

# An efficient cobalt (II) catalyzed oxidation of secondary alcohols to carbonyl compounds with *N*-bromosuccinimide

Vishal B. Sharma, Suman L Jain, Bir Sain\*

Chemical and Biosciences Division, Indian Institute of Petroleum, Dehradun –248005, India

Received 30 July 2004; received in revised form 29 September 2004; accepted 7 October 2004

Available online 13 November 2004

## Abstract

A variety of activated and non-activated secondary alcohols were selectively oxidized to the ketones with *N*-bromosuccinimide using cobalt (II) acetylacetonate as catalyst.

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**Keywords:** Oxidation; Secondary alcohol; Cobalt; *N*-bromosuccinimide; Ketones

## 1. Introduction

The oxidation of secondary alcohols to carbonyl compounds is one of the important synthetic transformations and apart from conventional stoichiometric oxidants notably chromium (VI) and manganese reagents which, produce copious amounts of heavy metal wastes [1–2], the use of molecular oxygen with a variety of metal catalysts has been reported in the literature [3–15], in pursuit to the development of eco-friendly synthetic methodologies. However, these procedures suffer from one or more drawbacks such as the use of expensive metal catalysts like ruthenium and palladium, oxidation of only activated alcohols such as benzylic and allylic, the need for a sacrificial aldehyde, and severe reaction conditions, for example, high temperature, pressure, leaving the scope for the further improvement in the catalytic oxidation of secondary alcohols to ketones. *N*-Bromosuccinimide, a cheap and convenient oxidant, has been widely used in a variety of oxidation reactions both under acidic and alkaline conditions [16–18]. Recently Itoh et al. [19] reported the oxidation of benzylic group with molecular oxygen in the presence of *N*-bromosuccinimide under photoirradiation. To the best of our knowledge there is no literature report on the

oxidation of secondary alcohols to carbonyl compounds using *N*-bromosuccinimide as oxidant. In continuation to our studies on oxidation [20–25] herein, we report for the first time a very simple and convenient methodology for the oxidation of both activated and non-activated secondary alcohols to the corresponding ketones in excellent yields with *N*-bromosuccinimide using cobalt (II) acetylacetonate as catalyst under very mild conditions (Scheme 1).

## 2. Experimental

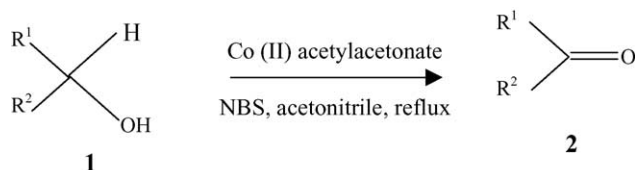
### 2.1. Materials

All the catalysts and substrates used were commercially available.

### 2.2. Oxidation of secondary alcohols to ketones (typical procedure)

To a stirred solution of benzhydrol (184 mg, 1 mmol) in acetonitrile (5 ml) was added *N*-bromosuccinimide (178 mg, 1 mmol), cobalt (II) acetylacetonate (13 mg, 5 mol%) and the reaction mixture was refluxed for 45 min. The reaction progress was monitored by TLC (SiO<sub>2</sub>). At the end of re-

\* Corresponding author. Tel.: +91 135 660071; fax: +91 135 660202.  
E-mail address: [birsain@iip.res.in](mailto:birsain@iip.res.in) (B. Sain).



action cobalt (II) acetylacetonate was removed by passing through a short column of silica gel by using ethyl acetate as eluent. The solvent was evaporated under vacuum and the residue thus obtained was purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded benzophenone (171 mg, 94%). Other alcohols were oxidized using this procedure and their reaction times and yields are given in the Table 1. The products were identified by comparing their physical and spectral data with those of authentic compounds reported in literature.

### 3. Results and discussion

The oxidation of a variety of activated and non-activated secondary alcohols to ketones was carried out using a catalytic amount of cobalt (II) acetylacetonate in the presence of an equimolar amount of *N*-bromosuccinimide. All the secondary alcohols studied were smoothly converted to the ketones in very good yields (Table 1). Among the various alcohols studied those containing a carbonyl moiety at the  $\alpha$ -position were found to be the most reactive and required shorter reaction times for their oxidation. Furthermore alcohols bearing aromatic substituents like benzhydrol (Table 1, entry 1) and  $\alpha$ -methyl benzylalcohol (Table 1, entry 2) were found to be more reactive than alicyclic and aliphatic alcohols. This method was not found to be suitable for the oxidation of primary alcohols.

