Citric Acid Catalyzed Synthesis of Hydrazones Schiff Bases of 2,4-Dinitrophenyl Hydrazine

Keywords: 2, 4 – dinitrophenyl hydrazine, Schiff bases, Citric acid, hydrazones

ABSTRACT
An efficient method for the Citric acid-catalyzed synthesis of hydrazones Schiff base using 2,4-dinitrophenyl hydrazine. We have synthesized a series of hydrazones using 2,4-dinitrophenyl hydrazine as a source of amine and substituted aromatic aldehydes and aromatic ketones as a carbonyl source. Synthesized compounds were characterized by FT-IR techniques. Synthesis of above hydrazones using citric acid as a catalyst proved to be a green and eco-friendly approach.
INTRODUCTION

Compounds containing azomethine group (\(-\text{CH} = \text{N}-\)) are known as Schiff’s bases and they are synthesized by condensation of primary amine with carbonyl compounds (aldehydes & ketones). [1] Recently there has been considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications. [2] Schiff base hydrazone compounds have been extensively used as versatile ligands in coordination chemistry and Schiff base hydrazone complexes are also very attractive model compounds for the elucidation of several biochemical processes. Hydrazones are used as intermediate in synthesis [3], as functional groups in metal carbonyls [4], in organic compounds [5, 6] and in particular hydrazone Schiff base ligands. [7-10] They also act as herbicides, insecticides, plant growth regulators and nematocides. [11-13] Hydrazones have been demonstrated to possess antimicrobial, anticonvulsant, analgesic, anti-inflammatory, anticancer activities. [14, 15] The chemistry of hydrazone derivatives has been investigated intensively in the last decade owing to their coordinative and pharmacological activity as well as their use analytical chemistry as metal extracting agents. [16, 17] The significance of Schiff bases like hydrazones lies in the fact that these compounds not only possess antimicrobial activities but also show greater tendency to form complexes. [18] In analytical chemistry hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determination. [19, 20] The above remarkable considerations, pharmaceutical and industrial applications encouraged us to synthesize hydrazone derivatives of 2, 4 dinitrophenyl hydrazine using Citric acid as a green catalyst.

MATERIALS AND METHODS

All chemicals were purchased either from S.D fine and Loba chemicals used without further purification. Melting points were taken in an open capillary and are uncorrected. FT-IR spectra were recorded on JASCO-FT-IR/4100, Japan, in KBr disc. All the reactions were carried out at room temperature.

General procedure for the synthesis of Hydrazones Schiff bases

A reaction mixture of 2,4-dinitrophenyl hydrazine (1 mmol), aromatic aldehydes/ketones (1 mmol) and citric acid (0.1 gm) in ethanol (15 ml) was stirred for specific time mentioned in
Table 3 at room temperature. Insoluble solid was gradually generated, then filter and wash with water. The crude product obtained was recrystallized from ethanol to afford pure products.

Scheme 1

Spectroscopic data of compound:

3b. IR (KBr in cm\(^{-1}\)): \(\nu = 3456 \text{ (-NH)}, 1620 \text{ (-C=N)}, 1512 \text{ (-NO}_2\))

3d. IR (KBr in cm\(^{-1}\)): \(\nu = 3456 \text{ (-NH)}, 1620 \text{ (-C=N)}, 1512 \text{ (-NO}_2\)}, 3268 \text{ (-OH)}, 1273 \text{ (-C-O)}

3g. IR (KBr in cm\(^{-1}\)): \(\nu = 3493 \text{ (-NH)}, 1616 \text{ (-C=N)}, 1512 \text{ (-NO}_2\))

The IR spectra of compounds 3b, 3d, and 3g indicate the formation of the Schiff base product by the absence of the carbonyl group (1700 cm\(^{-1}\)) band and the appearance of strong band in the region of (1616-1620 cm\(^{-1}\)). Hence, this band indicates that the formation of hydrazones derivatives.

RESULTS AND DISCUSSION

To optimize the reaction conditions, 2,4-dinitrophenyl hydrazine and benzaldehyde as a model reaction to examine the effect of various solvents, such as water, acetone, methanol and ethanol with citric acid as catalytic materials. The best solvent effect was observed in ethanol and hence, we have used ethanol as solvent for the synthesis of hydrazones as derivatives.
Scheme 2 Model reaction

Table 1 Effect of various solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Acetone</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>Methanol</td>
<td>81</td>
</tr>
</tbody>
</table>

*aAll reactions were carried out using citric acid at room temperature. *bIsolated yields.

After optimization of solvent effect, the reaction was performed employing various acid catalysts such as H$_2$SO$_4$, HNO$_3$, acetic acid and citric acid. It was noted that none of the catalyst other than citric acid was promising for considerable yields. Best catalytic activity was performed citric acid as a catalyst in ethanol as a solvent.

Table 2 Effect of various catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$SO$_4$</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>HNO$_3$</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>Acetic acid</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Citric acid</td>
<td>94</td>
</tr>
</tbody>
</table>

*Citation: Dinore J.M et al. Ijprr.Human, 2016; Vol. 6 (1): 349-354.*
Reaction conditions: 2,4-dinitrophenyl hydrazine (1 mmol), benzaldehyde (1 mmol) catalyst (0.1 gm) and ethanol 15 ml. \(^a\) Isolated yields

To explore the scope and generality of the present method, variety of different substituted aromatic aldehydes and ketones possessing electron rich and electron deficient groups gave good to excellent yields (89-96 %) and reaction were completed within 2-6 min in ethanol at room temperature (Table 3).

Table 3 Citric acid catalyzed synthesis of hydrazones Schiff bases

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R(^1)</th>
<th>Time (min)(^a)</th>
<th>Yields (%)(^b)</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C(_6)H(_5)</td>
<td>H</td>
<td>3</td>
<td>94</td>
<td>240-242</td>
</tr>
<tr>
<td>3b</td>
<td>p-ClC(_6)H(_4)</td>
<td>H</td>
<td>4</td>
<td>92</td>
<td>254-256</td>
</tr>
<tr>
<td>3c</td>
<td>p-OCH(_3)C(_6)H(_4)</td>
<td>H</td>
<td>5</td>
<td>91</td>
<td>230-232</td>
</tr>
<tr>
<td>3d</td>
<td>o-OHC(_6)H(_4)</td>
<td>H</td>
<td>4</td>
<td>90</td>
<td>238-240</td>
</tr>
<tr>
<td>3e</td>
<td>p-NO(_2)C(_6)H(_4)</td>
<td>H</td>
<td>2</td>
<td>96</td>
<td>239-241</td>
</tr>
<tr>
<td>3f</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>4</td>
<td>91</td>
<td>126-128</td>
</tr>
<tr>
<td>3g</td>
<td>C(_6)H(_5)</td>
<td>CH(_3)</td>
<td>5</td>
<td>90</td>
<td>135-137</td>
</tr>
<tr>
<td>3h</td>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_5)</td>
<td>6</td>
<td>89</td>
<td>237-239</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 2,4-dinitrophenyl hydrazine (1 mmol), benzaldehyde (1 mmol) catalyst (0.1 gm) and ethanol 15 ml. \(^b\)Isolated yields

CONCLUSION

In conclusion, we have synthesized hydrazones Schiff bases using simple and convenient method with a short reaction time and easy work up. Present method offers remarkable advantages such as non-toxic, non-corrosive and an inexpensive reaction condition.

ACKNOWLEDGEMENTS

The authors express their thanks to the authorities of IndraRaj Arts and Science College, Sillod for the providing laboratory facilities.
REFERENCES