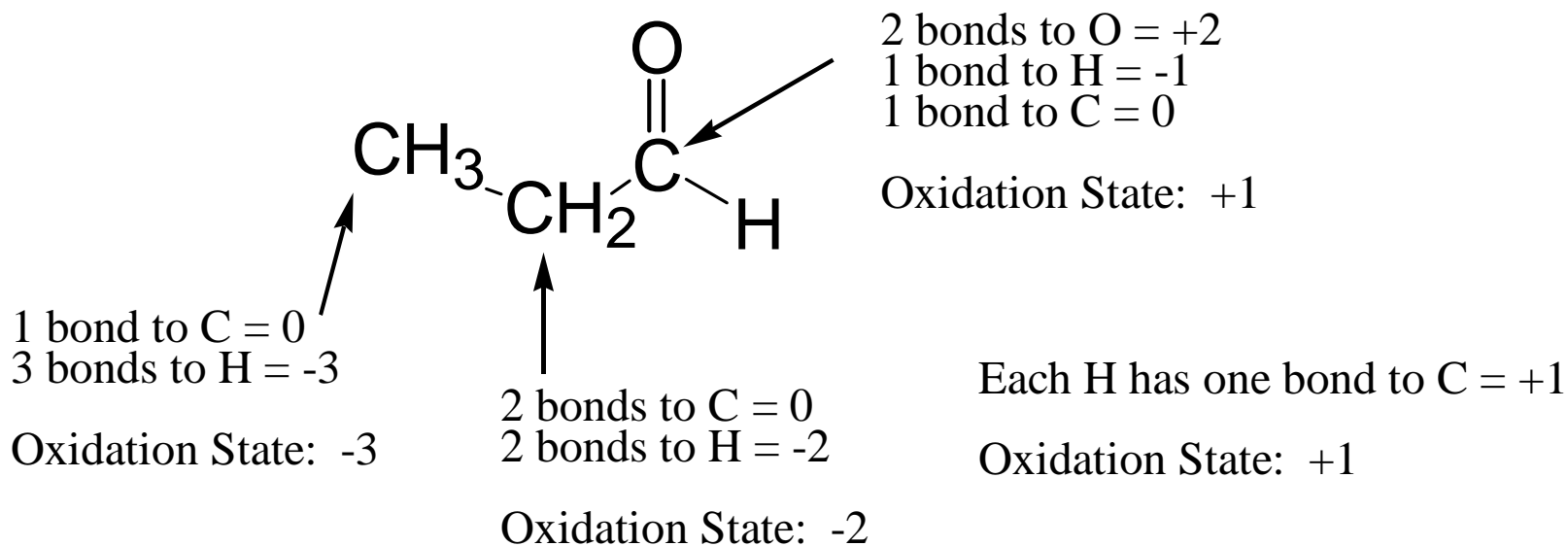


Oxidation/Reduction Reactions

Oxidation States

- Carbon oxidation states are assigned on the basis of the electronegativity of attached atoms
 - For each bond to a more electronegative atom give +1
 - For each bond to a less electronegative atom give -1
 - For each bond to carbon give 0



Carbon Reduction Reactions

1. Alkyl halides \rightarrow alkanes
2. Alkyl halides \rightarrow organometallics
3. Alkenes \rightarrow alkanes
4. Alkynes \rightarrow alkenes
5. Alkynes \rightarrow alkanes
6. Carbonyls \rightarrow alcohols

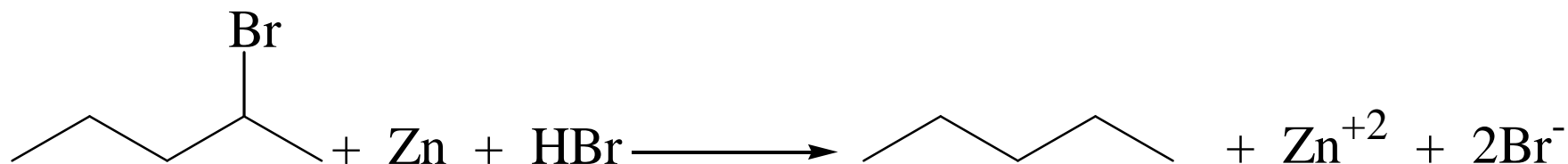
Carbon Oxidation Reactions

7. Alkenes \rightarrow diols
8. Alkenes \rightarrow carbonyls
9. Alkenes \rightarrow dihalides
10. Alkenes \rightarrow alcohols
11. Alkenes \rightarrow epoxides
12. Alcohols \rightarrow carbonyls

