

Efficient aerobic oxidation of alcohols using a novel combination *N*-hydroxy phthalimide (NHPI) and a recyclable heterogeneous cobalt complex

Fatemeh Rajabi^a, Babak Karimi^{b, c, *}

^a Department of Chemistry, Sharif University of Technology, PO Box 11365-9516, Tehran, Iran

^b Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), PO Box 45195-159, Gava Zang, Zanjan, Iran

^c Institute for Fundamental Research, Farmanieh (IPM), PO Box 19395-5531, Tehran, Iran

Received 10 November 2004; received in revised form 7 January 2005; accepted 8 January 2005

Abstract

A novel combination between *N*-hydroxy phthalimide (NHPI) and a silica based cobalt (II) interphase catalyst (**1**) efficiently catalyzes the aerobic oxidation of various types of alcohols to the corresponding carbonyl compounds. The catalyst **1** shows high thermal stability and also could be recovered and reused in combination with NHPI for at least five reaction cycles without considerable loss of reactivity.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Alcohols; Oxidation; *N*-hydroxy phthalimide; Molecular oxygen; Supported reagents

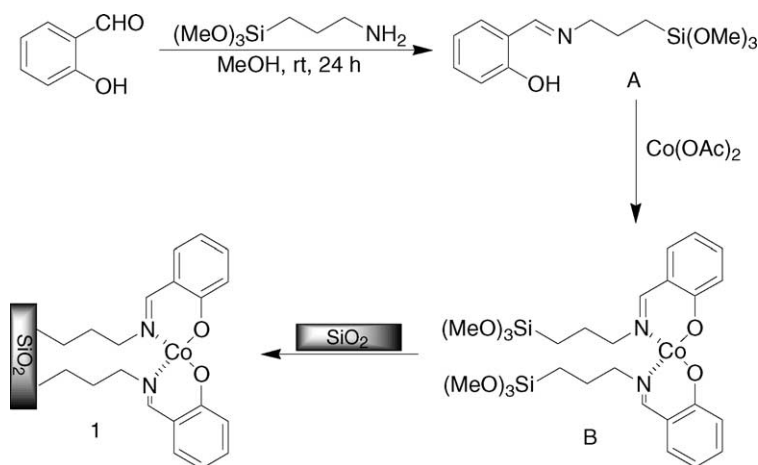
1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds is one of the most frequently used and important transformation in organic chemistry as demonstrated by a plethora of methods and procedures that have been developed for this purpose [1]. Unfortunately, the traditional methods for oxidation of alcohols suffer from the drawbacks such as the use of at least a stoichiometric amount of oxidants and bring about a large quantity of harmful by-products. Thus, from the standpoint of the so-called green and sustainable chemistry, another approach to construct cleaner catalytic systems for oxidation of alcohols using molecular oxygen (O₂) has been becoming increasingly attractive in recent years [2–4].

In recent years, *N*-hydroxy phthalimide (NHPI) has been recognized as a valuable catalyst for aerobic oxidation of various organic compounds under mild reaction conditions [5]. Especially, it has been shown that NHPI in combination with Co(II) salts and *m*-chloro perbenzoic acid (*m*-CPBA)

is an efficient method for oxidation of alcohols to the corresponding carbonyl compounds with molecular oxygen under normal pressure and temperature [6]. It is believed that the phthalimide *N*-oxyl (PINO) radical generated in situ from the reaction of O₂ and NHPI is able to abstract a hydrogen atom from the organic substrates. The newly formed carbon radical then rapidly reacts with O₂ to give ultimately oxygenated products. While using this protocol a considerable progress is being achieved, the protocol needs to use *m*-CPBA as co-reagent and owing to the homogeneous reaction conditions, the catalyst is difficult to recover and reuse. One way to circumvent this problem is to anchor one or more components of the catalytic systems onto a large surface area solid carrier to create new organic–inorganic hybrid (interphase) catalysts [7]. However, it is shown that PINO radical is not stable well under the aerobic oxidation conditions and it finally decomposes via a self decomposition kinetics [8]. Therefore, one approach to the problem of recyclability of NHPI/Mⁿ⁺ is to create a system based on NHPI itself and a recoverable metal salt. Along this hypothesis, we now report on a successful and novel combination of homogeneous NHPI with a supported cobalt catalyst instead of homogeneous Co(II) counterparts.

