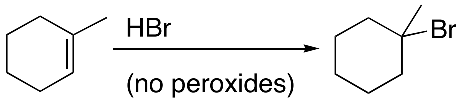
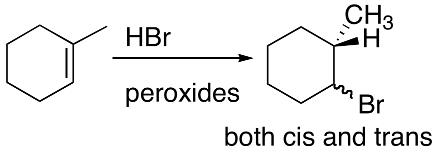
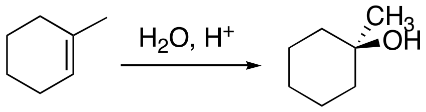
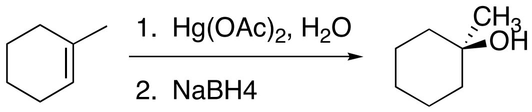
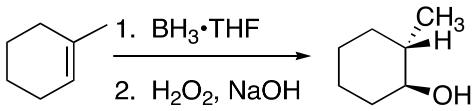
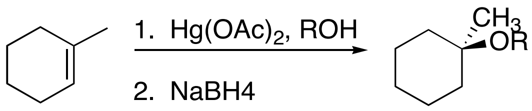
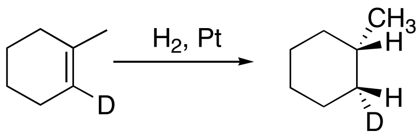
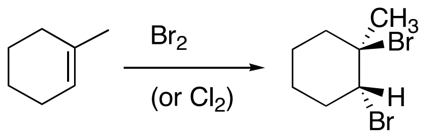
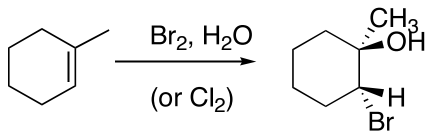
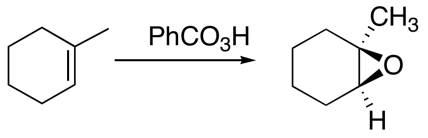
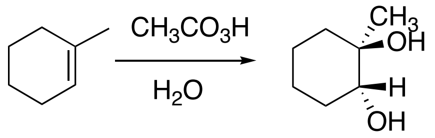
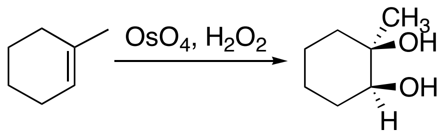
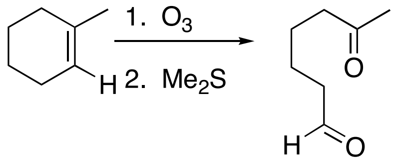
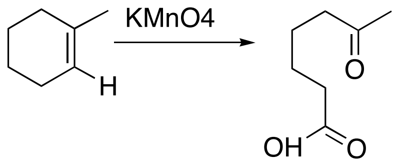
Summary of Alkene Reactions, Ch. 7. Memorize Reaction, Orientation where Appropriate, Stereochemistry where Appropriate, and Mechanism where Appropriate.

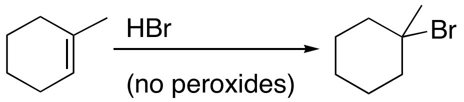
-all are drawn using 1-methylcyclohexene as a prototype alkene, because both orientation and stereochemistry effects are readily apparent.

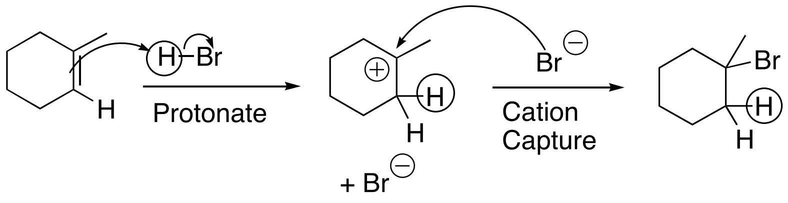
		Orientation	Stereo	Mechanism
1		Markovnikov	None	**Be able to draw completely**
2		Anti-Markovnikov	**Nonselective. Both cis and trans**	**Be able to draw propagation steps.**
3		Markovnikov	None	**Be able to draw completely**
4		Markovnikov	None	Not responsible
5		Anti-Markovnikov	**Cis**	Not responsible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

		Orientation	Stereo	Mechanism
8		None	**Trans**	**Be able to draw completely**
9		Markovnikov	**Trans**	**Be able to draw completely**
10		None	**Cis**	Not responsible
11		None	**Trans**	**Be able to draw acid-catalyzed epoxide hydrolysis**
12		None	**Cis**	Not responsible
13	 Note: H-bearing alkene carbon ends up as aldehyde.	None	None	Not responsible
14	 H-bearing alkene carbon ends as carboxylic acid	None	None	Not responsible

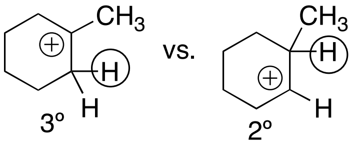
Summary of Mechanisms, Ch. 6 + 7. Alkene Synthesis and Reactions.

1





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



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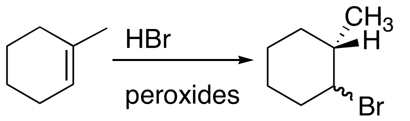
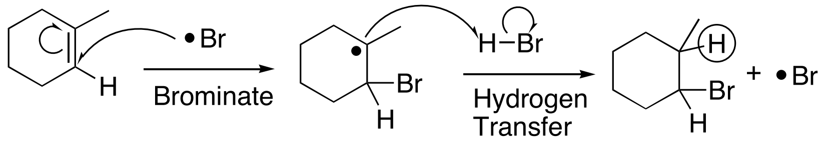
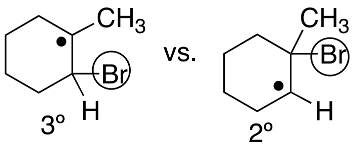


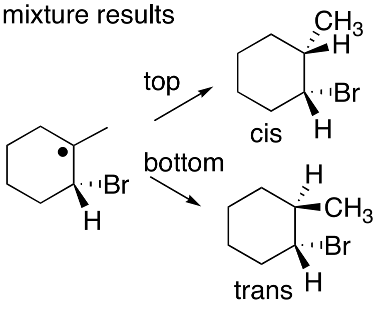
both cis and trans



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



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



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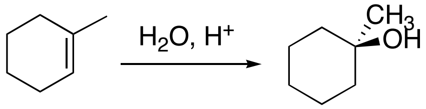
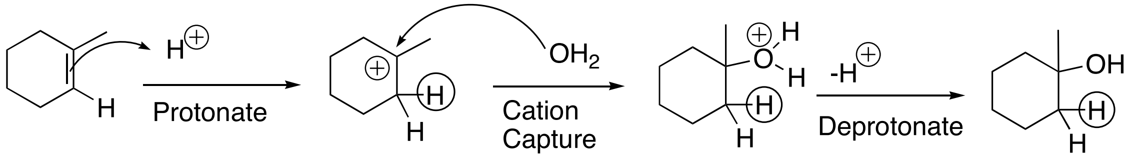
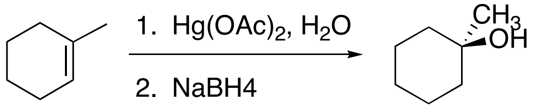
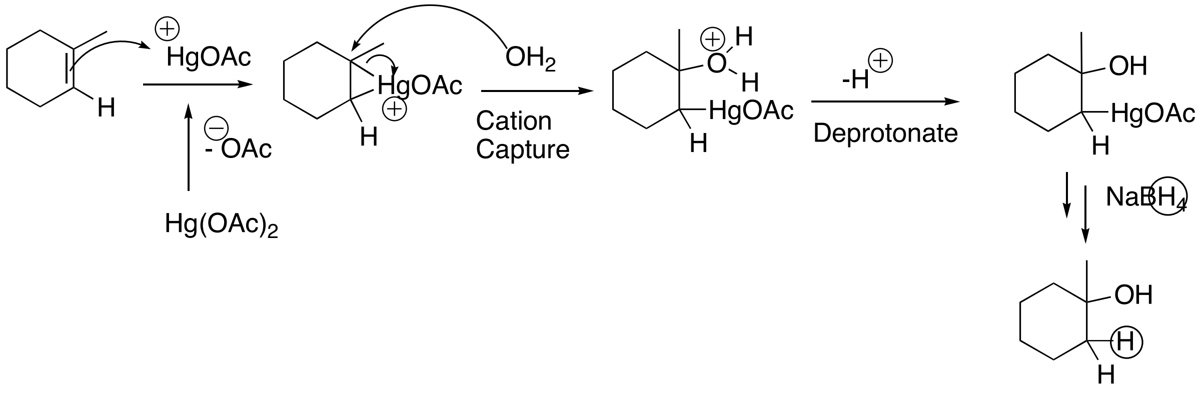




Note: For unsymmetrical alkenes, protonation again occurs at the <u>less</u> substituted end of the alkene, in order to produce the <u>more</u> stable radical intermediate (3° > 2° > 1°)

