

Short communication

# A catalytic and transition metal-free method for the chemoselective oxidation of alcohols to their corresponding carbonyl compounds using periodic acid or iodic acid in the presence of a catalytic amount of KBr

Mohammad Ali Zolfigol<sup>a,\*</sup>, Farhad Shirini<sup>b</sup>,  
Gholamabbas Chehardoli<sup>a</sup>, Eskandar Kolvari<sup>a</sup>

<sup>a</sup> Faculty of Chemistry, Bu-Ali Sina University, Post Box No. 4135, Hamadan 6517838683, Iran

<sup>b</sup> Department of Chemistry, College of Science, Guilan University, Rasht, Iran

Received 23 September 2006; accepted 18 October 2006

Available online 24 October 2006

## Abstract

Chemoselective oxidation of various alcohols was proceeded by using a catalytic amount of KBr in the presence of periodic acid or iodic acid and wet SiO<sub>2</sub> under mild and heterogeneous conditions with moderate to excellent yields.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Periodic acid; Iodic acid; Alcohols; Chemoselective oxidation; Catalytic amount of KBr; Oxidation

In recent years, the search for environmentally benign chemical processes or methodologies has received much attention from chemists, because they are essential for the conservation of the global ecosystem. The development of heterogeneous catalysts for fine chemical synthesis has become a major area of research, as the potential advantages of these materials (simplified recovery and reusability; the potential for incorporation in continuous reactors and micro reactors) over homogeneous systems can lead to novel environmentally benign chemical procedures for academia and industry [1]. From this viewpoint, catalytic oxidation is a valuable process because the use of stoichiometric reagents that are often toxic poses inherent limitations from both economical and environmental viewpoints regarding product purification and waste management [2].

The selective oxidation of alcohols to aldehydes and ketones is a highly desirable and much sought after transformation both in industrial chemistry as well as in organic synthesis, due to the wide-ranging utility of these products as important precursors and intermediates for many drugs, vitamins and fragrances [1]. In particular, the controlled oxidation of primary alcohols to aldehydes without forming over-oxidized products is a chal-

lenging task for chemists. Numerous methods are available for alcohol oxidation; however, the development of newer methods and methodologies is currently gaining much attention due to the significance of this reaction [3].

A combination of an oxidizing agent and Br<sup>-</sup> as an oxidizing system for the above-mentioned transformation have been reported previously. Especially, oxidation of primary alcohols to aldehydes with hydrogen peroxide as an oxidizing agent by using a suitable catalyst such as methyltrioxorhenium and bromide ions as co-catalysts [4], oxoammonium salt and bromide ions [5] and/or hydrobromic acid [6] have been described. Also combination of oxone<sup>®</sup> and Br<sup>-</sup> was used for the oxidation of alcohols [7]. Recently, we reported trichloroisocyanuric acid/KBr in the presence of wet SiO<sub>2</sub> for the catalytic oxidation of alcohols [8].

Application of solid acids in organic transformation have very important role because, solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes [9]. Among solid acids, oxidation of alcohols with periodic acid (HIO<sub>4</sub>·2H<sub>2</sub>O) with various catalysts has been well documented. In recent years, periodic acid has been employed for oxidation of alcohols with various catalysts, such as pyridinium fluorochromate, pyridinium chlorochromate,

\* Corresponding author. Tel.: +98 811 8257407; fax: +98 811 8257407.  
E-mail addresses: [zolfi@basu.ac.ir](mailto:zolfi@basu.ac.ir), [mzolfigol@yahoo.com](mailto:mzolfigol@yahoo.com) (M.A. Zolfigol).

Table 1

Oxidation of alcohols **1** to their corresponding carbonyl compounds **2** using periodic acid (**I**) or iodic acid (**II**), a catalytic amount of KBr (**III**) and wet SiO<sub>2</sub> in the chloroform at room temperature

