CHAPTER V

Poly (N-vinyl-2-pyrrolidone)-Cu(OAc)$_2$: An Efficient and Reusable Catalyst for Sulffimidation
CHAPTER V

Poly (N-vinyl-2-pyrrolidone)-Cu(OAc)$_2$: An Efficient and Reusable Catalyst for Sulfindation

Introduction

The vast chemistry of sulfoxides and sulfonium ylides make them very useful reagents in organic synthesis. These compounds are important synthetic intermediates for the construction of various chemically and biologically significant molecules.\textsuperscript{1} Several successful methods have been developed for the synthesis of these compounds.\textsuperscript{2} But Sulfimides, the nitrogen analogues of sulfoxides although have been widely used as important auxillaries for chiral ligands and structural units in pseudopeptides,\textsuperscript{3} are less investigated due to scarcity of appropriate nitrogen sources, as opposed to oxidants that are available in wide variety and forms.\textsuperscript{4}

Thus there have been many excellent methods developed for oxidation in terms of stereoselectivity, mildness of reaction conditions, atom-efficiency and ecological benignity; however the number of nitrogen-atom-transfer reactions satisfying such terms has been very limited.\textsuperscript{3}

In view of this, development of efficient methods for selective imidation of sulfides to sulfimides has been desired for many years. However, only a few of them have been found to yield the desired products in high yields under mild conditions.

State of the Art

In 1983, Groves and Takahashi reported that irradiation of Mn(porphyrin)(azide) complex gave a nitride-Mn species that underwent aziridination by treatment with trifluoroacetic anhydride in the presence of olefins, via an N-trifluoroacetyl nitrenoid
species. Later, nitride-Mn(salen) complex was also reported to undergo aziridination under similar conditions.

Mansuy et al. demonstrated for the first time that PhI=NTs could convert Fe and Mn complexes into corresponding nitrenoid species for aziridination and allylic amination reactions, depending on the olefin used (Scheme 1).

![Scheme 1](image)

Evans et al. reported enantioselective aziridination of olefins using bis(oxazoline)-copper complexes (Scheme 2).

![Scheme 2](image)

Jacobsen and co-workers studied the mechanistic aspects of the aziridination reaction using Cu(I) (diimine) catalyst.
Later, Bolm and co-workers\textsuperscript{3i} reported Fe(acac)$_3$ catalyzed imidation of sulfides and sulfoxides (Scheme 3).

\[
\begin{align*}
\text{R}^1 \text{S}^\text{O} \text{R}^2 & \quad \text{Fe(acac)$_3$ (5mol\%)} \\
& \quad \text{R$_3$SO$_2$NH$_2$ PhH-O} \\
& \quad \text{CH$_3$CN, rt} \\
\text{R}^1 \text{S} \text{R}^2 & \quad \text{R}^3 \text{O}_2\text{S-N} \quad \text{R}^1 \text{S} \text{R}^2 \\
& \quad \text{up to 95\%}
\end{align*}
\]

**Scheme 3**

Latour and co-workers\textsuperscript{9} have reported amidation of thioanisole using a non-heme iron complex (Scheme 4).

**Scheme 4**

Sharpless and co-workers\textsuperscript{10} reported metal free reactions in presence of chloramine-T with moderate yields and longer reaction times (Scheme 5).

\[
\begin{align*}
\text{R}^1 \text{S}^\text{O} \text{R}^2 + \text{Cl-N-SO$_2$R}^3 & \quad \text{MeCN, 16h} \quad \text{r.t.} \\
& \quad \text{Na$^+$} \\
\text{R}^1 \text{S}^\text{O} \text{R}^2 & \quad \text{R}^1 \text{S}^\text{O} \text{R}^2 \\
& \quad \text{up to 98\%}
\end{align*}
\]

**Scheme 5**
Later, Bolm and co-workers\textsuperscript{11} described sulfitidation using 4-nitobenzenesulfonamide (NsNH\textsubscript{2}) and iodobenzene diacetate [PhI(OAc)\textsubscript{2}] (Scheme 6).

