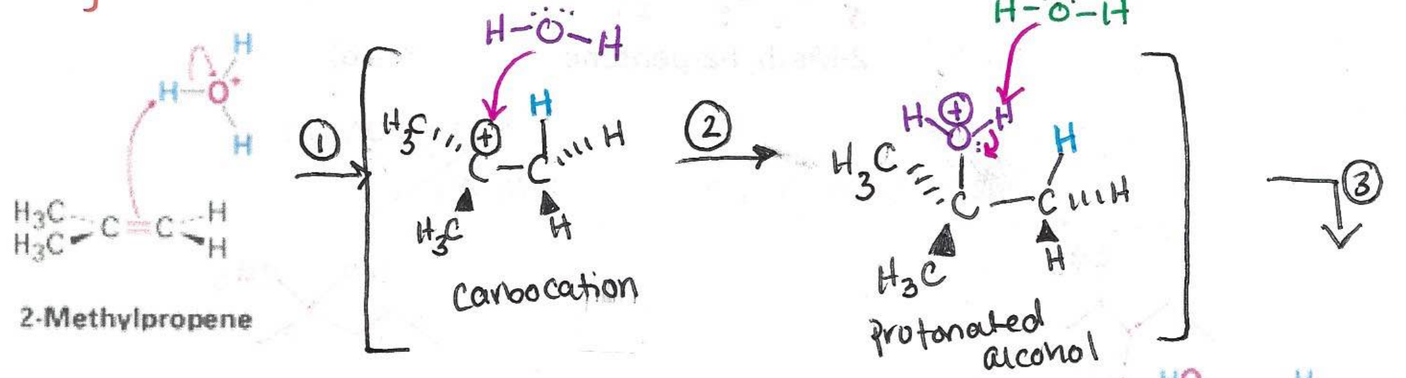
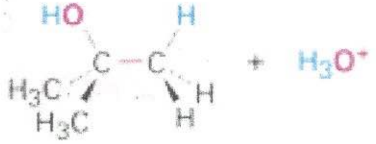
11/7/17

Review of Alcohol Reactions
Chapter 17

Hydration of Alkenes

↳ adding water to alkenes to yield alcohols





2-Methyl-2-propanol

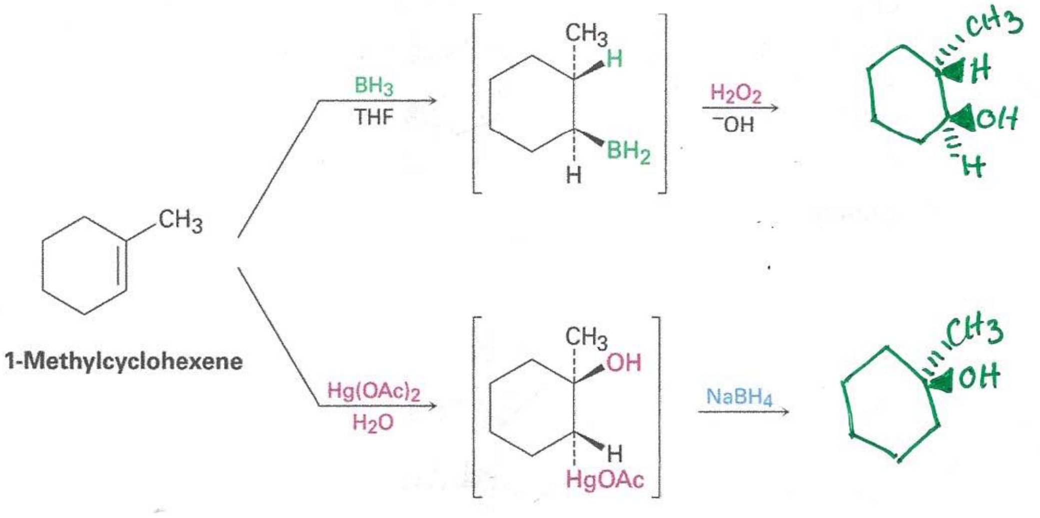
① a hydrogen atom on the electrophile H_3O^+ is attacked by π electrons from the nucleophilic double bond, leaving the carbon atom w/ a positive ⊕ charge

② nucleophilic water donates an electron pair to the positive charged atom forming a C-O bond and leaving a ⊕ charge on the protonated alcohol

③ water acts as a base to remove H^+, regenerating the H_3O^+ and neutral alcohol product

