Introduction

Nickel boride (Ni₂B), first reported in the pioneering work of Schlezinger and Brown¹ and traditionally used as a catalyst for hydrogenation,² has more recently found a niche as a reducing agent in its own right.³ Its ease of preparation, handling, and versatility as a reducing agent promise nickel boride its deserved attention from academic and industrial sectors. Nickel boride has been employed for a wide range of transformations including reductive dehalogenation of organic halides⁴, reductive amination of carbonyl compounds,⁵ desulfurization of a variety of thioxo compounds,⁶ deoxygenation of sulfoxides and selenoxides,⁷ and reducing of nitrogen functionalities.⁸ Of late, the reagent is being explored in the form of a nickel boride silica nanocomposite catalyst for hydrogen production from NaBH₄ hydrolysis.⁹

Preparation and Properties

The reagent can be generated by using nickel(II) salts in conjunction with sodium borohydride in protic conditions to deposit finely divided black precipitates of nickel boride.¹⁰

<table>
<thead>
<tr>
<th>Abstracts</th>
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<td>(A) The reduction of α,β-unsaturated five-membered lactones and lactams to saturated lactones and lactams has been achieved using nickel boride.¹¹ Ex situ generated SC-1 nickel boride is used for the selective 1,4-hydrogenation of α,β-unsaturated ketones and aldehydes.¹²</td>
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\[
\begin{align*}
\text{NiCl₂, NaBH₄} & \quad \text{MeOH, 5–10 °C} \\
\text{O} & \quad \text{H} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

(B) The chemoselective reduction of double bonds in chalcones, α,β-unsaturated ketones, aldehydes, carboxylic acids, and esters using nickel boride has been reported.¹³ The rapid reduction of chalcones to tetrahydrochalcones has also been achieved.¹⁴

\[
\begin{align*}
\text{NiCl₂, NaBH₄} & \quad \text{dry MeOH, r.t.} \\
\text{R₁, R₂, R₃, R₄, R₅} & \quad \text{OMe, Cl, Br, H} \\
\end{align*}
\]

(C) The chemoselective cleavage of benzyl esters with nickel boride affords carboxylic acids in good yields. Dibenzyl esters are also successfully cleaved. Methyl, ethyl, t-butyl, and trityl esters are reported to be not affected under the reaction conditions, thereby imparting selectivity.¹⁵

\[
\begin{align*}
\text{R(COOBn)₂} & \quad \text{NiCl₂·6H₂O, NaBH₄} \\
\text{MeOH, r.t.} & \quad \text{R(COOH)₂} \\
\text{RCOOBn} & \quad \text{NiCl₂·6H₂O, NaBH₄} \\
\text{MeOH, r.t.} & \quad \text{RCOOH} \\
\end{align*}
\]
(D) In situ generated nickel boride has been described to efficiently reduce carbonyl compounds to alcohols. Benzopyrones have been reduced to cis-benzopyran-4-ols.

(E) Nickel boride has proved to be an efficient reducing agent for various nitrogen functionalities. It is reported to reduce nitriles to amines, the concept being modified to obtain Boc-protected nitriles. Further, Ni,B-BER has been reported to reduce oximes into amines. Recently, nickel boride has been utilized to reduce the hydrazine functionality developing a novel method towards 4-aminoquinolines.

(F) Recent efforts have been directed to study the feasibility of new materials to be used as support for boron nickel catalysts. Ni/SiO₂–NaBH₄ is reported to achieve the reduction of different aliphatic and aromatic functional groups with 100% conversion and selectivity.

\[
\begin{align*}
R_1&COR_2 & \overset{\text{NiCl₂, NaBH₄}}{\text{dry THF, r.t.}} & \overset{5-15 \text{ min}}{\text{NiCl₂, NaBH₄}} & \overset{\text{dry MeOH, r.t.}}{R_1'CH(OH)R_2} \\
R_1 = & \text{Me, MeO; R₂ = Ar, R₃ = H;} & \text{R₂ = Alk, R₃ = H;} & \text{R₂ = H, R₃ = Ar}
\end{align*}
\]

**References**