

Selective Oxidation of Alcohols with a New Reagent: Iron(III) Nitrate Supported on Aluminum Silicate

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Abstract: A selective and effective oxidation of alcohols, except aliphatic alcohols, such as 1-hexanol or 1-octyl alcohol, to the corresponding aldehydes and ketones using a new reagent, iron(III) nitrate supported on aluminum silicate, under heterogeneous conditions with reflux with 85–98% yield is described.

Keywords: alcohol, aluminum silicate, iron (III), nitrate nonahydrate, oxidation

INTRODUCTION

Iron(III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], a relatively nontoxic chemical, has been widely used as a multipurpose reagent for the transformation of a variety of organic functional groups. For example, the selective oxidation of alcohols, oxidative coupling of thiols, carbonyl group deprotections, synthesis of azides and iminophosphoranes, aromatization of

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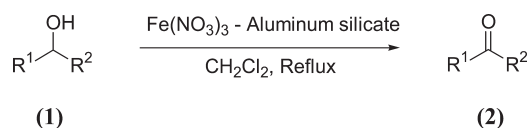
1,4-dihydropyridines, and regioselective nitration of phenols have all been reported using this reagent.^[1]

So far, iron(III) nitrate nonahydrate supported on several inorganic materials has been employed as an oxidizing reagent for the selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. Typical examples reported in the literature are iron(III) nitrate supported on K 10-clay,^[2] silica gel,^[3] graphite,^[4] and kieselguhr.^[5] These supported reagents have achieved good selectivity under mild reaction conditions and convenient isolation of the products. Although a diversity of $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ supported reagents described previously are available for the oxidation transformation, they have some common stability problems. Therefore, to develop new methods or reagents is still an interested topic for organic chemists, especially in the search of stable, versatile, and selective oxidants such as iron(III) nitrate-based reagents.

RESULTS AND DISCUSSION

Previously, we have described that aluminum silicate is a good inorganic solid support of both chromic acid^[6] and potassium permanganate^[7] for the selective oxidation of alcohols to carbonyl compounds. In connection with our previous studies,^[6,7] we now report that iron(III) nitrate supported on aluminum silicate is a new reagent suitable for the selective oxidation of primary and secondary alcohols (**1**) into the corresponding aldehydes and ketones (**2**) (Scheme 1).

The present reagent is easily prepared. First, the acetone solvate of iron(III) nitrate nonahydrate is obtained by concentration under vacuum of an acetone solution of iron(III) nitrate nonahydrate. It seems that the solvate is in a viscous form with a brown color, to which aluminum silicate is added. Rotary evaporation of the solvent under vacuum affords the desired powdered reagent. In our cases, the temperature of the reaction procedure was kept colder than 35°C, since at higher temperatures it will lead to an unstable reagent, which will decompose with evolution of nitrogen dioxide.^[1] The process for the oxidation is very simple. After combining the alcohols with the iron(III) nitrate hydrate supported on aluminum silicate, the mixture was refluxed and the expected products were obtained. In our cases, a 1 to 1.2 molar ratio of the substrate to the oxidant was employed, and except



Scheme 1.

oxidation of cyclohexanol, the reactions were completed within 1 h with high yield, for instance, 98% yield for the oxidation of benzyl alcohol to benzaldehyde. Meanwhile, we have observed that aliphatic alcohols, such as 1-hexanol or 1-octyl alcohol, were not efficiently oxidized under these conditions, even though they had been performed at longer reaction time. The mechanism of the present oxidation is the same as the well-known one described previously in the literature.^[1] Our results are listed in Table 1.

Comparing with some of the other existing iron(III) nitrate hydrate – supported reagents cited previously, the main advantage of the present method is that the solid reagent is more stable, which means it can be stored in a dark brown vacuum desiccator at room temperature at least 3 months without loss of activity. In addition, the reaction time of the present oxidation is comparatively shorter.

CONCLUSION

In conclusion, the present iron(III) nitrate nonahydrate supported on aluminum silicate reagent under heterogeneous conditions with reflux is a new and efficient method for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, except oxidation of aliphatic alcohols, such as 1-hexanol or 1-octyl alcohol.

EXPERIMENTAL

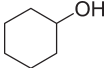
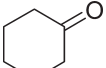
Preparation of Iron(III) Nitrate Supported on Aluminum Silicate Reagent

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4 g, 10 mmol) is added to acetone (60 mL), and the mixture is stirred vigorously for 10 min. Aluminum silicate (15 g; $D50: \leq 1.5$ micron; $d: 2.1 \text{ g/cm}^3$; Sasin Chemical New Material Co., Ltd.) is then added in small amounts, and stirring is continued for another 10 min. The solid (18.3 g), $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent, which can be directly used for oxidation, is obtained by evaporation of the solvent from the resulting suspension in a rotary evaporator at temperatures less than 35°C under vacuum. This new $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent can be stored in a dark brown vacuum desiccator without losing activities.

