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Cobalt Catalysed Allylic and Benzylic Oxidations with Dioxygen in the Presence of Ethyl 2-oxocyclopentanecarboxylate

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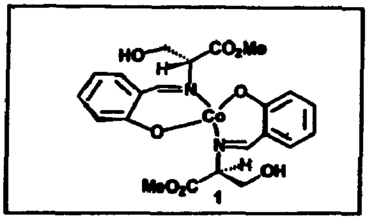
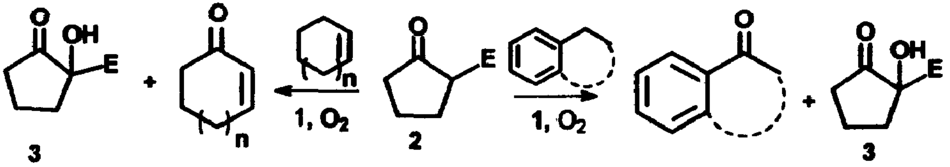
Abstract: *An efficient allylic and benzylic oxidation of various cyclic alkenes and benzylic compounds respectively can be achieved with dioxygen in the presence of ethyl 2-oxocyclopentanecarboxylate* **2** *and catalytic amount of cobalt(II) Schiff's base complex* **1**.

We have recently demonstrated[1] that various acyclic alkenes can be epoxidised with dioxygen in the presence of ethyl 2-oxocyclopentanecarboxylate **2** and catalytic amount of [bis(salicylidene-N- (methyl-3-hydroxypropionate)][2] abbreviated as CoSANSE **1**. The reaction is believed to occur via the in situ formation of a cobalt(III) superoxide complex which transfers the oxygen atom to **2** and alkene to afford the corresponding tertiary alcohol **3** and epoxide respectively. Interestingly, the cyclic alkenes do not undergo epoxidation and they are instead allylically oxidised to the corresponding allyl alcohol or enones whereas benzylic substrates undergo oxidation to the corresponding ketones in excellent yields (Scheme I). This communication describes a preliminry account of our finding on this useful transformation. A mixture of alkene (5 mmol), **2** (10 mmol) and catalyst **1** (5 mol %) were stirred at 25 ° C in acetonitrile (60 ml) under dioxygen balloon for 30 -35 h. Removal of solvent followed by aqueoues work up and purificaion by distillation over kugerhorl afforded the corresponding allyl alcohol or enone in good yields (table I). Cyclopentene was mainly converted to the corresponding alcohol **4** wereas cyclohexene and cyclooctene were oxidised to a mixture of corresponding alcohols and ketones **5** and **6** respectively (table I, entries

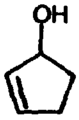
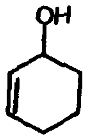
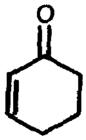
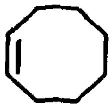
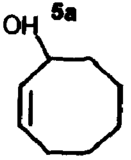
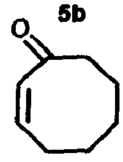
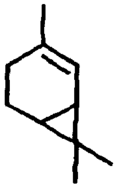
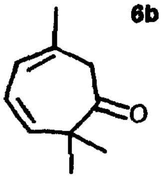
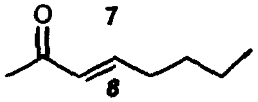




(SCHEME I)

I, entries 1-3). Interestingly, Δ^3-carene provided the cycloheptadienone **7** as the only product in very high yield (table 1, entry 4). Surprisingly, (Z)-2-octene underwent allylic oxidation to give the rearranged (E)-enone **8** exclusively (table I , entry 5) along with the epoxide of (Z)-2-octene as the minor product. Benzylic substrates also undergo oxidation to the corresponding ketones under the above mentioned experimental conditions. Thus, diphenyl methane, ethyl benzene, tetralin and fluorene were oxidised following this protocol to afford the correspondng ketones in good yields (table II, entries 1-2 and 4-5).

Table I. CoSANSE Catalysed Allylic Oxidations with Molecular Oxygen

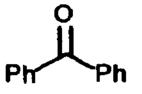
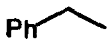
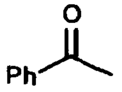
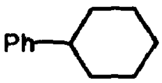
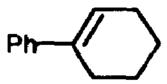
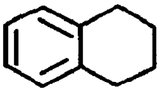
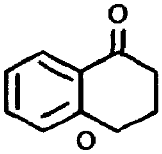
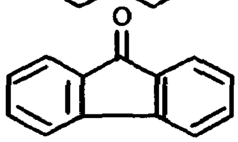
entry	*alkene*	*product*	*(% yield)*[a]
1		 **4**	(71)
2		 **5a**  **5b**	2:1(65)[b]
3		 **6a**  **6b**	1:1(56)[b]
4		 **7**	(67)
5		 **8**	(51)

[a] Isolated yield. [b] *Ratio determined from the ^1H NMR of the crude reaction mixture.*

Cyclohexyl benzene underwent smooth trans formation to 1-phenyl cyclohex-1-ene in moderate yield (table II, entry 3). These transformations are complete within 15-17h at 60 ° C under atmospheric pressure of dioxygen and all the reactions yielded the tertiary alcohol **3** in quantitative yield (yield based on **2**. The allylic oxidation of alkenes is known to occur via metal-catalysed autoxidation process [3], however, in the present case the reaction seems to be proceeding via a different pathway. We have observed that these reactions do not occur using catalytic amount of **2**, however, as we increase the quantity of **2**, then the allylic and benzylic oxidations proceed quite smoothly. Thus, in the oxidation of cyclohexene, increasing the quantity of **2** from 0.1 equivalent to 1 equivalent we see a considerable increase in the yields of **5a** and **5b**. Further, enhancement in the yield of **5a** and **5b** were also observed by using 2 equivalents of **2**.

