

L. H. Klemm\* and Joseph J. Karchesy (2)

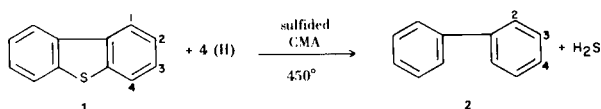
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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Desulfurization of dibenzothiophene is effected in 82% yield by means of methanol and a sulfided cobaltous oxide-molybdenic oxide-aluminum oxide catalyst at 450° and *ca.* one atmosphere pressure in a flow system. The methanol serves as a hydrogen donor and methylating agent to form biphenyl (main product), 3- and 4-methylbiphenyls, and fluorene.

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Commercially, removal of organically bound sulfur from coal and crude oils is effected by means of hydrodesulfurization (HDS), a process which normally employs a catalyst of sulfided cobaltous oxide-molybdenic oxide-aluminum oxide (designated CMA), a flow system, temperatures of 250-450°, and hydrogen gas at 10-300 atmospheres pressure (3,4). Because of the difficulties and hazards of handling hydrogen at high pressures, one would like to devise modified desulfurization methods which employ a hydrogen-donor solvent (instead of hydrogen gas) and atmospheric pressure, but still retain the advantages of a flow system. We now report the successful attainment of this goal with a CMA catalyst, methanol in the dual role of *in situ* hydrogen donor plus methylating agent, a temperature of 450° ( $\pm 200^\circ$ ), and dibenzothiophene (1) as substrate (0.8-2 g. scale) (5,6). The principal reaction is shown in equation 1.



Aspects of reaction 1 were investigated with a variety of reactor packings, *viz.* glass beads, sulfided alumina,

unsulfided CMA, and sulfided CMA (categorized as three modifications: CMA-1, obtained by activation *in situ* with a mixture of methanol and hydrogen sulfide; CMA-2, obtained by activation *in situ* with hydrogen sulfide alone; and CMA-3, obtained by activation with hydrogen sulfide alone and stored in a desiccator for later usage). Results with CMA-1 were the most successful, as indicated subsequently.

For desulfurization a solution of 1 in methanol was added dropwise in a stream of nitrogen carrier gas at *ca.* 1 atmosphere pressure to a reactor tube bearing a catalyst bed maintained at a constant temperature (250-650°) in a flow system. Effluent products were collected in cold traps and analyzed both qualitatively and quantitatively. Results are presented in Table I.

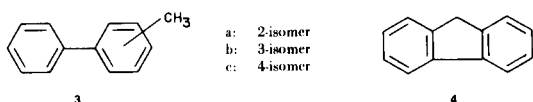
Table I shows that desulfurization of dibenzothiophene by means of methanol and a sulfided CMA catalyst yields three hydrocarbon products, *viz.* biphenyl (2, the major component), mixed monomethylbiphenyls (3), and fluorene (4, in smallest quantity). Combined yields of these products ranged from 40% (run 8) to 82% (run 3) in our studies. While optimal conditions for desulfurization were only broadly established, it appears (*cf.* runs 1-3, as

Table I

Desulfurization of Dibenzothiophene (1) by Means of Methanol and a Catalyst (a)

Run No.	Catalyst or Packing	Sulfiding Time, hours	Reaction Temp., °C	Reaction Time, hours	Yields of Products, mole %				Isomeric Ratio 3a:3b:3c
					2	3	4	1 (b)	
1	CMA-1	2	250	8	20	4	none	25	0.8:1.4:1
2	CMA-1	2	350	8	68	4	trace		trace:1.8:1
3 (c)	CMA-1	2	450	8	71	8	3	~0	~0:2.0:1
4	CMA-2	0.8	450	8	37	2	1	1	(d)
5	CMA-2	1.5	450	8	61	4	3		(d)
6	CMA-3	1	450	8	52	14	1	17	(d)
7	CMA-3	1	550	8	57	<1	<1	<1	(d)
8	CMA-3	1.2	650	10	40	trace	trace	trace	
9	CMA	0	450	6	~10	none	none	(e)	
10	glass beads	--	450	4	none	none	none	100	
11 (f)	alumina	2	450,630	8	trace			90 (g)	

