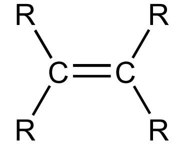
Reactions of Alkenes - Chapter 8 (Klein)

Chapter Outline

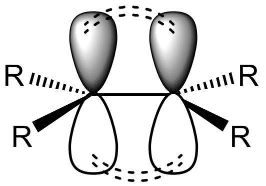
I. Alkene & Alkyne nomenclature (8.2, 8.3, 9.2)
II. Addition reactions & addition of HX (8.1, 8.4, 8.5)
III. Addition of H_2O (add -H and -OH across pi bond)
  A) Acid-catalyzed hydration, H_3O^+(8.6)
  B) Oxymercuration-Demercuration (8.7)
  C) Hydroboration-Oxidation (8.8)
IV. Addition of Br_2 and Br_2/H_2O (8.10)
V. Hydrogenation, add -H and -H (8.9)
VI. Oxidation reactions
  A) Epoxidation (8.10) *skip ring-opening reactions*
  B) Syn Dihydroxylation (8.11)
  C) Ozonolysis (8.12)
VII. Summary & synthesis strategies (8.14, 8.15)

Recall:



alkenes are planar
(*sp^2 hybridized C atoms)*

Recall:



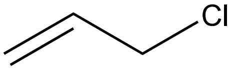
π bond is formed by
overlapping *p* orbitals
3-D sketch: *p* orbitals are
orthogonal to *sp^2* plane

Recall:
- π bonds are higher energy than σ bonds
- π bonds are electron-rich (can react as a **nucleophile** or a **base**)

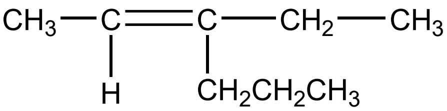
I. Alkene & Alkyne nomenclature (8.3, 9.2)

Alkene IUPAC Rules: Identify the longest parent carbon chain that contains the π bond(s). Number from the end closer to the π bond. Change the alk**a**ne "a" to an "e" to give "**#-alkene**," where # is the first carbon in the double bond (or the number can be inserted into the name "alk-#-ene"). Don't forget to include the configuration where stereochemistry is appropriate (*cis, trans, E, Z;* see Klein 5.11). A compound with two double bonds is called "**#,#-alkadiene**" (triene, tetraene...).

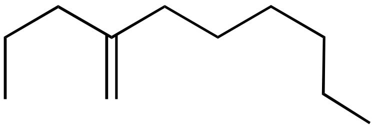
alkane	**alkene**	**alkyne**
CH_3-CH_3	$CH_2=CH_2$	$HC\equiv CH$
eth**a**ne		eth**y**ne
	(ethylene)	(acetylene)



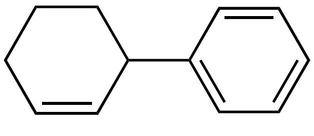
(allyl chloride)



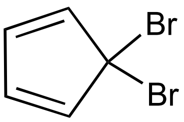
$$\mathrm{CH_3{-}\underset{H}{\underset{|}{C}}{=}\underset{CH_2CH_2CH_3}{\underset{|}{C}}{-}CH_2{-}CH_3}$$



2-propyl-1-octene
(*note Educator error!*)
also: 2-propyloct-1-ene

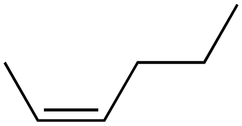


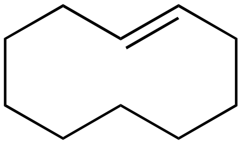
(double bond in a ring ***defines C-1 and C-2***,
and ***cis stereochemistry*** assumed)

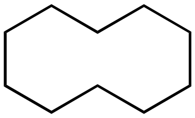


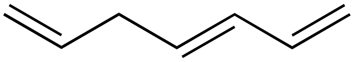
Alkene Nomenclature: Stereochemistry

* for alkenes with two groups (and two H atoms), use cis or trans.

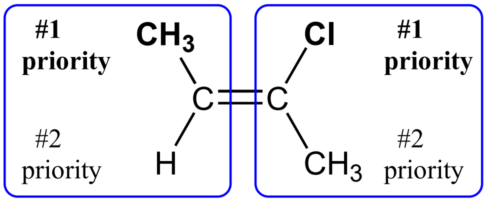




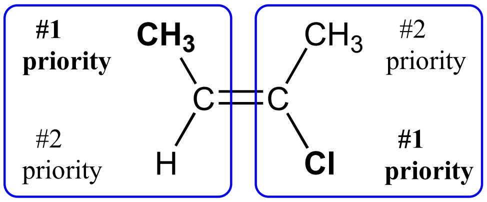




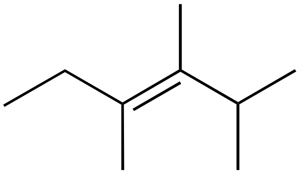
* for alkenes with more than two groups, stereodescriptors (*E)* and (*Z)* are used (see Klein Ch. 5)



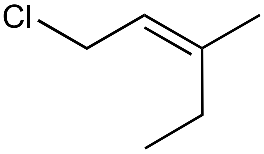
Are the higher priority groups on ***"ze same side"*** **?** Yes! (*Z*)-2-chloro-2-butene



Are the higher priority groups on ***"ze same side"*** **?** No! (*E*)-2-chloro-2-butene



IUPAC:______________________________

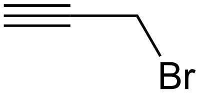


IUPAC:______________________________

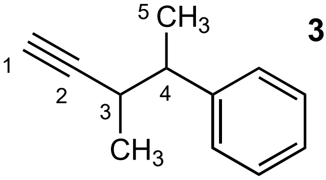
Alkyne IUPAC Rules: Change the alk**a**ne "a" to an "y" to give "**#-alkyne**," where # is the first carbon in the triple bond. A compound with two double bonds is called "**#,#-alkadiyne**" (or triyne...)

