CHM 2120 - Assignment 3 - ANSWERS

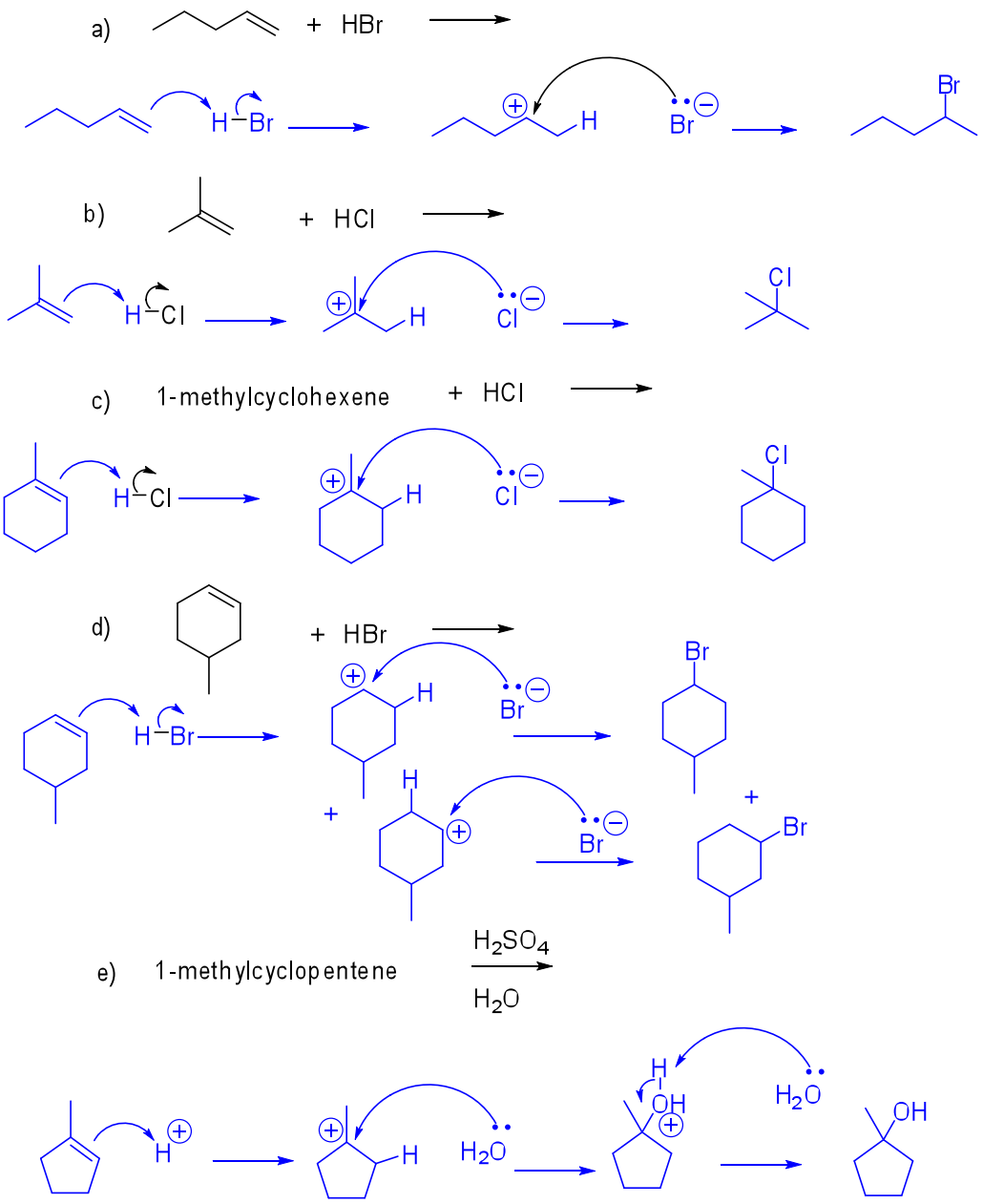
In this assignment:

- Electrophilic addition reactions
- Radical substitution reactions
- Anti-Markovnikov addition to alkenes
- Syntheses

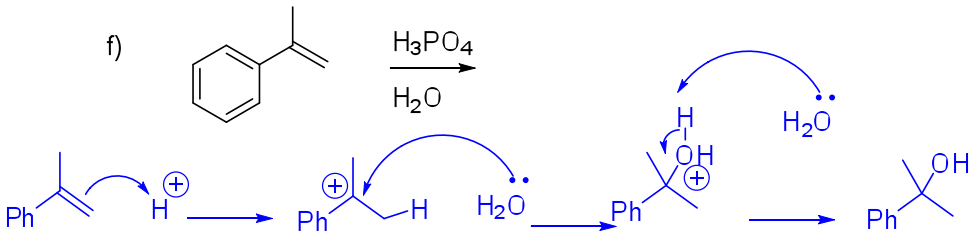
Note: Some questions were taken directly from CHM1321 assignments. You can choose to review your notes from last year or repeat the assignments.

