Nickel bromide as a hydrogen transfer catalyst

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Catalysed transfer hydrogenation of a range of organics is achieved using NiBr₂ in alkaline PrOH

During our studies on NiX₂(PPh₃)₂ complexes (X = halogen, py = 2-pyridyl, n = 1–3), some of which are water-soluble,1 a report appeared on the use of a NiCl₂(PPh₃)₂–NaOH–PrOH system for transfer hydrogenation of ketones and aldehydes.2 Our Ni(0) pyridylphosphines, under corresponding conditions, were of comparable activity, but some ‘blank tests’ soon revealed that NiCl₂·6H₂O had similar activity, while anhydrous NiBr₂ or NiI₂·6H₂O had much higher activity. For example, 90% conversion of cyclohexanone to cyclohexanol was attained after 1 h of refluxing in an alkaline PrOH solution containing NiBr₂, whereas conversions of only 14 and 24%, respectively, were achieved with NiCl₂(PPh₃)₂ and NiBr₂(PPh₃)₂. Because these conversions are comparable under conditions in which aldehydes are reduced to alcohols within 5 min, it seems unlikely that NiBr₂ has an influence on the reaction mechanism.3,7 3,7–11

Table 1 NiBr₂ catalysed transfer hydrogenation of organics

<table>
<thead>
<tr>
<th>Substrate</th>
<th>% Conversion (time, h)</th>
<th>% Conversion (time, h)</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone</td>
<td>99.9 (0.5)</td>
<td>29.1 (0.5)</td>
<td>Cyclohexanol</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>60.1 (4), 99.4 (24)</td>
<td>65.4 (4), 98.8 (24)</td>
<td>1-Phenylethanol</td>
</tr>
<tr>
<td>Butan-2-one</td>
<td>55.2 (2), 97.2 (24)</td>
<td>8.4 (2), 18.5 (24)</td>
<td>Butan-2-ol</td>
</tr>
<tr>
<td>Pentan-2-one</td>
<td>31.0 (24), 99.9 (48)</td>
<td>12.2 (24), 27.8 (48)</td>
<td>Pentan-2-ol</td>
</tr>
<tr>
<td>Oct-1-ene</td>
<td>99.9 (0.5)</td>
<td>0.0 (0.5)</td>
<td>n-Octane</td>
</tr>
<tr>
<td>Cyclohex-2-en-1-one</td>
<td>73.0 (48)</td>
<td>20.0 (48)</td>
<td>Cyclohexanone</td>
</tr>
<tr>
<td>Heptan-1-ol</td>
<td>92.2 (4)</td>
<td>83.0 (4)</td>
<td>Cyclohexanold</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>14.1 (0.5), 19.2 (48)</td>
<td>4.0 (0.5), 14.0 (48)</td>
<td>Aniline</td>
</tr>
<tr>
<td>4-Nitrobenzaldehyde</td>
<td>38.0 (24)</td>
<td>12.5 (24)</td>
<td>ABA, NBA, AB</td>
</tr>
</tbody>
</table>

* In 24 h, no conversion for: (i) oct-2-ene, but-3–2-ene, pentan-2,4-diene, hexane-2,5-diene, 2-propionic acid, MeCN, PhCN and benzene, and < 5% for cyclooctene and cod. 8 In presence of base only, no NiBr₂ · 2% ketone, 71% alcohol, 4% ketone, 16% alcohol, 10.5% 4-aminobenzaldehyde (ABA), 21.9% 4-nitrobenzyl alcohol (NBA), 5.6% 4-aminobenzaldehyde (AB), 3.6% ABA, 7.4% NBA, 1.5% AB.

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cyclohexanone hydrogenation; also the addition of Hg(0), an inhibitor for colloidal activity, to a ‘fresh’ system gave only a 7% decrease in conversion (cf. Table 1). Further, the solid inorganic residue obtained after a hydrogenation of cyclohexanone was re-used three more times for repeat conversions, when only slow deactivation of the catalyst was noted: 1st run, 99.9% conversion after 0.5 h; 2nd, 95% (3 h); 3rd, 92% (7 h); 4th, 63% (3 h).

Of interest, addition of up to 4 equiv. of PPh₃ to the NiBr₂ system has no effect on the rate of hydrogenation of cyclohexanone, and also NiBr₂(PPh₃)₂ is unstable in the alkaline medium (with dissociation of the phosphine), implying that in the earlier work on the NiCl₂(PPh₃)₂ system the precursor catalyst may be simply NiCl₂.

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Notes and references
† A glass vessel (35 mL) equipped with a Teflon-coated magnetic stirrer was charged in air with NiBr₂, NaOH and iPrOH, and the mixture heated at 95 °C to yield a pale-green solution. After this was cooled to rt, the vessel was fitted with a condenser and charged with substrate; the mixture was then refluxed, and samples were withdrawn for GC and NMR analysis (Table 1). The NiBr₂:NaOH:substrate ratios were 1:85:250 in all cases, with [NiBr₂] between 1–6 mM.