

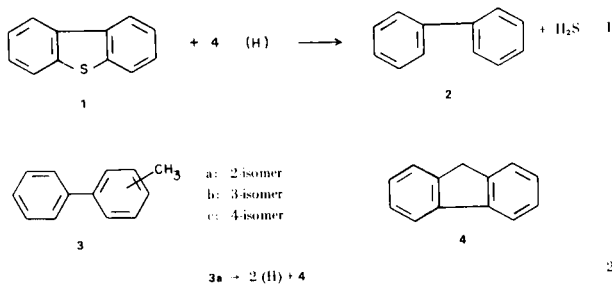
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Products were determined from reaction of biphenyl-2-thiol (5) with methanol in a packed flow reactor at elevated temperatures and *ca.* atmospheric pressure. At 450-550° thermolysis of 5 gives small yields of dibenzothiophene (1) and biphenyl (2). With sulfided alumina, products vary with reaction temperature from 82% *S*-methyl-5 at 250° to only 1 plus 2 at 550°. At 450° with sulfided cobaltous oxide-molybdenic oxide-aluminum oxide (CMA-1), 5 and its isomers give mainly desulfurization to 2 (81%), plus *C*-methylation to methylbiphenyls and fluorene. With CMA-1 at 450° the arrays of products from 1 and 5 are closely similar.

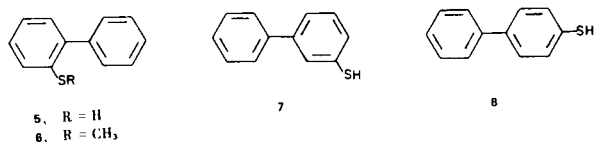
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In the previous paper in this series (3) we described a procedure for reductive desulfurization of dibenzothiophene (1) to form biphenyl (2) by means of sulfided cobalt oxide-molybdena-alumina catalyst (especially CMA-1) and methanol in a flow system at 250-550° and *ca.* atmospheric pressure (equation 1). Byproducts also formed are monomethylbiphenyls (3a-3c) and fluorene (4). It was



proposed that isomers 3 result from direct free radical methylation of 1, followed by desulfurization; while 4 is produced by catalytic dehydrogenation of 3a, as per equation 2. In separate experiments it was found that neither methylation nor desulfurization of 1 can be effected by means of methanol plus glass beads (*i.e.* by a thermal process) or methanol plus sulfided alumina. In the present paper we explore the possibility that biphenyl-2-thiol (5) [or its chemisorbed equivalent] can qualify as a plausible intermediate in the reaction. In particular we compare the arrays of products which result on treating 5 with methanol plus CMA-1, sulfided alumina, or glass beads with those found from CMA-1, methanol, and 1. For comparative purposes we also report products formed from the isomeric biphenylthiols 7 and 8 plus CMA-1 and methanol.

In hydrodesulfurization (HDS) of various organosulfur



compounds by means of a CMA catalyst at 325-425° and hydrogen pressures up to 36 atm. Obolentsev *et al.* (4-6) reported that 1 reacts differently from other substrates

(*e.g.* thiophene derivatives and dialkyl sulfides, which form identifiable thiol intermediates). Compound 1, which hydrogenolyzed more slowly than most other substrates used, yielded hydrogen sulfide and 2 – without a detectable intermediate step (such as formation of 5) or hydrogenation of the aromatic ring. Bartsch and Tanielian (7) in HDS at 300-375° and hydrogen pressures < 1 atm. and Doyle (8) in desulfurization by hydrogen transfer from tetralin at 350° in an autoclave also found that 2 was the only organic product from 1 when a CMA catalyst was used. Other workers (9) obtained phenylcyclohexane and bicyclohexyl from HDS of 1 in the presence of a CMA or molybdenum disulfide catalyst. None of these workers investigated 5 as a substrate compound. Sergienko and Perchenko (10) effected HDS of sulfides, thiols, and benzothiophene by means of a mixed nickel-tungsten sulfide catalyst at 200° and 200 atm. pressure. They reported that 1 is inert under these conditions and proposed that HDS is a two stage process involving a thiol intermediate.

