

Cobalt (II) Catalyzed Oxidation of Aldehydes to Carboxylic Acid with Molecular Oxygen

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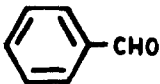
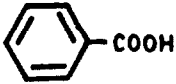


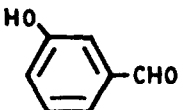
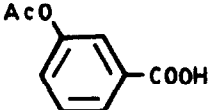
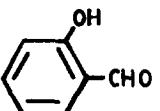
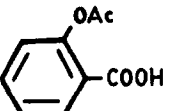
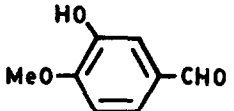
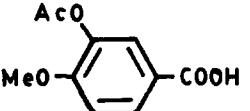
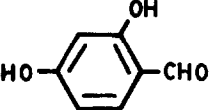
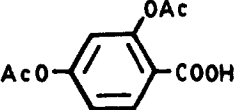

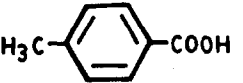

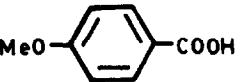
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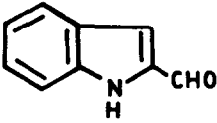
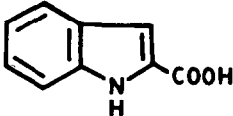
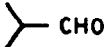
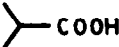
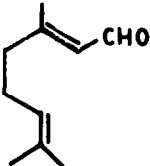
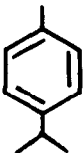
Key Words : Oxidation, Aldehydes, Molecular oxygen

Abstract : A variety of aromatic and some aliphatic aldehydes are efficiently transformed to the corresponding carboxylic acid in presence of catalytic amount of Cobalt (II) chloride, molecular oxygen and acetic anhydride at room temperature. Phenolic aldehydes undergo acylative oxidation to give the corresponding acylated carboxylic acid.

The propensity of cobalt complexes to bind¹ with molecular oxygen and the role of such dioxygen-cobalt complexes in the oxidation of various organic molecules² has been a subject of intensive research over the last several decades. These oxidations have been exploited in a controlled and synthetically useful³ manner to give rise to variety of oxidised organic molecules. The metal catalysed oxidation of aldehydes with molecular oxygen is well known, however, the synthetic potential of such transformation have scarcely been exploited. We have recently shown⁵ that cobalt complexes efficiently promote the incorporation of oxygen atom into various organic molecules using molecular oxygen under extremely mild condition. We now show that cobalt (II) chloride catalyses the oxidation of aldehydes to carboxylic acid in presence of molecular oxygen and acetic anhydride. Typically, dry cobalt (II) chloride (15 mg) was dissolved in dry dichloroethane (30 ml) and aldehyde (5 mmol), acetic anhydride (15 mmol) was added to the deep blue solution. The mixture was stirred under an oxygen balloon for 15-20 h at ambient temperature (25°C) and the progress of the reaction was monitored by TLC. Removal of dichloroethane gave a residue which was taken into ethyl acetate and the organic layer was washed with water and dried (MgSO₄). Purification by crystallization gave the carboxylic acid in very high yield (Table 1). A variety of aldehydes can be oxidised by this procedure and the phenolic aldehydes were also acetylated, besides oxidation, under these conditions⁶ to give the corresponding acylated carboxylic acids (entries, 2-6). Interestingly salicylaldehyde can be converted into aspirin by this procedure in high yields (entry, 4). The indole-aldehyde was smoothly transformed to the corresponding acid (entry,

Table: Cobalt(II) Chloride Catalysed Oxidation of Aldehydes to Carboxylic acids in presence of Molecular Oxygen and Acetic Anhydride

Entry	Aldehyde	Acid	Yield (%)
1.			41 %
2.			93 %
3.			79 %
4.			71.5 %
5.			73.2 %
6.			68.5 %
7.			62 %
8.			68 %

9.			72 %
10.			77 %
11.			22 %
12.	$C_6H_{13}^nCHO$	$C_6H_{13}^nCOOH$	35 %
13.			61 %

10) without the acetylation of the amino group. The aliphatic aldehydes were also oxidised under these conditions in moderate to good yields. However, the oxidation of citral gave p-cymene⁷ as one of the product and the reaction mixture was devoid of the corresponding carboxylic acid (entry, 13). p-Nitrobenzaldehyde and p-dimethylaminobenzaldehyde were recovered unchanged under these reaction conditions. These reactions can also be performed in benzene as solvent, however, no oxidation was observed in the absence of acetic anhydride in either of the solvents. Also the change of the reaction medium to more polar solvents (e.g., DMF or acetonitrile) did not bring about any oxidation of the aldehydes. However, phenolic aldehydes were acylated in DMF without affecting the aldehydic group.

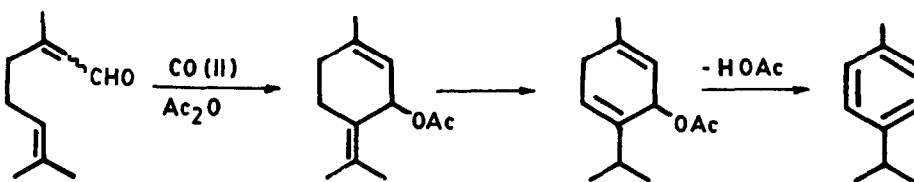
The role of acetic anhydride during this reaction is not clear at the moment although it is certain that its presence has a dominant effect on these oxidations. The mechanism of these reactions may have some similarity with that reported by Bawn and coworkers^{4b,c} for the metal catalyzed autooxidation of benzaldehyde and acetaldehyde. We are currently engaged in

the studies on the mechanistic aspects of these reactions.

In conclusion, cobalt (II) chloride catalyzed oxidation of aldehydes with molecular oxygen is a mild and efficient route to carboxylic acid whereas the acylative oxidation of phenolic aldehydes is a highly valuable method for a double functional group manipulation in one step.

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