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LETTERS

Cobalt(II)-catalyzed oxidation of alcohols into carboxylic acids and ketones with hydrogen peroxide

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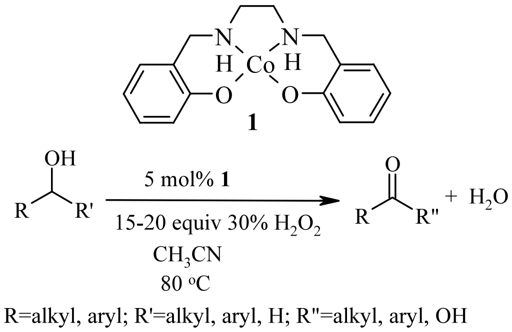
Abstract—The oxidation of aliphatic and aromatic alcohols into the corresponding carboxylic acid analogues and ketones has been carried out using 30% H_2O_2 and cobalt(II) complex **1** in good to high yields. The reaction is safe, clean and functions in the absence of additives.

The selective oxidation of alcohols into carbonyl compounds is one of the most important fundamental reactions in organic chemistry both at the laboratory and industrial level and numerous methods have been developed using a variety of reagents for this purpose.[1] Recent demand for eco-friendly chemical processes has encouraged the development of several clean reactions[2] and awaits further development of high yielding, clean and economical methods for the oxidation of alcohols. Herein, we wish to report the oxidation of aliphatic and aromatic alcohols into carboxylic acids and ketones in good to high yields with cobalt(II) complex[3] **1** in the presence of H_2O_2 under atmospheric oxygen (Scheme 1).



Scheme 1.

Reaction of ethylenediamine with 2 equiv. of salicylaldehyde followed by $NaBH_4$ reduction in methanol at ambient temperature provided salen–H_4 which was further reacted with $Co(OAc)_2$ under a nitrogen atmosphere to afford complex **1** as a green powder.[3] In the presence of a catalytic amount of **1**, the oxidation of 4-chlorobenzyl alcohol was examined with H_2O_2 in acetonitrile. We were pleased to find that the alcohol was oxidized to a 1:6 mixture of the corresponding aldehyde and carboxylic acid in 15% yield (17 h). Alternatively, the reaction could be carried out under heating (80°C) within 7 h to afford the carboxylic acid in 74% yield (Table 1, entry 3 and Scheme 2).[4] A controlled experiment in the absence of **1** using the same reaction conditions gave no reaction and the starting alcohol was recovered. $Co(OAc)_2$ and Co^{II}salen were also examined as the catalysts for this reaction, however, these systems were less effective compared to the protocol using **1**. The reaction with Co^{II}salen provided a 1:17 mixture of the corresponding aldehyde and carboxylic acid in a 34% yield, while the $Co(OAc)_2$ catalyzed process afforded only the aldehyde in 9% yield (Scheme 2).

The oxidations of other alcohols were then examined using the optimized reaction conditions (Table 1)[4] and aromatic alcohols, 4-bromo-, 2-nitro-, 3-nitro-, 4-nitro-, 4-methoxy- and 3,4,5-trimethoxybenzyl alcohol, phenylethanol and diphenylmethanol, were oxidized to the corresponding carboxylic acids and ketones in high yields. The progress of the oxidation of phenylethanol is shown in Figure 1. It is noteworthy to mention that no oxidation was observed in the aromatic ring of benzylic substrates. Similarly, aliphatic alcohols, decyl- and cetyl alcohols, 2-methylcyclopentanol and cylohex-

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Keywords: oxidation; alcohols; catalyst; hydrogen peroxide; cobalt(II) complex.

