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# Cobalt Catalyzed Oxidation of Cyclic Alkenes with Molecular Oxygen : Allylic Oxidation Versus Double Bond Attack

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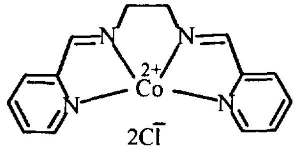
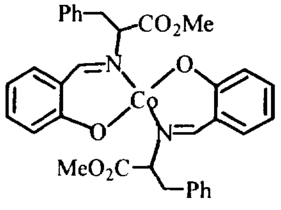
***Abstract :*** *Cobalt(II) Schiff's base complex 1 and 2 exhibit a remarkable chemoselectivity during oxidation of cyclic alkenes with molecular oxygen in the presence of 2- methylpropanal. Catalyst 1 encourages the oxidation of double bond to give epoxide as the major product whereas catalyst 2 promotes mainly the allylic oxidation leading to allylic alcohols or enones.*

Transition metal complex catalyzed oxidation of organic substrates with molecular oxygen is gaining importance as a viable[1] alternative to the environmentally hazardous metal oxide based reagents. Recent studies from our group has shown[2] that various cobalt(II) complexes derived from Schiff base catalyse the oxidation of alkenes and alcohols in the presence of molecular oxygen and 2- methylpropanal. We now show that the cobalt[3,2d] catalyst **1** and **2** exhibit an interesting chemoselectivity during the oxidation of cyclic alkenes by a combined use of molecular oxygen and 2- methylpropanal. These studies indicate that the oxidation of cyclic alkenes with **1** provides epoxide whereas catalyst **2** promotes the formation of allylically oxidized products (Scheme 1).

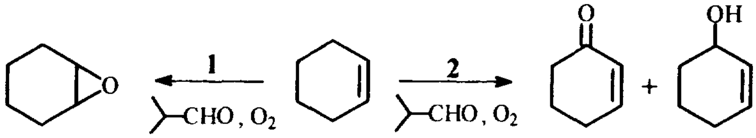
A mixture of alkene (5 mmol), 2- methylpropanal (10 mmol) and catalyst **1** or **2** (5 mol%) were stirred at 25° C in acetonitrile (60 ml) under dioxygen balloon for 10-15 h. Removal of solvent followed



**1**



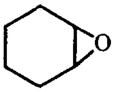
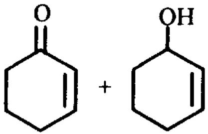
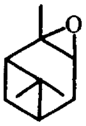
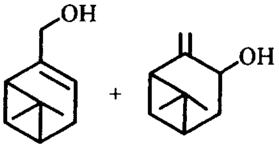
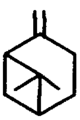
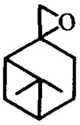
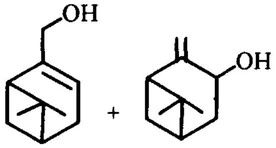
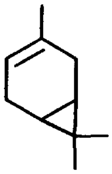
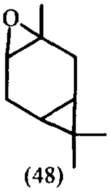
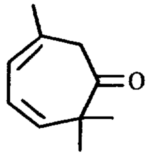
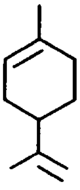
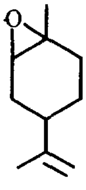
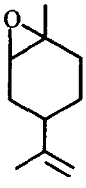
**2**



Scheme 1

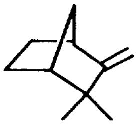
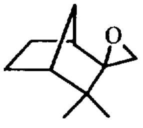
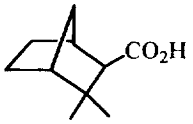
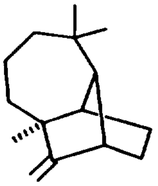
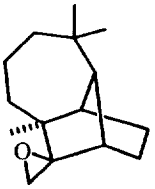
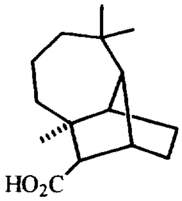
by aqueous work-up and purification by column chromatography or distillation using a Kugelrohr apparatus afforded corresponding epoxide or allylically oxidized product (table 1). Thus in the presence of catalyst **1** , cyclohexene can be converted to the corresponding epoxide as the major product, whereas a mixture of cyclohexenone and cyclohexenol are obtained predominantly under the aegis of catalyst **2** (table 1, entry 1). Similarly, α- and β- pinenes afford mainly the corresponding epoxides in the presence of catalyst **1**

