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# Catalytic Reaction. 1. Catalytic 1,4-Hydrogenation of *α,β*–Unsaturated Aldehydes and Ketones using SC-1 Nickel Boride[1]

Christopher M. Belisle, Yvette M. Young and Bakthan Singaram*

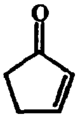
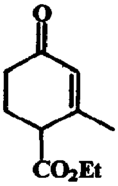
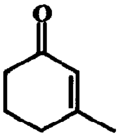
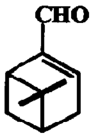
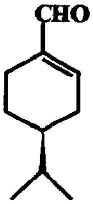
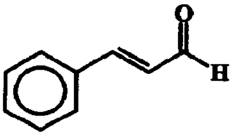
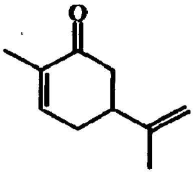
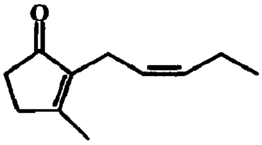
*Department of Chemistry and Biochemistry, University of California, Santa Cruz California 95064 USA*

***Abstract:*** *Ex-situ generated SC-1 nickel boride (SC-1 $Ni_2B$), prepared by refluxing nickel chloride and sodium borohydride in methanol, is used in the selective 1,4-hydrogenation of α, β–unsaturated ketones and aldehydes at one atmospheric pressure. Previous studies of in-situ generated $Ni_2B$ have had the disadvantage of the undesirable side reaction of sodium borohydride with the various functional groups. In contrast, our catalyst cleanly gives the corresponding saturated aldehyde or ketone with no detectable amounts of saturated alcohol. Furthermore, the degree of substitution of the double bond plays a significant role in the rate of hydrogenation. While unsaturated carbonyl compounds containing di- and tri- substituted double bonds are readily hydrogenated, tetra-substituted double bond containing carbonyl compounds are highly unreactive.*

Recently we disclosed our results on 1,2-reduction of *α,β*–unsaturated carbonyl compounds to the corresponding allylic alcohols using lithium pyrrolidinoborohydride.[2] In continuation of this project, we were interested in a complimentary procedure for the 1,4-reduction of *α,β*–unsaturated carbonyl compounds to the corresponding saturated carbonyl compound. A search of the literature showed that due to its ease of preparation and economic feasibility, $Ni_2B$ facilitated reduction of unsaturated systems has been successful.[3,4] Reduction of various unsaturated systems have previously been studied with *in-situ* generated $Ni_2B$.[3,5,6] However, the major draw back of this method has been its application to the reduction of systems easily reduced by sodium borohydride ($NaBH_4$).[5,7,8,9] The reduction of *α,β*–unsaturated aldehydes and ketones with *in-situ* generated $Ni_2B$ yielded mixtures of the corresponding saturated aldehydes/ketones and saturated alcohols. Consequently, *in-situ* prepared $Ni_2B$ 1,4-reductions were limited to *α,β*–unsaturated esters, *α,β*–unsaturated carboxylic acids and other compounds with functional groups that were stable to $NaBH_4$.[10,11,12,13]

It had been assumed previously that *in-situ* generated $Ni_2B$ was free of $NaBH_4$ and that the catalyst was only participating in a pure hydrogenation mode.[5,7,8] However, we found even if the *in-situ* generated $Ni_2B$ was filtered and washed with MeOH, the hydrogenation of cyclohexenone led to 95% cyclohexanol. We speculated that this undesired over-reduction of *α,β*–unsaturated aldehydes and ketones may be due to the residual $NaBH_4$ incorporated into the colloidal catalyst. It occurred to us that by refluxing the $Ni_2B$ in methanol, any residual $NaBH_4$ would be destroyed providing a new $Ni_2B$ catalyst that would give exclusive 1,4-reduction of *α,β*–unsaturated aldehydes and ketones. Herein we report our findings on the application of this new catalyst (SC-1 $Ni_2B$) for the hydrogenation of *α,β*–unsaturated carbonyl compounds.

**Table 1. Reduction of α,β-Unsaturated Carbonyl Compounds with SC-1 Ni$_2$B**

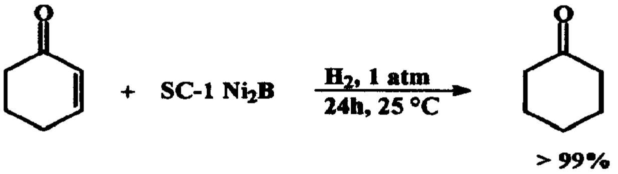
| Substrate | 1,4 : 1,2 | Yield % | Substrate | 1,4 : 1,2 | Yield % |
|---|---|---|---|---|---|
|  | >99:1 | >99 % |  | >99:1 | 83 % |
|  | >99:1 | 78 % |  | >99:1 | 96 % |
|  | >99:1 | 96 % |  | >99:1 | 93 % |
|  | >99:1[a] | 82 % |  | >99:1[b] | 97 % |

[a] The exocyclic double bond was also hydrogenated. [b] Only the exocyclic bond was hydrogenated.

