formed via the intermediate 5a) in the presence of methanol under the aforementioned conditions (equations 2-4, left to right; written in the form of balanced redox
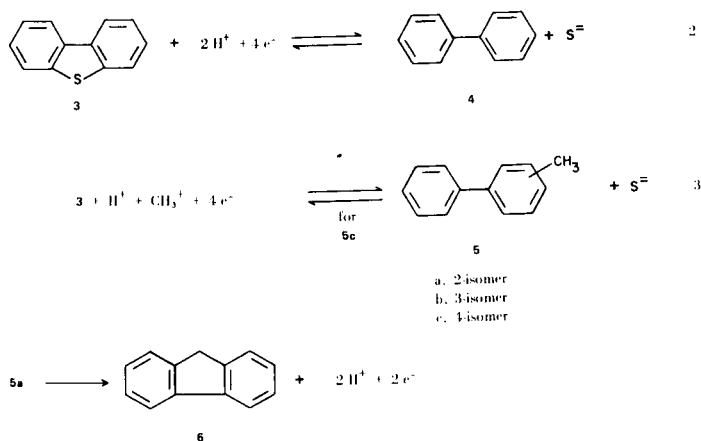
half-reactions). The present paper concerns the reverse processes of 4 → 3 and 5c → 3 and an investigation of the possibility that a biphenylthiol (7) (perhaps chemisorbed) is an intermediate in the former transformation.
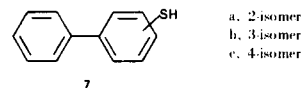

a. 2-isomer
b. 3-isomer
c. 4-isomer

Table 1 presents results from the various runs, which were conducted in the same flow apparatus as was used for sulfur extrusion reactions (4-7). In general, a stream of hydrogen sulfide gas and a solution of substrate compound (4, 5c, or 7) in benzene were passed through a heated column (at 350-630°) packed with CMA-1, sulfided alumina, or glass beads (used to check for the occurrence of thermal non-catalyzed processes). Effluent mixtures were analyzed both qualitatively and quantitatively.

As is evident from control runs 8-11 the benzene solvent is inert on glass beads at 450°, but it does react to give a small yield (0.3-1%) of dibenzothiophene (3) and a trace amount of biphenyl (4) on alumina or CMA-1 at 450-550°. Since the molar ratio of benzene/substrate used in the regular runs is large (40:1 to 160:1), however, corrections to the yields of 3 produced from the substrate for the presence of the solvent become appreciable (8). Both total (based on the assumption that the benzene is chemically inert) and corrected (shown in brackets) mole % yields are given in Table I. The correction for the presence of benzene in experiments with CMA-1 at 550° (see runs 3 and 13) is so large as to make close comparison of yields (particularly above 450°) questionable. Run 13 illustrates an extreme situation, wherein the uncorrected yield of 3 from biphenyl-2-thiol (7a) exceeds 100% but the corrected yield of 3 at 550° is lower than that at 450° (run 12). Runs 4 and 5 (compare 2 and 3, respectively) were made with n-heptane (instead of benzene) in an effort to avoid complications due to the solvent. However, with heptane the percentage conversion of biphenyl was decreased markedly at both 450° and 550°. In fact, results from run 5 (with heptane at 550°) approximate those from run 2 (with benzene at 450°) (9). For comparison purposes (10) it seemed preferable to focus on a temperature of 450° for most of our studies, so that benzene was used as the solvent in all additional runs.

Runs 1-3, 6 and 7 show that biphenyl undergoes sulfur bridging in the presence of catalysts CMA-1 and alumina,

Table I

Sulfur Bridging of Biphenyl (4) and Derivatives with Hydrogen Sulfide under Various Reaction Conditions (a)

Run No.	Substrate No.	Wt. (g)	Catalyst or Packing	Reaction Temp. °C	Yields of Products 3 (b,c)	4 (b)	S_8 (d,e)
1	4	2	CMA-1	350	25	65	0.12
2	4	2	CMA-1	450	49 [42]	30 [30]	0.58
3	4	2	CMA-1	550	91 [63]	7 [6]	0.21
4 (f)	4	1	CMA-1	450	11	72	
5 (f)	4	1	CMA-1	550	41	38	
6	4	1	Al_2O_3	550	47 [27]	48 [45]	
7	4	1	glass beads	550	none	92	
8	none	(g)	CMA-1	450	0.3 (h)	trace	
9	none	(g)	CMA-1	550	1 (h)	trace	0.00
10	none	(g)	Al_2O_3	550	0.3 (h)	0.03 (h)	
11	none	(g)	glass beads	450	none	none	
12	7a	1	CMA-1	450	74 [46]	trace	0.15
13	7a	1	CMA-1	550	132 [32]	2 [1]	
14	7a	1	glass beads	450	54 [54]	2 [2]	
15 (i)	7a	1	glass beads	450	15 [15]	3 [3]	
16	7b	1	CMA-1	450	79 [54]	1 [1]	
17	7c	1	CMA-1	450	110 [86]	2 [2]	
18	7c	1	Al_2O_3	550	67 [45]	36 [33]	
19	5c	1	CMA-1	450	39 [32]	6 [6]	0.03 (j)
20	5c	0.3	Al_2O_3 (k)	630	40	30	1.0 (ℓ)

