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A Study of Hydroboration of Alkenes and Alkynes with Pinacolborane Catalyzed by Transition Metals

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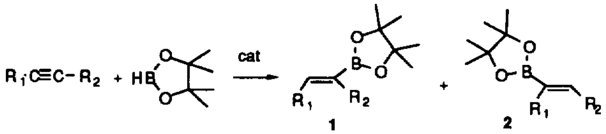
Abstract *Pinacolborane (PBH) is an excellent stoichiometric hydroboration reagent for alkenes and alkynes in the presence of catalytic amounts of transition metals. While Wilkinson's catalyst causes isomerization of internal alkenes, $Rh(CO)(PPh_3)_2Cl$ gives the internal alkyl pinacolboronates in excellent regioselectivity. Rhodium and also nickel are extremely effective catalysts for the hydroboration of alkynes with PBH .*

Since its discovery, transition metal-catalyzed hydroboration has almost exclusively utilized catecholborane(CBH).[2,3] However, many unresolved problems are associated with the use of CBH. At least 1.5 equiv of CBH is required[4] for hydroborations due to intrinsic side reactions such as alkene isomerization, hydrogenation, vinylboronate ester formation[5] and BH_3 addition.[6] Another significant problem is the degradation of CBH under the condition of the reaction.[7] Equally frustrating are the moisture and chromatography instability of the resulting catecholboronates. Thus, an alternative to CBH is highly desirable. As part of our program to develop and investigate new boron/metal systems and reactions, we have recently disclosed that pinacolborane (PBH) is a very effective hydroborating reagent for alkynes in the presence of Cp_2ZrHCl as catalyst.[8] However, while $Cp_2Zr(Cl)H$ is an excellent catalyst for hydroboration of alkynes, it is not compatible with many functional groups. We also recently reported that Wilkinson's catalyst caused isomerization of internal alkenes and provided terminal alkyl pinacolboronates.[9] Pinacolboronates unlike catecholboronates are insensitive to moisture and can be easily chromatographed, making their isolation, purification and analysis a simple affair. In the present study we have expanded the scope of hydroborations with PBH by employing more functionalized alkenes, and we have explored other transition metal catalysts.

Alkynes. Uncatalyzed hydroboration with dioxaborinanes or with PBH requires either elevated temperatures or two equiv of PBH.[10] Transition metal-catalyzed hydroboration of alkynes has not received much attention.[3a] Thus Burgess and coworkers report that the hydroboration of phenylacetylene with CBH catalyzed by rhodium complexes gave rise to a complex mixture of products.[6] We now have found that in the presence of Wilkinson's catalyst, **A**, PBH cleanly hydroborates phenylacetylene to give the regioisomers **1** and **2** in a ratio of 48:52. No other products were obtained (Table 1, entry 4).[11] Changing one phosphine group to a CO ligand ($Rh(CO)(PPh_3)_2Cl$, **B**) profoundly influenced the ratio of regioisomers and gave essentially pure anti-Markovnikov product. Remarkably, also $CpNiPPh_3(Cl)$, **C**, gave almost pure **2** Table 1, entry 6).[12] In general we found that Wilkinson's catalyst gave varying amounts of internal hydroboration, depending on the sterics of the substituents. In itself this is remarkable and suggests that fine tuning of ligands could possibly provide pure Markovnikov products. However, to the case in point, either catalyst **B** or **C** reversed the trend and provided essentially pure terminal alkenyl pinacolboronates in essentially quantitative yields. Unlike catalyzed hydroborations with CBH no other products could be detected by GCMS. One internal alkyne was examined, 3-hexyne. Hydroboration proceeded smoothly to give the internal product (Table 1, entry 15). As was the case with phenylacetylene, 1-trimethylsilyl-1,3-pentadiyne gave a mixture of **1** and **2** with catalyst **A**, but provided the terminal hydroboration product with either **B** or **C**. Reaction times with rhodium based catalysts were shorter than those for nickel.

