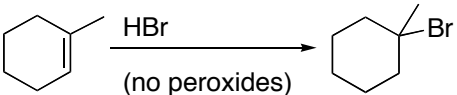
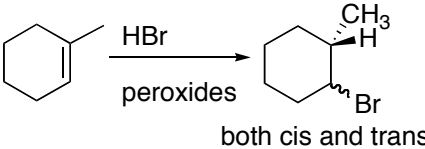
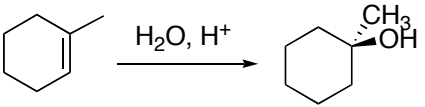
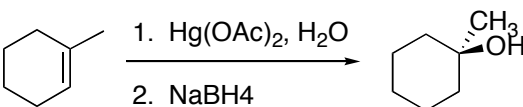
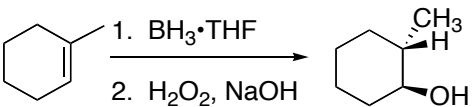
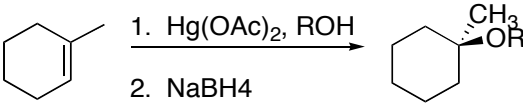
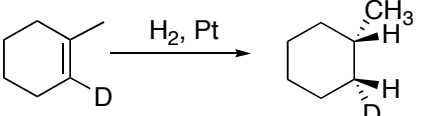
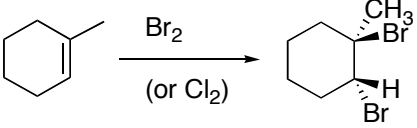
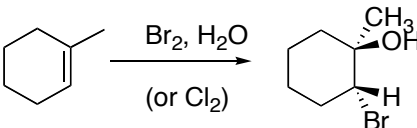
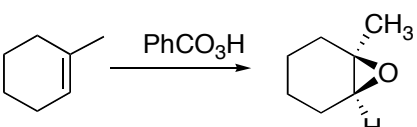
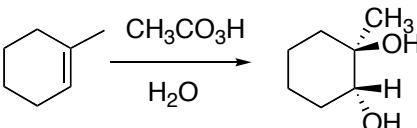
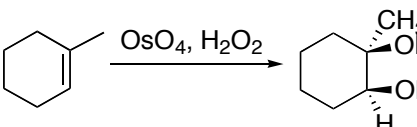
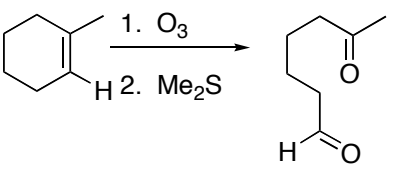
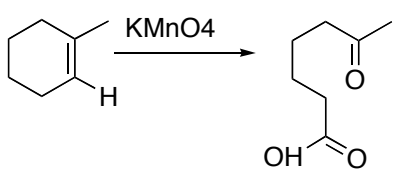


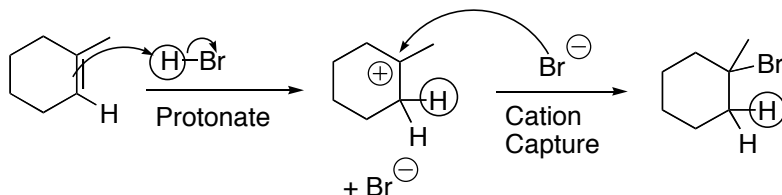
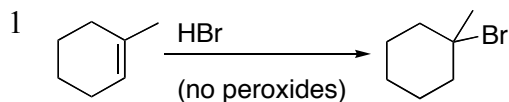
Summary of Alkene Reactions, Ch. 7.**Memorize Reaction, Orientation where Appropriate, Stereochemistry where Appropriate, and Mechanism where Appropriate.**

-all are drawn using 1-methylcyclohexene as a prototype alkene, because both orientation and stereochemistry effects are readily apparent.

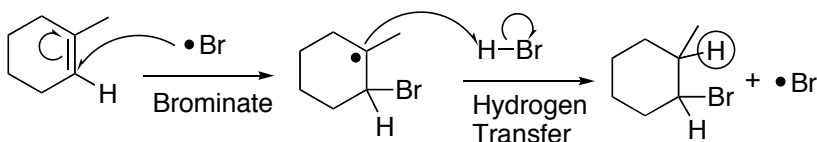
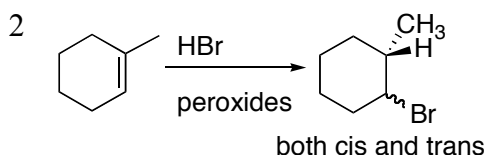
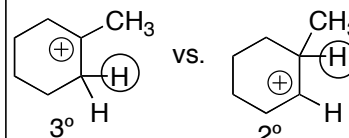
		<u>Orientation</u>	<u>Stereo</u>	<u>Mechanism</u>
1		Markovnikov	None	<u>Be able to draw completely</u>
2	 both cis and trans	Anti-Markovnikov	Nonselective. Both cis and trans	<u>Be able to draw propagation steps.</u>
3		Markovnikov	None	<u>Be able to draw completely</u>
4		Markovnikov	None	Not responsible
5		Anti-Markovnikov	<u>Cis</u>	Not responsible
6		Markovnikov	None	Not responsible
7		None	<u>Cis</u>	Not responsible

- Pd/C or PtO₂ can be used instead of Pt

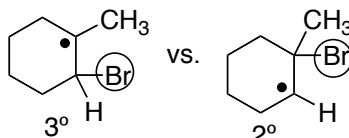
		<u>Orientation</u>	<u>Stereo</u>	<u>Mechanism</u>
8		None	<u>Trans</u>	<u>Be able to draw completely</u>
9		Markovnikov	<u>Trans</u>	<u>Be able to draw completely</u>
10		None	<u>Cis</u>	Not responsible
11	<p>• other RCO₃H work</p> 	None	<u>Trans</u>	<u>Be able to draw acid-catalyzed epoxide hydrolysis</u>
12		None	<u>Cis</u>	Not responsible
13	<p>• oxidant "NMO" can replace H₂O₂</p>  <p>Note: H-bearing alkene carbon ends up as aldehyde.</p>	None	None	Not responsible
14	<p>• Zn/H₃O⁺ can replace Me₂S</p>  <p>H-bearing alkene carbon ends as carboxylic acid</p>	None	None	Not responsible

Summary of Mechanisms, Ch. 6 + 7.**Alkene Synthesis and Reactions.**

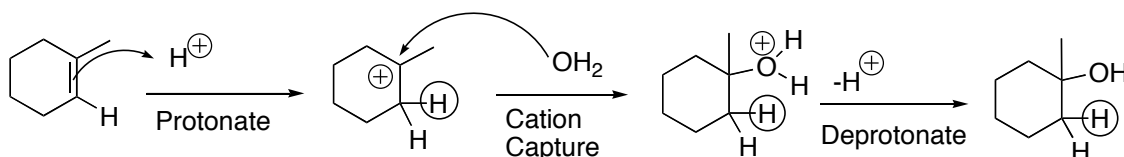
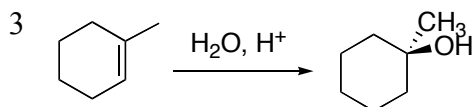
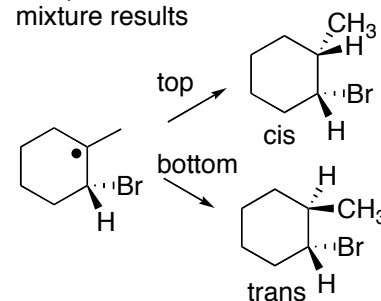
Note: For unsymmetrical alkenes, protonation occurs at the less substituted alkene carbon so that the more stable cation forms ($3^\circ > 2^\circ > 1^\circ$), in keeping with the product stability-reactivity principle



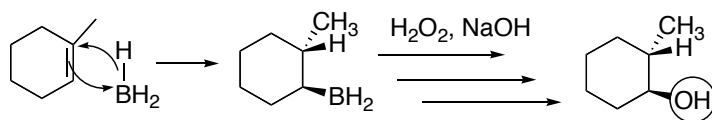
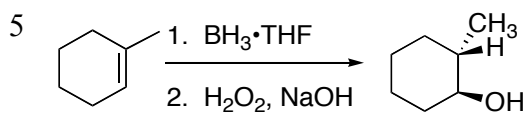
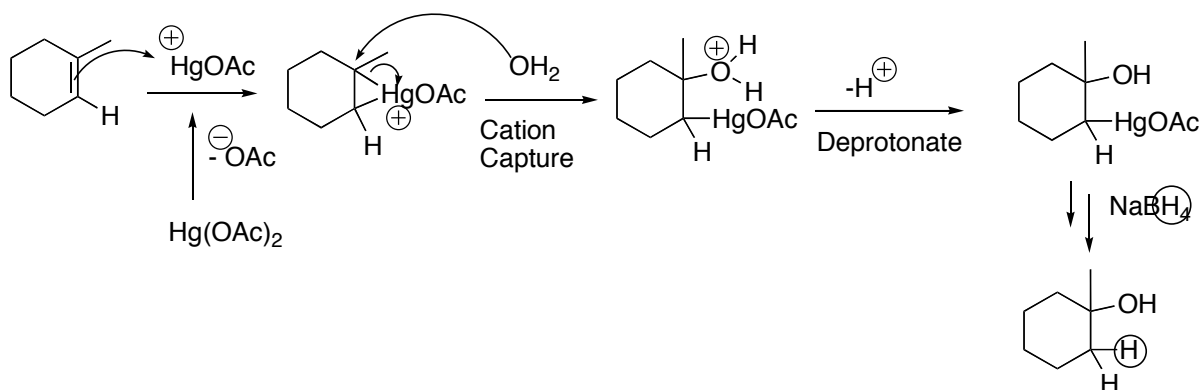
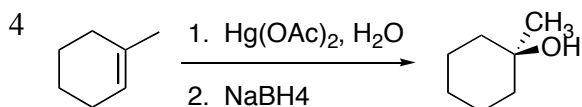
Note 1: For unsymmetrical alkenes, bromination occurs at the less substituted alkene carbon so that the more stable radical forms ($3^\circ > 2^\circ > 1^\circ$), in keeping with the product stability-reactivity principle



