

Metal-Free Oxidation of Alcohols to Their Corresponding Carbonyl Compounds Using NH_4NO_3 /Silica Sulfuric Acid

Amin Zarei

Department of Science, Fasa Branch, Islamic Azad University, Post Box No 364, Fasa 7461713591, Fars, Iran

E-mail: aj_zarei@yahoo.com

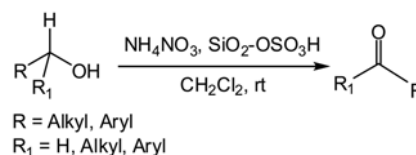
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A metal-free and efficient procedure for the oxidation of alcohols into the corresponding carbonyl compounds has been described using ammonium nitrate in the presence of silica sulfuric acid under mild and heterogeneous conditions. The use of non-toxic and inexpensive materials, simple and clean work-up, short reaction times and good yields of the products are among the advantages of this method.

Key Words : Oxidation, Alcohols, Ammonium nitrate, Silica sulfuric acid

Introduction

The oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important functional group transformations in organic chemistry which has received the most attention over years. Different methods have traditionally been employed for the oxidation of alcohols to their corresponding carbonyl compounds. Representative oxidants for this purpose include KMnO_4 ,¹ MnO_2 ,² Cr(VI) ,³ HNO_3 ,⁴ hypervalent iodine,⁵ activated dimethyl sulfoxide (DMSO),⁶ peroxides⁷ and electrophilic halogens.⁸ Although these methods have some synthetic advantages individually, they still suffer from some drawbacks such as low yields, long reaction times, the use of toxic heavy metal reagents, harsh reaction conditions, inconvenient and tedious work-up, using excess amount of oxidant and side reactions. Moreover, several reagents such as Oxone/palygorskite,⁹ bismuth(III) oxide,¹⁰ and polymer bromide-DMSO,¹¹ Solid-supported Pd(0) ,¹² ion-supported methyl sulfoxide and oxalyl chloride,¹³ and catalytic methods using metals have been developed for these transformations.¹⁴ Additionally, metal nitrates supported on inorganic supports have been used as oxidizing reagents. Iron (III) nitrate supported on silica gel (Silfen),¹⁵ iron (III) nitrate or copper (II) nitrate supported on K10-clay (Clayfen or Claycop),¹⁶ iron (III) nitrate mixed with HZSM-5 zeolite (Zeofen)¹⁷ and ferric nitrate activated by heteropoly acids¹⁸ are the reagents employed for the oxidation processes. However, the use of harmful transition metals and the stability of these reagents face problems. For example, Clayfen should be kept under *n*-pentane.¹⁸ Thus, the search for environmentally friendly as well as economical oxidation processes continues. On the other hand; recent rapidly growing environmental concerns need much greener transition-metal-free oxidation protocols.¹⁹ In the present study, a metal-free, simple, mild, and swift procedure for the oxidation of alcohols is report by using ammonium nitrate in the presence of silica sulfuric acid (SSA)²⁰ (Scheme 1).



Scheme 1

Experimental

Silica sulfuric acid was prepared according to previous works.²¹ All reagents were purchased from Merck and Aldrich and used without further purification. The products were characterized by comparison with authentic samples and by spectral data (IR, ^1H NMR, ^{13}C NMR, and MS). ^1H NMR spectra were recorded at 300 MHz. The spectra were measured in CDCl_3 using tetramethylsilane as the internal standard. GC analysis was run with Shimadzu GC-14A.

General Procedure for the Oxidation of Active Benzylic Alcohols Using Substoichiometric Amount of Ammonium Nitrate in the Presence of Silica Sulfuric Acid. Ammonium nitrate (0.032 g, 0.4 mmol) and silica sulfuric acid (0.175 g, 0.7 mmol) were mixed together in a mortar and were gently ground by a pestle to obtain a homogeneous reagent. Then, this reagent was slowly added to a vigorous stirring mixture of the corresponding active benzylic alcohol (1 mmol) and dichloromethane (5 mL). The reaction was carried out at room temperature for the appropriate reaction time (Table 4, entries 1-19). After completion of the reaction (monitored by TLC or GC), the reaction mixture was filtered off and the residue was washed with CH_2Cl_2 (3×5 mL). The combined organic layer was washed with NaHCO_3 (5%) and dried over Na_2SO_4 . The solvent was removed under reduced pressure to obtain almost pure carbonyl compound. Further purification was performed by column chromatography on silica gel and using cyclohexane-EtOAc (3:1) as eluents.