In our studies, runs (Table I) were conducted in the same manner as used for desulfurization of 1 previously (3). At 450° the arrays of products formed from either 1 or 5 with CMA-1 are identical [compare run 3, Paper V; and run 7, Table I]. Moreover, total yields of aromatic hydrocarbon products are 82% and 88%, and observed molar ratios (4:3b:3c) of minor products formed are 1.1:2.0:1.0 and 1.2:1.6:1.0, respectively. We consider these quantitative differences to be sufficiently small as to make the formation of 5 (probably chemisorbed) as an intermediate in the transformation 1 → 2 plausible (but not requisite). The clear result from this comparison is that methylation of the aromatic ring need not precede cleavage of a C-S bond in 1.

Runs 8 and 9 show that the isomeric biphenylthiols 7 and 8 likewise yield the same array of products as from 1 and 5; but, especially for the 4-thiol (8), there are noticeable quantitative variations in the ratios of the minor components. All of the thiols give high yields (81 ± 2%) of 2.

Although dibenzothiophene fails to react with methanol in the presence of sulfided alumina (3), thiol 5 does react under these conditions (runs 1-4) with results that vary as

Table I

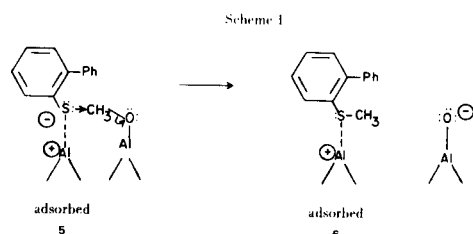
Transformations of Biphenylthiols with Methanol Plus a Catalyst (a)

Run No.	Substrate	Catalyst or Packing	Reaction Temp., °C.	Yields of Products, mole %				
				2	3(b)	4(b)	6(c)	1(c)
1	5	sulfided Al ₂ O ₃	250	none			82	none
2	5	ditto	350	1			79	none
3	5	ditto	450	22			50	1
4	5	ditto	550	36			none	27
5	5	glass beads	450	22			none	18
6	5	ditto	550	9			none	26
				Molar ratio 4:3b:3c				
7	5	CMA-1	450	81	5	>2	1.2:1.6:1.0	
8	7	CMA-1	450	83	3	2	1.4:1.6:1.0	
9	8	CMA-1	450	80	2	2	0.4:0.6:1.0	

(a) All runs were made with 1 g. of substrate, 150 ml. of methanol, and 75 g. of alumina (or the equivalent bulk volume of other tube packing). Yields were determined by gas chromatography and relate directly to the moles of substrate used (rather than to the moles of products formed). (b) A blank space indicates that none of this compound was detected. (c) not detected in runs 7-9.

a function of reaction temperature in the range 250-550°. Thus, at 250° only *S*-methylation occurs to form thioether **6**; at 450° both *S*-methylation and desulfurization to **2** are observed; while at 550° both desulfuration and cyclization to **1** are significant, but no methylation is found. Comparison of the yields of products from runs 3 and 4 with those from 5 and 6, respectively (latter runs conducted under thermolytic, rather than catalytic, conditions), indicates that *S*-methylation is catalyzed by alumina, cyclization to **1** is a thermal process, and desulfurization of **5** to **2** may involve both thermal and catalyzed processes. Total yields of products from thermolyses are only fair (35-40%). Reduction to **2** is much greater with CMA-1 than with either alumina or glass beads. It is significant that only CMA-1 gives *C*-methylation of **5** (*vide infra*). Moreover, it is clear that if the transformation of **1** into **2** in the presence of CMA-1 involves the two-step process **1** → **5** → **2**, neither the first nor the second step can be ascribed either predominantly to action of heat or to the presence of an alumina component in the catalyst.

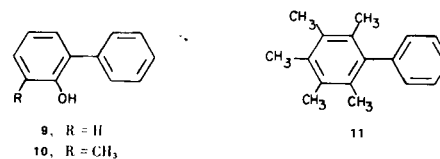
Mechanistic rationalizations for the processes of *S*-me-



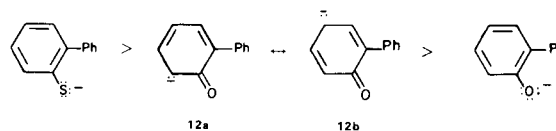
thylation and thermal cyclization are presented in Schemes 1 and 2.