![Scheme 6](image)

**Scheme 6**

Initially, sulfinimides were prepared in its chiral form either by conversion from enantiomerically pure sulfoxides\textsuperscript{12} or by kinetic resolution of racemic sulfinimides in the presence of an optically active base.\textsuperscript{13} Later, Catalytic asymmetric sulfitidation using PhI=NTs as nitrene donor in the presence of chiral Cu(I) bis(oxazoline) complex has been described by Uemura et al.\textsuperscript{14} with moderate enantioselectivity albeit longer reaction time (Scheme 7).

![Scheme 7](image)

**Scheme 7**

Katsuki et al. reported asymmetric sulfitidation with good enantioselectivity using Mn(salen)\textsuperscript{15} and Ru(salen)\textsuperscript{16} complexes (Scheme 8).
Owing to several economic and environmental advantages of heterogeneous catalysts, like easy separation of the products reusability of the catalysts, heterogeneous catalytic reactions are one of the most important ones and widely used in the industry. Various supports have been used over the years to immobilize metal catalysts, one of the important group among them are the polymers.

Polymer supported catalysts have been of great interest due to several advantages such as the ease of product separation, isolation and reuse of the catalyst. But the use of insoluble polymers as supports have some drawbacks as the reactivity and selectivity of the supported catalysts is lesser than the unsupported analogs.
In recent years, there have been intense efforts to develop methods to recover and reuse homogeneous catalysts. Poly (vinylpyrrolidone) (PVP) (Figure 1) is a water soluble, biocompatible, physiologically inert polyamide polymer exhibiting unusual colloidal and complexing properties.

![Figure 1. Molecular structure of PVP](image)

PVP stabilized nanoscale metal colloids have been reported for selective hydrogenation reactions (Scheme 9)

![Scheme 9](image)

Hu et al. reported PVP-CuCl\(_2\) catalyst for the oxidative carbonylation of methanol to dimethyl carbonate (Scheme 10).

![Scheme 10](image)

Wang and co-workers reported PVP supported nanosized palladium metal colloids for Sonogashira and Suzuki coupling reactions (Schemes 11 and 12).
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\[
\text{Scheme 11}
\]

\[
\text{Scheme 12}
\]

Recently, Kantam et al.\textsuperscript{24} have reported catalytic sulfimidation of various sulfides by using microencapsulated Cu(acac)\textsubscript{2} and Cu(acac)\textsubscript{2} immobilized in ionic liquids using PhI=NTs (Scheme 13).

\[
\text{Scheme 13}
\]

There is a need for the development of new and efficient catalyst for the imidation of sulfides with high selectivity, high atom efficiency and reusability.

Present Work

In this chapter, an efficient sulfimidation reaction using poly(vinylpyrrolidone) supported cupric acetate in the presence of PhI=NTs \([(N-(p-

\[
\text{Scheme 14}
\]

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Results and Discussion

Synthesis and Characterization of PVP-Cu(OAc)$_2$

The preparation of PVP-Cu(OAc)$_2$ was based on the literature procedure.$^{22}$ Cupric acetate (0.150 g) was added to a solution of PVP (Mw 40,000, 1g) in methanol (50 mL) and the mixture was refluxed under nitrogen atmosphere for 12h. The resulting solution was concentrated under reduced pressure to give powdered PVP-Cu(OAc)$_2$ (Cu 0.467 mmol/g). The copper content in the catalyst was found to be 2.93% by AAS analysis. The resulting catalyst was characterized by powdered X-ray photoelectron spectroscopy (XPS), TGA-MS, Electron spin resonance spectroscopy, UV-Vis Diffuse Reflectance Spectroscopy (UV-DRS) and FTIR spectroscopic techniques.