1. Provide a mechanism for the following transformations (only product is required for h and i):

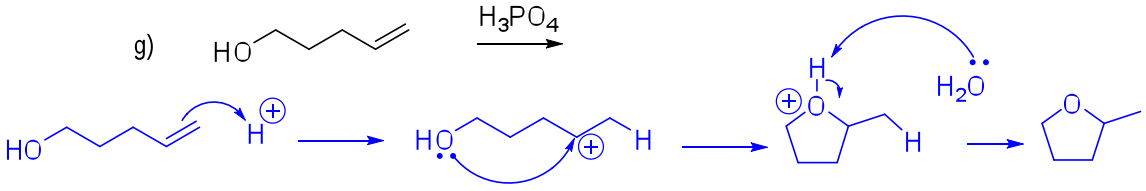
   For radical reactions, chain termination steps are not shown



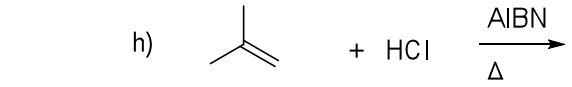
f)



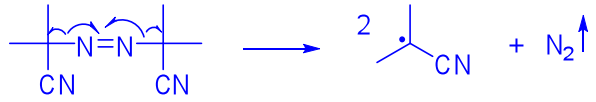
g)



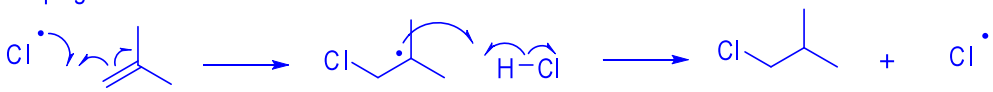
h)



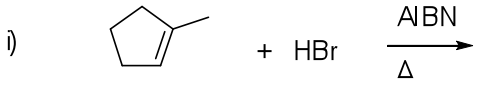
Initiation:



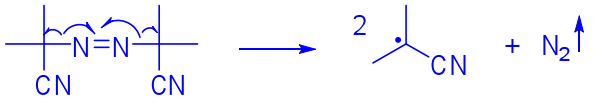
Propagation



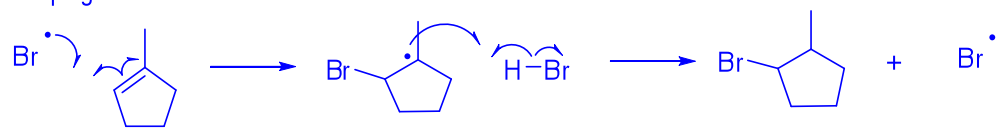
i)



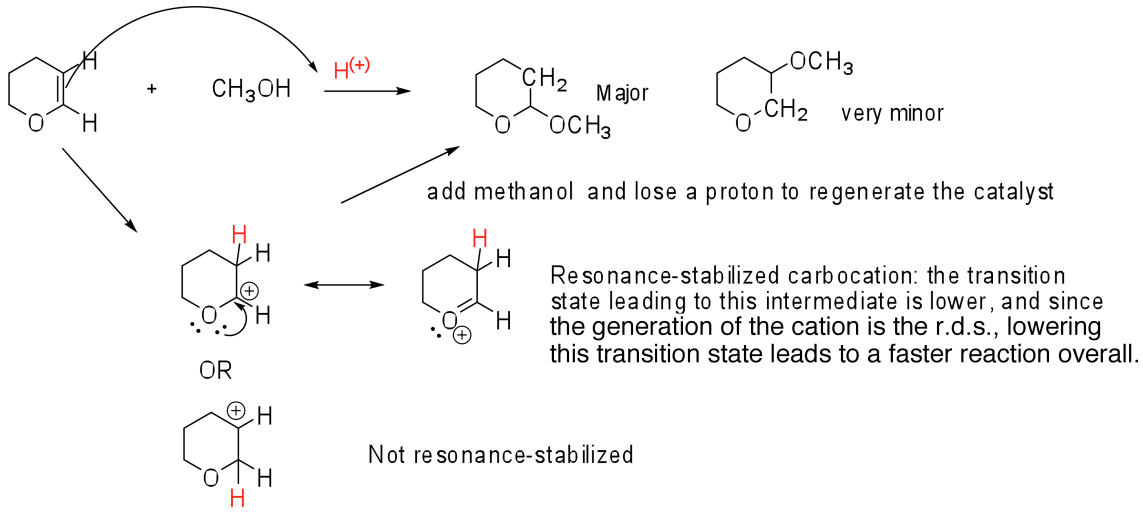
Initiation:



