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A Versatile Cobalt(II)-Schiff Base Catalyzed Oxidation of Organic Substrates with Dioxygen: Scope and Mechanism

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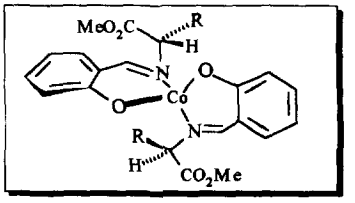
Abstract: Cobalt(II) complex **1a-f** derived from Schiff bases act as efficient catalysts during the oxidation of wide range of organic substrates(e.g. alkenes, alcohols, benzylic compounds and aliphatic hydrocarbons) with dioxygen in the presence of aliphatic aldehydes or ketones or ketoesters. EPR studies on **1a-f** complexes suggest that the aliphatic carbonyl compounds promote the formation of a cobalt(III)-superoxo species responsible for the oxidation of organic compounds. These studies also demonstrate the role of ligands on cobalt in controlling the chemoselectivity of these oxidations. A plausible mechanistic rational is also provided for these oxidations. © 1997 Elsevier Science Ltd.

Introduction

Oxidation of organic molecules by oxygen activation has attracted the attention[1-11] of organic and inorganic chemists over the last few decades. The impetus for these studies is provided by an urge to understand various oxidation reactions that are involved in many fundamental biological processes[1,12] such as energy transformation and storage, as well as biosynthesis of aminoacids, hormones, etc. Several model studies using transition metal complexes have been reported in an attempt[13-23] to mimic various mono and dioxygenases enzymes. These studies have engaged the attention of synthetic chemists a great deal and their efforts have culminated in providing a deeper insight into the intricacies involved during oxygen activation and its subsequent transfer to organic molecules.



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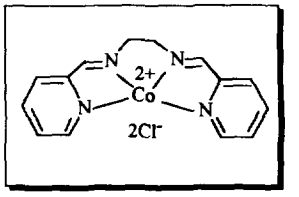
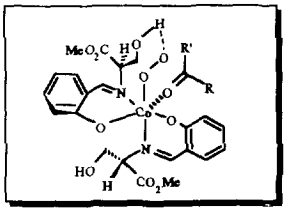


1f

R= -CH_2OH **(a)**
-CH_2Ph **(b)**
-CH_2Ph 4'-OH **(c)**
-$CH(CH_3)_2$ **(d)**
-$CHCH_3OH$ **(e)**



1g

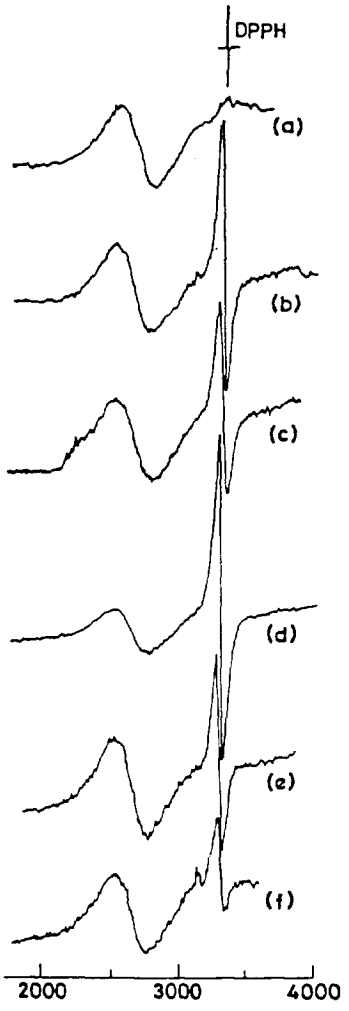


Fig. 1. EPR spectra at ambient temperature in CH_3CN and dioxygen. [a] Catalyst **1a** *(g_{iso} =2.5201) after 1h. [b] Catalyst* **1a** *and aldehyde* **8b** *(g_{iso} =2.0149) after 1.5 h. [c] Catalyst* **1a** *and aldehyde* **8a** *(g_{iso} =2.0112) after 2.5h. [d] Catalyst* **1a** *and ketoester* **8e** *(g_{iso} =2.0187) after 1.5h. [e] Catalyst* **1a** *and ketoester* **8d** *(g_{iso} =2.0189 after 2.5h. [f] Catalyst* **1a** *and cyclohexanone (g_{iso} =2.0 110) after 1.5 h.*

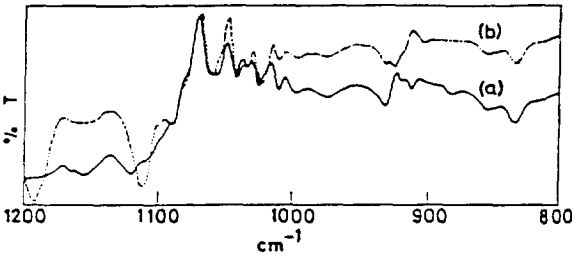


Fig. 2. IR spectra of catalyst **1a** *and ester* **8e** *at ambient temperature in CH_3CN and dioxygen. [a] After 10 min. [b] After 2.5 h.*

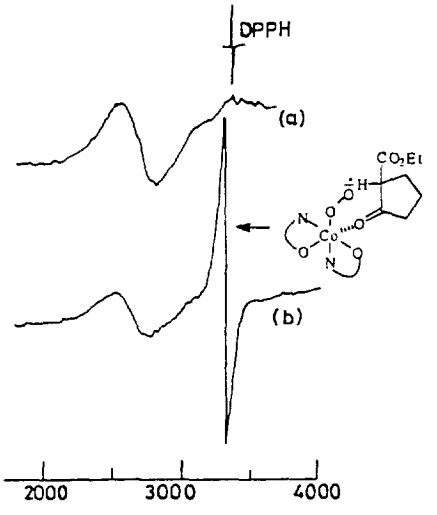


Fig.3. EPR spectra at ambient temperature in CH_3CN and dioxygen. [a] Catalyst **1b** *and ester* **8e** *(g_{iso}=2.5201) after 2.5 h. [b] Catalyst* **1a** *and ester* **8e** *(g_{iso}=2.0187) after 2.5 h.*

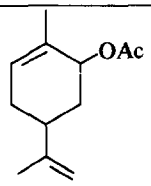
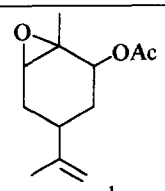
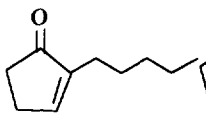
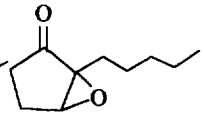
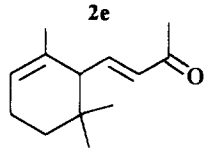
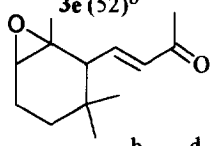
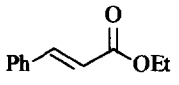
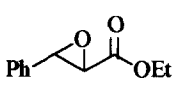
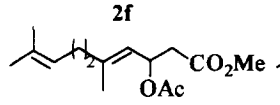
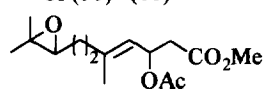
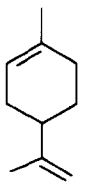
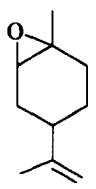
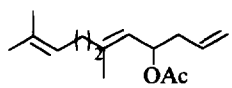
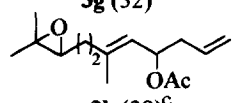
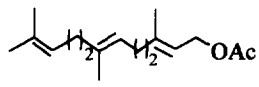
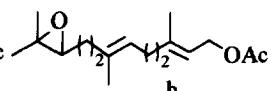
Cobalt(II) Schiff base complexes are known to bind dioxygen in the presence of an axial donor ligand. In their pioneering studies Basolo and coworkers[24] have established that monomeric cobalt(III)-dioxygen adducts are formed in the presence of strong coordinating ligands like substituted pyridine and DMF. They have also shown that these ligands occupy the axial position of the resulting octahedral complex arising due to dioxygen capture. It is known that four coordinated cobalt(II) complexes are very poor dioxygen binders whereas corresponding five coordinated complexes readily bind dioxygen at ambient pressure of oxygen. The binding of an axial fifth ligand leads to a square pyramidal geometry which raises the d_z^2 orbital above to d_{xy} and the latter configuration is known to be necessary prerequisite for oxygenation. The latter studies have indicated that other basic ligands also encourage the formation of monomeric dioxygen adduct. In view of the fascinating chemistry associated with cobalt(III)-dioxygen complex, we have undertaken a study on the formation and the reactivity of monomeric cobalt(III)-dioxygen complexes. We now demonstrate that aliphatic aldehydes and ketones can also act as a good ligand to the cobalt(II) Schiff base complexes in promoting the formation of monomeric cobalt(III)-dioxygen complexes.

