Asian Journal of Chemistry Vol. 21, No. 5 (2009), 3617-3621

Oxidation of Benzylic and Aliphatic Secondary Alcohols to Carbonyl Compounds with $KBrO_3/CeCl_3{\cdot}7H_2O$ System in Wet CH_3CN

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Potassium bromate in presence of $CeCl_3{\cdot}7H_2O$ effectively oxidizes benzylic and aliphatic secondary alcohols to the corresponding carbonyl compounds *i.e.*, primary alcohols selectively to aldehydes and secondary ones to ketones. The reactions are carried out in refluxing wet CH_3CN within 1.5-8.0 h. This oxidation system is quite ineffective for the oxidation of aliphatic primary alcohols. The chemoselective oxidation of benzylic or aliphatic secondary alcohols over aliphatic primary alcohols is achieved perfectly with $KBrO_3/CeCl_3{\cdot}7H_2O$ system.

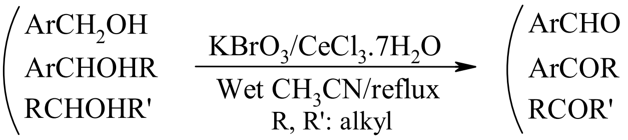
Key Words: Oxidation, Alcohols, $KBrO_3$, $CeCl_3{\cdot}7H_2O$, Aldehydes, Ketones.

INTRODUCTION

Sodium bromate and potassium bromate are commercially available stable solids and because of the capability of bromate anion in multi-electron transfer and high oxidation state of bromine, +5, these reagents potentially are strong oxidants and could be considered as interesting candidates for the oxidation of organic compounds. However, according to the literature, bromate itself is not able to oxidize organic compounds and therefore these reagents have not found many applications as an oxidizing agent in the field of organic synthesis. Bromates are usually used in aqueous media in the presence of co-reactants such as $NaHSO_3$[1], $KHSO_4$[2], H_2SO_4[3], *n*-Bu_4NHSO_4[4], silica chloride/wet SiO_2[5], silica sulfuric acid[6], HBr[7], Br_2[8], NH_4Cl[9], CAN[10], $HClO_4$[11] and ion exchange resin[12] for different oxidation purposes. Most of these oxidation systems suffer from disadvantages such as strong acidic conditions, overoxidation, bromination and tedious work-up procedure.

In the recent years, the effect of Lewis acids as promoters or catalysts for the oxidation of organic compounds with different oxidants has been reported. The literature review shows that the combination system of bromates with $FeCl_3$[13,14], $SnCl_4{\cdot}5H_2O$[15], $MnCl_2$[16] and $ZrOCl_2{\cdot}8H_2O$[17] has been reported for the oxidation of functional groups. Recently, the synergistic effect of Ce(IV) and Ce(III) ions with bromate anion as $(NO_3)_3CeBrO_3$[18] and $Ce(BrO_3)_3$[19] has been reported for the oxidation of alcohols, acyloins, arylarenes and sulfides. The preliminary preparation of these oxidants and the lack of selectivity in their oxidation systems prompted us to study the synergistic effect of Ce(III) ion with bromate anion in a simple and convenient procedure for the selective oxidation of alcohols.

In continuation of our research program directed to the application of $KBrO_3$ in organic synthesis[14-16], herein, we wish to report oxidation of benzylic and aliphatic secondary alcohols into the corresponding aldehydes and ketones by the combination system of $KBrO_3/CeCl_3 \cdot 7H_2O$ in refluxing wet CH_3CN (**Scheme-I**).



$$\begin{pmatrix} ArCH_2OH \\ ArCHOHR \\ RCHOHR' \end{pmatrix} \xrightarrow[\substack{\text{Wet } CH_3CN/\text{reflux} \\ R,\ R'\text{: alkyl}}]{KBrO_3/CeCl_3.7H_2O} \begin{pmatrix} ArCHO \\ ArCOR \\ RCOR' \end{pmatrix}$$

Scheme-I

EXPERIMENTAL

All reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. IR and ^1H NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and 300 MHz Bruker Avance spectrometers, respectively. The products were characterized by a comparison with authentic samples (melting or boiling points) and their ^1H NMR or IR spectra. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

A typical procedure for oxidation of benzyl alcohol to benzaldeyde with $KBrO_3/CeCl_3 \cdot 7H_2O$ system: In a round-bottomed flask (10 mL) equipped with magnetic stirrer and condenser, to a solution of benzyl alcohol (0.108 g, 1 mmol) in CH_3CN-H_2O (3:0.2 mL), $CeCl_3 \cdot 7H_2O$ (0.373 g, 1 mmol) and $KBrO_3$ (0.501 g, 3 mmol) was added. The reaction mixture was then stirred under reflux condition for 3 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/2). At the end of reaction, distilled water (5 mL) was added to the reaction mixture and it was stirred for an additional 5 min. The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Et_2O: 5/2) gave the pure benzaldehyde (0.1 g, 95 %, Table-1).

