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An Excellent Nickel Boride Catalyst for the *cis*-Selective Semihydrogenation of Acetylenes

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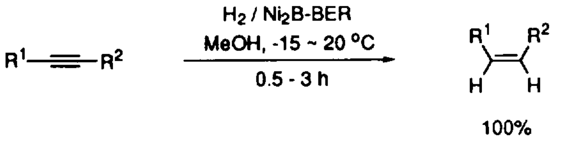
Abstract: Internal alkynes were hydrogenated quantitatively to the corresponding *cis*-alkenes over nickel boride (Ni_2B), prepared on borohydride exchange resin (BER) in methanol under hydrogen atmosphere. Further hydrogenation was very slow under the reaction conditions, and pure *cis*-alkenes were conveniently isolated in excellent yields. Hydroxy and ester functional groups did not interfere with the semihydrogenation.

The catalytic *cis*-selective semihydrogenation of acetylenes on heterogeneous catalysts is one of the important methods in organic synthesis.[1-3] Indeed, the synthesis of pure *cis*-olefins is often a key step during the synthesis of important substances such as pheromones[2] or other natural products.[3] Although numerous studies have been devoted to this problem, no catalyst of general applicability has been reported so far that exhibits a quantitative yield of *cis*-olefins.[4-9] Ni-based catalysts such as P-2 nickel[4] and Nic,[5] and Pd-based catalysts such as Lindlar catalyst,[6] Pdc,[7] Pd/W,[8] and montmorillonite-diphenylphosphine-palladium(II) chloride complex[9] are reported to be excellent for both quantitative bond selectivity (alkene / [alkene + alkane] ratio) and stereoselectivity (Z / [Z + E] ratio). However, all of these hydrogenations must be interrupted at the point of one equiv of hydrogen absorption; and some of these methods require a considerable work in the preparation of catalysts. Moreover, none of these catalysts gives complete selectivity.

Recently, we studied the reducing properties of borohydride exchange resin[10]-nickel boride (BER-Ni_2B) in methanol, and reported that this system is excellent for the selective reductions of halides,[11(a),(b)] nitro compounds,[11(c)] and azides.[11(d)] In the course of these studies, we found that Ni_2B prepared on BER has an excellent selectivity in the semihydrogenation of acetylenes.

The semihydrogenation of 2-butyne-1,4-diol is representative. A nickel boride catalyst[12] was prepared on resin by adding nickel acetate (0.1 mmol) to BER[10] (1.0 mmol) in methanol (7 mL) at 0 °C under hydrogen atmosphere (1 atm).[13] Immediately, black coating of nickel boride was observed. 2-Butyne-1,4-diol (1.0 mmol) in methanol (1.0 mL) was added together with *n*-decane as an internal standard. Glpc analysis showed that *cis*-2-butene-1,4-diol had been formed quantitatively in 60 min and remained unchanged until 180 min. In a preparative run, 2-butyne-1,4-diol (10 mmol) was treated with BER (10 mmol) and $Ni(OAc)_2$ (1 mmol). After 1 h reaction at 0 °C, Ni_2B-BER was filtered; and the methanol was removed by rotary evaporator to give

Scheme 1



R^1, R^2 = Alkyl, Aryl, $-CH_2OH$, -COOMe

pure *cis*-2-butene-1,4-diol in 94% isolated yield.

The results are summarized in Table 1. As shown there, all the alkynes tested were hydrogenated quantitatively to give the corresponding *cis*-alkenes. The semihydrogenation of 2-hexyne was completed in 45 min and remained unchanged until 90 min. A small amount of hexane (1%) was noticed after 120 min (entry 1). The hydrogenation of 3-hexyne was similar to 2-hexyne (entry 2); but 1-phenyl-1-propyne was