Problem

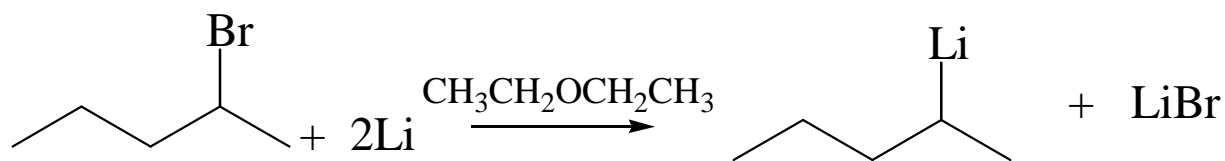
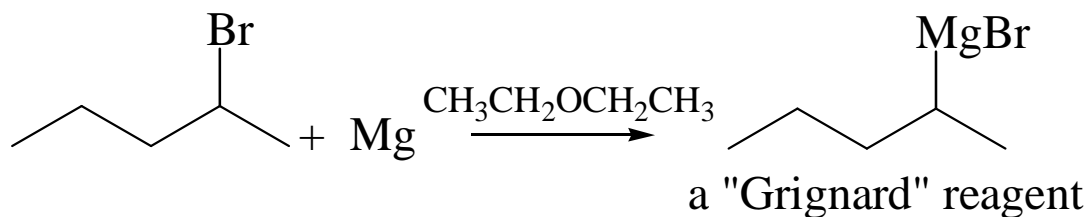
- Demonstrate why your assigned reaction involves either oxidation or reduction at carbon – you may want to draw a specific example of reaction that is described generically by functional group
- Decide if another reaction category (based on net result) also applies to your reaction

Reduction of Alkyl Halides - I

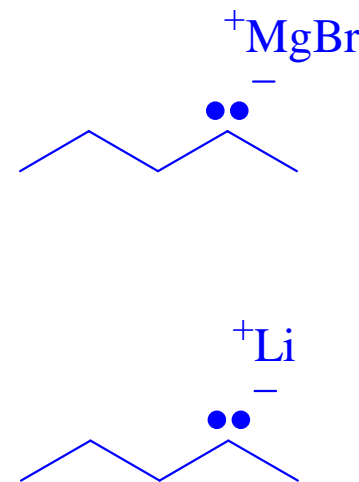


- Zn is a reducing agent because it has two valence electrons that can easily be lost to provide a more stable electron configuration
- The carbon attached to bromine is in the zero oxidation state (and most reducible), while other carbons in the alkyl halide are either -2 or -3 (and less reducible)
- An intermediate organometallic ($\text{R-Zn}^{+2}\text{Br}^-$) is thought to be formed during the reaction

Reduction of Alkyl Halides - II

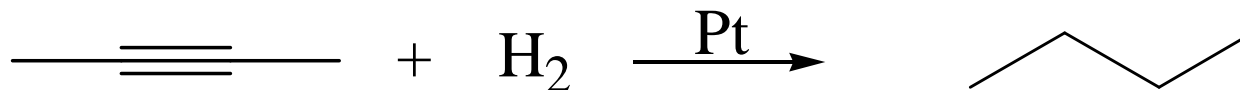


These act like:



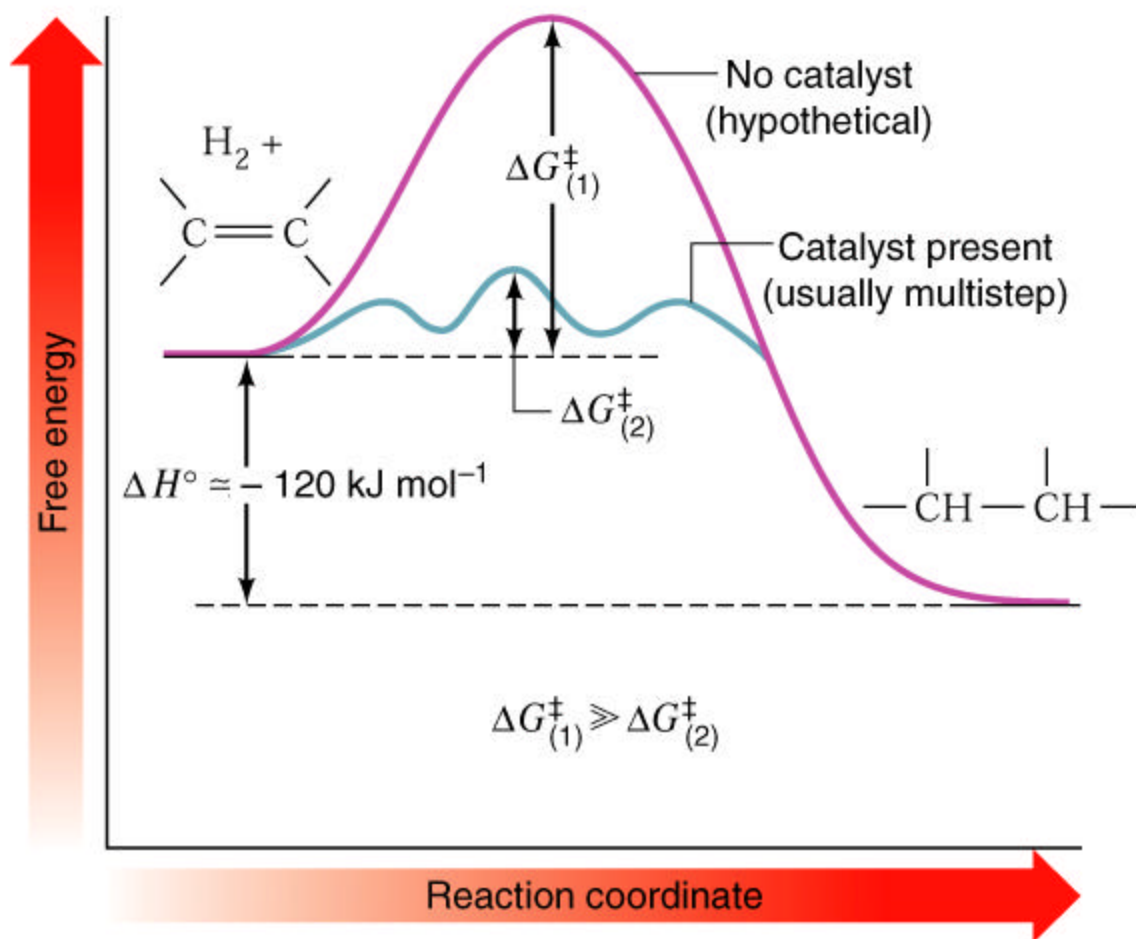
- Nucleophilic carbon atoms are extremely useful in substitution reactions that produce more complex carbon skeletons
- Reactions of alkyl halides with metals are therefore often NOT followed by treatment with acid (as in the previous example) to produce the alkane