(a) Except in runs 4, 5 and 8-11, the substrate was used as a solution in benzene (25-75 ml.). Except in run 20, 75 g. of oxide catalyst or a column length of 42 cm. of glass beads was placed in the reactor. (b) In mole %, as determined by gas chromatography. Yields relate directly to the moles of substrate used (rather than to the total moles of products formed). (c) Numbers in brackets are mole % yields corrected for the contribution by the benzene solvent (see runs 8-11), as based on the assumption of additivity by weight. (d) In grams, obtained from Soxhlet extraction of the spent packing by means of benzene. (e) A blank in this column indicates that the yield was not determined. (f) n-Heptane (50 ml.) was used instead of benzene. (g) Blank run with benzene. (h) Based on benzene used. (i) Nitrogen, instead of hydrogen sulfide, was used as the carrier gas. (j) Also 5% of 5c was recovered. Only 1% of a methyldibenzothiophene (identification only tentative) was extracted from the spent catalyst. (k) Only 25 g. of catalyst was used. (ℓ) Also 11% of 5c was recovered.

but that sulfur insertion is not effected thermally. With CMA-1 the yield of dibenzothiophene (3) increases with increasing temperature in the range 350-550° and (at least at 550°) is higher than with alumina. Particularly significant is the finding that, at 350° and 450°, CMA-1 catalyzes both sulfur bridging (4 → 3) and the reverse reaction of sulfur extrusion (3 → 4) (5,6). Thus, the reaction (equation 2) can be driven either to the right or to the left by changing the reactant (methanol or hydrogen sulfide, respectively), in the same manner as occurs in the phenanthrene-phenanthro[4,5-bcd]thiophene system (equation 1). Therefore, CMA-1 exhibits the characteristics (normally associated with a true catalyst) (11a) of fostering both forward and reverse reactions under one set of external conditions, even though the systems are operating far from a state of equilibrium (12). This reversibility, however, is not shown by sulfided alumina which fails to catalyze desulfurization of 3 in the presence of methanol (6).

A thermodynamically reversible process (as may be implied by equations 1 and 2) should involve the same intermediate(s), if any, and the same transition complexes

for proceeding in either direction (11b). It has already been shown (as based on yields of products) that biphenyl-2-thiol (7a) (probably chemisorbed, rather than free in the mobile phase) qualifies as a plausible (though certainly not a requisite) intermediate in the transformation 3 → 4 (7). Runs 12 and 14 (cf. run 2) show also that 7a could be an intermediate in the CMA-1 catalyzed conversion 4 → 3 but the result is ambiguous since cyclization of 7a to 3 occurs thermally to approximately the same extent [corrected yield of 3, 50 ± 4%]. A mechanism for the thermal cyclization was suggested previously (7). Surprisingly, when 7a in a stream of nitrogen gas (rather than hydrogen sulfide) was passed over glass beads (run 15) at 450° the yield of 3 was decreased markedly.

If one assumes that 7a is, indeed, an intermediate, it is not clear why the thiylation step (4 → 7a) should occur selectively (or exclusively) at C-2. Runs 16-18 (with the isomeric biphenylthiols 7b and 7c) were made in order to check on the possibility that thiylation of biphenyl does, indeed, give all three biphenylthiol isomers but that only 7a undergoes cyclization to dibenzothiophene. The results indicate, however, that every one of

the isomeric biphenylthiols is converted into **3**. In fact the yield of **3** from reaction of biphenyl-4-thiol over CMA-1 catalyst (run 17) is considerably larger than from reaction of the 2-thiol. One can visualize several plausible pathways from **7b** and **7c** to **3**. An attractive possibility is that a 3- or 4-thiol group serves merely to anchor the biphenyl molecule to the catalyst surface while sulfur bridging is occurring at C-2 and C-2'. Desulfurization at C-3 or C-4 then removes this relatively strong anchoring bond and permits desorption of **3** to take place (13,14).

