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Cobalt(II) Porphyrin : A Versatile Catalyst for the Oxidation of Organic Substrates with Dioxygen and 2-Methyl Propanal

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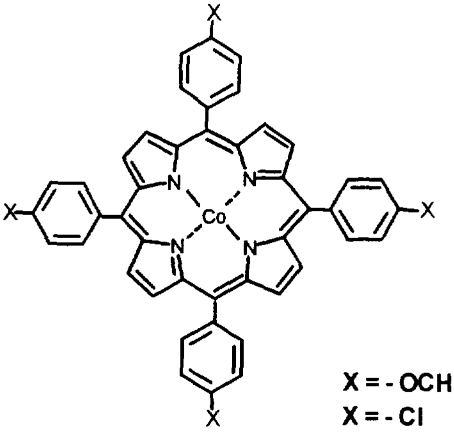
Abstract : *Cobalt(II)-porphyrin 1 is a versatile catalyst as it promotes the oxidation of wide range of organic substrates at ambient condition by using a combination of molecular oxygen and 2-methyl propanal.*

Metal catalysed oxidation of organic substrates is gaining importance as a viable alternative[1] to metal promoted stoichiometric oxidations. We have recently demonstrated that Co(II) Schiff's base complexes act as an effective catalyst in oxidising olefinic substrates in the presence of dioxygen[2,3] and an aldehyde. These catalysts are however only effective during oxidation of double bond or allylic oxidation. We now show that Co(II) porphyrin[4] complex **1** is extremely versatile in oxidising wide range of organic substrates by employing a combination of 2-methyl propanal and dioxygen. Following accounts describe the versatility of this catalyst.

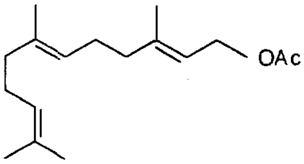
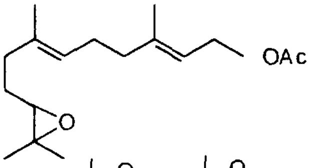
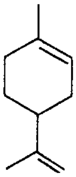
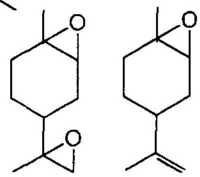
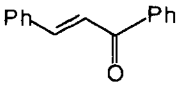
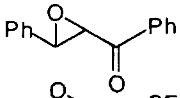
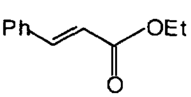
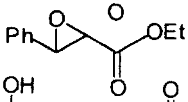
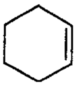
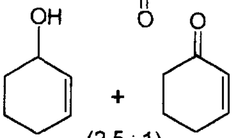
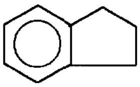
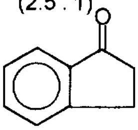
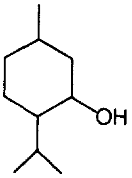
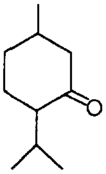
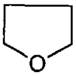
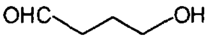
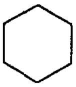
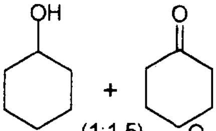
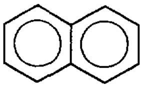
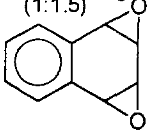


1

$X = -OCH_3$ (1a)
$X = -Cl$ (1b)
$X = -CH_3$ (1c)
$X = -O\underset{\underset{\displaystyle O}{\|}}{C}CH_3$ (1d)

Typically, Co(II) porphyrin catalyst **1** (5 mol%), organic substrate (1 mmol) and 2-methyl propanal (2 mmol) are taken in acetonitrile and the resulting mixture is stirred under oxygen balloon at room temperature for 3 hours. Aqueous work up followed by column chromatography or distillation afforded the corresponding product in moderate to good yields. According to this protocol, farnesyl acetate is oxidized to the corresponding monoepoxide in quantitative yields (Table 1, entry 1). It is interesting to note that chemoselective monoepoxidation of the farnesyl acetate is achieved as a careful analysis of reaction mixture

Table 1: Co(II) Porphyrin (1a) Catalysed Oxidation of Organic Substrates Using 2-methylpropanal

Entry	Substrate	Products[c]	Yield(%)[a,b]
1.			80
2.		 (2.3 : 1)	100[e]
3.			83
4.			51
5.		 (2.5 : 1)	81
6.			86[b]
7.			76
8.			94
9.		 (1:1.5)	26
10.			46