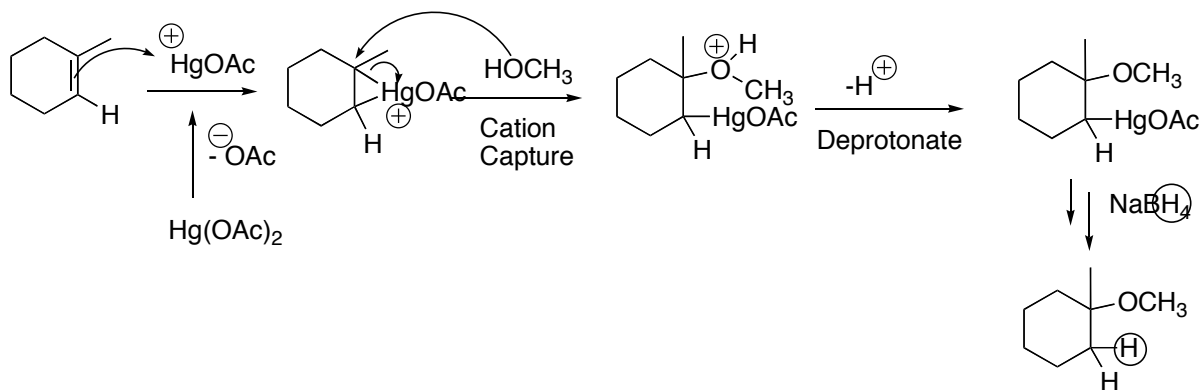
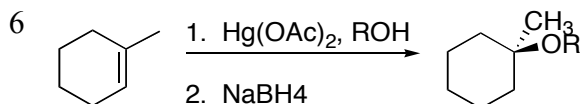
Note 2: Hydrogenation of the radical comes from either face, thus cis/trans mixture results



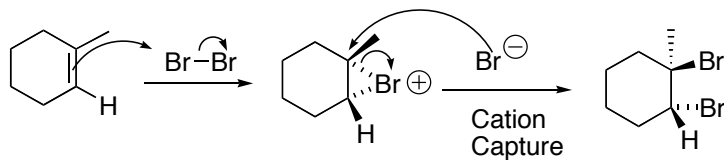
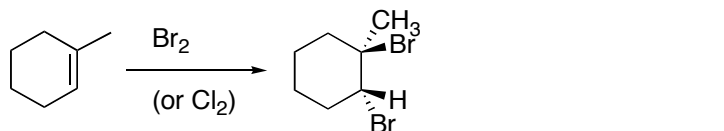
Note: For unsymmetrical alkenes, protonation again occurs at the less substituted end of the alkene, in order to produce the more stable radical intermediate ($3^\circ > 2^\circ > 1^\circ$)

Notes

- concerted addition of B-H across C=C
-explains the cis stereochemistry
- the B-H addition is Markovnikov; the B is δ^+ , the H is δ^-
- The $\text{H}_2\text{O}_2, \text{NaOH}$ process is complex, but replaces the B with OH with complete retention of stereochem
-the explains why the cis stereochemistry established in step one is preserved in step

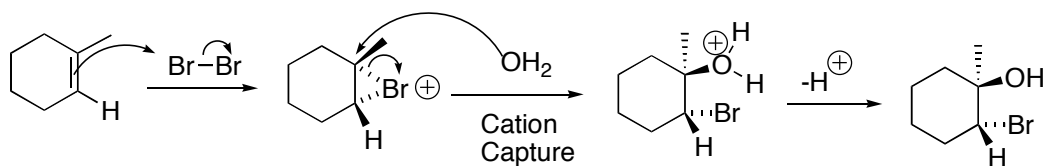
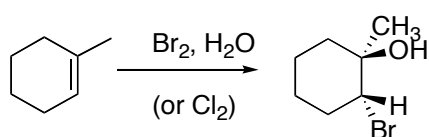


8

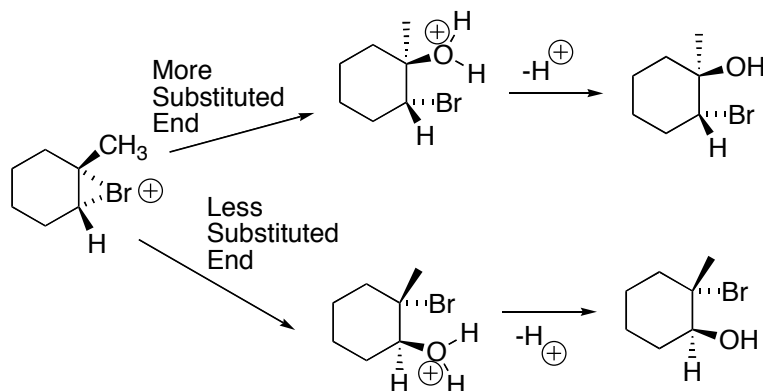
3 Notes

1. Cation intermediate is cyclic bromonium (or chloronium) ion
2. The nucleophile captures the bromonium ion via backside attack -this leads to the trans stereochemistry
3. The nucleophile attacks the bromonium ion at the *more* substituted carbon

9

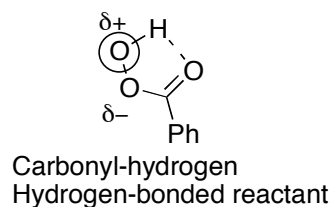
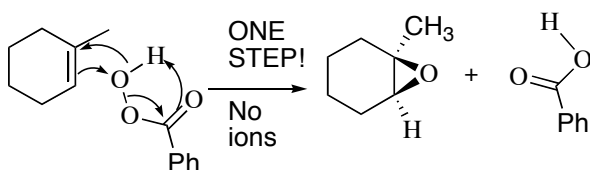
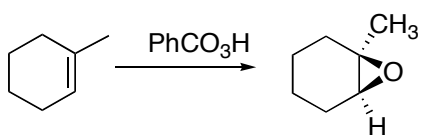
4 Notes

1. Cation intermediate is cyclic bromonium (or chloronium) ion
2. The nucleophile captures the bromonium ion via backside attack (ala $\text{S}_\text{N}2$) -this leads to the trans stereochemistry
3. The nucleophile attacks the bromonium ion at the *more* substituted carbon -this explains the orientation (Markovnikov)
 - a. There is more + charge at the more substituted carbon
 - b. The $\text{Br}-\text{C}$ bond to the more substituted carbon is a lot weaker



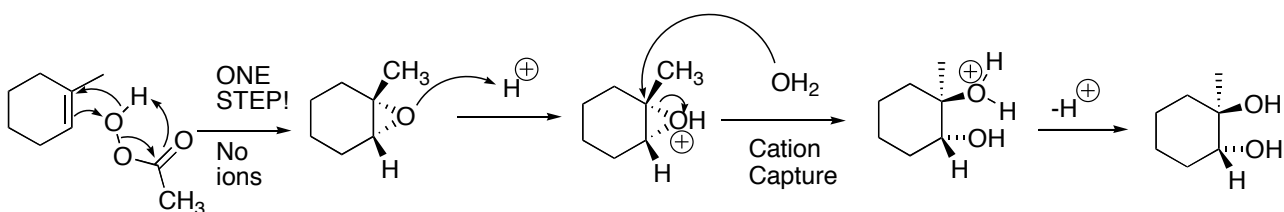
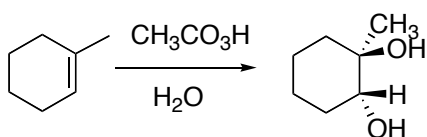
4. Alcohols can function in the same way that water does, resulting in an ether OR rather than alcohol OH .

10

Notes

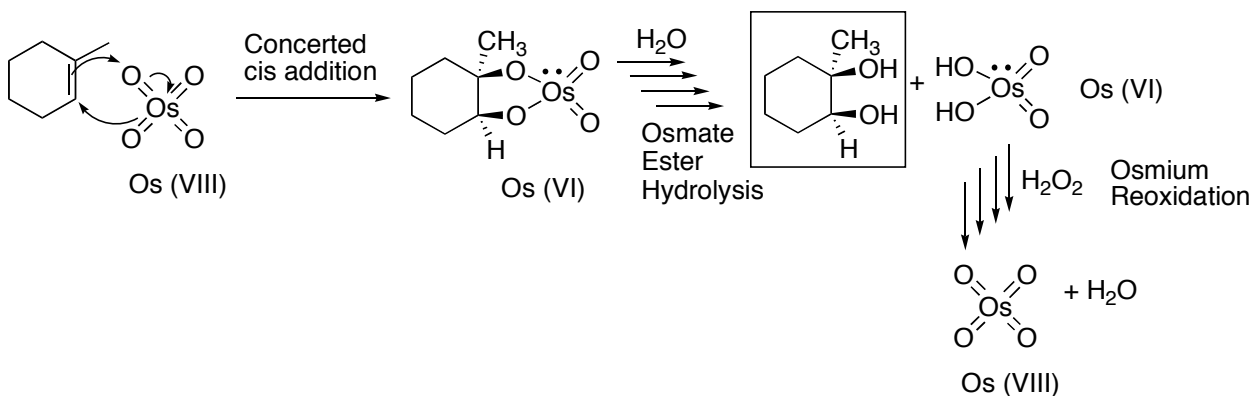
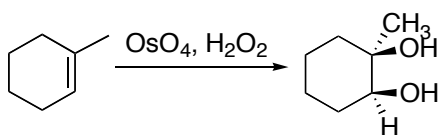
1. Complex arrow pushing
2. No ions required
3. The carbonyl oxygen picks up the hydrogen, leading directly to a neutral carboxylic acid
-The peracid is already pre-organized for this' via internal H-bonding between carbonyl and H

11

Notes:

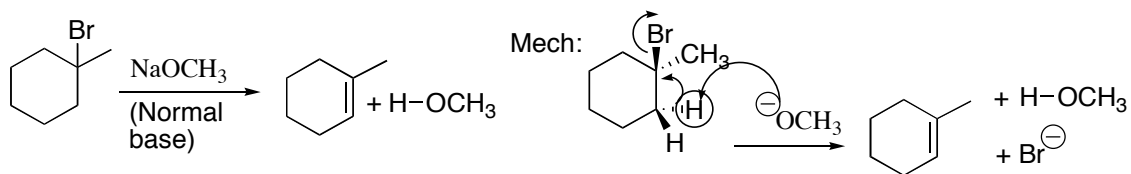
- a. The nucleophile (water) attacks from the more substituted end of the protonated epoxide
 - More δ^+ charge there
 - The C-O bond to the more substituted end is much weaker
- b. The nucleophile adds via $\text{S}_{\text{N}}2$ -like backside attack. Inversion at the top stereocenter, but not the bottom, explains the trans stereochemistry.