Results and Discussion

We have earlier shown[25] that certain ketoester and aldehydes promote the oxidation of alkenes and alcohols with dioxygen in the presence of catalytic amount of cobalt(II) Schiff base complexes. These carbonyl compounds help in the formation of cobalt(III)-dioxygen complex and subsequently act as a reducing agent[26] during oxygen atom transfer to organic substrates. We have carried out extensive EPR study on these reactions and found that the cobalt(II) complex **1a** forms a monomeric adduct of dioxygen in the presence of certain ketones and aldehydes. Thus mixing an equal amount of catalyst **1a** and aldehyde or ketone in acetonitrile under ambient oxygen pressure gives initially the EPR signal at 2662 G (g_{iso} 2.5021) due to cobalt(II) complex as the reaction progresses a new sharp EPR signal appears at ~ 3332 G whose formation could be due to the capture[27] of dioxygen by cobalt(II) complex. The EPR spectra of the cobalt(III)-dioxygen adduct in the presence of different aldehydes and ketones are shown in figure 1 and it is clearly evident that aliphatic aldehydes and cyclic ketones encourage the formation of the monomeric dioxygen complex whose presence is clearly inferred from the appearance of the sharp signal at ~3332 G. The appearance of this sharp signal is a clear indication of the formation of an oxygen centered radical of the type Co-O-O·. The intensity of this signal also reflects the extent of coordination to the metal center by the carbonyl group. Thus it is evident that 2-methylpropanal **8b** (Fig. 1b) and β-ketoester **8e** (Fig. 1d) encourage, a great deal, the formation of monomeric cobalt(III)-dioxygen complex. It is interesting to note that no EPR signal at ~3332 G is observed in the absence of carbonyl compound. The formation of cobalt(III)-superoxo complex is also revealed[28] by IR spectra of the reaction mixture. Thus in the presence β-ketoester **8e** the initial IR spectrum (Fig. 2a) changes to the spectrum (Fig. 2b) after 2.5 h where absorption at 1195 cm^{-1} strongly suggests the presence of a Co-O-O· species.

The strong tendency of catalyst **1a** to form cobalt(III)-dioxygen complex appears to be due to the stabilization of cobalt(III)-dioxygen adduct **1g** by hydrogen bonding between the OH proton of ligand and the terminal oxygen atom of the bound dioxygen (Fig. 3a). This becomes quite obvious by comparing the EPR of **1a** with a structurally similar catalyst devoid of OH group i.e. **1b**, in the presence of β-ketoester **8e** (Fig. 3b). Thus, the EPR recorded under these conditions for catalyst **1a** shows the sharp signal after 1.5 h whereas no such signal is observed in case of **1b** even after 2.5 h, however, for the latter catalyst the sharp signal at ~3332 G appears only after 5 h (Fig. 3). This clearly reveals that hydrogen bonding in catalyst **1a** encourages the formation of monomeric cobalt(III)-dioxygen complex and this makes **1a** an efficient oxygen transfer agent. A similar stabilization of dioxygen by hydrogen bonding has recently, been reported by Chang and coworkers[29] on related Cobalt(II) porphyrin systems. A recent report by Harris and Loew[30] has shown that iron(III) dioxygen complex in P450*cam* is also stabilized by the hydroxy group of threonine.

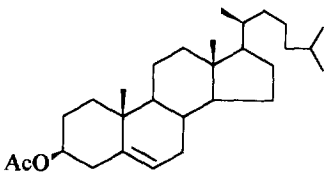
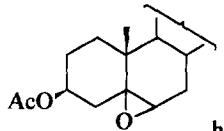
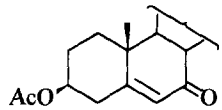
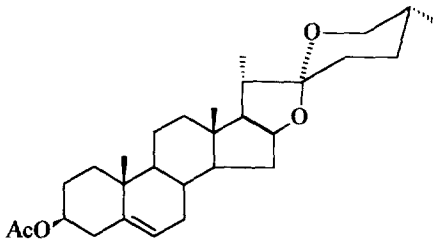
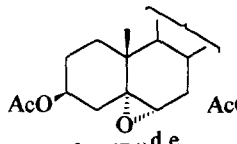
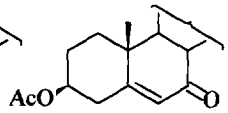
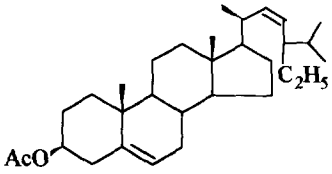
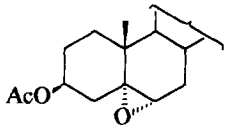
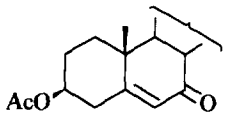
Table 1. Cobalt(II) Catalysed Epoxidation of Alkenes with Dioxygen

Entry	Alkene	Products (yield %)[a]	Entry	Alkene	Products (yield %)[a]
1	 **2a**	 **3a** (66)[d]	5	 **2e**	 **3e** (52)[b]
2	 **2b**	 **3b** (49)[d]	6	 **2f**	 **3f** (50)[b] (66)[d]
3	 **2c**	 **3c** (68)[d]	7	 **2g**	 **3g** (32)[c]
4	 **2d**	 **3d** (53)[c](54)[d]	8	 **2h**	 **3h** (28)[c]
			9	 **2i**	 **3i** (32)[b]

[a]*Isolated yield.* [b]*Catalyst* ***1a*** *and 2-methylpropnal* ***8b*** *were used.* [c]*Catalyst* ***1a*** *and ketoester* ***8e*** *were used.* [d]*Catalyst* ***1f*** *and* ***8b*** *were used.* [e]***8b*** *and* ***8e*** *were oxidised to isobutyric acid* ***13*** *and tertiary alcohol* ***12*** *respectively.*

The reactivity of different alkenes in the presence of catalysts **1a** and **1f**[31] , and 2-methylpropanal **8b** or β-ketoester **8e** are presented in table 1 and according to this protocol, alkenes are epoxidized readily in a highly regioselective manner. Thus, methyl styrene **2a**, cyclopentenone derivative **2b** and ethyl cinnamate **2c** afforded good yield of epoxides in the presence of catalyst **1f** and 2-methylpropanal (Table 1, entries 1-3). A highly regioselective epoxidation of cyclic dienes **2d-f** can also be achieved by catalyst **1a** or **1f** under these reaction conditions to give the corresponding monoepoxides **3d-f** respectively. Interestingly, no diepoxide was observed in any of these reactions (Table 1, entries 4-6) and the ring double bond were epoxidized exclusively. The acyclic diene **2g** and trienes **2h-i** underwent monoepoxidation in the presence of catalyst **1a** in moderate yields (Table 1, entries 7-9). It is interesting that the highly substituted double bond was epoxidized exclusively.

Table 2. Cobalt(II) Catalyzed Epoxidation with 2-Methylpropanal in the Presence of Dioxygen

Entry	Alkene	Catalyst	Products (Yield, %)[a]
1	 **2j**	**1a**	 **3j:3k** (α:β) (3:1) (81)[b]
2		**1a**	**3j:3k** (α:β) (3:1) (77)[c]
3		**1f**	**3j** (α) (72)[d,e]  **3l** (16)
4	 **2k**	**1f**	 **3m** (74)[d,e]  **3n** (10)
5	 **2l**	**1f**	 **3o** (71)[d,e]  **3p** (19)

[a] *Isolated yield.* [b] *Catalyst* ***1a*** *and* ***8b*** *were used.* [c] *Catalyst* ***1a*** *and* ***8e*** *were used.* [d] *Catalyst* ***1f*** *and* ***8b*** *were used.* [e] *Only the trace of the corresponding β-diastereomer was obtained.*

without formation of any di or triepoxide and apart from monoepoxide the unreacted diene or triene were isolated from the reaction mixture. *The oxidized product derived from aldehydes are the corresponding mixture of carboxylic acid 13 and anhydride whereas β-ketoester 8e gives rise to the tertiary alcohol 12 as the byproduct during this epoxidation. However, the quantification of these byproducts could not be achieved due to the over oxidation and loss during aqueous sodium bicarbonate work up. It is also noteworthy that inspite of the chiral nature of catalysts 1a-e, no enantioselectivity was observed during expoxidations.*

Epoxidation of steroids was also undertaken by using catalysts **1a** and **1f** under these reaction conditions (Table 2). Accordingly, cholesteryl acetate **2j** can be transformed to the corresponding epoxide **3j** and **3k** as 3:1 mixture of diastereomers[32] in which the α-epoxide **3j** was found to be major isomer (Table 2, entry 1). There was no difference in the diastereomeric ratio by changing the carbonyl compounds from **8b** to **8e** (Table 2, entry 2). Surprisingly, the epoxidation of **2j** in the presence of catalyst **1f** gave the corresponding α-epoxide **3j** as the major product along with a trace of β-epoxide **3k** and in addition to the α-epoxide **3j** a small amount of the corresponding enone **3l** was also formed under these conditions (Table 2, entry 3). Similarly, diosgenin acetate **2k** was transformed to a mixture of α-epoxide **3m** and enone **3n** in good yields (Table 2, entry 4) and once again a trace amount of the corresponding β-epoxide was detected in this reaction. In a similar way the selective epoxidation of Stigmasterol acetate **2l** can be achieved in the presence of **1f** to give a mixture of α-epoxide **3o** and enone **3p** (Table 2, entry 5). It is note worthy that no epoxide arising due to the oxidation of chain double bond in Stigmasterol acetate **2l** was detected in the reaction mixture. The results obtained under the catalysis of **1a** and **1f** are quite interesting as the latter catalyzes an unusual allylic oxidation to give enones which is not observed in the case of former catalyst. The highly selective α-epoxidation in the presence of catalyst **1f** is also surprising for which no rational explanation is presently available.

