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Cobalt(II) Catalysed Epoxidation of Unfunctionalised Alkenes with in Situ Generated Hydroperoxide from Methyl-2-oxocyclopentane Carboxylate and Molecular Oxygen

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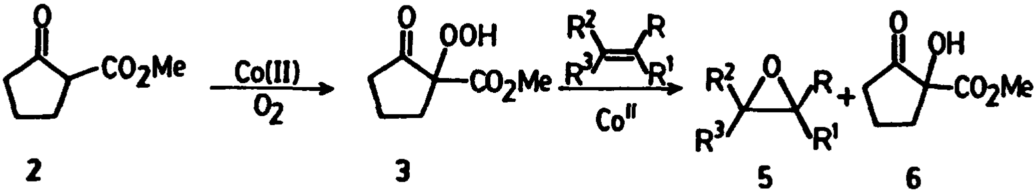
Abstract:*Cobalt(II) complexicatalyses the epoxidation of unfunctionalised alkenes by in situ generated hydroperoxide from methyl-2-oxocyclopentane carboxylate and molecular oxygen.*

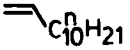
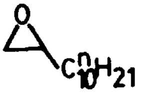
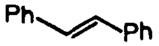
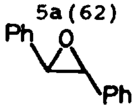
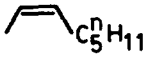
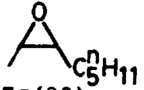
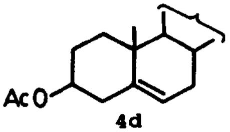
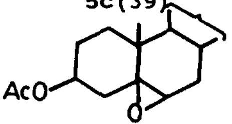
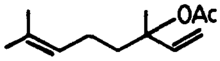
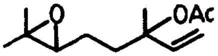
The epoxidation of alkenes by molecular oxygen in the presence of a metal catalyst has been a subject of intensive research over the last few[1] years. A direct oxidation by molecular oxygen seldom results in any meaningful reaction, however , the activation by a suitable trap promises to be a good route for its transfer to an organic substrate. We have recently demonstrated[2] that 1,3-dicarbonyl compounds undergo oxidative addition to alkenes in the presence of cobalt(II) and oxygen to give the corresponding oxygenated product. While exploring this reaction with methyl-2-oxocylopentane carboxylate in the presence of the cobalt(II) catalyst and oxygen, we discovered the exclusive formation of the corresponding hydroperoxide 3. Interestingly, the latter reaction when conducted in the presence of unfunctionalised alkenes 4 afforded the corresponding epoxide 5 and the alcohol 6 (Scheme 1). A brief account of these findings is described below



SCHEME 1

A mixture of alkene 4 (5 mmol), methyl-2-oxocyclopentane carboxylate 2 (10 mmol) and cobalt(II)complex[3](5 mol%) in acetonitrile were stirred at 25°C under oxygen baloon for 20-25 h. Removal of the solvent followed by the usual work up and chromatography afforded the epoxide 5 and alcohol 6 in good yields(table 1). The geometrically pure alkenes i.e.,(E)-stilbene and (Z)-octene, afforded the corresponding anti and syn epoxides respectively whereas cholesteryl acetate was efficiently transformed to the mixture of the corresponding α and β epoxides (table 1, entry 4). Selective monoepoxidation of the internal double bond in linalool acetate can be achieved without the concomitant formation of diepoxide(table, entry 5)

Table 1. Cobalt(II) Catalysed Epoxidation of Alkenes with Methyl 2-oxocyclopentane carboxylate and Molecular Oxygen

Entry	Alkene	Epoxide(Yield %)
1	 **4a**	 5a(62)
2	 **4b**	 5b(64)
3	 **4c**	 5c(39)
4	 **4d**	 5d(77)
5	 **4e**	 5i(71)

In conclusion, the cobalt(II) catalysed epoxidations by in situ generated hydroperoxide is synthetically useful transformation and it provides a good and efficient alternative to tertiary butylhydroperoxide promoted epoxidatioins.

REFERENCES AND NOTES

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3. The cobalt(II) complex*i*was prepared by reacting equivalent amount of $CoCl_2$and Schiff's base derived from salicylaldehyde and methyl ester of L-serine in acetonitrile under nitrogen at ambient temperature.

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