General Procedure for the Oxidation of Inactive Benzylic Alcohols and Saturated Alcohols Using Ammonium Nitrate in the Presence of Silica Sulfuric Acid. Ammonium nitrate (0.08 g, 1 mmol) and silica sulfuric acid (0.43 g, 1.7 mmol)

were mixed together in a mortar and were gently ground by a pestle to obtain a homogeneous reagent. Then, this reagent was slowly added to a vigorous stirring mixture of the corresponding alcohol (1 mmol) and dichloromethane (5 mL). The reaction was carried out at room temperature for the appropriate reaction time (Table 4, entries 21-37). After completion of the reaction (monitored by TLC or GC), the reaction mixture was filtered off and the residue was washed with CH_2Cl_2 (3×5 mL). The combined organic layer was washed with NaHCO_3 (5%) and dried over Na_2SO_4 . The solvent was removed under reduced pressure to obtain almost pure carbonyl compound. Further purification was performed by column chromatography on silica gel and using cyclohexane-EtOAc as eluents.

The Spectral Data of Some Representative Products.

1-(4-Methoxyphenyl)-3-phenylpropane-1-one (Table 4, entry 14): White solid; mp 96-98 °C; IR (KBr) cm^{-1} : 3040, 2915, 1670, 1600, 1570, 1500, 1450, 1420, 1255, 1170, 1020, 980, 840, 780, 745, 700. ^1H NMR (300 MHz, CDCl_3): δ 7.95 (2 H, d, $J = 8.87$ Hz), 7.37-7.2 (5 H, m), 6.92 (2 H, d, $J = 8.87$ Hz), 3.86 (3 H, s), 3.25 (2 H, t, $J = 8.05$ Hz), 3.05 (2 H, t, $J = 8.05$ Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 198, 163.2, 141.5, 130.5, 130.2, 128.5, 127.9, 126.3, 113.7, 55.5, 40.5, 30.5. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 79.97; H, 6.71%. Found: C, 79.84; H, 6.83%.

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethanone (Table 4, entry 15): Yellow solid; mp 114-116 °C; IR (KBr) cm^{-1} : 3055, 2930, 1680, 1600, 1510, 1450, 1350, 1340, 1270, 1175, 990, 825, 730. ^1H NMR (300 MHz, CDCl_3): δ 8.3 (2 H, d, $J = 8.65$ Hz), 8.1 (2 H, d, $J = 8.7$ Hz), 7.55 (2 H, d, $J = 8.65$ Hz), 7.06 (2 H, d, $J = 8.7$ Hz), 4.43 (2 H, s), 4 (3 H, s). ^{13}C NMR (75 MHz, CDCl_3): δ 195, 165, 143.2, 131.5, 131.1, 130, 124.4, 115, 110.6, 56, 46. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_4$: C, 66.41; H, 4.83; N, 5.16%. Found: C, 66.38; H, 4.89; N, 5.09%.

(2-Methoxynaphthalene-1-yl) (phenyl)methanone (Table 4, entry 16): Light cream solid; mp 125-127 °C; IR (KBr) cm^{-1} : 3060, 2916, 2830, 1660, 1590, 1500, 1450, 1250, 1070, 880, 780, 690. ^1H NMR (300 MHz, CDCl_3): δ 8-7.85 (4 H, m), 7.6-7.35 (7 H, m), 3.85 (3 H, s). EIMS m/z (%): 262 (M^+ , 62), 245 (16), 185 (100), 142 (15), 105 (15), 77 (30). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.42; H, 5.38%. Found: C, 82.28; H, 5.45%.

4-Nitro-4'-phenylbenzophenone (Table 4, entry 30): Bright yellow solid; mp 163-165 °C; IR (KBr) cm^{-1} : 3060, 1650, 1600, 1515, 1355, 1280, 935, 845, 755, 730, 700. ^1H NMR (300 MHz, CDCl_3): δ 8.37 (2 H, d, $J = 9.1$ Hz), 7.97 (2 H, d, $J = 9.1$ Hz), 7.88 (2 H, d, $J = 8.65$ Hz), 7.74 (2 H, d, $J = 8.65$ Hz), 7.66 (2 H, d, $J = 8.4$ Hz), 7.5 (3 H, m). EI MS m/z (%): 303 (M^+ , 70), 181 (100), 153 (30), 152 (53), 76 (15). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{NO}_3$: C, 75.24; H, 4.32; N, 4.62%. Found: C, 75.36; H, 4.43; N, 4.51%.