Table 3. Epoxidation of Cholesteryl benzoate under Different Catalysts using Dioxygen

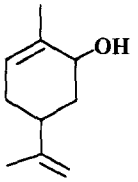
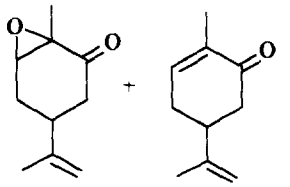
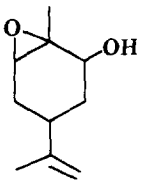
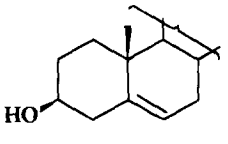
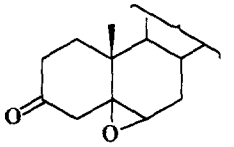
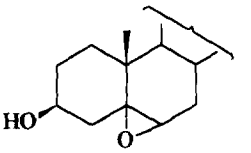
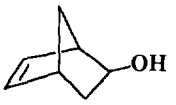
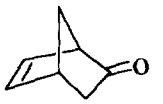
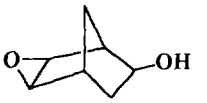
Entry	Catalyst	Epoxide (ratio α:β)	Ref.	Entry	Catalyst	Epoxide(ratio α:β)
1	Ni(dmp)	31:69	34	4	Co(II) **1a**	75:25[a]
2	Mn(dmp)	20:80	34	5	Co(II) **1f**	> 90:< 10[a]
3	Ru(TMP)(O_2)	< 10:> 90	35			

[a] *Ratio for the epoxidation of cholesteryl acetate.*

Similarly, the epoxidation[33] with molecular oxygen and 2-methylpropanal in the presence of a catalytic amount of metal ion nickel(II)[34], Mn(II)[34], or Ru(TMP)(O_2)[35]) led to the formation of the hindered 5,6-β-epoxide as the major product (Table 3, entries 1-3) whereas the less hindered 5,6-α-epoxide was obtained as the major product when Co(II) **1f** was used as catalyst. (Table 3, entry 5).

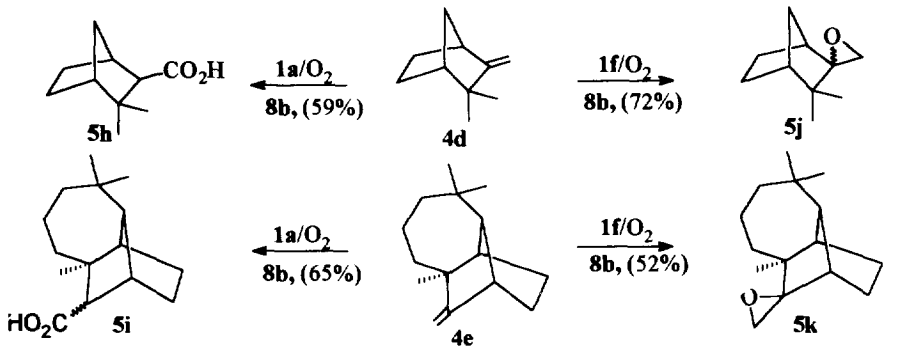
Catalysts **1a** and **1f** also show a remarkable difference in chemoselectivity during the oxidation of certain olefinic alcohols (Table 4). Thus, using catalyst **1a**, dioxygen and 2-methylpropanal **8b**, carveol **4a** can be oxidized to a mixture of epoxide **5a** and enone **5b** whereas the catalysis under **1f** selectively converts it to

Table 4. Cobalt(II) Catalysed Epoxidation of Alkenes with Dioxygen and 2-Methylpropnal

Entry	Alkene	Products (yield, %)[a,b]	
		Catalyst **1a**	Catalyst **1f**
1	 **4a**	 **5a** (28) **5b** (33)	 **5c** (36)
2	 **4b**	 **5d** (69), α:β (1:1)	 **5e** (49), α:β (1:4)
3	 **4c**	 **5f** (43)	 **5g** (76)

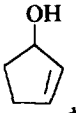
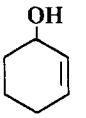
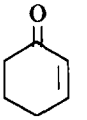
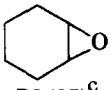
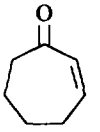
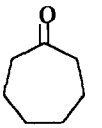
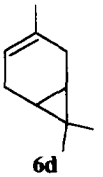
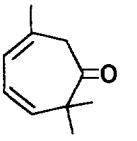
[a] *Isolated yield.* [b] *2-Methylpropanl* ***8b*** *was oxidized to carboxylic acid* ***13*** *as byproduct.*

the corresponding epoxy alcohol **5c** (Table 4, entry 1). This result demonstrates that catalyst **1a** gives rise to an active oxygen species which reacts with both alcohol and double bond functionality whereas **1f** provides a species which selectively reacts with double bond. Cholesterol **4b** also exhibits a similar behavior in the presence of catalyst **1a** or **If** as indicated by its conversion to the corresponding epoxy ketone **5d** in the presence of **1a** and epoxy alcohol **5e** under the aegis of **1f** (Table 4, entry 2). Norborneol **4c** is oxidized to the ketone **5f** in the presence of catalyst **1a** whereas the corresponding epoxy alcohol **5g** is obtained in the presence of **1f** (Table 4, entry 3). Interestingly, camphene **4d** is directly transformed to a diastereomeric mixture of the carboxylic acid **5h** in the presence of **1a** whereas the corresponding epoxide **5j** can be obtained as a mixture of diastereomers if **1f** is used as the catalyst (Scheme 1). A similar behavior is observed with longifolene **4e** which can be oxidized to the corresponding diastereomeric mixture of carboxylic acid **5i** under the influence of catalyst **1a** whereas the diastereomeric mixture of longifolene epoxide **5k** is the major product under the catalysis of **1f** (Scheme 1). Oxidation of cyclic alkenes can also be catalyzed by **1a**, **1b** and **1f** . It is interesting to note that allylic oxidation of cyclic alkenes is the predominant path in the presence of catalyst **1a**, 2-methylpropanal or β-ketoester **8e** and dioxygen. As indicated in table 5, cyclopentene **6a**, cyclohexene **6b** and cycloheptene **6c** were oxidized to a mixture of the corresponding allylic alcohols **7a**,**7b** and enones **7c**, **7f** respectively in good yields (Table 5, entries 1-2 and 5). A similar behavior is also exhibited in the presence of



Scheme 1

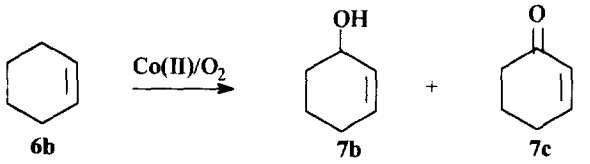
Table 5. Cobalt Catalyzed Allylic Oxidation in the Presence of Dioxygen and 2-Methylpropanal

Entry	Alkene	Catalyst	Products (Yield, %)[a,e]
1	 6a	1a	 7a (71)[d]
2	 6b		 7b 65(1:2)[d]  7c
3		1b	70(1:2)[d]
4		1f	 7d (87)[c] 7c (13)[c]
5	 6c	1a	 7e 67(1:3)  7f
6	 6d	1f	 7g(35)[f]  7h(35)[f](68)[d]

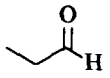
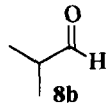
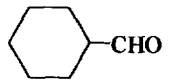
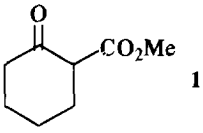
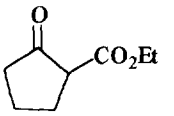
[a]Isolated yield. [b]Ratio determined from ^{1}H NMR. [c]GC. yield. [d]8e was used as reducing agent. [e]8b and 8e were oxidised to carboxylic acid 13 and tertiary alcohol 12 respectively. [f]Yield obtained in the presence of 1f and 2- methylpropanal.

catalyst **1b** (Table 5, entry 3). On the other hand, no allylic oxidation of cyclohexene is observed in the presence of catalyst **1f** however, high yield of cyclohexene oxide **7d** is obtained under these conditions (Table 5, entry 4). 3-Carene **6d** underwent allylic oxidation followed by rearrangement to give cycloheptadienone **7h** as a major product in the presence of catalyst **1a** and β-ketoester **8e** whereas if 2-methylpropanal is used as reducing agent, a mixture of 3-carene epoxide **7g** and cycloheptadienone **7h** were obtained (Table 5, entry 6). The reactions presented in table 5 provide very attractive chemoselectivity by merely changing the ligand around cobalt and this difference may be arising due to the formation of different active oxygen species. It is also evident from these results that reducing agents e.g. **8b** or **8e** also have some influence on the outcome of the reactions as noticed during the oxidation of 3-carene (Table 5, entry 6).

Table 6. Oxidation of Cyclohexene in the Presence of Dioxygen and Different Carbonyl compounds



6b **7b** **7c**

Entry	Carbonyl compound	Catalyst	Products[a,b,c] ratio **7b** : **7c** (Yield%)
1	 **8a**	**1a**	(1:2) (55)
2	 **8b**	**1a**	(2:1) (72)
3	 **8c**	**1a**	(3:2) (33)
4	 **8d**	**1a**	(2:1) (68)
5	 **8e**	**1a**	(2:1) (65)
6		**1b**	(1:2) (53)
7		**1d**	(2:3) (59)
8		**1e**	(1:3) (57)

[a] Isolated yield. [b] Ratio determined from ^1H NMR spectra. [c] Aldehydes and ketoesters are transformed to carboxylic acids 13 and tertiary alcohols 12 respectively.