Runs 19 and 20 show that 4-methylbiphenyl (**5c**) also undergoes sulfur bridging in the presence of either CMA-1 or alumina, but that concomitant demethylation to yield **3** occurs (equation 3, right to left). The reversibility shown in equations 2 and 3, however, only applies to the use of CMA-1 in our studies.

In summary, the pathway for the conversion of **4** into **3** (i.e. for sulfur bridging) remains uncertain. The overall process is catalyzed both by CMA-1 and alumina, and is not simply a thermal reaction. No intermediates have been isolated. However, on the basis of products formed under bridging conditions, any of the isomeric biphenylthiols qualifies as an intermediate, though only biphenyl-2-thiol (**7a**) can cyclize directly to **3**. If a two-step process, **4** → **7a** → **3** is involved, the first step (thiylation) is catalyzed, while the second step (cyclization) is either thermal or catalyzed (or both). Compound **7a** (probably chemisorbed) is a plausible intermediate in both sulfur insertion (**4** → **3**) and sulfur extrusion (**3** → **4**) in the presence of CMA-1. Reaction via **7a** would involve the making or breaking (respectively) of carbon-sulfur bonds one at a time. However, results thus far do not exclude the attractive alternative that both carbon-sulfur bonds form or break in a concerted manner.

EXPERIMENTAL

Syntheses of biphenylthiols (**7**), pre-conditioning of catalysts and glass beads, general procedure, and analytical methods were described previously (6,7). The following modifications were used in the present studies. Flow of hydrogen sulfide gas was continued (no nitrogen used, except in run 15) during the reaction proper, while 0.3-2 g. of substrate [biphenyl (**4**), biphenylthiol (**7a, 7b** or **7c**), or 4-methylbiphenyl (Aldrich, purified by sublimation in vacuo) (**5c**)] in 25-75 ml. of benzene was added from the dropping funnel (rate of 25 ml./hour). Additional benzene was sometimes added to wash the column. In some cases the

spent catalyst was extracted with benzene over a period of 4 hours in a Soxhlet apparatus. The residue, after filtration and evaporation of the extract, was weighed and analyzed qualitatively and quantitatively for organic components (generally none found) by gas chromatography. Elemental sulfur (estimated by difference) was identified qualitatively in various residues by recrystallization from chloroform plus melting point determination.

By-products from control runs 8 and 9 (with benzene only) were tentatively identified by tlc on silica gel as benzenethiol and diphenyl sulfide. Gas chromatography also indicated the formation of diphenyl disulfide.

REFERENCES AND NOTES

(1) This investigation was supported by research grant No. MPS 75-04116 from the National Science Foundation. For Paper VII in this series, see reference 4.

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

(3) L. H. Klemm and W. Hsin, J. Heterocyclic Chem., 13, 1245 (1976).

(4) L. H. Klemm, J. J. Karchesy and R. F. Lawrence, ibid., 15, (1978).

(5) L. H. Klemm and J. J. Karchesy, ibid., 14, 353 (1977).

(6) Paper V: L. H. Klemm and J. J. Karchesy, ibid., 15, 65 (1978).

(7) Paper VI: L. H. Klemm and J. J. Karchesy, ibid., 15, (1978).

(8) While it is uncertain how one should make these corrections, we have based them on the assumption that the weights of **3** and **4** formed from a given volume of benzene remain constant, irrespective of the quantity of substrate used.

(9) If one assumes that adsorbed molecules of biphenyl undergo rapid sulfur bridging on a limited number of adsorption sites, then the conversion **4** → **3** will be fostered by rapid elution of adsorbed **3** from the catalyst surface. Both increased temperatures and benzene (as compared to heptane) should promote more rapid desorption of **3** and may account for these observations.

(10) A temperature of $450°$ was found to be desirable for desulfurization of **3** with methanol and CMA-1 (6).

(11) F. Daniels and R. A. Alberty, "Physical Chemistry," 4th ed., John Wiley and Sons, New York, N. Y., 1975, (a) p. 338, (b) p. 319.

(12) We have not yet attempted to establish equilibrium concentrations of reactants and products in a closed system at $450°$ and 1 atmosphere pressure.

(13) It seems very unlikely that a 3- or 4-thiol intermediate is involved in the desulfurization process **3** → **4**.

(14) Efforts to detect biphenylthiols in the effluent products from runs 12-18 by means of thin-layer or gas chromatography have not been successful. Known biphenylthiols fail to give a a detector signal in our gc apparatus.