

Cobalt (II) Schiff base catalyzed aerobic oxidation of secondary alcohols to ketones

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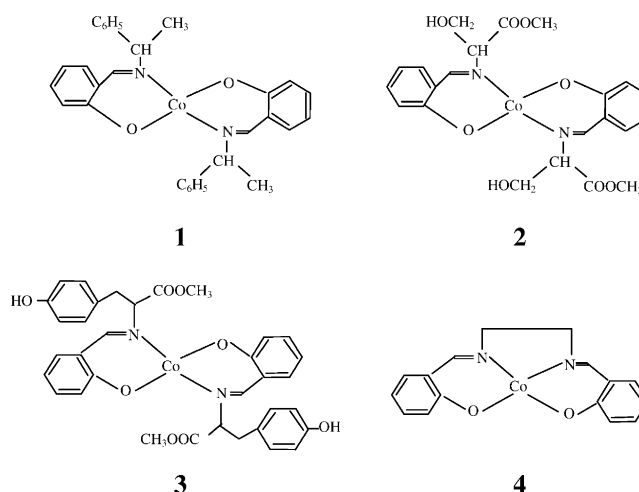
Abstract

A variety of secondary alcohols were efficiently oxidized to corresponding ketones in excellent yields with molecular oxygen using cobalt (II) Schiff base complexes as catalyst. In general, alcohols having a carbonyl moiety at their α -position were found to be more reactive and required lesser reaction time for their oxidation. While benzoin derivatives showed higher reactivity as compared to the acyloins, among the benzoin derivatives those having electron-donating groups were found to be more reactive. Among the various cobalt Schiff base complexes studied, bis[2-[(1-phenylethyl)imino]methyl]phenolato-*N,O*-cobalt (**1**) was found to be most efficient catalyst for this transformation.
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Keywords: Cobalt Schiff base complexes; Secondary alcohols; Ketones; Oxidation; Molecular oxygen

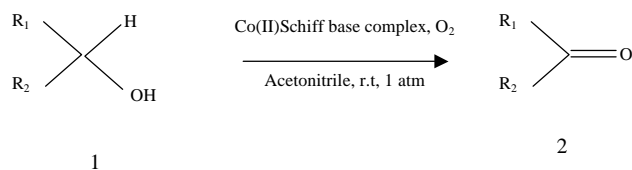
1. Introduction

The propensity of cobalt complexes to bind with molecular oxygen [1,2] and the use of such dioxygen–cobalt complexes as catalysts in various oxidation reactions has been a subject of intensive research in the recent years [3,4]. The dioxygen–cobalt complexes formed from cobalt complexes in presence of oxygen are known to catalyze a variety of organic reactions like oxidation of thiols [5], phenols [6,7], aldehydes [8,10] and hydrocarbons [11,12] involving hydrogen abstraction or one electron transfer. Cobalt Schiff base complexes; bis[2-[(1-phenylethyl)imino]methyl]phenolato-*N,O*-cobalt (**1**) [13], bis[methyl *N*-[(2-hydroxyphenyl)methylene]-L-serinato-*N,O*^N, O^{1'}]-cobalt (**2**) [14], bis[methyl *N*-[(2-hydroxyphenyl)methylene] L-tyrosinato-*N,O*^N]-cobalt (**3**) [15], [*N,N'*-bis(*o*-hydroxybenzylidene)ethylenediamine]-cobalt (**4**) [16] are known to bind with molecular oxygen and use of such dioxygen–cobalt complexes as catalysts and aldehyde as sacrificial agent [17,18] has led to the development of several synthetically important methodologies like epoxidation of olefins [13,19–21], oxidation of sulfides to sulfones [22,23] and imines to oxaziridines [24].



The oxidation of secondary alcohols to carbonyl compounds is an important synthetic transformation and various stoichiometric oxidants notably chromium(VI) and manganese reagents, producing copious amounts of heavy metal wastes have been used to accomplish this reaction [25,26]. Molecular oxygen is an attractive oxidant and development of synthetic methodologies using molecular oxygen as the sole oxidant is the rewarding goal both from economical and environmental points of view [27–30]. In this context aerobic oxidation of secondary alcohols to

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Scheme 1.

ketones by using metal catalysts such as hydrated RuCl_3 [31], $\text{RuO}_2 \cdot \text{H}_2\text{O}$ [32], combination of cobalt and ruthenium [33,34], tetrapropylammonium perruthenate [35], Ru^{+3} -exchanged hydroapatite [36], ruthenium complex along with Co-salen [37], Ru–Al–Mg hydrotalcites [38], Pd(II) hydrotalcite [39], $\text{Pd}(\text{OAc})_2$ [40], Ru-TEMPO [41], $\text{CuCl} \cdot \text{Phen}$ [42], $\text{Cu}(\text{OAc})_2$ [43] and cobalt complexes with 2-methylpropanal as sacrificial agent [44] has been reported in the literature. However these reported procedures are suffer from one or more of the drawbacks such as the use of expensive metal catalysts like ruthenium and palladium, addition of bases like potassium carbonate, requirement of sacrificial aldehyde and severe reaction conditions for example high pressure. In continuation to our studies on oxidation using molecular oxygen as primary oxidant [45–47], herein we now report the first successful cobalt (II) Schiff base complexes catalyzed oxidation of secondary alcohols to corresponding ketones in excellent yields with molecular oxygen as the sole oxidant without use of additive (Scheme 1).