Results and Discussion

Initially, to optimize the reaction conditions, oxidation of benzyl alcohol, as a model compound, was set in the

presence of several acidic catalysts in dichloromethane. As shown in Table 1, in the absence of SSA, the oxidation reaction did not proceed after 60 minutes at room temper-

Table 1. Oxidation of benzyl alcohol to benzaldehyde using NH_4NO_3 in the presence of various acids at room temperature^{a,b}

Entry	Acid	Benzyl alcohol/ Acid/ NH_4NO_3	Time (min)	Yield (%)
1	None	1 : 0 : 0.4	60	0
2	SSA	1 : 0.7 : 0.4	25	86
3	$\text{H}_3\text{PW}_{12}\text{O}_{40}$ ^c	1 : - : 0.4	30	trace
4	HZSM-5 ^c	1 : - : 0.4	30	0
5	Montmorillonite-K10 ^c	1 : - : 0.4	30	0
6	Amberlyst-15H ^{+c}	1 : - : 0.4	30	trace
7	$\text{H}_2\text{SO}_4/\text{SiO}_2$	1 : 0.7 : 0.4	30	72
8	Al_2O_3 ^c	1 : - : 0.4	30	0
9	SiO_2 ^c	1 : - : 0.4	30	0
10	TsOH	1 : 0.7 : 0.4	30	trace
11	$[\text{Hmim}]\text{HSO}_4^-$	1 : 0.7 : 0.4	30	trace
12	H_2SO_4	1 : 0.7 : 0.4	30	trace

^aReaction conditions: NH_4NO_3 (0.4 mmol), catalyst (0.7 mmol) and benzyl alcohol (1 mmol) were carried out in 5 mL of CH_2Cl_2 . ^bThe yields refer to the isolated pure products. ^c0.2 g of the catalyst was used.

Table 2. Oxidation of benzyl alcohol to benzaldehyde using various metal nitrates in the presence of SSA at room temperature^{a,b}

Entry	Metal Nitrate	Time (min)	Yield (%)
1	NH_4NO_3	25	86
2	NaNO_3	25	15
3	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	30	62
4	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	30	78
5	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	30	85
6	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	30	56
7	$\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$	25	85
8	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	30	45
9	$\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$	30	30

^aReaction conditions: metal nitrate (0.4 mmol), SSA (0.7 mmol) and benzyl alcohol (1 mmol) were carried out in 5 mL of CH_2Cl_2 . ^bThe yields refer to the isolated pure products.

Table 3. Oxidation of benzyl alcohol to benzaldehyde using NH_4NO_3 and SSA in various solvents and under solvent-free conditions^{a,b}

Entry	Solvent	Time (min)	Yield (%)
1	EtOAc	60	trace
2	Et_2O	60	trace
3	Acetone	60	trace
4	MeCN	60	trace
5	H_2O	25	0
6	<i>n</i> -Hexane	25	75
7	CH_2Cl_2	25	86
8	Solvent-free ^c	25	80

^aReaction conditions: NH_4NO_3 (0.4 mmol), SSA (0.7 mmol) and benzyl alcohol (1 mmol) were carried out in 5 mL of solvent at room temperature.

^bThe yields refer to the isolated pure products. ^c NH_4NO_3 (0.4 mmol), SSA (0.7 mmol) and benzyl alcohol (1 mmol) were ground at room temperature.

Table 4. Oxidation of various alcohols using NH_4NO_3 activated by SSA at room temperature^{a,b}

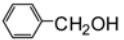
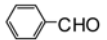
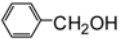
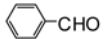
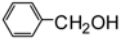
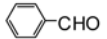
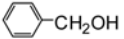
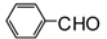
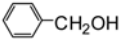
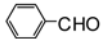
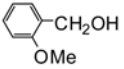
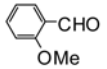
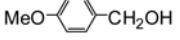