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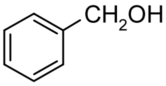
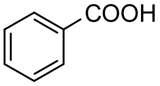
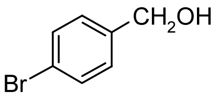
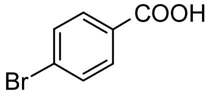
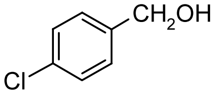
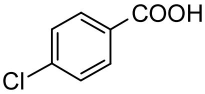
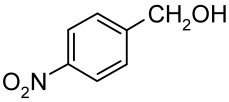
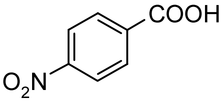
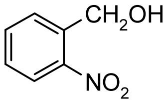
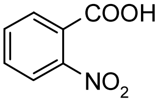
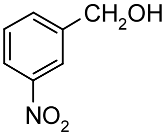
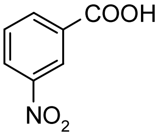
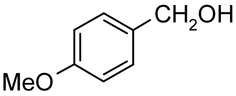
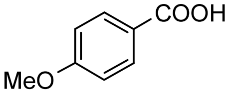
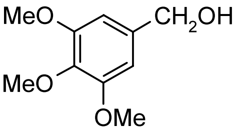
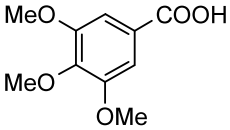
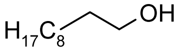
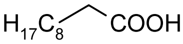
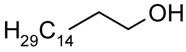
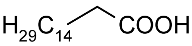
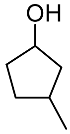
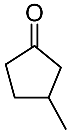
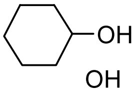
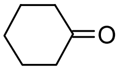
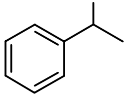
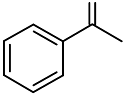
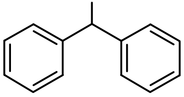
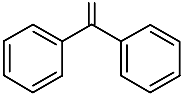
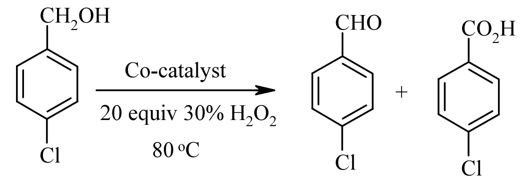
Table 1. Oxidation of alcohols to carboxylic acids and ketones with catalyst **1** and 30% H_2O_2

Entry	Substrate	Time (h)	Product	Yield (%)[a,b,c]
1		6		76
2		7		75
3		7		74
4		9		74
5		9		72
6		7		76
7		5		78
8		4		80
9		10		55
10		11		59
11		4		77[d]
12		4		82[d]
13		3		92[d]
14		3		89

[a]Substrate (3 mmol), catalyst (5 mol%) and 30% H_2O_2 (6.8 ml, 60 mmol) were stirred in acetonitrile (5 ml) at 80 °C under atmospheric oxygen. [b]Isolated yield. [c]The identity of the products has been ascertained by ^{1}H NMR, IR and mass spectroscopy, by melting points (solids), and by comparison with authentic samples. [d]GC yield.



Complex **1**	-	74%
Co^{II}salen	1.9%	32.1%
$Co(OAc)_2$	9%	-

Scheme 2.

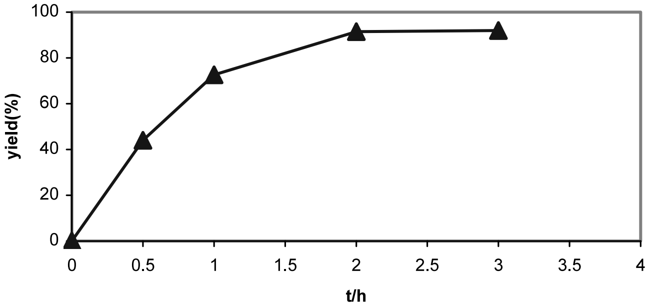
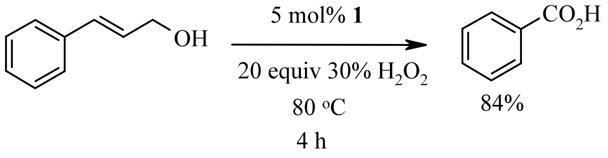


Figure 1. Progress of the oxidation of phenylethanol to acetophenone.