4





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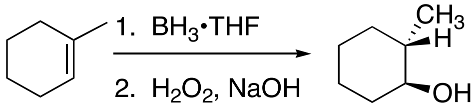
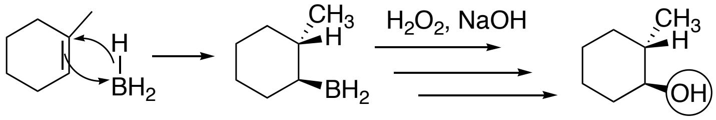
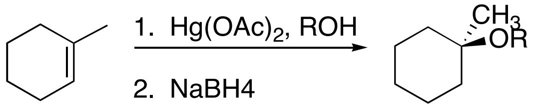
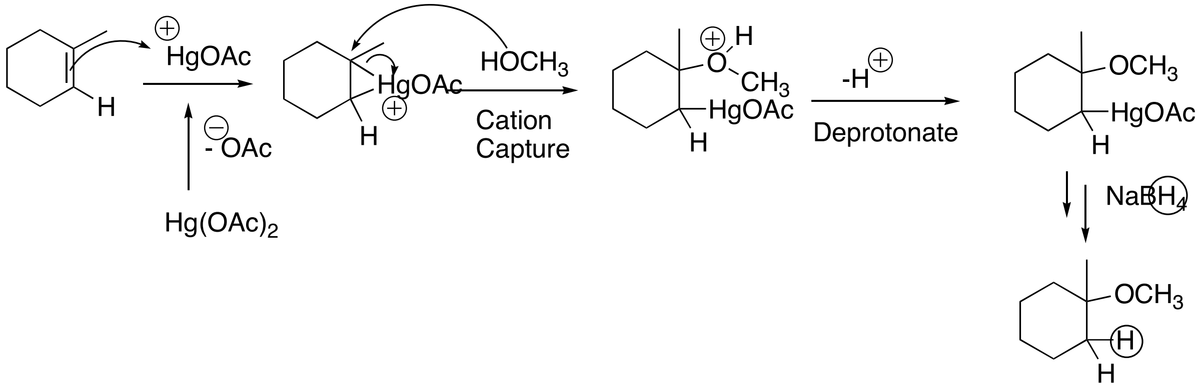




Notes
a. concerted addition of B-H across C=C
-explains the cis stereochemistry
b. the B-H addition is Markovnikov; the B is δ+, the H is δ-
c. The H_2O_2, NaOH process is complex, but replaces the B with OH with complete retention of stereochem
-the explains why the cis stereochemistry established in step one is preserved in step 2.

6





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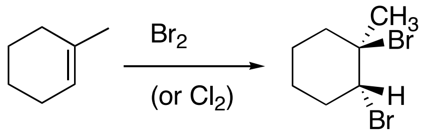
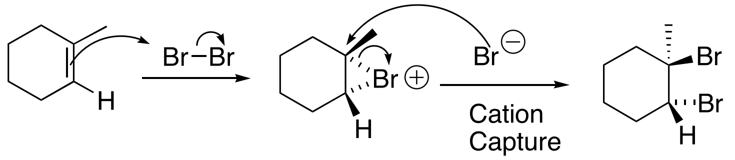
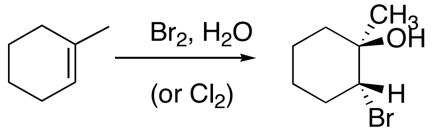
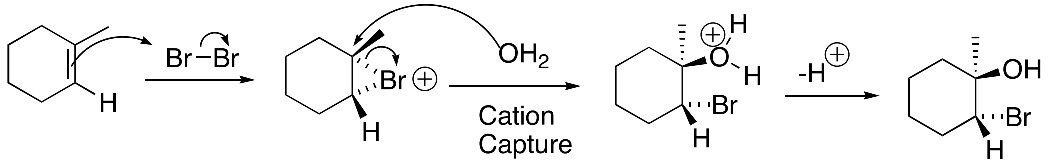




3 Notes
1. Cation intermediate is cyclic bromonium (or chloronium) ion
2. The nucleophile captures the bromonium ion via backside attack
-this leads to the trans stereochemistry
3. The nucleophile attacks the bromonium ion at the *more* substituted carbon

9

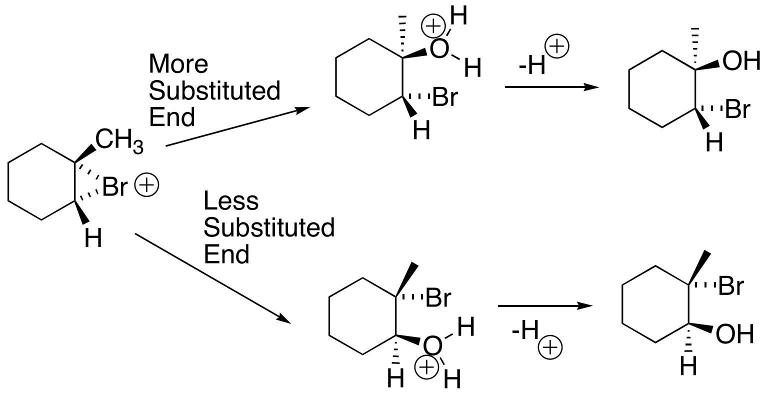




4 Notes
1. Cation intermediate is cyclic bromonium (or chloronium) ion

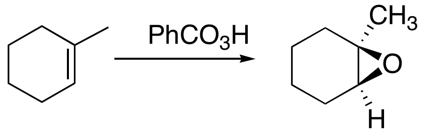
2. The nucleophile captures the bromonium ion via backside attack (ala SN2)
-this leads to the trans stereochemistry

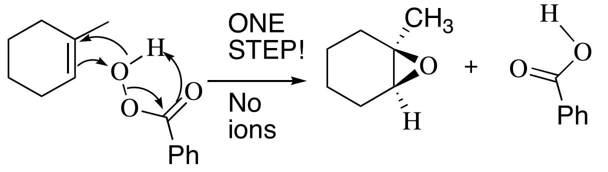
3. The nucleophile attacks the bromonium ion at the *more* substituted carbon
-this explains the orientation (Markovnikov)
a. There is more + charge at the more substituted carbon
b. The Br-C bond to the more substituted carbon is a lot weaker

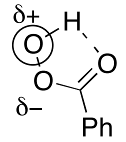


4. Alcohols can function in the same way that water does, resulting in an ether OR rather than alcohol OH.

10



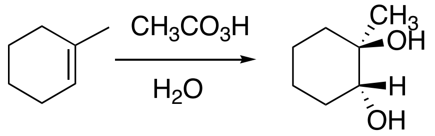


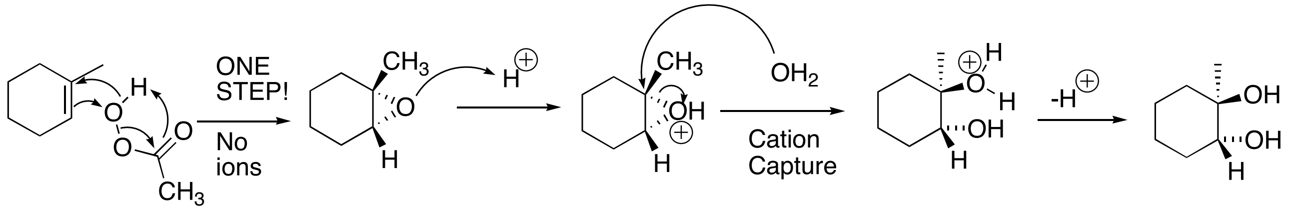


Carbonyl-hydrogen
Hydrogen-bonded reactant

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

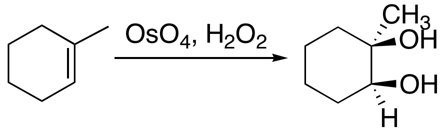
11

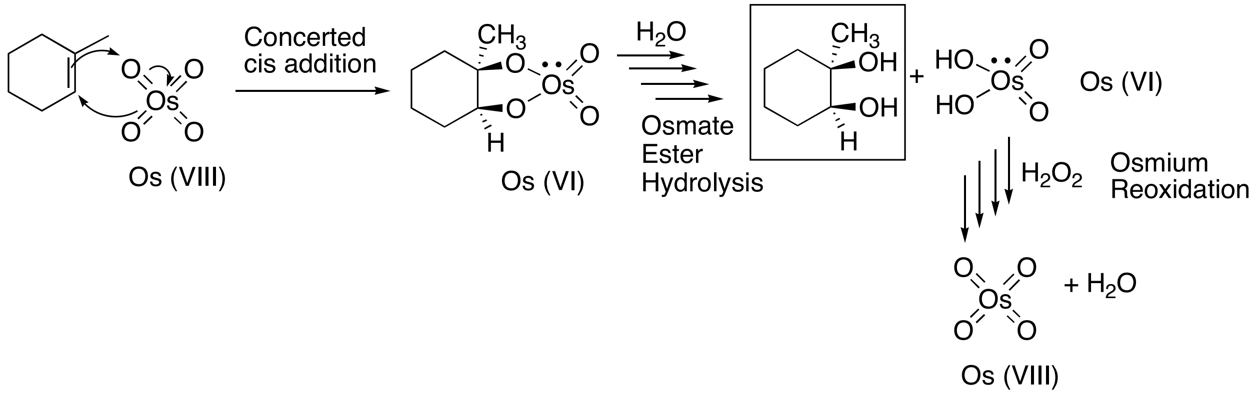




Notes:
a. The nucleophile (water) attacks from the more substituted end of the protonated epoxide
  - More δ+ charge there
  - The C-O bond to the more substituted end is much weaker
b. The nucleophile adds via S$_N$2-like backside attack. Inversion at the top stereocenter, but not the bottom, explains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

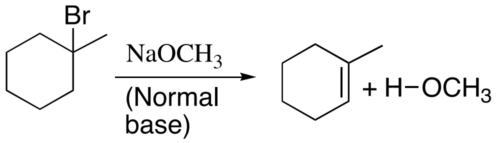
12



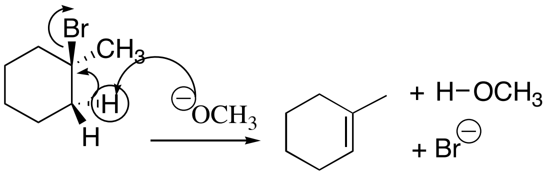


Chapter 7 Reactions and Mechanisms, Review

E2 On R-X, Normal Base

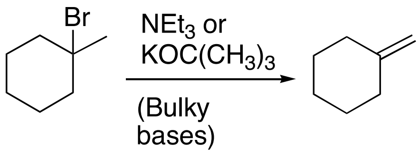


Mech:

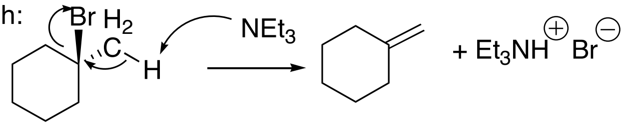


Notes
1. Trans hydrogen required for E2
2. Zaytsev elimination with normal bases
3. For 3° R-X, E2 only. But with 2° R-X, S_N2 competes (and usually prevails)
4. Lots of "normal base" anions.

