CHEM 203

Topics Discussed on Oct. 14

Hydroboration reaction: the addition of a B–H bond across the π system of an alkene

Alkylboranes or organoboranes: compounds containing a C–B bond

Rich chemistry and technological importance of alkylboranes

Lewis acidic character of the B atom in an alkylborane and possible formation of mono, di-, trialkylboranes through multiple cycles of the above reaction, until all B-H bonds have reacted

E.g., with ethylene:

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH}_2 \\
\text{H} &\text{B} \\
\text{H} &\text{H}
\end{align*}
\]

\[
\text{CH}_3\text{CH}_2\text{B} \quad \rightarrow \quad \text{repeat}
\]

\[
\begin{align*}
\text{monoethylborane:} & \quad \text{a monoalkyl borane} \\
\text{diethyl borane:} & \quad \text{a dialkyl borane}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{B} &\text{CH}_2\text{CH}_3 \\
\text{ox. st. } &\text{ }-1
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{B} &\text{CH}_2\text{CH}_3 \\
\text{ox. st. } &\text{ }-2
\end{align*}
\]

Important reaction of alkylboranes: oxidation of the C–B bond with H\textsubscript{2}O\textsubscript{2} / aq. NaOH leading to the formation of alcohols

\[
\begin{align*}
\text{H}_3\text{C} &= \text{CH}_2 \\
\text{B} &\text{R}
\end{align*}
\]

ox. st. = –3

\[
\begin{align*}
\text{HO} &\text{O} \\
\text{HO} &\text{OH}
\end{align*}
\]

ox. st. = –1

\[
\begin{align*}
\text{HO} &\text{H} \\
\text{HO} &\text{O} \text{OH}
\end{align*}
\]

ox. st. = –2

\[
\begin{align*}
\text{HO} &\text{OH}
\end{align*}
\]

(aq. NaOH)

Description of the overall process shown above as the hydroboration / oxidation of alkenes

General mechanism of the oxidation of boranes with H\textsubscript{2}O\textsubscript{2} / NaOH (aq.)

\[\text{HO}^{-} \rightarrow \text{HO} \rightarrow \text{HO}^{-} \quad \text{oxidation state of peroxy O's } = -1\]

Then . . .

\* deprotonation of H\textsubscript{2}O\textsubscript{2} and formation of the hydroperoxy anion:

\[
\begin{align*}
\text{HO}^{-} &\rightarrow \text{HO}^{-} \\
pK_a &\approx 12 \\
\text{H} &\text{O} \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{HO} &\text{H} \\
pK_a &\approx 16 \\
\text{HO} &\text{OH}
\end{align*}
\]

hydroperoxy anion

\* significant nucleophilicity of the hydroperoxy anion and facile addition thereof to the B atom of an organoborane
The oxygen atoms in the peroxy linkage "want" electrons, because they strive to attain the oxidation state of \(-2\). Additional electrons can be accommodated into the O–O \(\sigma^*\) orbital.

Hyperconjugative interactions between the C–B \(\sigma\) bond and the O–O \(\sigma^*\) orbital begin to weaken the O–O \(\sigma\) bond and the terminal OH group begins to depart by taking the pair of electrons connecting it to the internal O atom (i.e., the O–O \(\sigma\) electrons) with it.

The departure of the OH group as HO\(^-\) would leave a highly unfavorable (+) charge on the O atom attached to B. An alkyl group migration occurring in concert with OH departure avoids formation of a highly energetic "O". Both O atoms thus reach the more favorable oxidation state of \(-2\).

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**note**: the alkylborane can certainly combine with OH\(^-\) or with water, both of which are Lewis basic and nucleophilic:

- B still has a vacant p-type orbital
- A 1,2-shift similar to the one seen in carbocation rearrangement

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**however**, such events are non-productive, in the sense that they promote no further reaction. Then, the resulting complexes A and B will simply equilibrate back with the staring alkylborane. Only when HOO\(^-\) connects to the B atom will the complex undergo further chemical change (oxidation to an alcohol, as seen above)
Regiochemical course of the hydroboration reaction of unsymmetrical olefins: the H atom of the H–B bond connects to the more highly substituted C atom of the alkene; the B atom, to the less highly substituted C:

![Reaction Diagram]

as the interaction between the B atom and the \( \pi \) system becomes stronger, the more highly substituted C atom acquires a greater fraction of positive charge (better hyperconjugative stabilization). Consequently, it is the more highly substituted, more positive C atom that captures the (formal) hydride from BH\(_3\).

Interesting consequence of the hydroboration / oxidation of unsymmetrical olefins: formation of "anti-Markownikov" alcohols. E.g.:

![Reaction Diagram 2]

WHEREAS

The hydroboration – oxidation process as a net "anti-Markownikov" addition of water to an alkene (i.e. the regioselectivity is opposite that of an acid-catalyzed hydration reaction)

Absence of rearrangements in the hydroboration reaction (no carbocation intermediates are formed); e.g.:
Stereochemical aspects of the hydroboration/oxidation reaction: the question of *syn* vs. *anti* addition of BH₃ to an alkene

e.g., with a more complex olefin such as 1-methylcyclohexene:

The hydroboration reaction as a strictly *syn* addition: B and H atoms must necessarily add from the same face of the π system.

Stereochemical aspects of the oxidation of alkylboranes to alcohols with H₂O₂ / aq. NaOH

The oxidation of boranes is a substitution reaction

General pattern of a substitution reaction (no mechanism implied):

\[ C\text{--}X + Y \rightarrow C\text{--}Y + X \]

Possible stereochemical outcomes of a generic substitution reaction:

**retention** of configuration: the substituting group, Y, enters with the same orientation as the departing group, X:

\[
\begin{align*}
\text{R}^1 & \quad \text{--} \quad \text{X} \\
\text{R}^2 & \quad \text{--} \quad \text{Y} \\
\text{R}^3 & \quad \text{--} \quad \text{X}
\end{align*}
\]

product resulting through **retention of configuration**

**inversion** of configuration: the substituting group, Y, enters with the opposite orientation relative to the departing group, X:

\[
\begin{align*}
\text{R}^1 & \quad \text{--} \quad \text{X} \\
\text{R}^2 & \quad \text{--} \quad \text{Y} \\
\text{R}^3 & \quad \text{--} \quad \text{X}
\end{align*}
\]

product resulting through **inversion of configuration**
loss of configuration: the substituting group, Y, enters partly with the same orientation and partly with the opposite orientation relative to the departing group, X

Strict retention of configuration observed during the oxidation of boranes, as a result of mechanistic constraints:

The hydroboration – oxidation process as a net "anti-Markownikov" syn addition of water to an alkene (i.e. the regioselectivity is opposite that of an acid-catalyzed hydration reaction)