Scheme 3.

anol, underwent oxidation to the corresponding carboxylic acids and ketones in moderate to good yields (entries 9–12). The oxidation of cinnamyl alcohol was also examined; however, it mainly afforded benzoic acid due to cleavage of the carbon–carbon double bond (Scheme 3).

In conclusion, the oxidation of aromatic and aliphatic alcohols to carboxylic acids and ketones has been described using cobalt(II) complex **1** in the presence of H_2O_2 in high yields. The reaction is simple, clean and generates water as the only by-product.

Acknowledgements

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References

1. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ley, S. V., Eds.; Pergamon Press: Oxford, 1991; Vol. 7, pp. 251–325.
2. (a) Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Chelle-Regnaut, I.; Gautier, A.; Brown, S. M.; Urch, C. J. *J. Org. Chem.* **1999**, *64*, 2433; (b) Dijksman, A.; Arends, I. W. C. E.; Sheldon, R. A. *Synlett* **2001**, 102; (c) Betzemeier, B.; Cavazzini, M.; Quici, S.; Knochel, P. *Tetrahedron Lett.* **2000**, *41*, 4343; (d) Coleman, K. S.; Coppe, M.; Thomas, C.; Osborn, J. A. *Tetrahedron Lett.* **1999**, *40*, 3723; (e) Wang, Y.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *Science* **1998**, *279*, 537; (f) Saint-Aman, E.; Menage, S.; Pierre, J. D.; Defrancq, E.; Gellon, G. *New. J. Chem.* **1998**, 393; (g) Chaudhuri, P.; Hess, M.; Muller, J.; Hildenbrand, K.; Bill, E.; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 9599; (h) Zhao, M.; Li, J.; Mano, E.; Song, Z.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J. *J. Org. Chem.* **1999**, *64*, 2564; (i) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936; (j) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1637; (k) Miyata, A.; Murakami, M.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7067; (l) Masutani, K.; Uchida, T.; Irie, R.; Katsuki, T. *Tetrahdron Lett.* **2000**, *41*, 5119; (m) Punniyamurthy, T.; Iqbal, J. *Tetrahedron Lett.* **1994**, *35*, 4007.
3. The reaction of salicylaldehyde (122 mg, 1 mmol) with ethylenediamine (30 mg, 0.5 mmol) in methanol (5 ml) afforded salen-H_2 as a lemon yellow powder in 81% (217 mg), which was further reacted with $NaBH_4$ (32 mg) in methanol (5 ml) for 2 h at ambient temperature. Removal of the solvent on a rotary evaporator followed by treatment with water afforded salen-H_4 as a colorless powder in 72% (162 mg) yield. The salen-H_4 (272 mg, 1 mmol) was then reacted with $Co(OAc)_2$ (195 mg, 1.1 mmol) in methanol (10 ml) at 50°C for 2.5 h. Evaporation of the solvent on a rotary evaporator gave a powder which was passed through a short pad of silica gel using a mixture of EtOAc and MeOH (15:5) to afford **1** as a green powder (83%, 300 mg): UV–vis (CH_3CN): λ_{max} 265, 387 nm; FAB^+ MS: 329 (M^+).
4. A solution of the alcohol (3 mmol), complex **1** (5 mol%) and 30% H_2O_2 (6.8 ml, 60 mmol) was stirred in acetonitrile (5 ml) at ca. 80°C under atmospheric oxygen for the appropriate time (see Table 1). The reaction mixture was then cooled to ambient temperature and dimethyl sulfide (50 μl) was added. After further stirring for 0.5 h at ambient temperature, the aqueous acetonitrile was removed by rotary evaporation under reduced pressure and the residue was passed through a short pad of silica gel using ethyl acetate and hexane to afford the analytically pure carboxylic acid.