To evaluate the catalytic effect of cobalt (II) acetylacetonate, the oxidation of benzhydrol was carried out under similar reaction conditions in the absence of catalyst, and the reaction was found to be very slow giving very poor yield of benzophenone (Table 2, entry 6). The use of cobalt (II) salts such as cobalt (II) acetate and cobalt (II) chloride as catalyst in place of cobalt (II) acetylacetonate gave almost equivalent yields but reaction times were found to be longer (Table 2). Further the oxidation of benzhydrol was also carried out with the use of Mn(acac)<sub>2</sub> and Fe(acac)<sub>2</sub> as catalyst in place of Co(acac)<sub>2</sub>, the reaction was found to be very slow. The results of these experiments are presented in Table 2. The effect of various solvents was also studied for this reaction. Among the various solvents studied like acetonitrile, 1,2-dichloroethane, methanol and toluene, acetonitrile was found to be most suitable.

The mechanism of this reaction is premature at this stage and the reaction probably involves the formation of Br rad-

Table 1  
Cobalt catalyzed aerobic oxidation of secondary alcohols to ketones with *N*-bromosuccinimide<sup>a</sup>

Entry	Substrate	Reaction time (h)	Yield (%) <sup>b</sup>
1		0.75	94
2		1.00	95
3		1.50	80
4		5.00	50
5		1.25	80
6		1.00	75
7		2.50	70
8		1.50	75
9		5.0	50
10		0.17	96
11		0.08	97
12		1.50	85
13		2.00	80

<sup>a</sup> Reaction conditions: secondary alcohol (1 mmol), *N*-bromosuccinimide (1 mmol), cobalt (II) acetylacetonate (5 mol%) in acetonitrile (5 ml) at reflux temperature.

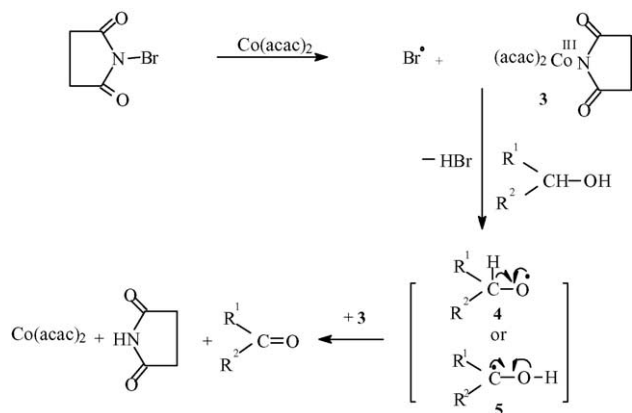
<sup>b</sup> Isolated yields.

Table 2  
Effect of various cobalt catalysts on the oxidation of benzhydrol<sup>a</sup>

Entry	Catalyst	Reaction time (h)	Yield (%) <sup>b</sup>
1	Co (acac) <sub>2</sub>	0.75	94
2	CoCl <sub>2</sub>	3.5	90
3	Co(OAc) <sub>2</sub>	4.0	92
4	Mn (acac) <sub>2</sub>	5.5	85
5	Fe (acac) <sub>2</sub>	6.5	82
6	–	10	20

<sup>a</sup> Reaction conditions: secondary alcohol (1 mmol), *N*-bromosuccinimide (1 mmol), catalyst (5 mol%) in acetonitrile (5 ml) at reflux temperature.

<sup>b</sup> Isolated yields.



Scheme 2.

ical 3 by the reaction *N*-bromosuccinimide with Co(acac)<sub>2</sub>. The abstraction of hydrogen by Br radical either from OH [26] or C–H bearing OH [27,28] yields intermediates 4 or 5, which on further reaction with 3 yields corresponding ketone (Scheme 2).

#### 4. Conclusion

In summary, we have developed a very easy and convenient methodology for the oxidation of both activated and non-activated alcohols to the corresponding ketones. The simplicity of the system, easy preparation/availability of the reagents and the versatility of the method towards a range of activated and non-activated alcohols make this cobalt catalyzed oxidation an attractive, and facile synthetic tool for the oxidation of secondary alcohols to ketones with *N*-bromosuccinimide.

#### Acknowledgements

We are thankful to Director, IIP for his kind permission to publish these results. Vishal B. Sharma and Suman L. Jain are thankful to CSIR, New Delhi, for award of research fellowship.

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