$HC\equiv CH$

(acetylene)



(propargyl bromide)

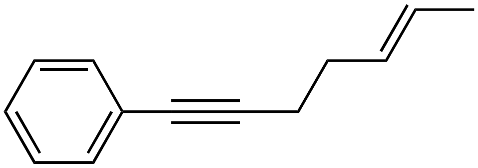


3-methyl-**4**-phenyl-1-hexyne *(note Educator error with doubly numbered C!)*

$CH_3\text{-}CH{=}CH{-}CH_2{-}C{\equiv}C{-}CH{=}CH_2$

1,6-octadien-3-yne (or octa-1,6-dien-3-yne)

(FYI an alkene has a higher priority than an alkyne)



SkillBuilder 9.1

Electrophilic Addition Reaction
I. Addition of HX (Hydrohalogenation, Klein 8.1 to 8.5)

$$CH_3{-}CH{=}CH_2 \quad + \quad HBr \longrightarrow$$

* a "regioselective" reaction (Br adds primarily to only one region/site)

* "**Markovknikov Addition**" is observed

Why this regioselectivity? Look at the mechanism (2 steps):

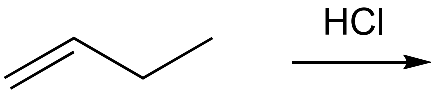
$$CH_3{-}CH{=}CH_2 \qquad H{-}Br \quad \rightleftharpoons$$

** Markovnikov Addition is favored because it involves the **more stable** carbocation intermediate**

- *more stable* means *lower Energy* carbocation intermediate
- more stable carbocation has lower-energy Transition State, making E_a smaller (smaller hill)
- the reaction involving the more stable carbocation is *faster* (kinetic effect)

SkillBuilders 8.1, 8.2

Predict the major product. Consider both **regiochemistry** and **stereochemistry**.

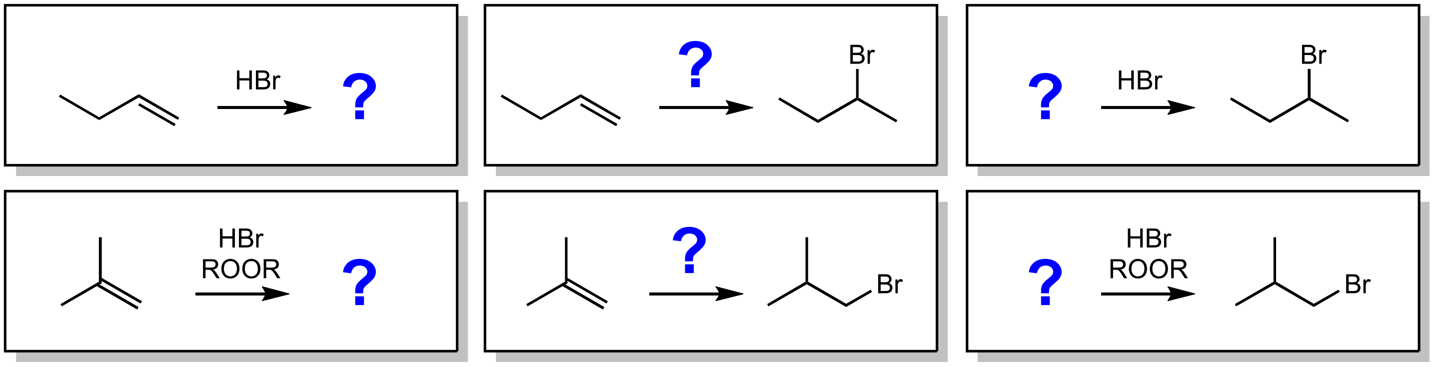


***Klein textbook note: Anti-Markovnikov** addition of HBr*
- *H adds to carbon with fewer H atoms*
- *takes place via a radical mechanism (Ch. 10)*
- *reagents used HBr with peroxides: **HBr/ROOR***

Start building up a set of flashcards to study O-Chem reactions and organize material. From any new reaction we learn in class, you can create **THREE** flashcards:

starting material $\xrightarrow{\text{reagent}}$ product

Sample Flashcards (Markovnikov and Anti-Mark. Addition of HBr to an Alkene)



predict the product **transform problem*** **retrosynthesis***

Useful for preparing for final, reviewing material in 2nd semester and *planning a synthesis.