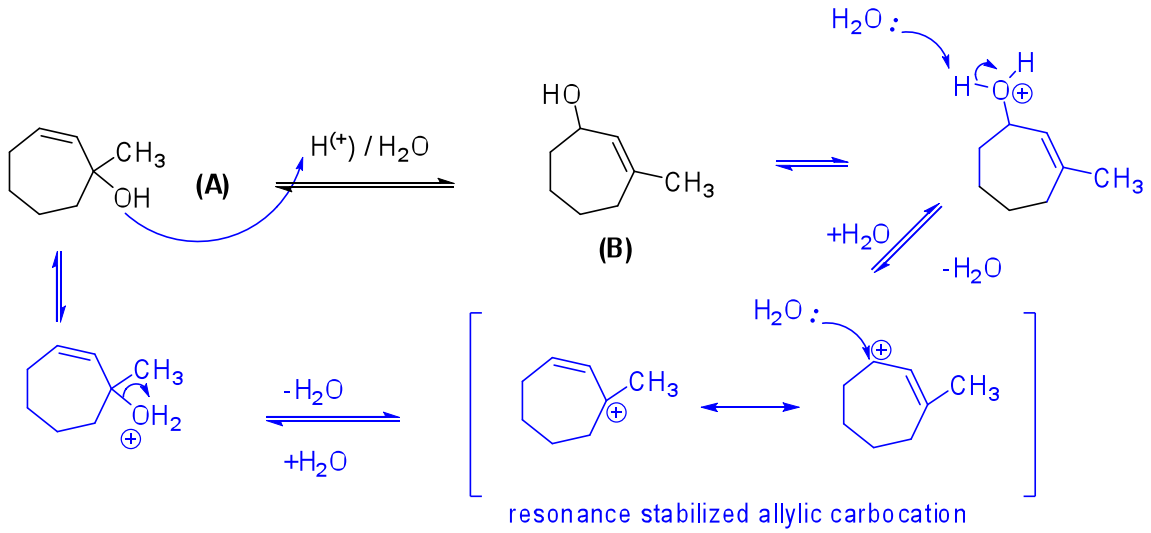
Propagation



2. Explain the formation of the major product:



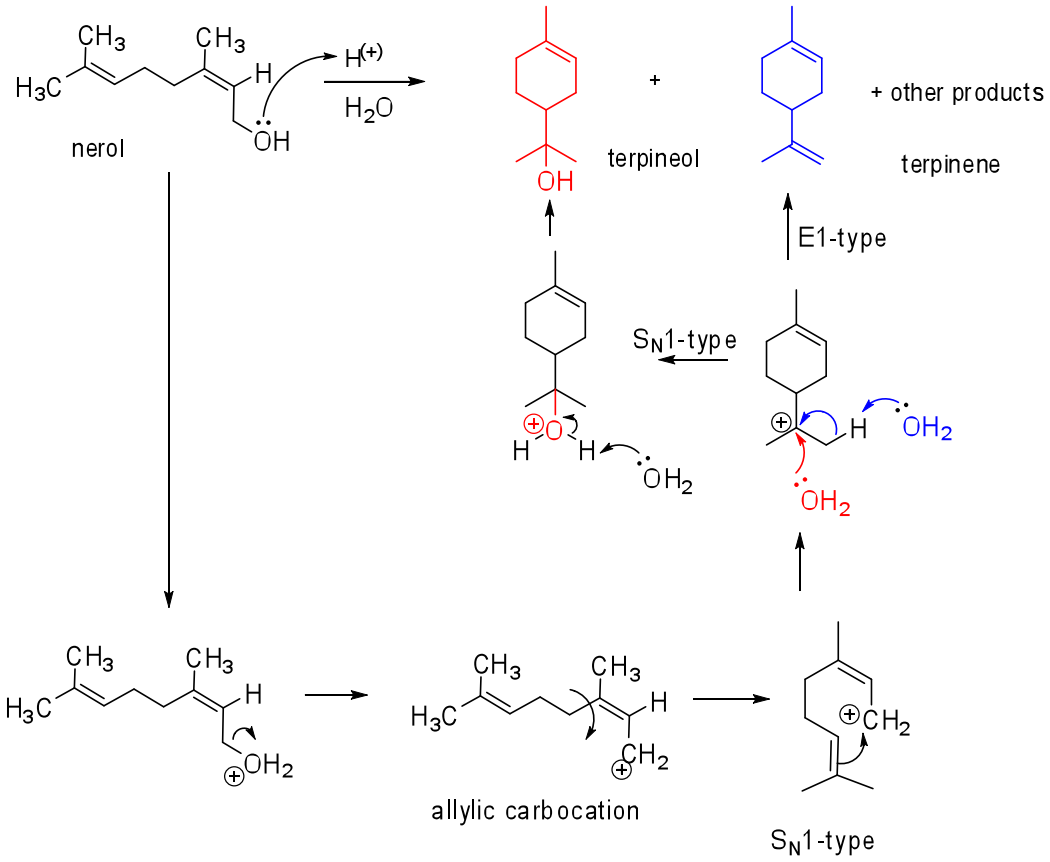
3. Draw the mechanism for the isomerization of (**A**) to (**B**), and vice versa. Which isomer dominates if the isomerization temperature is 100 °C (i.e. which is the most stable isomer)?



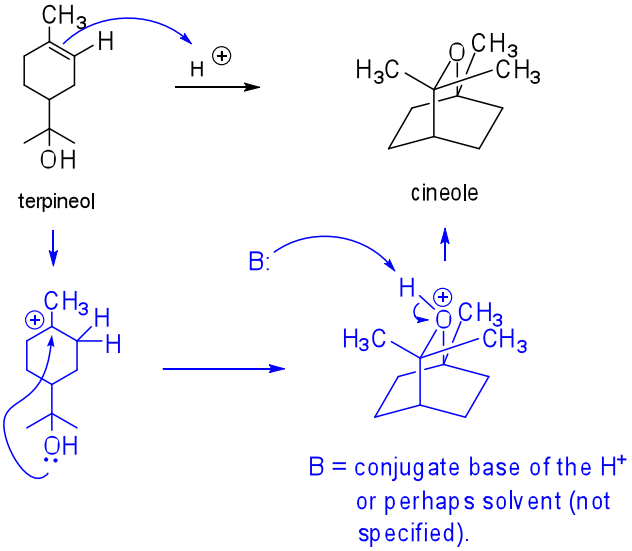
B is preferred under the high temp. [thermodynamic control conditions]

The most stable alkene, B, is preferred under high temperatures.

4. The natural product nerol when warmed with acid leads to a number of cyclic products including terpineol and terpinene. Explain the formation of these two products from Nerol and the isomer called geraniol , where the double bond at C2 has the E geometry are the major constituents of rose oil. Terpineol and terpinene are found in tea tree oil.

