

## Catalytic Desulfurization of Condensed Thiophenes by Means of Methanol (1)

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

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

Received January 5, 1977

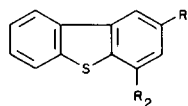
Desulfurization of dibenzothiophene, two methyl-dibenzothiophenes, and phenanthro[4,5-*bcd*]-thiophene to give 60-80% yields of hydrocarbon products was effected by means of a sulfided molybdena catalyst plus methanol at 450° and a pressure of *ca.* one atmosphere. The methanol functions both as an *in situ* hydrogen donor and as a methylating agent.

*J. Heterocyclic Chem.*, 14, 353 (1977).

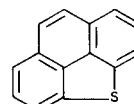
Sir:

The search for new methods for removal of chemically-bound sulfur from coal and crude oil holds widespread current interest. Commercially, hydrodesulfurization (HDS) employs a catalyst (oftentimes sulfided CoO-MoO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>), a flow system, and hydrogen gas at high pressure (3). In a bench-scale laboratory process desulfurization is effected by use of Raney nickel as a reactant (converted into nickel sulfide), a batch process, and hydrogen (held on the surface of the nickel) at *ca.* one atmosphere pressure (4). We now report that condensed thiophenes **1-4** can be successfully desulfurized by a modification of the HDS procedure which employs methanol (as an *in situ* hydrogen source, plus a methylating agent) at *ca.* one atmosphere pressure. It has been suggested (3) that dibenzothiophene (**1**) is representative of the least reactive sulfur-containing compounds in the HDS process, while 4-methyldibenzothiophene (**2**) is reported to be inert toward desulfurization by Raney nickel (5). Compounds **1-3** have been isolated from petroleum (6), while **4** was identified amongst the products from HDS of coal (7).

In our procedure a solution of **1-4** (1 g.) in 150 ml. of methanol was added dropwise in a stream of nitrogen gas over a period of eight hours to a vertically mounted vycor tube, heated at 450° and packed with 75 g. of pre-treated (*in situ*, with 50 ml. of methanol plus hydrogen sulfide for a period of two hours), pelletized Harshaw Co-Mo-0693 T catalyst (8). Hot catalyst was then washed with more methanol. Products were collected from the effluent, separated by preparative gas chromatography, and identified by physical methods including pmr, infrared, and high resolution mass spectrometry, m.p., and direct



1. R<sub>1</sub> = R<sub>2</sub> = H
2. R<sub>1</sub> = H; R<sub>2</sub> = Me
3. R<sub>1</sub> = Me; R<sub>2</sub> = H

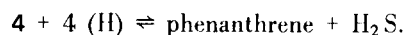


4

comparison with authentic samples. Quantitative analyses of the crude reaction mixtures were performed by means of gas chromatography with a column of Carbowax 20M TPA on Chromosorb (at 160° with naphthalene as internal standard for substrates **1-3**; at 215° with fluorene as internal standard for **4**). Mole percentage yields of products obtained follow: From **1** (3 runs) - biphenyl, 67-74; methylbiphenyls (separable mixture of 3- and 4-isomers, with only a trace of the 2-isomer), 7-9; fluorene, 3; recovered **1** plus other, <2. From **2** (2 runs) - biphenyl 18-21; methylbiphenyls, 32-36; dimethylbiphenyls (mixed isomers), 8-9; fluorene and methylfluorenes, 5; S-bearing products, <3. From **3** (1 run) - biphenyl, 10; methylbiphenyls, 44; dimethylbiphenyls, 8; fluorene, 2; other, *ca.* 0. From **4** (2 runs) - phenanthrene, 48-51; methylphenanthrenes (mixed isomers), 11-12; other, *ca.* 0.

Salient features of the reaction are the formation of 60-80% combined yields of desulfurized products from each substrate used, the appearance of very little sulfur-bearing compound in the effluent, and the occurrence of both methylation and demethylation of the benzene ring (probably prior to the desulfurization step). Control runs show that biphenyl, 3-methylbiphenyl, fluorene, and 4,5-methylenephenanthrene (not found amongst the products

from 4) are not appreciably altered when used as substrates under the reaction conditions. However, 2-methylbiphenyl is dehydrogenated to fluorene under these conditions. The reversible nature of the insertion and extrusion of heterosulfur bridges is exemplified by the equation



This reaction can be driven to the right or to the left under the influence of the same heterogeneous catalyst (9).

Current efforts are being directed toward establishing optimum conditions for the reaction, elucidating mechanistic aspects, and altering the extent of alkylation in the hydrocarbon products. For preparative usage and structural determinations one may prefer that alkylation be negligibly small; while for conversion of coal into oil, extensive alkylation seems desirable.

## REFERENCES AND NOTES

- (1) Paper IV in the series on The Insertion and Extrusion of Heterosulfur Bridges. For Paper III see reference 9. This investigation was supported by research grant no. MPS 75-04116 from the National Science Foundation.
- (2) Research Associate and Visiting Assistant Professor, 1975-1977.
- (3) B. C. Gates, "The Fundamental Organic Chemistry of Coal", J. W. Larsen, Ed., Proceedings of NSF Workshop, Univ. of Tenn., Knoxville, Tenn., July, 1975, pp. 157-169.
- (4) G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, **12**, 356 (1962).
- (5) W. Carruthers, *Nature*, **176**, 790 (1955).
- (6) J. Ashby and C. C. Cook, "Advances in Heterocyclic Chemistry", A. R. Katritzky and A. J. Boulton, Eds., Vol. 16, Academic Press, New York, N.Y., 1974, pp. 183-185.
- (7) S. Akhtar, A. G. Sharkey, J. L. Schultz, and P. M. Yavorsky, "Organic Sulfur Compounds in Coal Hydrogenation Products", ERDA report, Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania, 1974.
- (8) Composition: 3% CoO, 12% MoO<sub>3</sub>, 85% Al<sub>2</sub>O<sub>3</sub>.
- (9) L. H. Klemm and W. Hsin, *J. Heterocyclic Chem.*, **13**, 1245 (1976).