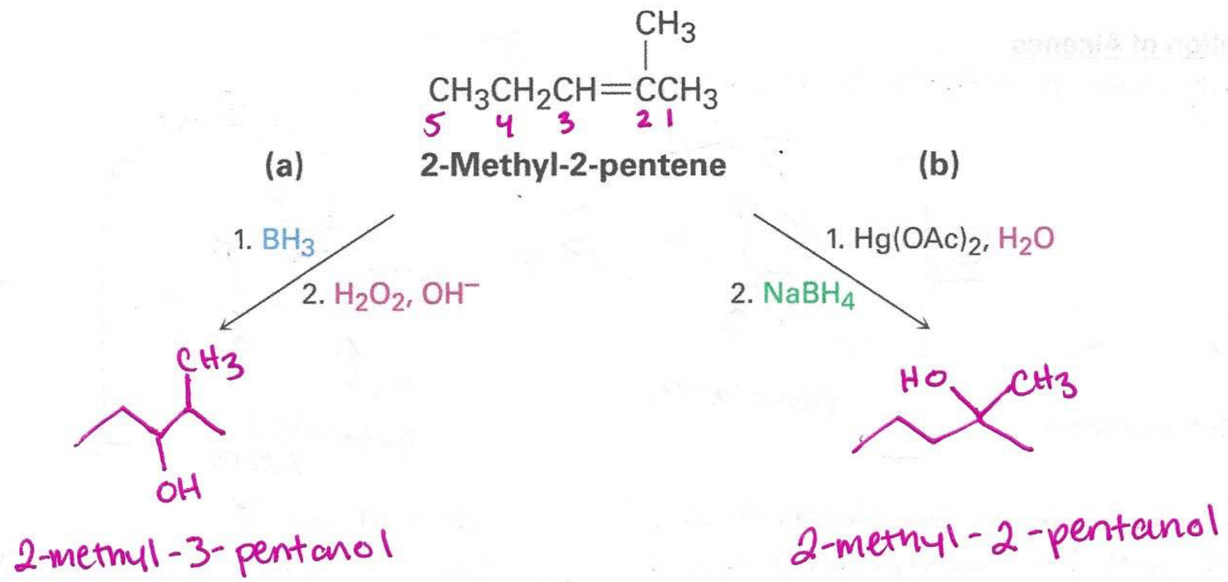
Hydroboration Oxidation yields the (syn) non-markovnikov hydration product

"syn" = adding to the same side of the previous alkene



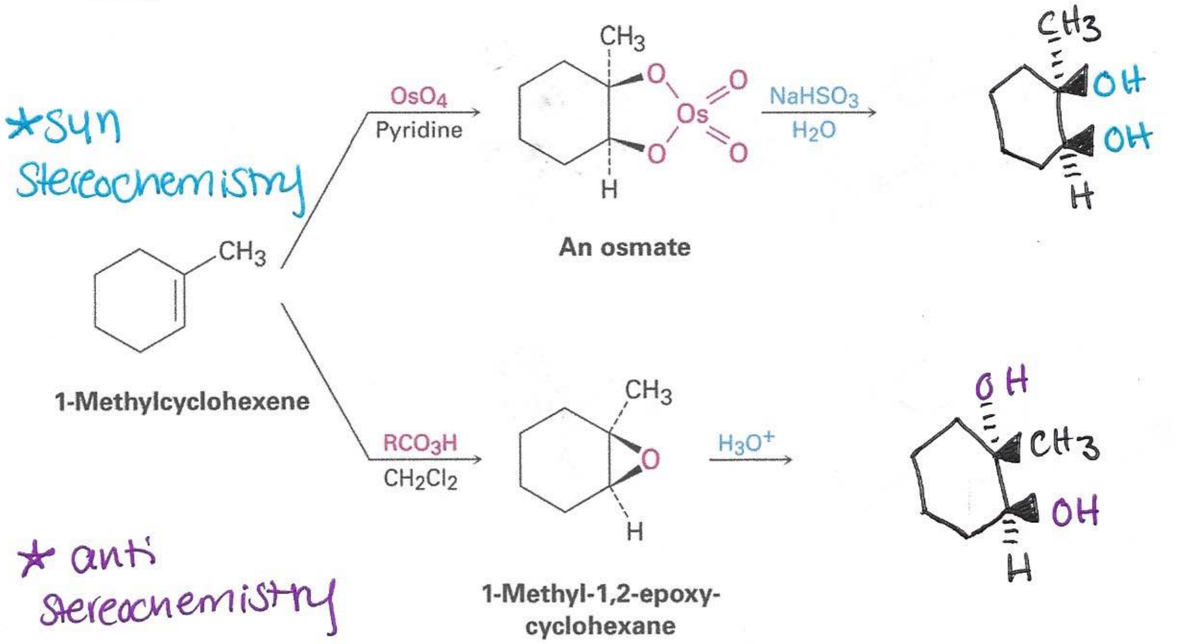
Oxymercuration - demercuration yields the markovnikov hydration product

What products would you obtain from the reaction below?



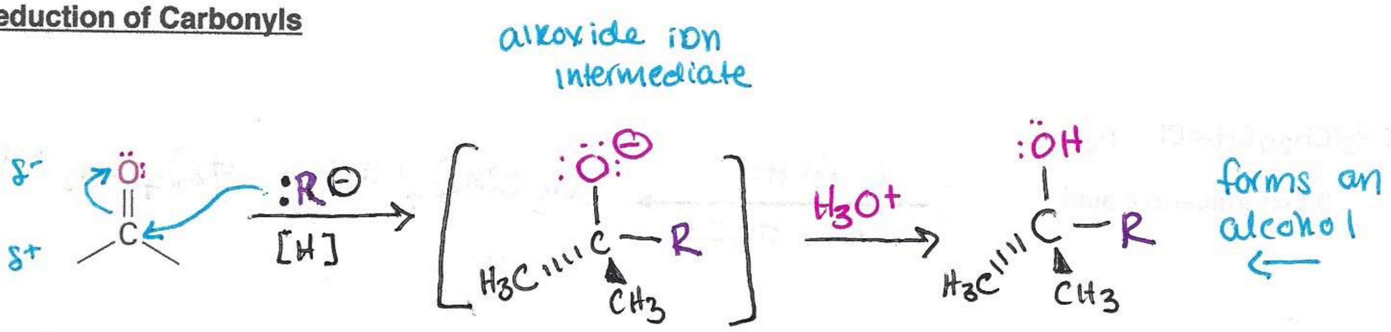
Preparation of 1,2-Diols

Hydrolation of alkenes w/ osimium tetroxide (w/ Reduction of sodium bisulfite) yields the cis 1,2-diol

