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

Compiled by Devanshi Magoo

Devanshi Magoo was born in 1983 in New Delhi, India. She received her B.Sc. degree in Chemistry from the Hindu College, University of Delhi, in 2004 and her M.Sc. in Organic Chemistry from the same university in 2006. After qualifying for the CSIR Junior Research Fellowship in 2006, she is presently working as senior research fellow towards her Ph.D. degree under the supervision of Prof. J. M. Khurana at the University of Delhi, India. Her research is focused on some novel synthetic methodologies and organic transformations along with enzyme inhibition studies.

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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 Schlezinger and Brown[1] 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 halides[4], 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

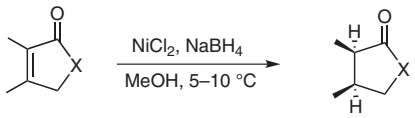
The reagent can be generated by using nickel(II) salts in conjunction with sodium borohydride in protic conditions to deposit finely divided black precipitates of nickel boride.[10]

$$4\ NaBH_4 + 2\ NiCl_2 + 9\ H_2O \longrightarrow Ni_2B + 3\ H_3BO_3 + 4\ NaCl + 12.5\ H_2$$

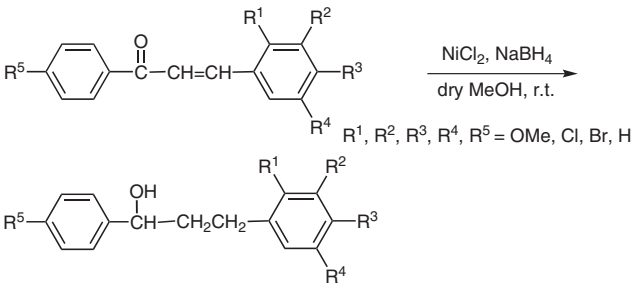
Scheme 1

Abstracts

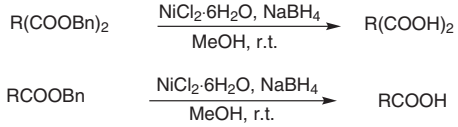
(A) The reduction of α,β-unsaturated five-membered lactones and lactams to saturated lactones and lactams has been achieved using nickel boride.[11] Ex situ generated SC-1 nickel boride is used for the selective 1,4-hydrogenation of α,β-unsaturated ketones and aldehydes.[12]



(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]



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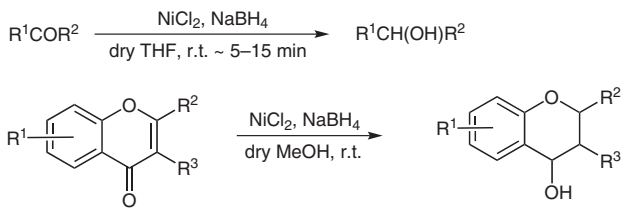
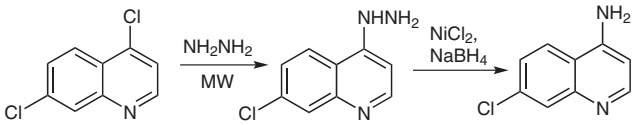
(D) In situ generated nickel boride has been described to efficiently reduce carbonyl compounds to alcohols.[16] Benzopyrones have been reduced to *cis*-benzopyran-4-ols.[17]

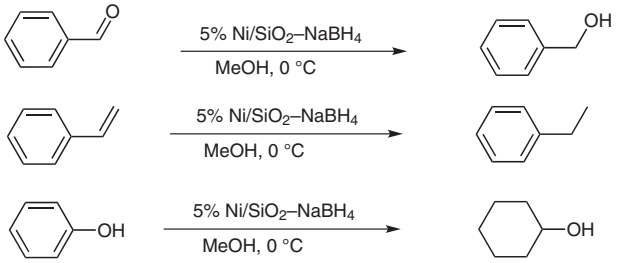


R^1 = Me, MeO; R^2 = Ar, R^3 = H;
R^2 = Alk, R^3 = H;
R^2 = H, R^3 = Ar

(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, Ni_2B-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/SiO_2–$NaBH_4$ is reported to achieve the reduction of different aliphatic and aromatic functional groups with 100% conversion and selectivity.[23]



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