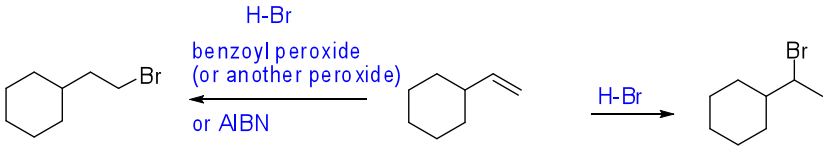


5. Cineol is a major constituent of the spice cardamon. The reaction shown below can occur under acid catalysis. Draw a mechanism for this conversion.

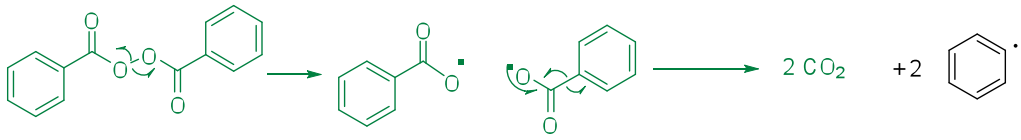


Note: Protonation of the OH does occur (reversible), however this does not lead to a productive reaction.

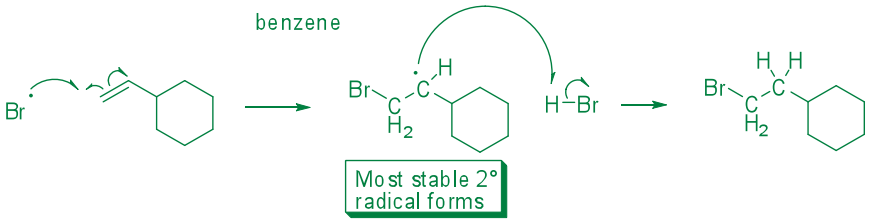
6. Give the reagents required to obtain each of the product from the alkene shown.

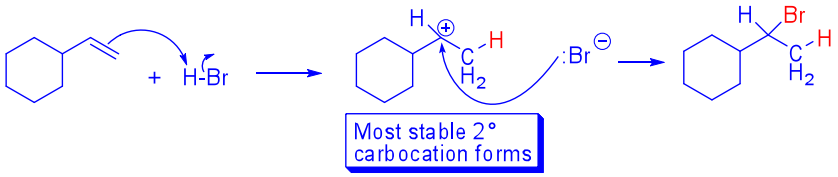


Mechanisms:

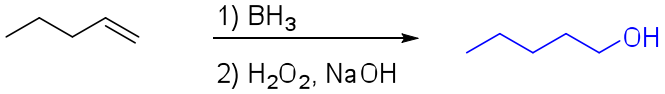


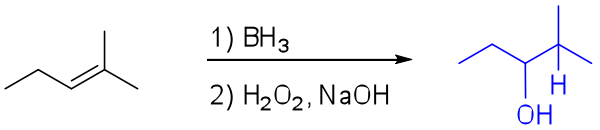
Use 'fish hooks to indicate moving one electron.

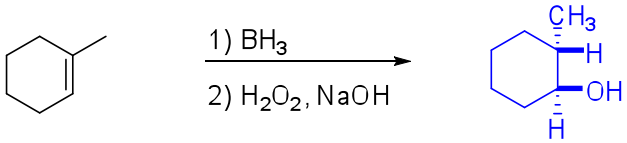


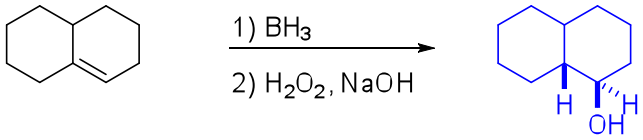


7. Give the product of the following transformations:

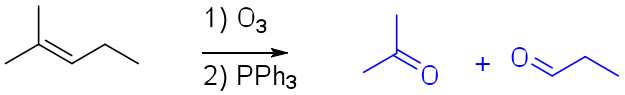
a) 

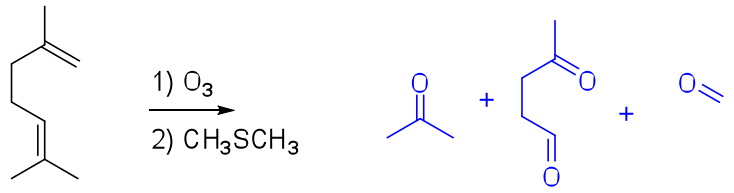
b) 

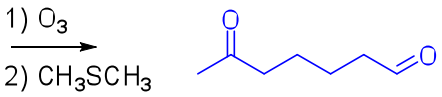
c) 

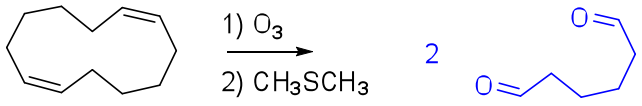
d) 

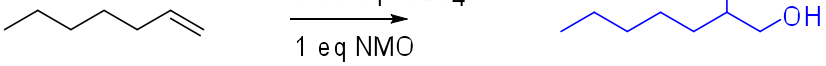
8. Predict the major product(s) of the following reactions:

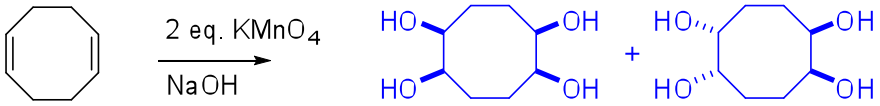
a) 