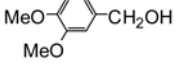
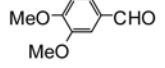
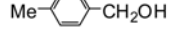
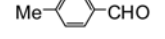
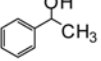
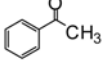
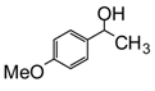
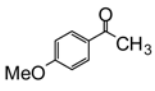
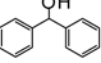
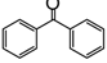
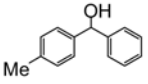
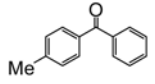
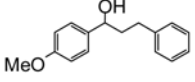
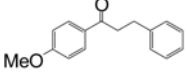
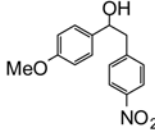
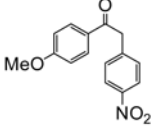
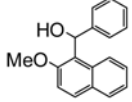
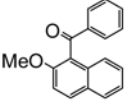


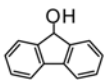
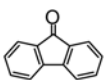
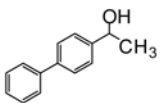
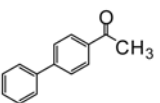
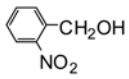
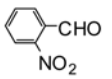
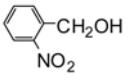
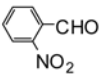
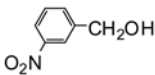
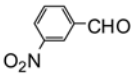
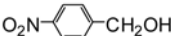

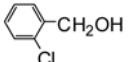
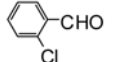
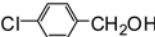
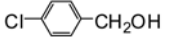
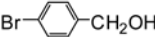
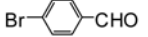
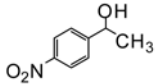
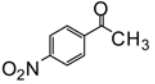
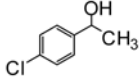
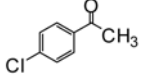
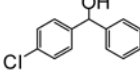
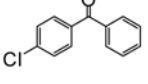
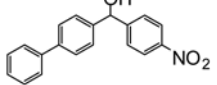
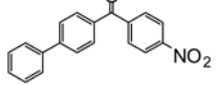
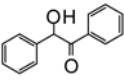
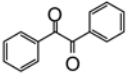
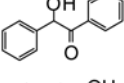
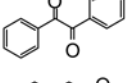


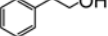
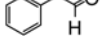
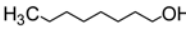
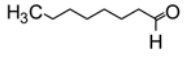

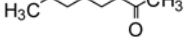


Entry	Alcohol	Alcohol/SSA/ NH_4NO_3	Product	Time (min)	Yield (%)
1		1 : 0.175 : 0.1		25	trace
2		1 : 0.35 : 0.2		25	30
3		1 : 0.52 : 0.3		25	62
4		1 : 0.7 : 0.4		25	86
5 ^c		1 : 0.875 : 0.5		25	85
6		1 : 0.7 : 0.4		25	85
7		1 : 0.7 : 0.4		25	87
8		1 : 0.7 : 0.4		25	88
9		1 : 0.7 : 0.4		25	86
10		1 : 0.7 : 0.4		30	84
11		1 : 0.7 : 0.4		30	86
12		1 : 0.7 : 0.4		40	83
13		1 : 0.7 : 0.4		40	82
14		1 : 0.7 : 0.4		35	80
15		1 : 0.7 : 0.4		40	77
16		1 : 0.7 : 0.4		40	80
17		1 : 0.7 : 0.4		30	87
18		1 : 0.7 : 0.4		40	85
19		1 : 0.7 : 0.4		30	84
20		1 : 0.7 : 0.4		60	trace
21		1 : 1.7 : 1		30	83

Table 4. Continued

Entry	Alcohol	Alcohol/SSA/NH ₄ NO ₃	Product	Time (min)	Yield (%)
22		1 : 1.7 : 1		30	86
23		1 : 1.7 : 1		30	88
24		1 : 1.7 : 1		30	85
25		1 : 1.7 : 1		30	88
26		1 : 1.7 : 1		30	89
27		1 : 1.7 : 1		30	86
28		1 : 1.7 : 1		30	87
29		1 : 1.7 : 1		45	84
30		1 : 1.7 : 1		45	78
31		1 : 1.7 : 1		45	15
32 ^d		1 : 1.7 : 1		15	62
33		1 : 1.7 : 1		60	trace
34 ^d		1 : 1.7 : 1		15	58
35 ^{d,e}		1 : 1.7 : 1		15	56
36 ^e		1 : 1.7 : 1		90	55
37 ^e		1 : 1.7 : 1		90	56