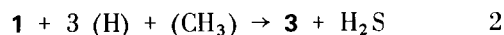
(a) All runs were made with 1 g. of substrate, 150 ml. of methanol, and (except for run 10) 75-90 g. of catalyst. Yields were determined by gas chromatography and relate directly to the moles of substrate used (rather than to the moles of products formed). (b) Recovered starting material. (c) Yields given are the average of three runs. Variations in mole % yields were  $\pm 3$  for 2,  $\pm 1$  for 3, and  $\pm 0.5$  for 4. (d) Not determined. (e) Hexamethylbenzene and various unidentified compounds were also formed (8). (f) Two separate runs at different temperatures. (g) See reference 8.



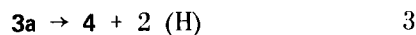
well as runs 6-8) that a reaction temperature of 450° and a sulfiding period of two hours *in situ* (cf. runs 3, 4, and 5) are desirable. These conditions are met by run 3, which also exhibits the following pertinent attributes. (a) No more than trace amounts of sulfur-bearing components appear in the reaction effluent. (b) In contrast to reactions with CMA-2 and CMA-3, neither elemental sulfur nor sloughed catalyst dust appear in the effluent in noticeable quantities when CMA-1 is used. (c) Yields are quantitatively reproducible (in contrast to runs with CMA-3, in particular) (See footnote c, Table I; and references 6 and 7). (d) Neither hydrogen gas nor high pressure (as employed in the HDS process) is used. In fact, operation occurs at a pressure only slightly greater than one atmosphere. (e) With CMA-1 (as well as with CMA-2 and CMA-3) the desulfurization process is, indeed, catalytic and dependent on the presence of a sulfided molybdena surface. Thus, use of glass beads plus methanol at 450° (run 10; presumably conditions conducive to thermal rather than catalytic transformation) gives no reaction. Also, unsulfided CMA at 450° (run 9) gives only a small amount of desulfurization, with the major products derived from self-condensation of methanol itself (8); while sulfided alumina (run 11) is inert as a catalyst (9). (f) As based on the products isolated, there is no evidence for hydrogenation of the aromatic rings along with hydrogenolysis of the C-S bonds. This contrasts with the situation which prevails in the commercial HDS process (10b,14,15), but it is consistent with results obtained for substrate 1 by various other workers (16-18).

In Table I are presented yields of the various isomeric monomethylbiphenyls (3) and fluorene (4). Comparison of runs 1-3 shows that the yields of 3 and 4 increase with increasing reaction temperature in the range of 250-450°. At the same time the percentage of 2-methylbiphenyl (3a) in mixture 3 decreases from 25 to ca. 0, while that of 3-methylbiphenyl (3b) increases from ca. 44 to 67. As a check on possible pathways to these products and interconversions amongst them we conducted a series of control runs which showed that under reaction conditions at 450° both 3a and 2-hydroxymethylbiphenyl yield 4; 3b (as well as 3a) undergoes limited demethylation to biphenyl but no other observed reaction; 4 undergoes some methylation, but no conversion to 3 or biphenyl; and biphenyl is recovered with only traces of 3 therein. On the basis of these results, plus those reported for desulfurization of 2- and 4-methyldibenzothiophenes and phenanthro[4,5-*bcd*]thiophene (6), we propose that generalized equation 2 (as well as equation 1) also applies to our desulfurization method. Thus, methanol serves in the dual

role of

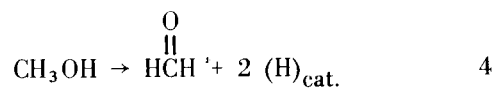


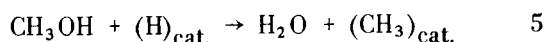
*in situ* hydrogen donor and methyl donor (i.e., methylating agent). As indicated by the control runs, methylation could occur by the direct transfer of chemisorbed methyl groups to the aromatic ring or by the indirect pathway of initial formylation (*vide infra*) of the ring and subsequent hydrogenolysis of the C-O bond. We favor the direct transfer, plus the formation of fluorene from 2-methylbiphenyl (equation 3), because the array of isolated products is consistent with expectations from this pathway (see below).