Entry	Substrate <b>1</b>	Product <b>2</b>	Reagent/catalyst/substrate (mmol) <sup>a</sup>			Time (h)	Yield (%) <sup>b</sup>
			<b>I</b>	<b>II</b>	<b>III</b>		
1	Benzyl alcohol	Benzaldehyde	2	–	0.2	1	68
2	Benzyl alcohol	– <sup>c</sup>	2	–	–	6.5	–
3	Benzyl alcohol	Benzaldehyde	–	3	0.3	2.83	100 <sup>d</sup>
4	4-Bromobenzyl alcohol	4-Bromobenzaldehyde	2	–	0.2	1.75	90
5	4-Bromobenzyl alcohol	4-Bromobenzaldehyde	–	3	0.3	4.66	80
6	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	2	–	0.2	3.75	35 <sup>e</sup>
7	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	2	–	0.2	1.5	92
8	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	–	3	0.3	4.5	79
9	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	2	–	0.2	1.75	82
10	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	–	3	0.3	2.16	70
11	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	2	–	0.2	1	100 <sup>d</sup>
12	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	2	–	0.4	1	100 <sup>d</sup>
13	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	–	3	0.3	2.5	100 <sup>d</sup>
14	4-Nitrobenzyl alcohol	– <sup>c</sup>	2	–	0.2	1	–
15	4-Nitrobenzyl alcohol	– <sup>c</sup>	–	3	0.3	4	–
16	4-Fluorobenzyl alcohol	4-Fluorobenzaldehyde	2	–	0.2	1.75	89 <sup>f</sup>
17	4-Fluorobenzyl alcohol	4-Fluorobenzaldehyde	–	3	0.3	3	100 <sup>d</sup>
18	4-Methoxybenzyl alcohols	– <sup>c</sup>	1	–	0.2	1	–
19	4-Methoxybenzyl alcohols	– <sup>c</sup>	–	3	0.3	6	–
20	1-Indanol	1-Indanone	2	–	0.2	0.45	75
21	1-Indanol	1-Indanone	–	3	0.3	2	80
22	2-Phenyl ethanol	2-Phenyl ethanal	–	3	0.3	100	100 <sup>d</sup>
23	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	2	–	0.2	2	100 <sup>d</sup>
24	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	–	3	0.3	3.5	100 <sup>d</sup>
25	Benzhydrol	– <sup>c</sup>	2	–	0.2	1	–
26	Benzhydrol	Benzophenone	1	–	0.2	2	75
27	Benzhydrol	Benzophenone	–	1	0.2	2	70
28	2-Menthol	2-Menthon	–	3	0.3	100	100 <sup>d</sup>
29	1-Cyclohexyl ethanol	1-Cyclohexyl ethanone	2	–	0.2	8.5	100 <sup>d</sup>
30	1-Cyclohexyl ethanol	1-Cyclohexyl ethanone	–	3	0.3	13	100 <sup>d</sup>
31	Cyclohexanol	Cyclohexanone	2	–	0.2	12	100 <sup>d</sup>
32	Cyclohexanol	Cyclohexanone	–	3	0.3	48	62 <sup>d</sup>
33	3-Pentanol	3-Pentanone	2	–	0.2	6	100 <sup>d</sup>
34	3-Pentanol	3-Pentanone	–	3	0.3	11	62 <sup>d</sup>
35	1-Octanol	1-Octanal	2	–	0.2	6.5	100 <sup>d</sup>
36	1-Octanol	1-Octanal	2	–	0.2	6.5	100 <sup>d</sup>

<sup>a</sup> Wet SiO<sub>2</sub>–substrate (0.2 g:1 mmol).

<sup>b</sup> Isolated yields.

<sup>c</sup> Mixture of products.

<sup>d</sup> GC yields.

<sup>e</sup> Without wet SiO<sub>2</sub>.

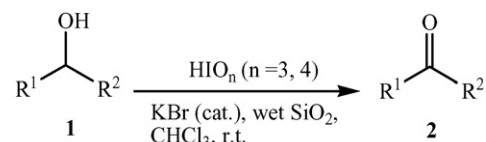
<sup>f</sup> Isolated as 2,4-dinitrophenylhydrazone derivative.

chromium(III) acetylacetonate and Fe(III)/2-picolinic acid [10]. In contrast to the periodic acid, there are two reports in literature about using iodic acid (HIO<sub>3</sub>) for the oxidation of alcohols. HIO<sub>3</sub>/wet montmorillonite K10 under microwave irradiation and HIO<sub>3</sub>/ammonium dichromate have been reported for the above-mentioned purpose [11].

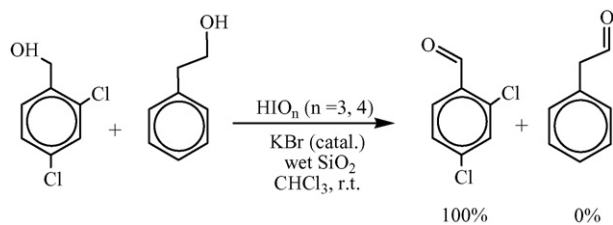
To the best of our knowledge all of the reported above-mentioned catalysts have toxic transition metal cations or reaction condition is harsh. Therefore, we decided to choose a safe and cheap catalyst for activation of periodic acid and iodic acid under mild condition.