E2, On R-X, Bulky Base



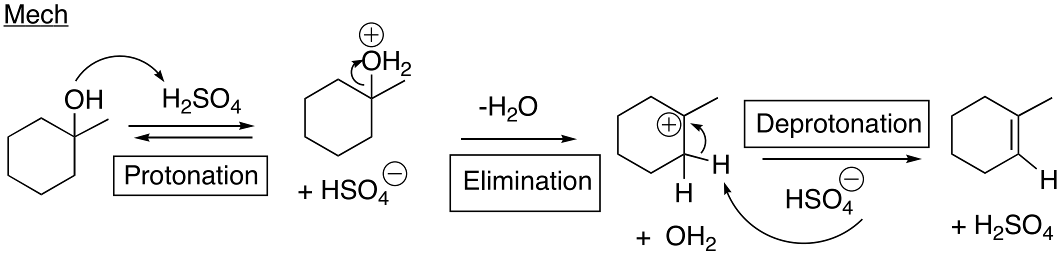
Mech:



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 NEt_3 and $KOC(CH_3)_3$ as bulky bases.

Acid-Catalyzed E1-Elimination Of Alcohols

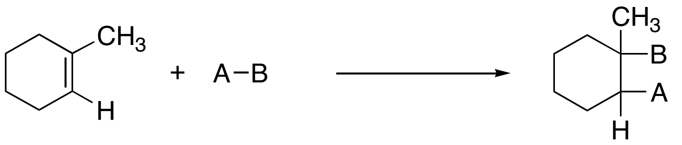
Mech



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

Ch. 6, 7 Reactions of Alkenes

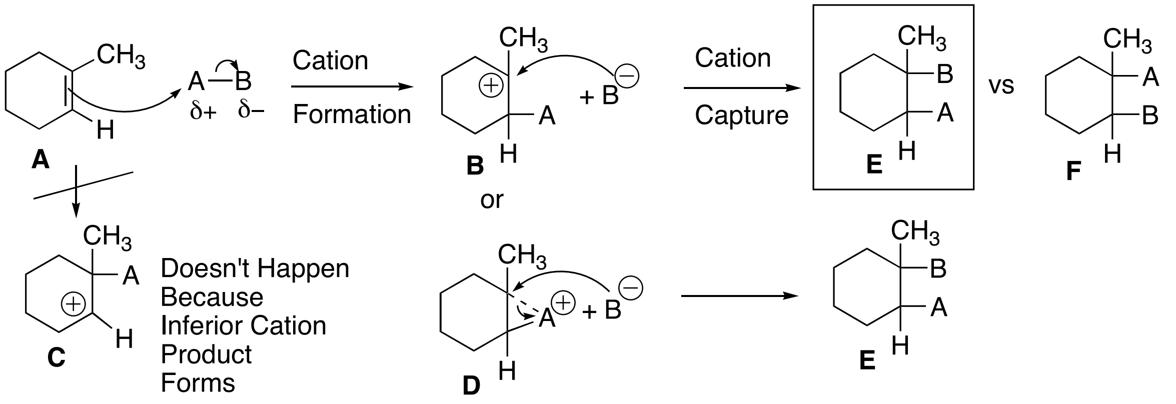
Introduction: 6.8



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 Mechanism



2 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 → B** or **A → 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

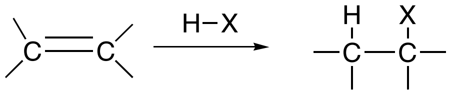
2. Relative Stereochemistry
    - Matters only if both the first and the second alkene carbons are transformed into chiral centers

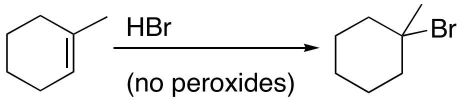
3. Mechanism

4. Relative Reactivity of Different Alkenes
    - Stability of cation formed is key

6.8,9 H-X Hydrogen Halide Addition: Ionic/Cationic Addition in the Absence of Peroxides (Reaction 1)

General:



		Orientation	Stereo	Mechanism
1		Markovnikov	None	**Be able to draw completely**

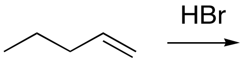
Markovnikov's Rule (For Predicting Products): When H-X (or any unsymmetrical species $A^{\delta+}B^{\delta-}$) adds to an unsymmetrical alkene:

- 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?

1



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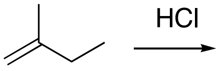

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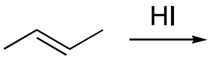

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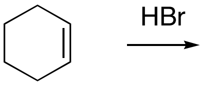

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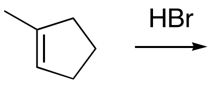

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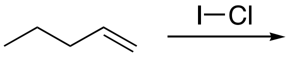
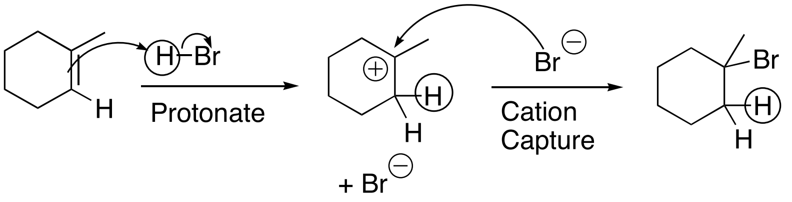
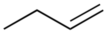


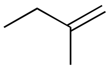
Mechanism

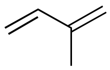


- Protonate first
- Capture cation second
- Cation formaton (step 1) is the slow step

Rank the Reactivity of the following toward HBr addition.



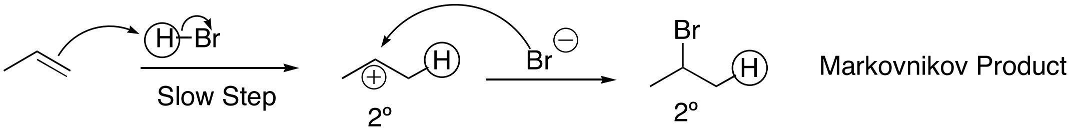




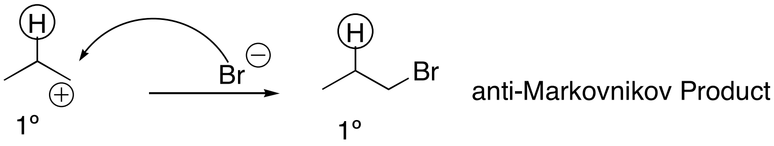
Issue:

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

- Formation of the most stable carbocation results in Markovnikov orientation

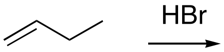


For unsymmetrical alkenes, protonation occurs at the less substituted alkene carbon so that the more stable cation forms (3° > 2° > 1°), in keeping with the product stability-reactivity principle

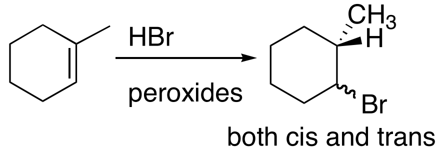


- This same logic applies anytime something adds to an alkene.
- You want to make the best possible intermediate in the rate-determining step.

Draw the mechanis for the following reaction:

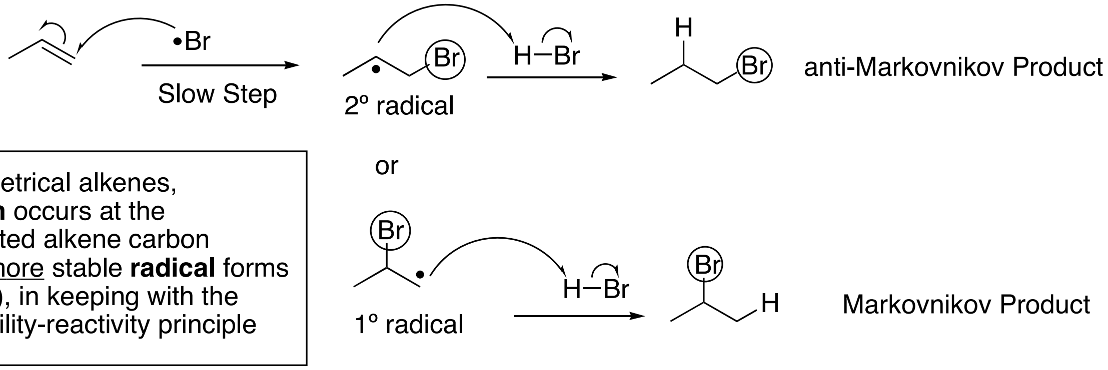


Rxn 2. Anti-Markovnikov Radical Addition of HBr with Peroxide Initiator: (no book)

2		Anti-Markovnikov	**Nonselective. Both cis and trans**	**<u>Be able to draw propagation steps.</u>**

- 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.