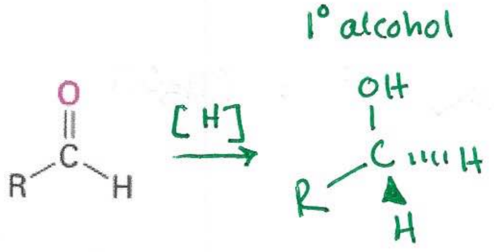


Acid Catalyzed hydrolysis of epoxides yields the trans 1,2-diol

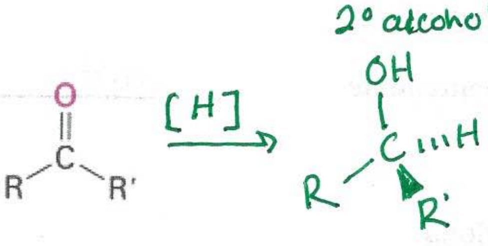
Reduction of Carbonyls



A carbonyl compound



An aldehyde



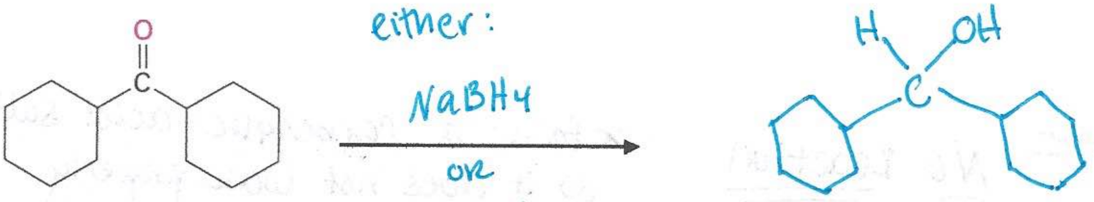
A ketone

Sodium Borohydride ($NaBH_4$) is a safe and common reduction reagent that reduces aldehydes

& ketones

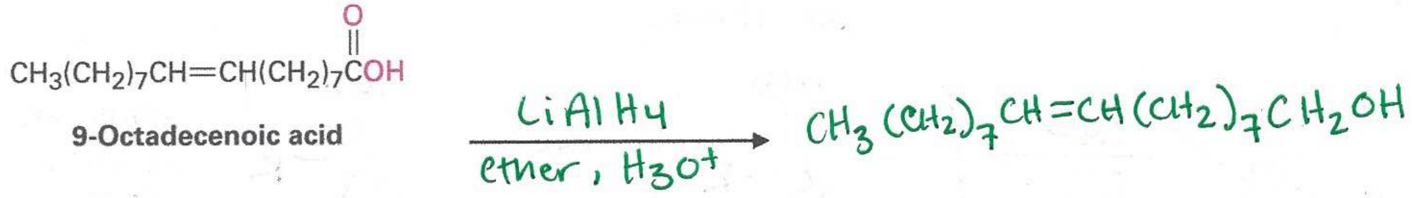
Lithium Aluminum Hydride ($LiAlH_4$) is a powerful & less specific reagent that reduces aldehydes

ketones, carboxylic acids & esters



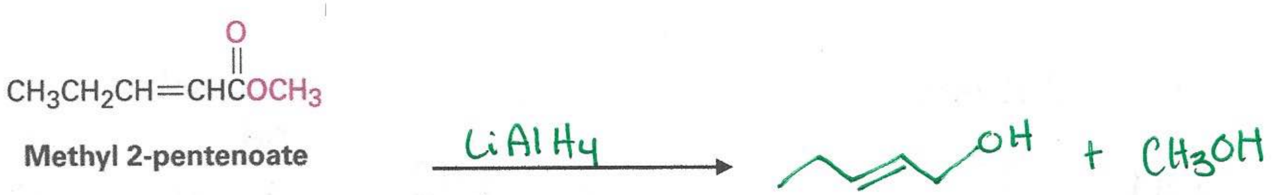
Dicyclohexyl ketone

(both will work w/ ketone)



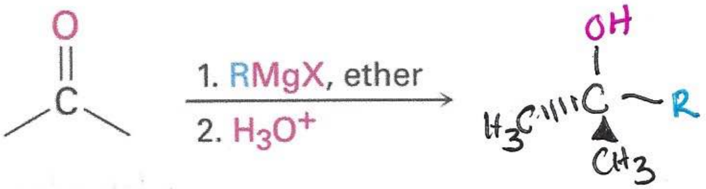
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{\overset{\displaystyle O}{\|}}{C}OH \xrightarrow[\text{ether, } H_3O^+]{LiAlH_4} CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$$