2. Experimental

2.1. Materials

Cobalt Schiff base complexes; bis[2-[(1-phenylethyl) imino]methyl] phenolato-*N,O*]-cobalt(**1**) [7], bis[methyl *N*-[(2-hydroxyphenyl) methylene]-*L*-serinato-*N,O^N O^N*]-cobalt(**2**) [8], bis[methyl *N*-[(2-hydroxyphenyl) methylene] *L*-tyrosinato-*N,O^N*]-cobalt(**3**) [9], [*N,N'*-bis(*o*-hydroxybenzylidene) ethylenediamine]-cobalt (**4**) [10] were prepared according to literature procedure. Benzhydrol and α -methyl benzylalcohol were prepared by reduction of their corresponding ketones following the literature procedure [48]. Borneol was purchased from Aldrich and used without further purification. Benzoin was prepared by benzoin condensation of aldehydes in presence of cyanide ions. Acyloins were prepared from acyloin condensation of esters in presence of sodium metal. Acetonitrile was dried by refluxing over CaH_2 and stored on 4 Å molecular sieves.

2.2. Oxidation of secondary alcohols to ketones (general procedure)

Secondary alcohol (1 mmol), cobalt Schiff base complex 1 (0.05 mmol, 5 mol%), and dry acetonitrile (5 ml) were taken

in a 50 ml double necked round bottomed flask fitted with a gas passing tube and a stirring bar. The mixture was then stirred at room temperature in the presence of molecular sieves (3 Å) with oxygen gas bubbled in at a slow rate. The progress of reaction was monitored by TLC (SiO_2 gel) and after completion; the molecular sieves were removed by filtration. The filtrate thus obtained was evaporated under reduced pressure and the residual mass was dissolved in a mixture of ethyl acetate/hexane (1:4) and then passed through a short column of silica gel using hexane/ethyl acetate (4:1) as eluent. Removal of solvent and usual workup gave corresponding ketones, which were identified by comparing their physical and spectral data with those of authentic compounds reported in literature.

3. Results and discussion

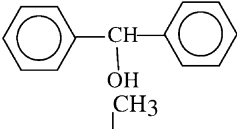
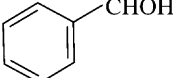
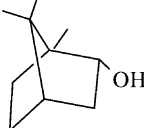
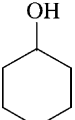
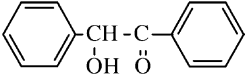
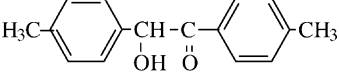
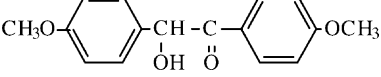
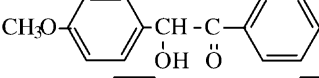
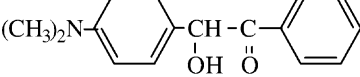
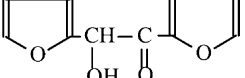
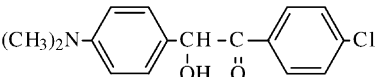
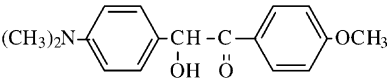
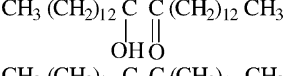
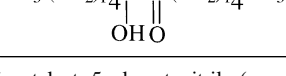
To evaluate the catalytic efficiency of various cobalt Schiff base complexes, the oxidation of 4,4'-dimethylbenzoin was studied with molecular oxygen using different cobalt Schiff base complexes as catalyst and acetonitrile as solvent in presence of molecular sieves. These results are presented in Table 1 and show that bis[2-[(1-phenylethyl) imino]methyl] phenolato-*N,O*]-cobalt(**1**) is most efficient catalyst for this transformation. In blank experiment no oxidation was observed under similar conditions in the absence of catalyst. To examine the versatility of cobalt Schiff base complex 1, a wide variety of secondary alcohols were oxidized to their corresponding ketones in excellent yields by simply bubbling molecular oxygen at room temperature into a solution of secondary alcohols and cobalt Schiff base complex 1 in acetonitrile in presence of molecular sieves (3 Å). These results are summarized in Table 1. Among the various secondary alcohols studied, those having a carbonyl moiety at their α -position were found to be most reactive and required lesser reaction time for their oxidation (Table 2, entry 5–14). Aromatic substituted alcohols were found to be more reactive and afforded better yields of their corresponding ketones as compared to aliphatic substituted alcohols (Table 2, entry 1, 2). Benzoin in general were showed higher reactivity as compared to acyloins (Table 1, entry 5–12) and among the benzoin studied, those sub-