<u>Mechanism, and Reason for AntiMarkovnikov Orientation</u>

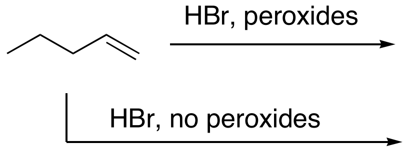


For unsymmetrical alkenes, **bromination** occurs at the <u>less</u> substituted alkene carbon so that the <u>more</u> stable **radical** forms (3° > 2° > 1°), in keeping with the product stability-reactivity principle

Examples, Predict the Products.

Does Markovnikov's Rule matter?

1



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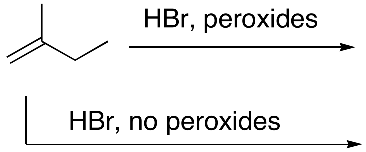

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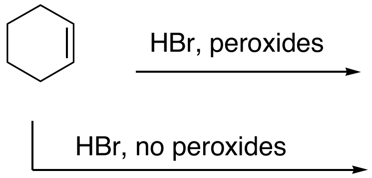
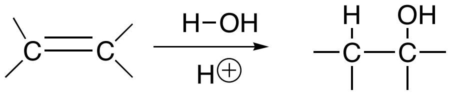
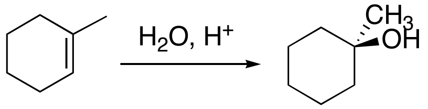


7.4 Addition of H-OH. Direct acid-catalyzed addition. (Reaction 3)

General:



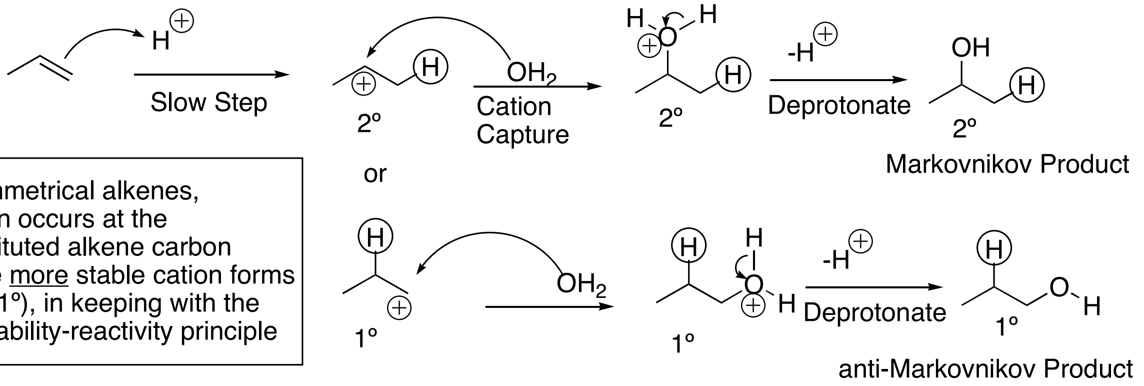
3		Markovnikov	None	**Be able to draw completely**

Markovnikov: $H^{\delta+}OH^{\delta-}$ → 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



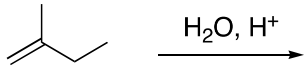
For unsymmetrical alkenes, protonation occurs at the less substituted alkene carbon so that the more stable cation forms (3° > 2° > 1°), in keeping with the product stability-reactivity principle

- 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 → 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?

1


2


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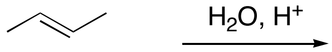

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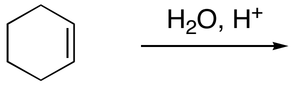

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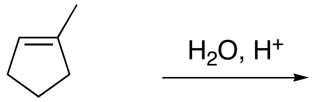
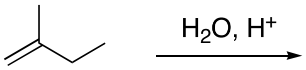


Problems with Acid-Catalyzed Addition of Water to Alkenes

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…
        - o Especially if you have to purify!
5. Obviously you can't get the reverse, anti-Markovnikov alcohol products.

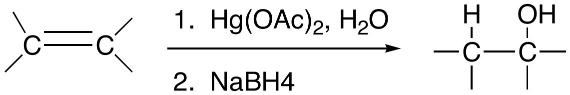
Each of these limitations, when they are a problem, can be solved by alternative recipes that indirectly add H-OH.

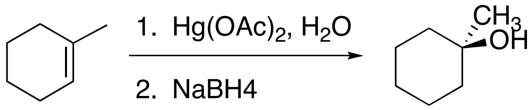
Draw the mechanism for the following reaction:



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

General:



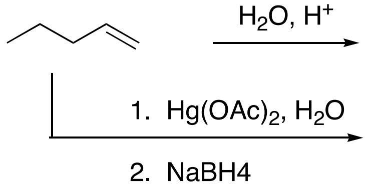
4		Markovnikov	Stereo: None	Mech: Not responsible

Notes:

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

Does Markovnikov's Rule matter?

1



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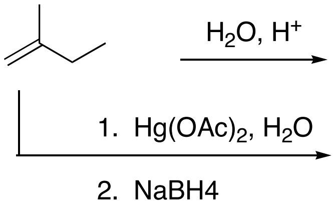
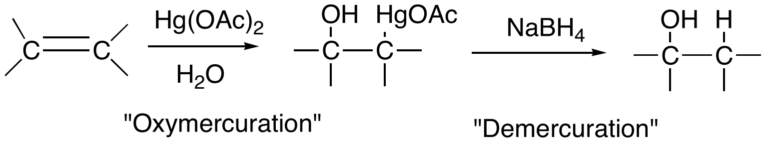


H_2O/H^+ vs Oxymercuration/Demercuration: Which should I use?

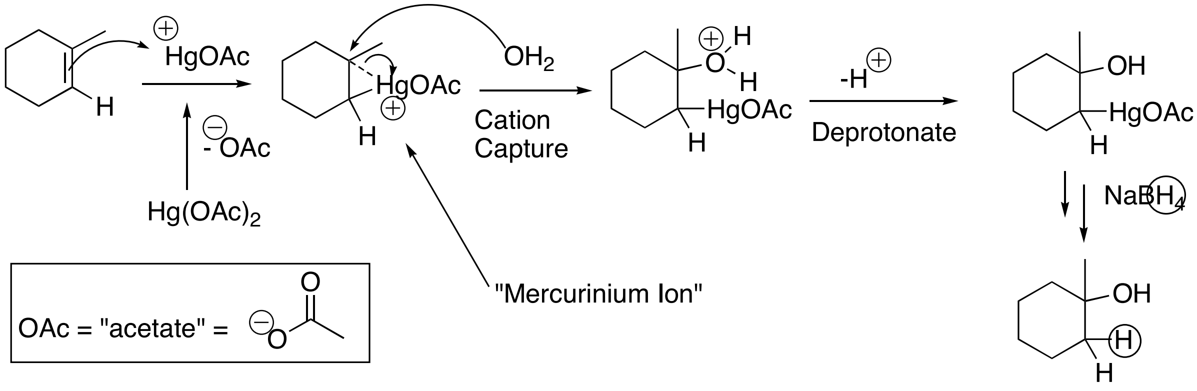
- Both normally give same product
- For predict-the-product problems, be able to handle either recipe
- **For provide-the-right-recipe problems, I will accept either answer.**
  - H_2O/H^+ is easier to write!
- In the real lab, the choice is decided on a case-by-case basis.
  - Default to H_2O/H^+
  - 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.)

Overall pathway:



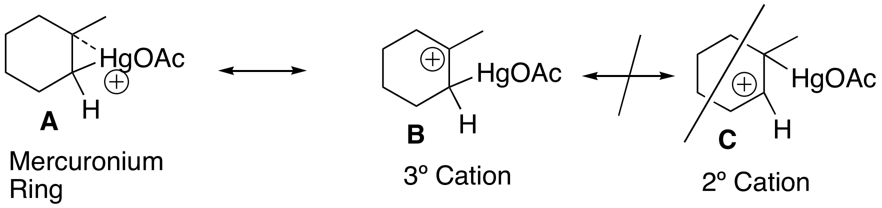
More Details for the Oxymercuration Phase



Notes:

1. "demercuration" with NaBH4 replaces the mercury with a hydrogen
2. The initial "oxymercuration" essentially adds $(HgOAc)^{\delta+}(OH)^{\delta-}$, 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

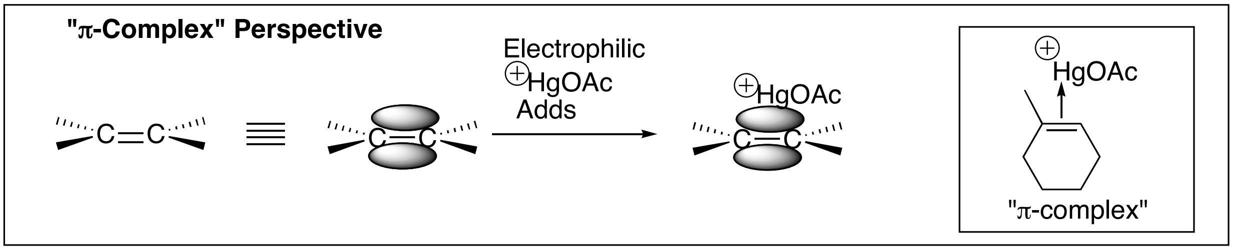
Mercuronium Ion



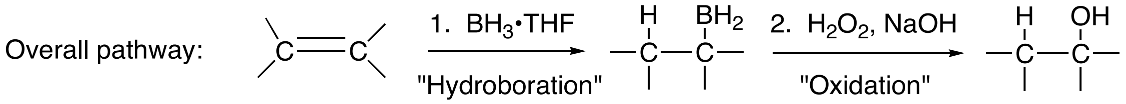
Both participation from structures **A** and **B** are required to explain everything

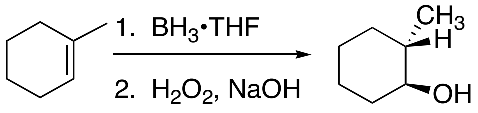
- **A** explains why you don't get cation rearrangments, ever: you don't have a free carbocation
- **A** also explains structure studies, which show that the mercury is weakly bonded to the more substituted carbon
- **B** helps to explain why water adds to the more substituted carbon, which has extensive 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.



