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Hydrogenation of alkenes or alkynes using decaborane in methanol

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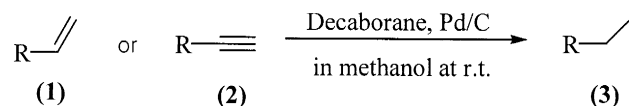
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Abstract

Alkenes and alkynes were reduced to corresponding alkanes in methanol using decaborane (B₁₀H₁₄) in the presence of Pd/C as catalyst under nitrogen in high yields. © 2000 Elsevier Science Ltd. All rights reserved.

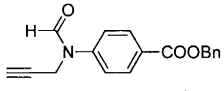
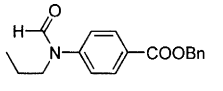
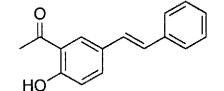
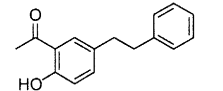
Heterogeneous catalytic transfer hydrogenation has found wide spread use in organic synthesis.¹ Selective, mild and effective reducing agents in transition metal catalyzed transfer hydrogenation have been an area of considerable interest. Some of the hydrogen donors for heterogeneous catalytic transfer hydrogenation have been known to be simple molecules² such as cyclohexene, cyclohexadiene, limonene, hydrazine, formic acid and formates, ammonium formate, phosphinic acid and phosphinates, and propan-2-ol. However, these hydrogen donors suffer from limitations in themselves: requiring reaction long times, yielding mixtures, and being less productive and effective.

It was reported that decaborane (B₁₀H₁₄) was rapidly decomposed in acetone and water to give boric acid and hydrogens.^{3,4} Encouraged by this result and as part of a continuing study of decaborane as reducing agent,⁵ we examined decaborane in heterogeneous catalytic transfer hydrogenation and found that a system of decaborane as hydrogen source and methanol as solvent is excellent for the slow generation of hydrogen. The reaction of alkenes or alkynes with decaborane in methanol in the presence of Pd/C at room temperature under nitrogen gave the corresponding products in high yields (Table 1). The reactions are extremely easy to carry out. The optimization of reaction condition allowed us to decrease the amount of decaborane down to 30 mol% and 10% Pd/C to 20 mol% at room temperature under nitrogen.⁶



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Table 1
Hydrogenation of alkenes and alkynes using decaborane

Entry	Substrate (1) or (2)	Time (h)	Product (3) ^a	Yield ^b (%)
1	Diethyl maleate	0.3	Diethyl succinate	98
2	4-Vinylbenzoic acid	1	4-Ethylbenzoic acid	92
3	4-Methylcinnamic acid	2.5	3-(4-Methylphenyl) propanoic acid	92
4	<i>N</i> -Vinylphthalimide	2.5	<i>N</i> -Ethylphthalimide	94
5	Phenyl crotonate	3	Phenyl butanoate	97
6	1,2-Diphenyl ethylene	8	1,2-Diphenyl ethane	96
7	Diphenyl acetylene	8	1,2-Diphenyl ethane	97
8		1		91
9		36		99

a) All products gave spectra consistent with the assigned structures. b) Isolated yields.

We found some chemoselectivity for this reaction. We observed the chemoselectivity against benzyl protecting group in our hydrogenation condition (entry 8): the selectivity was reported in the presence of amine as poison.⁷ Ketone group of acetophenone was not reduce under our reaction condition (entry 9). The reaction seemed to be relatively fast in the unsaturated hydrocarbon with electron-withdrawing group compared with those with electron-donating groups (Table 1).

We are unsure whether the real hydrogenating agent is hydrogen molecules generated by the decomposition of decaborane followed by absorption onto the palladium catalyst, or whether it is hydride absorbed onto the palladium catalyst from decaborane directly. The detailed study of this reaction and its application to other systems are underway.

In conclusion, we report the hydrogenation of unsaturated hydrocarbons with decaborane in the presence of Pd/C at rt under nitrogen to give the corresponding saturated alkanes in high yields.

Acknowledgements

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6. In a typical experimental procedure, 4-vinylbenzoic acid (100 mg, 0.68 mmol) was stirred with decaborane (25 mg, 0.20 mmol) and 10% Pd/C (20 mg) in methanol (10 ml) at rt under nitrogen for 1 h. After the reaction, acetone and silica gel was added to the reaction solution and stirred for 10 min to remove the remaining decaborane. The solution was concentrated under reduced pressure and was chromatographed on a short silica gel pad using a solution of ethyl acetate and *n*-hexane (1:4) to give a 4-ethylbenzoic acid in high yield (92%).
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