# Oxidation of Cyclic Ketones by Hydrogen Peroxide Catalysed by Group 6 Metal Peroxo Complexes

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*Summary* Molybdenum peroxo complexes stabilized by picolinato and pyridine-2,6-dicarboxylato ligands catalyse oxidation of cyclic ketones by $H_2O_2$ to lactones and their derivatives; this represents a catalytic analogue of the Baeyer–Villiger reaction.

Peroxo complexes of high valency Group 6 metals have been reported only as stoicheiometric reagents for oxidation of olefins[1] and alkali metal enolates.[2] We now report the first example of the use of molybdenum peroxo complexes as catalysts for the Baeyer–Villiger oxidation[3] of cyclic ketones by $H_2O_2$ to lactones and their derivatives.

Peroxo complexes containing monodentate ligands such as $Mo(O)(O_2)_2(hmpa)(H_2O)$ (**1**)[4] (hmpa = hexamethylphosphoric triamide) decompose readily and are not suitable as catalysts for oxidation of cyclic ketones. However, peroxo complexes stabilized by polydentate ligands[5] such as the picolinato in $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)](H_2O)$ (**2**) and the pyridine-2,6-dicarboxylato in $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (**3**) have proved successful; the best results are obtained with the complex (**3**).

In a typical run, a solution of 90% aqueous $H_2O_2$ (1·17 g) in acetonitrile (2·5 ml) was added to a solution of (**3**) (0·32 g) and cyclopentanone (2·6 g) in acetonitrile (20 ml) and the resulting mixture was heated to 60 °C. After 24 h, δ-valerolactone (45%) and 5-hydroxypentanoic acid (15%) were obtained. When the oxidation was carried out in methanol, methyl 5-hydroxypentanoate was formed. In the absence of (**2**) or (**3**) no lactones or their derivatives were obtained. Addition of radical scavengers such as 2,6-di-t-butyl-4-hydroxytoluene had no effect on the reaction rate and the product yields. The results of the oxidation of other ketones are summarized in the Table.

Table. Reaction of cyclic ketones with $H_2O_2$ catalysed by complex (**3**)[a]

| Ketone | Solvent | Product | Combined yield/% | Catalyst turnover |
|---|---|---|---|---|
| Cyclopentanone | MeCN | δ-Valerolactone and 5-hydroxypentanoic acid (66:34) | 60 | 19 |
| ,, | MeOH | Methyl 5-hydroxypentanoate | 40 | 12 |
| 2-Methylcyclopentanone | MeCN | 5-Methylvalerolactone | 82 | 25 |
| ,, | MeOH | Methyl 5-hydroxyhexanoate and methyl 5-oxohexanoate (62:38) | 83 | 25 |
| Cyclohexanone | MeCN | ε-Caprolactone | 10 | 3 |
| 2-Methylcyclohexanone | MeCN | 6-Methylcaprolactone | 10 | 3 |
| ,, | MeOH | Methyl 6-hydroxyheptanoate and methyl 6-oxoheptanoate (47:53) | 87 | 26 |

[a] All reactions were carried out at 60 °C with equimolar quantities of cycloalkanone and $H_2O_2$ and with a molar ratio of cycloalkanone:catalyst of 30:1. The identity of the products was ascertained by g.l.c., n.m.r., and mass spectra, and by comparison with authentic samples. The quantitative analysis was carried out by g.l.c. and n.m.r. spectrometry employing biphenyl as the internal standard.

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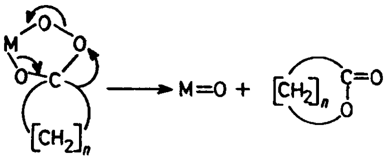
† The identity of the peroxide was determined by i.r. and n.m.r. spectroscopy, elemental analysis, and by comparison with an authentic sample.

A competing reaction is the formation of oligomeric peroxides. For example, in the case of cyclohexanone, tricyclohexylidene triperoxide was isolated from the reaction mixture.† This increased tendency of cyclohexanone to form oligomeric peroxides, when compared with other cyclic ketones, qualitatively correlates with the high values of the equilibrium constants for addition of nucleophiles to cyclohexanone.[6]



(4)

It is proposed that the carbonyl group of the ketone inserts into the molybdenum–oxygen bond of the peroxo species to form a metallo-ozonide (**4**; M = Mo). A similar stable ozonide (**4**; M = Pt) is formed in the reaction of ketones with bis(triphenylphosphine)platinum peroxide.[7] As expected, the molybdenum intermediate (**4**; M = Mo) reacts further due to the tendency of high valency molybdenum to form metal–oxo bonds. Formation of the oxo complex is substantiated by the isolation of a new complex formed from (**2**) when the $H_2O_2$ added to the reaction mixture is depleted. The i.r. spectrum of this new complex displays three bands at 900, 920, and 950 $cm^{-1}$, characteristic of a trioxo species, and no peroxo band originally observed at 850 $cm^{-1}$. These data and elemental analysis correspond to an oxo complex of the formula $Mo(O)_3(C_5H_4NCO_2H)$ (MeOH). The catalytic cycle is completed by conversion of the oxo complex back into the peroxo complex by interaction with $H_2O_2$ as has been demonstrated for $V^{V}$[8] and $Mo^{VI}$[9] oxo complexes. The analogy between the Baeyer–Villiger oxidation and the rearrangement of the intermediate (**4**) is further supported by the exclusive migration of the most substituted species in the case of 2-methylcycloalkanones (Table).

Lactones are the precursors for the hydroxyalkanoic acids and their esters (Table). This is supported by the observation that, in methanol and in the presence of catalytic quantities of (**2**) or (**3**) the lactones are rapidly solvolysed to the corresponding methyl hydroxyalkanoates.

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[1] H. Mimoun, I. S. deRoch, and L. Sajus, *Tetrahedron*, 1970, **26**, 37.

[2] E. Vedejs, *J. Amer. Chem. Soc.*, 1974, **96**, 5945.

[3] Baeyer–Villiger oxidation has been achieved with 90% $H_2O_2$ in combination with an excess of acid anhydrides or $BF_3 \cdot OEt_2$. Recently the use of a new reagent generated from benzeneseleninic acid and a 10 molar excess of 30% aqueous $H_2O_2$ has been reported: P. A. Grieco, Y. Kokoyama, S. Gilman, and Y. Ohfune, *J.C.S. Chem. Comm.*, 1977, 870.

[4] H. Mimoun, I. S. deRoch, and L. Sajus, *Bull. Soc. chim. France*, 1969, 1481.

[5] S. E. Jacobson, R. Tang, and F. Mares, *Inorg. Chem.* in the press.

[6] J. Hine, 'Structural Effects on Equilibria in Organic Chemistry,' Wiley-Interscience, New York, 1975, p. 257.

[7] S. Otsuka, A. Nakamura, Y. Tatsumo, and M. Miki, *J. Amer. Chem. Soc.*, 1972, **44**, 3761.

[8] K. Weighardt, *Inorg. Chem.*, 1978, **17**, 57.

[9] S. E. Jacobson, R. Tang, and F. Mares, unpublished results.