Neodymium acetylacetonate. A new heterogeneous catalyst for transfer hydrogenation of carbonyl compounds

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Neodymium acetylacetonate, Nd(acac)$_3$H$_2$O, has been found to exhibit high activity towards the transfer hydrogenation of carbonyl compounds using 2-propanol as hydrogen source under truly heterogeneous phase to afford the corresponding alcohols in 63-81% yield.

Reduction of organic compounds is important synthetically both in the laboratory and in the industry. In comparison with catalytic reduction using molecular hydrogen, transfer reduction using H-donors such as ammonium formate, isopropanol, etc has real and potential advantages since it avoids the risks and constraints associated with high pressure reactors. Of all the methods available for addition of hydrogen to organic compounds heterogeneous catalytic transfer hydrogenation reactions have been relatively less explored. Heterogeneous catalyst derived from Rh, Ru, Pd, Ni, Ir, Pt, Co are known to promote hydrogenation process. These catalysis are generally in the form of finely divided metals, metals supported on carbon or skeletal metals like Raney Ni. Both salts and complexes of Pd, Pt, Ru, Ir, Rh, Fe, Ni, and Co have been used as catalysts for the transfer of hydrogen from molecular hydrogen or hydrogen donors to organic substrates. But all these salts or complexes catalyze transfer hydrogenation in homogeneous condition. Although many transition metals are known as catalysts for the transfer hydrogenation process, no such reports are available in the literature for the complexes of inner transition metals. Herein, we report for the first time the use of Nd(acac)$_3$3H$_2$O for the transfer hydrogenation of carbonyl compounds. Interestingly, unlike other metal complexes, this catalyst shows activity in a heterogeneous manner for transfer hydrogenation with the aid of isopropanol as hydrogen donor (Scheme I).

The catalyst Nd(acac)$_3$3H$_2$O was prepared according to literature procedure. Table I summarizes the results of transfer hydrogenation of various ketones and aldehydes which underwent reduction in refluxing in propan-2-ol. Potassium hydroxide is necessary as promoter for this catalytic process to occur. Evidently, aliphatic, alicyclic and aromatic aldehydes and ketones undergo reduction readily under these conditions. Reduction of aromatic aldehydes goes faster than ketones but yields are slightly lower. We have also tested the catalytic activity of this complex in formic acid as hydrogen source but reaction did not proceed at all. The colour of the complex turns to white from violet when it was heated in formic acid. This may be due to deactivation of the catalyst to form neodymium oxides. The neodymium catalyst was filtered and recycled once in case of acetophenone and yields are found to be reduced considerably (entry 12, Table I).

\[
\text{R, } R_2 = \text{alkyl, aryl, } H
\]

Scheme I

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Table I—Transfer hydrogenation of carbonyl compounds with \( \text{Nd(acac}_3 \cdot 3\text{H}_2\text{O)} \)

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Substrate</th>
<th>H-Donor</th>
<th>Period (hr)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetophenone</td>
<td>Propan-2-ol</td>
<td>24</td>
<td>No reaction</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>Acetophenone</td>
<td>Propan-2-ol/KOH</td>
<td>24</td>
<td>1-Phenylethanol</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>4-Methyl acetophenone</td>
<td>Propan-2-ol/KOH</td>
<td>20</td>
<td>1-(4-Methylphenyl)ethanol</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>4-Chloroacetophenone</td>
<td>Propan-2-ol/KOH</td>
<td>20</td>
<td>1-(4-Chlorophenyl)ethanol</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexanone</td>
<td>Propan-2-ol/KOH</td>
<td>20</td>
<td>Cyclohexanol</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>1-Tetralone</td>
<td>Propan-2-ol/KOH</td>
<td>24</td>
<td>1-Tetralol</td>
<td>67</td>
</tr>
<tr>
<td>7</td>
<td>Octanal</td>
<td>Propan-2-ol/KOH</td>
<td>24</td>
<td>Octyl alcohol</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>Benbazylide</td>
<td>Propan-2-ol/KOH</td>
<td>16</td>
<td>Benzyl alcohol</td>
<td>74</td>
</tr>
<tr>
<td>9</td>
<td>4-Methoxybenzaldehyde</td>
<td>Propan-2-ol/KOH</td>
<td>12</td>
<td>4-Methoxybenzaldehyde</td>
<td>76</td>
</tr>
<tr>
<td>10</td>
<td>Acetophenone</td>
<td>HCO(\text{H}_2\text{O})</td>
<td>12</td>
<td>No reaction</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>Acetophenone</td>
<td>HCO(\text{H}_2\text{O})/HCO(\text{NH}_4)</td>
<td>24</td>
<td>1-Phenylethanol</td>
<td>50</td>
</tr>
</tbody>
</table>

(a) Reaction conditions: Substrate, 4 mmoles; Catalyst, 0.08 mmole; KOH, 0.4 mmole; ProOH, 10 mL. Temp. 82°C; (b) All products have been characterized by IR, \(^1\)H and \(^13\)C NMR and MS; (c) Isolated yield after chromatographic purification.

In conclusion, \( \text{Nd(acac}_3 \cdot 3\text{H}_2\text{O}) \) in conjunction with KOH serves as good catalyst for transfer hydrogenation of aldehydes and ketones in heterogeneous manner. This catalyst does not show any activity in formic acid, which may be due to decomposition of the catalyst in acidic medium.

Experimental Section

A mixture of carbonyl compound (4.17 mmole), \( \text{Nd(acac}_3 \cdot 3\text{H}_2\text{O}) \) (0.083 mmole, 2 mol%) and KOH (0.2 mmole) in propan-2-ol (10 mL) was refluxed for 24 hr. After completion of reaction the catalyst was filtered and solvent was removed from the filtrate to get a crude mass. The crude mass was dissolved in ether, washed with brine, dried over anhydrous \( \text{Na}_2\text{SO}_4 \) and evaporated. Crude product was chromatographed on silica gel using petroleum ether-ethyl acetate to give the corresponding alcohol.

Spectral data for selected compounds

1-(4-Chlorophenyl)ethanol: Yield 71%; IR (neat): 3500-3100, 2950, 1590, 1410, 1250, 1200, 1060, 1010 cm\(^{-1}\); \(^1\)H NMR (200 MHz, CDCl\(\text{3}\)): \( \delta \) 1.5 (d, \( J=6.7 \text{ Hz} \), 3H), 2.1 (bs, 1H), 4.85 (q, \( J=7.4 \text{ Hz} \), 2H); MS (m/z, % rel. intensity): 156 (M\(^+\), 21), 141 (100), 111 (22), 107 (29), 91 (5), 77 (38).

1-Tetralol: Yield 67%, IR (neat): 3500-3100, 2860, 1430, 1200, 1050, 1020 cm\(^{-1}\); \(^1\)H NMR (200 MHz, CDCl\(\text{3}\)): 1.7-2.1 (m, 5H), 2.65-2.9 (m, 2H), 4.75 (t, 1H, \( J=6.8 \text{ Hz} \)), 7.1 (d, \( J=6.8 \text{ Hz} \), 1H), 7.2 (d, \( J=6.8 \text{ Hz} \), 1H).

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Reference