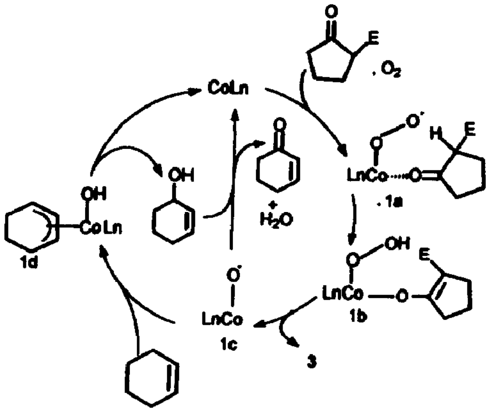
It is interesting to note that during the oxidation of cyclohexene in the presence of two equivalents of **2**, the formation of enone **5b** is more than **5a**. *When the oxidation of cyclohexene was carried out in the presence of radical trap, ie. 2,4,6-tritertiarybutylphenol, no inhibition of product formation was observed.* This observation also rules out the occurrence of this reaction via metal catalysed autoxidation process. An EPR study has also indicated[4] the formation of superoxocobalt(III) species 1a from **2**, dioxygen and catalyst 1. The formation of the superoxo species is only observed in the presence of **2** and this clearly indicates that the latter is helping the uptake of oxygen by catalyst 1, a similar observation has been reported[5] by Basolo and coworkers in related cobalt complexes. Thus, the catalytic cycle for this reaction may be initiated by the formation of 1a which may lead to the formation of cobalt enolate 1b via intramolecular hydrogen transfer. The rapid intramolecular hydroxylation of 1b will lead to **3** and the reactive cobalt oxo complex 1c, which may abstract an allylic hydrogen atom to provide allylic alcohol **5a** via the complex 1d. It is clear that the allylic alcohol is also prone to oxidation[6] by 1c and thus, this would require more of the latter compound in order to achieve high conversion of alkene

Table II. CoSANSE Catalysed Benzylic Oxidations with Molecular Oxygen

entry	benzylic compounds	product	(% yield)[a,b]
1			(69)
2			(45)
3			(47)
4			(61)
5			(66)

[a] Yield of the isolated product. [b] Reaction condition: CoSANSE (5 mol%) ethyl 2-oxocylopentane carboxylate (10 mmol) and benzylic compound (5 mmol) were taken in acetonitrile (60 mL) and heated at 60° C for 15 h under oxygen balloon.

to the corresponding alcohol or enone. Due to this competetive reactions (ie. allylic oxidation versus alcohol oxidation), more of 1c will be consumed which in turn would require more of **2** for high yield of conversion of alkenes to alcohol or ketone. Thus, the dependence of **2** on the overall yield of this reaction may be understood if we invoke the formation of 1c as the reactive species. A species analogous to 1c has already been proposed[7] by Kochi and coworkers during the cobalt catalysed oxidation of alkenes with iodosylbenzene. Inlight of this, the formation of **7** and **8** can be understood by the rearrangement followed by the oxidation of the initially formed allylic radical from the corresponding alkenes.



In conclusion, cobalt(II) complex **1** catalysed allylic and benzylic oxidation with dioxygen and ketoester **2** constitutes a novel methodology which will have wide applications in organic synthesis. We are currently pursuing studies on the mechanistic aspects of this reaction.

References and Notes

1. Punniyamurthy, T.; Bhatia, B.; Iqbal,J., *Tetrahedron Lett.* **1993**, 34, 4657.
2. Serine methyl ester hydrochloride(5mmol) was reacted with triethylamine (7.5mmol) and 2-hydroxy benzaldehyde (5 mmol) in 20ml of ethyl alcohol at ambient temperature for 5h to give the schiff's base ligand as an oil. The purified ligand (5 mmol) and Cobalt(II) chloride (2.5 mmol) were stirred in acetonitrile (25 ml) solvent under nitrogen atmosphere for 15h at room temperature. Removal of the solvent followed by crystallisation in chloroform yielded the CoSANSE as a green coloured powder in good yield. Complex **1** was assigned tetrahedral geometry based on UV-Vis and magnetic moment value.
3. For autoxidation of olefins see: a). Sheldon, R.A.; Kochi, J.K. *Metal-Catalysed Oxidations of Organic Compounds*, Academic Press: New York, 1981. and references therin.
4. EPR study of this reaction has indicated that superoxide complex 1a is formed in the presence of **2**. The g-value(2.0187) obtained from the EPR of the reaction mixture indicates the formation of monomeric cobalt-superoxide species[5]. A detailed study on the formation of cobalt-superoxide from **1** in the presence of carbonyl compounds will be published soon.
5. For the formation of oxygen adduct from cobalt-schiff's base complexs see: a).Crumbliss, A.L.; Basolo, F. J. *Am. Chem. Soc.*,**1970**, 92, 55. b). Mirioun., *Comprehensive Coordination Chemistry* ; Pergamon Press: Oxford,Vol.6,1987.
6. See the accompanying paper.
7. Koola,J.D.; Kochi,J.K. *J. Org. Chem.* **1987**, 52, 4545.

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