We prepared the new SC-1 Ni$_2$B catalyst by the following procedure. A 200-mL RB flask fitted with a condenser and septum, was charged with NiCl$_2$ · 6H$_2$O (20 mmol) and methanol (20 mL). The flask was flushed with nitrogen several times and was finally equipped with positive nitrogen pressure through a mercury bubbler. It was then reacted with a 1M solution of NaBH$_4$ in methanol (50 mL, 50 mmol) over a period of 15 minutes at 0 °C.[14] A black precipitate was formed upon the addition of NaBH$_4$ and the colloidal suspension was stirred at 25 °C for 1 hour. The reaction mixture was then refluxed for 3 hours to destroy any residual NaBH$_4$ to give SC-1 Ni$_2$B. The catalyst thus prepared can be stored up to six months at 25 °C with no loss in activity.

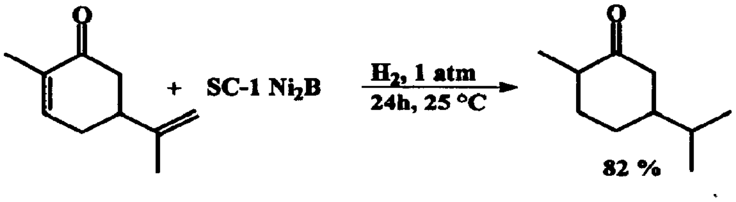
The hydrogenation of $\alpha,\beta$-unsaturated aldehydes and ketones with SC-1 $Ni_2B$ was done as follows. A 50-mL RB flask fitted with a septum and stir bar was charged with SC-1 $Ni_2B$ in methanol (5 mmol in 10 mL) and the $\alpha,\beta$-unsaturated aldehyde or ketone (10 mmol). The flask was then evacuated and flushed with hydrogen several times and was finally equipped with one atmosphere of hydrogen pressure through a mercury bubbler. The reaction was then stirred at 25 °C for 24 hours. The total reaction mixture was then centrifuged and the supernant was isolated and filtered. Removal of the solvent gave an essentially analytically pure sample. It was analyzed by capillary GC and characterized by IR, $^1H$ and $^{13}C$ NMR. The results are summarized in Table 1.

The hydrogenation of $\alpha,\beta$-unsaturated aldehydes and ketones with SC-1 $Ni_2B$ gave exclusively the corresponding saturated aldehyde or ketone with no by-product resulting from the reduction of the carbonyl group (eq. 1).[15]

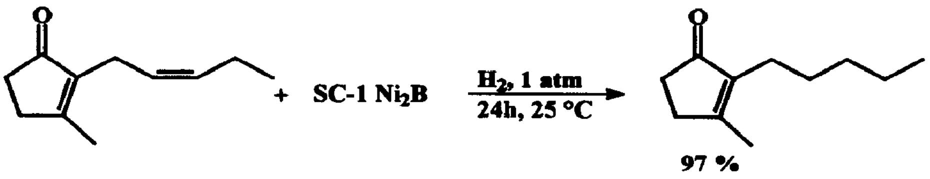


(1)

The degree of olefin substitution had a major effect on the rate of hydrogenation of $\alpha,\beta$-unsaturated carbonyl compounds. Di-substituted and tri-substituted compounds were readily accommodated whereas tetra-substituted systems were unreactive. Furthermore, isolated carbon-carbon double bonds were also readily hydrogenated with SC-1 $Ni_2B$, demonstrating the same steric sensitivity to double bond substitution (eq. 2 and 3)



(2)



(3)

We have shown that SC-1 $Ni_2B$ prepared in refluxing methanol cleanly gave 1,4 reduction of $\alpha,\beta$-unsaturated aldehydes and ketones with no saturated alcohol byproduct resulting from the reduction of the carbonyl group. We are currently exploring the applications of SC-1 $Ni_2B$ modified with chiral ligands in the regioselective and stereoselective hydrogenation of organic compounds.

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14. The $NaBH_4$ / methanol solution was made and maintained at 0 °C.
15. The following procedure for the hydrogenation of *trans*-cinnamaldehyde is representative. In a 50-mL round-bottomed flask fitted with a stir bar and septum, *trans*-cinnamaldehyde (10 mmol ,1.32 g) was dissolved in of methanol (5 mL). The flask was then charged with SC-1 $Ni_2B$ (5 mmol) in methanol (5 mL). The flask was then evacuated and flushed with hydrogen and finally filled with one atmosphere of hydrogen pressure through a mercury bubbler. The reaction was then stirred at 25°C for 24 hours. The reaction mixture was then centrifuged and the supernant isolated and filtered through Celite®. The solvent was then evaporated under reduced vacuum to give analytically pure dihydrocinnamaldehyde; 1.33g (9.9 mmol, 99% yield). The clear oil was analyzed by capillary gas chromatography (HP 5890A fitted with a 30m 10% methyl silicate column) , FT-IR (Perkin Elmer spectrometer 1600) and $^1H/^{13}C$ NMR (Bruker 250 MHz.). IR (neat): 3028, 2927, 2825, 2724, 1724, 1603, 1496, 1451, 1405 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.78 (dt, $J = 8$, 1 Hz., 2H), 2.97 (t, $J = 7$ Hz., 2H), 7.19-7.34 (m, 5H), 9.83 (t, $J = 1$ Hz., 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 28.2, 45.3, 126.4, 128.3, 128.7, 140.4, 201.6.

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