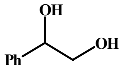
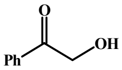
A typical procedure for competitive oxidation of 2-octanol over 1-octanol with $KBrO_3/CeCl_3 \cdot 7H_2O$ system: In a round-bottomed flask (10 mL) equipped with magnetic stirrer and condenser, to a solution of 1-octanol (0.13 g, 1 mmol) and 2-octanol (0.13 g, 1 mmol) in CH_3CN-H_2O (3:0.2 mL), $CeCl_3 \cdot 7H_2O$ (0.373 g, 1 mmol) and $KBrO_3$ (0.668 g, 4 mmol) was added. The reaction mixture was then stirred under reflux condition for 3 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/2). At the end of reaction, distilled water (5 mL) was added to the reaction mixture and it was stirred for an additional 5 min. The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Et_2O: 5/2) gave the pure 2-octanone as a sole product of oxidation and 1-octanol as an intact material (Table-2, entry 3).

TABLE-1
OXIDATION OF ALCOHOLS TO CARBONYL COMPOUNDS WITH $KBrO_3/CeCl_3·7H_2O$ SYSTEM[a]

Entry	Substrate	Product	Molar ratio Subs./ $KBrO_3$/Ce(III)	Time (h)	Yield (%)[b]
1	Benzyl alcohol	Benzaldehyde	1:3:1	3.0	95
2	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	1:3:1	4.0	93
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	1:3:1	4.0	92
4	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	1:3:1	4.5	92
5	2-Methylbenzyl alcohol	2-Methylbenzaldehyde	1:4:1	4.0	90
6	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	1:4:1	6.0	40
7	2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	1:4:1	4.0	90
8	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	1:4:1	8.0	93
9	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	1:4:1	4.5	93
10	4-*tert*-Butylbenzyl alcohol	4-*tert*-Butylbenzaldehyde	1:3:1	3.0	94
11	3-Pyridylmethanol	3-Pyridinecarbaldehyde	1:4:1	1.5	97
12	1-Phenylethanol	Acetophenone	1:4:1	4.5	99
13	1-Phenyl-1-propanol	Propiophenone	1:4:1	3.3	98
14	Benzoin	Benzil	1:4:1	8.0	99
15	(1S)-(-)-Borneol	(1S)-(-)-Camphor	1:4:1	3.0	95
16	(-)-Menthol	(-)-Menthone	1:4:1	8.0	96
17	2-Octanol	2-Octanone	1:4:1	3.0	94
18	1-Octanol	No reaction	1:5:1	10.0	–
19	2-Phenylethanol	No reaction	1:5:1	10.0	–
20	3-Phenyl-1-propanol	No reaction	1:5:1	10.0	–

[a] All reactions were carried out in refluxing CH_3CN-H_2O (3:0.2 mL).
[b] Yield refer to isolated pure products.

TABLE-2
COMPETITIVE OXIDATION OF ALCOHOLS WITH $KBrO_3/CeCl_3·7H_2O$ SYSTEM[a]

Entry	Substrate	Product	Molar ratio Subs./ $KBrO_3$/Ce(III)	Time (h)	Conversion (%)
1	Benzyl alcohol 1-Octanol	Benzaldehyde 1-Octanol	1:3:1	3.0	100 0
2	1-Phenylethanol 2-Phenylethanol	Acetophenone 2-Phenylethanol	1:4:1	4.5	100 0
3	2-Octanol 1-Octanol	2-Octanone 1-Octanol	1:4:1	3.0	100 0
4			1:4:1	3.0	100

[a] All reactions were carried out in refluxing CH_3CN-H_2O (3:0.2 mL).

RESULTS AND DISCUSSION

The preliminary observations showed that $KBrO_3$ is quite ineffective for the oxidation of benzyl alcohol under different conditions. However, it is found that when benzyl alcohol was allowed to react with 3 molar equivalents of $KBrO_3$ in the presence of 1 molar equivalent of $CeCl_3·7H_2O$ in refluxing CH_3CN-H_2O (3:0.2 mL), benzaldehyde was obtained as a sole product in 95 % yield within 3 h. This achievement prompted us to evaluate the applicability of this synthetic tool for the oxidation of other alcohols. Table-1 shows the general trend for molar equivalents of $KBrO_3/CeCl_3·7H_2O$, reaction times and yields in oxidation of structurally different benzylic and aliphatic secondary alcohols into the corresponding aldehydes and ketones.

The reactions were completed within 1.5-8.0 h with high to excellent yields of products. In the case of aliphatic primary alcohols this oxidation system is quite ineffective and 1-ocatnol, 2-phenylethanol and 3-phenyl-1-propanol were recovered from the reaction mixture after 10 h (entries 18-20). Therefore, we used this result successfully for the chemoselective oxidation of benzylic or aliphatic secondary alcohols over aliphatic primary alcohols with $KBrO_3/CeCl_3·7H_2O$ system. The results of this investigation are summarized in Table-2.

Conclusion

In this study, we have shown that the combination system of $KBrO_3/CeCl_3·7H_2O$ is an effective system for oxidation of benzylic and aliphatic secondary alcohols into the corresponding aldehydes and ketones in refluxing wet CH_3CN. The reactions were completed within 1.5-8.0 h with high to excellent yields of products. Oxidation of aliphatic primary alcohols was not carried out with this oxidation system. The chemoselective oxidation of benzylic or aliphatic secondary alcohols over aliphatic primary alcohols was achieved perfectly with $KBrO_3/CeCl_3·7H_2O$ system.

ACKNOWLEDGEMENT

The authors are gratefully acknowledged the Research Council of Urmia University for financial support of this work.

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(*Received*: 9 June 2008; *Accepted*: 10 February 2009) AJC-7233