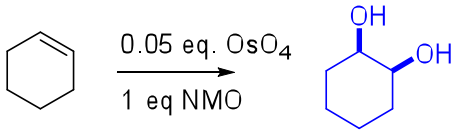
b) 

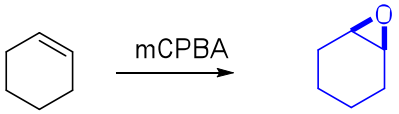
c) 1-methylcyclohexene 

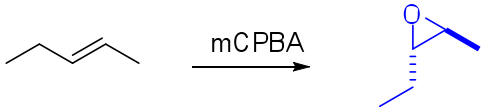
d) 

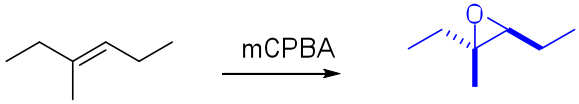
e) 

f) 

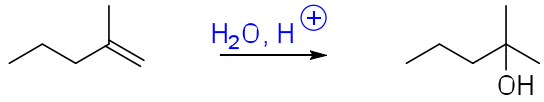
g) 

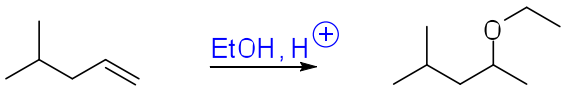
h) 

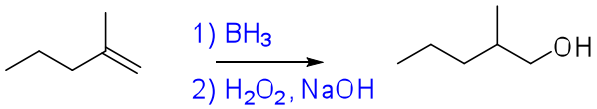
i) 

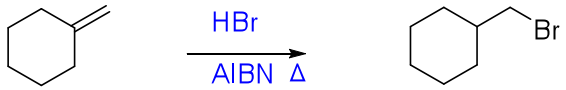
j) 

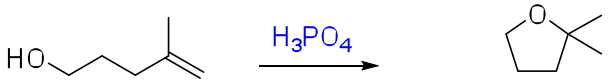
9. Show how you could effect the following transformations. Include stereochemistry where appropriate

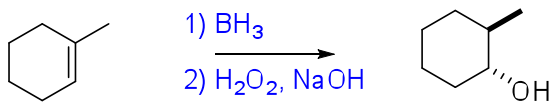
a) 

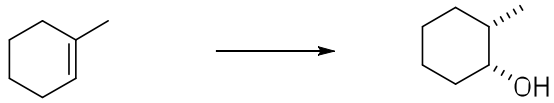
b) 

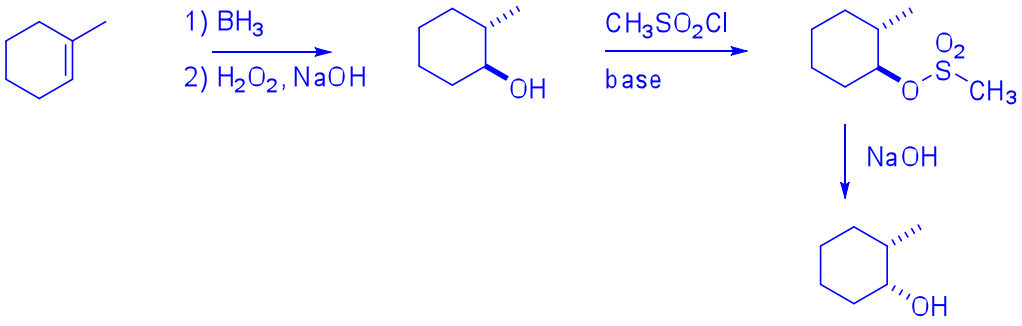
c) 

d) 