II. Addition of Water

A) Acid-Catalyzed Hydration of Alkenes (Klein 8.6)

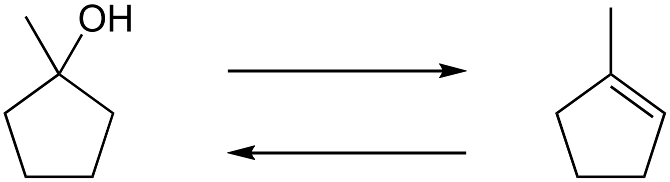
alkene

$$H_2\ddot{O}\!: \qquad H{-}A \longrightarrow$$

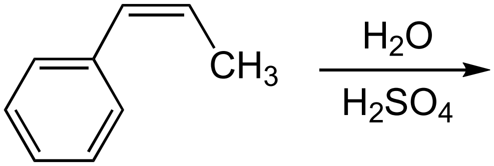
strong acid

Mechanism (3 steps, **P.A.D.**)

Note: the acid-catalyzed **hydration** mechanism is the exact reverse of alcohol **dehydration** mech.



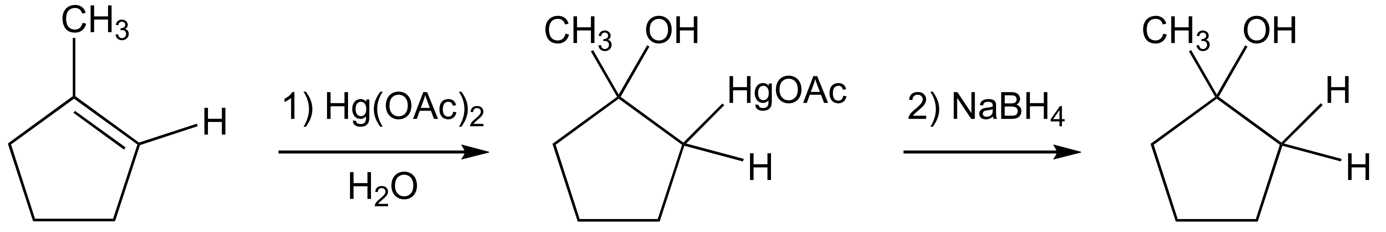
Predict the major product:



SkillBuilder 8.3

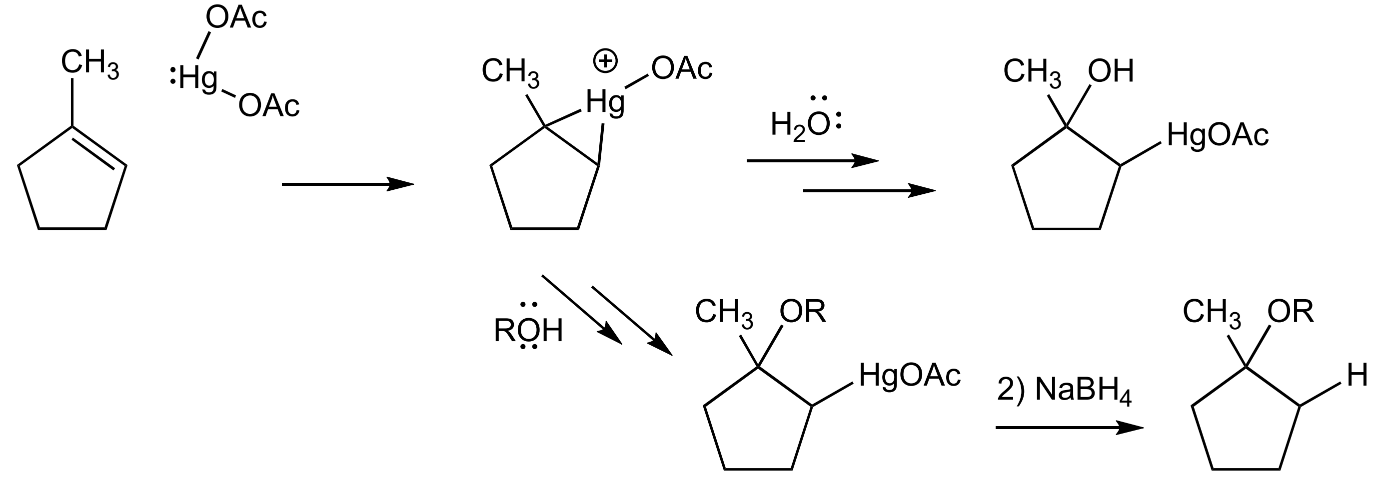
Alternative "Hydration" Methods

B) Oxymercuration-Demercuration, a 2-step process (Klein 8.7)



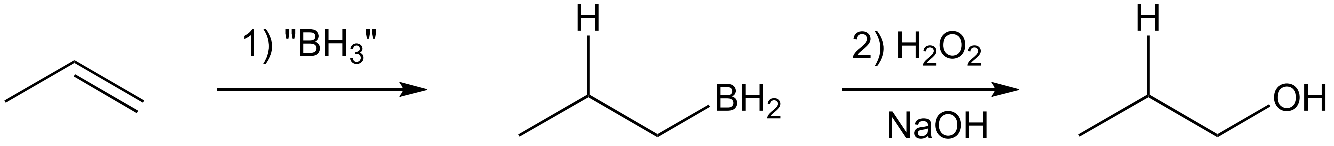
- * gives Markovnikov addition of H_2O
- * generally higher yielding than H_3O^+
- * no carbocation in mechanism, so no rearrangements

