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Cis-dioxomolybdenum(VI) Complexes as New Catalysts for the Meyer-Schuster Rearrangement.

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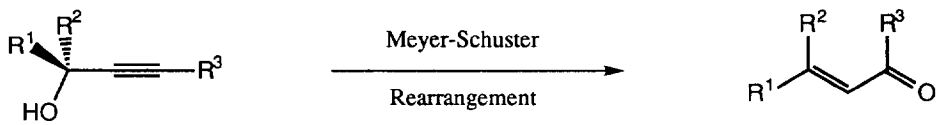
Abstract: We describe a new catalytic system for the isomerisation of propargylic alcohols into α,β-ethylenic carbonyl derivatives (Meyer-Schuster rearrangement)[1], based on the combination of dioxomolybdenum(VI) catalysts and sulfoxides.

The Meyer-Schuster rearrangement of α-acetylenic alcohols (scheme 1) leads to α,β-unsaturated carbonyl compounds which are important organic intermediates, particularly in the synthesis of natural products of biological, pharmaceutical or cosmetic interest[2,3] such as vitamin-A and its derivatives, terpens (for the synthesis of vitamins A, E, K, flavours and perfumes) and carotenoids.

Scheme 1



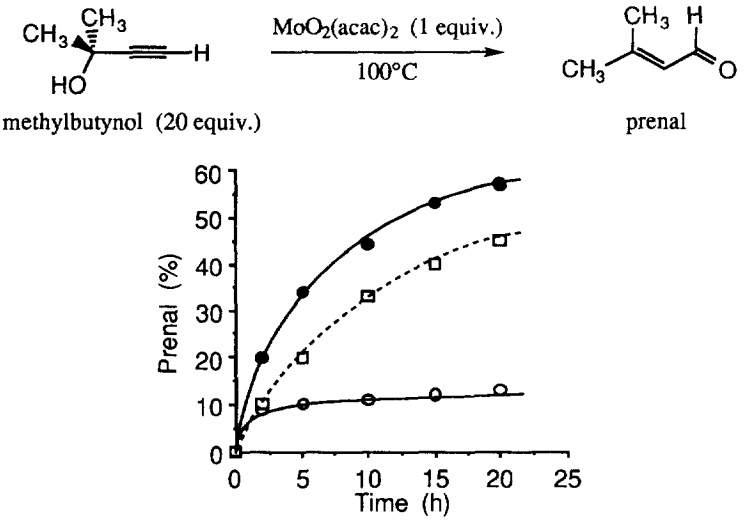
This rearrangement can been achieved by using a variety of catalysts such as strong acids which are unselective,[1,4] oxovanadium(V) complexes which need elevated temperatures,[5-7] MoO_3 which needs also elevated temperatures (150-170°C) and gives only poor yields,[5] n-Bu_4NReO_4/*p*-TsOH which works at 25°C but is unselective (dehydration due to the presence of the acid),[8] and ziconium(IV) catalysts in association with CuCl.[9] To date, the best results were obtained using a catalytic system based on the couple $Ti(OR)_4$/CuCl.[10,11] In the present paper, we describe the use of molecular *cis*-dioxomolybdenum(VI) catalysts to isomerise propargylic alcohols.

In contrast with oxovanadium catalysts, dioxomolybdenum(VI) complexes (5% mol) alone do not catalyse the Meyer-Schuster rearrangement of 2-methyl 3-butyn 2-ol (methylbutynol), only incomplete conversion being observed in this case (see figure 1). However, when dimethylsulfoxide is used as solvent or cosolvent (*ca* 2 equiv DMSO/substrate), catalytic isomerisation takes place as shown in figure 1.

Other sulfoxides, or pyridine-N-oxide, can as well serve as promoters (see table 1). Yet our best results

were obtained with dibutylsulfoxide (entries 1-3).[9,12] Both rates and selectivities are further increased by addition of a catalytic amount of carboxylic acid (compare entries 1 and 2). Such an effect has already been observed in the isomerisation of propargylic alcohols catalysed by siloxovanadium[6a] or titanium[7b] catalysts.