^aThe yields refer to the isolated pure products. ^bThe products were characterized from their spectral data (IR, ¹H NMR, ¹³C NMR, and MS) and compared with authentic samples. ^cBenzoic acid was obtained in 5% yield. ^dThe reaction was carried out in 5 mL of 1,2-dichloroethane under reflux conditions. ^eThe yields refer to GC analysis.

ature. However, in the presence of silica sulfuric acid this reaction was efficiently carried out after 25 minutes at room temperature (Table 1, entry 2). To compare the activity of SSA with other acidic catalysts, we studied the activity of Montmorillonite-K10, HZSM-5 zeolite, H₃PW₁₂O₄₀, H₂SO₄ supported on silica gel, Amberlyst-15H⁺, Al₂O₃, SiO₂, *p*-toluenesulfonic acid, 1-methylimidazolium hydrogensulfate ([Hmim]HSO₄⁻),²² as an acidic ionic liquid, and sulfuric acid for the oxidation of benzyl alcohol in the presence of substoichiometric amount of ammonium nitrate. It was found that SSA was the best solid acid for this purpose. This is probably due to the high surface area of SiO₂ (300-600

m².g⁻¹)²³ as a support which a number of -OSO₃H groups are immobilized on it.^{20,21}

The oxidation of benzyl alcohol to benzaldehyde was also studied with other metal nitrates under the same reaction conditions. As shown in Table 2, most of these metal nitrates were effective oxidants for this transformation. However, some of these salts are toxic, harmful and expensive. In addition, ammonium nitrate is more inexpensive and more abundant than those metal nitrates. Furthermore, NH₄NO₃/SSA is easily prepared and does not need any precautions for its handling.

Moreover, the effect of solvent on the oxidation of benzyl

alcohol to benzaldehyde was studied. Therefore, the oxidation of benzyl alcohol was carried out in different solvents and also under solvent-free conditions. It was found that in comparison with other conditions, the yield of the reaction in dichloromethane was higher and the reaction time was shorter (Table 3, entry 7). It is clear that the solvents with lone pair electrons, can act as the weak Lewis bases. Therefore, proton transfers between oxygen or nitrogen of these solvents and a strong acid are usually fast.²⁴ In the present work, nitrate ion (NO_3^-), as a relatively weak base, reacted with silica sulfuric acid to generate nitronium ion (NO_2^+).^{20d} Then, the oxidation process was followed by this ion.²⁵ We think that using the solvent with proton transfer ability (Table 3, entry 1-5), can compete with nitrate ion for abstracting proton of SSA leading to decrease the reaction rate extremely. In comparison with *n*-hexane, the yield of the product was higher in dichloromethane. This may be due to higher dielectric constant of dichloromethane than *n*-hexane. Also, the yield of the product was lower in solvent-free conditions than that in dichloromethane. It might be due to lower homogeneity under solvent-free conditions (Table 3, entry 8). Therefore, we employed this oxidation system for the oxidation of various alcohols to their corresponding carbonyl compounds in dichloromethane.

To optimize the molar ratio of $\text{NH}_4\text{NO}_3/\text{SSA}$, oxidation of benzyl alcohol (1 mmol) to benzaldehyde in dichloromethane was studied using different molar ratio of $\text{NH}_4\text{NO}_3/\text{SSA}$ (Table 4, entries 1-5). The best molar ratio was 0.4/0.7 of $\text{NH}_4\text{NO}_3/\text{SSA}$ (Table 4, entry 4). By increasing the molar ratio of $\text{NH}_4\text{NO}_3/\text{SSA}$, over oxidation of benzyl alcohol to benzoic acid was observed (Table 4, entry 5).

By using substoichiometric amount of ammonium nitrate supported on silica sulfuric acid, active benzylic alcohols (with electron-donating groups on aromatic rings) were converted to their corresponding carbonyl compounds in good yields at room temperature (Table 4, entries, 4, 6-19). These reactions were carried out under mild and heterogeneous conditions and the products were extracted by simple filtration. Over oxidation of aldehydes to the corresponding carboxylic acids and aromatic nitration were not observed in any cases studied using the present reaction conditions. For the oxidation of inactive benzylic alcohols (with electron-withdrawing groups on aromatic rings), and also primary and secondary saturated alcohols, it was necessary to increase the molar ratio of $\text{NH}_4\text{NO}_3/\text{SSA}$ to obtain quantitative amount of products in short reaction times (Table 4, entries 21-37).