Oxymercuration Mechansim **(FYI - will not be on exams)**



(FYI we will see *Alkoxymercuration* reaction in Ch.13)

Alternative "Hydration" Methods
C) Hydroboration-Oxidation, a 2-step process (Klein 8.8)



**** add H_2O with __________________________________ regiochemistry ****

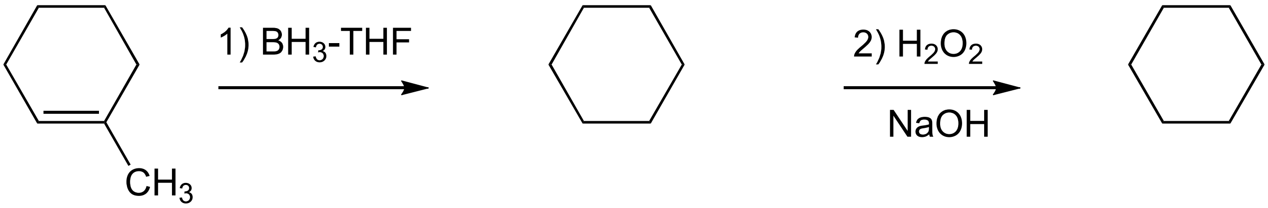
Hydroboration mechanism

regioselective

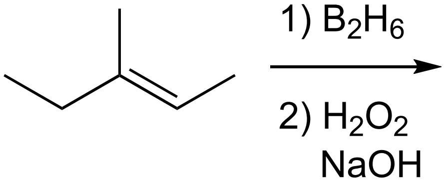
* bulky Boron atom goes to less hindered carbon

stereoselective

* B and H add at the *same time* to the *same face* of the alkene



Predict the major product.

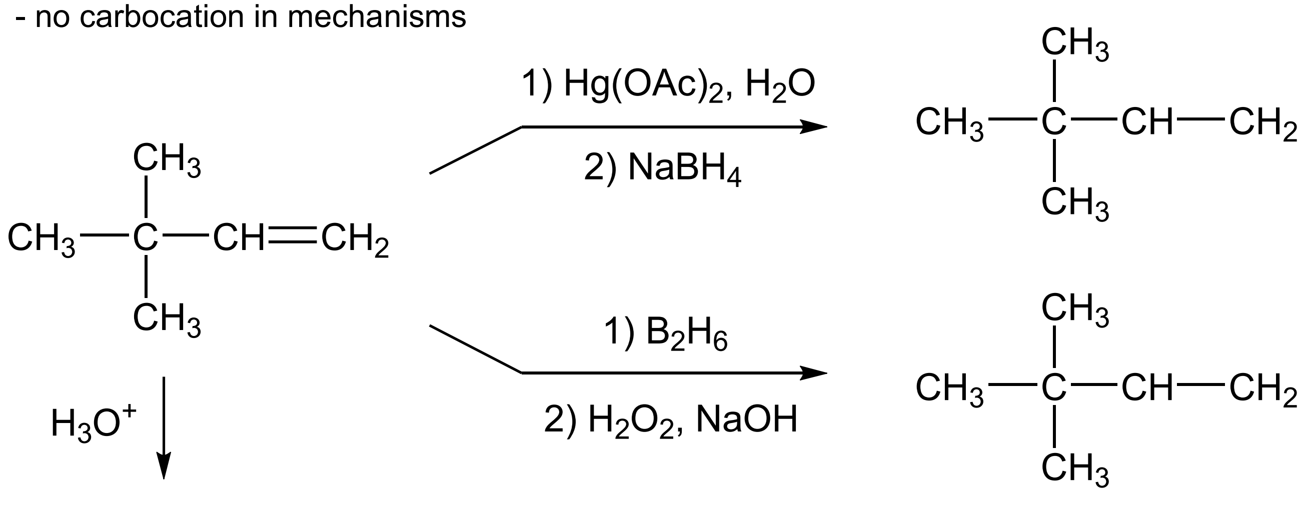


* what are we adding?
* where are we adding it?
(*i.e.*, regiochemistry?)
* what is stereochemistry?

SkillBuilder 8.4

Synthetic Utility of "alternate" hydration methods

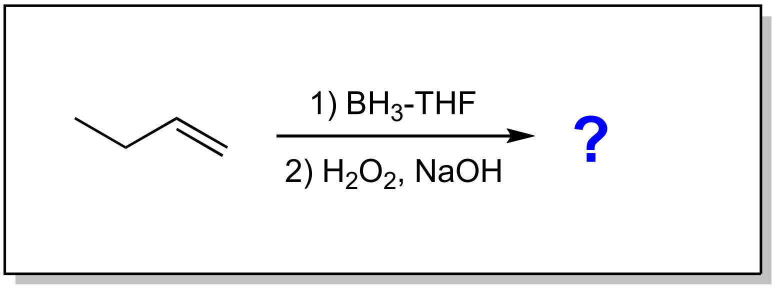
- can add H_2O with Markovnikov or anti-Markovnikov regiochemistry
- no carbocation in mechanisms



