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Oxidation of Alcohols by Ferric Nitrate in the Presence of Barium Chloride or Silica Sulphuric Acid under Mild Heterogeneous Conditions

Davood Habibi,[a*] Mohammad Ali Zolfigol,[a*] Farhad Shirini,[b] Maliheh Safaiee,[a] Masumeh Abedini [b] and Payam Rahmani [a]

[a] *Faculty of Chemistry, Bu-Ali Sina University, Hamadan, 6517838683, Iran.*
[b] *Department of Chemistry, Faculty of Science, Guilan University, Rasht, Iran.*

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ABSTRACT

Oxidation of various alcohols were carried out by the mixtures of $Fe(NO_3)_3.9H_2O$ and $BaCl_2.2H_2O$ or $Fe(NO_3)_3.9H_2O$ and silica sulphuric acid under mild and heterogeneous condition with good to excellent yield.

KEYWORDS

Oxidation, ferric nitrate, barium chloride, silica sulphuric acid, heterogeneous or solvent-free conditions.

1. Introduction

Selective oxidation of alcohols to their corresponding aldehydes and ketones is an important transformation in organic chemistry which has received the most attention over the years, especially in the search of versatile and selective reagent for this purpose. Various methods have been reported and used for oxidation of alcohols.1 For example, supported transition metals could oxidize the internal and external alcohols such as zeolite NaY-supported ruthenate.[2] Recently aerobic oxidation of alcohols by $Fe(NO_3)_3$ $FeBr_3$ efficiently accomplished.[3] In addition, ferric nitrate can oxidize alcohol in the presence of heteropoly acid.[4]

Traditional alcohol oxidation employs the strongest stoichiometric inorganic oxidizing reagents, such as PCC, $Na_2Cr_2O_7$,[5] $K_2Cr_2O_7$,[6] NaClO, $KMnO_4$,[7] MnO_2,[8] and so on.[9] These procedures are quite useful in laboratory-scale reactions, but these oxidants are usually expensive, hazardous or toxic, and they can produce a large amount of inorganic wastes which damage the environment seriously in bulk-scale reaction. On the other hand, any reduction in the amount of sulphuric acid needed or any simplification in handling procedures is required for risk reduction, economic advantage and environment protection. In addition, the separation of the products from the acid is often a difficult and energy consuming process that habitually implies a basic aqueous work-up. Other drawbacks against such oxidants and their use in multistage organic synthesis, in spite of their power, are their lack of selectivity, strong protic and aqueous conditions, low yields of the products and tedious work-up.

Therefore, we decided to investigate new reagent systems to overcome the above limitations. In addition, for our purpose a clean and easy work-up were also important. We also find that the solid acid is an excellent candidate for sulphuric acid replacement in organic reactions such as sulfonation of activated aromatic rings and destruction of acid-sensitive functional groups without any limitations. In addition, silica sulphuric acid is an excellent proton source for reactions in terms of convenience, cheapness, easy production and insolubility in all organic solvents.[10]

2. Results and Discussion

Two different catalytic systems (I: the mixture of ferric nitrate and barium chloride, and II: the mixture of ferric nitrate and silica sulphuric acid) have been used for the selective oxidation of varieties of primary, secondary and benzylic alcohols to their corresponding carbonyl compounds under mild conditions (Scheme 1). All results are given in Tables 1 and 2.

The mechanism for the first catalytic system (the mixture of $Fe(NO_3)_3.9H_2O$ and $BaCl_2.2H_2O$) can be suggested as follows:

$$\begin{aligned}
&2H_2O + BaCl_2 \rightleftharpoons Ba(OH)_2 + 2HCl\\
&HCl \longrightarrow H^+ + Cl^-\\
&Fe(NO_3)_3 \rightleftharpoons Fe^{3+} + 3NO_3^-\\
&3H^+ + NO_3^- \longrightarrow H_3O^+ + NO_2^+\\
&RCH_2OH + NO_2^+ \longrightarrow RCH_2O^+HNO_2\\
&RCH_2O^+HNO_2 \longrightarrow RCH_2ONO_2 + H^+\\
&RCH_2ONO_2 + Cl^- \longrightarrow RCHO + HCl + NO_2^-
\end{aligned}$$

The mechanism for the second catalytic system (the mixture of $Fe(NO_3)_3.9H_2O$ and silica sulphuric acid can be suggested as follows:

$$\begin{aligned}
&SiO_2\text{-}O\text{-}SO_3H \longrightarrow SiO_2\text{-}O\text{-}SO_3^- + H^+\\
&Fe(NO_3)_3 \rightleftharpoons Fe^{3+} + 3NO_3^-\\
&3H^+ + NO_3^- \longrightarrow H_3O^+ + NO_2^+\\
&RCH_2OH + NO_2^+ \longrightarrow RCH_2O^+HNO_2\\
&RCH_2O^+HNO_2 \longrightarrow RCH_2ONO_2 + H^+\\
&RCH_2ONO_2 + Cl^- \longrightarrow RCHO + HCl + NO_2^-
\end{aligned}$$

A combination of ferric nitrate and barium chloride or ferric nitrate and silica sulphuric acid can act as solid oxidation

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* To whom correspondence should be addressed.
E-mail: dhabibi@basu.ac.ir and zolfi@basu.ac.ir

Table 1 Oxidation of different alcohols to their corresponding carbonyl compound * by the mixture of $Fe(NO_3)_3.9H_2O$ and $BaCl_2.2H_2O$ (mole ratio 0.25:0.05) ** at 90°C under the solvent-free conditions.

