Oxygen Atom Transfer in Dialkyldioxo-molybdenum or -tungsten Complexes. A Case of Dialkyldioxo–Alkylalkylideneoxohydroxometal Tautomerism

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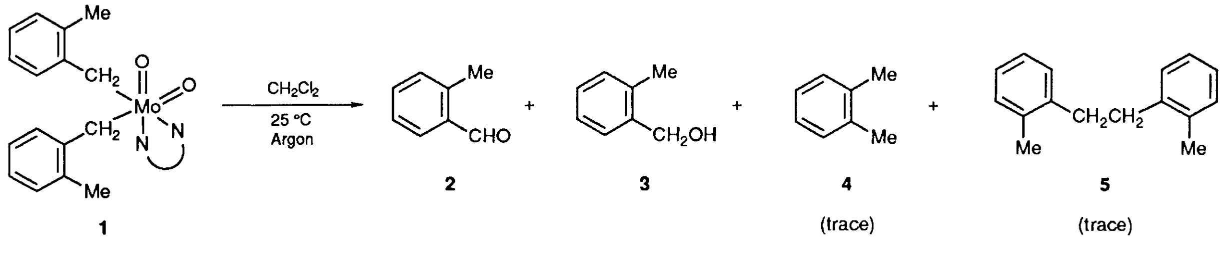
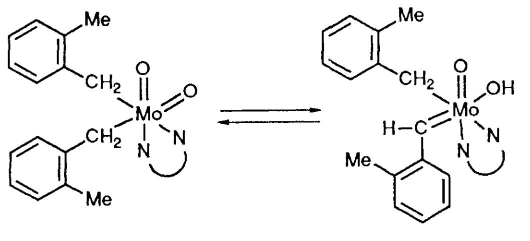
Reaction of bipyridylbis-2-(methylbenzyl)dioxomolybdenum or the tungsten analogue in solution, at room temperature, yields 2-methylbenzaldehyde and 2-methylbenzyl alcohol as the main products; their formation is rationalized in terms of a pseudo 'keto–enol' tautomeric equilibrium.

Metal–oxo compounds have been for many years a subject of interest in heterogeneous catalytic processes,[1] as well as, more recently, homogeneous systems.[2] Our interest in the chemistry of this type of complex had lead us to study them as models for oxygen atom transfer to alkyl groups. The metals of initial choice have been group VI metals and more specifically the bis(2-methylbenzyl)dioxomolybdenum(VI) and bis(2-methylbenzyl)dioxotungsten(VI) complexes. The





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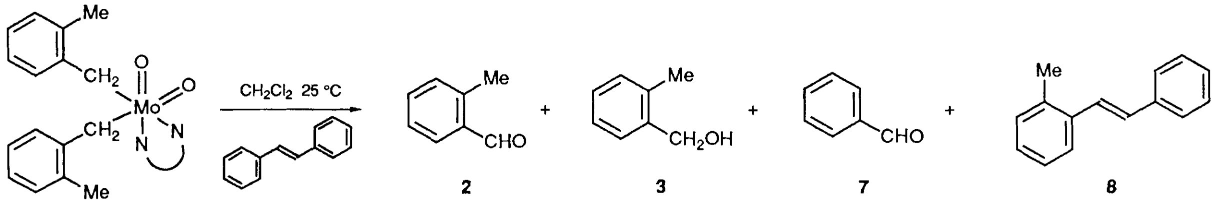

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reaction of MO_2X_2(bipy), (X = Cl, Br; M = Mo, W; bipy = bipyridyl), and 2-methylbenzylmagnesium bromide in tetrahydrofuran (THF) at −70 °C, following Schrauzer's method,[3] gives after recrystallization from CH_2Cl_2, the desired dialkyldioxobipyridyl compound as yellow orange crystalline products. The ^1H and ^{13}C NMR spectra as well as IR data are in accord with the reported analogous complexes.[3]†

These compounds are quite stable solids, however, we have found that they slowly react in solution producing oxygenated organic products. When a solution of bipyridyl bis(2-methylbenzyl)dioxomolybdenum **1** in CH_2Cl_2 is stirred under an inert atmosphere at 25 °C for several hours, a precipitate is slowly formed. Analysis of the resulting solution shows the presence of approximately equimolar amounts of 2-methylbenzaldehyde **2** and 2-methylbenzyl alcohol **3** as well as 2,2′-dimethyl-1,2-diphenylethane **5** and traces of *o*-xylene **4**.‡ The nature of the solvent does not seem to have any effect on the reaction path since besides CH_2Cl_2, acetonitrile, THF, dimethylformamide or dioxane can be used instead.