FTIR spectroscopy

The FTIR analysis of PVP, fresh and used PVP-Cu(OAc)$_2$ has been carried out and the IR spectrum (Figure 1) of PVP showed a characteristic stretching band corresponding to amide carbonyl group at 1657 cm$^{-1}$ whereas in PVP-Cu(OAc)$_2$, there is a red shift of the amide carbonyl group to 1631 cm$^{-1}$ with a shoulder at 1637 cm$^{-1}$ indicating the interaction of the metal ion with amide carbonyl moiety of PVP.$^{22}$ Both PVP and PVP-Cu(OAc)$_2$ showed characteristic bands at 2925 and 3418 cm$^{-1}$ originating from the amide group of PVP.
Figure 2. IR spectra of (a) PVP, (b) fresh catalyst and (c) used catalyst.
X-ray photoelectron spectroscopy (XPS)

The XPS survey scan of PVP-Cu(OAc)$_2$ showed the presence of oxygen (535 eV), nitrogen (400 eV), carbon (285 eV) and copper (935 eV). High resolution narrow scan for Cu 2p in PVP-Cu(OAc)$_2$ catalyst showed binding energy peaks at 934.9 and 955.1 eV (Table 1) corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ photoelectron transitions respectively characteristic of Cu in +2 oxidation state. The observed binding energies peaks of N 1s (398.9 eV) and O 1s (531.2 eV) in PVP-Cu(OAc)$_2$ are close to N 1s (399.0 eV) and O 1s (531.8 eV) peaks in PVP. These results indicate the electronic modification of Cu(II) on coordination with the amide moiety of PVP and thus, Cu(II) being immobilized on the polymer. However, XPS spectrum of the used catalyst showed the presence of both Cu(I) and Cu(II) states (Fig. 3b).

Table 1. XPS data for the binding energies (eV) of PVP, PVP- Cu(OAc)$_2$ and used PVP-Cu(OAc)$_2$

<table>
<thead>
<tr>
<th>XPS peak</th>
<th>PVP</th>
<th>PVP-Cu(OAc)$_2$</th>
<th>Used PVP-Cu(OAc)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_{1s}$</td>
<td>399.0</td>
<td>398.9</td>
<td>398.6</td>
</tr>
<tr>
<td>O$_{1s}$</td>
<td>531.8</td>
<td>531.2</td>
<td>531.2</td>
</tr>
<tr>
<td>Cu 2p$<em>{3/2}$, 2p$</em>{1/2}$</td>
<td>-</td>
<td>934.9, 955.1</td>
<td>(934.6, 955.6), (932.4, 952.0)$^a$</td>
</tr>
</tbody>
</table>

$^a$ Binding energy of Cu in +1 oxidation state
Figure 3. XPS high resolution narrow scan of Cu 2p in (a) PVP-Cu(OAc)$_2$ fresh catalyst and (b) PVP-Cu(OAc)$_2$ used catalyst

**ESR and UV DRS spectroscopy**

ESR and UV-Vis-DR spectroscopy have been used to understand the coordination of Cu$^{2+}$ ions in PVP. Both the fresh and used catalysts exhibit axial ESR spectra of Cu$^{2+}$ ions at room temperature with resolved hyperfine structure (Fig. 5). The observed hyperfine splitting parameters for the fresh and used catalyst are $g_{||} = 2.38, 2.37$; $g_{\perp} = 2.08, 2.07$, and $A_{||} = 14, 13$ mT respectively. The UV-Vis-DRS spectra (Fig. 6) showed
a characteristic absorption band at 700-750 nm corresponding to d-d transitions between \( T_{2g} \) and \( E_g \) terms typical for isolated Cu(II) ions in an octahedral environment with slight tetragonal distortion. Another peak is observed around 300 cm\(^{-1}\) which can be ascribed to the n-\( \pi^* \) transition of the carbonyl group in PVP. The shoulder around 350 cm\(^{-1}\) is due to the presence of the carbonyl group in the copper acetate. These results are in good agreement with the ESR and UV-Vis DR spectra of Cu\(^{2+}\) ions in various zeolites.\(^{25}\)

![Figure 4](image)

**Figure 4.** ESR spectra of Cu\(^{2+}\) ions in (a) fresh and (b) used PVP-Cu(OAc)\(_2\) catalyst at the X-band recorded at room temperature.
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Fig. 5. UV-Vis-DR spectrum of (a) fresh PVP-Cu(OAc)$_2$ (b) Cu(OAc)$_2$ (c) used PVP-Cu(OAc)$_2$ and (d) PVP.