* Corresponding author. Tel.: +98 241 424 2239; fax: +98 241 424 9023.
E-mail address: karimi@iasbs.ac.ir (B. Karimi).



Scheme 1.

The supported cobalt (II) catalyst is built up from the direct grafting of mesoporous silica by a silica precursor-Schiff base Co(II) complex according to the known literature procedure with slight modification (Scheme 1) [9].

Quantitative determination of the functional group contents of the surface bound compound **1** was performed with thermogravimetric analysis (TGA). Typically, an organic group loading at ca. 0.3 mmol g⁻¹ is obtained. Further characterization of **1** was also performed using DRIFT-IR and atomic absorption spectroscopy (AA) and also comparison of its IR with those obtained from aminopropyl silica (AMPS).

2. Experimental

2.1. General remarks

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products unless otherwise stated. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. ¹H NMR and ¹³C NMR spectra were recorded on a 500 MHz spectrometer in CDCl₃ as the solvent and TMS as internal standard. All products are known and all of the isolated products gave satisfactory IR and NMR spectra.

2.2. General procedure for aerobic oxidation of acetals to esters using NHPI/1 system under O₂ (1 atm)

A solution of NHPI (1 mmol, 10 mol%) and **1** (0.25 mol% of cobalt content, 0.083 g) in CH₃CN (15 mL) was prepared in a two-necked flask. To this solution alcohol (10 mmol) was added and the resulting mixture was stirred at 60 °C under an oxygen atmosphere (1 atm, balloon filled) for the indicated optimized time as shown in Table 1. After completion of the reaction, the reaction mixture was filtered off and the catalyst **1** was then rinsed twice with CH₃CN (15 mL) and reused;

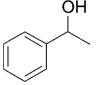

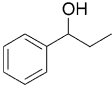

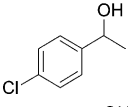
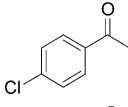
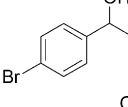
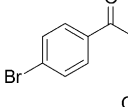
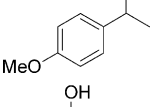
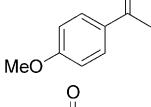
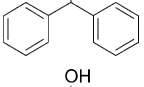
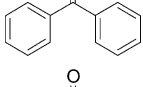
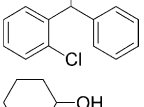
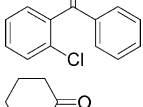
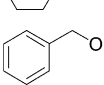
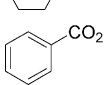
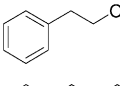
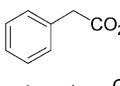
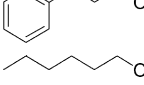
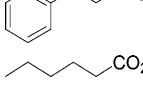
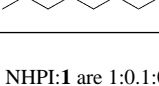
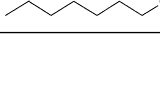
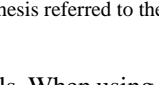
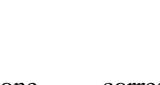
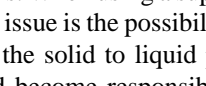
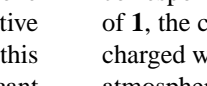
the products were purified by flash chromatography through a short pad of silica gel with an appropriate solvent to give the corresponding carbonyl compound in good to excellent yields.

