SYNLETT Spotlight 330

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Nickel Boride

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Dedicated to my honorable mentor Prof. J. M. Khurana

Introduction

Nickel boride (Ni_2B), first reported in the pioneering work of Schleisinger 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 NaBH_4 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

Scheme 1

Abstracts

(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

(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

(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

(D) In situ generated nickel boride has been described to efficiently reduce carbonyl compounds to alcohols.¹⁶ Benzopyrones have been reduced to *cis*-benzopyran-4-ols.¹⁷

(E) Nickel boride has proved to be an efficient reducing agent for various nitrogen functionalities. It is reported to reduce nitriles to amines,¹⁸ the concept being modified to obtain Boc-protected nitriles.¹⁹ Further, Ni₂B-BER has been reported to reduce oximes into amines.²⁰ Recently, nickel boride has been utilized to reduce the hydrazine functionality developing a novel method towards 4-aminoquinolines.²¹

(F) Recent efforts have been directed to study the feasibility of new materials to be used as support for boron nickel catalysts.²² Ni/SiO₂-NaBH₄ is reported to achieve the reduction of different aliphatic and aromatic functional groups with 100% conversion and selectivity.²³

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