McCall, *et al.*, (19) found that free radical phenylation of molten 1 by means of benzoyl peroxide at 110° or by benzenesulfonyl chloride at 250-270° gives an isomeric ratio of monophenyldibenzothiophenes of 1-:2-:3-:4- = 30.7:12.3:21.1:32.1. Analogously, free radical methylation of 1 in the same isomeric ratio (20), followed by desulfurization plus dehydrogenation of 3a (as in equation 3), should yield a molar ratio of hydrocarbon products of 4:3b:3c = 1.4:2.1:1.0. This predicted ratio compares favorably with the experimentally determined ratio of 4:3b:3c = 1.1:2.0:1.0 (obtained directly from run 3) or 1.6:2.0:1.0 (after correction for the 68% observed yield in the transformation 3a → 4, see Experimental). While initial attack on 1 by a hydroxymethyl free radical (followed by subsequent reactions) could yield a similar molar ratio of products, no intermediates to justify the postulation of such a pathway were found. Contrariwise, methylation by means of electrophilic attack on 1 should occur almost exclusively at C-2, and to a minor extent at C-4 (21). Then, only 3-methylbiphenyl (3b) would be obtained upon desulfurization. Moreover, experimental results indicate that 1 is highly resistant to nucleophilic attack (21). Thus, we rationalize the formations of 3 and 4 in our desulfurizations as occurring through initial free radical methylation of 1.

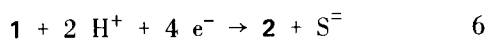
Hydrogen transfer from methanol should yield either formaldehyde or carbon monoxide (or both) as a by-product of the desulfurization reaction (equation 1). While no check was made for formation of the latter compound, formaldehyde was trapped in the effluent from a control run and identified as its 2,4-dinitrophenylhydrazine derivative. The function of methanol in desulfurization may, then, be represented by equation 4 (22); with perhaps attendant generation of a source of activated methyl groups, as shown in equation 5. Additionally, the presence of carbon monoxide could modify the catalytic surface (23).





Doyle (18) and Kirby and Swift (24) have also effected desulfurization by means of CMA catalysts and hydrogen-donor solvents (partially hydrogenated aromatic hydrocarbons and cyclohexane, respectively). Both concluded that molecular hydrogen formed as an intermediate. This was especially clear in the former case, where gaseous hydrogen accumulated in the autoclave reactor when dibenzothiophene (**1**) was used as a substrate. Inasmuch as the molar ratio of methanol:1 used in our desulfurizations is very large (690:1) it seems highly likely that molecular hydrogen is also produced in quantity in our reactor. Since Bartsch and Tanielian (16) have found that **1** (dissolved in *n*-dodecane) is hydrodesulfurized to biphenyl by means of CMA at 350-400° and atmospheric pressure it may well be that our desulfurizations also involve molecular hydrogen (or its adsorbed equivalent) as an intermediate. Be that as it may our method avoids any need to introduce gaseous hydrogen *per se* into the reactor (25).

The reduction half-reaction corresponding to equation 1 is shown in equation 6, where the sequence of steps which involve interaction of a molecule of **1**, two protons,



and four electrons is not yet clearly established. Since **1** is not attacked by lithium aluminum hydride in refluxing ether (26), does not react with alumina plus methanol (conditions believed to foster Meerwein-Ponndorf-type hydride transfer from methanol) (27), and generally resists nucleophilic attack (21,28) it seems very unlikely that the initial attack on **1** is effected by a hydride ion (or its equivalent). A pertinent role of the molybdenum in the CMA catalyst is certainly that of electron-transfer agent, as illustrated by the transformation  $\text{Mo(VI)} \rightleftharpoons \text{Mo(V)} \rightleftharpoons \text{Mo(IV)}$  (29). The significance of these oxidation states was discussed by Hercules and coworkers (30). The failure of alumina to act as a catalyst in desulfurization may then be ascribed primarily to the reluctance of Al(III) to either accept or donate one or more electrons.