In continuation of our studies on the oxidation of alcohols [12] and also using of periodic acid and iodic acid in organic transformation [13], we have found that these two solid acids in

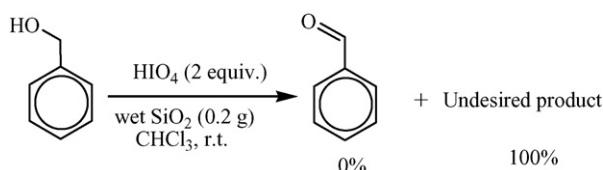
the presence of a catalytic amount of KBr can be oxidized alcohols to aldehydes and ketones under mild and heterogeneous condition. Herein we wish to report a very mild, simple, cheap and chemoselective method for the oxidation of alcohols to the corresponding carbonyl compounds using periodic acid or iodic acid (HIO<sub>n</sub>, n = 3, 4) and a catalytic amount of KBr in the pres-



Scheme 1.



Scheme 2.



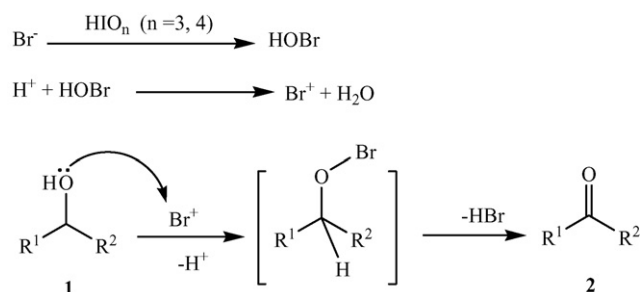
Scheme 3.

ence of wet SiO<sub>2</sub> in chloroform. Different types of alcohols (I) were subjected to the oxidation reaction in the presence of periodic acid (I) or iodic acid (II), catalytic amounts of KBr (III) and wet SiO<sub>2</sub> in chloroform at room temperature (Scheme 1 and Table 1).

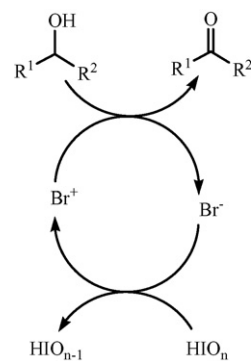
For showing the chemoselectivity of the described system some competitive reactions were design. A mixture of an equal amounts of 2,4-dichloro benzyl alcohols and 2-phenyl ethanol was subjected to oxidation in the presence of reagents under the reaction conditions given in entries 23 and 24 of Table 1 (Scheme 2). Reaction of benzyl alcohol with HIO<sub>4</sub> in the absence of catalyst (i.e. KBr) produces an undesired product (entry 2, Scheme 3). As is showing in the entry 4, reaction time in the absence of wet SiO<sub>2</sub> is long (entries 6 and 7).

These studies clearly reveal that the described method is a suitable catalytic procedure for the chemoselective oxidation of benzylic alcohols in the presence of aliphatic analogous. A plausible mechanism for the oxidation is shown in Scheme 4 based on literature [6,7], our observations and obtained results from catalytic activity of Br<sup>-</sup> [8] (Schemes 4 and 5).

In conclusion, chemoselectivity, the cheapness and availability of the reagents, easy and clean work-up and high yields make this method suitable for multi-step synthetic chemistry. We believe that the present methodology could be an important addition to the existing methodologies.



Scheme 4.



Scheme 5.

## 1. Experimental section

### 1.1. Typical procedure

A suspension of compound **1** (1 mmol), solid acid (I–II), wet SiO<sub>2</sub> (50% w/w) and KBr in CHCl<sub>3</sub> (6 ml) was stirred at room temperature for the specified time (see Table 1). The progress of the reaction was monitored by TLC. When the reaction was complete the suspension was filtered. The residue was washed with CHCl<sub>3</sub> (20 ml). Anhydrous Na<sub>2</sub>SO<sub>4</sub> (3 g) was added to the filtrate and filtered off after 20 min. The crude products were obtained after evaporation *in vacuo* and purified by recrystallization from methanol, ethanol or ethanol/water except for products which were volatile or oils.

### Acknowledgements

Financial support for this work by the Research Council of Bu-Ali Sina University, Hamadan, Iran, and Guilan University, Rasht, Iran (as a Common project) is gratefully acknowledged.

