Pressure mediated reduction of aromatic nitro compounds with hydrazine hydrate

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Reduction of aromatic nitro compounds to primary amines has been carried out with hydrazine hydrate under moderate nitrogen pressure. Under optimized reaction conditions of 2.0 MPa of nitrogen pressure at 150°C nitrobenzene is reduced to aniline in 89.7% yield. Under identical reaction conditions reductions of several other aromatic nitro compounds to their amines have been achieved in moderate to high yield.

Hydrazine is a powerful reducing agent. It is not only rich in hydrogen content but also its decomposition to nitrogen and hydrogen is an exothermic process (ΔH = 95.459 kJ mol⁻¹) and thermodynamically highly favourable. Anhydrous hydrazine is a potent explosive and therefore, requires careful handling. In contrast, hydrazine hydrate requires no special care in handling, and therefore, it is in this form most commonly used.

Reduction with hydrazine hydrate is reportedly carried out either in the presence of an oxidizing agent, an alkali or a catalyst. While the reduction is carried out in an open vessel it is the aerial oxygen that acts as the oxidizing agent. Some other oxidizing agents reportedly used are potassium periodate, hydrogen peroxide and ferri cyanide. Presence of an oxidizing agent presumably facilitates the generation of diimide which is considered responsible for the reducing act. Reduction of a carbonyl compound with hydrazine hydrate in the presence of a base, for example in Wolff-Kishner reduction, most probably takes place via intermediate formation of a monosubstituted diimide.

Some of the reportedly used catalysts in the reduction of aromatic nitro compounds using hydrazine hydrate are Raney Ni, Pd, Pt, graphite, Montmorillonite and activated carbon. While some of these catalysts are expensive, and not readily available, others need rigorous experimental conditions such as use of absolute ethanol, high temperature and long reaction time. Herein it is being reported that reduction of aromatic nitro compounds can be successfully carried out with hydrazine hydrate in easily available commercial ethanol under moderate nitrogen pressure without need of any oxidant or a catalyst.

Experimental Procedure

Materials

Hydrazine (80%) was procured from Loba Chemie Pvt. Ltd. and ethanol (90%) was of commercial grade. Nitro compounds, except the amides, were procured from commercial sources and used as such. Nitrobenzamides were prepared in the laboratory from the corresponding nitrobenzoic acids.

Method

All reactions were carried out in a medium pressure desk-top autoclave supplied by BERGHOF GmbH, Germany, with intake capacity ranging from 75 to 250 mL.

Reaction conditions were optimized with nitrobenzene as the substrate. All other reactions were carried out under the conditions found to be optimum with nitrobenzene. The procedure given here is the generalized one. For exact quantities of reactants and solvent in each reaction one should refer to the tables.

Calculated quantities of nitro compounds, ethanol (90%), and hydrazine hydrate (80%) were introduced into a PTFE-liner. The liner was placed into the autoclave, the autoclave was closed and it was then purged with nitrogen. Desired nitrogen pressure was applied from a N2-cylinder and the temperature of the reaction mixture was raised to the desired level. The autoclave was maintained at the desired temperature for the specified reaction time while the reaction mixture inside was stirred all the while. At the end of the reaction time (time period counted from the moment the autoclave reached the desired...
temperature to the moment the heating was switched off) the autoclave was allowed to cool down to room temperature without any help of cooling device.