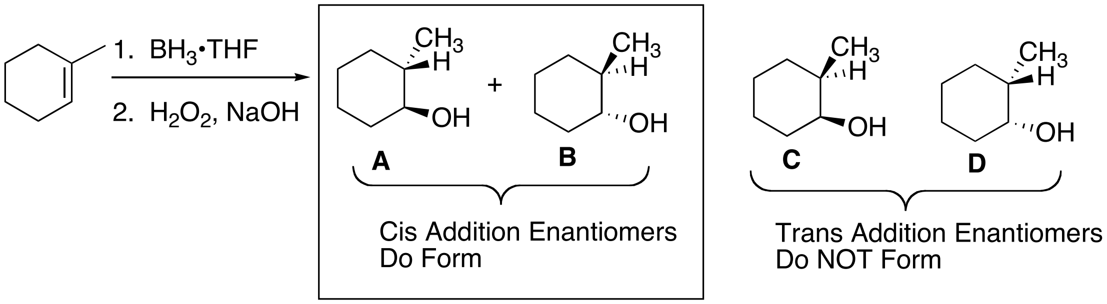
7.5 Indirect anti-Markovnikov Addition of H-OH via Hydroboration/Oxidation. Reaction 5.



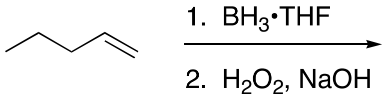
5	 plus enantiomer	Anti-Markovnikov	**<u>Cis</u>**	Not responsible

Notes:

1. **<u>Anti-Markovnikov orientation</u>**: the **<u>OH ends up on the less substituted end</u>** of an unsymmetrical alkene; the H adds to the more substituted end
2. **<u>Cis addition. Both the H and the OH add from the same side</u>**.
3. When does cis/trans addition stereochemistry matter?
   - Only <u>when both alkene carbons turn into chiral centers</u> 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
4. **<u>Chiral products are Racemic (two enantiomers form) but not optically active</u>**
   - 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.

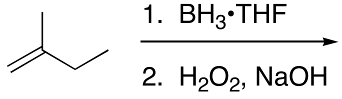


Examples, Predict the Products.

	Does Markov. Matter?	Does Stereo Matter?
1 		

Does Markov. Matter?

Does Stereo Matter?

2


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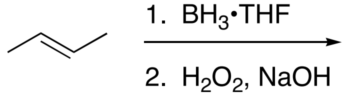

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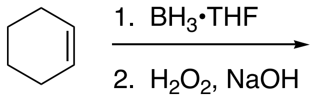

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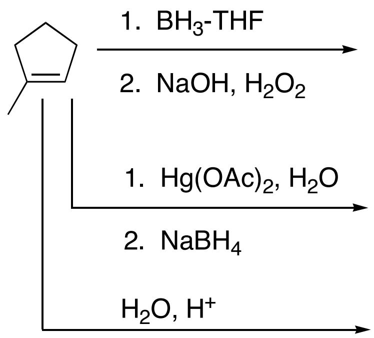
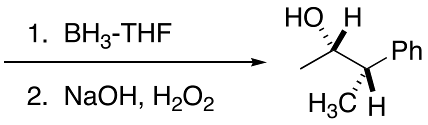
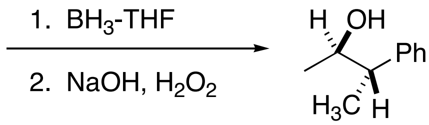


1. Which starting alkenes would produce the following products following hydroboration-oxidation? Factor in the stereochemistry of the products in considering what starting materials would work.

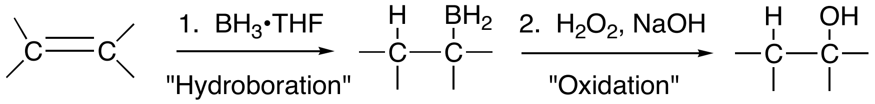




2. Fill in recipes for converting 1-butene into the three derivatives shown.

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

Overall pathway:



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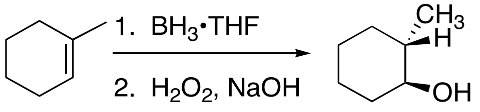
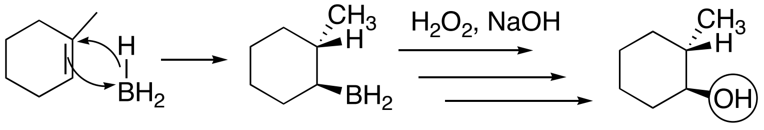
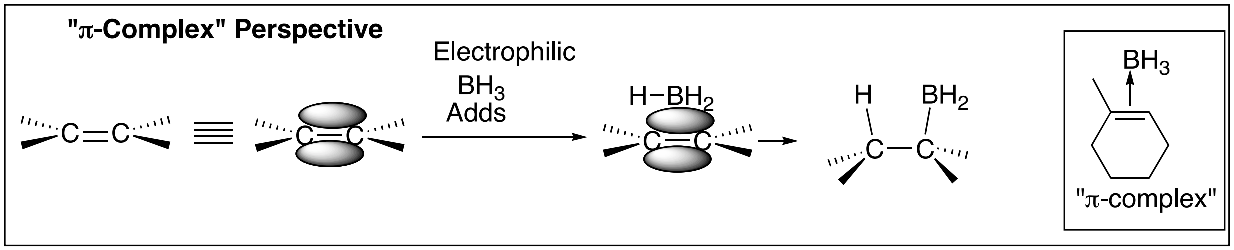
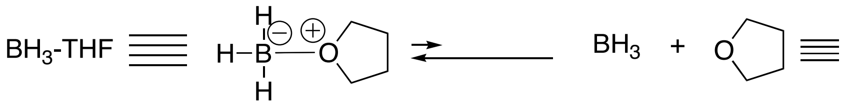








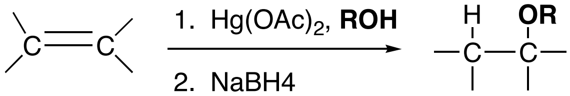
"THF" = Tetrahydrofurn

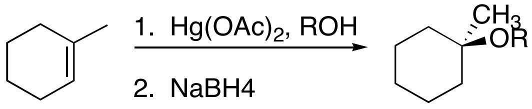
Notes

1. Free BH_3 is actually the electrophile
2. Because **BH_3 doesn not have octet rule**, the boron is very **electrophilic** for an extra electron pair
3. BH_3-THF is a convenient complex in which the oxygen provides the extra electron pair. But the complex is weak, and always provides a small equilibrium amount of free, reactive BH_3
4. The electrophilic boron originally makes a π-complex, but then you get actual hydroboration via a 4-centered ring
5. The key is that both the boron and the hydrogen enter from the same side of the alkene
    - **concerted addition of B-H across C=C**
    - **cis addition**
6. Why do you get the orientation?
    - the B-H addition actually does follow Markovnikov's rule
        - $H_2B\delta+H\delta-$ The B is δ+, the H is δ-, because boron is a semi-metal and less electronegative than hydrogen! The only case this chapter where the hydrogen is δ- rather than δ+
    - Sterics: The Boron end is pretty big, so it prefers to go to the less substituted, less hindered end of the alkene for steric as well as electronic reasons.
7. The NaOH/H_2O_2 workup is complex and beyond our scope, but replaces the B with OH with complete retention of stereochem
    - the cis stereochemistry established in the hydroboration one is preserved in the oxidation.

