Pergamon

Tetrahedron Letters 39 (1998) 5655–5658

TETRAHEDRON
LETTERS

Oxidations Catalysed by Rhenium(V) Oxides 2. Clean Sulfide Oxidation by Urea-Hydrogen Peroxide

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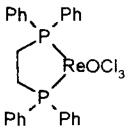
Received 17 April 1998; accepted 26 May 1998

Abstract: Three rhenium(V) oxo phosphine complexes and methyltrioxorhenium have been used as catalysts for oxidation of sulfides to sulfoxides with urea-hydrogen peroxide as oxidant in acetonitrile; partial enantioselective oxidation of methylphenyl sulfide was observed with methyltrioxorhenium in the presence of a (+)-camphor derived pyrazine carboxylic acid.

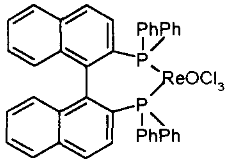
As part of our ongoing search for catalytic processes for clean oxidation using hydrogen peroxide we have investigated the potential of several rhenium based catalysts. In the preceding paper we demonstrated the use of methyltrioxorhenium (MTO) **1**[1] as a catalyst for oxidation of furans to enediones in a nonaqueous system employing the commercially available urea-hydrogen peroxide (UHP) complex. We have also completed a preliminary study of rhenium(V) oxide - UHP combinations for sulfide to sulfoxide oxidation in nonaqueous media. Although MTO is known to catalyse sulfide oxidation[2], this rhenium(V) oxide is currently accessible only through an inefficient synthesis requiring expensive chemicals. We have therefore looked at other rhenium(V) species as alternatives.

$MeReO_3$ (1)

$Re(PPh_3)_2OCl_3$ (2)



(3)



(4)

Arterburn and co workers[3] have successfully used Re(V)$OCl_3(PPh_3)_2$ **2** as a catalyst for sulfide oxidation employing one equivalent of diphenyl sulfoxide as oxidant, a process which yields one equivalent of diphenyl sulfide as a by-product. To our knowledge this catalyst, which is readily

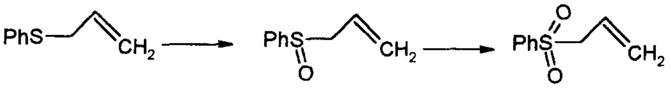
PII: S0040-4039(98)01100-9

available from inexpensive precursors[4], has not been used in conjunction with hydrogen peroxide.

We now report the clean oxidation of a variety of sulfides (Table 1) using UHP as oxidant with complex **2** as catalyst at room temperature. The process is devoid of sulfone formation, a byproduct common to most other peroxide-based oxidations. These oxidations exhibited striking solvent effects. We found that reaction rates were very slow in chloroform and dichloromethane, but increased dramatically in acetonitrile. The results in Table 1 were obtained using one equivalent each of sulfide and UHP in acetonitrile containing 2-3 mol% of catalyst **2**. Control experiments confirmed that no oxidation occurred in the absence of catalyst. As expected aliphatic sulfides were oxidised more rapidly than aryl alkyl sulfides.

We have synthesized two other rhenium(V) oxide complexes **3** and **4** utilising bidentate phosphine ligands. Comparison of their oxidising power with that of catalyst **2** revealed significant differences. Whereas **3** was less active than **2**, as revealed by longer oxidation times for methyl benzyl sulfide and methyl phenyl sulfide, catalyst **4** led to faster reaction times for both these sulfides when compared with catalyst **2**. Both catalyst **3** and **4** were found to be more robust than catalyst **2** under our reaction conditions. N-phthaloyl L-methionine (entry 6) was oxidised to sulfoxide with a de of 60%. To complete this survey of rhenium(V) oxo species as catalysts for sulfide oxidation utilising UHP, we have examined the performances of MTO under comparable conditions. Although MTO is known to catalyse sulfide oxidation, it has previously been used only in chloroform or dichloromethane. Here too we have observed a striking solvent effect in switching to acetonitrile. For example, the MTO-catalysed oxidation of methyl phenyl sulfide with UHP is complete in about 10 minutes in acetonitrile as compared to 36 hours in chloroform.

