Hexacarbonylmolybdenum as a Reagent and Homogeneous Catalyst in Reactions with α-Halogeno-sulphoxides

By HOWARD ALPER* and GERVAIS WALL

(*Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada* KIN 6N5)

Summary Hexacarbonylmolybdenum functions as both reagent and catalyst in its reaction with α-bromo sulphoxides to give thioacetals in good yields.

METAL carbonyls are important as reagents and as catalysts for organic synthesis.[1] Recent examples include the synthesis of 1,3-diketones by treatment of iodobenzene with tetracarbonylnickel in the presence of enamines,[2] the rhodium carbonyl-catalysed oxidative cleavage of carbon–carbon bonds in ketones to acids,[3] and the dimerization of azirines by group VI metal carbonyls.[4] We now report a useful and novel reaction of molybdenum hexacarbonyl with α-bromo-sulphoxides, in which the metal carbonyl functions as both reagent and catalyst.

α-Bromo sulphoxides (**1**), easily prepared by bromination of sulphoxides,[5] react with [Mo(CO)$_6$] in dry 1,2-dimethoxyethane (DME) to give thioacetals in good yields (Table). The yields are better, in some cases, than those from the conventional route. A by-product was the *gem*-dibromide (**3**), which was isolated for R^2 = Me. This reaction represents a simple and novel approach to 1,3-disulphides, several derivatives of which are important pharmacological agents (*e.g.* probucol).[6] [W(CO)$_6$] and [Cr(CO)$_6$] were essentially inert under identical conditions to those for [Mo(CO)$_6$].

$$\underset{(1)}{\mathrm{R^1SOCHR^2Br}} + [\mathrm{Mo(CO)_6}] \xrightarrow{\mathrm{DME}} \underset{(2)}{\mathrm{R^1SCHR^2SR^1}} + \underset{(3)}{\mathrm{R^2CHBr_2}}$$

The mole ratio of α-halogeno-sulphoxide to [Mo(CO)$_6$] was 2 : 1, indicating that one of the steps in the deoxygenation–coupling process is catalytic. α-Bromo-sulphoxides are not converted into thioacetals by use of a catalytic amount of the metal carbonyl. Sulphoxides, such as (**4**), can undergo deoxygenation to sulphides [*e.g.* (**5**)] with an equimolar, but not catalytic, quantity of [Mo(CO)$_6$].[7]

$$\underset{(4)}{p\text{-}\mathrm{MeC_6H_4S(:O)Me}} \xrightarrow[\text{DME, 24 h, Heat}]{[\mathrm{Mo(CO)_6}]} \underset{(5)}{p\text{-}\mathrm{MeC_6H_4SMe}}$$

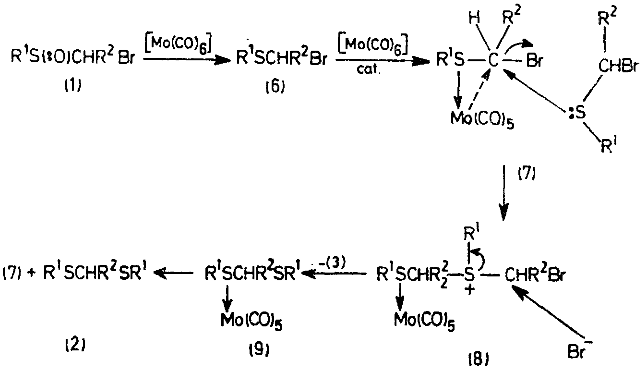
We propose that the initial step in the reaction of (**1**) with [$Mo(CO)_6$] involves stoicheiometric deoxygenation of (**1**) to the α-bromo-sulphide (**6**) which can then react further in the presence of a catalytic amount of [$Mo(CO)_6$] to give (**2**) (Scheme). The catalytic nature of the latter process was demonstrated by the conversion of chloromethyl phenyl sulphide into bis(phenylthio)methane (**2**; R^1 = Ph, R^2 = H) in 88% yield, by use of a 10:1 mole ratio of α-chloro-sulphide to [$Mo(CO)_6$]. (**2**) was not formed in the absence of [$Mo(CO)_6$]. Thus, (**6**) can react with the metal carbonyl to give the ligand-substitution product (**7**). The latter can then form a complexed sulphonium bromide (**8**) by displacement of bromine from (**7**), the displacement being assisted by the metal (β-effect). Carbon–sulphur bond cleavage of (**8**) would then generate (**9**) and the *gem*-dibromide (**3**). The 1,3-disulphide may result by ligand exchange of (**9**) with (**6**), regenerating (**7**).

TABLE

Reaction of the α-bromosulphoxides (**1**) with [$Mo(CO)_6$][a]

(**1**) R^1	R^2	Yield of (**2**)[b] (%)
Ph	H	56
Ph	Et	44
p-MeC_6H_4	H	64
p-BrC_6H_4	H	75
m-MeC_6H_4	H	67
m-MeC_6H_4	Me	38[c]
β-Naphthyl	H[c,d]	81[c,e]
Pr^n	Et	48

[a] 2:1 mole ratio of (**1**):[$Mo(CO)_6$]. Reflux times 23—27 h. [b] The products were identified by comparison of m.p. or b.p. and spectral results (i.r., n.m.r., mass spectra) with literature data. [c] New compound. Satisfactory elemental analyses were obtained. [d] M.p. 90—91 °C. [e] M.p. 87—88 °C.



SCHEME

In a typical experiment, a mixture of (**1**; R^1 = β-naphthyl, R^2 = H) (8·31 mmol) and [$Mo(CO)_6$] (4·15 mmol) in dry DME (50 ml) was refluxed with stirring for 23 h (N_2 atmosphere). The solution was cooled and filtered, and flash evaporation of the filtrate gave a solid. The latter was treated with n-hexane, filtered, and the filtrate was evaporated to give the crude thioacetal. Pure (**2**; R^1 = β-naphthyl, R^2 = H), m.p. 87—88 °C (81%), was obtained by chromatography on silica gel using n-hexane as eluant.

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[7] It was previously noted (H. Alper and E. C. H. Keung, *Tetrahedron Letters*, 1970, 53) that [$Mo(CO)_6$] did not deoxygenate sulphoxides using short reaction times (1—3 h). After 24 h, however, 50% yields of sulphides such as (**5**) could be obtained. Deoxygenation of α-bromo-sulphoxides would take place more readily, owing to the activating effect of the halogen atom.