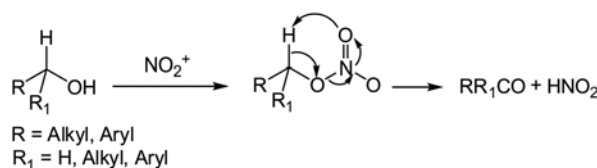
In order to show the merit of the present method, a number of competitive reactions were performed. Using substoichiometric amount of ammonium nitrate in the presence of silica sulfuric acid, benzyl alcohol was competitively converted to benzaldehyde in the presence of 4-nitrobenzyl alcohol and 2-phenylethanol (Table 5, entries 1, 2). Moreover, it was notable that some functional groups were almost intact during the oxidation process (Table 5, entries 3-5).

On the basis of these results, two mechanisms for the oxidation of alcohols using $\text{NH}_4\text{NO}_3/\text{SSA}$ are suggested

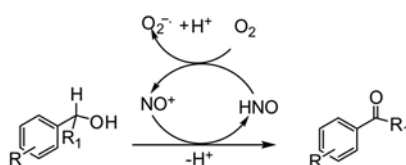
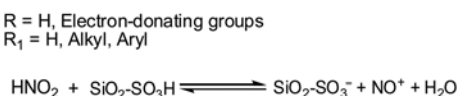
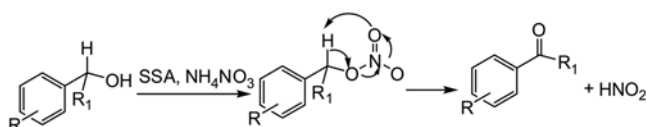
Table 5. Competitive oxidation of benzyl alcohol to benzaldehyde in the presence of some functional groups using $\text{NH}_4\text{NO}_3/\text{SSA}$ ^a

1	
2	
3	
4	
5	

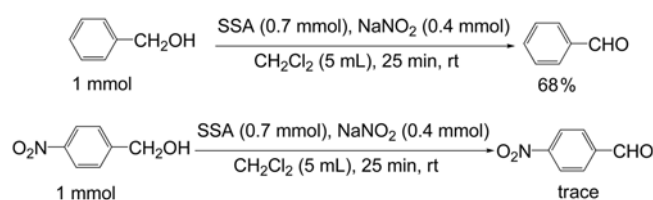
^aBased on GC and TLC analysis.



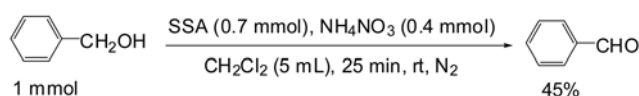
Scheme 2



Scheme 3



Scheme 4



Scheme 5

(Scheme 2 and 3). First, nitronium ion (NO_2^+) is generated by using a mixture of ammonium nitrate and silica sulfuric acid.^{20d} For inactive benzylic alcohols and also saturated alcohols, the oxidation reactions are carried out by NO_2^+ (Scheme 2).²⁵ However, for active benzylic alcohols, after the generation of nitrosonium ion (NO^+), this ion follows out the oxidation process in the presence of molecular oxygen (Scheme 3).²⁶

To clarify these mechanisms, we studied the oxidation of benzyl alcohol and 4-nitrobenzyl alcohol using substoichiometric amount of NaNO_2 in the presence of SSA. Nitrosonium ion (NO^+) is generated by using a mixture of sodium nitrite and silica sulfuric acid.^{20a} As shown in Scheme 4, NO^+ was not suitable for the oxidation of 4-nitrobenzyl alcohol as an inactive benzylic alcohol. This ion, however, was an effective oxidant for the oxidation of benzyl alcohol. The results showed that nitronium ion was a useful oxidant for the oxidation of inactive benzylic alcohols. However, the oxidation of active benzylic alcohols was carried out by both nitronium ion and nitrosonium ion. Ultimately, by comparison the present results, it is found that NO_2^+ is more reactive oxidant than NO^+ .

Finally, in order to approve the oxidation mechanism, the oxidation of benzyl alcohol to benzaldehyde was studied by using a substoichiometric amount of NH_4NO_3 in the presence of SSA under an atmosphere of nitrogen. As shown in Scheme 5, the yield of the reaction is low because, in the absence of molecular oxygen in the reaction mixture, NO^+ is not regenerated via the oxidation of HNO .²⁶

Conclusion

In conclusion, a simple and efficient method for the metal-free oxidation of alcohols to their corresponding carbonyl compounds was introduced by using ammonium nitrate in the presence of silica sulfuric acid. The use of non-toxic and inexpensive materials, simple and clean work-up, short reaction times, good yields of the products and mild reaction conditions were the advantages of the described method.

