Modified Molybdenum Carbonyl Species; Excellent Reagents for the Desulphurization of Thiols

By HOWARD ALPER*† and CLAUDE BLAIS

(*Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada* K1N 9B4)

Summary Thiols can be desulphurized in good yields by treatment with molybdenum hexacarbonyl either in acetic acid or when pre-adsorbed on to silica

THE removal of sulphur from fossil fuels is a subject of considerable current interest Initial model experiments with thioketones (the most readily desulphurized organic substrates) indicated the potential of metal carbonyls as desulphurization reagents[1] We now report that molybdenum species, generated by appropriate modification of molybdenum hexacarbonyl, are good reagents for the extrusion of sulphur from thiols or mercaptans ‡

It is known that molybdenum hexacarbonyl reacts with acetic acid to give mainly molybdenum(II) compounds such as tetrakis(acetato)dimolybdenum [2,3] These molybdenum(II) species, generated *in situ* , proved to be exceedingly use-

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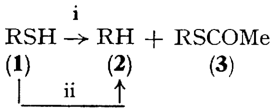
† E W R Steacie Fellow

‡ Raney nickel can also be used However, sulphides are often formed from aromatic thiols, and in any event, high Raney nickel to substrate ratios are required (C A Buehler and D E Pearson, 'Survey of Organic Syntheses,' vol 1, Wiley, New York, 1970, p 15

ful for converting thiols into hydrocarbons. Experimentally, a thiol (**1**), dissolved in acetic acid, was added to an acetic acid solution of molybdenum hexacarbonyl preheated to 115—120 °C [1·5 : 1·0 mole ratio of $Mo(CO)_6$: (**1**)]. The reaction mixture, after being heated for 3·0—3·5 h, was poured into water, and the products were extracted with ether or chloroform. The reaction is of broad applicability with good yields of hydrocarbons (**2**) being obtained for different aromatic, benzylic, and aliphatic thiols (Table). The bridgehead thiol, adamantane-1-thiol, was an exception and gave instead the thioester (**3**). Thioesters were also formed in low yield as by-products of several of the other thiol–Mo^{II} reactions.



$$\begin{tikzcd} \underset{(\mathbf{1})}{\text{RSH}} \arrow[r, "\text{i}"] \arrow[r, bend right, "\text{ii}"'] & \underset{(\mathbf{2})}{\text{RH}} + \underset{(\mathbf{3})}{\text{RSCOMe}} \end{tikzcd}$$

i, $Mo(CO)_6$, HOAc, 115—120 °C, 3·0—3·5 h; ii, $Mo(CO)_6$, SiO_2, tetrahydrofuran, room temp. to 45 °C.

The deposition of metal carbonyls on refractory oxides is another subject attracting significant attention.[4] The desulphurization of thiols can be achieved under gentle conditions using molybdenum hexacarbonyl on silica. The metal carbonyl was adsorbed onto silica (the latter was dried at 350—500 °C) and the mixture, after being heated at 1·0—1·5 h at 125—140 °C (conditions for the generation of sub-carbonyl species),[4] was cooled to room temperature and treated with a tetrahydrofuran solution of the thiol. Desulphurization occurred at room temperature or at 40—45 °C (Table). Lower yields resulted with the use of toluene as the solvent.

TABLE. Yields of products[a] (**2**) and (**3**) obtained from reactions of the thiols RSH (**1**) and $Mo(CO)_6$

R	% Yield[b]	
	(**2**)	(**3**)
Ph_3C	76[c,d]	—
"	72[e]	—
β-Naphthyl	63[d]	4[d]
"	90[e]	—
9-Phenanthryl	48[d]	5[d]
p-$MeOC_6H_4CH_2$	92[d]	—
"	54[e]	—
2,5-$Cl_2C_6H_3$	71[d]	20[d]
1-Adamantyl	—	58[d]
$C_{12}H_{25}$	83[d]	6[d]

[a] Products were identified by comparison with authentic samples. [b] Yields are of pure materials. [c] A trace of hexaphenylethane was also detected. [d] Using $Mo(CO)_6$–HOAc; [e] Using $Mo(CO)_6$–SiO_2.

Acknowledgement is made to the Natural Sciences and Engineering Research Council for support of this research.

(*Received*, 15*th October* 1979; *Com.* 1093.)

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[1] H. Alper and H. N. Paik, *J. Org. Chem.*, 1977, **42**, 3522.
[2] A. B. Brignole and F. A. Cotton, *Inorg Synth*, 1972, **13**, 87.
[3] A. Bino, M. Ardon, I. Maor, M. Kaftory, and Z. Dori, *J. Amer. Chem. Soc.*, 1976, **98**, 7093.
[4] A. Brenner, *J.C.S. Chem. Comm*, 1979, 251; A. Brenner, D. A. Hucul, and S. J Hardwick, *Inorg. Chem.*, 1979, **18**, 1478, and references cited therein.