12



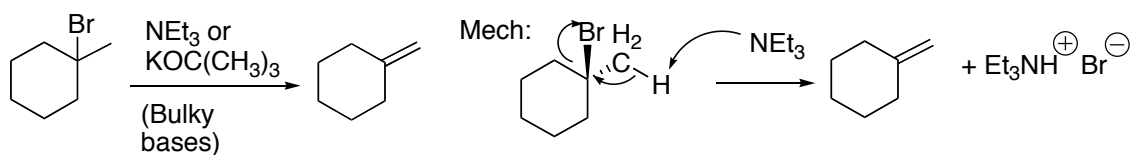
Chapter 7 Reactions and Mechanisms, Review

E2
On
R-X,
Normal
Base

Notes

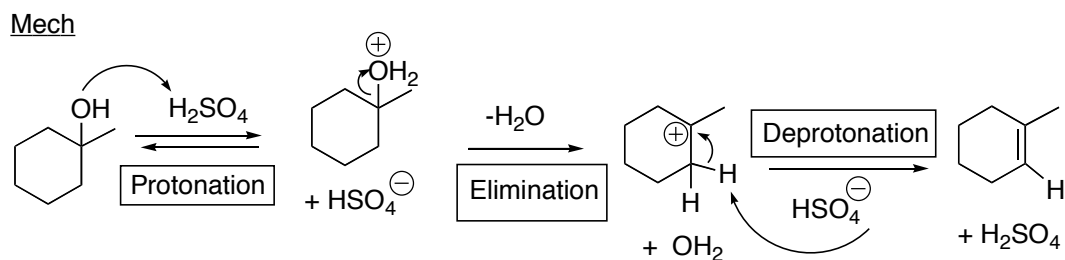
1. Trans hydrogen required for E2
2. Zaytsev elimination with normal bases
3. For 3° R-X, E2 only. But with 2° R-X, S_N2 competes (and usually prevails)
4. Lots of “normal base” anions.

E2,
On
R-X, Bulky
Base

Notes:

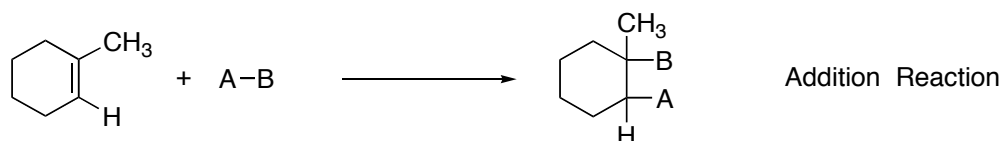
1. Hoffman elimination with Bulky Bases
2. E2 dominates over S_N2 for not only 3° R-X but also 2° R-X
3. Memorize NEt₃ and KOC(CH₃)₃ as bulky bases.

Acid-
Catalyzed
E1-
Elimination
Of
Alcohols

Notes:

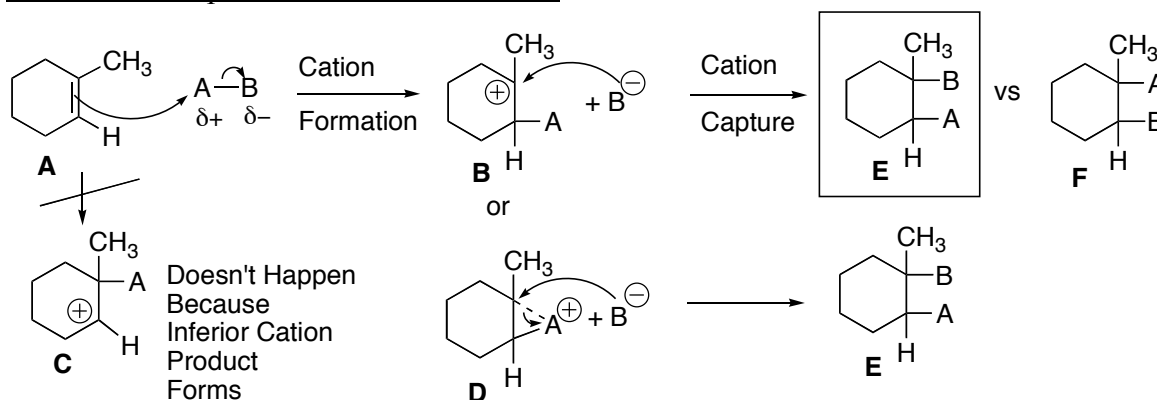
1. Zaytsev elimination
2. Cationic intermediate means 3° > 2° > 1°
3. 3-Step mechanism

Ch. 6, 7 Reactions of Alkenes

Introduction: 6.7

Addition Reaction

1. Thermodynamics: Usually exothermic
 - $1 \pi + 1 \sigma \rightarrow 2 \sigma$ bonds
2. Kinetics: π bond is exposed and accessible

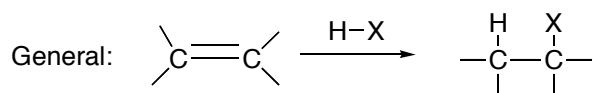
Generic Electrophilic Addition Mechanism2 Steps: Cation formation and cation capture

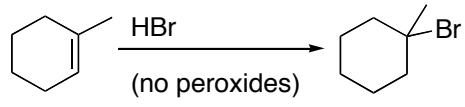
- Cation formation is the slow step
 - Cation stability will routinely determine the orientation in the first step
 - Which is preferred, $A \rightarrow B$ or $A \rightarrow C$?
- Often the cation is a normal cation **B**. Sometimes 3-membered ring cations **D** will be involved.
- In some cases, the cation will be captured by a neutral species (like water), in which case an extra deprotonation step will be involved

4 Aspects to Watch For

1. Orientation
 - Matters only if both of two things are true:
 - a. The alkene is unsymmetrical, and
 - b. The electrophile is unsymmetrical
2. Relative Stereochemistry
 - Matters only if both the first and the second alkene carbons are transformed into chiral centers
3. Mechanism
4. Relative Reactivity of Different Alkenes
 - Stability of cation formed is key

6.7,8 H-X Hydrogen Halide Addition: Ionic/Cationic Addition in the Absence of Peroxides
(Reaction 1)



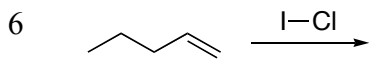
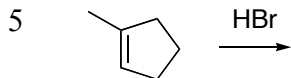
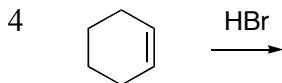
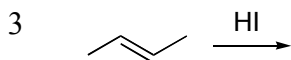
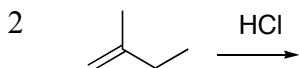
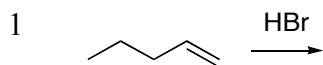
		<u>Orientation</u>	<u>Stereo</u>	<u>Mechanism</u>
1		Markovnikov	None	<u>Be able to draw completely</u>

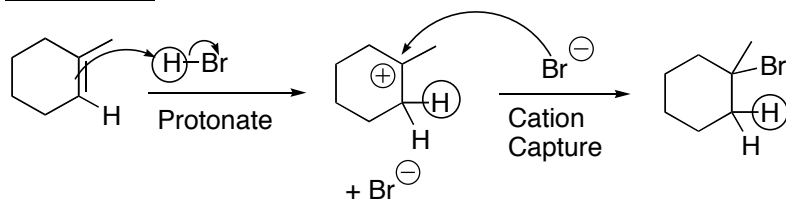
Markovnikov's Rule (For Predicting Products): When H-X (or any unsymmetrical species $A^{\delta+}B^{\delta-}$) adds to an unsymmetrical alkene:

- the H^+ (or $A^{\delta+}$) adds to the less substituted carbon (the one with more H's)
- the X^- (or $B^{\delta-}$) adds to the more substituted carbon (the one with more non-H's).
- Note: Markovnikov's rule does not apply if either the alkene or the atoms that are adding are symmetrical

Examples, Predict the Products.

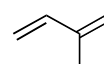
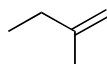
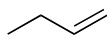
Does Markovnikov's Rule matter?



Mechanism

- Protonate first
- Capture cation second
- Cation formation (step 1) is the slow step

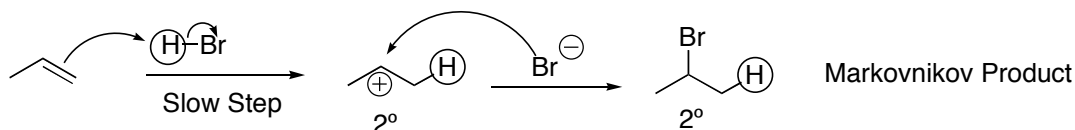
Rank the Reactivity of the following toward HBr addition.



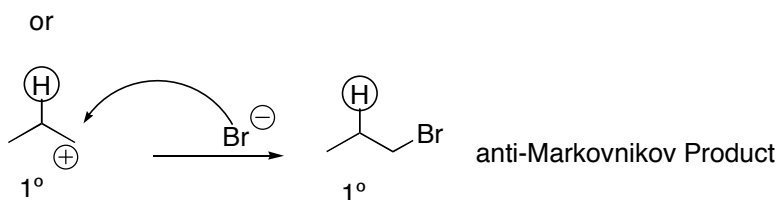
Issue:

Why Does Markovnikov's Rule Apply? Product/Stability Reactivity Rule.

- Formation of the most stable carbocation results in Markovnikov orientation

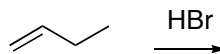


For unsymmetrical alkenes, protonation occurs at the less substituted alkene carbon so that the more stable cation forms (3° > 2° > 1°), in keeping with the product stability-reactivity principle

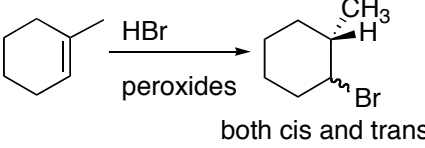


- This same logic applies anytime something adds to an alkene.
- You want to make the best possible intermediate in the rate-determining step.