**Table 1. Catalyst 1 or 2 Catalysed Oxidation of Cyclic Alkenes with Molecular Oxygen**

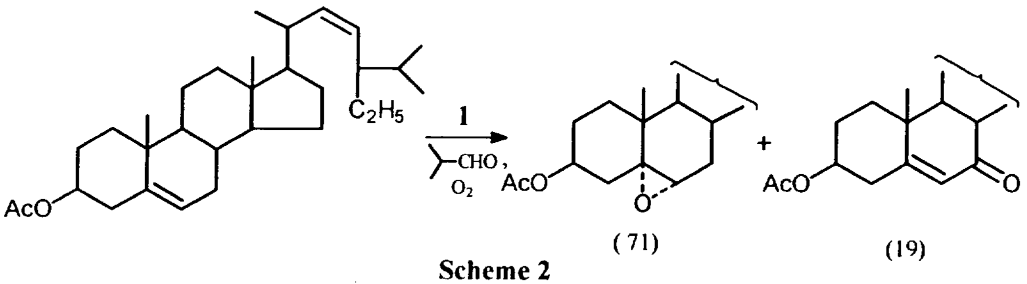
| Entry | Alkene | Product(s) (Yield %)$^{a,c}$ | |
|---|---|---|---|
| | | Catalyst **1** | Catalyst **2** |
| 1 |  | <br>(87) | <br>2:1 (70) |
| 2 |  | <br>(70) | <br>(50)$^b$ |
| 3 |  | <br>(64) | <br>(52)$^b$ |
| 4 |  | <br>(48) | <br>(48) |
| 5 |  | <br>(54) | <br>(53) |

*a) Isolated yield. b) An equal mixture of allylic alcohols are obtained. These reactions are also accompanied by ~ 40% of some unidentifiable products. c) The epoxides were obtained as mixture of diastereomers*

**Table 2. Catalyst 1 or 2 Catalysed Oxidation of Exocyclic Double Bond with Dioxygen**

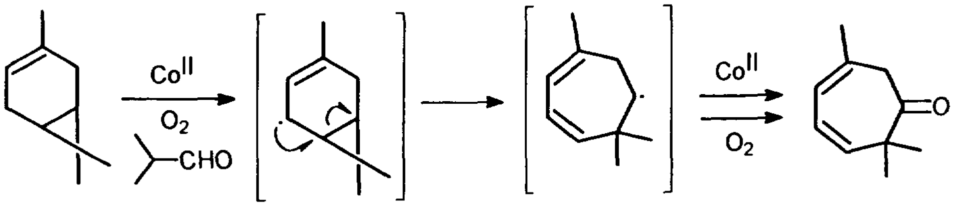
| Entry | Alkene | Product(s) Yield(%) | |
|---|---|---|---|
| | | Catalyst **1** | Catalyst **2** |
| 1 |  | <br>(72) | <br>(50) |
| 2 |  | <br>(52) | <br>(51) |

whereas a mixture of allylic alcohols were obtained when reaction was performed using catalyst **2** (table 1, entries 2 and 3). The latter reaction also afforded ~40% of unidentifiable products. Interestingly, 3-carene underwent ring enlargement followed by oxygenation to give cycloheptadienone as the major product in the presence of catalyst **2** while usual epoxidaton was observed with catalyst **1** (table 1, entry 4). Surprisingly, oxidation of limonene did not exhibit any difference in chemoselectivity using catalyst **1** or **2** as the corresponding epoxide was obtained as the sole product under the catalysis by either of these catalysts (table 1, entry 5). On the other hand the difference in the product formation in catalysis under the aegis of **1** or **2** is observed during oxidation of camphene and longifolene as the corresponding epoxides are obtained using **1** whereas catalyst **2** promotes the formation of corresponding carboxylic acid as the major product (table 2, entries 1 and 2). Surprisingly, catalyst **1** also showed some tendency for allylic oxidation during the oxidation of stigmasteryl acetate as it afforded the α- epoxide as the major product in addition to small amount of the enone (Scheme 2). It is interesting to note that the double bond in the

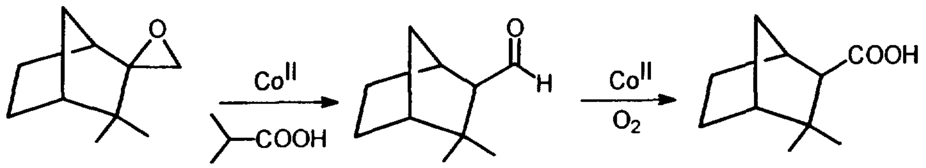


**Scheme 2**

side chain remains unaffected under these conditions. The oxidative rearrangement of 3-carene to cycloheptadienone may be initiated by allylic radical rearrangement to give cycloheptadiene radical which subsequently incorporates the dioxygen to give enone via a Haber-Weiss process (eq. 1). The formation of carboxylic acid under catalysis by **2** from camphene or longifolene may be explained by a rearrangement of the initially formed epoxide to give aldehyde which is subsequently oxidized to the carboxylic acid in the presence of cobalt catalyst and dioxygen (eq. 2).



(eq. 1)



(eq. 2)

The difference in the chemoselectivity in these oxidations is apparently due to the effect of ligand around cobalt in catalyst **1** and **2**. The diverse nature of complex **1** (charged) and complex **2** (neutral) may be responsible for the formation of various reactive species (i.e., $O_2^{\cdot}$, $O_2^{-}$, $O_2^{2-}$ etc.) thereby resulting in different chemoselectivity. We are currently studying the effect of ligands in order to tune the reactivity of these catalysts.

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3. Catalyst **1** was prepared by reacting $CoCl_2$ (1 equiv.) and Schiff's base ligand (derived from 2-pyridine carboxaldehyde and ethylenediamine) (1 equiv.) in acetonitrile at ambient temperature under nitrogen atmosphere.

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