9-Octadecenoic acid

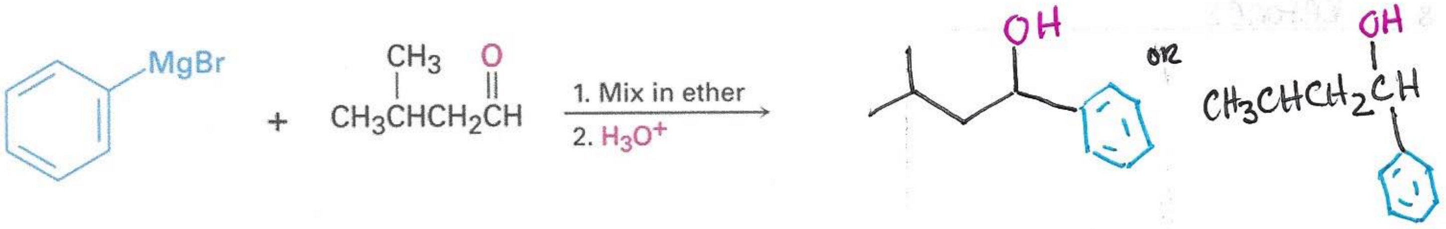


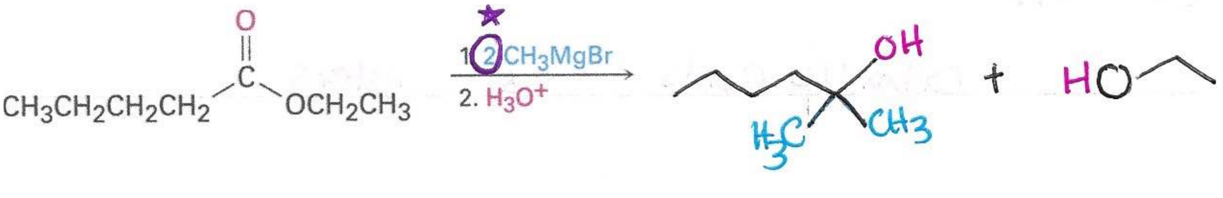
Methyl 2-pentenoate

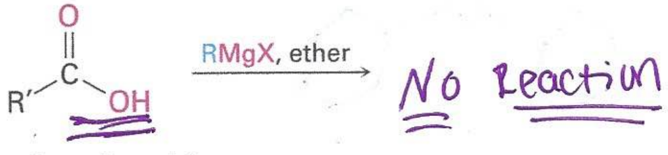
Grignard Reactions



* Grignard reagents react w/ carbonyl compounds to yield alcohols

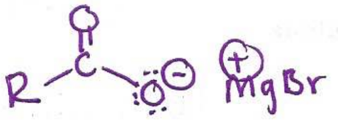




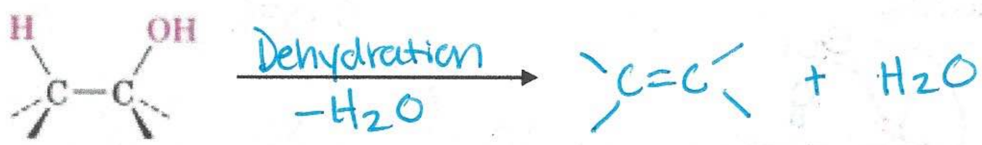


A carboxylic acid

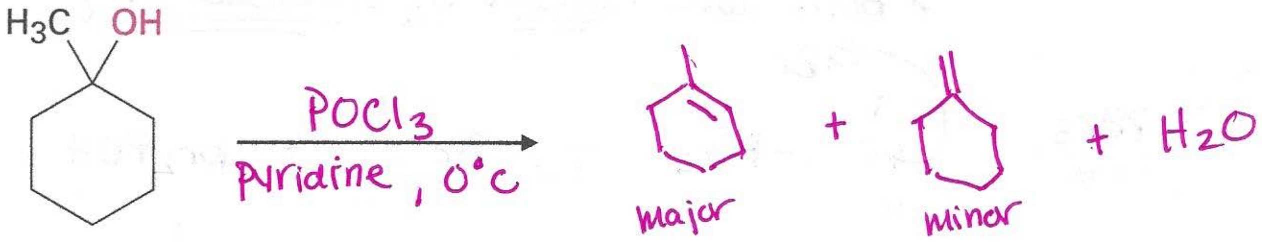
* forms a carboxylic acid salt so it does not work properly