Catalytic activity of PVP-Cu(OAc)$_2$ in sulfitidation reaction

In the preliminary experiments, sulfitidation of thioanisole using PhI=NTs in the presence of PVP-Cu(OAc)$_2$ has been studied in various solvents under nitrogen atmosphere (Table 2). The reaction was found to be more efficient in acetonitrile compared to methanol, ethanol and 2-propanol and there was no reaction in DMF, DMSO and water.
Table 2. Effect of solvents for the sulfimidation of thioanisole with PhI=NTs using PVP-Cu(OAc)$_2$\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>Methanol</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>2-Propanol</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$O</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: Thioanisole (0.5 mmole), PhI=NTs (0.5 mmol), catalyst (0.025 g, 2.3 mol %), solvent (3 mL) under nitrogen atmosphere for 0.6 h

Different nitrene donors were evaluated for the synthesis of sulfimides and the results are shown in (Table 3). PhI=NTs was found to be more efficient nitrene donor compared to chloramine-T and bromamine-T.

Table 3. Sulfimidation of thioanisole using different nitrene donors.

<table>
<thead>
<tr>
<th>Nitrene donor</th>
<th>Time (h)</th>
<th>Yield (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhI=NTs</td>
<td>0.6</td>
<td>98</td>
</tr>
<tr>
<td>Chloramine-T</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Bromamine-T</td>
<td>12</td>
<td>18</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Isolated Yields

Different sulfides were studied for the reaction under the optimized conditions using PVP-Cu(OAc)$_2$ as catalyst and the corresponding sulfimides were obtained in good to excellent yields (Table 4). However, the reaction in the presence of Cu(OAc)$_2$. H$_2$O gave
the product in 50% yield (Table 4, entry 1). Aliphatic as well as aromatic sulfides were equally effective for the reaction. Aromatic sulfides with electron-releasing substituents were found to be more reactive than aromatic sulfides with electron-withdrawing substituents (Table 4, entries 2 and 3). Whereas, sterically hindered sulfides, diphenyl sulfide required longer reaction time (Table 4, entry 5).

Further, when the reaction was applied to allylic sulfides, there was no aziridination of the double bond. Instead, [2,3] sigmatropic rearrangement with the formation of sulfonamide through a sulfinamide intermediate has been observed. Allylic sulfides were less reactive and required longer reaction times when compared to aliphatic sulfides (Table 4 entries 8 and 9). The catalyst was reused for several cycles and showed consistent activity (Table 4, entry 1). The leaching of the metal after the fourth cycle was determined by AAS analysis and was found to be 2%.
Table 4. Sulfimidation of sulfides with PhI=NTs using PVP-Cu(OAc)$_2$\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sulfide</th>
<th>Time (min)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Sulfide" /></td>
<td>40</td>
<td><img src="image2" alt="Product" /></td>
<td>98, 95\textsuperscript{b}, 48\textsuperscript{c}</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Sulfide" /></td>
<td>35</td>
<td><img src="image4" alt="Product" /></td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Sulfide" /></td>
<td>120</td>
<td><img src="image6" alt="Product" /></td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="Sulfide" /></td>
<td>40</td>
<td><img src="image8" alt="Product" /></td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9" alt="Sulfide" /></td>
<td>210</td>
<td><img src="image10" alt="Product" /></td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td><img src="image11" alt="Sulfide" /></td>
<td>30</td>
<td><img src="image12" alt="Product" /></td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td><img src="image13" alt="Sulfide" /></td>
<td>40</td>
<td><img src="image14" alt="Product" /></td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td><img src="image15" alt="Sulfide" /></td>
<td>50</td>
<td><img src="image16" alt="Product" /></td>
<td>78\textsuperscript{d}</td>
</tr>
<tr>
<td>9</td>
<td><img src="image17" alt="Sulfide" /></td>
<td>180</td>
<td><img src="image18" alt="Product" /></td>
<td>72\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} *Reaction condition*: Sulfide (0.5 mmole), PhI=NTs (0.5 mmol), catalyst (0.025 g, 2.3 mol %), acetonitrile (3 mL) under nitrogen atmosphere for 0.5 to 3.5 h.