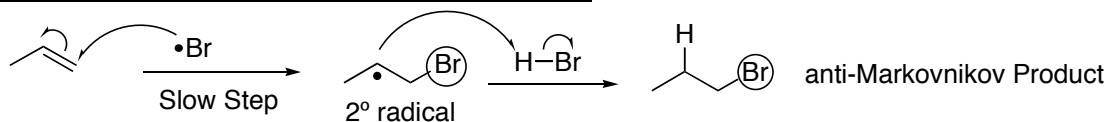
Draw the mechanism for the following reaction:



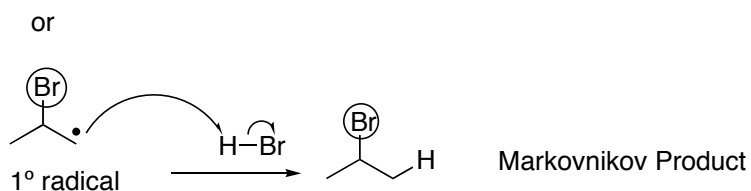
Rxn 2. Anti-Markovnikov Radical Addition of HBr with Peroxide Initiator: (no book)

2	 <p>both cis and trans</p>	Anti-Markovnikov	Nonselective. Both cis and trans	<u>Be able to draw propagation steps.</u>
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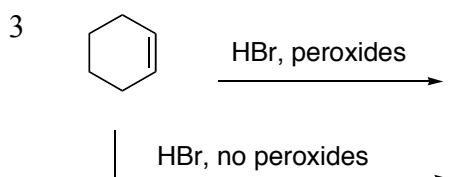
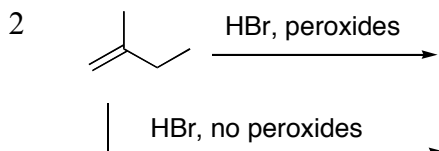
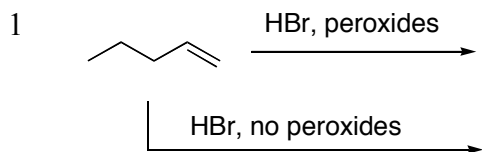
- Peroxides are radical initiators, and cause the mechanism to shift to a radical mechanism
- With peroxides, the orientation is reversed to anti-Markovnikov: now the Br adds to the less substituted end and the H adds to the more substituted end of an unsymmetrical alkene
 - No peroxides: Br goes to more substituted end
 - With peroxides: Br goes to less substituted end
- The anti-Markovnikov radical process works only with HBr, not HCl or HI
- The radical process is faster, and wins when peroxides make it possible. In the absence of peroxides, the slower cationic process happens.

Mechanism, and Reason for AntiMarkovnikov Orientation

For unsymmetrical alkenes, **bromination** occurs at the less substituted alkene carbon so that the more stable **radical** forms ($3^\circ > 2^\circ > 1^\circ$), in keeping with the product stability-reactivity principle

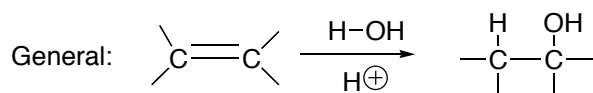


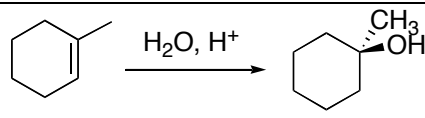
Examples, Predict the Products.



Does Markovnikov's Rule matter?

7.4 Addition of H-OH. Direct acid-catalyzed addition. (Reaction 3)



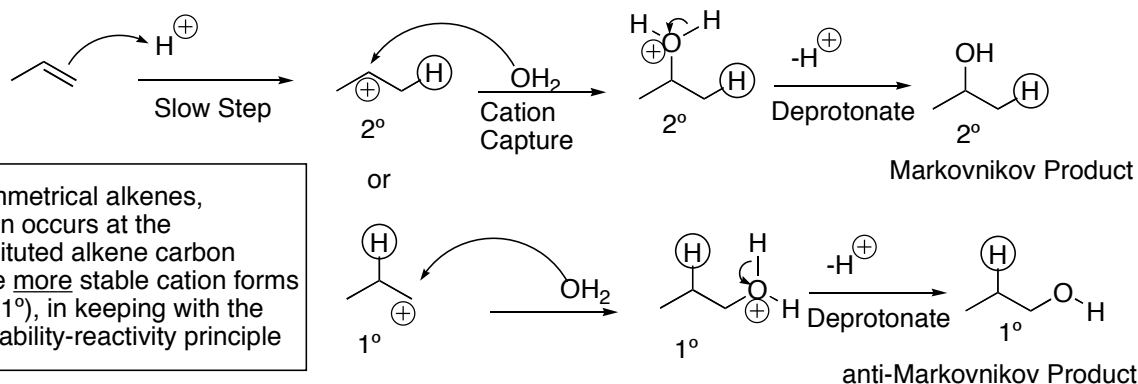
3		Markovnikov	None	<u>Be able to draw completely</u>
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Markovnikov: $\text{H}^{\delta+}\text{OH}^{\delta-} \rightarrow$ H adds to the less substituted end of the alkene, OH adds to the more substituted end

- **OH ends up on more substituted end of the alkene**

Mechanism: 3 Steps.

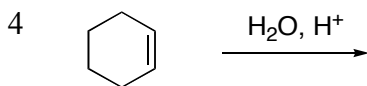
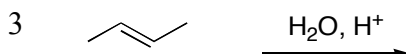
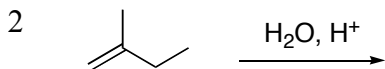
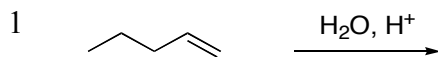
1. Protonation
2. Cation Capture
3. Deprotonation



- The sequence in which key step (cation capture in this case) is sandwiched by proton on-proton off protonation-deprotonation is super common for acid-catalyzed reactions.
 - **Whenever you see an acid-catalyzed process, expect to use H^+ in first step and to deprotonate in the last step**
- Cation stability dictates reactivity
- Cation stability explains why the Markovnikov orientation occurs. This involves the more substituted, more stable carbocation product in the rate-determining step.
- The actual reaction is an equilibrium.
 - The reverse of alcohol dehydration to make alkenes!
 - A key drive is to have excess water. That pushes the equilibrium to the alcohol side.
 - Under alcohol \rightarrow alkene conditions, the equilibrium is often driven to the alkene side by having no water, or by distilling off the lower-boiling alkene as it forms.

Examples, Predict the Products.

Does Markovnikov's Rule matter?



Problems with Acid-Catalyzed Addition of Water to Alkenes

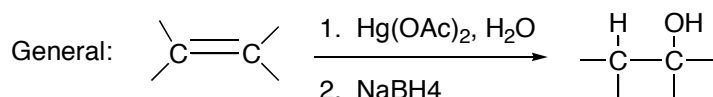
1. Alkenes with poor water solubility often don't add very well.
 - Can't drive the equilibrium strongly to the alcohol side in that case
 - Solvent mixtures can often help, but not always good enough
2. Alcohol/Alkene equilibrium sometimes poor
3. Carbocation rearrangements can be a problem
4. The degree of Markovnikov selectivity isn't always satisfactory
 - 99:1 isomer selectivity is a lot nicer than 90:10...
 - Especially if you have to purify!
5. Obviously you can't get the reverse, anti-Markovnikov alcohol products.

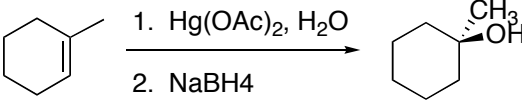
Each of these limitations, when they are a problem, can be solved by alternative recipes that indirectly add H-OH.

Draw the mechanism for the following reaction:



7.4 Indirect Markovnikov Addition of H-OH via Oxymercuration/Demercuration. Reaction 4.

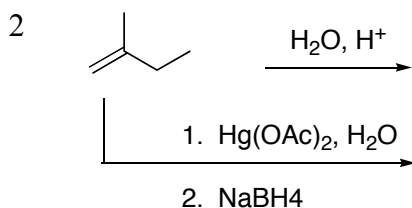
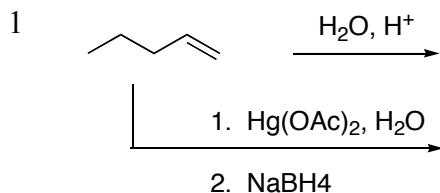


4		Markovnikov	Stereo: None	Mech: Not responsible
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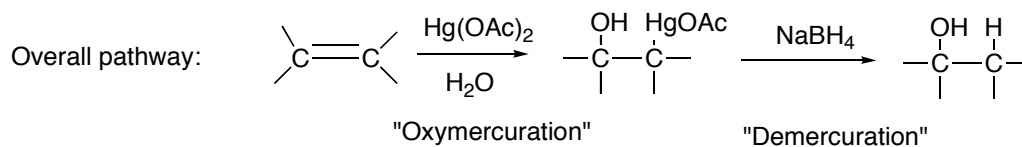
Notes:

- Often higher yields, cleaner, faster, and easier
- No restrictions
- No cation rearrangements
- Very strong**, often superior **Markovnikov selectivity**
 - OH adds to the more substituted end, H to the less substituted end

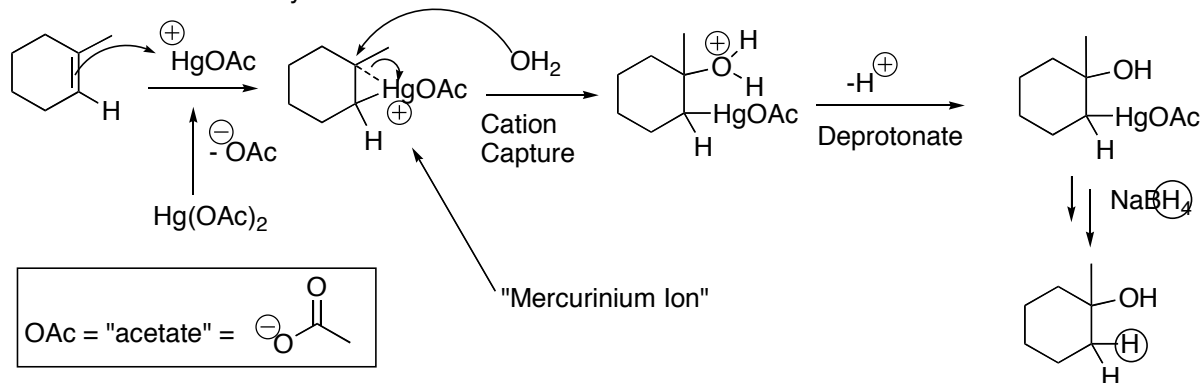
Does Markovnikov's Rule matter?

H₂O/H⁺ vs Oxymercuration/Demercuration: Which should I use?

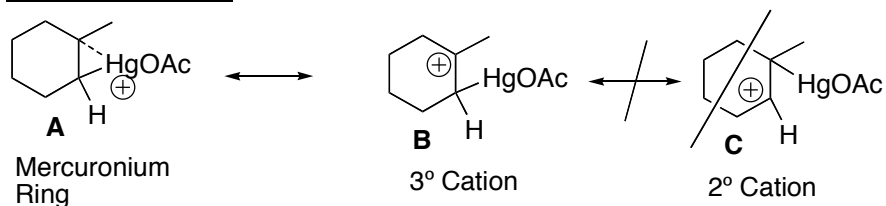
- Both normally give same product
- For predict-the-product problems, be able to handle either recipe
- For provide-the-right-recipe problems, I will accept either answer.**
 - H₂O/H⁺ is easier to write!
- In the real lab, the choice is decided on a case-by-case basis.
 - Default to H₂O/H⁺
 - Go to oxymercuration/demercuration when direct acid-catalyzed hydration doesn't work as well as you'd like

Mechanism (For interest sake. Not for memorization, not for test.)