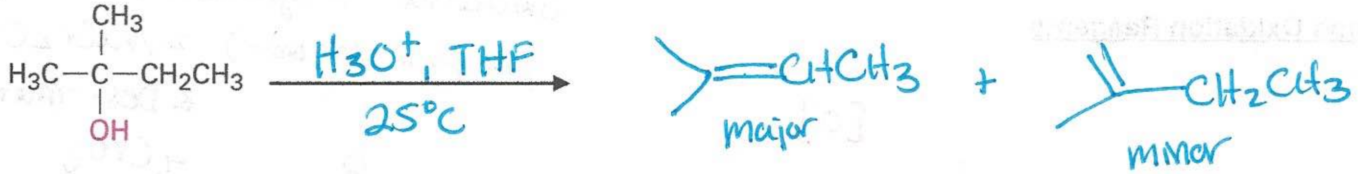
Dehydration Reactions



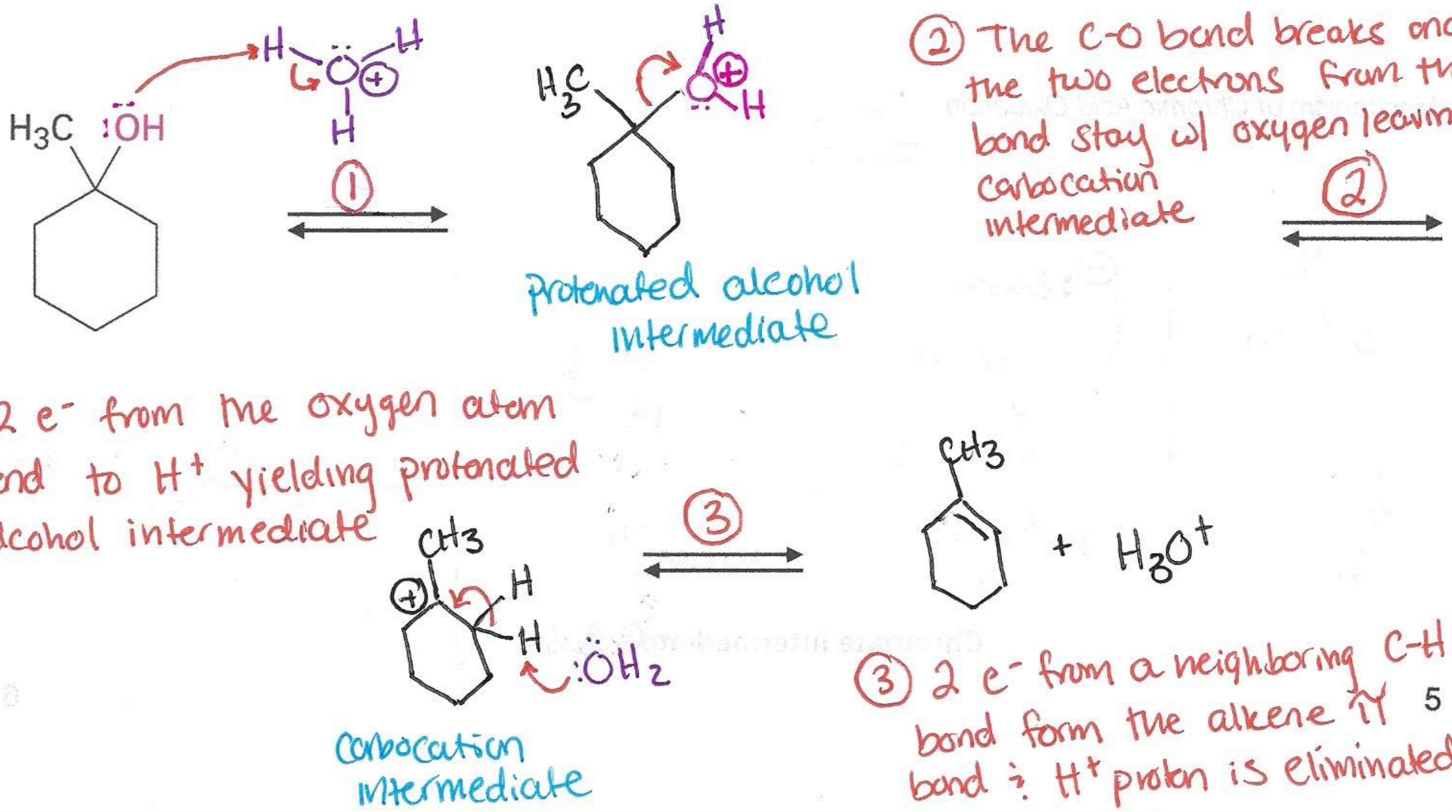
Dehydration with Phosphorous Oxychloride (phosphoryl chloride)