Reduction of Alkenes and Alkynes



- Alkenes and alkynes can be reduced to alkanes
- A source of hydrogen atoms is required
- A catalyst is required (since neither alkenes nor alkynes are sufficiently polar to provide good ‘handles’ for reactions to start)
 - Pt, Ni, Pd and many other solid metals can catalyze this reaction

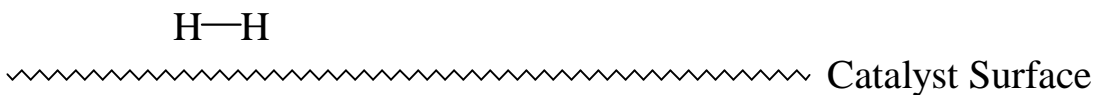
Catalyst Function



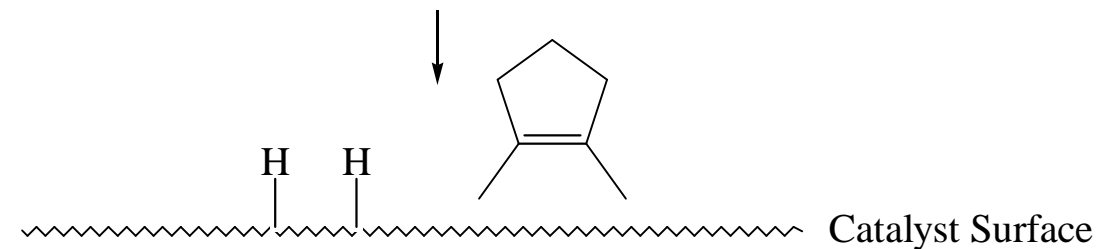
Catalysts increase reaction **RATES** and thus must lower the activation energy – this does not change the overall favorability of the reaction