Oxidation of cyclohexene has been carried out in the presence of different carbonyl compounds and cobalt catalyst **1a**, **1b**, **1d** and **1e** and in each case a mixture of cyclohexenol **7b** and cyclohexenone **7c** were obtained (Table 6). It is noteworthy that the oxidation of cyclohexene in the presence of catalyst **1a** is highly facilitated by aldehydes **8a-c** which act as reducing agent (Table 6, entries 1-3). The cyclic ketoester **8d** also act as an efficient reducing agent in the presence of catalyst **1a** to afford a mixture of cyclohexenol and

cyclohexenone in good yields (Table 6, entry 4). On the other hand the reactions using β-ketoester **8e** are comparatively slower, however, the yield of the products are not very different in either of these cases (Table 6, entries 1-5). β-Ketoester **8e** also acts as a good reducing agent in the presence of catalyst **1b**, **1d**, and **1e** and as indicated the ratio of alcohol **7b** and enone **7c**, and the chemical yields are not very different from reactions described in entries 5-8 (Table 6). It is clearly evident from the results in table 6, that aldehydes **8a-c** and β-ketoester **8d-e** perform a very efficient role as reducing agent during the oxidation of cyclohexene using dioxygen and cobalt(II) catalysts.

Table 7. Cobalt(II) Catalysed Benzylic Oxidations in the Presence of Dioxygen

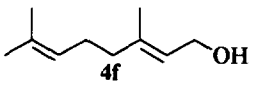
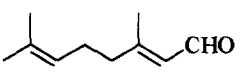
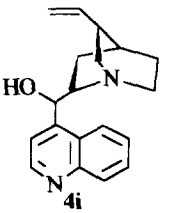
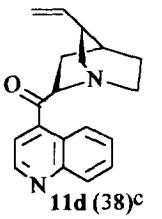
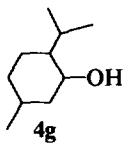
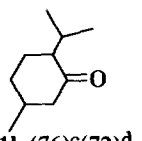
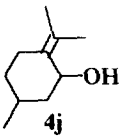
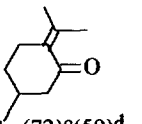
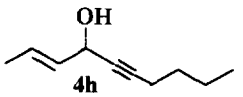
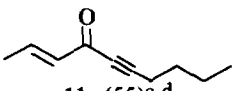
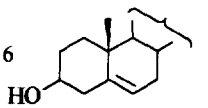
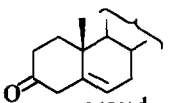
Entry	Benzylic compound	Products (yield, %)[a,c]	Entry	Benzylic compound	Products(yield, %)[a,c]
1	Diphenylmethane (**9a**)	Benzophenone (**10a**) (69)[b,c] (62)[d]	6	Tetralin (**9f**)	Tetralone (**10f**) (61)[c] (88)[d]
2	Ethylbenzene (**9b**)	Acetophenone (**10b**) (45)[b,c] (70)d	7	Indane (**9g**)	Indanone (**10g**) (70)[d]
3	Propylbenzene (**9c**)	Propiophenone (**10c**) (75)[d]	8	Indene (**9h**)	2-Indanone (**10h**) (42)[b,d]
4	Fluorene (**9d**)	Fluorenone (**10d**) (66)[b,c] (51)d	9	Isopropylbenzene (**9i**)	Acetophenone (**10b**) (39)[d]
5	Cyclohexylbenzene (**9e**)	Cyclohex-1-ene-benzene (**10e**) (47)[b,c]	10	Dibenzylether (**9j**)	Benzoic acid (**10j**) (80)[d]

*[a]HPLC yield. [b]Isolated yield. [c]Catalyst **1a** and **8e** were used. [d]Catalyst **1c** and **8b** were used. [e]**8b** and **8e** were transformed to carboxylic acid **13** and tertiary alcohol **12** respectively.*

Benzylic substrates **9** are also oxidized to the corresponding ketones **10** under the influence of catalyst **1a** or **1c**, reducing agent and dioxygen (Table 7). Thus, diphenylmethane **9a**, ethylbenzene **9b**, propylbenzene **9c** and fluorene **9d** were oxidized to the corresponding ketones **10a-d** respectively in the presence of catalyst **1a** and β-ketoester **8e** under dioxygen atmosphere (Table 7, entries 1-4). Same transformation can also be achieved in the presence of catalyst **1c** and 2-methylpropanal. Cyclohexyl benzene **9e** can be oxidized to cyclohex-1-ene benzene **10e** by using catalyst **1a** and β-ketoester **8e** (Table 7, entry 5). Tetralin **9f** is oxidized to tetralone **10f** by using catalyst **1a** or **1c**, however, better yields were obtained in the presence of latter catalyst (Table 7, entry 6). In a similar fashion, indane **9g** underwent oxidation to indanone **10g** in the presence of catalyst **1c** and 2-methylpropanal (Table 7, entry 7). Surprisingly, indene **9h** gave 2-indanone **10h** under the influence of catalyst **1c** whereas isopropyl benzene **9i** gave acetophenone **10i** (Table 7, entries 8-9). The latter reactions may be proceeding via initial oxidation of benzylic position followed by α-cleavage whereas the product arising from the former reaction may be obtained by the rearrangement of the initially formed epoxide. Dibenzyl ether **9j** underwent complete oxidation in the presence of catalyst **1c** to give benzoic acid **10j** in good yields (Table 7, entry 10).

Catalyst **1a** is also very efficient in oxidizing primary and secondary alcohols to the corresponding aldehydes and ketones respectively in the presence of 2-methylpropanal or β-ketoester **8e** and dioxygen (Table 8). It is noteworthy that during oxidation of geraniol **4f** only the alcohol oxidation is observed and no product arising due to the oxidation of double bond was isolated (Table 8, entry 1). Similarly, menthol **4g** was smoothly oxidized to the corresponding carbonyl compound **11b** using either **8b** or **8e** (Table 8, entry 2). The alkyne alcohol **4h** was also selectively oxidized to the corresponding ketone **11c** without any observable oxidation of triple or double bonds (Table 8, entry 3). Cinchonine **4i** was also selectively oxidized in moderate yield to the corresponding carbonyl compound **11d** (Table 8, entry 4). The cyclic allylic alcohol **4j** was smoothly oxidized to the corresponding ketone **11e** using **8b** or **8e** as reducing agent (Table 8, entry 5). In the same fashion, cholesterol **4b** can be oxidized to the corresponding carbonyl compound **11f** (Table 8, entry 6).

Table 8. Cobalt(II) Complex 1a Catalyzed Oxidation of Alcohols with Dioxygen

Entry	Alcohol	Products(yield, %)[a,e]	Entry	Alcohol	Products(yield, %)[a,e]
1	 **4f**	 **11a** (47)[b,d]	4	 **4i**	 **11d** (38)[c]
2	 **4g**	 **11b** (76)[c](72)[d]	5	 **4j**	 **11e** (72)[c](59)[d]
3	 **4h**	 **11c** (55)[c,d]	6	 **4b**	 **11f** (52)[d]

*[a]Isolated yield. [b]HPLC yield. [c]**8b** was used as reducing agent. [d]**8e** was used as reducing agent. [e]**8b** and **8e** were transformed to carboxylic acid **13b** and alcohol **12** respectively.*

oxidation of alkenyl alcohols clearly indicates that the alcoholic group is more prone to oxidation than double bond under these reaction conditions. However, concomitant oxidation of alcohol and double bond may be achieved under the catalysis of **1a** if 2-methylpropanal is used as reducing agent (Table 4, entry 2). This difference in the outcome of the reactions on changing the reducing agents is not surprising and it may be attributed to the formation of different active oxygen species by using reducing agents with different stereo electronic environment.

We have conducted the oxidation of some organic substrates and their yields have been determined based on alkene and carbonyl compounds. Thus Cholesteryl acetate in the presence of catalyst **1a** and 2-methylpropanal **8b** gave the product **3j** and **3k** in 81% based on alkene whereas yield of these epoxides are 30% based on carbonyl compound **8b**. A similar epoxidation of D-limonene with 2-methylpropanal **8b** and catalyst **1f** afforded **3d** in 50% yield based on alkene whereas the yield becomes 22% when based on carbonyl compound. Similar epoxidation of D-limonene using catalyst **1a** and cyclic ketoester **8e** affords the corresponding epoxide 54% yield based on alkene, whereas it becomes 25% based on carbonyl compound (Table 9, entries 2-3). A similar trend is also observed with 3-carene with catalyst **1a** and cyclic ketoester **8e** where the yields of epoxide are higher when calculated from alkene as compared with that from **8e**. This studies thus, indicate that aldehyde is also undergoing oxidation to carboxylic acids, where alkenes do not undergo any other oxidation apart from epoxidation.

