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Effective oxidation of alcohols by Iron(III)-Schiff base-triphenylphosphine complexes

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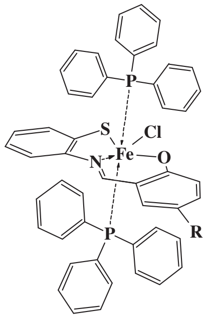
ABSTRACT

Iron(III)-Schiff base-triphenylphosphine complexes catalyze the oxidation of alcohols to their corresponding carbonyl compounds in presence of hydrogen peroxide in good yields.

The transformation of alcohols into aldehydes and ketones is of paramount importance in organic chemistry, both for laboratory scale experiments and in the manufacturing processes. Whereas the oxidation of primary and secondary alcohols into the corresponding aldehydes and ketones is a fundamental reaction in organic synthesis, still many oxidation processes use non-environmentally friendly oxidants.[1] In recent years, there has been an increasing need for search of catalytic oxidations with inexpensive green oxidants, such as molecular oxygen or hydrogen peroxide. Accordingly, several studies have been recently reported for the oxidation of alcohols with molecular oxygen or hydrogen peroxide catalyzed by transition metal salts or complexes of V,[2] Pd,[3] Mo,[4] Ru,[5] Co,[6] Cu,[7] etc. Though extensive research efforts have been invested in the development of many of these metal catalyzed reactions, there are only a few reports of using cheap and less toxic iron catalysts for the oxidation of alcohols to carbonyls so far.[8] In particular, iron-catalyzed reactions have several practical advantages over the analogous palladium or nickel-mediated reactions. The low cost and ample supply of iron salts coupled with their environmentally benign nature and lack of toxicity make them ideal for industrial scale synthesis of fine chemicals.

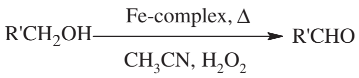
Very recently, we developed an efficient method for the selective oxidation of alcohols to the corresponding aldehydes and ketones using iron(III) complexes [**FeL$_1$**–**FeL$_4$**] containing triphenylphosphine and a Schiff base, *N*-(2-mercaptophenyl)salicylideneimine and its derivatives (Fig. 1) as a catalyst using periodic acid at ambient temperature in acetonitrile medium.[9] As a part of our ongoing research toward iron-catalyzed oxidation chemistry, herein, we report the catalytic oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds in good to high yields with iron(III) complexes using H_2O_2 in acetonitrile (Scheme 1). This procedure is very simple, mild, and clean and works efficiently without any additives.

The oxidation of benzyl alcohol, as a standard substrate, was first investigated in order to optimize the reaction variables such as solvent, temperature, alcohol/oxidant molar ratio, and length of the reaction time. We checked first the activity of **FeL$_1$** in



Complex	R
FeL$_1$	H
FeL$_2$	Cl
FeL$_3$	Br
FeL$_4$	NO$_2$

Figure 1. General structure of the complexes.



$$R'CH_2OH \xrightarrow[CH_3CN,\ H_2O_2]{Fe\text{-complex},\ \Delta} R'CHO$$

Scheme 1. Conversion of alcohols to carbonyl compounds.

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Table 1
Optimization of reaction conditions for oxidizing benzyl alcohol to benzaldehyde[a]

Entry	Amount of **FeL_1** (mmol)	Amount of oxidant (mmol)	Yield[b] (%) $CH_3CN–H_2O_2$ system
1	0	5.0	2.4
2	0.01	5.0	22.0
3	0.02	5.0	46.5
4	0.03	5.0	74.4
5	0.04	5.0	80.1
6	0.05	5.0	79.7
7	0.04	0	1.7
8	0.04	1.0	43.3
9	0.04	2.0	60.2
10	0.04	3.0	69.9
11	0.04	4.0	74.6
12	0.04	6.0	79.9

[a] 1 mmol benzyl alcohol, 10 mL CH_3CN, 90 min, 80 °C.
[b] GC yield, average of three trials.

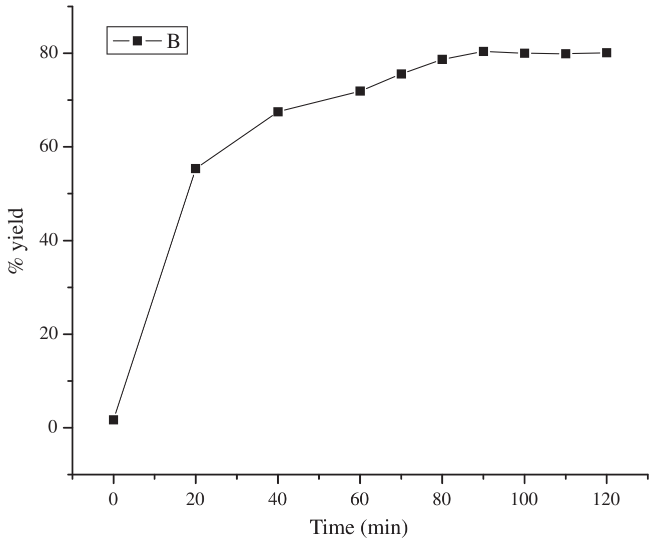


Figure 2. Effect of time on the yield of benzyl alcohol to benzaldehyde.