Catalysts are **INVOLVED** in the reaction, but are not consumed

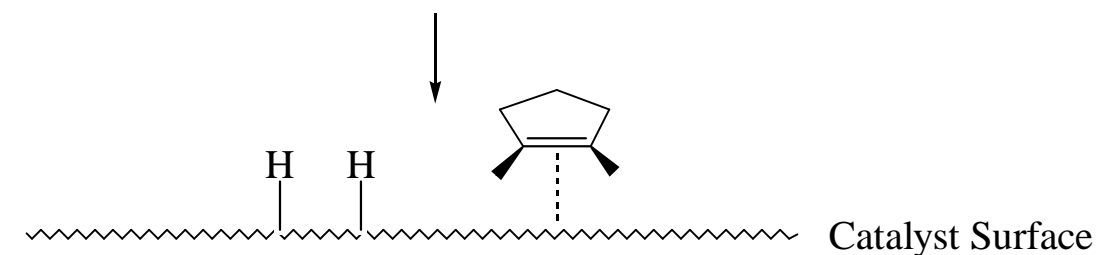
Reduction to Alkanes - Mechanism



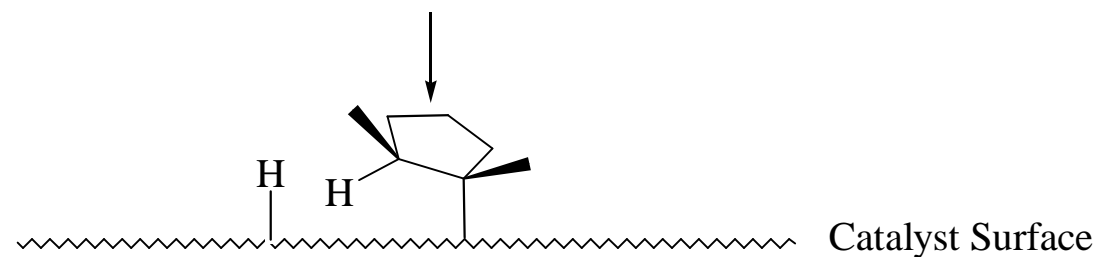
Hydrogen approaches catalyst



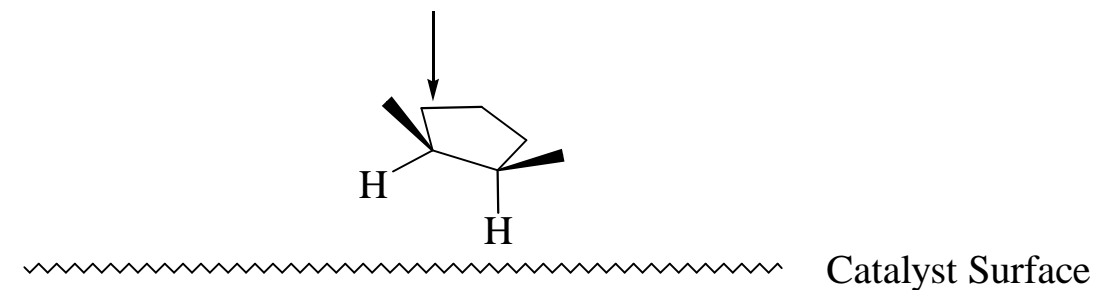
Hydrogen reacts with catalyst



Pi bond interacts with catalyst



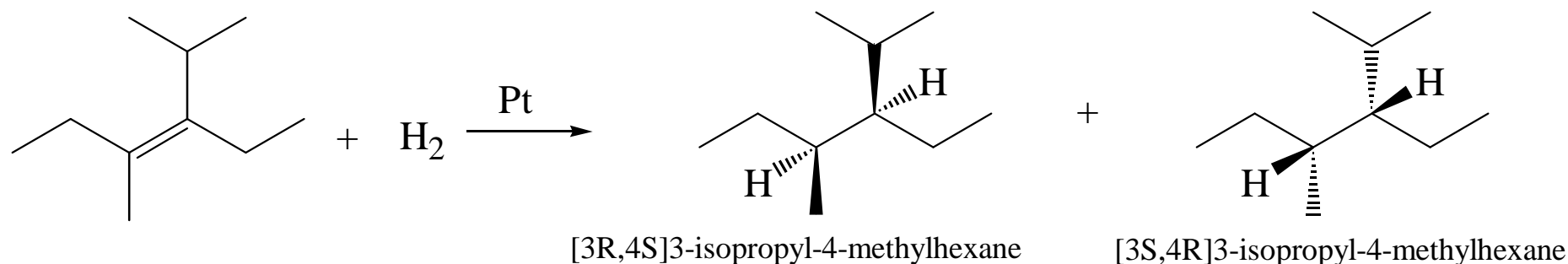
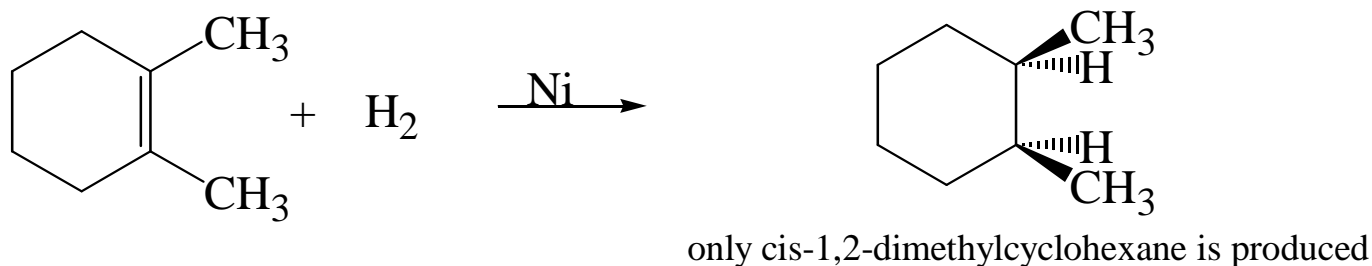
Pi bond reacts with nearby H atom



Second H atom is rapidly added

Mechanism Consequence - Stereoselectivity

- Due to the rapid addition of both hydrogen atoms at the catalyst surface – they are added to the same face of the pi bond (syn addition)



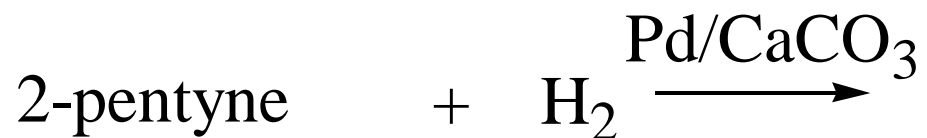
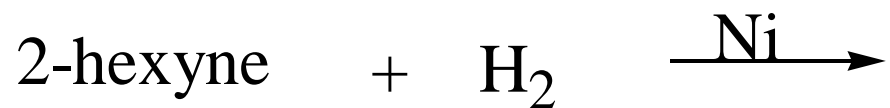
(no [3R, 4R] or [3S, 4S] are produced)