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References

- (a) Shabani, A.; Lee, D. G. *Tetrahedron Lett.* **2001**, 42, 5833-5836. (b) Mirjalili, F.; Zolfigol, M. A.; Bamoniri, A.; Zarei, A. *Bull. Korean Chem. Soc.* **2003**, 24, 400-402.
- (a) Matsubara, J.; Nakao, K.; Hamada, Y.; Shioiri, T. *Tetrahedron Lett.* **1992**, 33, 4187-4190. (b) Aoyama, T.; Sonoda, N.; Yamauchi, M.; Toriyama, K.; Anzai, M.; Ando, A.; Shioiri, T. *Synlett* **1998**, 35-36. (c) Struve, G.; Seltzer, S. J. *J. Org. Chem.* **1982**, 47, 2109-2113. (d) Lou, J. D.; Xu, Z. N. *Tetrahedron Lett.* **2002**, 43, 6149-6150.
- (a) Lou, J. D.; Xu, Z. N. *Tetrahedron Lett.* **2002**, 43, 8843-8844. (b) Mirjalili, F.; Zolfigol, M. A.; Bamoniri, A.; Zarei, A. *Phosphorus Sulfur and Silicon* **2003**, 178, 1845-1849. (c) Hajipour, A. R.; Mallakpour, S.; Khoei, S. *Synlett* **2000**, 740-742. (d) Cardillo, G.; Orena, M.; Sandri, S. *Synthesis* **1976**, 394-396.
- (a) Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; Palmieri, G. *Synth. Commun.* **1988**, 18, 69-75. (b) Strazzolini, P.; Runcio, A. *Eur. J. Org. Chem.* **2003**, 526-536. (c) Barrett, A. G. M.; Braddock, D. C.; McKinnell, R. M.; Waller, F. J. *Synlett* **1999**, 1489-1490. (d) Minisci, F.; Porta, O.; Recupero, F.; Punta, C.; Gambarotti, C.; Pierini, M.; Galimberti, L. *Synlett* **2004**, 2203-2205.
- (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, 102, 2523-2584. (b) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, 44, 3656-3665. (c) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, 113, 7277-7287. (d) More, J. D.; Finney, N. S. *Org. Lett.* **2002**, 4, 3001-3003. (e) Surendra, K.; Krishnaveni, N. S.; Reddy, M. A.; Nageswar, Y. V. D.; Rao, K. R. *J. Org. Chem.* **2003**, 68, 2058-2059.
- (a) Muncusco, A. J.; Huang, S. L.; Swern, D. J. *J. Org. Chem.* **1978**, 43, 2480-2482. (b) Tidwell, T. T. *Synthesis* **1990**, 857-870.
- (a) Sharma, V. B.; Jain, S. L.; Sain, B. *Synlett* **2005**, 173-175. (b) Bogda, D.; Lukasiewicz, M. *Synlett* **2000**, 143-145. (c) Chhikara, B. S.; Chandra, R.; Tandon, V. *Synlett* **2005**, 872-874. (d) Liu, C.; Han, J.; Wang, J. *Synlett* **2007**, 643-645. (e) Ferguson, G.; Ajjou, A. N. *Tetrahedron Lett.* **2003**, 44, 9139-9142.
- (a) Zolfigol, M. A.; Shirini, F.; Ghorbani Choghamaran, A. *Synthesis* **2006**, 2043-2046. (b) Mirafzal, G. A.; Lozeva, A. M. *Tetrahedron Lett.* **1998**, 39, 7263-7266. (c) Hanessian, S.; Wong, D. H.; Therien, M. *Synthesis* **1981**, 394-396. (d) Arterburn, J. B. *Tetrahedron* **2001**, 57, 9765-9788.
- Wu, S.; Ma, H.; Lei, Z. *Synlett* **2010**, 2818-2822.
- Malik, P.; Chakraborty, D. *Synthesis* **2010**, 3736-3740.
- Prasanna, T. S. R.; Mohanaraju, K. *Tetrahedron Lett.* **2011**, 52, 6971-6973.
- Bandna, Aggarwal, N.; Das, P. *Tetrahedron Lett.* **2011**, 52, 4954-4956.
- Tsuchiya, D.; Moriyama, K.; Togo, H. *Synlett* **2011**, 2701-2704.
- (a) Dewan, A.; Sarma, T.; Bora, U.; Kakati, D. K. *Tetrahedron Lett.* **2011**, 52, 2563-2565. (b) Moyer, S. A. Funk, T. W. K. *Tetrahedron Lett.* **2010**, 51, 5430-5433.
- (a) Hirano, M.; Ukawa, K.; Yakabe, S.; Morimoto, T. *Synth. Commun.* **1997**, 27, 1527-1533. (b) Hirano, M.; Komiya, K.; Yakabe, S.; Clark, J. H.; Morimoto, T. *Org. Prep. Proced. Int.* **1996**, 28, 705-708. (c) Hirano, M.; Ukawa, K.; Yakabe, S.; Morimoto, T. *Org. Prep. Proced. Int.* **1997**, 29, 480-484. (d) Khadilkar, B.; Borkar, S. *Synth. Commun.* **1998**, 28, 207-212. (e) Hirano, M.; Komiya, K.; Morimoto, T. *Org. Prep. Proced. Int.* **1995**, 27, 703-706.
- (a) Heravi, M. M.; Ajami, D.; Mojtahedi, M. M.; Ghassemzadeh, M. *Tetrahedron Lett.* **1999**, 40, 561-562. (b) Varma, R. S.; Dahiya, R. *Tetrahedron Lett.* **1998**, 39, 1307-1308. (c) Laszlo, P.; Cornelis, A. *Synthesis* **1985**, 909-918. (d) Laszlo, P.; Cornelis, A. *Synthesis* **1980**, 849-850.
- Heravi, M. M.; Ajami, D.; Mojtahedi, M. M.; Ghassemzadeh, M. *Chem. Commun.* **1999**, 833-834.
- Firouzabadi, H.; Iranpoor, N.; Amani, K. *Synthesis* **2003**, 849-412.
- (a) Lee, J. C.; Lee, J. Y.; Lee, J. M. *Bull. Korean Chem. Soc.* **2005**, 26, 1300-1302. (b) Oda, Y.; Hirano, K.; Satoh, T.; Kuwabata, S.;