[a] Isolated yield. [b] Yield determined by HPLC. [c] Ratio determined from ^{1}H-NMR of the reaction mixture. [d] Crude yield (as this epoxide is very labile and decomposes during purification on column chromatography using silica gel). [e] Mixture of diastereomers are obtained.

showed the absence of any other regio-isomeric epoxide. The oxidation of limonene afforded a mixture of mono and diepoxide in quantitative yield (Table 1, entry 2). The diepoxide is always found to be major isomer in limonene oxidation. Interestingly the α-β unsaturated carbonyl compounds are also epoxidised under these conditions as chalcone and ethyl cinnamate are transformed to the corresponding epoxides in preparatively useful yields (Table 1, entries 3 & 4). The oxidation of cyclohexene afforded a mixture of cyclohexenol and cyclohexenone in good yields (Table 1, entry 5) and no trace of corresponding epoxide was observed in the reaction mixture. Similarly benzylic oxidation of indane afforded indanone in good yields (Table 1, entry 6). Even the secondary alcohol, menthol, was oxidised to the corresponding ketone according to this protocol (Table 1, entry 7). Interestingly tetrahydrofuran was also oxidised to the corresponding hydroxy aldehyde in quantitative yields (Table 1, entry 8). Surprisingly, even cyclohexane underwent oxidation to a mixture of cyclohexanol and cyclohexanone under these conditions (Table 1, entry 9). Naphthalene underwent oxidation to afford a labile diepoxide which decomposed on column chromatography and any attempt to purify it by other techniques proved futile (Table 1, entry 10).

Table 2: Co(II) Porphyrin Catalyzed Oxidation of Indane to Indanone using Molecular Oxygen

Entry	Catalyst	Yield (%)[a,b]
1.	1a	86
2.	1b	82
3.	1c	54
4.	1d	26

[a]Determined by HPLC analysis. [b]Reaction conditions : hydrocarbon (10 mmol), 2-methylpropanal (20 mmol) and ***1(a-d)*** *(~5 mmol%) were stirred in acetonitrile (15 ml) for 12-15h under dioxygen at r.t.*

We have also carried out the effect of substituents in the porphyrin ring during the oxidation of indane and cyclohexane. Interestingly, some substituent effect is observed during the oxidation of indane to indanone as indicated in table 2. Thus catalyst **1a** proved to be highly efficient during this oxidation giving rise to a high yield of indanone . Similarly, catalyst **1b** also proved quite efficient during this oxidation , to afford a high yield of indanone (Table 2, entry 2) . On the other hand catalyst **1c** & **1d** gave moderate to low yields of this product (Table 2, entries 3 & 4).

In a similar fashion the functionalization of cyclohexane could also be carried out by using catalyst **1a-d** under these conditions to afford a mixture of cyclohexanol and cyclohexanone respectively and in accordance with the previous observation , **1a** showed better catalytic activity during these oxidations. A slight improvement in the yields of oxidized products of cyclohexane can be obtained if these reactions are carried out under 1 atm pressure of dioxygen , and as the results in table 3 indicate **1a** proved to be more efficient than **1c-1d**, however there is no noticeable difference in the ratio of cyclohexanol and cyclohexanone during these oxidations. These observations suggest that substituents in the para position of aromatic ring in porphyrin plays quite an effective role during these oxidations and as indicated methoxy group appears to enhance the catalytic activity of **1a** during the oxidation of indane and cyclohexane.

Table 3: Co(II) Porphyrin Catalysed Oxidation of Cyclohexane with Molecular Oxygen

Entry	Catalyst	Conversion(%)[a] at ambient dioxygen pressure	Yield (%)[c,d,e] Cyclohexanol: Cyclohexanone	Conversion(%)[b] at 1 atm dioxygen pressure	Yield (%)[c,d,e] Cyclohexanol: Cyclohexanone
1.	1a	17	12(30:70)	41	26(44:56)
2.	1b	14	10(50:50)	31	24(39:61)
3.	1c	11	8(50:50)	25	20(50:50)
4.	1d	8	7(44:56)	19	16(40:60)

[a,b] *Determined by GC analysis.* [c] *Yield of the isolated products.* [d] *The ratio is determined by* ^{1}*H NMR analysis.* [e] *Reaction conditions : hydrocarbon (10 mmol), 2-methylpropanal (20 mmol) and* ***1(a-d)*** *(~5 mmol%) were stirred in acetonitrile (15 ml) for 12-15h under dioxygen at r. t.*

In conclusion, Co(II) porphyrin complex is a extremely versatile catalyst for the oxidation of alkenes, alcohols, aliphatic, benzylic and aromatic hydrocarbons by employing a combination of dioxygen and 2-methylpropanal at ambient conditions. Studies are in progress to delineate the mechanism of this reaction.

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