Alkyne Reduction to Alkenes - I

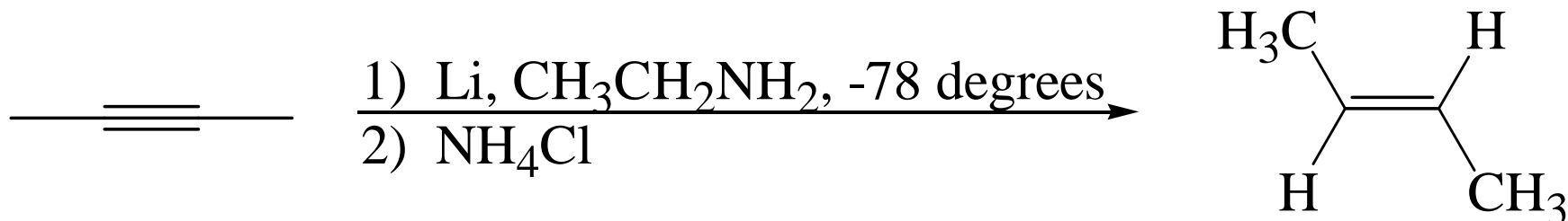
- The catalysts previously mentioned (Ni, Pt, Pd) are highly active and reduce alkynes to alkanes without stopping at alkenes
- Less active catalysts (Ni_2B = P-2 catalyst, Pd/CaCO_3 = Lindlar's catalyst) will stop at the Z-alkene

Problem

- What products do you predict for the following reactions?

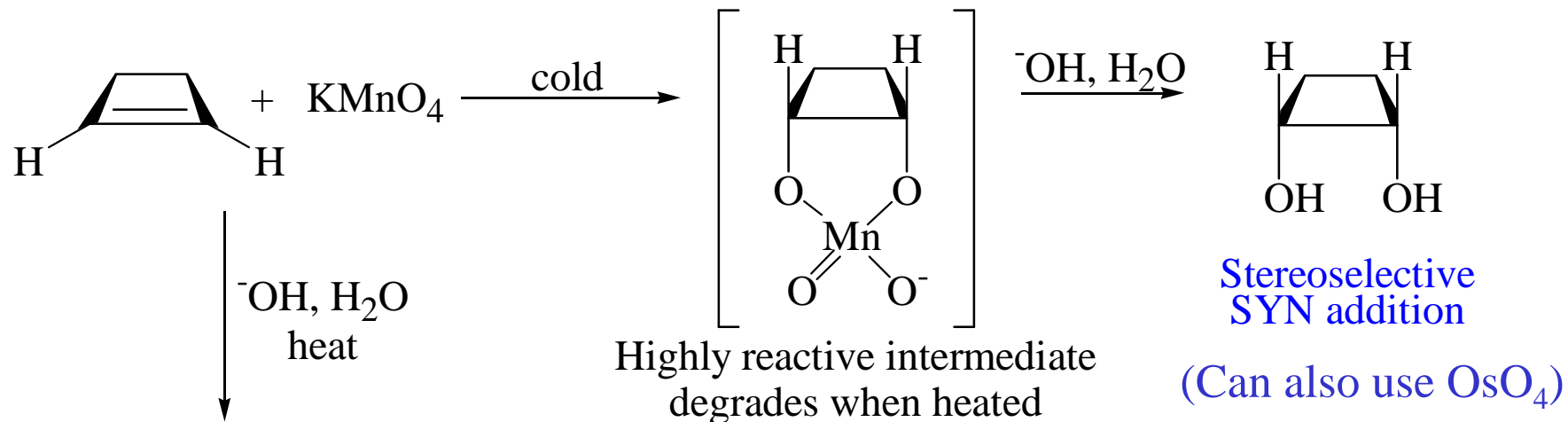


Anti Hydrogen Addition



- Why the difference?
 - The reaction consumes the metal ($\text{Li} \rightarrow \text{Li}^+$), rather than being catalyzed at a metal surface (and is thus called a dissolving metal reduction)
 - The two hydrogen atoms are added in solution (from the solvent), and the thermodynamically more stable product is formed since the alkyne is surrounded by solvent and they can add from any side

