Metal-Free Catalytic Oxidation of Sulfides to Sulfoxides with Ammonium Nitrate, Ammonium Hydrogen Sulfate and Ammonium Bromide as Catalyst

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A general and metal-free catalytic oxidation of aliphatic and aromatic sulfides to their corresponding sulfoxides via combination of ammonium nitrate (NH₄NO₃), supported ammonium hydrogen sulfate on silica gel (NH₄HSO₄–SiO₂) and a catalytic amount of ammonium bromide (NH₄Br) in the presence of wet SiO₂ (50%, w/w) has been investigated. The reactions were carried out heterogeneously and selectively in short reaction times in CH₂Cl₂ at room temperature. This protocol is mild and efficient compared to other reported methods.

Keywords: sulfides, sulfoxide, ammonium hydrogen sulfate (NH₄HSO₄), ammonium nitrate (NH₄NO₃), ammonium bromide (NH₄Br), homoselectivity

Introduction

The chemoselective oxidation of sulfides to their corresponding sulfoxides is of interest for organic chemists, both for fundamental research and for a variety of applications. Sulfoxides are valuable synthetic intermediates for the synthesis of chemically and biologically significant molecules.1–3 Sulfoxides are also valuable materials in C–C bond-forming4–5 and molecular rearrangements.6–8 Additionally some of biologically active sulfoxides play an important role as therapeutic agents such as anti-ulcer,9–11 antibacterial,12 anti-atherosclerotic,13,14 among others. Although a wide variety of oxidizing systems has been applied for the oxidation of sulfides to the sulfoxides such as H₂O₂/silica sulfuric acid,15 urea hydrogen peroxide (UHP)/Mn(III),16 Me-IBX,17 H₂O₂/VO(acac)₂,18 N-bromosuccinimide,19 H₂O₂/NBS,20 H₂O₂/Cr(III),21 1-benzyl-4-aza-1-azonia-bicyclo[2.2.2]octane tribromide,22 BF₃-based ionic liquid/UHP,23 H₂O₂/1,1,1-trifluoracetone,24 some of these methods still suffer from some drawbacks like overoxidation to sulfones, low selectivity, low yields of products, tedious work-up, toxicity, and expensive reagents or catalysts.

In the last few years, heterogeneous reagents and catalysts are used increasingly in organic functional group transformation.25–28 The development of efficient and new catalytic systems for various organic transformations is an active research area with the aim to develop milder reaction conditions.29 Finding molecules which are able to catalyze the reaction between others is an important contribution of molecular chemists to increase the efficiency of chemical reactions whereby our daily life based on consumption of chemicals is shifted closer to an ecologically and economically tolerable equilibrium with our environment.30

Results and Discussion

Recently we have introduced different approaches for the in situ generation of bromonium ion (Br⁺), which effectively applied for the oxidation of different types of organic compounds.31–36 In continuation of this investigation we decided to explore catalytic and metal-free media for the in situ generation of Br⁺. Meanwhile we were interested to use ammonium nitrate (NH₄NO₃) as very cheap, nontoxic
and commercially available oxidizing material. Ammonium nitrate is used in fertilizer industry and as an explosive in mining operations. It has been also used widely in different organic transformations such as: cleavage of THP ethers, acetals and acetonides, nitrogenation of arenes, dethioacetalization, coordination of ammonium nitrate to crown ethers.

However, the low oxidizing power of ammonium nitrate is the main drawback to its application. Therefore we decide to activate this reagent with supported ammonium hydrogen sulfate on silica gel (NH$_4$HSO$_4$–SiO$_2$). Therefore a mixture of NH$_4$NO$_3$, NH$_4$HSO$_4$–SiO$_2$ (50%, w/w) and catalytic amounts of NH$_4$Br in the presence of wet SiO$_2$ (50%, m/m), as metal free catalytic media, was combined for the in situ generation of Br$^*$. Consequently, we disclosed a new heterogeneous catalytic protocol for the chemo and homoselective oxidation of sulfides to the sulfoxides using combination of ammonium nitrate, ammonium hydrogen sulfate and wet SiO$_2$ (50%, w/w) in the presence of catalytic amounts of NH$_4$Br.

Obviously, solvent plays an important role in organic transformations, and hence it was decided to investigate the solvent effect and also find an appropriate solvent for the oxidation of sulfides. However, we screened different solvents for the oxidation of dibenzyl sulfide, as a typical example. The oxidation of dibenzyl sulfide was carried out using a mixture containing 1 mmol of dibenzyl sulfide, NH$_4$NO$_3$ (1.2 mmol), NH$_4$HSO$_4$–SiO$_2$ (50%, w/w) (1.2 mmol), NH$_4$Br (0.02 mmol) and 0.2 g of wet SiO$_2$ (50%, w/w) in 5 mL of solvent at room temperature. As is evident from Table 1, oxidation of dibenzyl sulfide was subjected to the oxidation reaction proceeds more rapidly and more selectively in dichloromethane compared to other solvents.

