Hydroboration of alkenes/alkynes is one of the most versatile reactions available. Most commonly, the resulting alkyl borane intermediates are not isolated, but are used in subsequent reactions for forming a wide range of functional groups.

Most examples that will be shown will involve oxidation to the alcohol.

Many Different Reagents

There are several reagent options available depending on selectivity/reactivity concerns. Generally, boranes (B–H compounds) can be prepared easily from inexpensive reagents. Many are air and moisture sensitive. Most are prepared by initial hydroboration of a different olefin with borane (BH₃).

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**Some Commonly used hydroborating agents**

- BH₃·SMe₂ (BMS, air stable, neat liquid, ~10 M)
- diisoamylborane (Sia₂BH)
- thexylborane (Thx₂BH)
- 9-borabicyclo-[3.3.1]nonane (9-BBN)
- pinacolborane (PinBH)
- catecholborane (CatBH)
- di(isopropylprenyl)borane (iPP₂BH)

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The addition of the first two alkyl groups is usually rapid. The addition of the third alkyl group is slower and quite dependent on the substitution pattern of the olefin.
Stereoselectivity With Acyclic Olefins

Hydroboration involves a four-membered transition state with syn-addition across the alkene/alkyne. Conversion of C–BR₂ into C–OH is stereospecific with retention of configuration. The boron usually ends up on the less substituted end of the olefin.

*trisubstituted olefins* – similar argument can be made for disubstituted, but regioselectivity now becomes important.

- **potential A¹,² interactions**
- **preferred**
- **potential A¹,³ interactions**

interaction of RM with boron ligands overrules any A¹,²

* but with BH₃, A¹,² will win out
Asymmetric Hydroboration

Asymmetric hydroborations were among the first examples of non-enzymatic transformations to proceed with high enantiomeric excess (J. Am. Chem. Soc. 1961, 83, 486).

Several reagents have been developed, but those derived from α-pinene (Brown) are still the most widely used.

**diisopinocamphenylborane** – sterically demanding reagent, reacts with unhindered alkenes

\[
\text{BH}_3\cdot\text{SMe}_2 \rightarrow \text{MeBH}_2 \quad \text{THF, rt, 16 h crystallize} \\
\text{Me} \quad \text{Me} \\
(+)-\alpha\text{-pinene (excess)} \quad > 99\% \text{ ee} \\
91\% \text{ ee} \\

\text{(note change in rotation)} \\
\text{solid, can be stored at 0 °C under N}_2
\]

\[
\text{J. Org. Chem. 1982, 47, 5065}
\]

**monoisopinocamphenylborane** – unhindered reagent, reacts with all classes of alkenes

\[
\begin{align*}
\text{Me} & \quad \text{BH}_3\cdot\text{SMe}_2 \rightarrow \text{MeBH}_2 \\
\text{Me} & \quad \text{Me} \quad \text{Me} \\
(+)-\alpha\text{-pinene (1 equiv)} & \quad (+)-\text{lpcBH}_2 \\
\text{THF, rt, 96 h} & \quad \text{THF} \\
4.5\% & \quad 91\% \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{BH}_3\cdot\text{SMe}_2 \\
\text{Me} & \quad \text{Me} \quad \text{Me} \\
\text{MeBH}_2 & \quad \text{MeBH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \quad \text{BH}_3\cdot\text{SMe}_2 \\
\text{Me} & \quad \text{Me} \quad \text{Me} \\
(+)-\text{lpcBH}_2 & \quad \text{MeBH}_2 \\
\text{THF} & \quad \text{THF} \\
4.5\% & \quad 91\% \\
\end{align*}
\]
Asymmetric Hydroboration

(-)-Ipc₂BH – 1,2-cis-olefins give high selectivity, others react slowly
(+)-IpcBH₂ – 1,2-trans- and trisubstituted olefins give high to moderate selectivity
1,1-disubstituted olefins are still troublesome, with no general reagent available

Conversion to Other Organoboron Compounds

Boronic acids, boronic esters, and organotrifluoroborates are useful intermediates for cross-coupling and other reactions. Their preparation from alkenes is complicated by needing to perform a monohydroboration with BH$_3$. Snieckus and co-workers reported a nice solution to this problem.

$$\text{RMg or RLi} \rightarrow \text{B(OMe)$_3$} \rightarrow \text{BH}_2 \text{H}_2\text{O} \rightarrow \text{boronic acids} \rightarrow \text{ROH} \rightarrow \text{boronic esters}$$

$$\text{R-BH}_2 \rightarrow \text{B(OR)$_2$} \rightarrow \text{potassium trifluoroborates}$$

$$\text{BH}_3$$

$$\text{iPP}_2\text{BH}$$

(similar steric demand & reactivity to Sia$_2\text{BH}$)

$$2.2\text{–}2.5\text{ equiv}$$ (inexpensive)

$$\text{R} = \text{alkene or alkyne}$$

$$\text{aq. CH}_2\text{O}$$

$$\text{allylation of CHO}$$

$$\text{R-B(OR)$_2$}$$

$$\text{R-B(OH)$_2$}$$

$$\text{R-BF}_3\text{K}$$