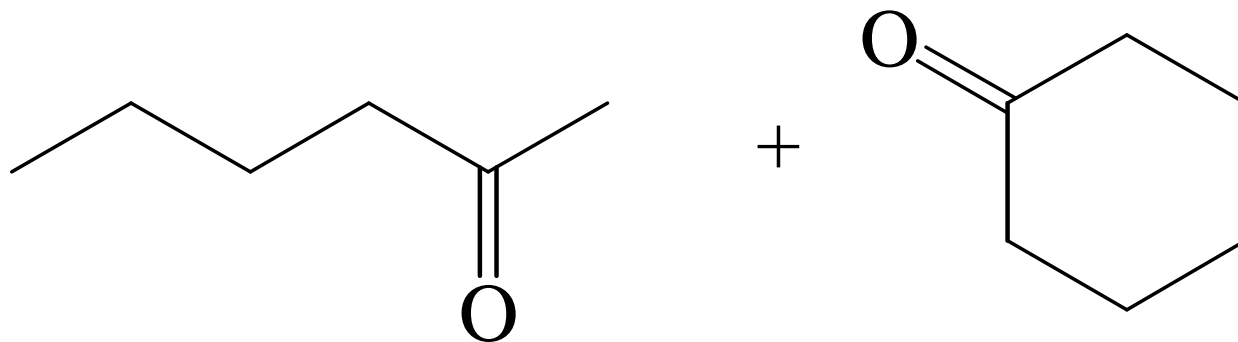
Alkene Oxidations



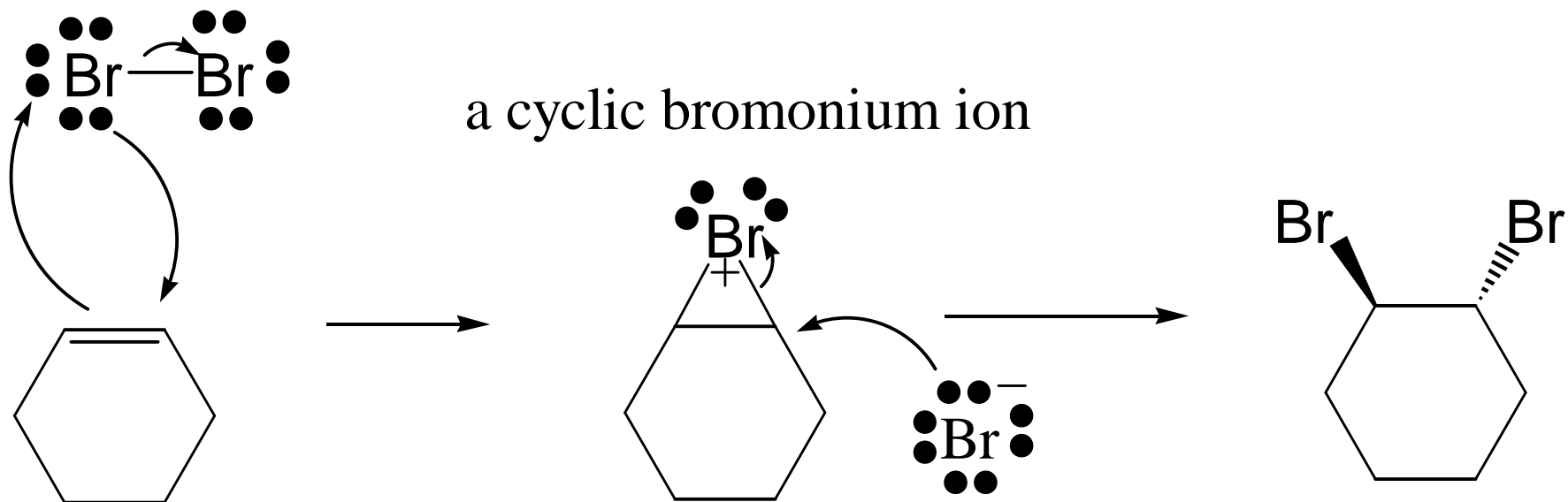
- The cleavage reaction at left was historically used as a means to determine the location of double bonds in complex molecules from natural sources
 - Cleavage of more highly substituted alkenes gives ketones, rather than carboxylic acids

Problem

- What initial structure would give the following products upon treatment with hot potassium permanganate in base?



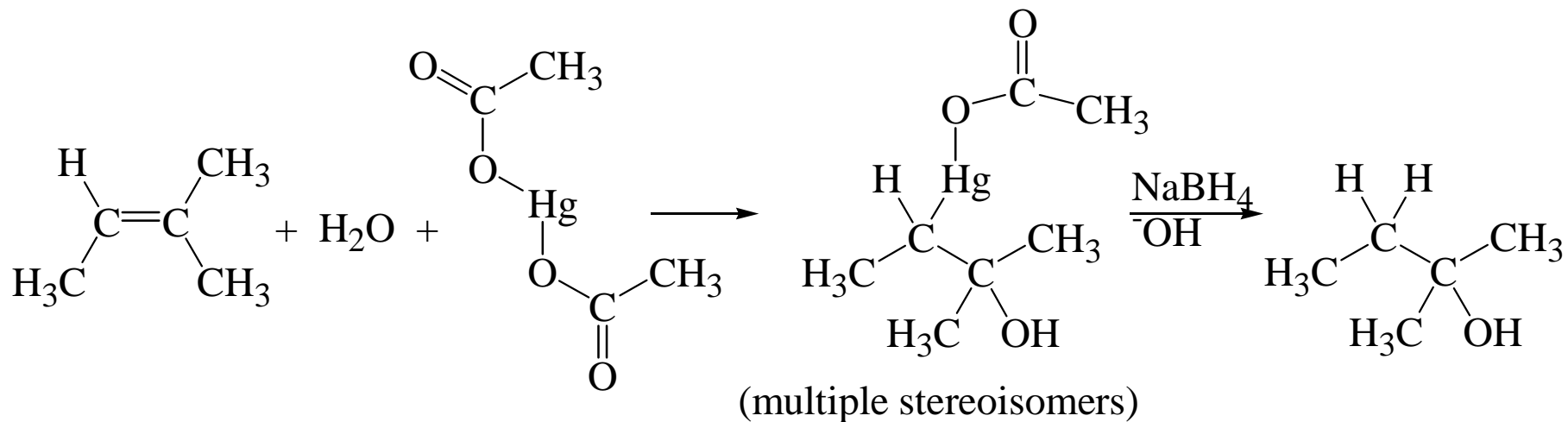
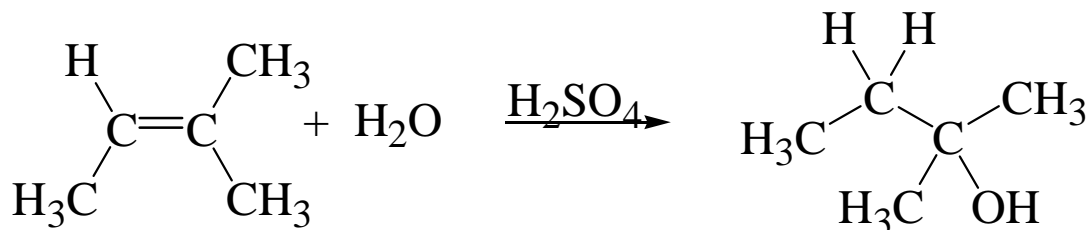
Halide Addition (review)