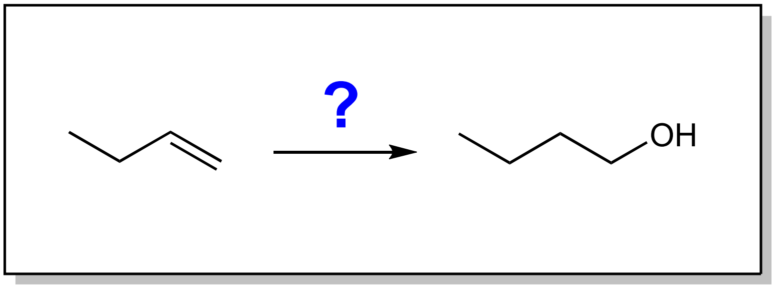
will rearrange!

More Sample Flashcards (Hydroboration-Oxidation of an Alkene)

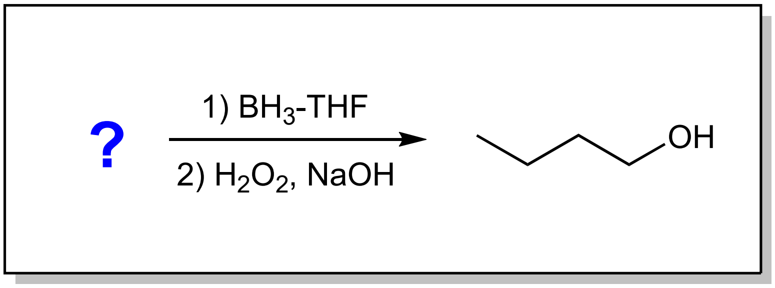
provide the "?" answer on the back of each card



predict the product



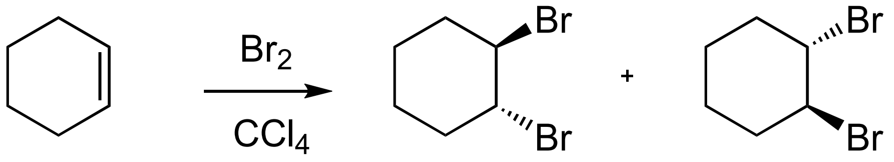
transform problem



retrosynthesis

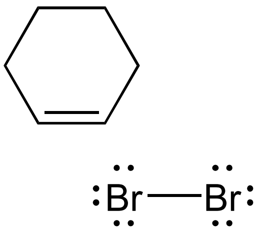
IV. Addition of Br_2 and Br_2/H_2O (Klein 8.10)

Bromination: Anti-Addition of Br_2

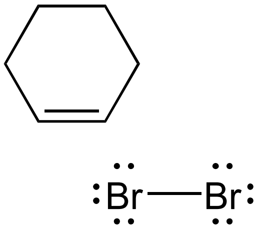


* <u>trans</u> product only (one Br up, one Br down)
* described as a *stereospecific* reaction
* Why *anti addition*? See mechanism!
  (two steps, via **bromonium ion** intermediate)

What is a **bromonium ion**?

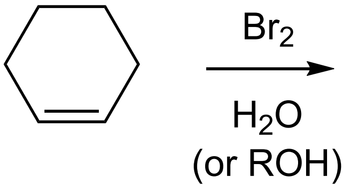


Bromination Mechanism

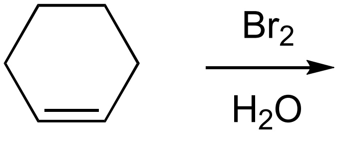


Br_2/H_2O: Halohydrin formation

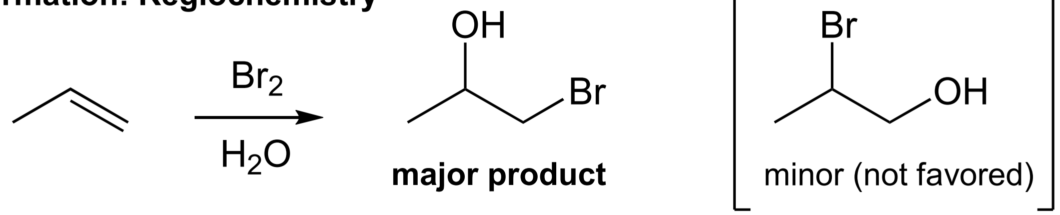
addition of other nucleophiles
to a bromonium ion



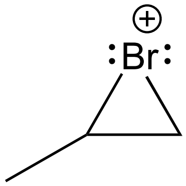
Halohydrin Formation: Mechanism



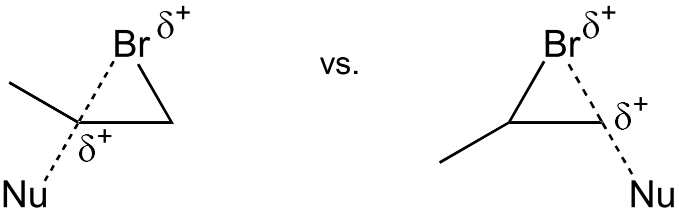
Halohydrin Formation: Regiochemistry



Why this regiochemistry? Look at the bromonium ion intermediate:

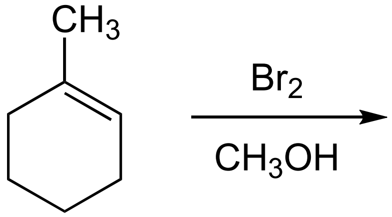


Transition
States:

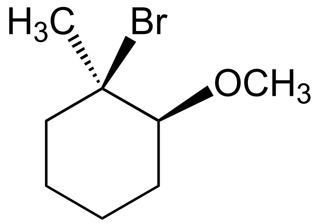


Example: Predict the major product.