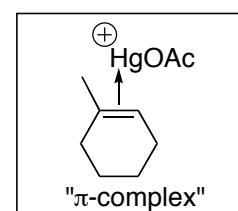
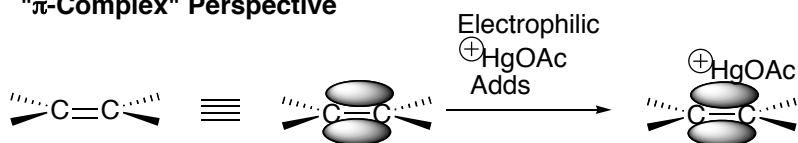
More Details for the Oxymercuration Phase

Notes:

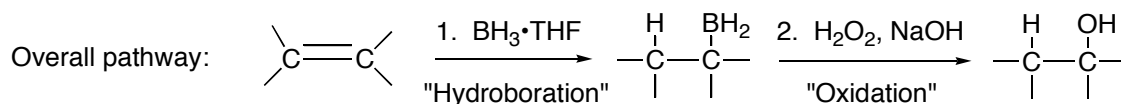
1. "demercuration" with NaBH_4 replaces the mercury with a hydrogen
2. The initial "oxymercuration" essentially adds $(\text{HgOAc})^{\delta+}(\text{OH})^{\delta-}$, and follows Markov.'s rule
3. The interesting new thing here is the "mercuronium" ion
4. This is normally drawn as a 3-ring, but can also be viewed as a resonance structure of a hybrid

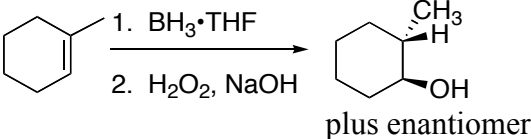
Mercuronium IonBoth participation from structures **A** and **B** are required to explain everything

- **A** explains why you don't get cation rearrangements, ever: you don't have a free carbocation
- **A** also explains structure studies, which show that the mercury is weakly bonded to the more substituted carbon
- **B** helps to explain why water adds to the more substituted carbon, which has extensive positive charge
- **C** doesn't contribute, isn't really involved
- In the real thing, there is a long, very weak and super breakable bond between mercury and the more substituted carbon. The bond to the less substituted carbon is much shorter and stronger.

" π -Complex" Perspective

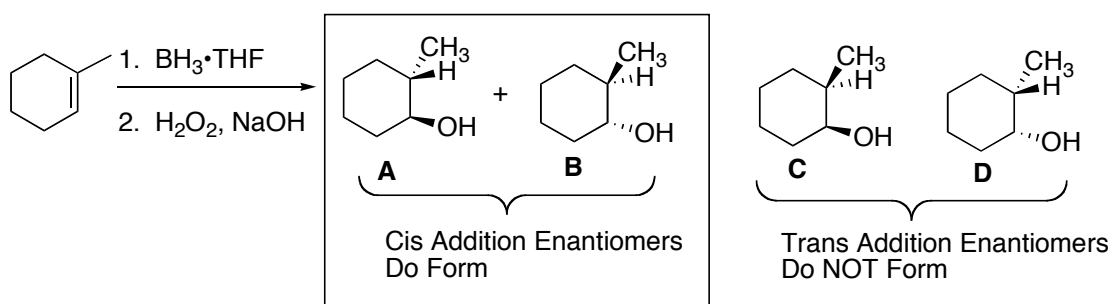
7.5 Indirect anti-Markovnikov Addition of H-OH via Hydroboration/Oxidation. Reaction 5.



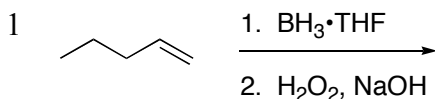
5	 <p>plus enantiomer</p>	Anti-Markovnikov	<u>Cis</u>	Not responsible
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Notes:

- Anti-Markovnikov orientation:** the OH ends up on the less substituted end of an unsymmetrical alkene; the H adds to the more substituted end
- Cis addition. Both the H and the OH add from the same side.**
- When does cis/trans addition stereochemistry matter?
 - Only when both alkene carbons turn into chiral centers in the product.
 - If one does but not both, then the relative stereochemistry doesn't matter
 - For Markovnikov additions involving H-Br or H-OH, the H usually adds to a carbon that already has an H, so that in the product it is not a stereocenter.
 - In anti-Markovnikov additions, much more common for both carbons to become chiral carbons
- Chiral products are Racemic (two enantiomers form) but not optically active**
 - When only one chiral center forms (often in the Markovnikov additions), any chiral product will always be racemic
 - When two chiral centers form, as in the example above, of the four possible stereoisomers, you get only two of them, in racemic mixture.

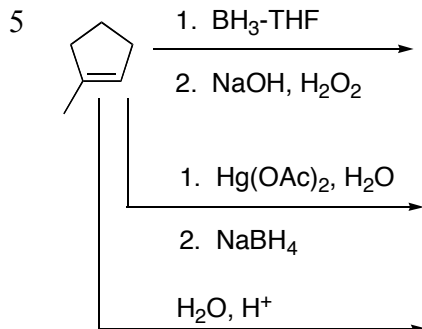
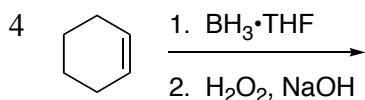
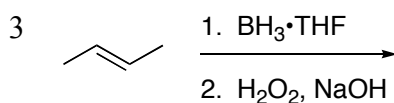
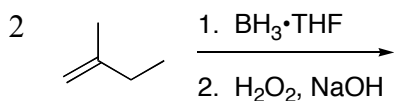


Examples, Predict the Products.

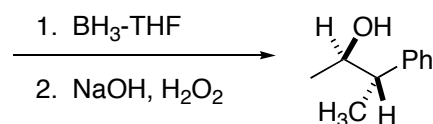
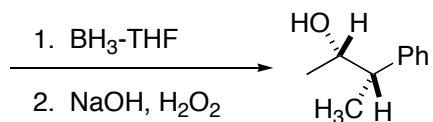


Does	Does
Markov.	Stereo
Matter?	Matter?

Does Markov. Matter?	Does Stereo Matter?
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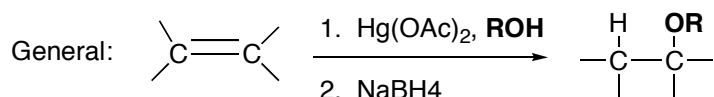
1. Which starting alkenes would produce the following products following hydroboration-oxidation? Factor in the stereochemistry of the products in considering what starting materials would work.

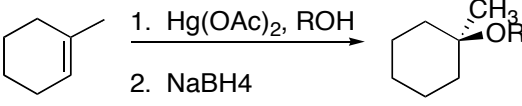


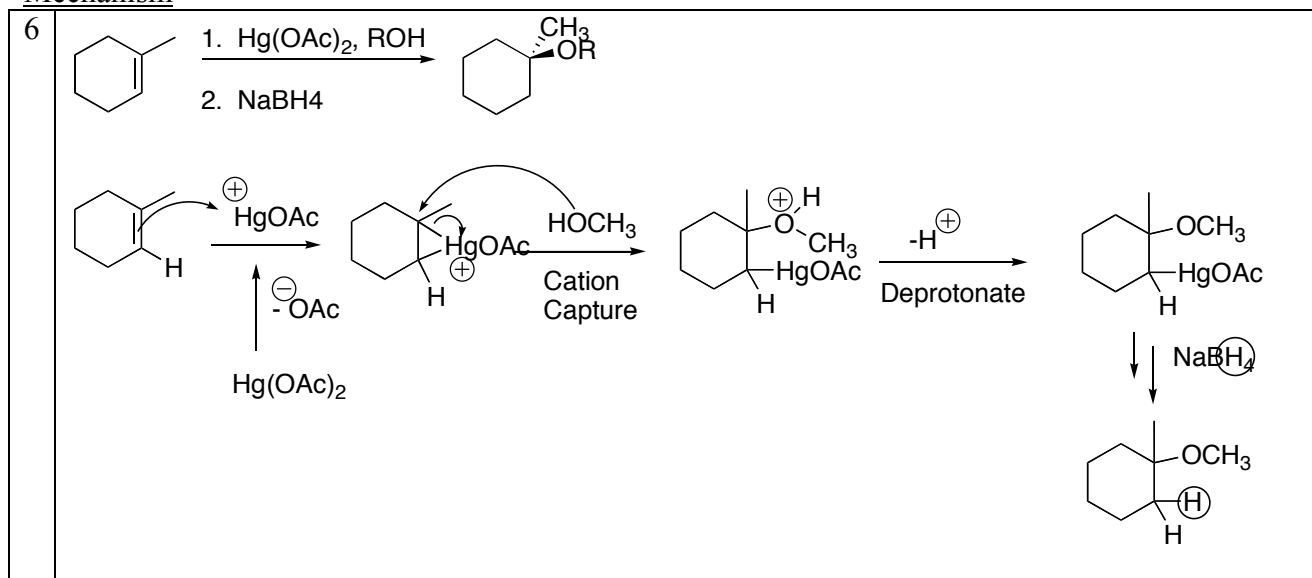
2. Fill in recipes for converting 1-butene into the three derivatives shown.



18.4; 7.4 Alkoxymercuration-Demercuration: Markovnikov Addition of H-OR (Reaction 6)

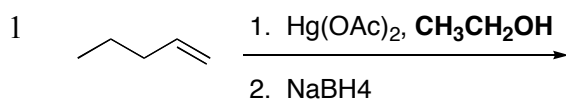


6		Markovnikov	Stereo: None	Mech: Not responsible
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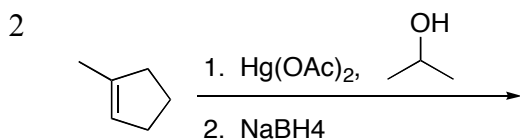
MechanismNotes:

- Everything is the **same as with oxymercuration-demercuration to form an alcohol, except you use an alcohol instead of water**
- This results in an oxygen with it's spectator carbon chain adding rather than an OH
- Strong Markovnikov orientation
 - The OR adds to the more substituted end of the alkene
 - The Hydrogen ends up on the less substituted end of the alkene
- The mechanisms are analogous.

Examples, Predict the Products.



Does Mark's Rule matter? Does Stereo?