Table 1. The Semihydrogenation of Representative Alkynes by using Ni_2B-BER in Methanol under Hydrogen Atmosphere

entry	alkyne	temp.(℃)	time(min)	products (%)
1	2-hexyne	0	45	*cis*-2-hexene (100)[a]
			90	*cis*-2-hexene (100)
			120	*cis*-2-hexene (99) hexane (1)
2	3-hexyne	0	60	*cis*-3-hexene (100)
			120	*cis*-3-hexene (100)
			180	*cis*-3-hexene (99) hexane (1)
3	1-phenyl-1-propyne	0	180	*cis*-1-phenyl-1-propene (100)
			360	*cis*-1-phenyl-1-propene (100)
4	2-butyne-1,4-diol	0	60	*cis*-2-butene-1,4-diol (100) [94][b]
			180	*cis*-2-butene-1,4-diol (100)
5	dimethyl acetylenedicarboxylate	-15	120	dimethyl maleate (100) [96]
			180	dimethyl maleate (100)
6	1-hydroxy-1-phenyl-2-octyne	20[c]	30	*cis*-1-hydroxy-1-phenyl-2-octene (100) [95]
			120	*cis*-1-hydroxy-1-phenyl-2-octene (100)
7	3-hydroxy-1-phenyl-1-octyne	20[c]	180	*cis*-3-hydroxy-1-phenyl-1-octene (100) [98]
			360	*cis*-3-hydroxy-1-phenyl-1-octene (100)

[a]Estimated by Glpc. [b]Isolated yields. [c]Only 5% hydrogenation in 1 h at 0 ℃.

hydrogenated somewhat more slowly, the semihydrogenation being completed in 180 min. No sign of overhydrogenation to propylbenzene was noticed until 360 min (entry 3). 2-Butyne-1,4-diol was readily hydrogenated at the similar rate with that of 3-hexyne (entry 4). The two hydroxy groups of 2-butyne-1,4-diol showed almost no effect on hydrogenation. On the other hand, dimethyl acetylenedicarboxylate was hydrogenated rapidly at 0 °C. The semihydrogenation was completed in 30 min, and 5% of overhydrogenation to dimethyl succinate was observed in 60 min. Fortunately, however, the selectivity could be enhanced by lowering the reaction temperature. Thus the semihydrogenation was completed in 120 min at -15 °C and remained unchanged until 360 min (entry 5). Sterically bulky propargyl alcohols were hydrogenated very slowly at 0 °C, showing only 5% hydrogenation in 1 h. However, the hydrogenations of 1-hydroxy-1-phenyl-2-octyne and 3-hydroxy-1-phenyl-1-octyne proceeded smoothly at 20 °C, the semihydrogenations being completed in 30 and 180 min, and remained unchanged until 120 and 360 min respectively (entries 6 and 7). The excellent selectivity seems to be due to the steric effect of bulky *cis*-alkenes, the corresponding semihydrogenated products; for a simple alkyne, such as 1-phenyl-1-propyne, exhibits considerable overhydrogenation at 20 °C.[14] Another advantage of the procedure is the simple work up. Since the reaction proceeds quantitatively, the separation of BER-Ni_2B by filtration and the evaporation of the solvent give essentially pure *cis*-alkenes.

In conclusion, the nickel boride catalyst prepared on BER in methanol is an excellent catalyst for the semihydrogenation of internal alkynes. The corresponding *cis*-alkenes are hereby obtained quantitatively for the first time.

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10. Borohydride Exchange Resin was prepared as follows: An aqueous solution of sodium borohydride (1 M, 500 mL) was stirred with wet chloride-form anion exchange resin [Amberlite IRA-400 (20 - 50 mesh), 200 g] for 15 min. The resulting resin was washed thoroughly with distilled water (3 x 100 mL). The borohydride form anion exchange resin was then dried in vacuo at 60 °C for 5 h to give 102 g of dried borohydride exchange resin (BER). The dried resin was analyzed for borohydride content by hydrogen evolution on acidification with 2 N HCl and the average hydride content of BER was found to be 3.0 mmol of BH_4^- per gram. The dried resin was stored under nitrogen in refrigerator (~ 4 °C). The hydride content was constant over 6 weeks.
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12. Three successive semihydrogenations of 2-butyne-1,4-diol could be carried out over the same catalyst, all in 1.0 h; however, the rate dropped sharply thereafter.
13. In the presence of Ni_2B, BER decomposes slowly in methanol evolving hydrogen. Therefore, the hydrogenation proceeds without supply of external hydrogen; however the hydrogenation is very slow. For example the hydrogenation of 2-butyne-1,4-diol proceeds only 24% in 1 h and 60% in 6 h.
14. Overhydrogenated propylbenzene (9%) and isomerized *trans*-1-phenyl-1-propene (1%) were observed together with 90% of *cis*-1-phenyl-1-propene in 60 min.

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