Table 1
Oxidation of 4,4'-dimethyl benzoin with molecular oxygen using different cobalt Schiff base complexes as catalyst^a

Entry	Catalyst	Reaction time (h)	Conversion (%)
1	Schiff base complex 1	0.75	100
2	Schiff base complex 2	1.50	100
3	Schiff base complex 3	1.75	100
4	Schiff base complex 4	4.00	100
5	–	12.00	0

^a 1 mmol substrate, 5 mol% catalyst, 5 ml acetonitrile (room temperature) under atmospheric pressure of O_2 in presence of 3 Å molecular sieves.

Table 2
Oxidation of secondary alcohols to ketones with molecular oxygen using cobalt Schiff base complex 1 as catalyst^a

Entry	Secondary alcohol	Reaction time (h)	Yield (%) ^b
1		3.00	96
2		5.50	94
3		20.00	40
4		15.00	45
5		2.50	95
6		0.75	96
7		0.50	97
8		1.25	95
9		1.50	96
10		0.50	97
11		2.50	90
12		1.00	92
13		12.00	65
14		12.00	70

^a 1 mmol substrate, 5 mol% catalyst, 5 ml acetonitrile (room temperature) under atmospheric pressure of O₂ in presence of 3 Å molecular sieves.

^b Isolated yields.

stituted with electron donating groups were found to be more reactive and required lesser reaction time for their oxidation. (Table 2, entry 6–9, 12).

To evaluate the catalytic effect of cobalt Schiff base complex 1, the oxidation of 4,4'-dimethyl benzoin was carried out with different catalyst concentration under similar

reaction conditions. These results are presented in Table 3 and show that the reaction time decreases with increase in catalyst concentration. Effect of reaction temperature was also investigated for this reaction under similar reaction conditions; these results are shown in Table 4. The oxidation of 4,4'-dimethyl benzoin was very slow at higher temperature

Table 3

Effect of catalyst concentration on the oxidation of 4,4'-dimethyl benzoin with molecular oxygen using cobalt(II) Schiff base complex as catalyst^a

Entry	Catalyst concentration (mol%)	Reaction time (h)	Conversion (%)
1	10.00	0.25	100
2	5.00	0.75	100
3	2.00	2.50	100
4	0.50	5.00	90

^a 1 mmol substrate, different catalyst concentration, 5 ml acetonitrile (room temperature) under atmospheric pressure of O₂ in presence of 3 Å molecular sieves.

Table 4

Effect of the reaction temperature on the oxidation of 4,4'-dimethyl benzoin with molecular oxygen using 5 mol% of cobalt(II) Schiff base as catalyst and acetonitrile as solvent^d

Entry	Reaction temperature (°C)	Reaction time (h)	Conversion (%)
1	90	10	80
2	25	0.75	100
3	10	0.33	100
4	0	0.08	100

^a 1 mmol substrate, different reaction temperature, 5 mol% catalyst, 5 ml acetonitrile under atmospheric pressure of O₂ in presence of 3 Å molecular sieves.

in refluxing acetonitrile and did not complete even after 10 h, while the same could be completed within 5 min at 0 °C. The higher reaction rates at lower temperature are probably due to the involvement of reversible dioxygen–cobalt complexes, which are favorably formed at lower temperatures, in these oxidation reactions [2].

Although the mechanism of this reaction is not clear at this stage, the reaction probably involves the formation of superoxo complexes by the reaction of cobalt complexes with molecular oxygen [49] and abstraction of hydrogen radical from more acidic hydroxyl group followed by radical coupling to yield ketones. The experimental observations that lower reaction temperature, which favors the formation of superoxo complexes, increases the reaction rates support this type of mechanism.

4. Conclusion

In summary, we have demonstrated, the first successful example of cobalt Schiff base complexes catalyzed oxidation of secondary alcohols to their corresponding ketones with molecular oxygen as the sole oxidant without using sacrificial aldehyde or additive. The simplicity of the system, non-hazardous nature of the catalyst and wide applicability make cobalt (II) Schiff base catalyzed oxidation an attractive, environmentally acceptable synthetic tool for the oxidation of secondary alcohols to ketones with molecular oxygen.

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