Oxidation state of alkene
carbons = -1

Oxidation state of halide
carbons = 0

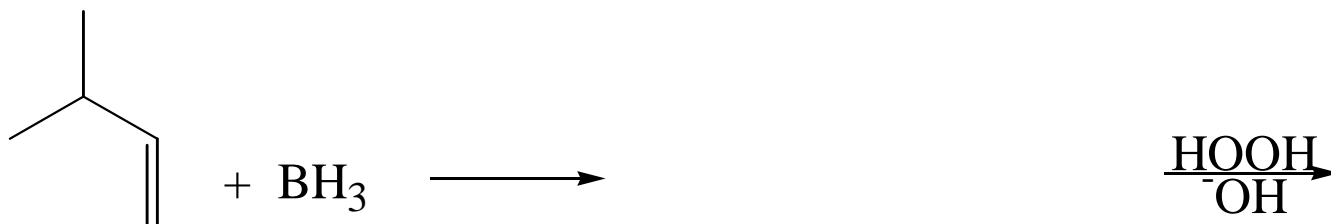
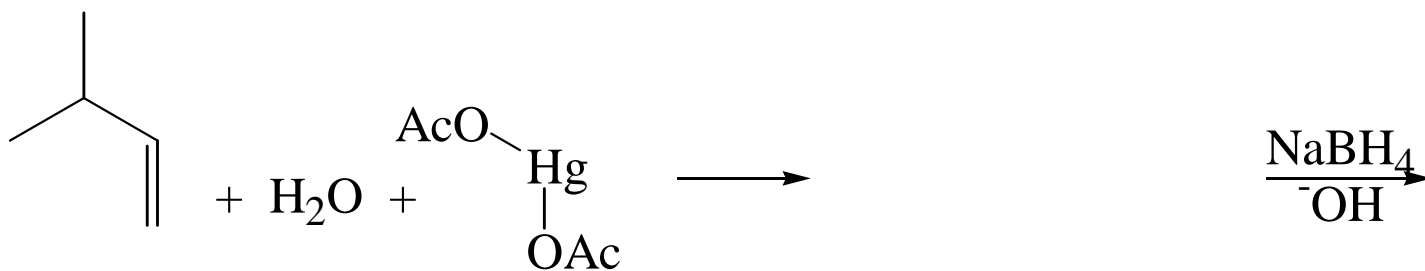
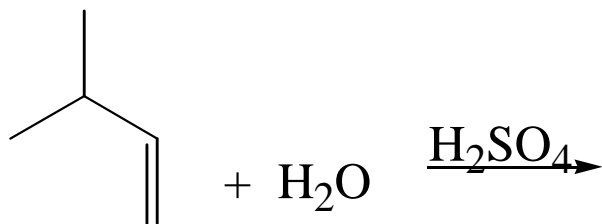
Alkenes \rightarrow Alcohols I



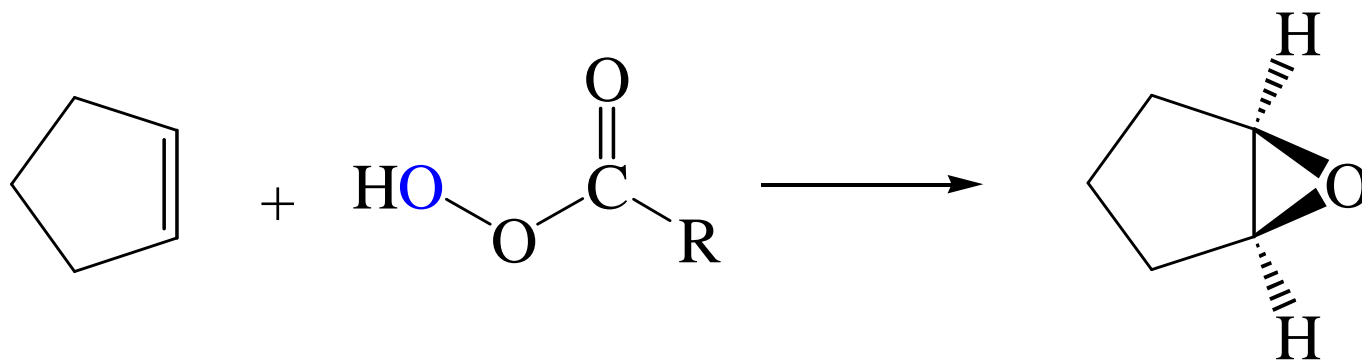
- Why two reactions to give the same product(s)?