Acid Catalyzed Dehydration



Mechanism of Acid Catalyzed Dehydration

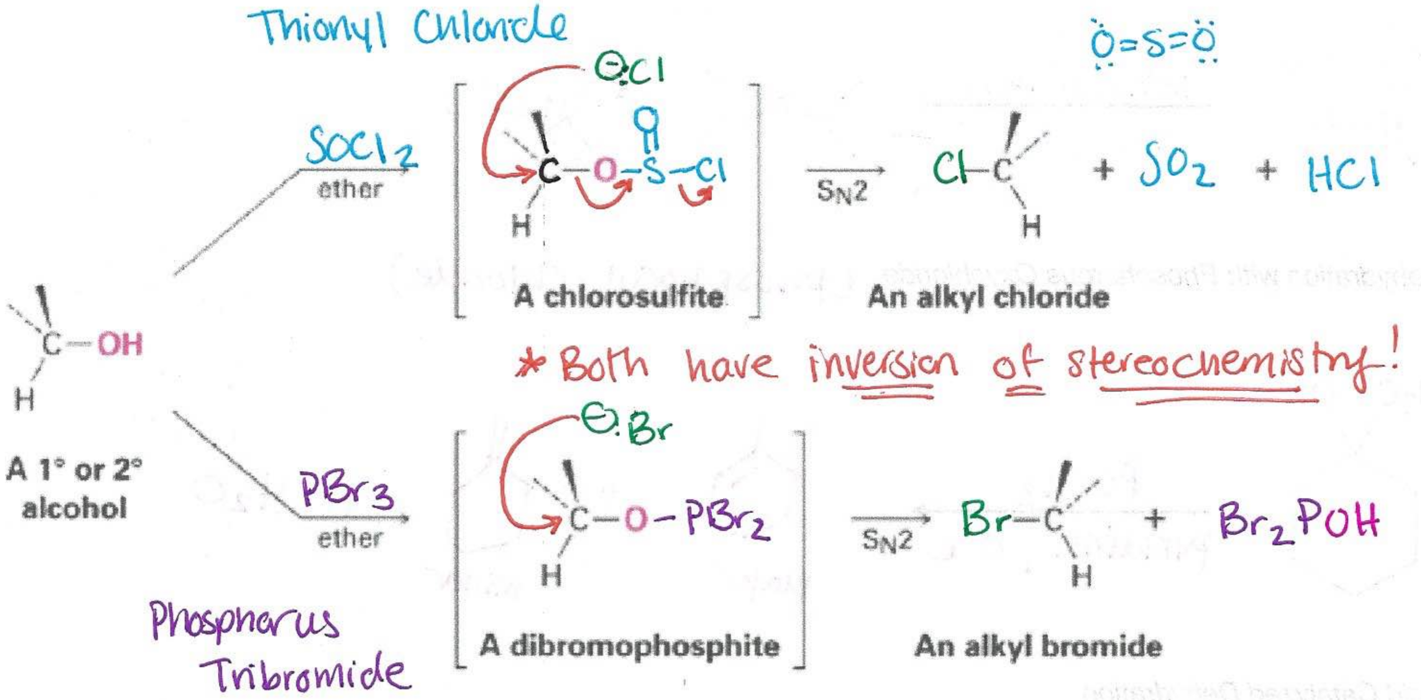


① 2 e⁻ from the oxygen atom bond to H⁺ yielding protonated alcohol intermediate

② The C-O bond breaks and the two electrons from the bond stay w/ oxygen leaving a carbocation intermediate

③ 2 e⁻ from a neighboring C-H bond form the alkene π bond ÷ H⁺ proton is eliminated

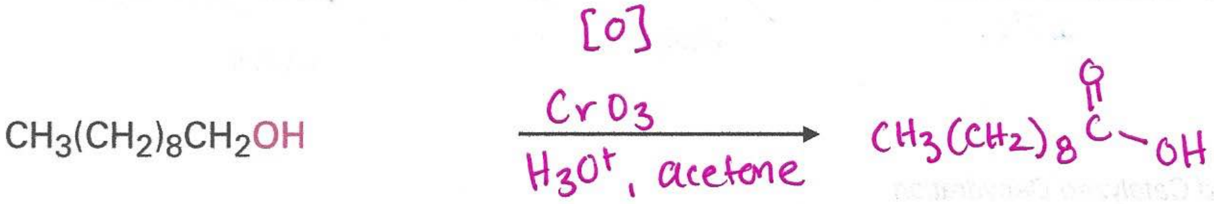
Conversion of Alcohols into Alkyl Halides



* Both have inversion of stereochemistry!

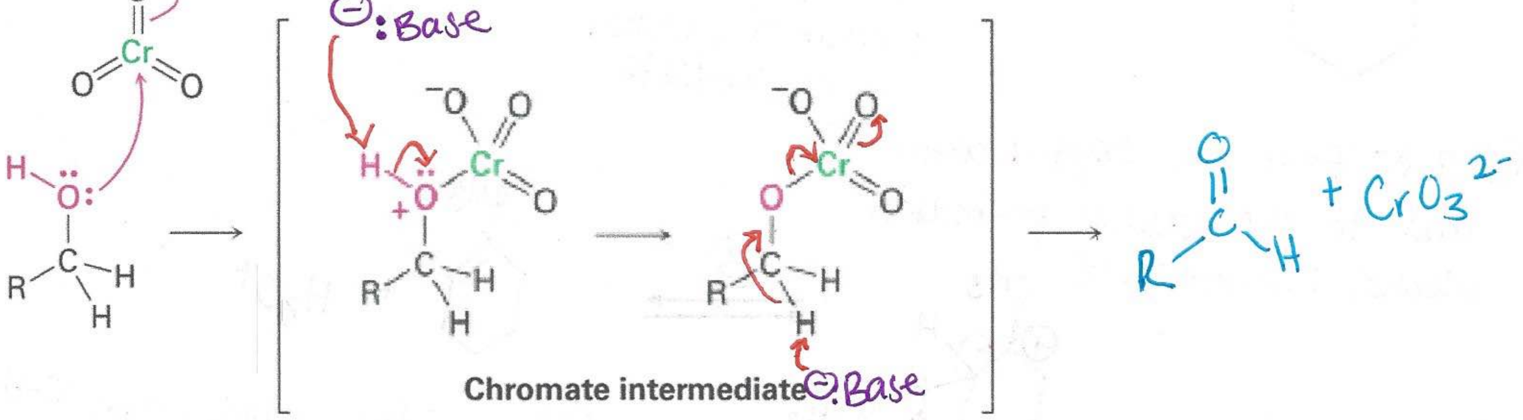
Common Oxidation Reagents

oxidation reagents: 1. $KMnO_4$
(no particular order) 2. $NaCr_2O_7$
3. Dess-Martin
4. CrO_3