## EXPERIMENTAL

### Molybdenum Catalysts Used.

The catalyzed reactions in this study involved the use of Harshaw pelletized Co-Mo-0603 T catalyst (designated CMA, containing 3% cobaltous oxide, 12% molybdic oxide, and 85% aluminum oxide) or a sulfided form of CMA (designated as CMA-1, CMA-2, and CMA-3, depending on the method of sulfidation). CMA-1 was obtained from CMA by *in situ* reduction-sulfidation with a mixture of methanol and hydrogen sulfide prior to the start of the reaction proper. Formation and use of CMA-1 is described in a subsequent paragraph.

Catalyst CMA-2 was also obtained by *in situ* treatment of CMA, but with hydrogen sulfide alone (in the preceding manner) for varying periods of time.

Catalyst CMA-3 was prepared by treatment of CMA with hydrogen sulfide alone, and then storage of the sulfided catalyst for later usage, according to the following procedure (31). Through a bed of CMA catalyst (180 g., 24 cm. deep) contained in a pyrex reactor tube was passed a slow stream (2 mmoles/minute) of hydrogen sulfide gas while the catalyst was being heated (*vide infra* for the description of a smaller apparatus) to 430° (sulfiding temperature). When this temperature had been stabilized and no more water vapor appeared to be issuing from the tube, the flow of hydrogen sulfide was increased (to 12 mmoles/minute) and maintained there for a period of 2-3 hours, whereupon sulfur was observed to begin issuing from the tube (32). The heater was turned off, the flow of hydrogen sulfide was stopped when the temperature had fallen to about 100°, and the cooled catalyst was stored in a desiccator until use (1-20 days later).

Catalyst CMA has a blue color [apparently due to the presence of mixed Mo(V) and Mo(VI) oxides (29)], while the sulfided catalysts are black (presence of Mo and Co sulfides).

### Methodology for Desulfurization - Use of CMA-1 Catalyst.

Reactions were conducted in a flow system, consisting of a vertically mounted combustion furnace (50 cm. long) bearing a vycor reactor tube (78 cm. long, 17 mm. i.d.) packed with 75 g. (42 cm. in length) of CMA catalyst (35). The temperature of the catalyst was measured by a thermocouple (inserted into a steel well) at the midpoint of the bed. The catalyst was heated (at ca. 8°/minute) to the reaction temperature, which was maintained constant ( $\pm 10^\circ$ ) throughout the reaction proper. When a temperature of 100° was reached, addition of both hydrogen sulfide [flow rate 160 ml./minute (36)] and methanol (added at ca. 20 drops per minute from a dropping funnel atop the reactor tube) was started. After 50 ml. of methanol had been added (over a period of ca. 2 hours) activation of the catalyst (*i.e.*, conversion of CMA into CMA-1) was complete. The carrier gas was changed to nitrogen (60 ml./minute) and a solution of 1 g. of dibenzothiophene (**1**) in 150 ml. of methanol was added from the dropping funnel (10 drops/minute) for the reaction proper (period of 8 hours). Then 50 ml. of methanol was added over a period of 2 hours. Heating was discontinued and the catalyst was allowed to cool under nitrogen.

During the reaction proper and the subsequent methanol washing, effluent from the bottom of the reactor tube was collected in air- and ice-cooled traps. The contents of these traps were extracted with ether (200 ml.) and water. Evaporation of the dried (sodium sulfate) ether extract left a crude reaction mixture which was analyzed as indicated in subsequent paragraphs.

Soxhlet extraction of the spent catalyst with benzene gave trace amounts of unidentified oily substances.

### Modified Procedures for Other Catalysts.

Alumina (Harshaw A1-0104 T) catalyst was sulfided and used in the same manner as employed for CMA-1. Runs with CMA, CMA-3, and glass beads (Pyrex) were conducted similarly except that nitrogen gas was employed while the reactor was being heated to reaction temperature (as well as during the subsequent operations).