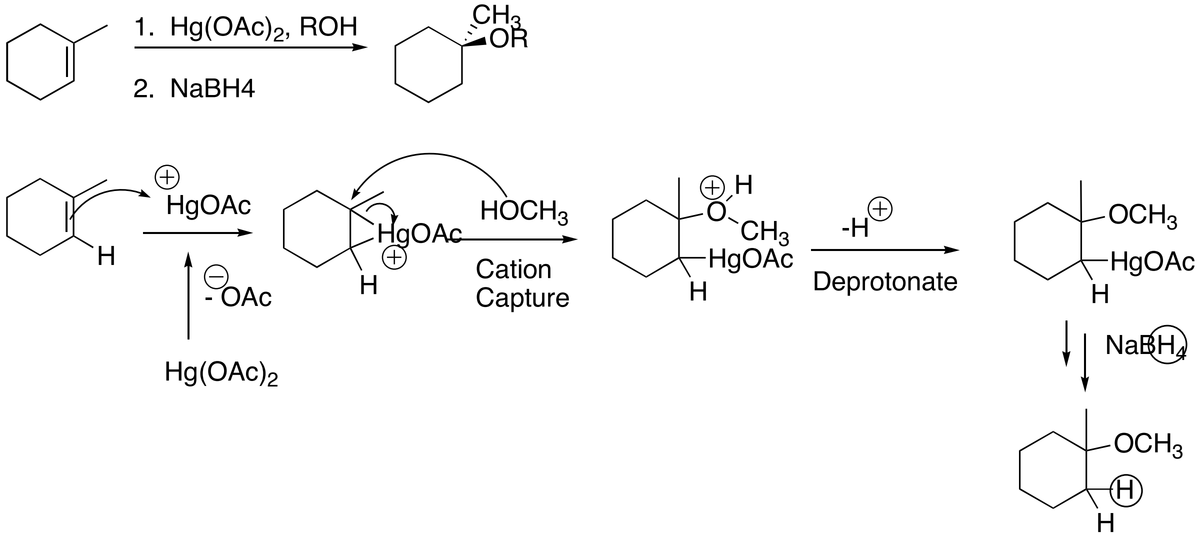
18.4; 7.4 Alkoxymercuration-Demercuration: Markovnikov Addition of H-OR (Reaction 6)

General:



6		Markovnikov	Stereo: None	Mech: Not responsible

Mechanism

6	

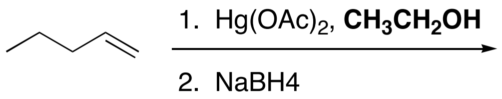
Notes:

1. Everything is the **<u>same as with oxymercuration-demercuration to form an alcohol, except you use an alcohol instead of water</u>**
2. This results in an oxygen with it's spectator carbon chain adding rather than an OH
3. 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
4. The mechanisms are analogous.

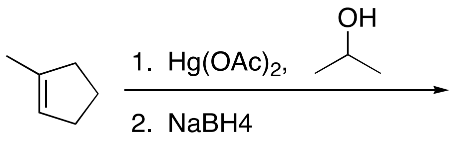
Examples, Predict the Products.

Does Mark's Rule matter? Does Stereo?

1



2

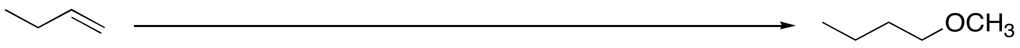


Ether Synthesis: Two Routes

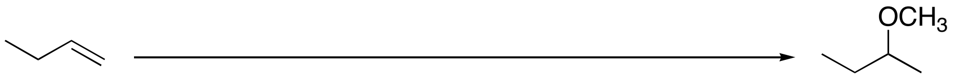
1. From Alkene and Alcohol: By Oxymercuration/Demercuration
2. From R-Br and Alkoxide Anion: By S_N2

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.

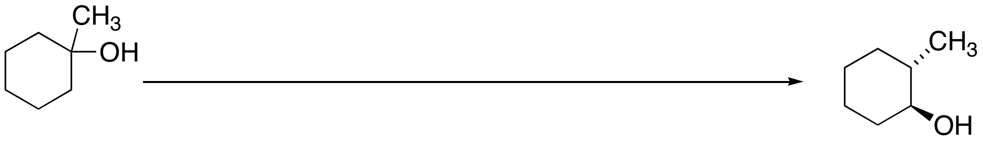
a.



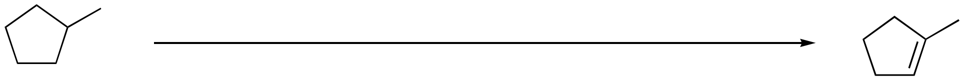
b.



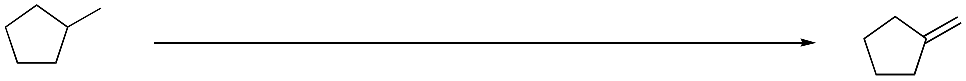
c.



d.

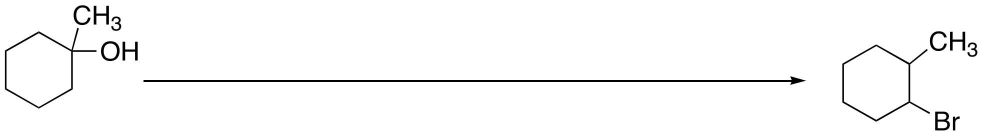


e.



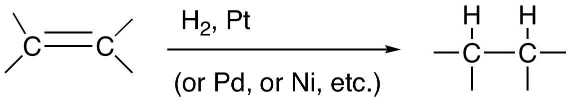
f.

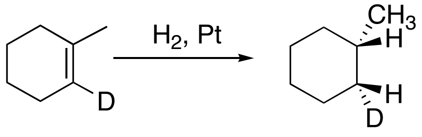
g.



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

General:



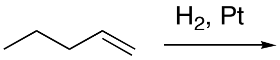
7	 plus enantiomer	Orientation: None	Stereo: **Cis**	Mech: Not responsible

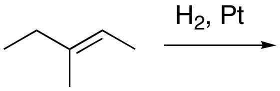
Notes:

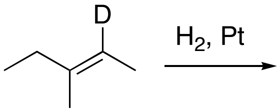
1. Since both atoms adding are the same (H), Markovnikov orientation issues don't apply
   - You're adding a hydrogen to both the more and less substituted alkene carbon!
2. Stereochemistry isn't often relevant, but when it is it's **cis**
   - Rarely relevant because if either alkene carbon has even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

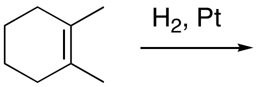
Examples, Predict the Products.

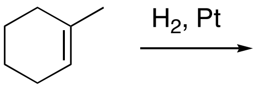
	Does Mark's Rule matter?	Does Stereo?

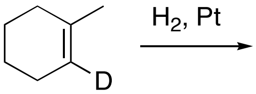
1 

2 

3 

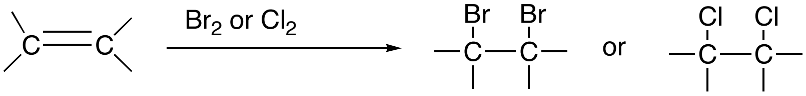
4 

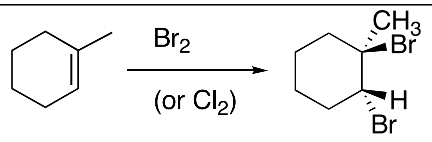
5 

6 

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

General:

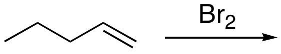
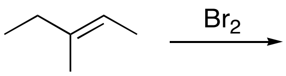
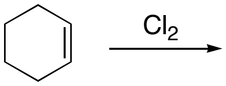
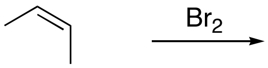


		Orientation	Stereo	Mechanism
8	 plus enantiomer	None	**Trans**	**Be able to draw completely**

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?
1				
2				
3				
4				
5				
6				

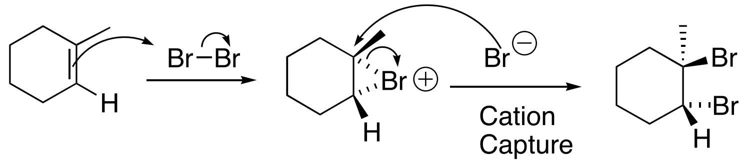
Notes:

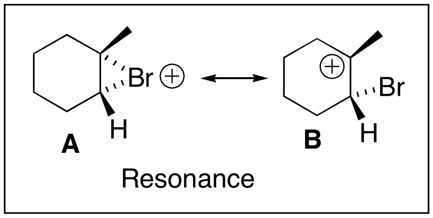
1. Cis and trans reactants give different products!
2. For any product (in this and other reactions), be able to identify whether it is chiral or not

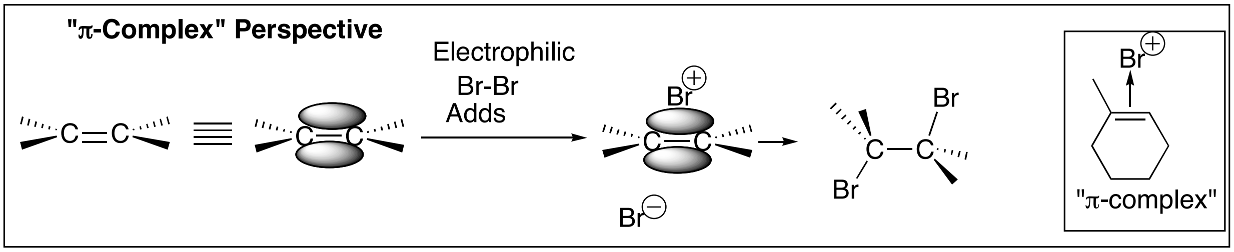
Chemical Test for Alkenes: Br_2 in CCl_4 solvent is reddish/brown color. Add a few drops to an unknown organic:

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

Mechanism (Very important)





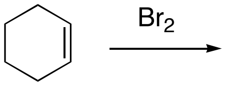


Notes

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 S_N2**
    - **Trans addition results**
7. **The nucleophile actually attacks at the more substituted carbon!**
    - This is contrary to S_N2 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 explains 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.