Table 1. Distribution of Pinacolboronates in the Hydroboration of Alkynes with PBH Catalyzed by Transition Metals for the Reaction[a]:

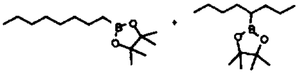
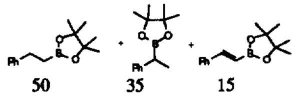
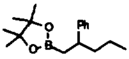
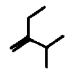
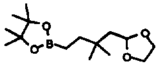
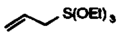
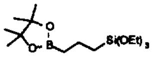
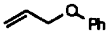
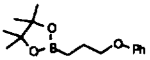
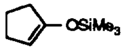
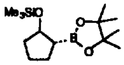
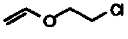
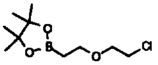
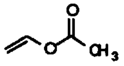
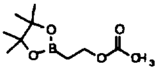
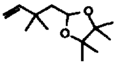
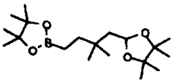
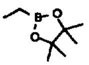
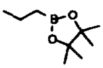


Entry	R_1	R_2	Catalyst[b]	1:2	Yield, % isolated[c]	Entry	R_1	R_2	Catalyst[b]	1:2	Yield, % isolated[c]
1	n-hexyl	H	A	71:29	99	13	t-butyl	H	A	99:1	99
2	n-hexyl	H	B	99:1	99	14	cyclopentyl	H	A	93:7	98
3	n-hexyl	H	C	99:1	98	15	n-propyl-	n-pr	A	--	99
4	phenyl	H	A	48:52	99	16	3-phenylpropyl	H	A	73:27	99
5	phenyl	H	B	98:2	99	17	3-phenylpropyl	H	B	99:1	99
6	phenyl	H	C	98:2	99	18	3-phenylpropyl	H	C	99:1	99
7	3-chloropropyl	H	A	40:60	99	19	-CH2-OCH$_3$	H	A	30:70	99
8	3-chloropropyl	H	B	99:1	99	20	-CH2-OCH$_3$	H	B	99:1	99
9	3-chloropropyl	H	C	99:1	98	21	-CH2-OCH3	H	C	99:1	99
10	isopropyl	H	A	79:21	99	22	$Me_3SiC{=}C\text{-}CH_2$	H	A	59:41	99
11	isopropyl	H	B	99:1	99	23	$Me_3SiC{=}C\text{-}CH_2$	H	B	99:1	99
12	isopropyl	H	C	99:1	98	24	$Me_3SiC{=}C\text{-}CH_2$	H	C	98:1	99

[a] Reaction conditions: 1 equiv PBH, 1 mol% catalyst, 3 h for rhodium or 18 h for nickel, 25 °C, 0.5 M in CH_2Cl_2. [b] A=$Rh(PPh_3)_3Cl$ (Aldrich); B=$Rh(CO)(PPh_3)_2Cl$ (Aldrich) ; C=$NiCpPPh_3Cl$, prepared according to: Yamazaki, H.; Nishido, T.; Matsumoto, Y.; Sumida, S.J.; Hagihara, N. *J. Organomet. Chem.* **1966**, *6*, 86. [c] All compounds are consistent with ^1H, ^{13}C and ^{11}BNMR data.

Alkenes. Much effort has been directed to metal-catalyzed hydroboration of alkenes, primarily in asymmetric synthesis and in stereoselectivity.[3b] We recently reported that $Rh(PPh_3)_3Cl$ catalyzes the hydroboration of alkenes with PBH. But *trans*-4-octene gave the terminal octyl pinacolboronate. Other internal alkenes behaved similarly. However we have now found that either catalyst **B** or **C** provide the internal octyl pinacolboronate in essentially quantitative yield (Table 2, entry 1). Similarly, styrene which provides a mixture of products with catalyst **A**, furnishes almost exclusively the terminal product, without any trace of vinyl boronates.[13,5] In the other cases examined, catalyst **A** cleanly gave the desired products. Of significance is the compatibility of PBH with various enols. Vinyl acetate was cleanly hydroborated to give the stable β-boraethylacetate (Table 2, entry 9). Other enols (Table 2, entries 7-8) were also cleanly hydroborated. No products attributable to *syn* elimination were detected.[14] In particular hydroboration of the chloro enol gave a highly functionalized pinacol boronate (Table 2, entry 8). Allylic ethers placed boron on the terminal carbon exclusively (Table 2 entries 5-6). Hydroboration was also compatible with a hindered acetal (Table 2, entry 10). Vinyl bromides behaved differently. Only the debrominated products were detectable. Since we have already shown that α-bromo pinacolboronates are stable compounds,[15] it would indicate that initial hydroboration occurred β to the bromine atom, followed by a fast *syn* elimination.[16] Hydroboration of the liberated alkene by another equiv of PBH furnished the observed product. The low yields are probably attributable to the volatility of ethylene and propene.