Scheme 1 depicts a surface S_N2-type reaction wherein an adsorbed anion of thiol **5** (from ionic dissociative adsorption of **5**) effects nucleophilic attack at the carbon

atom of an adjacent chemisorbed methoxide group. The weakly adsorbed **6** which is produced is then desorbed and carried into the effluent. This transformation is analogous to the limited *O*-methylation which occurs for 1- and 2-naphthols in the presence of methanol and plain alumina at temperatures below 450° (11,12). In these naphthol reactions, however, methylation takes place predominantly on the aromatic ring (*i.e.* one obtains *C*-methylation), as likewise occurs for phenol (13), indanol (14), and hydroxybiphenyls (including **9**) (15). The occurrence of *S*-methylation in **5** and the failure of **9** to undergo *O*-methylation under identical reaction conditions (see Experimental) are consistent with the generalization (found for reactions in solution) that nucleophilicity toward an

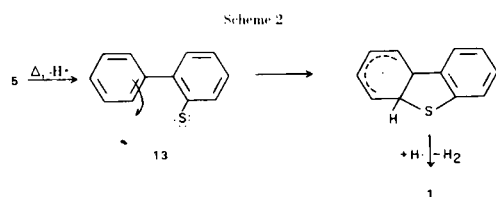


sp³ carbon by the PhS⁻ ion is greater than by the PhO⁻ ion (16). At least for reactions with alumina-methanol one can now extend this generalization to give the order for nucleophilicity



where resonance carbanion structures **12** are invoked to account for the formation of products **10** and **11** (17-19).

It is apparent that the foregoing order of nucleophilicity does not apply to the reaction of **5** with methanol-CMA-1. Probably a different reaction mechanism is involved in bringing about *C*-methylation.



It is expected that the thermal cyclization shown in Scheme 2 will be assisted by the presence of a surface (glass beads or alumina) for retention of the hydrogen atom and the free radical 13, interaction between these intermediates, and energy transfers; *i.e.* the surface serves merely to foster physical adsorption rather than chemisorption.

EXPERIMENTAL (20)

Synthesis of Biphenyl-2-thiol (5).

According to a modified procedure of Newman and Hetzel (21), a solution of 0.3 mole of 2-hydroxybiphenyl (Aldrich) in potassium hydroxide, water, and tetrahydrofuran (50 ml.) was treated with a solution of 0.4 mole of *N,N*-dimethylthiocarbamyl chloride (Aldrich) in 80 ml. of tetrahydrofuran. The benzene extract was washed with water, dried (sodium sulfate), concentrated, and chromatographed on a column of 600 g. of silica gel (J. T. Baker, no. 3405). Elution with benzene (500 ml.) gave a glass which crystallized from methanol; yield 40.6 g. (53%) of *O*-2-biphenyl *N,N*-dimethylthiocarbamate, m.p. 111-112°, reported (22) m.p. 102-104°.

The crude product from heating 25 g. of the preceding *O*-ester at 255-265° for 3 hours in an atmosphere of nitrogen was hydrolyzed by means of potassium hydroxide, water, and ethylene glycol. The chloroform solution of the acidified mixture was dried (sodium sulfate), evaporated, dissolved in a minimum amount of benzene, and percolated through a short column of alumina (petroleum ether as eluent) to give a glass. Crystallization from ethanol-dichloromethane (19:1 by volume) gave 8 g. (44%) of biphenyl-2-thiol as prisms, m.p. 38-39°, reported m.p. 38-39° (23), 40-42° (24).

Exact mass: Calcd. for $C_{12}H_{10}S$, 186.050. Found: 186.052.

Biphenyl-3-thiol (7) and Biphenyl-4-thiol (8).

Thiols 7 and 8 were synthesized from the corresponding hydroxybiphenyls in the general manner used for 5. The intermediate *O*-4-biphenyl *N,N*-dimethylthiocarbamate (83%, m.p. 141-142°) (22) gave thiol 8 (47%), m.p. 106-109° from ethanol, raised to 108-109° by sublimation at 95°/0.6 mm.; pmr δ 3.46 (s, 1, SH) and 7.1-7.6 ppm (m, 9, aromatic H); reported m.p. 108-110° (25), 111-112° (26).