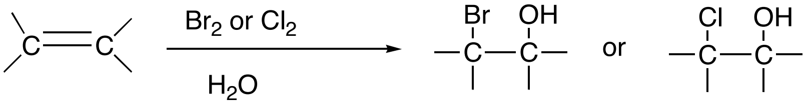
Solvent Limitation: Solvents that are nucleophilic (water or alcohols…) successfully compete with bromide or chloride in the cation capture step.

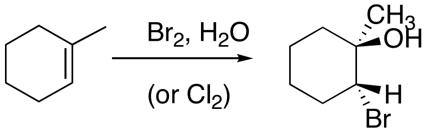
Draw the mechanism for:



7.**3** Br-OH or Cl-OH Addition. Markovnikov Addition, Trans Addition, to form "Halohydrins" (reaction 9)

General:

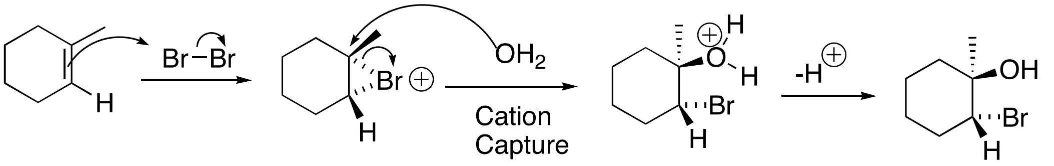


		Orientation	Stereo	Mechanism
9	 plus enantiomer	Markovnikov	**Trans**	**Be able to draw completely**

Notes:

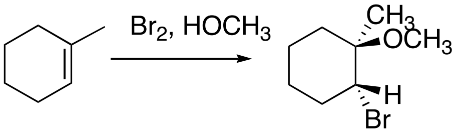
1. **Markovnikov Orientation**
   - OH adds to more substituted alkene carbon
   - Br or Cl adds to less substituted alkene carbon
   - This literally follows Markovnikov's Rule, since the relative electronegativity makes for BrOH (or ClOH) is Brδ+(OH)δ-
2. **Trans addition**
3. **Solvent** matters: whenever you see Br_2 or Cl_2 recipes, check whether there is a water (or alcohol) solvent

Mechanism

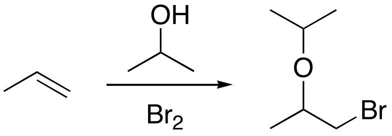


1. 3 Steps:
   a. bromonium formation (cation formation)
   b. cation capture/nucleophile addition
   c. deprotonation (since the nucleophile was neutral)
2. The mechanism is closely analogous to the Br_2 or Cl_2 additions
3. Water is a better bromonium (chloronium) capture nucleophile than bromide (or chloride) anion
   a. The large population of water molecules in the solvent give it a statistical advantage
   b. 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.
   c. 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
4. Notice that the water attacks the **more substituted** carbon of the bromonium (chloronium) ion

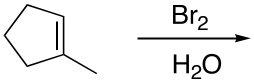
Alcohol Reactions



Alcohols Give Haloethers



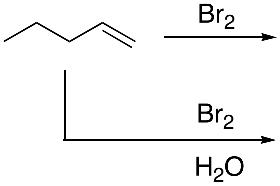
Draw the mechanism for the following reaction:



Examples, Predict the Products.

Does Mark. matter?	Does Stereo?	Chiral?

1



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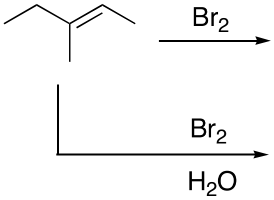

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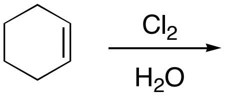

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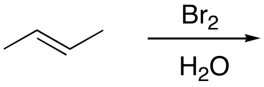

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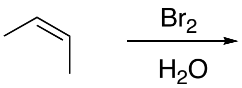
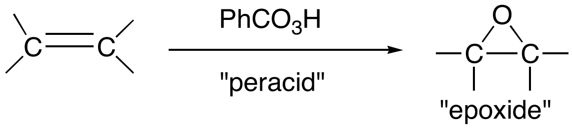
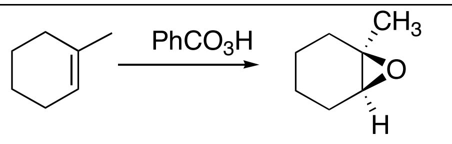


18.7 Epoxidation. Addition of one Oxygen (Reaction

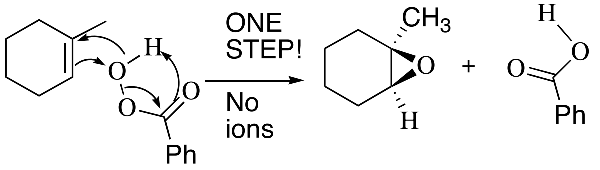
General:

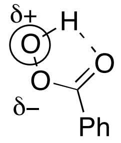


10	 plus enantiomer	None	<u>**Cis**</u>	Not responsible

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**

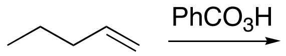
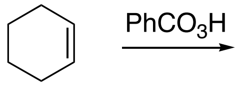
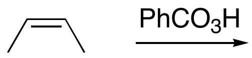
<u>Mechanism: No test Responsibility</u>




Carbonyl-hydrogen
Hydrogen-bonded reactant

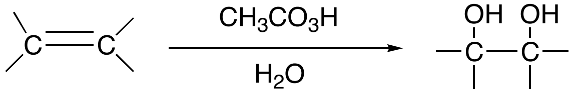
- Any peracid with formula RCO₃H has an extra oxygen relative to a carboxylic acid.
- Any peracid can deposit the extra oxygen onto the p-bond to make the epoxide
- No ions are actually involved, because the leaving group is the neutral carboxylic acid

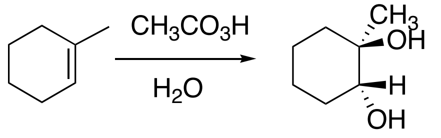
Examples, Predict the Products.

		Does Mark. matter?	Does Stereo?	Chiral?
1				
2				
3				
4				

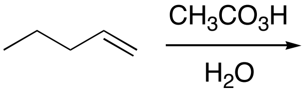
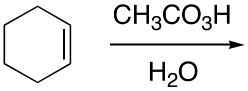
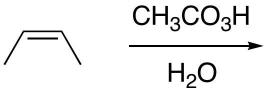
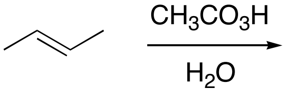
18.8 Trans OH-OH addition. Epoxidation in water. The initially formed epoxide undergoes Acid-Catalyzed Ring Opening. Reaction 11.

General:

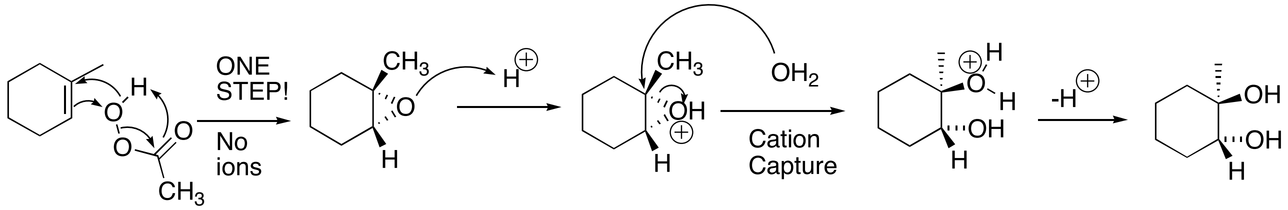


11	 plus enantiomer	None	**Trans**	**Be able to draw acid-catalyzed epoxide hydrolysis**

Examples, Predict the Products.

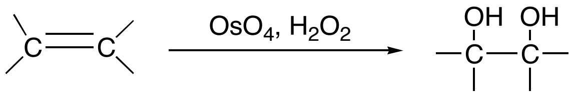
		Does Mark. matter?	Does Stereo?	Chiral?
1				
2				
3				
4				

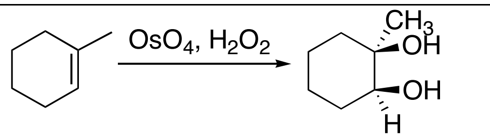
Mech

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 c. The nucleophile adds via S_N2-like backside attack. Inversion at the top stereocenter, but not the bottom, explains the trans stereochemistry.

7.8 Cis OH-OH addition. Catalytic Osmylation. Reaction 12.

General:

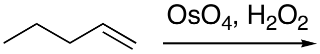


12	 plus enantiomer	None	**Cis**	Not responsible

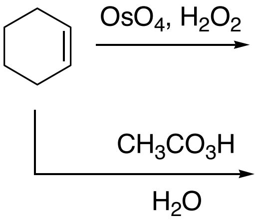
Examples, Predict the Products.

Does Mark. matter?	Does Stereo?	Chiral?