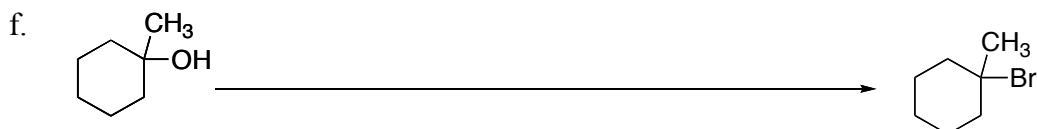
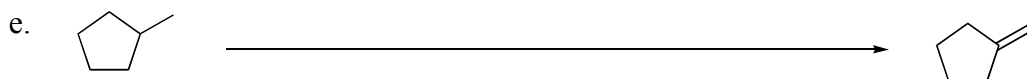
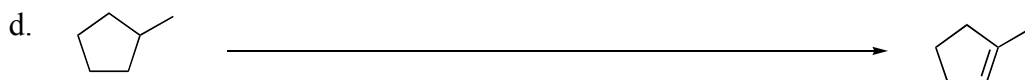
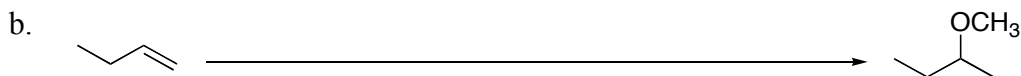
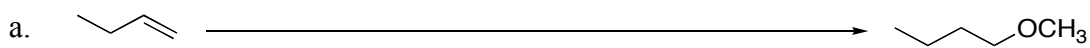


Ether Synthesis: Two Routes

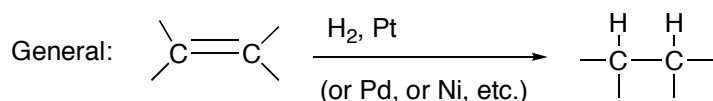
1. From Alkene and Alcohol: By Oxymercuration/Demercuration

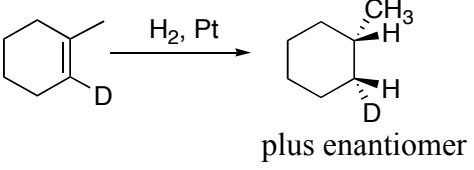
2. From R-Br and Alkoxide Anion: By S_N2 3. **Multistep Syntheses:** Design Reactants for the Following Conversions

- Note: It is often most strategic to think backward from product to precursor.
- Then think back how you could access the precursor from the starting material.
- There may sometimes be more than one suitable route.



7.7. H-H addition. Catalytic Hydrogenation (Reaction 7)



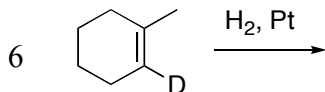
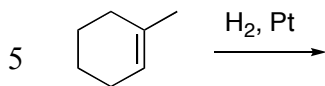
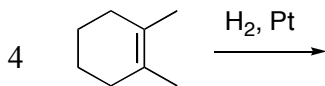
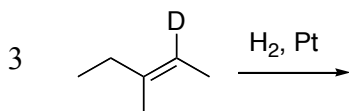
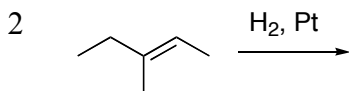
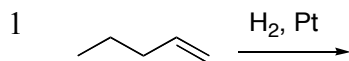
7	 <p>plus enantiomer</p>	Orientation: None	Stereo: Cis	Mech: Not responsible
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Notes:

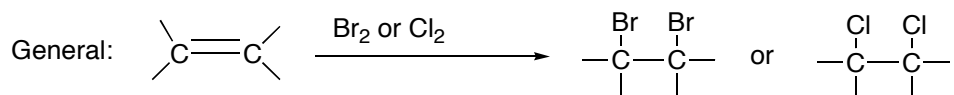
- Since both atoms adding are the same (H), Markovnikov orientation issues don't apply
 - You're adding a hydrogen to both the more and less substituted alkene carbon!
- Stereochemistry isn't often relevant, but when it is it's **cis**
 - Rarely relevant because if either alkene carbon has even one hydrogen attached, addition of an additional hydrogen will result in an achiral carbon.
- The reaction is substantially exothermic
- But some kind of transition-metal catalyst is required to activate the otherwise strong H-H bonds. Pd, Pd/C, Pt, Pt/C, PtO₂, Rh, Rh/C, Ni, Ni/C, etc all work variably well.

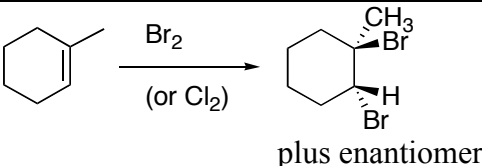
Examples, Predict the Products.

Does Mark's Rule matter? Does Stereo?



7.2 X-X Dihalogen Addition: Trans Addition (Reaction 8)



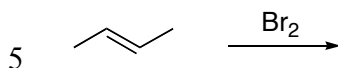
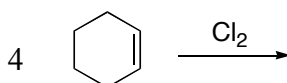
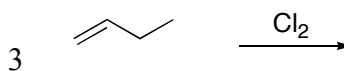
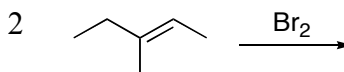
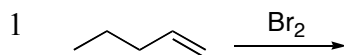
		<u>Orientation</u>	<u>Stereo</u>	<u>Mechanism</u>
8	 <p>plus enantiomer</p>	None	<u>Trans</u>	<u>Be able to draw completely</u>

Notes:

1. **Orientation: Non-issue**, since you're adding the same atom to each alkene carbon
2. **Trans addition**
3. **Solvent** matters: to get X-X addition, you need a solvent other than water or alcohol.
 - With water or alcohol, you get different products, see reaction 9

Examples, Predict the Products.

Does Mark. Matter? Does Stereo? Chiral?

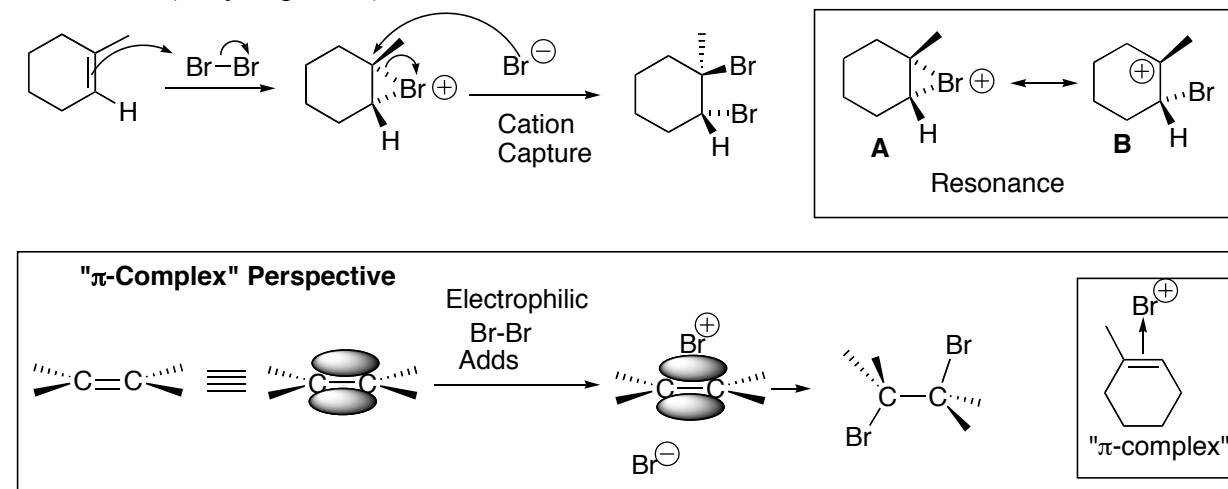
Notes:

1. Cis and trans reactants give different products!
2. For any product (in this and other reactions), be able to identify whether it is chiral or not

Chemical Test for Alkenes: Br_2 in CCl_4 solvent is reddish/brown color. Add a few drops to an unknown organic:

- If the color stays reddish/brown \rightarrow the unknown does not contain any alkenes
- If the reddish/brown color goes away \rightarrow the unknown did have an alkene that is reacting with the bromine

Mechanism (Very important)



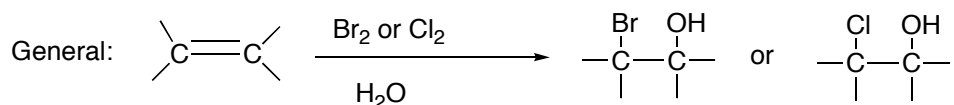
Notes

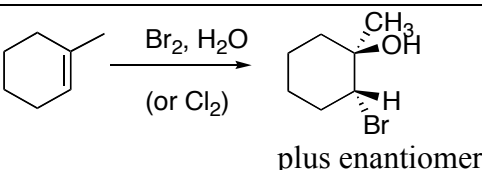
1. **Cation Formation: Step 1**
2. **Cation capture: Step 2**
3. Br_2 and Cl_2 are exceptionally good electrophiles
4. **The cation that forms is a 3-membered ring**
 - "Bromonium ion"
 - "Chloronium ion"
5. Or, it can be viewed as a π -complex, with a halogen cation sitting on a p-bond
6. When the nucleophile captures the cation, it must come in from the opposite face
 - **Backside attack, ala $\text{S}_{\text{N}}2$**
 - **Trans addition results**
7. **The nucleophile actually attacks at the more substituted carbon!**
 - This is contrary to $\text{S}_{\text{N}}2$ expectations!
8. Resonance pictures **A** and **B** help to explain things
 - a. The cyclic form **A** explains stereochemistry
 - If acyclic form **B** was all there was, you wouldn't need backside attack and you wouldn't get trans stereochemistry
 - b. Form **B** helps explain why the nucleophile attacks the more substituted carbon.
 - Of the two carbons, the more substituted one has the positive charge and is thus more electrophilic, in spite of steric issues.

Solvent Limitation: Solvents that are nucleophilic (water or alcohols...) successfully compete with bromide or chloride in the cation capture step.