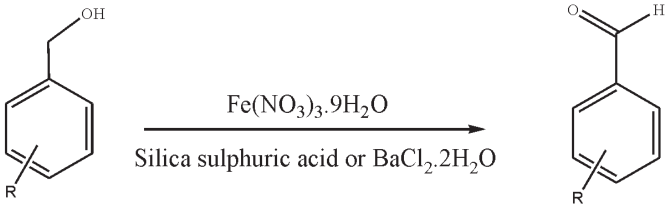
Entry	Substrate	Products	Time (min) ***	Isolated yield
1	2-Adamanthanol	2-Adamanthanone	40	100
2	2-Bromobenzylalcohol	2-Bromobenzaldehyde	25	90
3	4-Bromobenzyl alcohol	4-Bromobenzaldehyde	20	90
4	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	10	100
5	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	25	90
6	4-Isopropylbenzylalcohol	4-Isopropylbenzaldehyde	20	90
7	4-*t*-Butylbenzylalcohol	4-*t*-Butylbenzaldehyde	30	90
8	4-Methoxybenzylalcohol	4-Methoxybenzaldehyde	10	90
9	2-Methylbenzyl alcohol	2-Methylbenzaldehyde	30	90
10	2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	120	60
11	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	130	70
12	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	40	100
13	1-Phenylethanol	Acetophenone	40	90
14	2-Phenylethanol	2-Phenylethanol	20	90
15	2-Phenyl-1-propanol	2-Phenyl-1-propanal	30	90
16	3-Phenyl-1-propanol	3-Phenyl-1-propanal	25	90
17	1-Phenyl-2-propanol	1-Phenyl-2-propanone	25	90

* All products are known and their spectra as well as physical data have been reported in the literature.
** Optimum conditions are reported after several ratios were experimented with.
*** Optimum conditions are reported after several temperatures were experimented with.

Table 2 Oxidation of selected alcohols to their corresponding carbonyl compound * by the mixture of $Fe(NO_3)_3.9H_2O$ (1 mmol) and silica sulphuric acid (0.15 g) in dichloromethane at 40°C.

Entry	Substrate	Product	mmol of substrate **	Time ***	Isolated yield
1	4-bromobenzyl alcohol	4-bromobenzaldehyde	0.6	5.5 h	90
2	4-chlorobenzyl alcohol	4-chlorobenzaldehyde	0.7	5.5 h	42
3	4-methoxy-benzyl alcohol	4-methoxybenzaldehyde	0.6	3.25 h	60
4	4-nitrobenzyl alcohol	4-nitrobenzaldehyde	0.7	9.5 h	72
5	2-phenylethanol	2-phenylethanal	1.5	5 days	Trace
6	3-phenyl-1-propanol	3-phenyl-1-propanal	1.5	5 days	Trace

* All products are known and their spectra as well as physical data have been reported in the literature.
** Optimum conditions are reported after several ratios were experimented with.
*** Optimum conditions are reported after several temperatures were experimented with.



Scheme 1

reagents which readily can be weighed, handled and used. These solids are easily separated from the products by simple filtration. These reagents are cheap, non-toxic and commercially available. Easiness of the procedure as well as work-up makes the method attractive for organic chemists.

Comparisons of the two systems indicated that the first method (catalysed by the mixture of $Fe(NO_3)_3.9H_2O$ and $BaCl_2.2H_2O$) is more efficient than the second one (catalysed by the mixture of $Fe(NO_3)_3.9H_2O$ and silica sulphuric acid) due to the short reaction time and high yield. The result indicated that the alcohols with strong electron-deficient group such as the nitro group are oxidized more slowly.

2. Experimental

General Procedure

I. *Oxidation of alcohols by the mixture of $Fe(NO_3)_3.9H_2O$ and $BaCl_2.2H_2O$ under solvent-free conditions*

$Fe(NO_3)_3.9H_2O$ (0.101 g, 0.25 mmol) and $BaCl_2.2H_2O$ (0.012 g, 0.05 mmol) were mixed together and added to the corresponding alcohol (1 mmol). The resulting mixture was mixed for appropriate time at 90°C and progress of the reaction monitored by TLC. After completion, structure of the product was characterized by its physical data as well as the IR and NMR spectra.

II. *Oxidation of alcohols by the mixture of $Fe(NO_3)_3.9H_2O$ and silica sulphuric acid in CH_2Cl_2*

$Fe(NO_3)_3.9H_2O$ (0.242–0.606 g, 0.0.6–1.5 mmol), silica sulphuric acid (0.15 g), the corresponding alcohol (1 mmol) and CH_2Cl_2 (5 mL) were placed in a flask and the resulting mixture stirred for the appropriate time at 40°C. Progress of the reaction was monitored by TLC. After completion, the resulting mixture was filtered off, solvent removed and the pure product obtained.

Structure of the product was characterized by its physical data as well as the IR and NMR spectra.

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