different solvents (methanol, acetonitrile, and acetone) with H_2O_2 as the oxidant. The best conversions have been observed in acetonitrile. The activity of **FeL_1** was studied at different temperature by taking benzyl alcohol as the model substrate in acetonitrile–H_2O_2 system. It was observed that at 80 °C, the system showed higher conversion. The optimization of other reaction conditions was studied by taking benzyl alcohol as substrate with **FeL_1** in acetonitrile–H_2O_2 system (Table 1). In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 2). It was observed that the yield remains constant after a reaction time of 90 min. The effect of the concentration of catalyst with respect to substrate was carried out at different substrate to catalyst ratios. A 0.04 mmol of catalyst was sufficient for the effective transformation of benzyl alcohol into benzaldehyde (Table 1, entry 5). The yield was insignificant when the reaction was carried in absence of catalyst (Table 1, entry 1). This observation reveals the catalytic role of iron(III) complexes. The reaction was studied at various substrates to oxidant ratios (Table 1). A minimum quantity of 5 mmol of the oxidant was necessary for the effective oxidation of benzyl alcohol to benzaldehyde (Table 1, entry 5). The catalytic activities of **FeL_2–FeL_4** in acetonitrile–H_2O_2 were carried out (Table 2).[10] From the Table 2, it is clear that the **FeL_1** in acetonitrile–H_2O_2 system showed good efficiency. The reported iron complexes in acetonitrile–H_2O_2 system are found to be more efficient compared with the reported work on iron complexes for the oxidation of alcohols to carbonyls.[8]

The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic, and cyclic alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Table 2. All the benzylic primary and secondary alcohols studied were oxidized smoothly to give aldehydes and ketones, respectively. Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols. All the reactions occurred with complete selectivity for ketones or aldehydes and no other products were detected in the reaction mixture. The over oxidation to carboxylic acid was ruled out by derivative test.

Table 2
Oxidation of alcohols catalyzed by Fe(III) complexes[a] in $CH_3CN–H_2O_2$ system

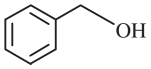
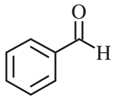
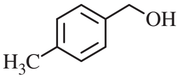
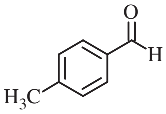
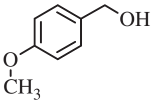
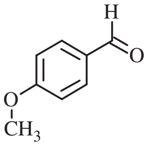
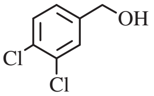
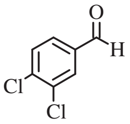
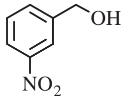
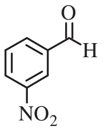
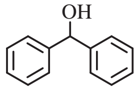
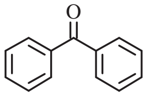
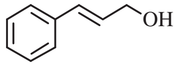
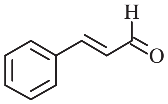
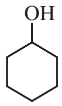
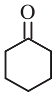
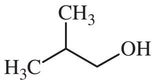
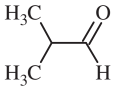
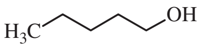
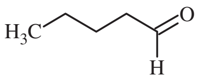
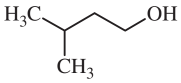
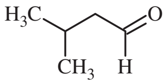
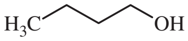
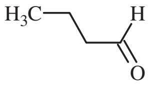
Alcohols	Product	Yield of carbonyl compound[b] (%)			
		FeL_1	**FeL_2**	**FeL_3**	**FeL_4**
		80.1	78.4	78.9	79.3
		79.5	77.5	78.2	78.6
		78.3	76.0	77.8	76.8
		82.6	81.2	81.7	82.0

Table 2 (*continued*)

Alcohols	Product	Yield of carbonyl compound[b] (%)			
		FeL$_1$	**FeL$_2$**	**FeL$_3$**	**FeL$_4$**
		79.7	77.2	76.3	77.8
		75.6	73.8	74.8	75.2
		71.9	70.8	71.4	69.8
		70.5	68.9	69.4	70.1
		36.8	33.6	35.2	36.1
		28.3	26.5	25.0	27.6
		23.1	20.6	22.6	22.9
		22.3	20.5	21.6	22.1

[a] 1 mmol alcohol, 5.0 mmol H_2O_2, 0.04 mmol **Fe**(III) complex, 10 mL CH_3CN, stirring at 80 °C.

[b] GC yield, average of three trials.

In conclusion, oxidation of alcohols using hydrogen peroxide, a mild oxidant, in the presence of catalytic amounts of synthesized iron(III) complexes provides a simple, safe, and efficient method for oxidation of aromatic alcohols to corresponding carbonyls with high yield.

References and notes

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9. Rani, S.; Bhat, R. B. *Inorg. Chem. Commun.*, doi:org/10.1016/j.inoche.2010.07.018.
10. Procedure: A solution of the complexes (0.04 mmol) in 10 ml acetonitrile was added to the solution of substrate (1 mmol) and H_2O_2 (5 mmol, 30%). The reaction mixture was stirred at 80 °C for 90 min. The residue was then extracted with a minimal volume of ether and dried over $MgSO_4$. The ether solution was then analyzed by GC using dichlorobenzene as internal standard.