- *what are we adding?*
- *where are we adding it?*
- *what is stereochemistry?*

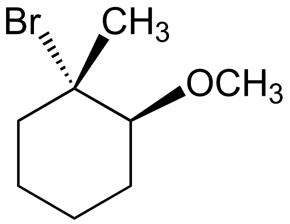


A)



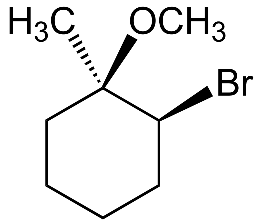
+ enantiomer

B)



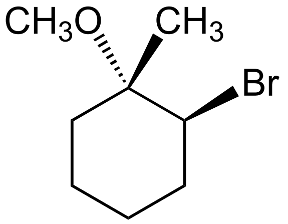
+ enantiomer

C)



+ enantiomer

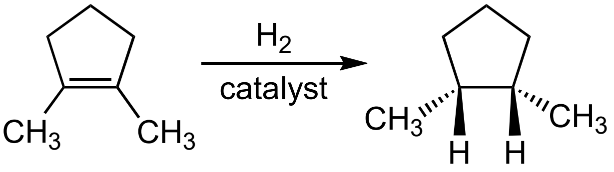
D)



+ enantiomer

SkillBuilder 8.6

V. Catalytic Hydrogenation (Klein 8.9)

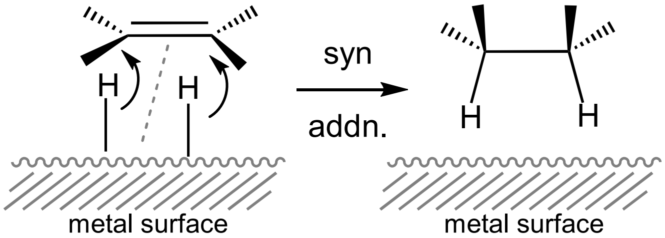


Features of catalytic hydrogenation:

- stereochemistry: syn addition gives cis H atoms
- this reaction needs a catalyst
- it is considered a reduction reaction
- it is an exothermic reaction (break π, form σ)

General process:

- alkene and hydrogen gas are adsorbed onto the metal surface
- metal delivers both hydrogen atoms to the same face of the alkene (syn addition)



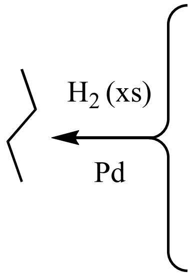
Heterogeneous Catalysts
Pd, Pt, Ni

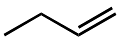
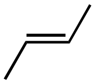
- these metals do NOT dissolve in the solvent

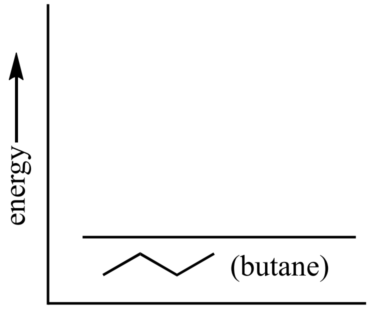
Homogeneous Catalysts, such as $RhCl[P(C_6H_5)_3]_3$

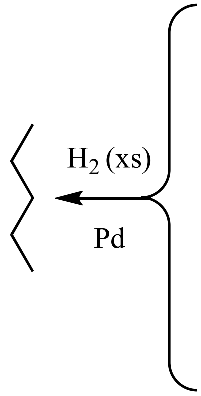
- Organometallic catalysts dissolve in organic solvents
- contain transition metals (Rh, Ru, Ir) and various organic ligands
- generally more selective for unhindered alkenes (due to sterics)

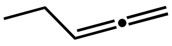
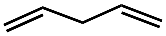
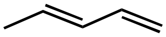
ΔH° **Hydrogenation** can be used as an indication of pi bond stability.

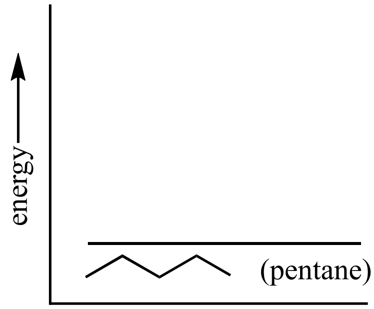


Alkene			ΔH° (kcal/mol)
	monosubt'd (terminal)	**A**	– 30.3
	*cis* disubt'd (internal)	**B**	– 28.6
	*trans* disubt'd (internal)	**C**	–27.6