Table 9. Oxidation of Various Organic Substrates Catalysed by Cobalt Complexes

Entry	Alkene	Carbonyl compound	Catalyst	(Yield, %)	Entry	Alkene	Carbonyl compound	Catalyst	(Yield, %)
1	Cholesteryl acetate **2j**	**8b**	**1a**	(**3j** & **3K**) 81^a 30^b	3	**2d**	**8e**	**1a**	(**3d**) 54^a 25^b
2	D-Limonene **2d**	**8b**	**1f**	(**3d**) 50^a 22^b	4	3-Carene **6d**	**8e**	**1a**	(**7h**) 68^a 27^b

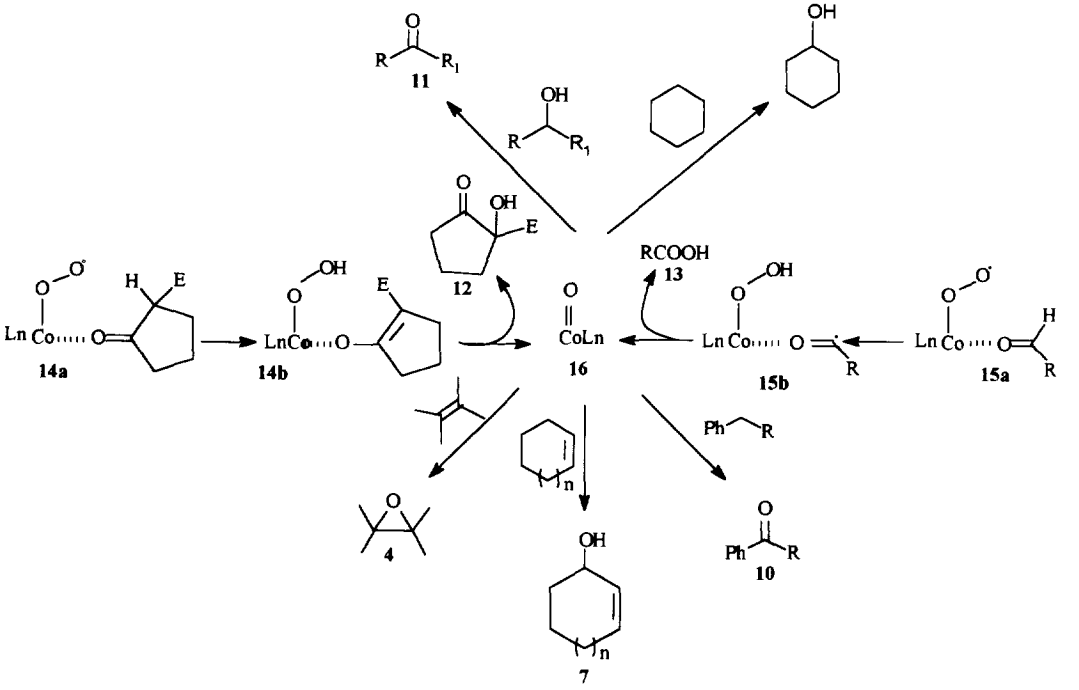
[a]Yield based on alkene. [b]Yield based on carbonyl compound. These reactions were carried out according to the general procedure in the experimental section.

Mechanism

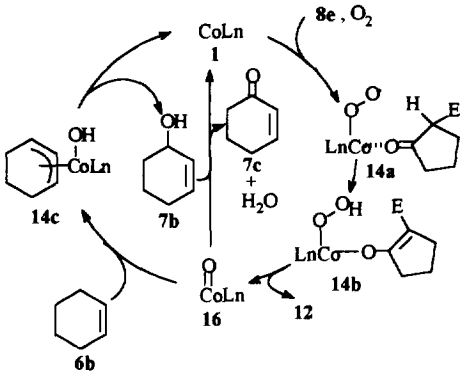
The mechanism of these reactions may have some similarities with that of cytochrome P-450 reactions where the presence of iron (IV)-oxo species has been proposed by Groves and coworkers[36]. The EPR studies on these reactions indicate that cobalt(III)-superoxo complex **1g** is formed initially by the assistance of carbonyl compounds and the sequential oxygen atom transfer from **1g** to carbonyl compound and an organic substrate (alkene, benzylic substrates etc.,) may be initiated by an intramolecular[37] hydrogen atom transfer from carbonyl compound to the terminal oxygen atom of bound dioxygen in complex **1g** (Scheme 2). The resulting cobalt enolate **14b** or complexed acyl radical **15b** may undergo an intramolecular hydroxylation to give the tertiary alcohol **12** or carboxylic acid **13** respectively and a highly reactive cobalt(IV)-oxo intermediate **16** where the latter species may transfer oxygen atom to organic substrates to give oxidized products (Scheme 2).

The intermediacy of this reactive species can also be inferred from the fact that wide range of organic substrates like alcohols, alkenes, benzylic substrates can be oxidized under these reaction conditions. The allylic oxidation of alkenes is known to proceed via metal catalyzed autoxidation process, however, in the present reactions it seems to be following a different pathway. It is observed that these reactions do not occur

using catalytic amount of **8e**, however, as we increase the quantity of **8e** then the allylic and benzylic oxidations proceed quite smoothly. Thus, in the oxidation of cyclohexene, increasing the quantity of **8e** from 0.1 equiv to 1 equiv, we see a considerable increase in the yields of **7b** and **7c**. Further increase in the yield of **7b** and **7c** were also observed by using 2 equiv of **8e**, the formation of enone **7c** is more than that of alcohol **7b**. When the oxidation of cyclohexene was carried out in the presence of radical trap *i.e. 2, 4, 6-tritertiarybutylphenol*, no inhibition of product formation was observed. This observation also rules out the occurrence of this reaction via metal catalyzed autoxidation or Fenton process. Thus, during the oxidation of cyclohexene, the reactive cobalt(IV)-oxo complex **16** may abstract an allylic hydrogen atom to provide allylic alcohol via the complex **14c** (Scheme 3). Since allylic alcohol is prone to oxidation by **16**, this would require more of the latter complex (i.e. **16**) in order to achieve higher conversion of alkene to the corresponding alcohol or enone. Due to this competitive reaction (allylic oxidation versus alcohol oxidation) more of **16** will be consumed which in turn would require more of **8e** for high yield of conversion of alkene to alcohol or ketone . Thus, the dependence of **8e** on the overall yield of this reaction may be understood if we invoke the formation of **16** as the reactive species analogous to latter has already been proposed by Kochi and coworkers[38] during the cobalt catalyzed epoxidation of alkenes by iodosyl benzene. Oxidative rearrangement of 3-carene may be initiated by allylic radical rearrangement to give cycloheptadiene radical which subsequently incorporates the dioxygen to give ketone **7h** via Haber-Weiss process.



Scheme 2



Scheme 3

The difference in the chemoselectivity during the epoxidation of cyclic alkenes under the influence of catalyst **1a** or **1f**, may be mainly due to the presence of different active oxygen species. Thus, the allylic oxidation of cyclic alkenes catalyzed by complex **1a** may be occurring due to the formation of **1g** which gives rise to a cobalt(IV)-oxo intermediate as the active species. On the other hand, complex **1f** may give rise to the formation of a peracid from aldehyde and dioxygen. Alternatively, catalyst **1f** may give rise to a hydrogen peroxide anion type of species which being nucleophilic will epoxidise α, β-unsaturated carbonyl compounds (Table 1, entries 4-5). Moreover unlike **1a** the EPR spectrum of catalyst **1f** does not show the formation of a cobalt(III) superoxo complex with dioxygen in the presence of carbonyl compound which again indicates that the catalyst **1f** gives rise to a different active species, which may be arising due to the difference between the geometry of complex **1a** and **1f**.

Table 10. Cobalt Catalysed Oxidation of Hydrocarbons in the Presence of Dioxygen and 2-Methylpropanal

Entry	Hydro-carbon	Conver-sion(%)[a]	Products	Yield (%)[c]	Entry	Hydro-carbon	Conver-sion(%)[a]	Product	Yield (%)[c]
1	Cyclo-hexane **17**	17	Cyclohexanol **18a** 21 Cyclohexanone **18b** 79		3	Methylcyclo-hexane **17c**	20	1-Methyl-cyclohexanol **18e**	70
2.	Cyclo-octane **17b**	13	Cyclooctanol **18c** 33 Cyclooctanone **18d** 67		4	Benzene **17e**	21[b]	1,4-Benzo-quinone **18g**	71[b]
					5	Anthra-cene **17f**	65[b]	9,10-Anthra-quinone **18h**	67[b]

[a]*Determined by GC analysis.* [b]*Determined by HPLC analysis.* [c]*Determined by GC analysis based on converted substrate.*

Finally, the presence of cobalt(1V)-oxo species **16** is also supported by the oxidation of cyclic aliphatic hydrocarbons under these conditions. Thus, cyclohexane can be converted into a mixture of cyclohexanol and cyclohexanone in 1:4 ratio whereas cyclooctane afforded a 1:2 mixture of the corresponding alcohol and ketone in moderate yields (Table 10, entry 1-2). Methyl cyclohexane can also be oxidized to give 1-methyl cyclohexan-1-ol as the major product, however, the reaction mixture also consisted of some unidentifiable products (~15%) (Table 10, entry 3). Similarly, benzene and anthracene can also be oxidized to the corresponding quinones under these conditions (Table 10, entries 4 and 5).