- Miura, M. *Tetrahedron Lett.* **2011**, 52, 5392-5394.
20. (a) Zolfigol, M. A. *Tetrahedron* **2001**, 57, 9509-9511. (b) Zolfigol, M. A.; Shirini, F.; Ghorbani Choghamarani, A.; Mohammadpoor-Baltork, I. *Green Chem.* **2002**, 4, 562-564. (c) Hajipour, A. R.; Mirjalili, B. B. F.; Zarei, A.; Khazdooz, L.; Ruoho, A. E. *Tetrahedron Lett.* **2004**, 45, 6607-6609. (d) Zolfigol, M. A.; Mirjalili, B. B. F.; Bamoniri, A.; Karimi, M. A.; Zarei, A.; Khazdooz, L.; Noei, J. *Bull. Korean Chem. Soc.* **2004**, 25, 1414-1416.
21. (a) Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Mirjalili, B. B. F.; Sheikhan, N.; Zahmatkesh, S.; Ruoho, A. E. *Synthesis* **2005**, 3644-3648. (b) Hajipour, A. R.; Zarei, A.; Ruoho, A. E. *Synth. Commun.* **2006**, 36, 1039-1050. (c) Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Ruoho, A. E. *Synth. Commun.* **2005**, 35, 2237-2241.
22. Hajipour, A. R.; Khazdooz, L.; Ruoho, A. E. *Catal. Commun.* **2008**, 9, 89-96.
23. Clark, J. H. *Catalysis of Organic Reactions by Supported Inorganic Reagents*; VCH: New York, 1994.
24. Smith, M. B.; March, J. *Advanced Organic Chemistry*; Wiley and Sons: New York, 2001; p 327-351.
25. Hajipour, A. R.; Rafiee, F.; Ruoho, A. E. *Synlett* **2007**, 1118-1120.
26. Matsumura, Y.; Yamamoto, Y.; Moriyama, N.; Furukubo, S.; Iwasaki, F.; Onomura, O. *Tetrahedron Lett.* **2004**, 45, 8221-8224.
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