7.3 Br-OH or Cl-OH Addition. Markovnikov Addition, Trans Addition, to form "Halohydrins" (reaction 9)



		<u>Orientation</u>	<u>Stereo</u>	<u>Mechanism</u>
9	 <p>plus enantiomer</p>	Markovnikov	Trans	<u>Be able to draw completely</u>

Notes:

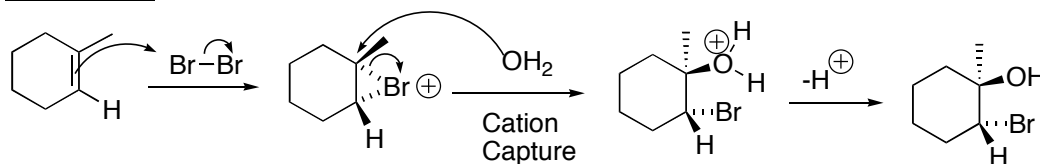
1. Markovnikov Orientation

- OH adds to more substituted alkene carbon
- Br or Cl adds to less substituted alkene carbon
- This literally follows Markovnikov's Rule, since the relative electronegativity makes for BrOH (or ClOH) is $\text{Br}\delta^+(\text{OH})\delta^-$

2. **Trans addition**

3. **Solvent** matters: whenever you see Br_2 or Cl_2 recipes, check whether there is a water (or alcohol) solvent

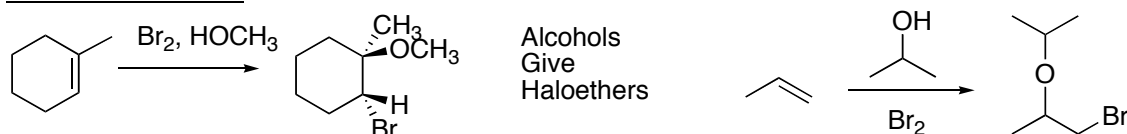
Mechanism



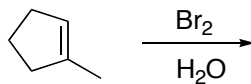
1. 3 Steps:

- bromonium formation (cation formation)
 - cation capture/nucleophile addition
 - deprotonation (since the nucleophile was neutral)
- The mechanism is closely analogous to the Br_2 or Cl_2 additions
 - Water is a better bromonium (chloronium) capture nucleophile than bromide (or chloride) anion
 - The large population of water molecules in the solvent give it a statistical advantage
 - When the bromide anion forms in step one, it is initially formed on the wrong side of the bromonium. It needs to swim around to the opposite side in order to attack. Usually water has already captured the cation before then.
 - Water really is inherently a better electron donor than bromide anion. This is why in water a proton goes onto water to make hydronium ion rather than going onto bromide to make covalent HBr
 - Notice that the water attacks the **more substituted** carbon of the bromonium (chloronium) ion

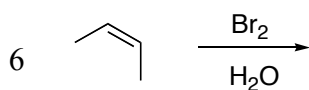
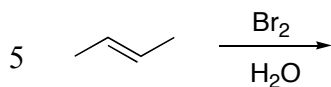
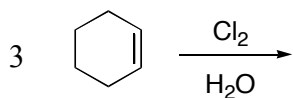
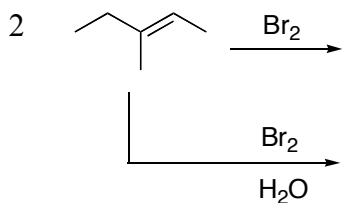
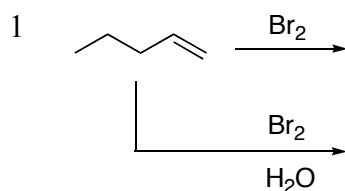
Alcohol Reactions



Draw the mechanism for the following reaction:



Examples, Predict the Products.

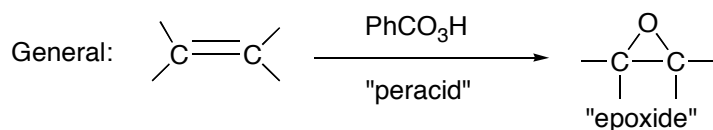


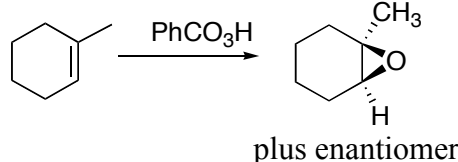
Does
Mark.
matter?

Does
Stereo?

Chiral?

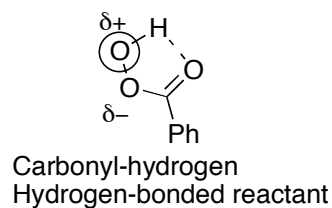
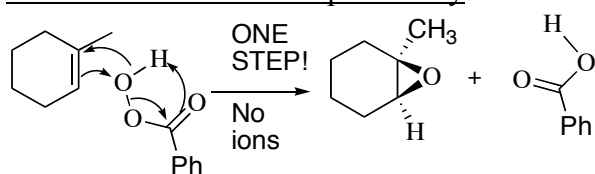
7.8 Epoxidation. Addition of one Oxygen (Reaction 10)



10	 <p>plus enantiomer</p>	None	Cis	Not responsible
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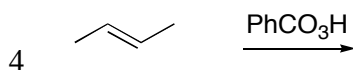
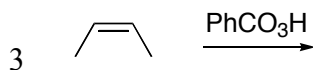
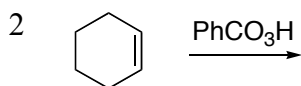
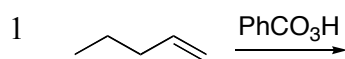
Notes:

1. No orientation issues, since the same oxygen atom connects to both bonds
2. **Cis addition: both oxygen bonds come from the same direction**

Mechanism: No test Responsibility

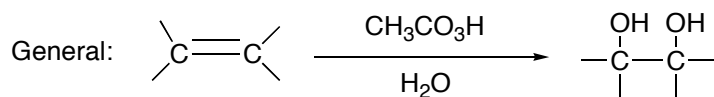
- Any peracid with formula RCO_3H has an extra oxygen relative to a carboxylic acid, and can do this reaction.
- To produce the epoxide, a non-aqueous organic solvent must be used. (If water is present, the epoxide is unstable, see reaction 10.)
- Any peracid can deposit the extra oxygen onto the p-bond to make the epoxide
- No ions are actually involved, because the leaving group is the neutral carboxylic acid

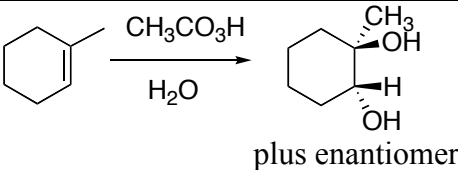
Examples, Predict the Products.



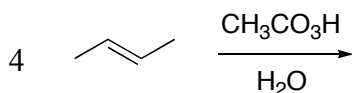
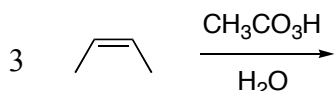
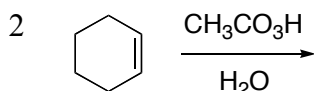
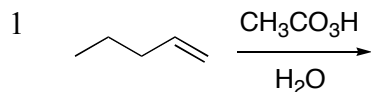
Does Mark. matter? Does Stereo? Chiral?

7.8 Trans OH-OH addition. Epoxidation in water. The initially formed epoxide undergoes Acid-Catalyzed Ring Opening. Reaction 11.



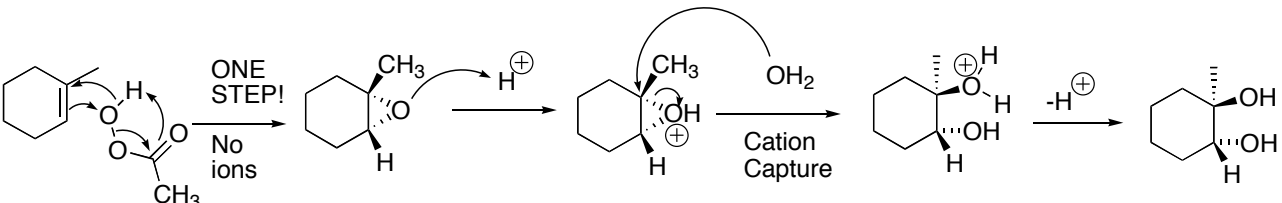
11	 <p>plus enantiomer</p>	None	<u>Trans</u>	<u>Be able to draw acid-catalyzed epoxide hydrolysis</u>
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Examples, Predict the Products.

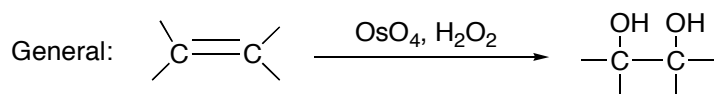


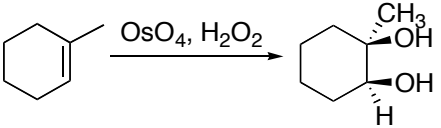
Does Mark. matter? Does Stereo? Chiral?

Mech

11	 <p>ONE STEP! No ions</p> <p>Cation Capture</p> <p>Notes:</p> <ol style="list-style-type: none"> The nucleophile (water) attacks from the more substituted end of the protonated epoxide <ul style="list-style-type: none"> More δ^+ charge there The C-O bond to the more substituted end is much weaker The nucleophile adds via $\text{S}_{\text{N}}2$-like backside attack. Inversion at the top stereocenter, but not the bottom, explains the trans stereochemistry.
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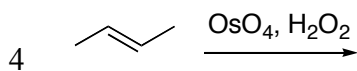
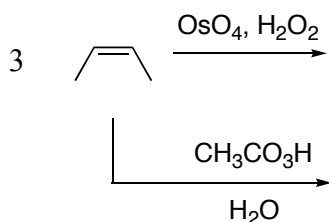
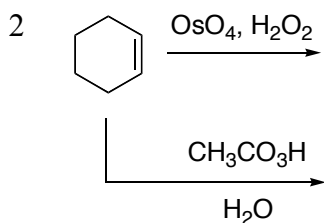
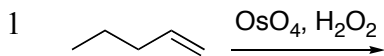
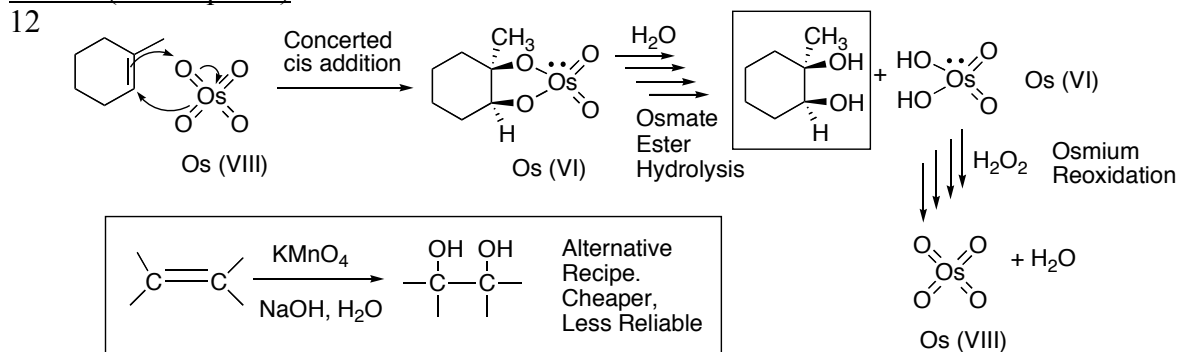
7.8 Cis OH-OH addition. Catalytic Osmylation. Reaction 12.