Thus it appears that the oxidation of hydrocarbons by **1a** is analogues to the oxidation of hydrocarbon by cytochrome P-450 model systems where the active oxygen species has been proposed to be an iron(IV)-oxo intermediate. This similarity in the two reactions lends credence to our proposal that cobalt(II) complex **1a** catalyzed oxidation with dioxygen are also proceeding via the intermediacy of an active cobalt(IV)-oxo **16** species.

In conclusion, the forgoing studies have demonstrated that cobalt(II) Schiff base complex **1a** reacts with dioxygen in the presence of certain ketone or aliphatic aldehyde or ketoester to give a cobalt(II) superoxo complex which leads to a reactive cobalt(IV)-oxo species by the reducing action of carbonyl compounds and it is this reactive species which is responsible for oxidation of wide range of organic molecules like alkene, alcohol, benzylic substrates, hydrocarbons etc. The results described here also indicate that the ligands around cobalt play very important role towards the formation of active oxygen species on interaction with dioxygen as evidenced from the diverse reactivity profile exhibited by catalysts **1a** and **1f.** These studies have also demonstrated that the cobalt(III)-superoxo complex can be stabilized by intramolecular hydrogen bonding as shown for catalyst **1a** and that is why latter is very versatile in catalyzing the oxidation of a wide range of organic substrates.

Experimental Section

Materials and Methods. Acetonitrile and acetic anhydride were purified[39] by the standard procedures. $CoCl_2$ was purchased from LOBA India Ltd., Bombay, and dried at 110^0 C for 3-4 h prior to use. Column chromatography was performed by using ACME silica gel (60-120 mesh). Aldehydes and alkenes were purchased commercially and purified prior to use. β-Ketoesters **8d-e** were prepared[40] by the standard procedure commercially. ^{1}H NMR spectra were recorded at 60, 80, and 400 MHz in CCl_4, $CDCl_3$. UV-vis spectra were recorded on Perkin-Elmer Lambda-2 spectrophotometer. HPLC was carried out on Shimadzu LC-6A liquid chromatography. GC was carried on 5765 Nucon Gas Chromatography. EPR spectra were recorded on Varian-100 series spectrophotometer in acetonitrile at ambient temperature. Magnetic moment (μ_{eff}) was calculated by Evans Method[41]. Mass spectra were recorded on a JEOL SX 102/DA-6000 spectrometer. Elemental analysis was conducted using a Coleman automatic C, H, and N analyzer. All the known compounds were characterized by comparison with the data from the literature.

[Bis(salicylidene-N-(methyl 3-hydroxypropionate)] cobalt (1a). L-serine methyl ester hydrochloride (0.79g, 5 mmol), anhydrous triethylamine (0.56g, 5.5 mmol) and salicylaldehyde (0.61g, 5 mmol) were stirred in ethyl alcohol (30 mL) for 5 h at 20^0 C. Triethylamine hydrochloride was filtered and the solvent was evaporated in

vacuum, the residue was purified by column chromatography eluting with acetonitrile to afford salicylidene-N-(methyl 3-hydroxypropionate) as red colored oil (0.86g, 77%): ^{1}H NMR ($CDCl_3$) δ 8.2 (s, 1H), 7.2-6.5 (m, 5H), 4.0-3.6 (m, 4H), 3.6 (s, 3H); IR (neat) 3450, 1720 cm^{-1}. The colored oil (0.56g, 2.5 mmol) was dissolved in dry acetonitrile (15 mL) and reacted with cobalt(II) chloride (0.16g, 1.25 mmol) under nitrogen atmosphere for 12 h at ambient temperature. Removal of the solvent in vacuum afforded **1a** (0.44g, 70%) as green colored powder. The geometry of **1a** was found to be tetrahedral based on UV-vis data and magnetic momen[t41,42] studies. UV-vis(CH_2Cl_2) λ_{max} 615, 632, 644 nm; μ_{eff} 4.58 μ_B (lit[41,42] μ_{eff} 4.59-4.77 μ_B); IR(CH_3CN) 3400, 1730 cm^{-1} ; MS (m/e) 504 (M^++1), 503(M^+) , 281, (100), 224, 77, 57.

[Bis(salicylidene-N-(methyl 3-phenyl propionate)] cobalt (1b). L-Phenylalanine methyl ester hydrochloride (1.08g, 5 mmol) was stirred with saturated bicarbonate solution (pH=7) in chloroform (20 mL) for 1 h at 0^0 C. The organic layer was separated and dried over anhydrous sodium sulfate. Removal of the solvent in vacuum gave the free ester which was stirred with salicylaldehyde (0.61g, 5 mmol) in ethyl alcohol (10 mL) for 3 h at 20^0 C. Removal of the solvent in vacuum followed by column chromatography eluting with ethyl acetate-hexane (1:4) yielded salicylidene-N-(methyl 3-phenyl propionate) (1.10g, 78%) as yellow colored oil: ^{1}H NMR ($CDCl_3$) δ 8.2(s, 1H), 7.3-7.0(m, 5H), 7.0-6.4(m, 5H), 4.0(t, 1H, J=6.0 Hz), 3.6(s, 3H), 2.5(d, 2H, J=6.5 Hz); IR (neat) 1720, 1620 cm^{-1}. The yellow colored oil (0.71g, 2.5 mmol) was dissolved in anhydrous acetonitrile(15 mL) and reacted with cobalt(II) chloride (0.16g, 1.25 mmol) according to the above reaction conditions to give **1b** (0.60g, 78%) as green colored powder. The geometry of **1b** was found to be tetrahedral based on UV-vis data and magnetic moment[41,42] studies: UV-vis ($ClCH_2CH_2Cl$) λ_{max} 613, 632, 664 nm; IR(CH_3CN) 1720 cm^{-1} ; μ_{eff} 4.60 μ_B (lit[41,42] μ_{eff} 4.59-4.77 μ_B); Conductivity (CH_3CN) 25 mΩ cm^2 mol^{-1} ; MS (m/e) 623 (M^+), 341 (100), 283, 282, 120, 77.

[Bis(salicylidene-N-(methyl 3-{4'hydroxy phenyl}propionate))] cobalt (1c). Triethylamine (0.75g, 7.5 mmol) was added drop wise to tyrosine methyl ester hydrochloride (1.16g, 5 mmol) in ethyl alcohol (20 mL) and the resulting mixture was stirred for 0.5 h after this salicylaldehyde (0.61g, 5 mmol) was added and the stirring was continued for 12 h at ambient temperature. Removal of solvent gave the residue which on treatment with water yielded yellow colored solid which was crystallized in ethyl alcohol to give salicylidene-N-(methyl-3-(4'-hydroxy phenyl propionate)) (1.14g, 77%): ^{1}H NMR ($CDCl_3$) δ 8.2(s, 2H), 7.3-7.0(m, 5H), 7.0-6.5(m, 4H), 4.0(t, 1H, J=6.0 Hz), 3.6 (s, 3H), 2.5 (d, 2H, J=6.5 Hz); IR (neat), 3335, 1730, 1620 cm^{-1} ; mp 170-172^0 C. The yellow colored solid (0. 74g, 2.5 mmol) and cobalt(II) chloride (0.16g, 1.25 mmol) were subjected to the above reaction conditions for 12 h to give **1c** (0.74g, 90%) as green colored powder. The geometry of **1c** was found to be tetrahedral based on UV-vis data and magnetic moment[41,42] studies: UV-vis(CH_3CN) λ_{max} 613, 630, 664 nm; IR(CH_3CN) 3335, 1720 cm^{-1} ; μ_{eff} 4.51 μ_B (lit[41,42] μ_{eff} 4.59-4.77 μ_B); MS (m/e) 655 (M^+), 357,298, 77(100), 63, 51, 39.

[Bis(salicylidene-N-(methyl 3-methyl butanoate)] cobalt (1d). Salicylidene-N-(methyl 3-methyl butanoate) was prepared from L-valine methyl ester hydrochloride (0.84g, 5 mmol) and salicylaldehyde (0.61g, 5 mmol) in ethyl alcohol (10 mL) as described for salicylidene-N-(methyl 3-phenyl propionate) as yellow colored oil after

purification on silica gel column chromatography (20% ethyl acetate in hexane): ^{1}H NMR ($CDCl_3$) δ 8.2 (s, 1H), 7.3-7.0 (m, 5H), 4.0 (d, 1H, J=6.5 Hz), 3.6 (s, 3H), 1.8-1.2 (m, 1H), 0.9 (d, 6H, J=6.0 Hz); IR (neat) 1730 cm^{-1}. The yellow colored oil (0.59g, 2.5 mmol) was dissolved in anhydrous acetonitrile (15 mL) and reacted with cobalt(II) chloride (0.16g, 1.25 mmol) according to the reaction conditions described for **1b** to give **1d** (0.48g, 72%) as green colored powder. The geometry of **1d** was found to be tetrahedral based on UV-vis data and magnetic moment[41,42] studies: UV-vis(CH_2Cl_2) λ_{max} 613, 629, 664 nm; IR(CH_3CN) 1720 cm^{-1} ; μ_{eff} 4.45 μ_B (lit[41,42] μ_{eff} 4.59-4.77 μ_B).