### References

- [1] D. Choudhary, S. Paul, R. Gupta, J.H. Clark, *Green Chem.* 8 (2006) 479.
- [2] P. Ferreira, E. Phillips, D. Rippon, S.C. Tsang, *Appl. Catal. B: Environ.* 61 (2005) 206.
- [3] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman, *Catal. Today* 57 (2000) 157.
- [4] J.H. Espenson, Z. Zhu, T.H. Zauche, *J. Org. Chem.* 64 (1999) 1191.
- [5] P.L. Anelli, C. Biffi, F. Montanari, S. Quici, *J. Org. Chem.* 52 (1987) 2559.
- [6] V.B. Sharma, S.L. Jain, B. Sain, *Synlett* (2005) 173.
- [7] (a) M. Bagherzadeh, *Tetrahedron Lett.* 44 (2003) 8943; (b) B.S. Koo, C.K. Lee, K.J. Lee, *Synth. Commun.* 32 (2002) 2115.
- [8] M.A. Zolfigol, F. Shirini, A.G. Choghamarani, *Synthesis* 12 (2006) 2043.
- [9] (a) See excellent review: H. Firouzabadi, A.A. Jafari, *J. Iran. Chem. Soc.*, 2 (2005) 85.; (b) See excellent review: P. Salehi, M.A. Zolfigol, F. Shirini, M. Baghbanzadeh, *Curr. Org. Chem.*, 10 (2006) 2171.;
- (c) M.A. Zolfigol, M. Bagherzadeh, S.E. Mallakpour, G. Chehardoli, A.G. Choghamarani, E. Kolvari, N. Koukabi, *Catal. Commun.*, 8 (2007) 256.
- [10] (a) M. Hunsen, *J. Fluorine Chem.* 126 (2005) 1356; (b) M. Hunsen, *Tetrahedron Lett.* 46 (2005) 1651; (c) L. Xu, M.L. Trudell, *Tetrahedron Lett.* 44 (2003) 2553; (d) S.S. Kim, I. Trushkov, S.K. Sar, *Bull. Korean Chem. Soc.* 23 (2002) 1331.
- [11] (a) F. Shirini, M.A. Zolfigol, M.R. Azadbar, *Russ. J. Org. Chem.* 37 (2001) 1600;

- (b) M.M. Hashemi, A. Rahimi, Z. Karimi-Jaberi, Y. Ahmadibeni, *Acta Chim. Slov.* 52 (2005) 86.
- [12] (a) M.A. Zolfigol, F. Shirini, I. Mohammadpoor-Baltork, A. Ghorbani-Choghamarani, M. Hajami, A.M. Sedaghat, *Mendeleev Commun.* (2005) 113;
- (b) B.F. Mirjalili, M.A. Zolfigol, A. Bamoniri, A. Zarei, *Bull. Korean Chem. Soc.* 24 (2003) 400;
- (c) F. Shirini, M.A. Zolfigol, M. Khaleghi, *Bull. Korean Chem. Soc.* 24 (2003) 1021;
- (d) F. Shirini, M.A. Zolfigol, B. Mallakpour, S.E. Mallakpour, A.R. Hajipour, *Aust. J. Chem.* 54 (2001) 405;
- (e) B.F. Mirjalili, M.A. Zolfigol, A. Bamoniri, Z. Zaghaghi, *J. Chem. Res., Synop.* (2003) 273;
- (f) B.F. Mirjalili, M.A. Zolfigol, A. Bamoniri, Z. Zaghaghi, A. Hazar, *Acta Chim. Slov.* 50 (2003) 563;
- (g) F. Shirini, M.A. Zolfigol, M. Khaleghi, *Phosphorus Sulfur* 178 (2003) 2107;
- (h) N. Iranpoor, H. Firouzabadi, M.A. Zolfigol, *Bull. Chem. Soc. Jpn.* 71 (1998) 905;
- (i) F. Shirini, M.A. Zolfigol, S. Torabi, *Lett. Org. Chem.* 2 (2005) 544.
- [13] (a) M.A. Zolfigol, G. Chehardoli, F. Shirini, S.E. Mallakpour, H. Nasr-Isfahani, *Synth. Commun.* 31 (2001) 1965;
- (b) D. Azarifar, H.G. Bosra, M.A. Zolfigol, M. Tajbaksh, *Heterocycles* 68 (2006) 175;
- (c) M.A. Zolfigol, M. Bagherzadeh, K. Niknam, F. Shirini, I. Mohammadpoor-Baltork, A.G. Choghamarani, M. Baghbanzadeh, *J. Iran. Chem. Soc.* 3 (2006) 73;
- (d) M.A. Zolfigol, A.G. Choghamarani, F. Shirini, H. Keypour, S. Salehzadeh, *Synth. Commun.* 31 (2001) 359;
- (e) F. Shirini, M.A. Zolfigol, M.M. Lakouraj, M.R. Azadbar, *Russ. J. Org. Chem.* 37 (2001) 1340;
- (f) F. Shirini, M.A. Zolfigol, M.R. Azadbar, *Synth. Commun.* 32 (2002) 315;
- (g) A.G. Choghamarani, *Synlett* (2006) 2347.