Eventually, we wish to report here the selective oxidation of wide range of aliphatic and aromatic sulfides 1 to the corresponding sulfoxides 2 using NH$_4$NO$_3$, supported ammonium hydrogen sulfate on silica [NH$_4$HSO$_4$–SiO$_2$ (50%, w/w)] II and catalytic amounts of NH$_4$Br III in the presence of wet SiO$_2$ (50%, w/w) in dichloromethane at room temperature with good to excellent yields (Scheme 1 and Table 2).

NH$_4$Br is the catalytic part of this oxidizing system. Therefore to investigate the catalytic role of NH$_4$Br dibenzyl sulfide was subjected to the oxidation reaction in the absence of catalyst. However, no sulfoxide was observed after 3 h (Table 1, entry 4). Also the necessity of wet SiO$_2$ (50%, w/w), as source of water, and NH$_4$HSO$_4$–SiO$_2$ (50%, w/w) were considered. Therefore to show the role of supported ammonium hydrogen sulfate on silica in this system, oxidation of dibenzyl sulfide was carried out in the absence of this reagent. Interestingly it was observed that the reaction did not proceed in the absence of NH$_4$HSO$_4$–SiO$_2$ (Table 1, entry 5). Also is evident from entry 6 of Table 1, that wet SiO$_2$ is necessary for the described system.

### Table 1. Oxidation of dibenzyl sulfide using NH$_4$NO$_3$, NH$_4$HSO$_4$–SiO$_2$ (50%, w/w) and catalytic amounts of NH$_4$Br in the presence of wet SiO$_2$ (50%, w/w) in different solvents at room temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>time / min</th>
<th>Yield / (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>30</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>Acetone</td>
<td>480</td>
<td>---$^c$</td>
</tr>
<tr>
<td>3</td>
<td>Chloroform</td>
<td>35</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>Dichloromethane</td>
<td>20</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>n-Hexane</td>
<td>162</td>
<td>---$^d$</td>
</tr>
<tr>
<td>6</td>
<td>Ethanol</td>
<td>480</td>
<td>---$^c$</td>
</tr>
<tr>
<td>7</td>
<td>Methanol</td>
<td>480</td>
<td>---$^c$</td>
</tr>
<tr>
<td>8</td>
<td>Ethyl acetate</td>
<td>80</td>
<td>96</td>
</tr>
</tbody>
</table>

$^a$Substrate : NH$_4$NO$_3$: NH$_4$HSO$_4$–SiO$_2$: NH$_4$Br : wet SiO$_2$ = 1 mmol : 1.2 mmol : 1.2 mmol : 0.2 mmol : 0.2 g. $^b$Isolated yield. $^c$No reaction. $^d$Reaction was complete but impurity of sulfoxide was observed.

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Scheme 1. Catalytic oxidation of sulfides to the corresponding sulfoxides.
It is of interest to note that the mentioned oxidizing system allowed the homoselective oxidation of thianthrene and bis-(methyl thio)-methane to their monosulfoxide derivatives (Scheme 2, entries 11 and 18).

Finally to show the chemoselectivity of the described system, two sulfides containing a hydroxy group were subjected to the sulfoxidation reaction, but alcohol oxidation did not occur under mentioned conditions, and primary hydroxyl group remained intact in the course of the reaction (Table 2, entries 8 and 12, Scheme 3).

In the first place, NH$_4$NO$_3$ reacts with NH$_4$HSO$_4$ to produce in situ HNO$_3$. Subsequently, auto ionization of HNO$_3$ generates nitronium ion (NO$_2^+$), which is able to convert bromide ion (Br$^-$) to bromonium (Br$_2^+$). In the last step reaction of bromonium ion with sulfide in the presence of water might generate the corresponding sulfoxide.

In summary herein we report a novel catalytic protocol for the chemo and homoselective oxidation of sulfides to the sulfoxides under metal-free, mild and heterogeneous conditions. This method offers the advantage of shorter reaction times, high selectivity, non toxic conditions, cost effective reagents and catalyst and easy workup. We believe that the present methodology could be an important addition to the existing methodologies.

**Experimental**

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, $^1$H NMR, and $^{13}$C NMR) and physical data with authentic samples.
Oxidation of dibenzyl sulfides 1c to dibenzyl sulfoxide 2c using NH$_4$NO$_3$, NH$_4$HSO$_4$-SiO$_2$ and NH$_4$Br as a typical procedure

NH$_4$NO$_3$ (0.096 g, 1.2 mmol), NH$_4$Br (0.0019 g, 0.02 mmol), NH$_4$HSO$_4$-SiO$_2$ (50%, w/w), (0.276 g, 1.2 mmol) and 0.2 g of wet SiO$_2$ (50%, w/w) were added to a solution of dibenzyl sulfide 1c (0.214 g, 1 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting mixture was stirred at room temperature for 20 min (the reaction progress was monitored by TLC) and then filtered. The residue was washed with CH$_2$Cl$_2$ (4×5 mL). Anhydrous Na$_2$SO$_4$ (1.5 g) was added to the filtrate and filtered off after 20 min. Finally CH$_2$Cl$_2$ was removed and the yield was 0.221 g (98%).

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References


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