[Bis(salicylidene-N-(methyl 3-hydroxy butanoate)] cobalt (1e). L-Threonine methyl ester hydrochloride (0.85g, 5 mmol), anhydrous triethylamine (0.56g, 5.5 mmol) and salicylaldehyde (0.61g, 5 mmol) in ethyl alcohol (30 mL) were subjected according to the reaction conditions described for salicylidene-N-(methyl 3-hydroxy propionate) to afford salicylidene-N-(methyl 3-hydroxy butanoate) as yellow colored powder (0.89g, 75%) after purification on silica gel column chromatography (25% ethyl acetate in hexane): ^{1}H NMR ($CDCl_3$) δ 8.2 (s, 1H), 7.2-6.5 (m, 5H), 4.0-3.6 (m, 3H), 3.6 (s, 3H), 0.9 (d, 3H, J=6.5 Hz); IR (neat) 3450, 1720 cm^{-1} ; mp 180-182^0 C. The yellow colored solid (0.59g, 2.5 mmol) was dissolved in anhydrous aectonitrile (15 mL) and reacted with cobalt(II) chloride (0.16g, 1.25 mmol) as described for **1a** to give **1e** (0.50g, 75%) as green colored powder. The geometry of **1e** was found to be tetrahedral based on UV-vis data and magnetic moment[41,42] studies: UV-vis(CH_2Cl_2) λ_{max} 613, 632, 664 nm; IR(CH_3CN) 3450, 1720 cm^{-1} ; μ_{eff} 4.52 μ_B (lit[41,42] μ_{eff} 4.59-4.77 μ_B).

General Procedure for Epoxidation and Allylic Oxidation. Aldehyde or β-ketoester (10 mmol), alkene (5 mmol) and cobalt (II) complex (~5 mol%) were stirred in anhydrous acetonitrile (30 mL) at ambient temperature under dioxygen balloon for 20-35 h. The solvent was removed in vacuum and the residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was washed with saturated sodium bicarbonate solution (3x15 mL), brine solution (3x10 mL). Drying over anhydrous sodium sulphate and evaporation yielded residue which was subjected to silica gel column chromatography. Compounds **7a-f** characterized by comparing their NMR, IR, GC data with standard samples.

General Procedure for the Oxidation of Benzylic compounds and Alcohols. Aldehyde or β-ketoester (10 mmol), alcohol (in the presence of molecular sieves (4 A^0)) or benzylic compound (5 mmol) and cobalt(II) complex (~5 mol%) were stirred in anhydrous acetonitrile (40 mL) at ambient temperature for 20-24 h or at 50-60^0 C for 10-12 h under dioxygen balloon. Usual work-up gave the residue which was purified by silica gel column chromatography or analyzed by HPLC. Compounds **10a-j** (Table 7) and **11a-b**, **11e-f** (Table 8) were characterized by comparing their NMR, IR and HPLC data with standard samples.

General Procedure for Hydrocarbon Oxidation. Hydrocarbons **17** (40 mmol), aldehyde **8b** (80 mmol) and cobalt(II) complex **1a** (~5 mol%) were stirred at ambient temperature for 12-15 h under 1 atm of oxygen in acetonitrile (30 mL). Removal of solvent yielded the residue which was dissolved in ethyl acetate (30 mL) and successively washed with sodium bicarbonate (5 x 20 mL) and brine solution (3 x 15 mL). Drying over

anhydrous sodium sulphate and removal of the solvent in vacuum, gave the crude compounds **18** which was subjected to GC, HPLC analysis or distilled by kugelrohr distillation. Compounds **18a-h** (Table 10) were prepared by this procedure and characterized by comparing their NMR, IR, GC, HPLC data with standard samples.

2, 3-Epoxy-2-Pentylcyclopentanone (3b). Alkene **2b** (0.52g, 3.4 mmol), aldehyde **8b** (0.49g, 6.8 mmol) and cobalt complex **1f** (~5 mol%) were reacted according to the reaction conditions described in the general procedure for 24 h to give **3b** (0.28g, 49%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane): ^{1}H NMR ($CDCl_3$)δ 3.8-3.6 (m, 1H), 2.4-1.7 (m, 4H), 1.6-1.2 (m, 8H), 0.9 (d, 3H, J=6.0 Hz); IR (neat) 1740, 1260, 1240 cm^{-1} .

Ethyl 2,3-epoxy-3-phenylpropionate (3c). Alkene **2c** (1.41g, 8 mmol), aldehyde **8b** (1.15g, 16 mmol) and cobalt(II) complex **1f** (~5 mol%) were subjected to the reaction conditions described above for 12 h to yield **3c** (0.86g, 56%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane): ^{1}H NMR (CCl_4)δ 7.5-7.1 (m, 5H), 4.2 (q, 2H, J=6.0 Hz), 4.0 (d, 1H, J=2.0 Hz), 3.3 (d, 1H, J= 2.0 Hz), 1.2 (t, 3H, J=6.0 Hz); IR (neat) 1720, 1260, 1240 cm^{-1} .

1,2-Epoxy 1-methyl-4-(1-methylethenyl)cyclohexane (3d). Alkene **2d** (1.36g, 10 mmol), aldehyde **8b** and cobalt(II) complex **1f** (~5 mol%) were subjected to the above reaction conditions to afford **3d** as a liquid (0.82g, 54%) after purification on silica gel column chromatography (5% ethyl acetate in hexane): ^{1}H NMR (CCl_4) δ 4.6 (s, 2H), 3.0 (m, 1H), 2.5 (q, 1H, J=5.0 Hz), 2.1-1.5 (m, 7H), 1.3-1.1 (m, 5H); IR (neat) 3080, 1640, 1360, 1250, 1240 cm^{-1} .

4-(2,6,6-trimethyl 2,3-epoxy cyclohexane)-3-buten-2-one (3f). Alkene **2f** (0.96g, 5 mmol), aldehyde **8e** (0.72g, 10 mmol) and cobalt(II) complex **1a** (~5 mol%) were reacted according to the above reaction conditions for 17 h to afford **3f** (0.52g, 50%) as an oil after purification on silica gel column chromatography (5% ethyl acetate in hexane): ^{1}H NMR (CCl_4)δ 7.1-6.0 (dd, 2H, J=12 Hz), 2.1 (s, 3H), 1.9-1.2 (m, 6H), 1.1 (s, 3H), 1.1 (s, 3H), 1.0(s, 3H), 0.8 (s, 3H). IR (neat) 1670, 1620, 1375, 1250 cm^{-1}.

Methyl 3-acetoxy-5,9-dimethyl-8,9-epoxydeca-4-enoate (3g). Alkene **2g** (0.67g, 2.5 mmol), ketoester **8e** (0.78g, 5 mmol) and cobalt(II) complex **1a** (~5 mol%) were subjected to the above described reactions conditions to provide **3g** (32%) as an oil. ^{1}H NMR ($CDCl_3$)δ 5.7-6.0(m, 1H), 5.1-5.4 (m, 1H), 3.7 (s, 3H), 2.6 (t, 1H, J=6.0 Hz), 2.05-2.3 (m, 4H), 2.1 (s, 3H), 1.7-1.9 (m, 2H), 1.6 (s, 3H), 1.1 (s, 3H), 1.0(s, 3H). IR (neat) 1735, 1375, 1250 cm^{-1}.

4-Acetoxy-6,10-dimethyl-9,10-epoxyundeca-1,5-diene (3h) was prepared as described above in 28% yield and characterized[25k] by comparing with literature data.

1-Acetoxy-3,7,11-trimethyl-10,11-epoxy dodeca-2,6-diene (3i). Alkene **2i** (0.53g, 2 mmol), aldehyde **8b** (0.30g, 4 mmol) and cobalt(II) complex **1a** (~5 mol%) were reacted according to the reaction conditions described in the above procedure to give **3i** (0.18g, 32%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane): ^{1}H NMR (CCl_4) δ 5.5-4.9 (m, 2H), 4.4 (d, 2H, J=6.0 Hz), 2.5 (t,

1H, J=6.0 Hz), 2.2-1.9 (m, 11H), 1.6 (s, 3H), 1.5 (s, 3H), 1.1 (s, 3H), 0.9 (s, 3H); IR (neat) 1720, 1365, 1230 cm^{-1}.

Compounds 3j and 3l. Cholesteryl acetate **2j** (0.42g, 1 mmol) in 1,2-dichloroethane (5 mL), aldehyde **8b** (0.15g, 2 mmol) and cobalt(II) complex **1f** (~5 mol%) were stirred in acetonitrile (20 mL) according to the above reaction conditions for 15 h to give **3j**[25b] (0.32g, 72%) and **3l** (0.07g, 16%) after column chromatography over silica gel (5% ethyl acetate in hexane). Data for **3l**: ^1H NMR ($CDCl_3$) δ 5.7 (s, 1H), 5.0-4.8 (m, 1H), 2.5 (m, 1H), 1.9 (s, 3H), 2.1-0.6 (m, 40 H); IR(KBr) 1720, 1660 cm^{-1} ; MS (m/e) 383 (100), 55, 43; mp 146-148^0 C.

Compounds 3m and 3n. Diosgenin acetate **2k** (0.20g, 0.44 mmol) in 1,2-dichloroethane (5 mL), aldehyde **8b** (0.06g, 0.88 mil) and cobalt(II) complex **1f** (~5 mol%) were reacted according to the above reaction conditions to provide **3m** (0.15g, 75%) and **3n** (0.02g, 10%) after column chromatography over silica gel (5% ethyl acetate in hexane). Data for **3m**: ^1H NMR ($CDCl_3$) δ 5.0-4.5 (m, 1H), 4.5-4.2 (m, 1H), 3.6-3.2(m, 2H), 3.1-2.8 (m, 1H), 1.9 (s, 3H), 2.1-0.6 (m, 36H); IR(KBr) 1720, 1375, 1250 cm^{-1} ; mp 174-176^0 C.

