

The Insertion and Extrusion of Heterosulfur Bridges. XI.
Desulfurizations of Condensed Thiophenes by Means of
Methanol and a Molybdena Catalyst (1)

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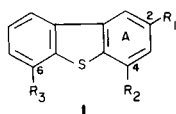
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Desulfurizations of 2-methyl- (**1b**), 4-methyl- (**1c**), and 4,6-dimethyldibenzothiophenes (**1d**), benzo[*b*]thiophene (**2**), and benzo[*b*]naphtho[2,1-*d*]thiophene (**5**) were effected by means of methanol and a sulfided CMA catalyst [a mixed oxide of Co(II), Mo(VI), and Al(III)] at 450°. Desulfurization was accompanied by processes of demethylation and ring hydrogenation in the case of **1d** and by both methylation and demethylation in the cases of **1b** and **1c**. Compound **2** gave ethylbenzene (80%), while **5** produced 2-phenylnaphthalene (69%).

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In previous papers (5-8) we reported the use of CMA catalysts [sulfided mixed oxides of Co(II), Mo(VI), Al(III)] plus methanol in a flow system at atmospheric pressure and 450° for desulfurizations of dibenzothiophene (**1a**), phenanthro[4,5-*bcd*]thiophene (**3**), and triphenyl[4,5-*bcd*]thiophene (**4**). We now report the extension of this desulfurization method to the substrates 2-methyl-, 4-methyl-, and 4,6-dimethyldibenzothiophenes (**1b-1d**), benzo[*b*]thiophene (**2**), and benzo[*b*]naphtho[2,1-*d*]thiophene (**5**).

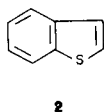


a, $R_1 = R_2 = R_3 = H$

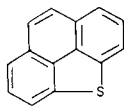
b, $R_1 = CH_3, R_2 = R_3 = H$

c, $R_2 = CH_3, R_1 = R_3 = H$

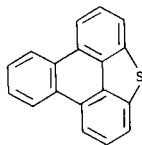
d, $R_1 = H, R_2 = R_3 = CH_3$



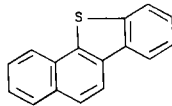
2



3



4



5

The monomethyldibenzothiophenes were successfully desulfurized by the methanol-CMA-1 method at 450° to yield mixtures of products which are closely analogous to those formed from dibenzothiophene under the same reac-

tion conditions (Table I). Total yields of desulfurized products (65% from **1b**, 68% from **1c**) were comparable from the two isomeric methyldibenzothiophenes but somewhat lower than from the parent substrate **1a** (82%). The major product formed from simple desulfurization of **1b** and **1c** is the expected 3-methylbiphenyl. However, both processes of methylation, as occurs with **1a**, and demethylation (to biphenyl), as occurs during sulfur-bridging of 4-methylbiphenyl with CMA-1 and hydrogen sulfide (9), are noted. Demethylation of **1c**, wherein the methyl group occupies a position *ortho* to the sulfur atom in ring A, is more extensive than is demethylation of **1b**, wherein the methyl group is *para* to the sulfur atom. Interestingly, however, the combined yields of biphenyl and 3-methylbiphenyl are identical, within experimental error, in these two cases. In addition, the array of other desulfurized products is closely similar from both methyldibenzothiophenes (10).

Because of the limited solubility of **1d**, in methanol, studies on desulfurization of this compound were conducted in a solvent of benzene-methanol (1:2) (8). The complex mixture of products, analyzed by gas chromatography-mass spectrometry, is presented in Table II. It is apparent from the data in Table II that **1d** undergoes three main transformations under these reaction conditions, specifically (a) demethylation, (b) desulfurization (by carbon-sulfur bond hydrogenolysis), and (c) ring

Table I

Products of Desulfurization of **1a-1c** at 450° with Methanol and CMA-1 Catalyst (a)

Substrate Used	Yields of Products, mole %						
	BP (b)	3-MeBP	4-MeBP	DiMeBP	Fl (c)	MeFl	S-Compounds
1a (d)	71	5.7	2.3		3		ca. 1 (e)
1b (f)	10	41	3.5	8	2	trace	
1c (g)	20	32	2.4	9	3	2	ca. 2 (h)

(a) All runs were made and product mixtures were analyzed by closely similar methodologies (*cf.* reference 6). (b) BP = biphenyl. (c) Fl = fluorene. (d) From reference 6; average of 3 runs. (e) Recovered **1a**. (f) One run only. (g) Average of 2 runs; variations in yields are 1-2% in BP and 3-MeBP and < 1% in the other products. (h) Consists of **1a**, **1c** and dimethyl-**1a**.

hydrogenation. While there was no clear evidence for ring methylation in this reaction, process (c) had not been observed previously in our desulfurization procedure.