The reaction mixture was taken out of the autoclave and was made strongly alkaline (except entries 10 and 11, Table 5) with 1N NaOH solution (10 to 15 mL). The alkaline solution was extracted thrice with diethyl ether (3×25 mL). The ether layer contained the product amine along with the unreacted nitro compound. The aqueous layer was discarded and the combined ether phase was washed with dilute hydrochloric acid (2×10 mL). While the product amine was washed away into the aqueous phase as its hydrochloride, the unreacted nitro compound and undesired tarry materials were left behind in the ether layer. The ether layer was discarded and the acidic aqueous layer was made strongly alkaline with 1N NaOH solution so as to liberate the product amine from its hydrochloride. This was followed by extraction with diethyl ether (3×25 mL). The ether layer was separated, washed with 10% sodium chloride solution (1×25 mL), dried over anhydrous sodium sulphate and filtered under suction. The solvent was removed by rotary vacuum evaporator and the last traces by high vacuum pump to yield the product amine in pure state. In case of entry 10 and 11, the solvent and the excess hydrazine were removed by heating the reaction mixture under vacuum and solid mass obtained were recrystallized from rectified spirit to yield the product as a crystalline solid. The purity of the products were ascertained by $^1$H NMR and comparing their IR and m.p. with those of authentic samples. The percentage of yield was calculated based on the number of moles of the nitro compound used and the amino compound obtained.

**Results and Discussion**

For maximizing the yield of the product the effect of different parameters such as temperature, time, pressure, etc. were studied in the order as discussed below. The optimized conditions as determined for nitrobenzene as the substrate are shown in the scheme.

The reductions of all other compounds have been carried out under these conditions although it is understood that these are not necessarily the optimized conditions for each of them.

**Effect of reaction temperature**

The reduction of nitrobenzene to aniline was studied at five different temperatures ranging from 80°C to 170°C (Table 1). Maximum yield of 89.70% could be achieved at 150°C. Higher temperature than this results in the decrease of the yield due to simultaneous increase of tarry materials at the cost of the product.

**Effect of reaction time**

Maximum yield of 89.70% could be achieved at a reaction time of 4 h (Table 2). Longer reaction time decreases the yield by destruction of the product with simultaneous increase in the quantities of tarry materials.

**Effect of nitrogen pressure**

Table 3 shows that maximum reaction pressure of 2.0 MPa (initial nitrogen pressure being 0.5 MPa) is beneficial for the reaction. Higher pressure than this tends to increase the amount of tarry materials at the cost of the product. When the reaction was carried out under one atmospheric pressure of nitrogen only 23.20% of yield (as compared to 89.70% under 2.0 MPa of N$_2$-pressure) could be achieved.

<table>
<thead>
<tr>
<th>Reaction temp (°C)</th>
<th>Max. reaction pressure (MPa)</th>
<th>Yield of aniline (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.0</td>
<td>21.00</td>
</tr>
<tr>
<td>100</td>
<td>1.1</td>
<td>65.07</td>
</tr>
<tr>
<td>120</td>
<td>1.3</td>
<td>62.80</td>
</tr>
<tr>
<td>150</td>
<td>2.0</td>
<td>89.70</td>
</tr>
<tr>
<td>170</td>
<td>2.2</td>
<td>61.40</td>
</tr>
</tbody>
</table>

@ Nitrobenzene 1 mL (9.7 mmol), ethanol (90%) 52.5 mL, hydrazine hydrate (80%) 25.0 mL, reaction time 4 h, initial N$_2$-pressure 0.5 MPa.

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Max. reaction pressure (MPa)</th>
<th>Yield of aniline (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.0</td>
<td>45.39</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>89.70</td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>63.87</td>
</tr>
</tbody>
</table>

@ Nitrobenzene 1 mL (9.7 mmol), ethanol (90%) 52.5 mL, hydrazine hydrate (80%) 25.0 mL, reaction time 150°C, initial N$_2$-pressure 0.5 MPa.
achieve maximum amount of the product. Higher amount than this amount of hydrazine does not make much quantitative change in the amount of the product.

Reduction of other nitro compounds

Under reaction conditions found to be optimum for the reduction of nitrobenzene, a couple of other nitro compounds have been reduced (Table 5). In most of the cases moderate to high yields have been achieved. Chloro, bromo and amide groups are unaffected.

Conclusion

Reduction of nitro compounds to industrially useful amines can be conveniently carried out using cheap and easily available hydrazine hydrate under moderate nitrogen pressure. This methodology is a potential alternative or even better than already known methods, which require expensive catalysts, reagents or rigorous reaction conditions.

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References