Figure 1: Isomerisation of methylbutynol.



methylbutynol (20 equiv.) prenal

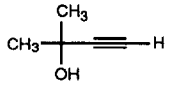
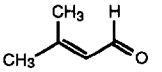
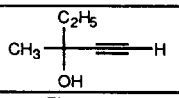
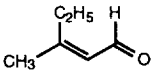
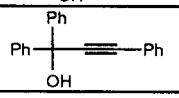
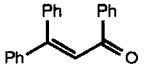
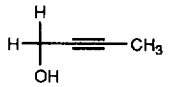
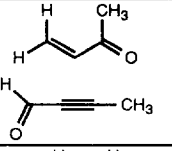
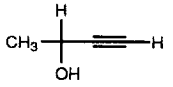
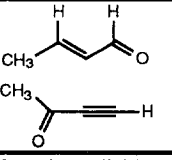
Conditions: methylbutynol 20 equiv., $MoO_2(acac)_2$ 1 equiv., 100°C.
(o) solvent : o-$C_6H_4Cl_2$; (□) solvent : DMSO; (•) solvent : o-$C_6H_4Cl_2$ + 40 equiv. DMSO.

A great range of molybdenum precursors can be used, *e.g.* MoO_2X_2 (X = 1/2 acac, OR, OAr or Cl), $MoO_2(NCS)_4(PPh_4)_2$ or even MoO_3. $MoO_2(acac)_2$ appears to give the highest isomerisation rate and selectivity.

The high selectivity obtained for methylbutynol is also found for other tertiary propargylic alcohols such as 3-methyl 1-pentyn 3-ol (entries 1-6). Whereas for more hindered alcohols like triphenylpropargylalcohol the reaction is very slow (entry 7). This was also found for vanadium and titanium catalysts. The molybdenum catalyst, however, is unsatisfactory for the rearrangement of primary and secondary alcohols, since side-products resulting from the oxidation of the alcohol function are formed extensively (entries 9-10). The use of the same couple MoO_2X_2 / sulfoxide in the catalytic oxidation of alcohols will be presented elsewhere.[13]

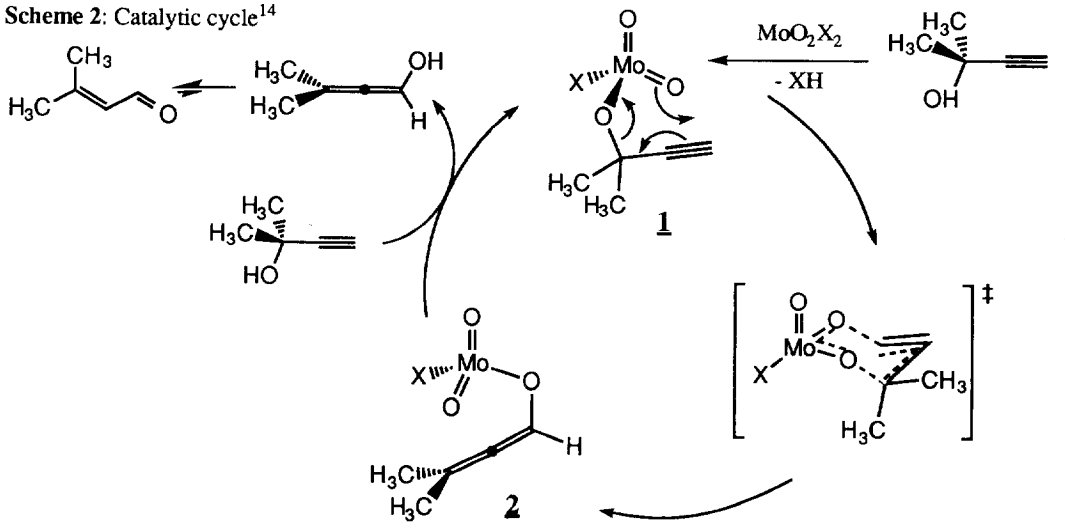
The general mechanism proposed[5] for oxo-metal complex catalysed isomerisation of propargylic alcohols would appear to apply in part to the molybdenum(VI) catalysis reported here (scheme 2): *i.e. (1)* formation of an alkynyloxo complex **1** by transesterification of the *cis*-dioxomolybdenum(VI) precursor, followed by *(2)* formation of the allenyloxo complex **2** by a [3,3]-sigmatropic rearrangement (where the oxo ligands play a key role) *via* a metallacyclic intermediate, and then*(3)* alkoxide exchange occurs with a further molecule of substrate, liberating the allenol which rearrange to the product *via* a prototropic shift. Complexes of type **1** could be isolated and characterised, but compounds **2** have not been detected.