O-3-Biphenyl *N,N*-dimethylthiocarbamate [74%; m.p. 77-82°, from methanol; pmr δ 3.30 and 3.42 (2s, 3 each, 2 methyl groups) and 7.0-7.8 ppm (m, aromatic H)] apparently contained *ca.* 10% of the 4-isomer as an impurity.

Exact mass: Calcd. for $C_{15}H_{15}NOS$, 257.087. Found: 257.087.

On cooling, an ether solution of the thermolysate from the preceding *O*-aryl thioamide deposited a solid mixture of isomeric *S*-aryl thioamides. Evaporation of the mother liquor then left isomerically pure *S*-3-biphenyl *N,N*-dimethylthiocarbamate as a liquid (36%); pmr δ 2.94 (s, 6, methyl groups) and 7.1-7.9 (m, 9, aromatic H).

Hydrolysis of the *S*-aryl thioamide yielded biphenyl-3-thiol (7), obtained as a colorless liquid (49%) from evaporative distillation at 130°/0.5 mm.; pmr δ 3.40 (s, 1, SH) and 7.0-7.7 (m, 9, aromatic H); ir (neat) 2560 (weak, SH), 750 and 700 cm^{-1} (strong); reported, pale yellow liquid, b.p. 103-162°/0.5 mm.; ir bands at 2570, 750, and 700 cm^{-1} (27).

Exact mass: Calcd. for $C_{12}H_{10}S$, 186.050. Found: 186.051.

Methodology for Reactions.

The apparatus, general procedure, preparation *in situ* of catalyst CMA-1, and analytical methods were described previously (3). Sulfided alumina catalyst was prepared *in situ* by passing a stream of hydrogen sulfide (160 ml./minute — measured at room temperature) through the reactor tube packed with 75 g. of alumina (Harshaw Al-0104 T) catalyst while methanol (50 ml.) was added dropwise over a period of 2 hours and the temperature was raised (during the first 45 minutes) from 100° to 450° (maintained constant thereafter). A flow of nitrogen gas (60 ml./minute) was substituted for the hydrogen sulfide. For reaction at 450° addition of a solution of 1 g. of 5 in 150 ml. of methanol was started immediately and the previous procedure was followed. For reaction at lower temperatures the tube was allowed to cool to the reaction temperature before initiating the reaction proper. For reaction at 550°, the reaction temperature was attained during the same sulfidation period. Effluents were extracted into methylene chloride, instead of ether.

For runs 5 and 6 the reactor tube was packed to the same height with pyrex glass beads, which were preconditioned *in situ* with hydrogen sulfide and methanol in the aforementioned manner.

Methyl 2-Biphenyl Sulfide (6).

This compound, isolated from run 2, was obtained as plates from methanol, m.p. 40-41° [reported 39-41° (24)]; pmr δ 2.30 (s, 3, methyl group) and 7.0-7.7 ppm (m, 9, aromatic H).

Exact mass: Calcd. for $C_{13}H_{12}S$, 200.066. Found: 200.064.

Reaction of 2-Hydroxybiphenyl (9) with Sulfided Alumina Plus Methanol.

Run 4 was repeated with 2-hydroxybiphenyl, instead of 5. Products obtained were the same as with non-sulfided alumina, *i.e.* 2,3,4,5,6-pentamethylbiphenyl (11) (11%) and 1,2,3,4-tetramethylfluorene (7%) (15). No biphenyl or thioether 6 was detected.

REFERENCES AND NOTES

- (1) This investigation was supported by research grant no. MPS 75-04116 from the National Science Foundation. For Paper V in this series see ref. 3.
- (2) Research Associate and Visiting Assistant Professor, 1975-1977.
- (3) L. H. Klemm and J. J. Karchesy, *J. Heterocyclic Chem.*, **15**, 65 (1978).
- (4) R. D. Obolentsev, A. V. Mashkina, A. R. Kuzyev, and G. P. Gribkova, *Khim. Seraorgan. Soedin. Soderzhashch. v. Neft. i Nefteprodukt., Akad. Nauk SSSR, Bashkirsk. Filial*, **4**, 166 (1961); *Chem. Abstr.*, **57**, 15048 (1962).
- (5) R. D. Obolentsev and A. V. Mashkina, *ibid.*, *Doklady 3-oi (Tret'ei) Nauch. Sessii, Ufa*, 228 (1957); *Chem. Abstr.*, **55**, 6464 (1961).
- (6) R. D. Obolentsev and A. V. Mashkina, *Khim. Serai Azotorg. Soedinenui, Soderzhashchikksya v Neft. i Nefteprodukt., Akad. Nauk. SSSR, Bashkirsk. Filial, No. 3*, 295 (1960); *Chem. Abstr.*, **56**, 11537 (1962).
- (7) R. Bartsch and C. Tanielian, *J. Catalysis*, **35**, 353 (1974).
- (8) G. Doyle, Preprint, Division of Petroleum Chem., American