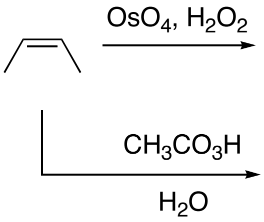
1



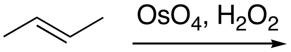
2



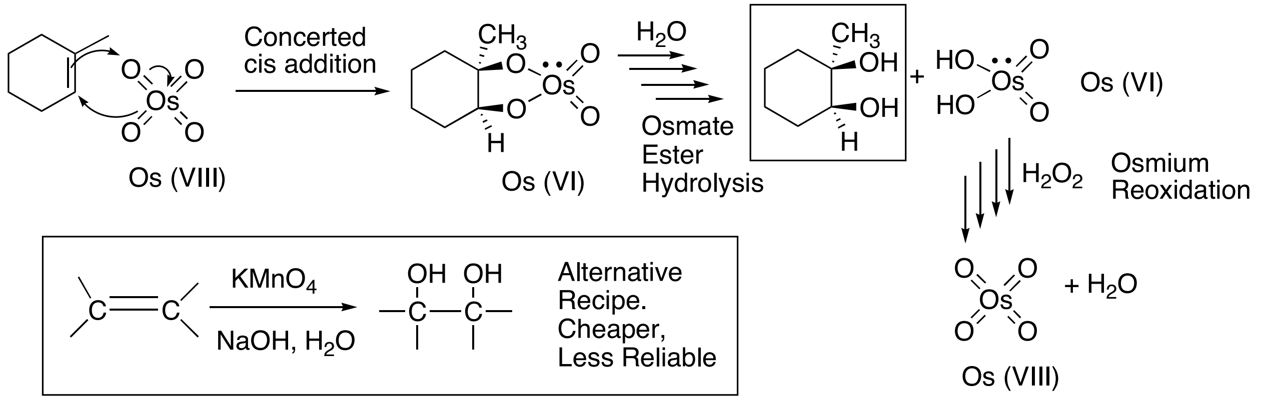
3



4



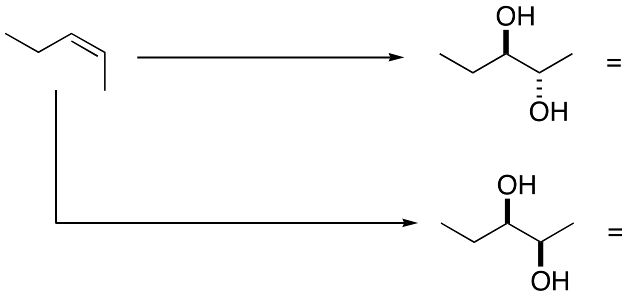
Mech: (Not required)

12	

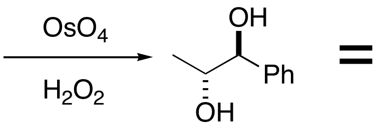
Stereochemically complementary methods

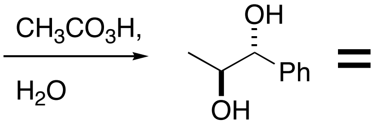
CH_3CO_3H/H_2O	trans	Skills: a. Given starting material and product, provide reagent b. Given product and reagent, what was the starting material?
OsO_4/H_2O_2	cis	

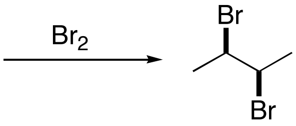
1. Given starting material and product, provide reagent. Consider stereo.

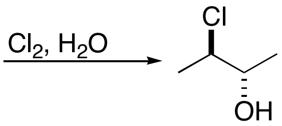


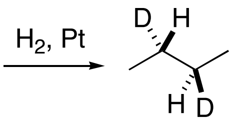
2. Stereochemistry Problems. Given product and reagent, what was the starting material?

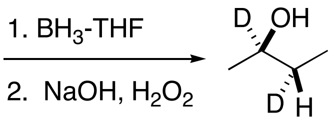


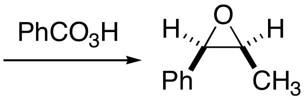






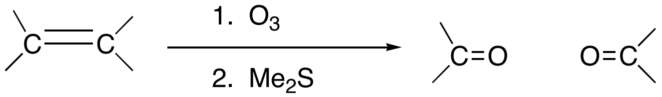


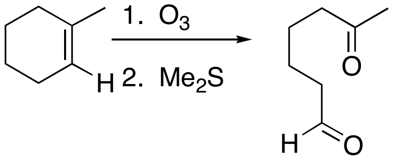




7.8 Ozonolysis. Cleavage of Alkenes. Reaction 13

General:



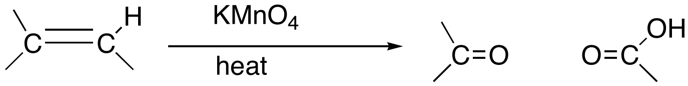
13	 Note: H-bearing alkene carbon ends up as aldehyde.	None	None	Not responsible

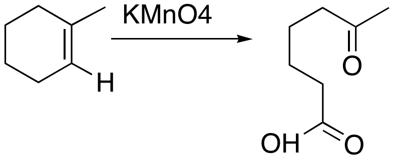
<u>Notes</u>

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**

7.8 Oxidative Cleavage of Alkenes by Permanganate. Reaction 14

General:

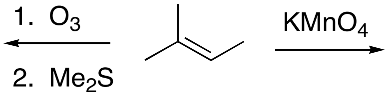


14	 H-bearing alkene carbon ends as carboxylic acid	None	None	Not responsible

<u>Notes</u>

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.**

1



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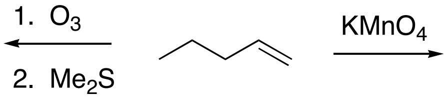
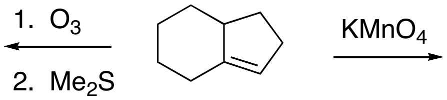
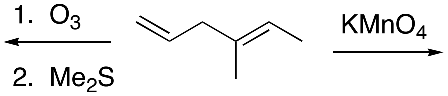


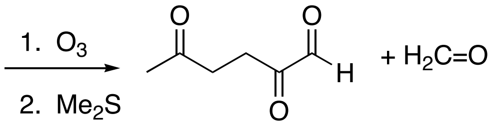
3

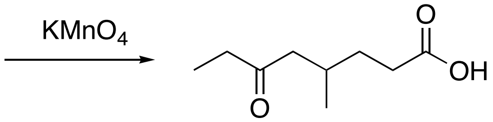


4.

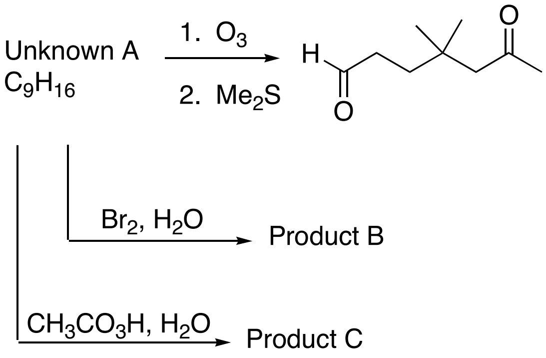


5. Identify reactants.



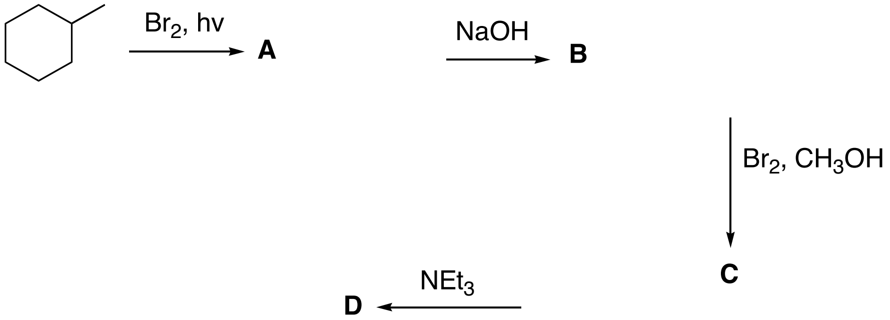


6. Identify A, B, and C.



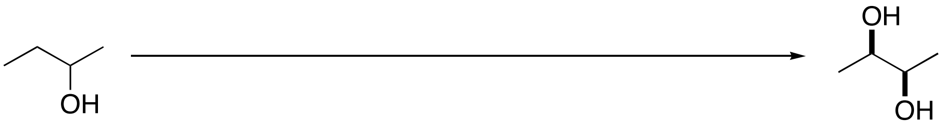
Review Problems.

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

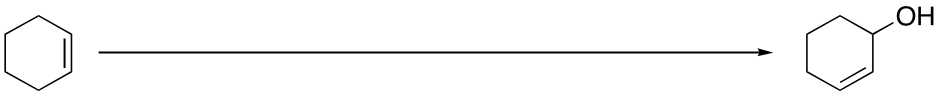


8. Design a synthetic plan for the following conversions. (Several on test)

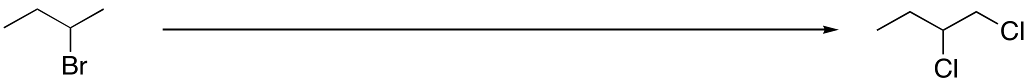
a.



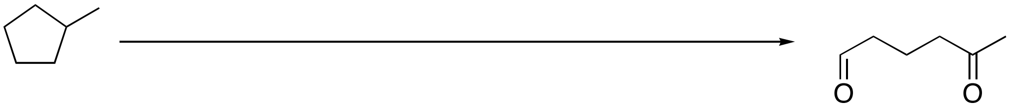
b.



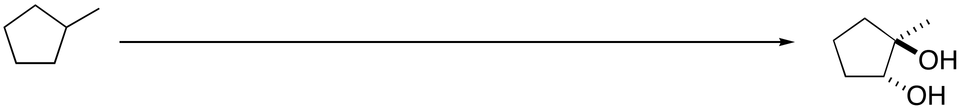
c.



d.



e.



f.

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**.