12	 <p>plus enantiomer</p> <ul style="list-style-type: none"> oxidant "NMO" can replace H₂O₂ 	None	Cis	Not responsible
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Examples, Predict the Products.

Does Mark. matter? Does Stereo? Chiral?

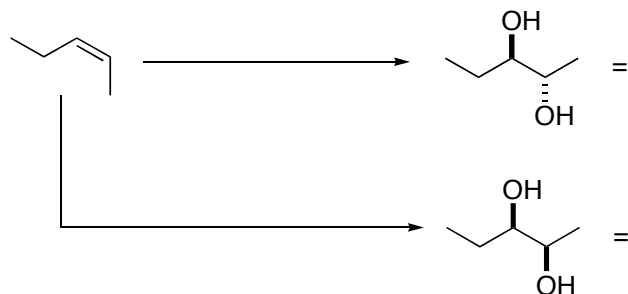
Mech: (Not required)

- An oxidizing agent, either H₂O₂ or "NMO", is used to reoxidize the osmium

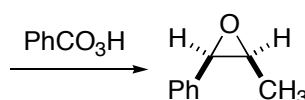
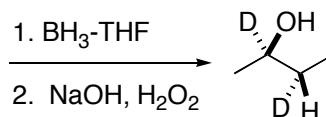
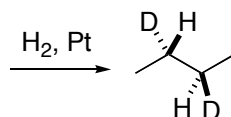
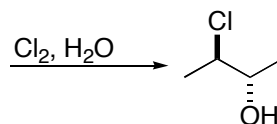
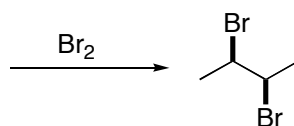
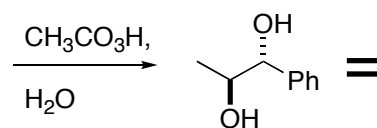
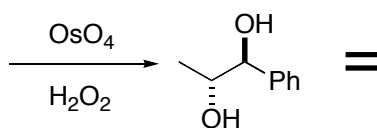
Stereochemically complementary methods

CH ₃ CO ₃ H/H ₂ O OsO ₄ /H ₂ O ₂	trans cis	Skills: a. Given starting material and product, provide reagent b. Given product and reagent, what was the starting material?
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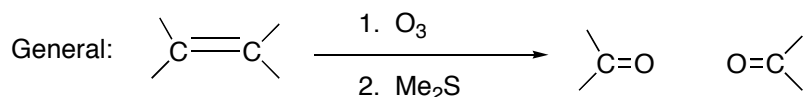
1. Given starting material and product, provide reagent. Consider stereo.

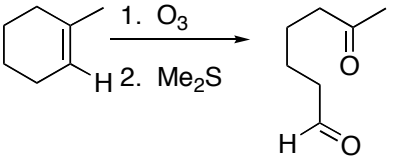


2. Stereochemistry Problems. Given product and reagent, what was the starting material?



7.9 Ozonolysis. Cleavage of Alkenes. Reaction 13

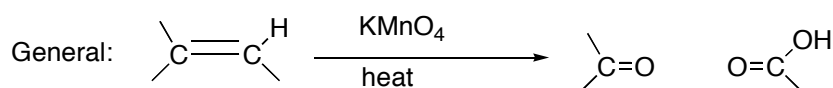


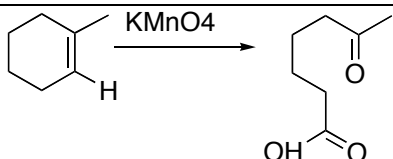
13	 <p>Note: H-bearing alkene carbon ends up as aldehyde.</p> <ul style="list-style-type: none"> • $\text{Zn/H}_3\text{O}^+$ can replace Me_2S 	None	None	Not responsible
----	---	------	------	-----------------

Notes

1. Double bond gets sliced in half
2. Get two corresponding carbonyls
3. Alkene bonds and nothing else are oxidized.
4. **Get ketones and/or aldehydes and/or formaldehyde**

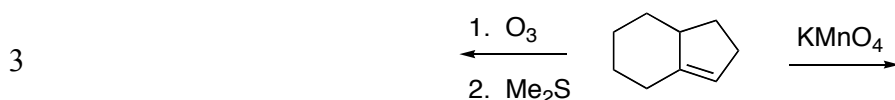
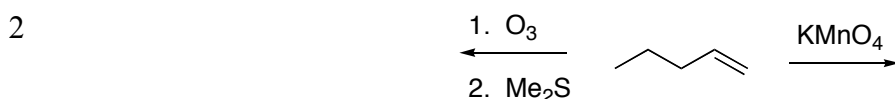
7.9 Oxidative Cleavage of Alkenes by Permanganate. Reaction 14



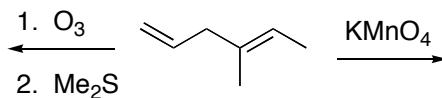
14	 <p>H-bearing alkene carbon ends as carboxylic acid</p>	None	None	Not responsible
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Notes

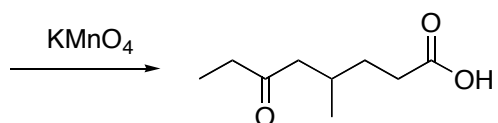
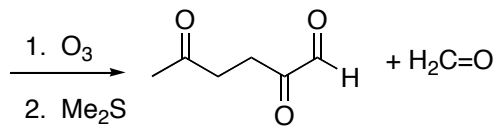
1. Double bond gets sliced in half
2. Get two corresponding carbonyls
3. Alkene C-H bonds are also oxidized to C-OH bonds.
4. **Get ketones and/or carboxylic acids and/or carbonic acid.**



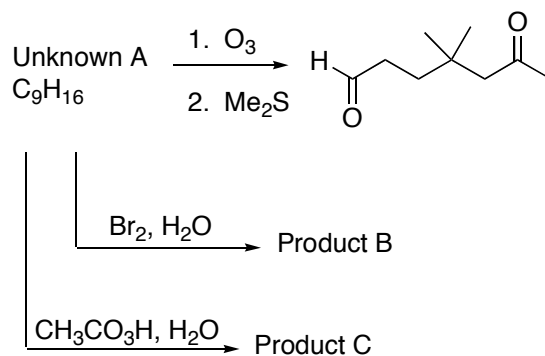
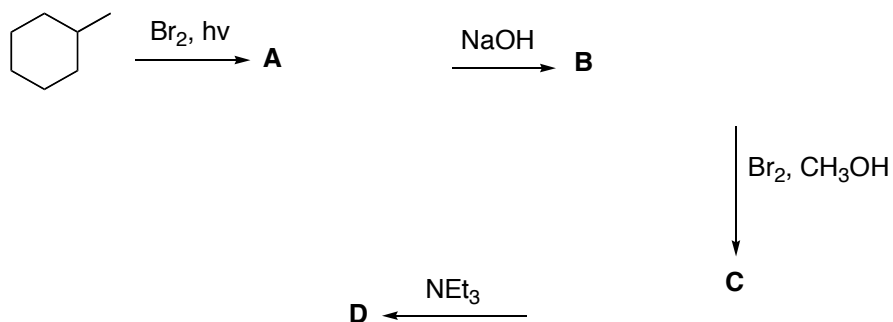
4.



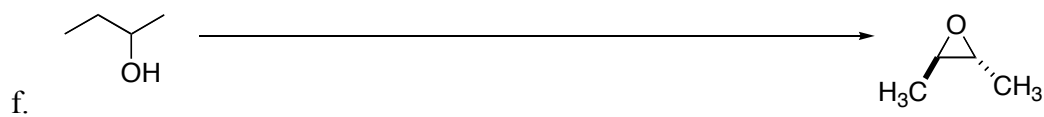
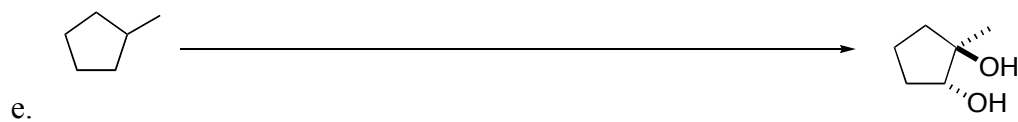
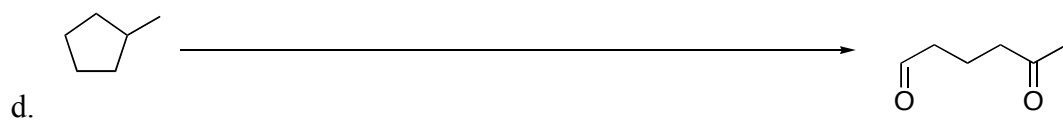
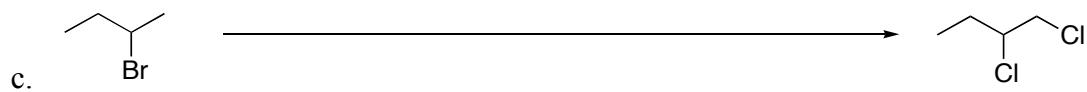
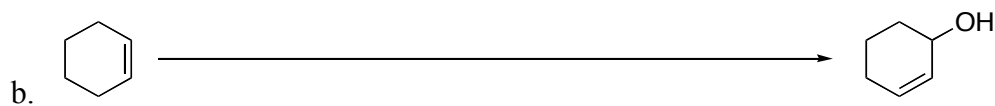
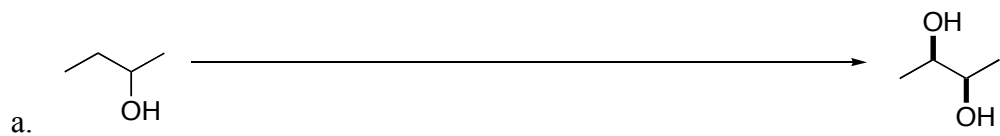
5. Identify reactants.



6. Identify A, B, and C.

Review Problems.7. "Roadmap format". Identify products **A-D**.

8. Design a synthetic plan for the following conversions. (Several on test)



9. What is a structure for C_3H_6 , if it reacts with Br_2 ?

Elements of Unsaturation Problems

10. What is a structure for $C_5H_{10}O$, if it does not react with H_2/Pt , but does react with H_2SO_4 to give 2 different isomeric alkenes C_5H_8 ?

11. What is a possible structure for C_5H_8 , if it reacts with H_2/Pt to give C_5H_{10} ?

12. Identify products **A-C**.

