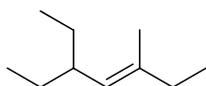


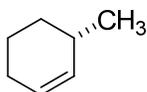
CHEMISTRY 31
Summer 2010 Final Exam
200 pts

Name: KEY

1. (6 pts) Provide the complete IUPAC name for each of the following compounds:

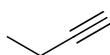


(Z)-5-ethyl-3-methyl-3-heptene

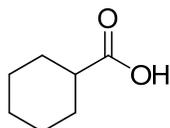


(S)-3-methylcyclohexene

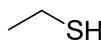
2. (10 pts) For each of the following compounds provide the functional group and the corresponding pKa value for the most acidic hydrogen.



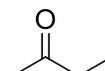
alkyne
25



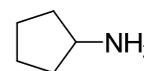
carboxylic acid
5



thiol
10

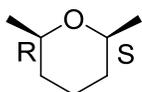


ketone
20

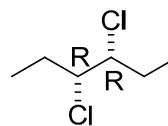


amine
36

3. (6 pts) For each compound given below determine if it is chiral or achiral (give answer below structure).

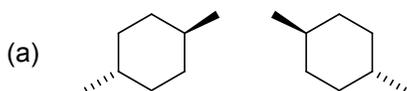


achiral (meso)

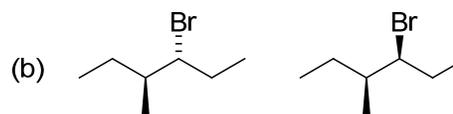


chiral

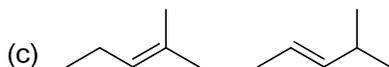
4. (12 pts) What is the relationship between each set of compounds below; identical, constitutional isomers, enantiomers, or diastereomers (give answers below structures).



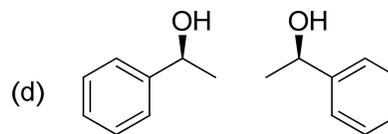
identical (superimposable!)



diastereomers



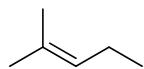
constitutional



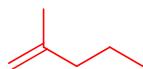
enantiomers

5. (30 pts) Answer each of the following questions by circling your answers:

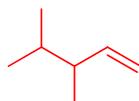
(a) Which of the following alkenes will isomerize to a new alkene with H_3PO_4 ? (circle all that apply)



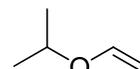
trisub best



di to tri sub

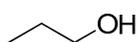


mono to tri sub



no way to move

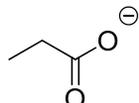
(b) Circle the strongest nucleophile and cross-out the weakest nucleophile from choices below:



neutral
weak base



neutral and hindered
weak base

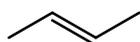


res stabilized
weak base

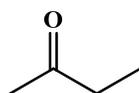


strongest base

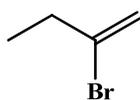
(c) Which of the following compounds cannot be prepared directly from an alkyne? (circle all that apply)



Li, NH_3



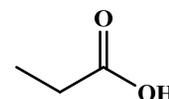
$\text{HgSO}_4, \text{H}_2\text{SO}_4$



HBr

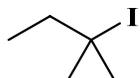


can't get Br here

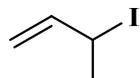


O_3

(d) Which substrate will react the fastest with hydroxide (OH^-) in DMSO to give a substitution product? (circle one answer)



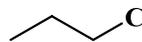
E2



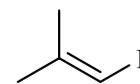
E2



SN_2 best LG

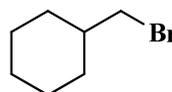
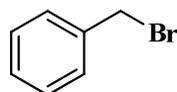
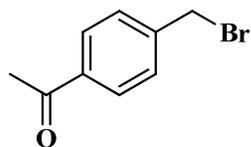