For investigation of the desulfurization of compound **5** we not only used a solvent of benzene-methanol (3:1) but also altered the catalyst to CMA-2 (activated with hydrogen sulfide alone, *i.e.*, *sans* methanol) (6). Experiments were conducted over the temperature range of 250-450°. At 250°, only unreacted **5** was recovered; while at 350°, products formed were 2-phenylnaphthalene (**6**) (42%), a small amount (1%) of monomethylphenylnaphthalene (**7**), plus some recovered **5** (8%). Despite the thermal instability of **5** (11) a better yield (69%) of **6** (without evidence for the presence of **5** or **7**) was obtained at 450°.

Table II
Products from Desulfurization of **1d** at 450°
with Methanol-Benzene and CMA-1 Catalyst

Product	Molecular	Retention	Yield
(a)	Wt. (b)	Time (c)	(Mole %)
BP (d)	154	1.0	(e)
3-MeBP	168	1.4	7
3,3'-DiMeBP	182	2.0	9
C ₁₄ H ₂₀	188	2.4-2.8	(f)
1c	198	8.8	6
1d	212	11.2	19 (g)

(a) Identified by gc-ms and (except for C₁₄H₂₀) comparison with authentic reference samples. (b) From molecular ion in ms. (c) Relative value, compared to BP as an internal standard. (d) BP = biphenyl. (e) Much of the BP probably arises from the benzene solvent used. (f) There are two or more overlapping gc peaks, which may correspond to isomers of dimethylhexahydroBP. (g) Recovered starting material.

Desulfurization of benzo[*b*]thiophene (**2**) was effected under the same reaction conditions as used with **1** (Table I), to yield ethylbenzene (**8**) as the main product (*ca.* 80% yield). Compound **8** has likewise been obtained by other workers from hydrodesulfurization of **2** at either atmospheric or elevated pressure (12) in the presence of CMA catalysts.

It is interesting to compare the preceding results with those from desulfurization runs on these same substrates with Raney nickel in refluxing methanol or ethanol. Compounds **2** and **5** gave **8** and **6** (respectively) in comparable yields (13-15), while treatment of **1b** with Raney nickel has not yet been reported. In contrast, Carruthers (16) found that W-2 Raney nickel fails to effect desulfurization of either **1c** or **1d**, though it readily converts dibenzothiophene (**1a**) into biphenyl (13). Carruthers suggested that **1c** and **1d** resist desulfurization because of "the presence of a substituent in a position flanking the sulphur atom." In contradistinction, however, Carruthers and Douglas (17) found that 2,3,6,7-, 2,3,6,8- and 2,4,6,8-tetramethyl-

benzothiophenes undergo desulfurization when refluxed with W-5 Raney nickel in ethanol. In preliminary runs we have now found that **1c** and **1d** are also largely desulfurized under the latter conditions, but we have not yet made a careful study of the products formed. It is apparent, then, that the facility of desulfurization is dependent on the nature of the Raney nickel used.

EXPERIMENTAL

Benzo[*b*]thiophene (**2**) (Aldrich) and 2- and 4-methyldibenzothiophenes (**1b** and **1c**) (18,19) were desulfurized by means of methanol and CMA-1 catalyst at 450° and quantitative analyses of the product mixtures were conducted by the methodology previously described (6). Because of uncertain losses by volatilization during concentration of the collected product, the estimated yield of ethylbenzene from **2** is only approximate.

For desulfurization of **5** (11) the CMA-2 catalyst was prepared by sulfidation of 93 g. of CMA (6) (column length 23 cm) at the reaction temperature (250°, 350°, or 450°) in a stream of hydrogen sulfide gas until evolution of water ceased and then for 2 hours longer, and then activation in a stream of nitrogen for 20 hours. The flow of nitrogen was continued for 5 hours while a solution of **5** (0.25-0.5 g.) in 60 ml. of benzene and 20 ml. of methanol was added dropwise. Column effluent was collected in benzene and analyzed for products. Only biphenyl (formed from the solvent) was found. The catalyst was extracted with benzene in a Soxhlet apparatus for 2-3 days. The yellow solid residue from evaporation of the extract was analyzed by gas chromatography with a mixed nitrate column (6) programmed from 190-305°. Products isolated and identified by m.p. and/or spectral methods were (in order of increasing retention time) biphenyl, methylbiphenyls, dibenzothiophene (?), 2-phenylnaphthalene, methylphenylnaphthalene (identified by mass spectrum), and recovered **5**.

4,6-Dimethyldibenzothiophene (m.p. 154-156°, **1d**) (20) was desulfurized in the manner used with the monomethyldibenzothiophenes. The product mixture was analyzed by gas chromatography on a column of 10% Carbowax 20M on 60-80 mesh acid-washed Chromosorb P maintained at 180°, with 9-methylanthracene used as an internal reference compound for quantitative analysis. The same packing was employed in a gc-ms apparatus (consisting of a Varian 1200 Aerograph plus a Hewlett-Packard 5930A mass spectrometer) in order to obtain the molecular ion for each major chromatographic peak.

REFERENCES AND NOTES

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- (4) Teaching Assistant, 1975-1976.
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