Problem

- Predict the products of the following alkene oxidation reactions:

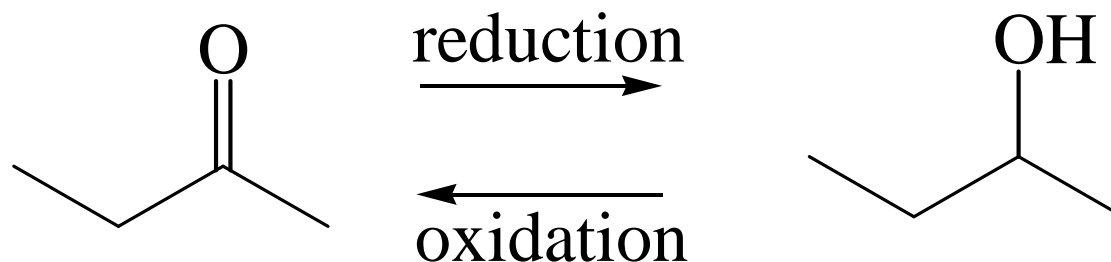


Alkenes \rightarrow Epoxides



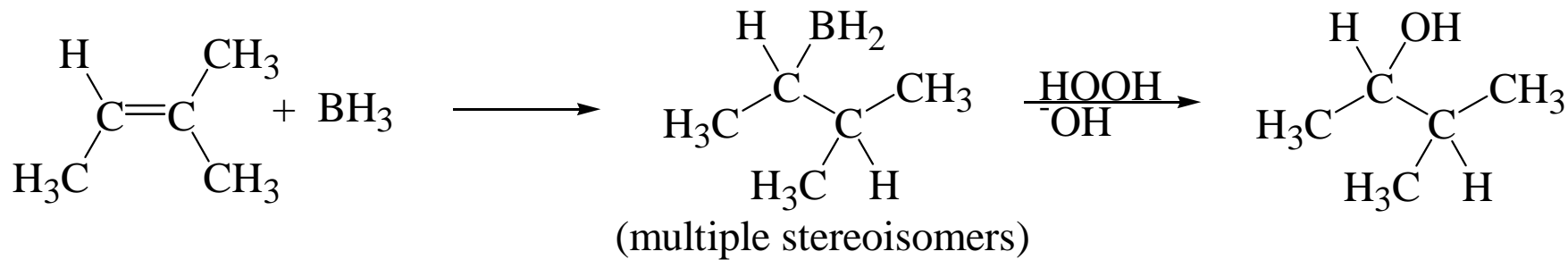
- Epoxides are highly strained and are easily attacked by nucleophiles (thus useful reagents)
- Peroxy acids are used to transfer an oxygen atom to the alkene
 - Common peroxy acids used:
 - Meta-chloroperbenzoic acid (MCPBA)
 - Magnesium monoperoxyphthalate (MMPP)

Carbonyls \rightleftharpoons Alcohols



- Reducing agents often used: NaBH_4 , LiAlH_4
– (both act as hydride donors)
- Oxidizing agents often used: KMnO_4 , H_2CrO_4 ,
pyridinium chlorochromate ($\text{C}_5\text{H}_6\text{N}^+ \text{CrO}_3\text{Cl}^-$)

Alkenes \rightarrow Alcohols II



- First step – hydroboration (stereoselective SYN addition as we saw previously)
- Second step – oxidation of carbon attached to boron (oxidation state = -2) to an alcohol (carbon oxidation state = 0) – stereochemical configuration of carbon UNCHANGED!
- Note regioselectivity is opposite previous two reactions

Summary of Oxidizing Agents

- Metals in high oxidation states
 - KMnO_4
 - OsO_4
 - H_2CrO_4
 - pyridinium chlorochromate ($\text{C}_5\text{H}_6\text{N}^+ \text{CrO}_3\text{Cl}^-$)
 - Less reactive than permanganate or chromate, will oxidize primary alcohols to aldehydes rather than continuing to the carboxylic acid
- Non-metals in higher than usual oxidation states
 - O_2
 - Peroxides
 - Peroxy acids
 - Br_2

Summary of Reducing Agents

- Elements (zero oxidation state) that prefer positive oxidation states
 - Zn
 - Mg
 - Li
 - H₂
- Atoms in negative oxidation states that prefer positive oxidation states (hydride in both cases)
 - LiAlH₄ (more reactive since Al is less electronegative than B)
 - NaBH₄ (less reactive since B is more electronegative than Al)
 - Note: These will only reduce POLAR bonds since hydride is nucleophilic!)