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The Semihydrogenation of Acetylenes over Pd Catalyst on BER in the Presence of CsI

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Abstract: In the presence of CsI, Pd catalyst on borohydride exchange resin (BER) in 95% ethanol exhibits a perfect selectivity for the semihydrogenation of acetylenes, providing the corresponding terminal olefins or *cis*-olefins quantitatively at room temperature.Copyright © 1996 Elsevier Science Ltd

The catalytic semihydrogenation of acetylenes over heterogeneous catalyst is one of the important methods in organic synthesis,[1,2] and was traditionally carried out by using Pd-based catalysts (e.g., Lindlar catalyst)[3] and Ni-based catalysts (e.g., P-2 nickel).[4] These catalysts are reportedly excellent in yield and selectivity; however, hydrogenation must always be interrupted at the point of one equiv of hydrogen absorption, and some of the methods require considerable work in the preparation of catalysts. Yet none of these catalysts give complete selectivity. Recently, we have demonstrated that pure *cis*-olefins can be obtained by the hydrogenation of internal acetylenes over Ni_2B on BER in methanol.[5] In the course of the study, we have found that metal halides generally inhibit the catalytic hydrogenation of acetylenes and olefins, and the effect is more severe to olefins. Although there were some reports on the inhibitory effect of alkali metal halides on the catalytic hydrogenation of olefins,[6] the modification of Lindlar catalyst has mainly been devoted to the addition of deactivating metals such as Pb and inhibitors such as quinoline.[1,3] We report here the semihydrogenation of acetylenes using Pd catalyst on BER in 95% ethanol in the presence of CsI.

The semihydrogenation of 3-hydroxy-1-octyne is representative. $Pd(OAc)_2$ (0.022 g, 0.1 mmol) in 95% ethanol solution (50 mL) was added to BER[7] (2.5 mmol) with gentle stirring under hydrogen atmosphere (1 atm) at room temperature to give a black coating of Pd on BER immediately. Reaction was started by adding CsI (0.78 g, 3 mmol) in 95% ethanol solution (50 mL) and 3-hydroxy-1-octyne (1.26 g, 10 mmol). After 30 min, Pd-BER was filtered, and the ethanol was removed by a rotary evaporator. Ether (30 mL) was added to the residue, and insoluble CsI was removed by filtration. Ether was evaporated under reduced pressure to yield pure 3-hydroxy-1-octene (1.24 g, 97%).

The results are summarized in Table 1. As Table 1 shows, terminal acetylenes, such as 1-heptyne, phenyl acetylene, and 3-hydroxy-1-octyne, were selectively hydrogenated to the corresponding olefins in 30 min by using BER (0.25 eq)-$Pd(OAc)_2$ (0.01 eq) in the presence of CsI (0.3 eq) in 95% ethanol at room temperature, and these olefins remained unchanged until 120-180 min (entries 1-3). On the other hand, the semihydrogenation of internal acetylenes was not practical under these conditions; 2-hexyne, for instance, was hydrogenated at a rate of only 25% in 180 min (entry 4). However, the semihydrogenation could be

Table 1. The Semihydrogenation of Representative Acetylenes over Pd Catalyst on BER in the Presence of CsI in 95% Ethanol at Room Temperature

entry	acetylene	method[a]	time (min)	products (%)
1	1-heptyne	A	30 (120)[b]	1-heptene (100)[c]
2	phenyl acetylene	A	30 (180)	styrene (100)
3	3-hydroxy-1-octyne	A	30 (180)	3-hydroxy-1-octene (100) [97][d]
4	2-hexyne	A	180	*cis*-2-hexene (25)
		B	180 (360)	*cis*-2-hexene (100)
5	3-hexyne	B	180 (360)	*cis*-3-hexene (100)
6	1-phenyl-1-propyne	B	180 (360)	*cis*-1-phenyl-1-propene (100)
7	dimethyl acetylenedicarboxylate	B	120 (180)	dimethyl maleate (100) [98]
8	1-hydroxy-1-phenyl-2-octyne	B	180 (360)	*cis*-1-phenyl-1-hydroxy-2-octene (100) [97]
9	3-hydroxy-1-phenyl-1-octyne	B	180 (360)	*cis*-1-phenyl-3-hydroxy-1-octene (100) [98]

[a]Method A : BER (0.25 eq), $Pd(OAc)_2$ (0.01 eq), CsI (0.3 eq), Method B : BER (0.5 eq), $Pd(OAc)_2$ (0.1 eq), CsI (0.3 eq). [b]Time for the 100% olefins remained unchanged. [c]Estimated by Glpc. [d]Isolated yields.

carried out successfully by using 0.1 eq of Pd on 0.5 eq of BER. Internal acetylenes tested, 2-hexyne, 3-hexyne, 1-phenyl-1-propyne, dimethyl acetylenedicarboxylate, 1-hydroxy-1-phenyl-2-octyne, and 3-hydroxy-1-phenyl-1-octyne, were all hydrogenated quantitatively to give the corresponding *cis*-olefins in 120-180 min, and remained unchanged in 180-360 min (entries 4-9). Hydroxy (entries 3, 8 and 9) and ester (entry 7) groups did not affect the selectivity and the rate of hydrogenation.

In conclusion, Pd catalyst on BER in 95% ethanol is excellent for the semihydrogenation of terminal and internal acetylenes in the presence of CsI.

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7. BER was prepared following the procedure reported in *Ref. 5*.

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