Table 1: Catalytic Isomerisation of Various Propargylic Alcohols.

Entry	Substrate#	Conditions: Promoter	Acid	Temp. (°C)	Time (h)	Product¶	Yield†	Selectivity‡
1		$Bu_2S{=}O$	-	100	5		56	92
2		$Bu_2S{=}O$	$Ar'CO_2H$[b]	100	5		90	99
3		$Bu_2S{=}O$	-	140	0.5		95	98
4		DMSO[a]	-	140	1		60	75
5		Py-O	$Ar'CO_2H$[b]	100	5		46	99
6		$Bu_2S{=}O$	$Ar'CO_2H$[b]	100	5		73[c]	99
7		$Bu_2S{=}O$	$Ar'CO_2H$[b]	100	5		10	50
8		$Bu_2S{=}O$	-	100	5		18[c] 9[d]	/
9		$Bu_2S{=}O$	-	100	5		30 10[d]	/

Conditions: Substrate 20 equiv, $MoO_2(acac)_2$ 1 equiv (0,077 M), promoter 40 equiv, o-dichlorobenzene 2g (solvent). # Commercial products (Aldrich) except for entry 7, ¶ each product were first characterised by GC-MS analysis, † in %, GC determination, ‡ selectivity = (yield/conversion)x100, [a] solvent: DMSO, [b] Ar'=^{t}BuC$_6$H$_4$ (5 equiv), [c] mixture of Z + E, [d] from oxidation of hydroxyl group.

Scheme 2: Catalytic cycle[14]



The presence of two oxo ligands on the catalyst may be at the origin of its relative efficiency, the second oxo group serving as an active spectator ligand by stabilising the cyclic intermediate (or transition state). The role of the carboxylic acid and of the sulfoxide remains obscure. The latter may serve to maintain molybdenum in oxidation state VI, since reduction to lower oxidation states, together with catalyst deactivation, appears to occur in its absence.[15]

We are currently investigating in more detail the mechanism of the rearrangement mediated by these molybdenum catalysts.

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12. *Typical reaction conditions:* Under an inert atmosphere, 39 mg of $MoO_2(acac)_2$ (0.119 mmol), 200 mg of 2-methyl-3-butyn-2-ol (2.377 mmol), 772 mg of dibutylsulfoxide (4.754 mmol), 156 mg of 4-tert-butyl-benzoic acid (0.594 mmol), 150 mg of n-nonane (internal standard, 1.190 mmol) and 2 g of 1,2-dichlorobenzene (solvent) were placed in a screw caps vial and heated to 100°C under stirring. After 5 hours, the yield and selectivity were determined by gas chromatography (chromatograph: HP 5890 II; column: HP-1, methylsilicon gum, 10 m x 0.53 mm x 2.65 μm; detector: FID): yield in prenal 90% (recovered alcohol: 9%). After 10 hours, the conversion is complete: yield in prenal 98%.
13. Lorber, C. Y.; Osborn, J. A. to be published.
14. *Nota*: X = OR, Cl, 1/2 acac, ... Sulfoxide ligands probably bound to molybdenum center are not represented in this scheme.
15. In the absence of promoter, the isomerisation is only stoichiometric, and a fraction of the propargylic alcohol is dehydrated into enyne.

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