Decomposition of dialkyldioxo-molybdenum and tungsten compounds has previously been reported but under less mild conditions (200–500 °C) and the formation of the products thus obtained (alkanes and alkenes) were rationalized in terms of free radical intermediates. The milder conditions used in the present study as well as the products obtained suggest a different reaction pathway. When the formation of aldehyde and alcohol is followed with time it is established that both are formed in a nearly parallel manner and that the aldehyde does not arise from the oxidation of the alcohol. This could possibly be explained by an oxygen atom transfer process from a unique intermediate arising from a tautomeric equilibrium between dialkyldioxo **1** and alkyalkylideneoxohydroxo species.

Formation of the alcohol can then be rationalized in terms of an α-elimination from **6** of alkyl and hydroxo groups whereas aldehyde fromation could arise from the oxo–alkylidene moiety.§ Interestingly such pseudo 'keto–enol' tautomerism does not seem to be operative with the mono-oxo analogue. Thus, when **1** is reduced to the dialkymono-oxomolybdenum(IV) complex with tri-n-butylphosphine, even a longer reaction time does not produce any aldehyde or alcohol.

The intermediacy of the alkylalkylideneoxohydroxo species was further supported by a metathesis reaction. When **1** was allowed to react under the same conditions but in the presence of stilbene, the reaction proceeded cleanly, although slowly, to give **2** and **3** as the main products as previously observed plus benzaldehyde which could be rationalized only *via* a metathetic process.

Interestingly, only a small amount of **8** was obtained and benzyl alcohol was not detected. Other minor products identified were **4** and **5** together with toluene. The metathetic ability of the reaction system could also be explained by the formation of a dioxoalkylidene intermediate by the α-elimination of *o*-xylene. This eventuality was discarded since *o*-xylene (<1%) appears well after the formation of aldehyde has started. Further investigation is presently underway in order to elucidate the exact nature of the oxygen transfer as well as the metathesis process.

Received, 2nd August 1990; Com. 0/03544K

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† *Spectroscopic data* for: bipyridyl bis(2-methylbenzyl)dioxomolybdenum: IR (KBr) ν_{Mo-O}/cm^{-1}, 920 s, and 889 s; ^1H NMR (CD_2Cl_2) δ 2.11 (s, CH_3, 6H) and 2.93 (s, CH_2, 4H); ^{13}C NMR (CD_2Cl_2) δ 19.69 (CH_3) and 45.51 (CH_2). For bipyridyl bis(methylbenzyl)-dioxotungsten IR (KBr) $\nu_{W=O}/cm^{-1}$ 904s and 890s; ^1H NMR (CD_2Cl_2) δ 2.20 (s, CH_3, 6H) and 2.45(s, CH_2, 4H).

‡ Formation of products was followed by GC or NMR spectroscopy using respectively 1,3,5-triisopropylbenzene and hexamethyldisiloxane as internal standards. They were identified by GC–MS and by comparison with authentic samples. After 7 days the yields based on **1** were **2** (33%), **3** (33%), **4** (<1%) and **5** (20%) for molybdenum and **2**(13%), **3**(11%), **4**(<1%) and **5**(13%) for tungsten. The insoluble solid was not identified but was shown electrochemically to contain reduced molybdenum species.

§ The non-involvement of the 2-methyl group was shown by performing the reaction with the 3-methyl analogue and observing the same type of reactivity.

Observation of **6** by ^1H or ^{13}C NMR was not conclusive primarily because of the formation of reduced paramagnetic molybdenum species during the reaction.‡