\textsuperscript{b} Yield after 4\textsuperscript{th} cycle.

\textsuperscript{c} In the presence of Cu(OAc)$_2$.H$_2$O (2.3 mol %). \textsuperscript{d}[2,3] sigmatropic rearrangement.
In order to extend the scope of this methodology, the asymmetric synthesis of sulfimides using 4, 4’-disubstituted bis(oxazolines) 1a and 1b (BOX) as chiral ligands was carried out under similar reaction conditions (Scheme 15). When bis(oxazoline) ligand 1a was used, higher ees were obtained in comparison to the reaction with 1b as the ligand. Sulfides with electron donating substituents gave higher ee’s when compared to the sulfides with electron withdrawing substituents (Table 5).

\[ \text{BOX (3-5 mol%) upto 68\% ee} \]

\[ \text{R'~SR} \]

\[ \text{PVP-Cu(OAc)}_2 \text{CH}_3 \text{CN} \]

\[ \text{Phl=NTs, rt} \]

\[ \text{BOX (3-5 mol%)} \]

\[ \text{upto 68\% ee} \]

\[ \text{1a R = t- butyl} \]

\[ \text{1b R = Ph} \]

**Scheme 15**
Table 5. Asymmetric sulfimidation of sulfides with PhI=NTs using PVP-Cu(OAc)$_2$.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Ligand</th>
<th>Time (min)</th>
<th>Isolated yield(^a)</th>
<th>% ee(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Substrate 1" /></td>
<td>la</td>
<td>35</td>
<td>95</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lb</td>
<td></td>
<td>96</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Substrate 2" /></td>
<td>la</td>
<td>40</td>
<td>95</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lb</td>
<td></td>
<td>92</td>
<td>24(^c)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Substrate 3" /></td>
<td>la</td>
<td>40</td>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lb</td>
<td></td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Substrate 4" /></td>
<td>la</td>
<td>120</td>
<td>78</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lb</td>
<td></td>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Substrate 5" /></td>
<td>la</td>
<td>40</td>
<td>88</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lb</td>
<td></td>
<td>85</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\)Reaction condition: Sulfide (0.5 mmol), PhI=NTs (0.5 mmol), catalyst (0.025g, 2.3 mol%), bis(oxazoline)/Cu = 2, acetonitrile (3 mL) were used.

\(^b\) The ee values were determined by HPLC using Daicel Chiralcel OJ-H column (hexane/2-propanol = 4 : 1, flow rate 1.0 mL/min).

\(^c\) With bis(oxazoline)/Cu = 1.

**Reusability study of the catalyst in asymmetric sulfimidation**

The catalyst was recovered, reused and the results are summarized in Table 6. The decrease in enantioselectivity in the recycle experiments can be explained by the TGA-MS studies of the bis(oxazoline) ligand in the fresh and the used catalyst.
Table 6. Recovery and reuse of PVP-Cu(OAc)₂-BOX catalyst for asymmetric sulffimidation of thioanisole.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cycle no</th>
<th>Isolated yield (%)</th>
<th>ee(^b)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>95</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>95</td>
<td>15, 50(^c)</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>95</td>
<td>15</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Reaction condition: Sulfide (0.5 mmol), PhI=NTs (0.5 mmol), catalyst (0.025 g) acetonitrile (3 mL) were used.  
\(^{[b]}\) 2\(^{\text{nd}}\) and 3\(^{\text{rd}}\) cycle ee\% obtained without the use of additional amount of ligand  
\(^{[c]}\) 3 mol\% of ligand added.