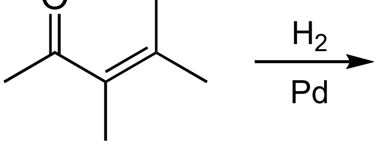




Diene			ΔH° (kcal/mol)
 1,2-pentadiene	**cumulated** (orthogonal p orbitals)	**A**	– 70.3
 1,4-pentadiene	**isolated** (unrelated p orbitals)	**B**	– 60.7 (~ ΔH° alkene x2)
 1,3-pentadiene	**conjugated** (aligned p orbitals)	**C**	–54.1



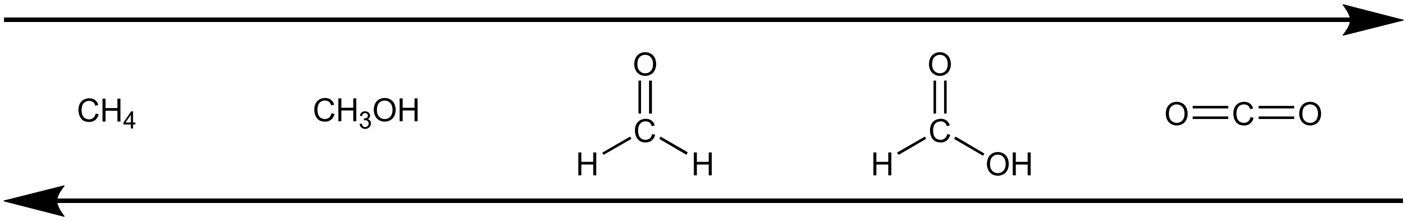
Predict the major product.



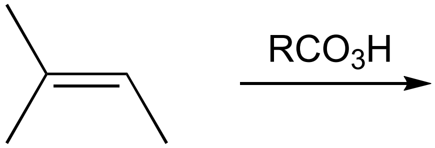
SkillBuilder 8.5

VI. Oxidation Reactions

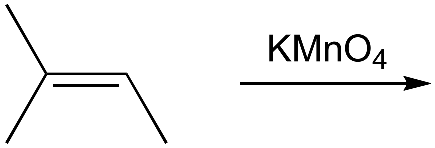
Redox Review



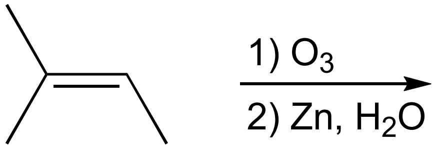
A. Epoxidation



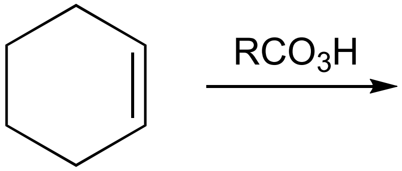
B. Dihydroxylation



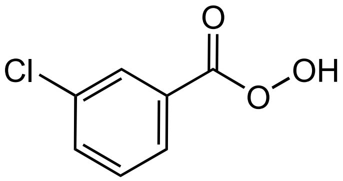
C. Ozonolysis



A. Epoxidation (Klein 8.10) ******Skip opening of epoxides (anti-dihydroxylation) & SkillBuilder 8.7**



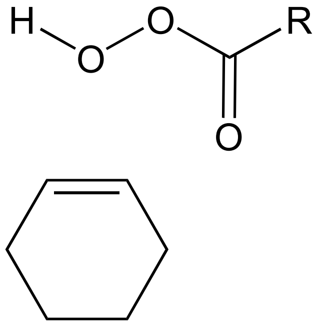
a common
RCO_3H



meta-chloroperoxybenzoic acid

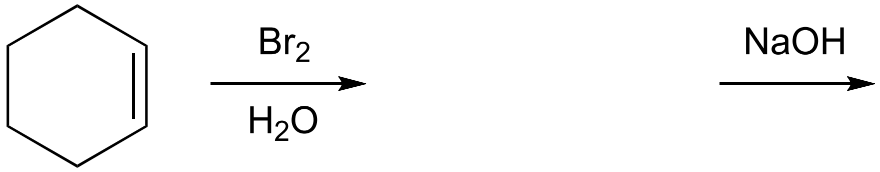
RCO_2H

General mechanism (FYI)

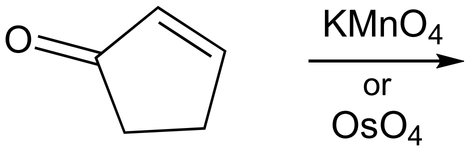


RCO_3H

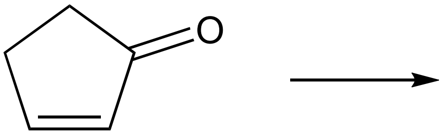
Alternate Epoxide Synthesis

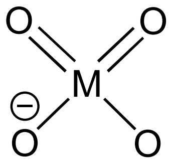


B. Syn Dihydroxylation (Klein 8.11)



General mechanism (concerted via cyclic intermediate):