Table 2. Distribution of Pinacolboronates in the Hydroboration of Alkenes with PBH Catalyzed by Transition Metals.[a]

Entry	Alkene	Catalyst	Product Ratio[b]			Yield, %
1	*trans*-4-octene					
		$\mathrm{Rh(PPh_3)_3Cl}$	100	0		92[c]
		$\mathrm{Rh(CO)(PPh_3)_2Cl}$	3	97		94
		$\mathrm{NiCp(PPh_3)Cl}$	1	99		97
2	styrene					
		$\mathrm{Rh(PPh_3)_3Cl}$	50	35	15	99[c]
		$\mathrm{Rh(CO)\ (PPh_3)_2Cl}$	99	1	0	99
		$\mathrm{NiCp(PPh_3)Cl}$	99	1	0	99
3	2-phenyl-1-pentene	$\mathrm{Rh(PPh_3)_3Cl}$				94
4		$\mathrm{Rh(PPh_3)_3Cl}$				99
5		$\mathrm{Rh(PPh_3)_3Cl}$				53
6		$\mathrm{Rh(PPh_3)_3Cl}$				90
7		$\mathrm{Rh(PPh_3)_3Cl}$				63
8		$\mathrm{Rh(PPh_3)_3Cl}$				91
9		$\mathrm{Rh(PPh_3)_3Cl}$				84
10		$\mathrm{Rh(PPh_3)_3Cl}$				97
11	vinyl bromide	$\mathrm{Rh(PPh_3)_3Cl}$				50
12		$\mathrm{Rh(PPh_3)_3Cl}$				50

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[a] For conditions, see footnote to Table 1. [b] All products are consistent with ^{1}H, ^{13}C and ^{11}B NMR data. [c] Reference 9.

In conclusion, we have demonstrated that catalyzed hydroboration of alkenes and alkynes with PBH occurs readily and gives products in essentially quantitative yields. The use of inexpensive nickel is especially interesting since it portends a facile asymmetric reaction with suitable ligands.

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(11) The following procedure for the $Rh(PPh_3)_3Cl$ catalyzed hydroboration of 1-octyne with PBH is typical and also applicable to the catalyzed hydroboration of alkenes: Pinacolborane (0.51 mmol) was added to a solution of $Rh(PPh_3)_3Cl$ (4.6 mg, 0.005 mmol) in CH_2Cl_2 (1.0 mL) at 25 °C. The solution was stirred for 2 min and 1-octyne (0.055 g, 0.50 mmol) was added. The reaction mixture was quenched with water (1 mL), extracted with ether (3 x 1 ml), and dried over Na_2SO_4 (0.5 g). If necessary, isolation of the products was achieved by silica gel chromatography (95:5, hexanes:ether). Yield: 118 mg, 99%. The above procedure is applicable to all rhodium catalysts. With $CpNiPPh_3Cl$ catalyzed hydroborations, the reactions were quenched after 18 h for both alkynes and alkenes.

(12) (a) For hydroboration of imines with copper and silver salts: Baker, R.T.; Calabrese, J.C.; Westccott. *J. Organomet. Chem.* **1995,** *498,* 109. However, nickel has been used in coupling reactions involving boron: (b) Mizojiri, R.; Kobayashi, Y. *J. Chem. Soc. Perkin Trans. 1* **1995,** 2073. (c) Kobayashi, Y.; Mizojiri, R.; Ikeda, E. *Synlett* **1995,** 571. (d) Trost, B.M.; Spagnol, M.D. *J. Chem. Soc. Perkin Trans. 1* **1995,** 2083.

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