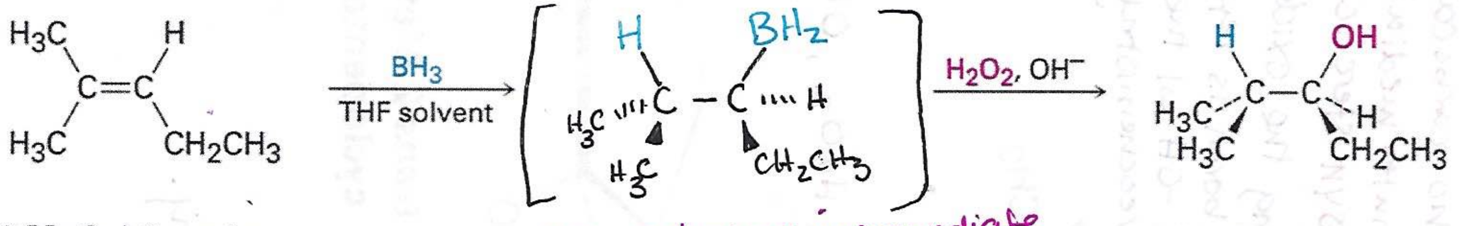
$$CH_3(CH_2)_8CH_2OH \xrightarrow[H_3O^+,\ acetone]{[O]\ \ CrO_3} CH_3(CH_2)_8COOH$$

Mechanism of Chromic Acid Oxidation CrO_3



Hydroboration Oxidation

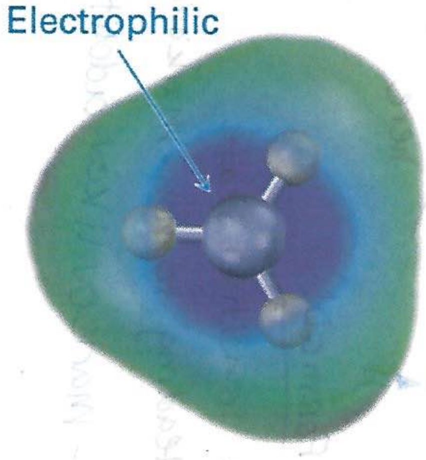
Addition of a B-H bond of borane (BH_3) to an alkene to yield an organoborane intermediate, RBH_2. Oxidation of the organoborane by reaction w/ basic hydrogen peroxide, H_2O_2, then creates the alcohol.

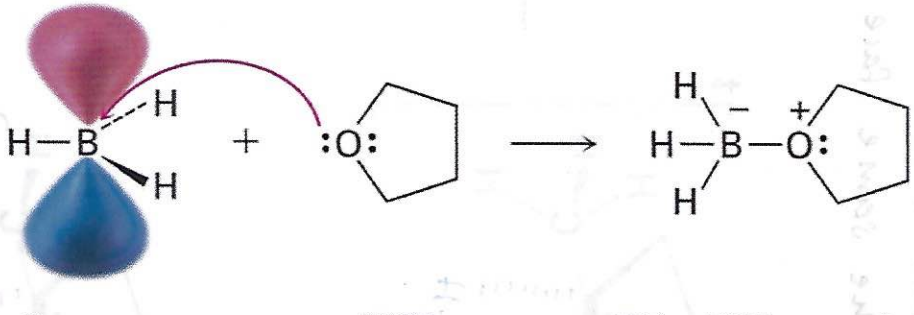


2-Methyl-2-pentene organoborane intermediate **2-Methyl-3-pentanol**

Borane is a very reactive Lewis acid because the boron atom only has 6 electrons in its valence shell. In tetrahydrofuran solution, BH_3 accepts an electron pair from a solvent molecule in a Lewis acid-base reaction to complete its octet and form a stable BH_3 − THF complex

Page 231 in textbook

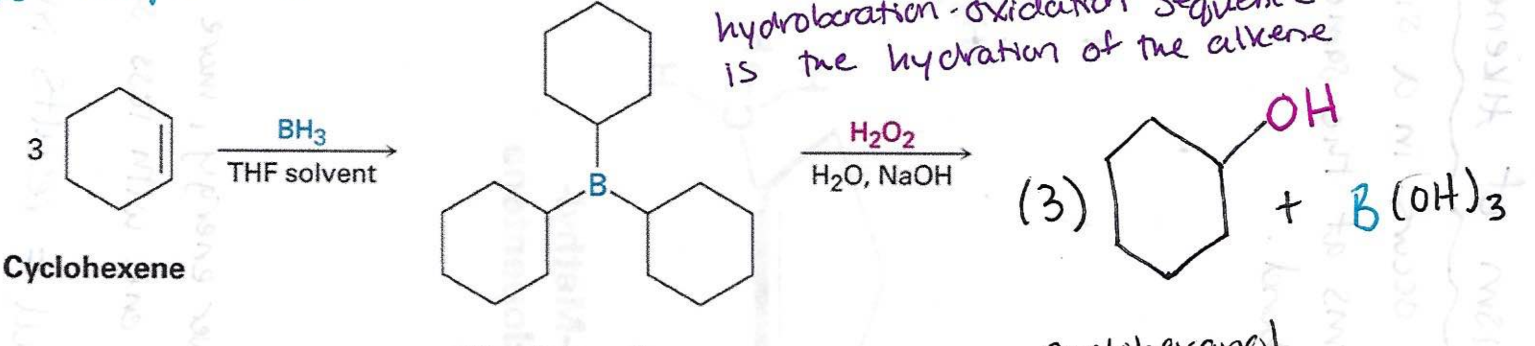




Borane **THF** **BH_3–THF complex**

When an alkene reacts w/ BH_3 in THF solution, rapid addition to the double bond occurs 3 times and a trialkyl borane, R_3B is formed. For example 1 molar equivalents of BH_3 adds to 3 molar equivialents of cyclohexene to yield tricyclohexylborane