3. Results and discussion

To test catalytic properties of NHPI combined with **1**, we selected the oxidation of alcohols using molecular oxygen. The optimized condition proved to be NHPI (10 mol%), **1** (0.25 mol% of cobalt content, 0.083 g), substrate (5 mmol), O₂ (1 atm) in CH₃CN (15 mL) under vigorous stirring at 65 °C. Thus, 1-phenyl ethanol as a model substrate was subjected to oxidize under these conditions for 24 h. The reaction mixture was filtered off and the catalyst **1** was then rinsed twice with CH₃CN (15 mL) and reused. The evaporation of the solvent followed by flash chromatography of the crude products through a short pad of silica gave acetophenone in 95% isolated yield, the purity of which was determined by GC and NMR to be more than 99% (Table 1, entry 1).

In two separate blank experiments, no considerable oxidation was observed under similar reaction conditions in the absence of either **1** or NHPI. To examine the versatility of the method, a variety of both aliphatic and benzylic secondary alcohols were allowed to oxidize using the above described reaction conditions (Table 1). It is worth mentioning that among the various types of secondary alcohols studied, those comprising two aromatic ring directly attached to the carbon bearing hydroxyl group are the most reactive and required lesser reaction time for their oxidation (Table 1, entries 6 and 7). This strongly suggests the intermediacy of a α -hydroxy radical intermediate. On the other hand, the oxidation of primary alcohols (both benzylic and aliphatic) using the presented protocol selectively furnishes the corresponding carboxylic acids in excellent yields (Table 1, entries 1–5, 8–13). These results clearly show the widespread applicability of the protocol for the oxidation of various types of struc-

Table 1
Aerobic oxidation of alcohols using NHPI combined with immobilized cobalt catalyst **1**

Entry	Substrate	Product	Time (h)	Yield (%) ^{a,b,c}
1			22	100
2			22	100
3			24	100
4			24	99
5			22	97 ^c
6			55	94
7			100	96 ^c
8			28	88
9			25	87 (13)
10			30	81 (7)
11			40	79 (2)
12			35	89 (5)
13			40	87 (4)

^a NMR yields.

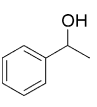
^b The ratios of substrate: NHPI:**1** are 1:0.1:0.0025.

^c The numbers in parenthesis referred to the yields of aldehydes.

turally diverse alcohols. When using a supported catalyst one of the most important issue is the possibility that some active metal migrates from the solid to liquid phase and that this leached Co(II) would become responsible for a significant extent of the catalytic activity. To rule out the contribution of homogeneous catalysis in the results shown in Table 1, the reaction was carried out in the presence of the solid **1** for 4 h and at that point the catalyst was filtered off. The liquid filtrate was then allowed to react, but no significant conversion was observed after 24 h under the presented reaction conditions. This clearly indicates that no active species were present in the supernatant. After obtaining these promising results, we moved toward testing the reusability of the catalyst **1**. Recycling experiments were examined for the oxidation of 1-phenylethanol. Thus, after the first run, which gave the

corresponding ketone in quantitative GC yield, after recovery of **1**, the catalyst was subjected to a second oxidation vessel charged with NHPI (10 mol%) in CH₃CN (15 mL) under O₂ atmosphere from which it gave the ketone in 99%. The average chemical GC yields for five consecutive runs was 96%,

Table 2
Recovery of immobilized cobalt catalyst **1** for the aerobic oxidation of 1-phenylethanol using NHPI combined with

Run	Alcohol	NHPI (mol%)	Time (h)	Yield (%) ^a
1st		10	22	100
2nd		10	22	99
3rd		10	24	99
3rd		10	24	96
4th		10	28	88

^a GC yields.

which clearly demonstrates the practical recyclability of this catalyst (Table 2).