Compounds 3o and 3p. Stigmasteryl acetate **2l** (0.30g, 0.66 mmol) in 1,2-dichloroethane (5 mL), aldehyde **8b** (0.1g, 1.3 mmol) and cobalt(II) complex **1f** (~5 mol%) were reacted according to the above reaction conditions to give **3o** (0.22g, 71%) and **3p** (0.06g, 19%) after column chromatography (5% ethyl acetate in hexane) as colorless solids. Data for **3o**: ^1H NMR ($CDCl_3$)δ 5.2-5.0 (m, 2H), 4.9-4.5 (m, 1H), 3.0 (m, 1H), 2.0 (s, 3H), 1.6-0.6 (m, 43H); IR(KBr) 1720, 1375, 1250 cm^{-1} ; MS (m/e) 471(M^+), 411, 105, 95, 83(100), 66, 55, 43; mp 137-139^0 C. Data for **3p**: ^1H NMR ($CDCl_3$)δ 5.8 (s, 1H), 5.2 (m, 2H), 5.0-4.7 (m, 1H), 2.5 (m, 1H), 2.0 (s, 3H), 1.6-0.6 (m, 40H); IR(KBr) 1720, 1660 cm^{-1} ; MS (m/e) 409 (100), 154, 136, 107, 91, 77, 69, 55, 51, 39 ; mp 152-154^0 C.

2,3-Epoxy-2-methyl-5-(1-methylethenyl)-cyclohexanone (5a). Alcohol **4a** (0.76g, 5 mmol), aldehyde **8b** (0.72g, 10 mmol), and cobalt(II) complex **1a** (~5 mol %) were subjected to the above reaction conditions for 24 h to give **5a** (0.23g, 28%) as an oil after silica gel column chromatography (5% ethyl acetate in hexane). ^1H NMR (CCl_4) δ 4.6 (s, 2H), 2.7-2.5 (t, 1H, J=6.0 Hz), 2.0-1.8 (m, 3H), 1.7 (s, 3H), 1.3-1.1 (m, 5H); IR(neat) 1715, 1360, 1240 cm^{-1}.

2,3-Epoxy-2-methyl-5-(1-methylethenyl)-cyclohexan-1-ol (5c). Alcohol **4a** (1.0g, 6.7 mmol), 2-methylpropanal (0.97g, 13.4 mmol) and cobalt(II) complex **1f** (~5 mol%) were reacted according to the above reaction conditions to afford **5c** (0.4g, 36%) as a liquid after silica gel column chromatography (10% ethyl acetate in hexane). ^1H NMR (CCl_4)δ 4.7 (s, 2H), 4.0-3.5 (m, 1H), 3.0 (m, 1H), 2.8-2.3 (m, 2H), 1.9-1.6 (m, 5H), 1.4-1.1 (m, 5H); IR(neat) 3440, 1370, 1250 cm^{-1} .

5,6-Epoxy Cholestenone (5d). Cholesterol **4b** (1.93g, 5 mmol), aldehyde **8b** (0.72g, 10 mmol) and cobalt(II) complex **1a** (~5 mol%) were reacted according to the above procedure for 25 h to afford **5d** (1.13g, 69%) after purification on silica gel column chromatography (10% ethyl acetate in hexane). ^1H NMR (CCl_4)δ 2.6-2.0 (m, 5H), 2.0-1.0 (m, 24H), 1.0-0.9 (m, 9H), 0.8 (s, 3H), 0.7 (s, 3H); IR(neat) 1715 cm^{-1} ; MS(m/e) 402 (M^+ +

1), 401 (M^+, 100), 133, 119, 105, 95, 81, 69, 55, 43, 29.

5,6-Epoxynorbornen-2-ol (5g). Alcohol **4c** (0.50g, 4.5 mmol), aldehyde **8b** (0.65g, 9 mmol) and cobalt(II) complex **1a** (~5 mol%) were reacted according to the above reaction conditions to afford **5g** (0.43g, 76%) as a liquid on silica gel column chromatography (10% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$)δ 4.4-4.1 (m, 1H), 3.4-3.0 (m, 2H), 3.0-2.6 (m, 2H), 2.5-2.2 (9m, 1H), 1.6-0.6 (m, 4H); IR(neat) 3400, 1375, 1250 cm^{-1}.

3,3,7-Trimethyl tricyclo[5.4.0.0] undecan-8-carboxylic acid (5i). Alkene **4e** (0.41g, 2 mmol), aldehyde **8b** (0.36g, 5 mmol) and cobalt(II) complex **1a** (~5 mol%) were reacted according to the above reaction conditions for 37 h to give **5i** (0.31g, 65%) as a solid after purification on silica gel column chromatography (3% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$)δ 11.0(s, 1H), 2.6-2.2 (m, 1H), 2.2-1.9 (m, 3H), 1.8-1.0 (m, 10H), 1.0 (s, 3H), 0.9 (s, 6H); IR(KBr) 3400, 1680 cm^{-1} ; MS(m/e) 236 (M^+), 219, 191, 135 (100), 109, 81, 55, 41, 29.

3-Epoxy 2,2-dimethylnorbornane (5j). Alkene **4d** (0.68g, 5 mmol), aldehyde **8b** (0.72g, 10 mmol) and cobalt(II) complex **1f** (~5 mol%) were subjected to the above reaction conditions for 12 h to afford **5j** (0.55g, 72%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane). ^{1}H NMR (CCl_4)δ 2.7 (s, 1H), 2.6 (s, 1H), 2.1-1.4 (m, 2H), 1.3-1.05 (m, 4H), 1.0-0.6 (m, 8H).

8-Epoxy-3,3,7-Trimethyltricyclo[5.4.0.0] undecane (5k). Alkene **4e** (0.51g, 2.5 mmol). aldehyde **8b** (0.36g, 5 mmol) and cobalt(II) complex **1f** (~5 mol%) were reacted according to the above reaction conditions for 15 h to give **5k** (0.28g, 51%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$)δ 2.6-2.2 (m, 2H), 2.2-1.9 (m, 3H), 1.8-1.0 (m, 10H), 1.0 (s, 3H), 0.9 (s, 3H), 0.8 (s, 3H); IR ($CDCl_3$) 1450, 1370 cm^{-1}

3,4-Epoxy-3,7,7-trimethylbicyclo[4.1.0]heptane (7g). Alkene **6d** (0.68g, 5 mmol), aldehyde **8b** (0.72g, 10 mmol) and cobalt(II) complex **1f** (~5 mol%) were reacted to the above reaction conditions to yield **7g** (0.36g, 47%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$)δ 2.9(m, 1H), 2.4-1.5 (m, 4H), 1.2(s, 6H), 0.8 (s, 3H), 0.5(m, 2H); IR(neat) 1370, 1250 cm^{-1}.

2,2-Dimethyl cyclohepta-3,5-diene-1-one (7h). Alkene **6d** (0.68g, 5 mmol), β-ketoester **8e** (7g, 7.5 mmol) and cobalt(II) complex **1a** (~5 mol%) were reacted according to the above reaction conditions for 40 h to give **7h** (0.51g, 68%) as a liquid after purification on silica gel column chromatography (3% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$)δ 6.3-5.6 (m, 3H), 2.7 (s, 2H), 2.0 (s, 3H), 1.2 (s, 6H); IR (neat) 1690, 1630 cm^{-1} ; UV-vis (MeOH) λ_{max} 267 nm.

2-Ene-5-enyne-4-oxo-decane (11c). 2-Ene-4-hydroxy-5-enyene decane **4h** (0.76g, 5 mmol), aldehyde **8b** (0.72g, 10 mmol) and cobalt(II) complex **1a** (~5 mol%) were subjected to the above reaction conditions to give **11h** (0.41g, 55%) as a liquid after purification on silica gel column chromatography (5% ethyl acetate in hexane). ^{1}H NMR (CCl_4)δ 7.2-6.6 (dq, 1H, J=6.4 Hz, J= 13.0 Hz), 6.0 (d, 1H, J=13.0 Hz), 2.2 (t, 2H, J=6.0 Hz), 2.0 (d, 3H, J=6.5 Hz), 1.7-1.0 (m, 4H), 0.9 (t, 3H, J=6.0 Hz); IR (neat) 2220, 1720, 1640 cm^{-1}.

Compound **11d.** Cinchonine **4i** (0.56g, 2 mmol), aldehyde **8b** (0.31g, 5 mmol) and cobalt(II) complex **1a** (~5 mol%) were subjected to the above described reaction conditions for 20 h to give **11d** (0.21g, 38%) as a liquid

after purification on silica gel column chromatography (15% ethyl acetate in hexane). ^{1}H NMR ($CDCl_3$) δ 8.1-7.6 (m, 6H), 6.2-5.8 (m, 1H), 5.1-5.0 (m, 2H), 3.6 (t, 1H, J=6.00), 3.1-2.8 (m, 4H), 2.6 (m, 1H), 2.3-1.8 (m, 5H); IR (KBr) 1690 cm^{-1}.

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