As can be seen in Fig. 6 and 7, the evolved gas fragments as a function of temperature showed the fragments m/Z values 15, 57, 84 and 126 a.m.u in both the catalysts resulting from the presence of tertiary butyl substituted bis(oxazoline) ligand in the catalyst. Remarkable changes were observed in the onset of the decomposition temperatures in both the fresh and used catalyst. In the fresh catalyst the onset of the ligand decomposition is observed at 425 °C whereas in the recovered catalyst it is observed at 250 °C, at much lower temperature. This clearly suggests that in the fresh catalyst, the ligand is chemisorbed where as in the recovered catalyst the ligand appears to be physically adsorbed, so the decrease in the onset of decomposition. These ligand molecules present on the surface of the support are responsible for the 15% ee’s in the recycle experiments, however consistent yield of the product was obtained in all the recycles. On the other hand, addition of fresh amounts of ligand after the first cycle gave the product with 50% ee. Therefore, it can be concluded that the immobilization of
bis(oxazoline) ligand-Cu complex by electrostatic interactions cannot be properly performed due to its low binding constant leading to the presence of ligand free copper on the support after the first cycle, which noticeably reduces the enantioselectivity.

![Fig. 6. TGA-MS of the fresh catalyst with t-butyl bis(oxazoline) ligand.](image-url)
Plausible Mechanism

A plausible mechanism of the sulfimidation reaction can be proposed on the basis of the literature reports. First the metal nitreneoid species (2) is formed by the interaction of PhI=NTs with the catalyst by the loss of the labile acetate ligand (L), then the intermediate sulfide-metal nitrene species (3) is formed in the next step by the interaction of the metal with the sulfide, this sulfide-metal-nitrene species subsequently losses the iodobenzene molecule and forms the S-N bond (4). This intermediate having sulfide moiety bonded directly to the nitrene species then forms the sulfimide product. The redox process involving Cu(II) and Cu(I) takes place during the course of the reaction which is detected by XPS analysis of the new catalyst and the used catalyst (Scheme 16).
Conclusions

In summary, PVP-Cu(OAc)$_2$ was synthesized, well characterized and employed as a catalyst for the sulfinidation of sulfides in the presence of PhI=NTs ([N-(p-tolylsulphonyl)imino]-phenyliodinane) as nitrene donor to afford the corresponding sulfinimides in good to excellent yields. In the presence of chiral bis(oxazoline) ligand, asymmetric induction occurs to afford chiral sulfinimides with moderate enantioselectivities. The catalyst can be reused for several cycles with consistent activity.
Experimental Section

General

X-ray photoelectron spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg-Kα anode. The pressure in the spectrometer was about 10⁻⁹ Torr. For energy calibration the carbon 1s photoelectron line is used. The carbon 1s binding energy was taken to be 285.0 eV. The spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products which were not obtained as pure species were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were in general, reproducible to within ± 0.1 eV. Diffuse reflectance UV-Vis absorption spectra for samples as KBr pellets were recorded on a GBC Cintra 10e in the range 200-800 nm with a scan speed of 400 nm/min. ESR spectra were recorded on JEOL JES-FA 200 ESR spectrometer operating in the X-band frequencies with a field modulation of 100 kHz. The microwave frequency was set at 9.45 GHz and the magnetic field was scanned between 225 mT to 425 mT. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer as KBr pellets. Thermogravimetric (TG), differential thermal analysis (DTA) and mass of the evolved gas during the thermal decomposition of the catalyst were studied on TGA/SDTA Mettler Toledo 851e system coupled to MS Balzers GSD 300T, using open alumina crucibles, containing samples weighing about 8-10mg with a linear heating rate of 10°C min⁻¹. NMR spectra were recorded on a Varian Gemini (200 MHz), Bruker Avance (300 MHz), Varian Unity (400MHz) spectrometer using TMS as an internal
standard and CDCl₃ as solvent. Mass spectra were obtained at an ionisation potential of 70 eV [scanned on VG 70-70H (micro mass)]. Only selected ions are presented here. Melting points were recorded on Barnstead electrothermal 9200 instrument and are uncorrected. CHNS analysis was performed on a Vario EL analyzer. High performance Liquid Chromatography (HPLC) was performed using AGILENT-1100 series liquid chromatograph equipped with a single pump and UV detector (fixed at 205 nm) using CHIRACEL-OJ-H capillary column with isopropanol/hexane as eluting agent. All the other solvents and chemicals were obtained from commercial sources and purified using standard methods. PVP (K=30) was purchased from Fluka. Cu(OAc)₂. H₂O was purchased from S.D Fine Chemicals, India. Iodobenzene diacetate, p-toluene sulfonamide and sulfides were purchased from Aldrich or Fluka and used without further purification. ACME silica gel (100–200 mesh) was used for column chromatography. Thin-layer chromatography was performed on Merck-precoated silica gel 60-F254 plates. All the other solvents and chemicals were obtained from commercial sources and purified using standard methods.

