

Titanium Catalysed Stereoselective Sulphoxidations with H₂O₂: Recent Developments

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Introduction

The discovery of efficient and atom-economic catalyst systems for asymmetric epoxidation is an important objective of catalytic chemistry. In this work, some new catalyst systems for the enantioselective oxidation of sulphides with hydrogen peroxide will be presented, as an alternative for the Kagan [1] and Modena [2] modified titanium(IV) isopropoxide – diethyltartrate / alkylhydroperoxide catalyst systems.

Experimental

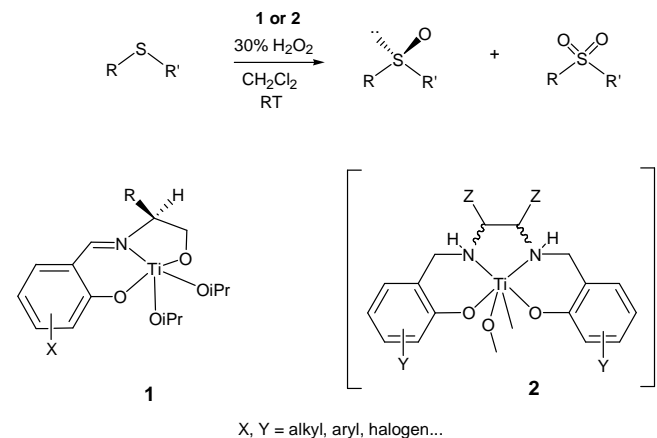
Prochiral sulphides were either commercial reagents or were prepared according to literature methods [3]. All other chemicals and solvents were commercial reagents and were used as received. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE-400 MHz spectrometer at 400.13 and 100.613 MHz, respectively, using 5 mm cylindrical tubes. The enantiomeric excess values (*ee*) were measured by ¹H NMR with a chiral shift reagent Eu(hfc)₃ or by HPLC on a Shimadzu LC-20 chromatograph with chiral stationary phases.

Results/Discussion

New catalyst systems for the asymmetric oxidation of sulphides to sulphoxides with H₂O₂ have been proposed (Scheme 1). They feature chiral ligands prepared from readily available precursors, a non-toxic metal, and a “green” oxidant, giving the sulphoxides in up to 97% *ee* with high efficiency (up to 500 turnovers).

The effect of temperature, solvent, concentration, catalyst and substrate structures on the oxidation chemo- and stereoselectivities has been examined.

Complexes of the type **2** have been found to be especially stereoselective (up to over 95% *ee*) in the oxidation of thioethers with both bulky substituents at the sulphur atom, the high enantiomeric excess originating in a tandem asymmetric oxidation and kinetic resolution processes. The latter process reduced the chemoselectivity due to an undesired sulphone formation. However, an improved method of the catalysts preparation has been developed which yielded the catalyst of the type **2** demonstrating high chemoselectivities (in the range of 80-90%) without loss of the high stereoselectivity.



Scheme 1. Stereoselective oxidation of sulphides to sulphoxides with hydrogen peroxide catalysed by complexes **1** and **2**.

References.

1. P. Pitchen, M. Desmukh, E. Dunach, H. B. F. Kagan, *J. Am. Chem. Soc.*, **106**, 8188 (1984)
2. F. Di Furia, G. Modena, R. Seraglia, *Synthesis*, 325, (1984).
3. Y. Jiang, Y. Qin, S. Xie, X. Zhang, J. Dong, D. Ma, *Org. Lett.*, **11**, 5250 (2009).