4. Conclusion

In conclusion, the novel combination of homogeneous NHPI and silica based cobalt (II) interphase catalyst **1** efficiently catalyzes the aerobic oxidation of a wide variety of both primary and secondary alcohols. The catalyst **1** could be recovered and reused for at least five reaction cycles without considerable loss of reactivity. Further applications of this novel catalyst combination for the aerobic oxidation of the other types of functional groups are underway in our laboratories.

Acknowledgments

The authors appreciate Institute for Advanced Studies in Basic Sciences (IASBS) and Institute for Fundamental Research (IPM) Research Council for support of this work. We also appreciate British Council of Iran for partial support of this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2005.01.016](https://doi.org/10.1016/j.molcata.2005.01.016).

References

- [1] (a) R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1984;
 - (b) M. Hudlicky, *Oxidations in Organic Chemistry*, ACS Monograph Series, American Chemical Society, Washington, DC, 1990;
 - (c) For a review on metal-mediated oxidations, see: W.J. Mijs, C.R.H. de Jonge, *Organic Syntheses by Oxidation with Metal Compounds*, Plenum, New York, 1986.
- [2] (a) R.A. Sheldon, in: L.L. Simandi (Ed.), *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Elsevier, Amsterdam, 1991, p. 573;
 - (b) B.R. James, in: L.L. Simandi (Ed.), *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Elsevier, Amsterdam, 1991, p. 195.
- [3] Ruthenium catalyst;
 - (a) R. Tang, S.E. Diamond, N. Neary, F. Mares, *J. Chem. Soc. Chem. Commun.* (1978) 562;
 - (b) M. Matsumoto, N. Watanabe, *J. Org. Chem.* 49 (1984) 3435;
 - (c) C. Bilgrien, S. Davis, R.S. Drago, *J. Am. Chem. Soc.* 109 (1987) 3786;
 - (d) J.-E. Backvall, R.L. Chowdhury, U. Karlsson, *J. Chem. Soc., Chem. Commun.* (1991) 473;
 - (e) S.-I. Murahashi, T. Naota, J. Hirai, *J. Org. Chem.* 58 (1993) 7318;
 - (f) G.Z. Wang, U. Andreasson, J.-E. Backvall, *J. Chem. Soc., Chem. Commun.* (1994) 1037;
 - (g) T. Inokuchi, K. Nakagawa, S. Torii, *Tetrahedron Lett.* 36 (1995) 3223;
 - (h) I.E. Marko, P.R. Giles, M. Tsukazaki, M.I. Chelle-Regnaut, C.J. Urch, S.M. Brown, *J. Am. Chem. Soc.* 119 (1997) 12661;
 - (i) R. Lenz, S.V. Ley, *J. Chem. Soc., Perkin Trans. 1* (1997) 3291;
 - (j) A. Hanyu, E. Takezawa, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* 39 (1998) 5557;
 - (k) K. Kaneda, T. Ya-mashita, T. Matsushita, K. Ebitani, *J. Org. Chem.* 63 (1998) 1750;

Copper catalysts;

 - (l) I.E. Marko, P.R. Giles, M. Tsukazaki, M.I. Chelle-Regnaut, C.J. Urch, S.M. Brown, *J. Org. Chem.* 63 (1998) 1756 (and the references cited therein);

Cobalt catalysts;

 - (m) T. Yamada, T. Mukaiyama, *Chem. Lett.* (1989) 519;
 - (n) A.K. Mandal, J. Iqbal, *Tetrahedron Lett.* 53 (1997) 7641;
 - (o) T. Iwahama, S. Sakaguchi, Y. Nishiyama, Y. Ishii, *Tetrahedron Lett.* 36 (1995) 6923;

Other metals;