The net effect of the 2 step hydroboration-oxidation sequence is the hydration of the alkene



Cyclohexene

Tricyclohexylborane

Cyclohexanol

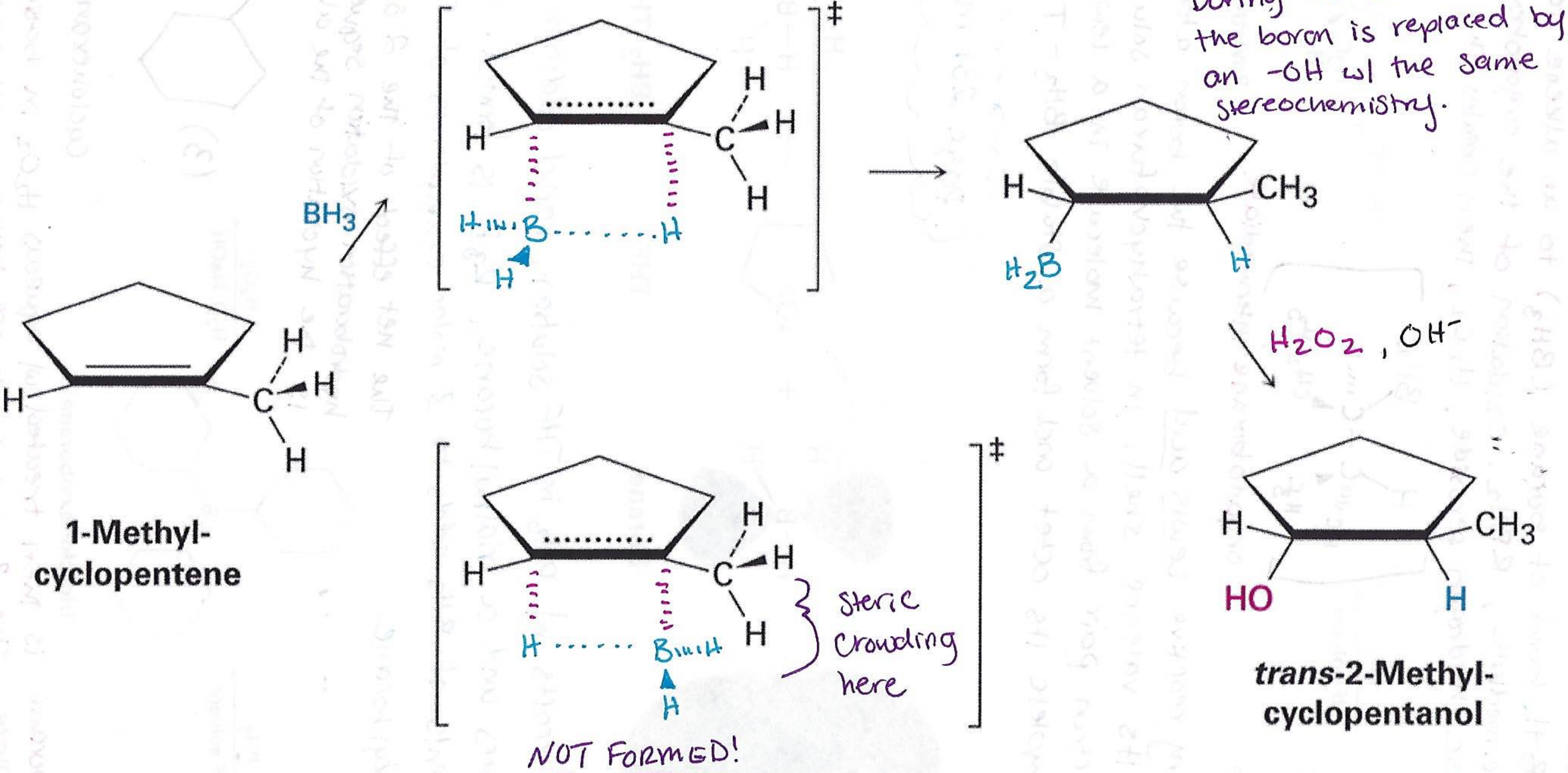
when tricyclohexylborane is then treated w/ aqueous H_2O_2 in basic solution, an oxidation takes place. The 3 C-B bonds are broken, -OH groups bond to the 3 carbons & 3 equiv. of cyclohexanol are produced.

Mechanism of Alkene hydroboration (page 232 in textbook)

Reaction occurs in a single step in which the C-H and C-B bond forms at the same time and on the same face of the double bond.

- ★ single step
- ★ no carbocation intermediate
- ★ syn stereochemistry

During the oxidation step the boron is replaced by an -OH w/ the same stereochemistry.



1-Methylcyclopentene

***trans*-2-Methylcyclopentanol**

The lower energy, more rapidly formed transition state is the one with less steric crowding, leading to non-markovnikov regiochemistry.

overall = results in a syn non-markovnikov addition of water!