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Cobalt-Catalyzed Selective Oxidation of Benzylic and Allylic Alcohols by Tert. Butyl Hydroperoxide

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COBALT-CATALYZED SELECTIVE OXIDATION OF BENZYLIC AND ALLYLIC ALCOHOLS BY tert. BUTYL HYDROPEROXIDE

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Abstract: The selective oxidation of benzylic and allylic alcohols by tert. BuOOH was catalysed by cobalt complexes.

The oxidation of primary and secondary alcohols to aldehydes and ketones is most frequently accomplished by the use of Group VI reagents in quantities ranging from stoichiometric to a large excess[1]. The oxidation of benzylic and allylic alcohols has also been achieved using tert. BuOOH in the presence of catalytic amount of CrO_3[2]. Kharasch and coworkers have demonstrated the oxidation of alcohols in alkaline media by tert. BuOOH in the presence of additives like

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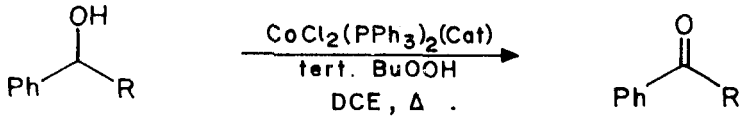
succinonitrile[3]. More recently the $RuCl_2(PPh_3)_3$[4] and $RhCl(PPh_3)_3$[5] catalysed oxidation of alcohols in the presence of tert. BuOOH has been reported. In addition to the use of precious metals, the Ru and Rh catalysed processes suffer from a parallel non productive decomposition of the tert. BuOOH which necessitates the slow addition of the reagent to the reaction mixture. The cleavage of tert. BuOOH by cobalt acetate and naphthenate has also been reported earlier[6]. So we decided to investigate the catalytic effect of cobalt phosphine complexes on the oxidation of alcohols by tert. BuOOH.

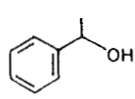
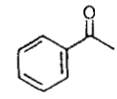
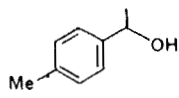
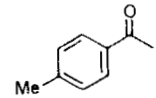
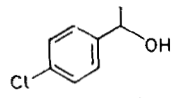
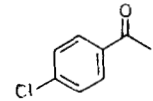
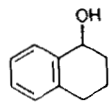
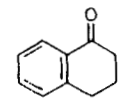
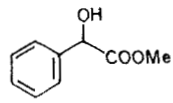
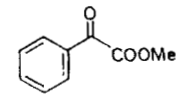
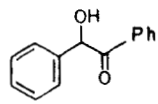
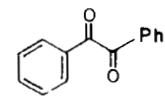
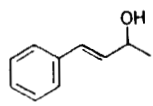
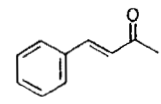
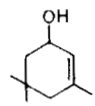
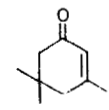
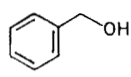
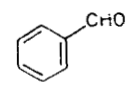
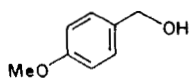
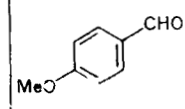
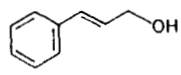
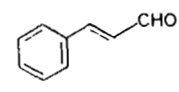
$CoCl_2(PPh_3)_2$ and $CoCl(PPh_3)_3$ can be easily prepared from $CoCl_2$[7]. In this communication we report the facile oxidation of allylic and benzylic alcohols in excellent yields by tert. BuOOH catalysed by these cobalt complexes. Table-1 lists the alcohols which undergo oxidation under these conditions.

SCHEME : I



R = H, Alkyl, Aryl, COOMe, COR', Vinyl

Table - 1 : $CoCl_2(PPh_3)_2$ catalysed oxidation of alcohols

Entry	Substrate	Time(h)	Product	Yield[b] (%)
1.		4·5		93
2.		4		95
3.		4		96
4.		5		78
5.		3		95
6.		2		80
7.		2·5		55[a]
8.		1·5		60[a]
9.		1·5		40
10.		1·5		40
11.		1·5		41

a = Catalyst $CoCl(PPh_3)_3$

b = Isolated yield

c = All products were characterised by IR & ^1H NMR

The reaction is selective for benzylic and allylic alcohols. Simple aliphatic and alicyclic alcohols were not oxidised under these conditions. Both mandelate ester and benzoin underwent oxidation in high yields. Other cobalt salts like $CoCl_2.6H_2O$ and $Co(OAc)_2$ were also effective for this reaction. Diphenylmethanol was oxidised to benzophenone at room temperature in presence of $CoCl(PPh_3)_3$ after 24 h.

The oxidation of benzyl alcohol and cinnamyl alcohol gave only 40-45 % yield of the corresponding aldehyde. About 40 % of the acid was also formed in both cases. $CoCl(PPh_3)_3$ proved to be a better catalyst for the oxidation of the allylic alcohols. While this work was underway there was a report on the $CuCl_2$/PTC catalysed oxidation of alcohols[8]. The use of PTC (Bu_4NBr) along with $CoCl_2.6H_2O$ similarly enables the oxidation of sec. phenethyl alcohol to acetophenone at room temperature in 24 h (74 % yield). Oxidation of benzyl alcohol on the other hand led only to the formation of acid and no aldehyde. While the use of PTC enables oxidation at lower temperature, simple refluxing of the reaction mixture enables the selective oxidation of benzylic and allylic alcohols without the use of PTC in shorter reaction times and in high yields.

In conclusion, $CoCl_2(PPh_3)_2$ serves as an excellent catalyst for the tert. BuOOH mediated selective oxidation of benzylic and allylic alcohols.

Experimental Procedure

In a typical experiment, 3 mMol of sec. phenethylalcohol, 6 mMol of tert. BuOOH (70 % solution), $CoCl_2(PPh_3)_2$ (7.5 mol %) were taken in 5 mL of dichloroethane and refluxed for 4-5 h. After the usual workup the product was purified by passing through a short column of silica gel.

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