Chemical Society National Meeting, Chicago, Ill., Aug., 1975.

(9) See papers cited in reference 7.

(10) S. R. Sergienko and V. N. Perchenko, *Doklady Akad. Nauk. SSSR*, **128**, 103 (1959); *Chem. Abstr.*, **54**, 1385 (1960).

(11) L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480, 1489, 1494 (1968); **35**, 1075 (1970).

(12) L. H. Klemm, C. E. Klopfenstein, and J. Shabtai, *ibid.*, **35**, 1069 (1970).

(13) N. M. Cullinane and S. J. Chard, *J. Chem. Soc.*, 821 (1945); E. Briner, W. Plüss, and H. Paillard, *Helv. Chem. Acta*, **7**, 1046 (1924); N. M. Cullinane, S. J. Chard, and C. W. C. Dawkins, *Org. Syntheses*, Coll. Vol. IV, 520 (1963).

(14) L. H. Klemm, R. Zell, and J. S. Shabtai, *J. Org. Chem.*, **39**, 698 (1974).

(15) L. H. Klemm and D. R. Taylor, *Org. Prep. Proced. Int.*, **8**, 163 (1976).

(16) J. Hine, "Physical Organic Chemistry", 2nd Ed., McGraw-Hill, New York, N. Y., 1962, p. 160; J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **14**, 271 (1963); R. Connor, "Organic Chemistry", Vol. I, 2nd Ed., H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 855.

(17) For a summary of the C- and O-alkylations of ambident phenoxide and naphthoxide anions see L. P. Hammett, "Physical Organic Chemistry", 2nd Ed., McGraw-Hill, New York, N. Y., 1970, pp. 243-244.

(18) The reluctance of thiophenols to undergo ring electrophilic substitution has been noted before; A. H. Herz and D. S. Tarbell, *J. Am. Chem. Soc.*, **75**, 4657 (1953); D. Walker and J. Lieb, *J. Org. Chem.*, **27**, 4455 (1962), and references cited therein.

(19) It has been noted that in water or a dipolar protic medium the mercaptide ion is also more basic toward carbon than is the alkoxide ion [E. C. Kooyman, "Organosulfur Chemistry", M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, pp. 5-6].

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

(21) M. S. Newman and F. W. Hetzel, *Org. Synth.*, **51**, 139 (1971).

(22) H. M. Relles and G. Pizzolato, *J. Org. Chem.*, **33**, 2249 (1968).

(23) A. J. Neale, T. J. Rawlings, and E. B. McCall, *Tetrahedron*, **21**, 1299 (1965).

(24) M. Janczewski and W. Wojtas, *Ann. Univ. Mariae Curie-Sklodowska, Sect. AA*, No. 21, 65 (1966); *Chem. Abstr.*, **69**, 51794u (1968).

(25) H. Niwa, *Tohoku Yakka Daigaku Kiyô*, **4**, 19 (1957); *Chem. Abstr.*, **52**, 7234e (1958).

(26) I. Heilbron, "Dictionary of Organic Compounds", 4th Ed., Oxford University Press, New York, N. Y., 1965, p. 2074.

(27) Private communication from Dr. Leslie M. Werbel, Warner-Lambert/Parke Davis, Ann Arbor, Mich. The sample of **7** (prepared by Dr. James Kaltenbronn by diazotization of 3-aminobiphenyl, treatment with potassium ethyl xanthate, and then hydrolysis with base) was homogeneous by vpc analysis. [E. F. Elslager and L. M. Werbel, British Patent No. 1,334,633 to Parke, Davis and Co.; *Chem. Abstr.*, **80**, 48026s (1974)].