Oxidation of Benzyl Alcohol to Benzaldehyde

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (2.2 g) is placed in a flask together with CH_2Cl_2 (15 mL), and the mixture is magnetically stirred. A solution of benzyl alcohol (108 mg, 1 mmol) in CH_2Cl_2 (3 mL) is added, and after 1 h

Table 1. Oxidation of alcohols with iron(III) nitrate supported on aluminum silicate reagent

Substrate ^a	Reaction time (h)	Product ^b	Yield ^c (%)	Mp/°C of 2,4-DNP	
				Found	Reported ^[8]
PhCH ₂ OH	1	PhCHO	98	236–239	237
PhCH=CHCH ₂ OH	1	PhCH=CHCHO	93	255–256	255
<i>p</i> -H ₃ CO-C ₆ H ₄ -CH ₂ OH	1	<i>p</i> -H ₃ CO-C ₆ H ₄ -CHO	90	253–254	254
CH ₂ =CHCH(OH)CH ₃	1	CH ₂ =CHC(O)CH ₃	89	139–140.5	139.5–140.5
CH ₃ CH ₂ CH(OH)CH ₃	1	CH ₃ CH ₂ C(O)CH ₃	85	113.5–115	115
	3		86	160–163	161–162
PhCH(OH)Ph	1	PhC(O)Ph	98	47–49 ^d	48–49 ^d

^aAll the substrates are commercially available.

^bAll the aldehydes and ketones have been described previously in the literature and were identified by their IR spectra or by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones.

^cYield of isolated product.

^dMp of benzophenone.

at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative thin-layer chromatography (TLC) with hexane–ethyl acetate (8:2) to afford 104 mg (98%) of benzaldehyde.

Oxidation of 3-Phenyl-2-propenol to 3-Phenyl-2-propenal

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (2.2 g) is placed in a flask together with CH_2Cl_2 (15 mL), and the mixture is magnetically stirred. A solution of 3-phenyl-2-propenol (134 mg, 1 mmol) in CH_2Cl_2 (3 mL) is added, and after 1 h at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 123 mg (93%) of 3-phenyl-2-propenal.

Oxidation of 4-Methoxybenzyl Alcohol to 4-Methoxybenzaldehyde

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (2.2 g) is placed in a flask together with CH_2Cl_2 (15 mL) and the mixture is magnetically stirred. A solution of 4-methoxybenzyl alcohol (138 mg, 1 mmol) in CH_2Cl_2 (3 mL) is added, and after 1 h at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 122 mg (90%) of 4-methoxybenzaldehyde.

Oxidation of 3-Buten-2-ol to 3-Buten-2-one

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (4.4 g) is placed in a flask together with CH_2Cl_2 (15 mL), and the mixture is magnetically stirred. A solution of 3-buten-2-ol (144 mg, 2 mmol) in CH_2Cl_2 (3 mL) is added, and after 1 h at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 124 mg (89%) of 3-buten-2-one.

Oxidation of 2-Butanol to 2-Butanone

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (4.4 g) is placed in a flask together with CH_2Cl_2 (15 mL), and the mixture is magnetically stirred. A solution of 2-butanol (148 mg, 2 mmol) in CH_2Cl_2 (3 mL) is added, and after 1 h at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The

combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 122 mg (85%) of 2-butanone.

Oxidation of Cyclohexanol to Cyclohexanone

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (2.2 g) is placed in a flask together with CH_2Cl_2 (15 mL), and the mixture is magnetically stirred. A solution of cyclohexanol (100 mg, 1 mmol) in CH_2Cl_2 (3 mL) is added, and after 3 h at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 84 mg (86%) of cyclohexanone.

Oxidation of Diphenylmethanol to Benzophenone

The $\text{Fe}(\text{NO}_3)_3$ -aluminum silicate reagent (2.2 g) is placed in a flask together with CH_2Cl_2 (15 mL), and the mixture is magnetically stirred. A solution of diphenylmethanol (184 mg, 1 mmol) in CH_2Cl_2 (3 mL) is added, and after 1 h at gentle reflux, the solid is filtered and washed with CH_2Cl_2 (3×5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 178 mg (98%) of benzophenone.

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