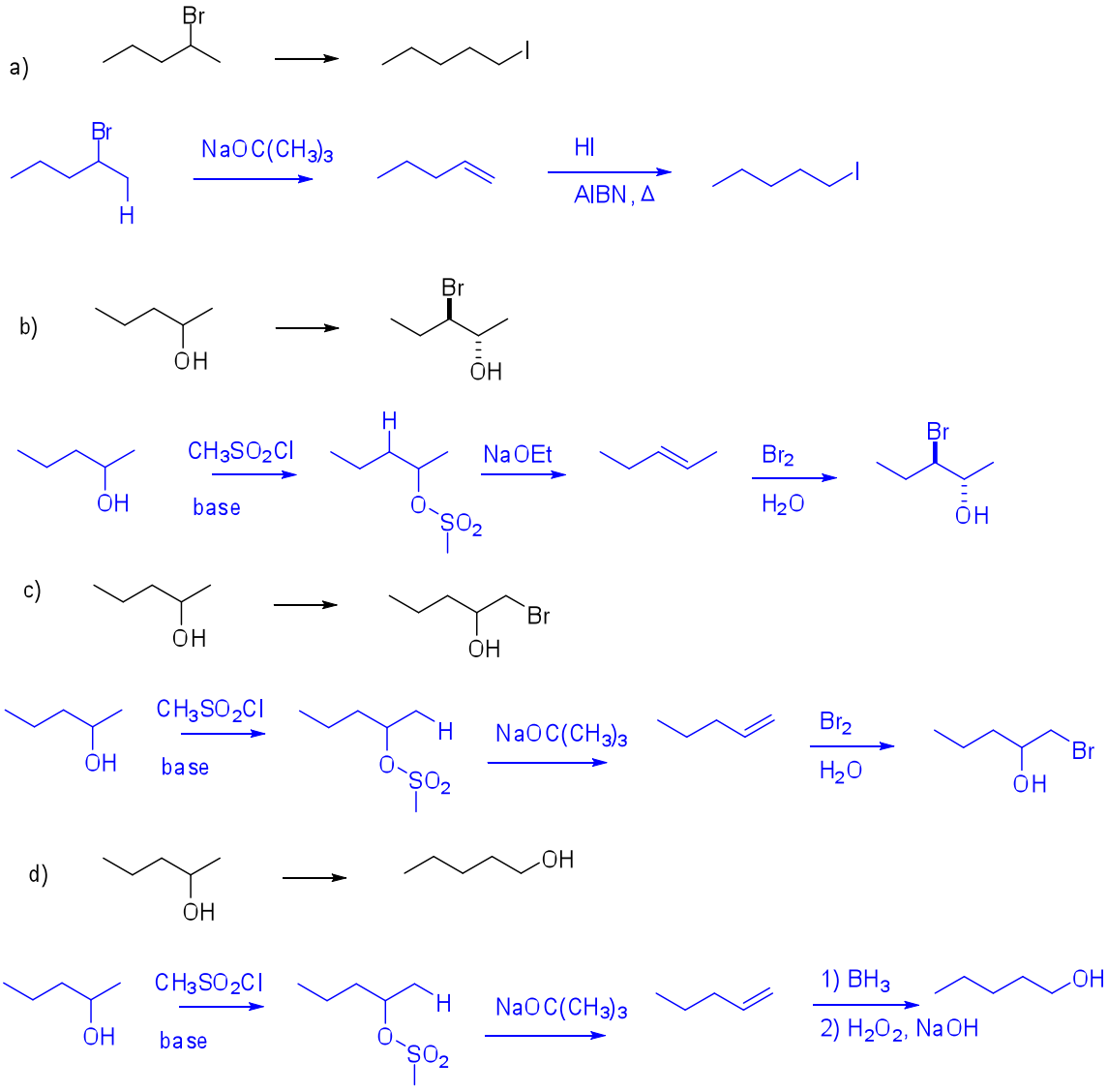
e) 

f) 

g) 

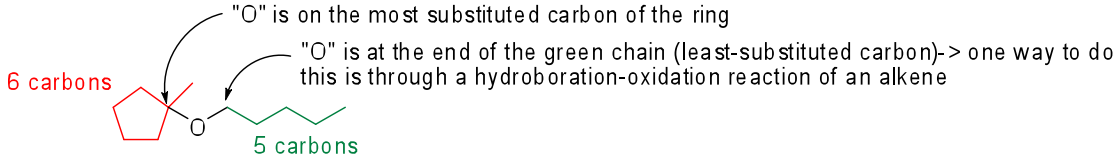


10. Propose methods to accomplish the following transformations (most require >1 step):



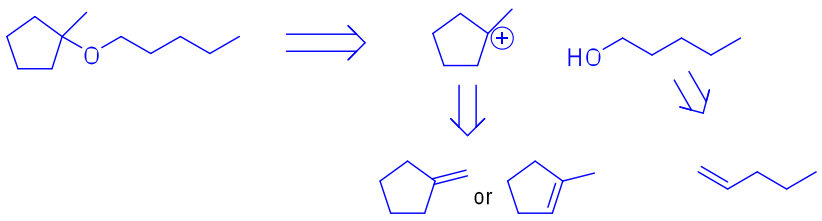
11. Propose a synthesis of each of the following starting with alkenes containing 6 carbons or less. You may use any additional reagents necessary, but all carbons in the products must be derived from alkenes with 6 carbons or less. A retrosynthesis and analysis are also required.

a) Analysis:

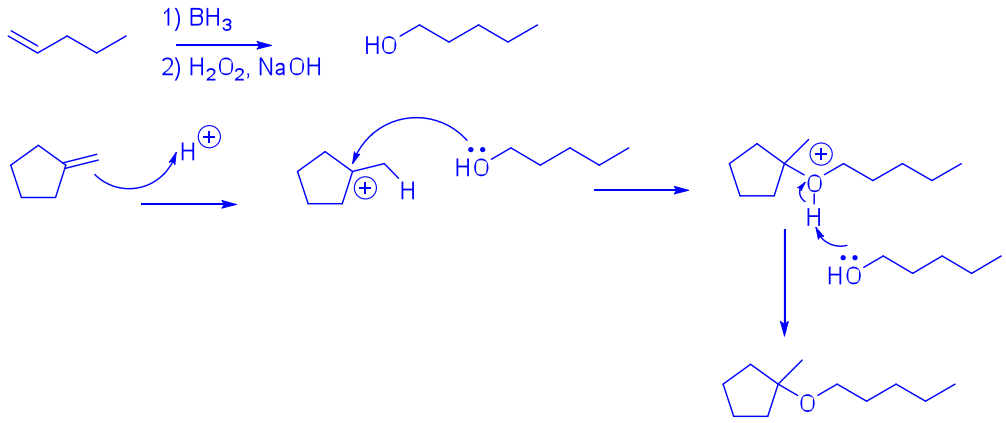


Stereochemistry: none to worry about
Regiochemistry: as described above

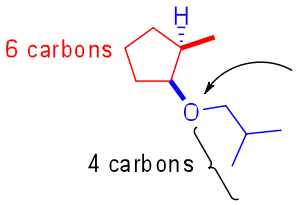
Retrosynthesis



Synthesis



b)