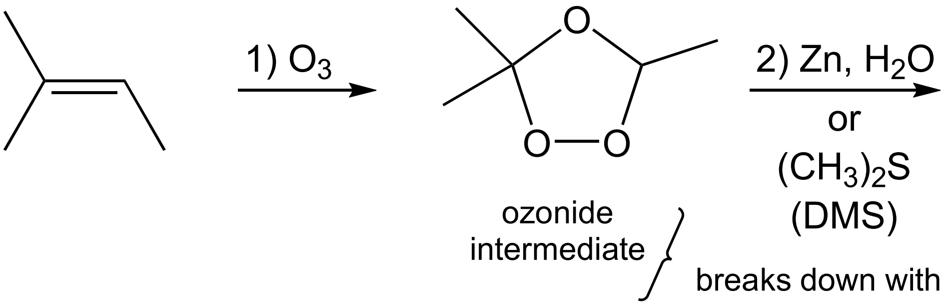




M = metal
(Os or Mn)

C. Ozonolysis (Klein 8.12)

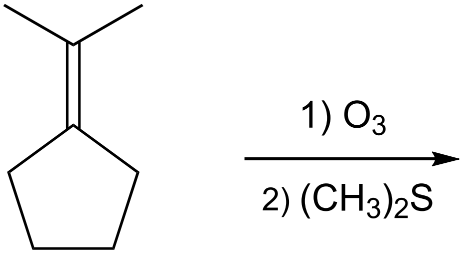
Consider ozone, O_3 Is it good or bad?

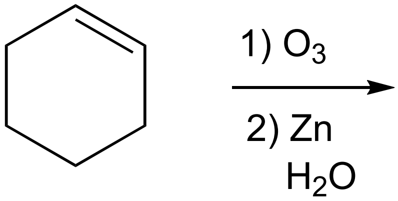


ozonide intermediate

breaks down with "reductive workup"

Predict the major product(s).





SkillBuilder 8.8

Note: Radical Additions to Alkenes will be covered with Chapter 10 (skip for now).

Chapter 8 recommended textbook problems (12 points homework credit!)
1-97, but skip SkillBuilder 8.7, 28-30, 35cg, 37, 39k, 62, 64d, 95.

CHM 3140 Organic Chemistry I, Cal Poly Pomona, Dr. Laurie S. Starkey
Chapter 8 (Klein) Summary: Reactions of Alkenes

I. Alkene & Alkyne Nomenclature (8.3, 9.2) ***SkillBuilder 9.1***
II. Electrophilic Additions (HBr, HCl) (8.1 – 8.5) ***SkillBuilders 8.1, 8.2***
  A) Markovnikov addition via carbocation
  B) HBr/peroxides gives anti-Markovnikov, via radical mechanism (Ch. 10)
III. Hydration (8.6 – 8.8)
  A) H_2O, H_2SO_4 (H_3O^+) – Markovnikov addition of -H and -OH via carbocation ***SkillBuilder 8.3***
  B) Oxymercuration/Reduction
    i) $Hg(OAc)_2$ followed by $NaBH_4$ to replace -Hg(OAc) with -H
    ii) Markovnikov addition of -H and -OH
  C) Hydroboration/Oxidation ***SkillBuilder 8.4***
    i) B_2H_6 followed by H_2O_2/NaOH to replace -B with -OH
    ii) Anti-Markovnikov regiochemistry and syn addition (stereochemistry)
IV. Bromination (Br_2) (8.10) ***SkillBuilder 8.6***
  A) anti addition via back-side attack on bromonium ion intermediate
  B) Br_2/H_2O gives trans halohydrin with Markovnikov regiochemistry
V. Hydrogenation (H_2) (8.9) ***SkillBuilder 8.5***
  A) syn addition of H–H (alkene $\rightarrow$ alkane)
  B) catalysts can be heterogeneous (Pd, Pt, Ni) or homogeneous (organometallic $RhCl[PR_3]_3$)
  C) reduction of alkynes (9.5)
    i) H_2/catalyst (Pd, Ni, Pt, $RhCl[PR_3]_3$) adds 2 equiv. to give alkane
    ii) H_2/poisoned cat. (Lindlar's catalyst) adds 1 equiv. to give cis alkene
    iii) Na/NH_3 (dissolving metal reduction of alkyne gives trans alkene)
VI. Oxidations
  A) epoxidation (using a peroxy acid: RCO_3H or mCPBA or H_2O_2)
    i) syn addition of -O- to give oxirane/epoxide
    ii) FYI: anti addition of two -OH groups if followed by H_3O^+ (will cover in CHM 3150)
  B) dihydroxylation (using $KMnO_4$ or OsO_4) (8.12)
    i) syn addition of two -OH groups via cyclic intermediate
  C) ozonolysis (break double bonds with O_3) (8.13) ***SkillBuilder 8.8***
    i) reductive workup (Zn/H_2O or Me_2S) gives aldehydes/ketones
VII. Predicting the products (summary) ***SkillBuilder 8.9***
  A) What groups are being added?
  B) Where are the groups being added? (regiochemistry, e.g., Markovnikov or anti-Mark.)
  C) What is the stereochemistry? (e.g., syn or anti addition)
VIII. Synthesis strategies
  A) Planning a one-step synthesis ***SkillBuilder 8.10***
  B) Moving an OH/Br/Cl group ***SkillBuilder 8.11***
    i) Elimination, followed by addition
  C) Moving a pi bond ***SkillBuilder 8.12***
    i) Addition, followed by elimination

SKIP: anti-dihydroxylation/epoxide ring openings (Section 8.11 and SkillBuilder 8.7)