 - (p) M.F. Semmelhack, C.R. Schmidt, D.A. Cortes, C.S. Chou, *J. Am. Chem. Soc.* 106 (1984) 3374;
 - (q) K.S. Coleman, M. Coppe, C. Thomas, J.A. Osborn, *Tetrahedron Lett.* 40 (1999) 3723.
- [4] For examples of Pd(II)-catalyzed aerobic oxidations, see;
 - (a) M.J. Schultz, C. vPark, M. Sigman, *Chem. Commun.* (2002) 3034;
 - (b) G.J. Ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Adv. Synth. Catal.* 344 (2002) 355;
 - (c) N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, *J. Org. Chem.* 66 (2001) 6620;
 - (d) G.J. Ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636;
 - (e) T. Nishimura, T. Onoue, K. Ohe, S. Uemura, *Tetrahedron Lett.* 39 (1998) 6011;
 - (f) K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* 41 (2002) 4538;
 - (g) T.F. Blackburn, J. Schwartz, *J. Chem. Soc., Chem. Commun.* (1977) 158;
 - (h) K. Kaneda, Y. Fujie, K. Ebitani, *Tetrahedron Lett.* 38 (1997) 9023;
 - (i) K.P. Peterson, R.C. Larock, *J. Org. Chem.* 63 (1998) 3185;
 - (j) For related examples of oxidative kinetic resolutions, see;
 - (k) E.M. Ferreira, B.M. Stoltz, *J. Am. Chem. Soc.* 123 (2001) 7725;
 - (l) J.T. Bagdanoff, E.M. Ferreira, B.M. Stoltz, *Org. Lett.* 5 (2003) 835;
 - (m) S.K. Mandal, D.R. Jensen, J.S. Pugsley, M.S. Sigman, *J. Org. Chem.* 68 (2003) 4600;

For example of Pd-catalyzed oxidation of alcohols using dichloroethane (DCE) see;

 - (n) G. Rothenberg, S. Humbel, J. Muzart, *J. Chem. Soc., Perkin Trans. 2* (2001) 1998;

For reviews aerobic oxidation of alcohols see;

 - (o) B.-Z. Zhan, A. Thompson, *Tetrahedron* 60 (2004) 2917;
 - (p) T. Mallat, A. Baiker, *Chem. Rev.* 104 (2004) 3037;
 - (q) J. Muzart, *Tetrahedron* 59 (2003) 5789.
- [5] (a) Y. Ishii, S. Sakaguchi, T. Iwahama, *Adv. Synth. Catal.* 343 (2001) 379, for more recent leading references see;
 - (b) S. Isozaki, Y. Nishiwaki, S. Sakaguchi, Y. Ishii, *Chem. Commun.* (2001) 1352;
 - (c) S. Sakaguchi, Y. Nishiwaki, T. Kitamura, Y. Ishii, *Angew. Chem. Int. Ed.* 40 (2001) 222;
 - (d) Y. Nishiwaki, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* 67 (2002) 5663;
 - (e) S. Sakaguchi, A. Shibamoto, Y. Ishii, *Chem. Commun.* (2002) 180;
 - (f) S. Yamamoto, S. Sakaguchi, Y. Ishii, *Green Chem.* 5 (2003) 300;

- (g) S. Sakaguchi, T. Hirabayashi, Y. Ishii, Chem. Commun. (2002) 516.
- [6] T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, J. Org. Chem. 65 (2000) 6502.
- [7] (a) Z.L. Lu, E. Lindner, H.A. Mayer, Chem. Rev. 102 (2002) 3543;
(b) A.P. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589;
(c) D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615.
- [8] (a) N. Koshino, B. Saha, J.H. Espenson, J. Phys. Chem. A 107 (2003) 4262;
(b) B. Saha, N. Koshino, J.H. Espenson, J. Phys. Chem. A 108 (2004) 425;
(c) C. Ueda, M. Noyama, H. Ohmori, M. Masui, Chem. Pharm. Bull. 35 (1987) 1372.
- [9] I.C. Chisem, J. Rafelt, M.T. Shieh, J. Chisem, J.H. Clark, R. Jachuck, D.J. Macquarrie, C. Ramshaw, K. Scott, Chem. Commun. (1998) 1949.