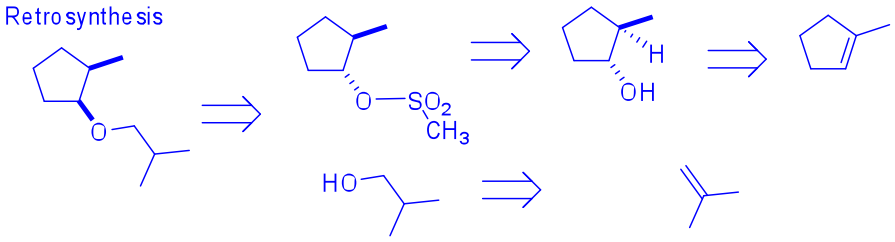


Regiochemistry: O is on the least-substituted carbon of the ring and of the blue chain (two hydroboration-oxidation reactions?

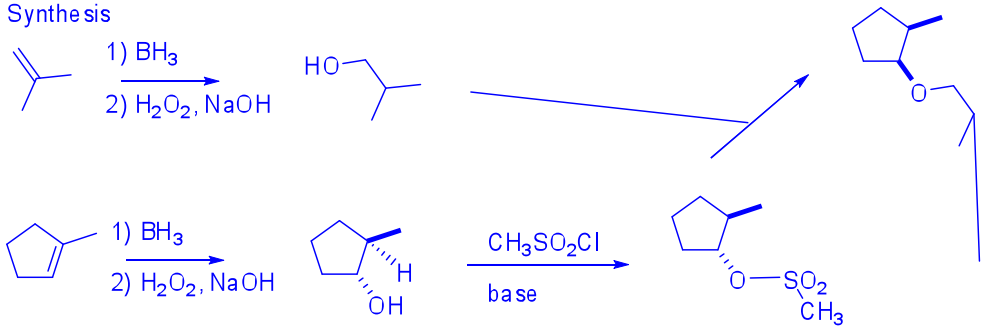
Note: a hydroboration-oxidation sequence results in the O and H(blue) being *syn*)

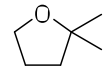
Stereochemistry: O and CH_3 are *syn*. O and H (shown) are *trans*

Retrosynthesis



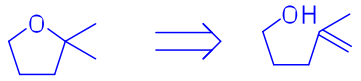
Synthesis



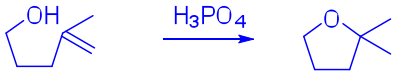
c) 

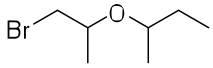
Analysis:
Already 6 carbons: no need to subdivide further
Stereochemistry: none to worry about
Regiochemistry: O is bound to the most substituted carbon of the ring and on a CH_2

Retrosynthesis



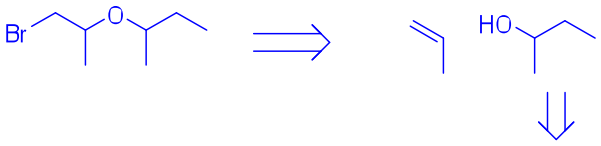
Synthesis



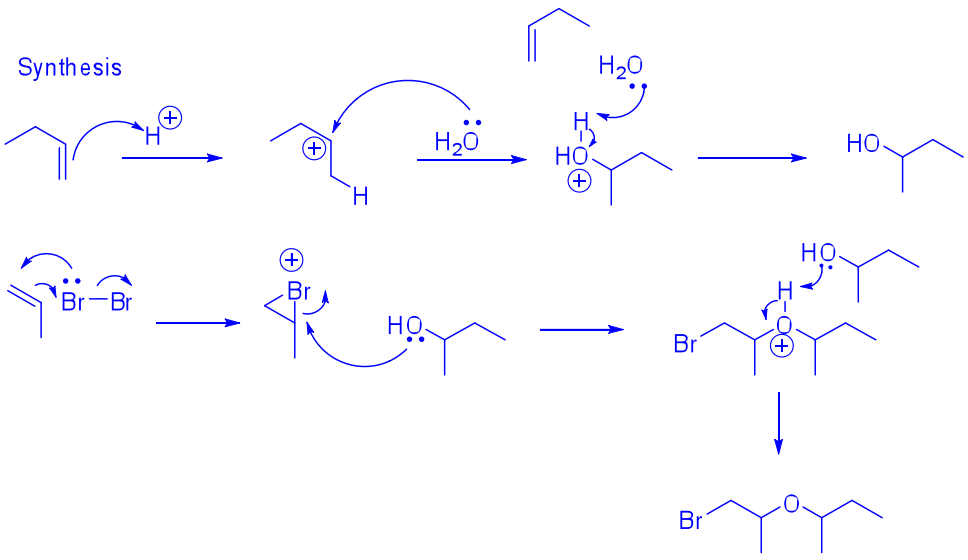
d) 

Analysis:
Two heteroatoms on adjacent carbons suggests that a bromination-type reaction of an alkene would be useful.
Stereochemistry: none to worry about
Regiochemistry: Br is on the least-substituted carbon; O is on the most substituted carbons (2)