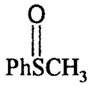
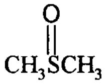
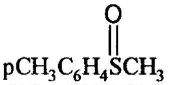
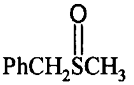
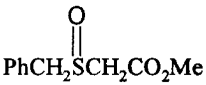
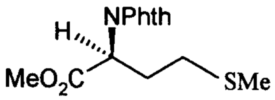
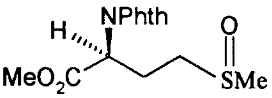
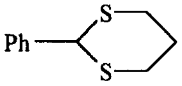
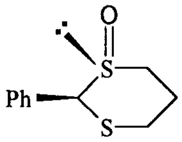
However, the MTO-UHP combination is less chemoselective than the rhenium(V) phosphine catalysts **2-4** in that oxidation can proceed further to the sulfone stage. However, with unsaturated sulfides, eg. equation 1, the sulfoxide and sulfone are consecutively formed without any concomitant epoxidation of the double bond.



Eq.1

Finally, we report some preliminary observations on attempts to realise enantioselection in sulfide oxidation catalysed by rhenium(V) oxo species. It is known that the presence of

TABLE 1. Oxidation of Sufides with UHP catalysed by Rhenium(V) oxide phosphine complex 2

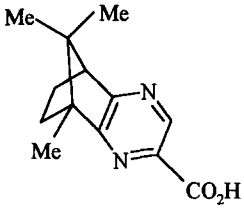
ENTRY	SUBSTRATE	PRODUCT	% YIELD
1	$PhSCH_3$	 $\mathrm{Ph\overset{\overset{O}{\Vert}}{S}CH_3}$	92
2	CH_3SCH_3	 $\mathrm{CH_3\overset{\overset{O}{\Vert}}{S}CH_3}$	90
3	$pCH_3C_6H_4SCH_3$	 $\mathrm{pCH_3C_6H_4\overset{\overset{O}{\Vert}}{S}CH_3}$	90
4	$PhCH_2SCH_3$	 $\mathrm{PhCH_2\overset{\overset{O}{\Vert}}{S}CH_3}$	90
5	$PhCH_2SCH_2CO_2Me$	 $\mathrm{PhCH_2\overset{\overset{O}{\Vert}}{S}CH_2CO_2Me}$	90
6			80
7			85[a], 88[b]

a -yield of monosulfoxide; b -yield of disulfoxide; Phth = phthaloyl

Typical procedure

To a solution containing benzyl methyl sulfide (138mg) in CH_3CN(2ml), UHP(100mg) and catalyst 1 (16mg) were added and stirred for 18h at room temperature. Solvent was removed under vacuum and the residue was extracted with (3x2ml) methylene chloride. Combined extracts were evaporated to yield benzyl methyl sulfoxide as an oil (140mg, 90%) of > 97% purity by ^{1}H NMR analysis.

pyrazine-2-carboxylic acid can accelerate the rate of oxidations with aqueous hydrogen peroxide catalysed by MTO and other oxometallic species[5]. Although the mechanism of this acceleration is unclear, the involvement of a Re(V)-pyrazine carboxylic acid complex is likely. Reasoning that a chiral pyrazine ligand might exert enantiocontrol on the oxygen transfer process we prepared the (+) camphor pyrazine carboxylic acid 5. Employing 5 as a potential co-catalyst in the MTO-UHP oxidation of methyl phenyl sulfide we obtained the corresponding sulfoxide with an ee of 15%.



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In conclusion, we have shown the versatility of UHP in sulfide oxidation with three different rhenium(V) phosphine catalysts in acetonitrile. Sulfone formation was not observed even when an excess of UHP was used. We have also demonstrated the first example of enantioselection, though limited, using a rhenium(V) oxide. The design of new chiral ligands for asymmetric oxidation using UHP is under study.

ACKNOWLEDGMENTS

We acknowledge support from the EU European Regional Development Fund and the Department of Education for Northern Ireland.

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6. Details of the synthesis of compound 5 will be published elsewhere.