**Synthesis of PVP-Cu(OAc)₂ catalyst**

The preparation of PVP-Cu(OAc)₂ was based on the literature procedure. Cupric acetate (0.150 g) was added to a solution of PVP (Mw 40,000, 1g) in methanol (50 mL) and the mixture was refluxed under nitrogen atmosphere for 12h. The resulting solution was concentrated under reduced pressure to give powdered PVP-Cu(OAc)₂ (Cu 0.467 mmol/g). The copper content in the catalyst was found to be 2.93% by AAS analysis.
Typical procedure for sulfitimination using PVP-Cu(OAc)₂

To acetonitrile (3 mL) were added PVP-Cu(OAc)₂ (0.025 g, 2.3 mol %), methyl phenyl sulfide (0.062 g, 0.5 mmol) and PhI=NTs (0.186 g, 0.5 mmol) and the reaction mixture was stirred at room temperature for the appropriate time as shown in Table 2. The reaction was monitored by the disappearance of PhI=NTs from the reaction mixture and by thin layer chromatography. After completion of reaction, the reaction mixture was concentrated and washed with 1:4 hexane/ethyl acetate. The combined organic extracts were concentrated and the crude solid was purified by recrystallization from iso-propanol and water or by column chromatography on silica gel (hexane/ethyl acetate, 20/80 v/v as eluent) to afford the pure product as white solid.

Representative examples

S-p-tolyl, S-methyl N-p-toluenesulfonyl sulfimide (Table 4, entry 2)

**Figure 8.** ¹H NMR (CDCl₃, 300 MHz): δ = 2.37 (s, 3H), 2.43 (s, 3H), 2.82 (s, 3H), 7.15 (d, 2H), 7.29 (d, J= 8.3 Hz, 2H), 7.59 (d, J= 8.3 Hz, 2H), 7.71 (d, J= 8.3 Hz, 2H).

**Figure 9.** ¹³C NMR (CDCl₃, 75 MHz): δ = 21.35, 21.40, 39.15, 43.38, 123.5, 125.82, 126.25, 129.12, 130.00, 129.08, 130.60, 132.72, 141.29, 141.29, 141.57, 143.32.

S-Phenyl, S-ethyl, N-p-toluenesulfonyl sulfimide (Table 4, entry 4)

**Figure 10.** ¹H NMR (CDCl₃, 300 MHz): δ = 1.21 (t, J= 6.7 Hz, 3H), 2.36 (s, 3H), 3.00 (q, J= 6.7, 12.8 Hz, 2H), 7.15 (d, J= 8.3 Hz, 2H), 7.50 (d, 2H, Ar-H), 7.70 (m, 5H).

**Figure 11.** ¹³C NMR (CDCl₃, 75 MHz): δ = 21.33, 47.82, 126.22 (2C), 126.25 (2C), 129.08 (2C), 129.77 (2C), 132.26 (2C), 141.30, 141.53.

Rest of the products were characterized similarly and the results obtained were similar to that reported in the literature.¹⁴,¹⁶,²⁶
Chapter V

References


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