### Analysis of Products Formed.

Products from the reaction mixtures were isolated by preparative gas chromatography on a Hewlett-Packard model 810 instrument with thermal conductivity detection. They were qualitatively identified by various physical methods such as pmr, infrared, and high resolution mass spectrometry, m.p., and direct comparison with authentic samples. Quantitative analyses of the crude reaction mixtures were performed by means of gas chromatography

on a Hewlett-Packard model 700 instrument with flame ionization detection and with disc integration. Naphthalene was used as an internal standard. Usually columns were packed with Carbowax 20M TPA on Chromosorb P (60-80 mesh) (1.2-m.) and maintained at 160°. However, Carbowax failed to separate 3- and 4-methylbiphenyls. For separations of these two isomers crude reaction mixtures were chromatographed on 2.4-m. mixed nitrate salt columns (37), with temperature programming (150-250°) used for isolation, but isothermal operation (at 120 ± 5°) used for quantitative analyses.

#### Byproducts from Methanol.

A quantity of 90 g. of CMA-3 catalyst was heated at 450° for 16 hours in a stream of nitrogen gas. Then 350 ml. of methanol was added dropwise to the reactor over a period of 8 hours. Effluent was passed into cold traps bearing 2,4-dinitrophenylhydrazine reagent (38). The yellow precipitate which formed in the first trap was collected by filtration (after dilution with water) and analyzed by paper chromatography (39). A spot corresponding to authentic formaldehyde 2,4-DNP was found, but there was none for acetaldehyde 2,4-DNP. The precipitate was recrystallized from aqueous ethyl acetate and shown to be identical (m.p., mixture m.p., pmr spectrum) with the authentic sample.

With catalyst CMA and sulfided alumina, methanol is also converted into small amounts of hexamethylbenzene (8), identified by m.p., high resolution mass spectrum, and especially by pmr spectrum (singlet at  $\delta$  2.2 ppm). No hexamethylbenzene was detected amongst products from sulfided CMA catalysts. However, needles of another minor product (not investigated further) were sometimes formed with these catalysts. Neither of these crystalline byproducts was detected from catalysis with CMA-1.

#### Control Runs with Miscellaneous Substrates.

A sample of 1 g. of 2-methylbiphenyl (Pfaltz and Bauer; mole % composition: 94.2 isomerically pure, 1.1 other isomers, 4.7 biphenyl, 0 fluorene - analyzed by gas chromatography) in 150 ml. of methanol was passed through CMA-1 catalyst at 450° (nitrogen gas; reaction time, 8 hours; mole % yields: 11, 2, 8, and 64, respectively). Fluorene was also obtained from 2-methylbiphenyl by means of the CMA-3 catalyst.

Passing a solution of 1 g. of 2-hydroxymethylbiphenyl [colorless liquid; exact mass found and calcd: 184.089; synthesized from biphenyl-2-carboxylic acid by means of sodium borohydride, aluminum chloride, and diglyme (40)] in 150 ml. of methanol through CMA-3 catalyst at 450° (nitrogen gas; reaction time, 4 hours) gave fluorene (32%) and 2-methylbiphenyl (1%).

From 0.5 g. of 3-methylbiphenyl (Pfaltz and Bauer; mole % composition from gas chromatography: 96.5 isomerically pure, 3.5 biphenyl), 75 ml. of methanol, and 37.5 g. of CMA-1 catalyst (450°, 4 hours) was obtained 0.409 g. of mixture containing 93.9 mole % 3-methylbiphenyl and 6.1 mole % biphenyl.

Treatment of 1 g. of fluorene in the manner used with 2-methylbiphenyl gave 7 mole % yield of methylfluorenes, 72% recovery of fluorene, and no other observed products. Similarly, biphenyl was recovered in 86% yield and only traces of methylbiphenyls were detected therefrom.

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(14) Hydrogenation of aromatic rings causes a decrease in octane rating of the product (10c).

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