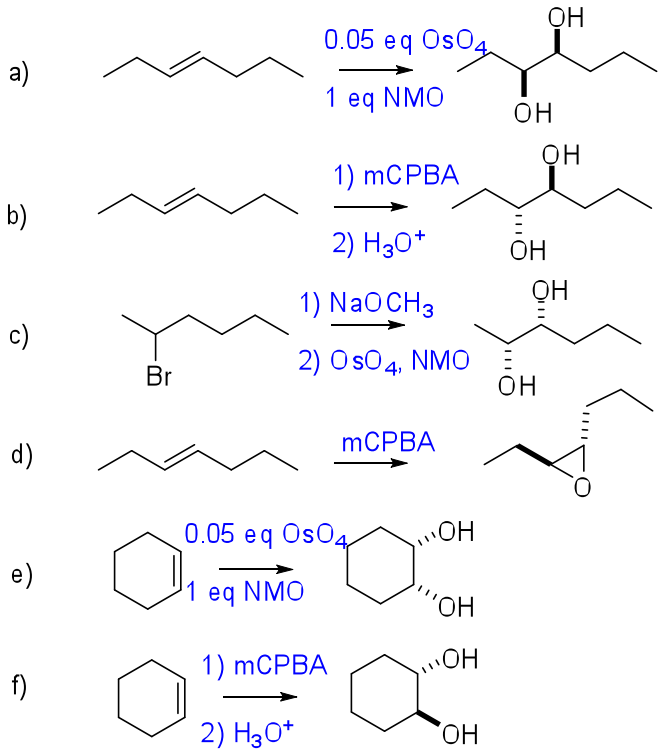
Retrosynthesis



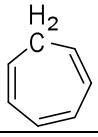
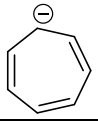
Synthesis

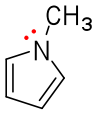
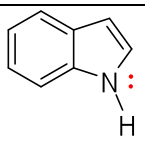
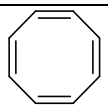
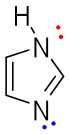
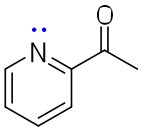
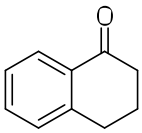
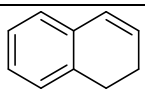
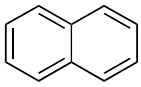
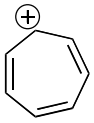


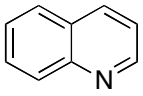
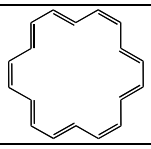
12. Propose efficient methods to achieve the following transformations (some may require more than one step):



13. Identify the aromatic, non-aromatic and anti-aromatic ring(s), if any, in the following molecules. Clearly explain each decision using the criteria given in class.

Part	Compound	Ring is planar?	All atoms sp^2-hybridized?	4n + 2 π electrons? (n=0,1,2…)	Aromatic? (conclusion)	Comments
a		Yes	Yes	6 (n = 1) Yes	YES	
b		No	No (CH_2 is sp^3)	Yes	NO – non-aromatic	
c		Yes	Yes	8 (n = 1.5) No	NO-antiaromatic	Compare to the tropylium (cation) from the notes
d		Yes	Yes	4 (n = 0.5) No	NO – antiaromatic	Compare to the pentadienyl anion
e		Yes	Yes	6 total (4 from π bonds, 2 from lone pair) Yes	YES	Red e⁻'s are in a p orbital; blue e⁻'s are in an sp^2 orbital

Part	Compound	Ring is planar?	All atoms sp^2-hybridized?	4n + 2 π electrons? (n=0,1,2…)	Aromatic? (conclusion)	Comments
f		Yes	Yes	6 (n = 1) Yes	YES	Red e^-'s are in a p orbital;
g		Yes	Yes	10 total (8 from π bonds, 2 from lone pair); n = 2 Yes	YES	Red e^-'s are in a p orbital;
h		No (see a model)	Yes	8 π e^-'s total No	NO – antiaromatic	
i		Yes	Yes	6 total (4 from π bonds, 2 from lone pair); n = 1 Yes	YES	Red e^-'s are in a p orbital; blue e^-'s are in an sp^2 orbital
J		Yes	Yes	6 total; n = 1 Yes	YES	The electrons from the carbonyl don't count (they are outside the ring); the blue e^-'s are in an sp^2 orbital
K		Yes	Yes	6 total; n = 1 Yes	YES (the ring on the left); the ring on the right is non-aromatic	The electrons from the carbonyl don't count (they are outside the ring);
L		Yes	Yes	6 total; n = 1 Yes	YES (the ring on the left); the ring on the right is non-aromatic	The electrons from the double bond outside the phenyl ring don't count
M		Yes	Yes	4 total; Not aromatic Satisfies the 4n rule (n=1)	NO - Antiaromatic	
N		Yes	Yes	6 total; n=1 Yes	Aromatic	The lone pair of electrons on the carbanion is in a p orbital
O		Yes	Yes	10 total; n=2 Yes	Aromatic	
P		Yes	Yes	6 total; n=1 Yes	Aromatic	The carbocation is sp^2 hybridized. The π electrons are delocalized through the empty p orbital on the carbocation

Part	Compound	Ring is planar?	All atoms sp^2-hybridized?	4n + 2 π electrons? (n=0,1,2…)	Aromatic? (conclusion)	Comments
Q		Yes	Yes	10 total; n=2 Yes	Aromatic	The lone pair of electrons on the N is in an sp2-hybridized orbital—it is perpendicular to the π system and is not involved in resonance
R		Yes	Yes	18 total; n=4 Yes	Aromatic	