SN_2 weaker LG



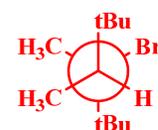
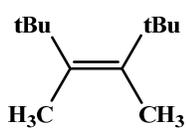
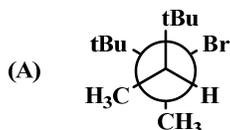
no sub or elim at all

(e) Which substrate will undergo the fastest $\text{S}_\text{N}1$ reaction? (circle one choice)



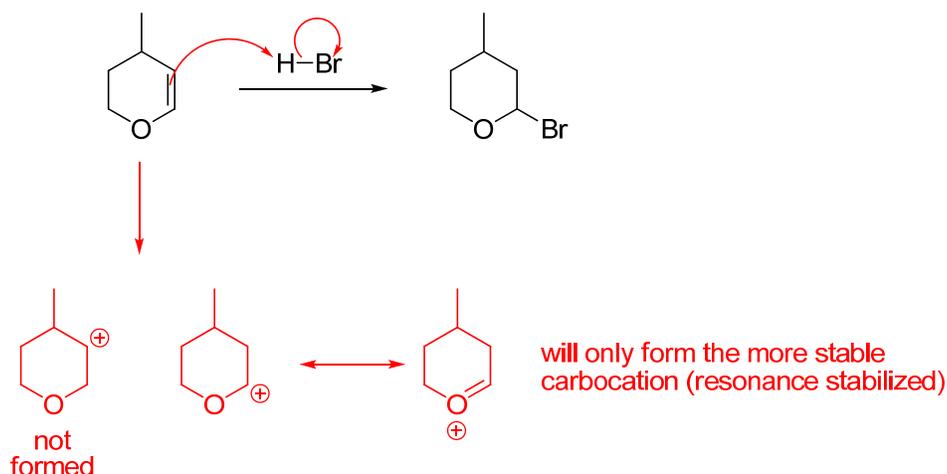
First, second, and fourth all have resonance stabilization. Fourth has best with full octets possible giving it the best resonance stabilization possible

(f) Which starting material, **A** or **B**, will give the following alkene in the *highest yield* when reacted with NaOH ? (circle one choice from **A** or **B**)



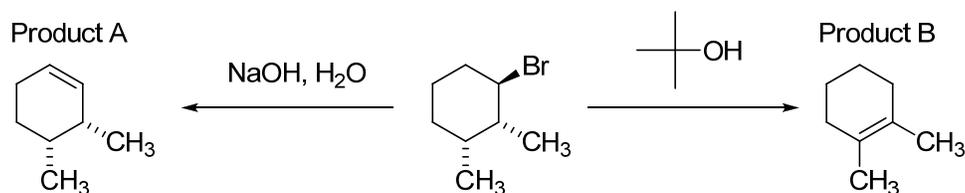
When H and Br anti, ONLY B would give Z alkene (A would give E alkene!)

6. (10 pts) Addition of HBr to the alkene shown below gives only the product provided. Explain why this is the only product generated. Note, a picture is worth a thousand words!



According to Markovnikov's rule, we will form the most stable carbocation intermediate. Adding H^+ to the bottom alkene carbon gives a secondary carbocation while adding H^+ to the top carbon of the alkene forms a more stable resonance stabilized carbocation. Since this is the only carbocation formed, this is the position that the Br^- will add to.

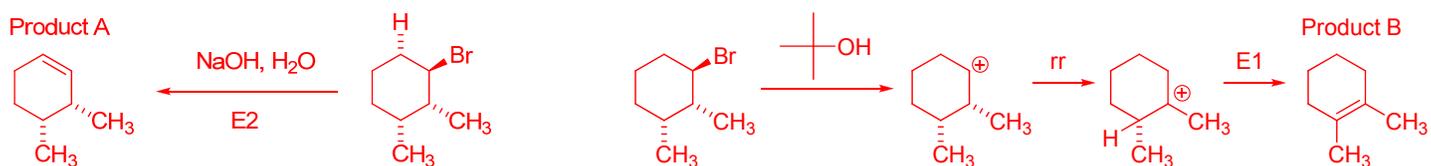
7. (12 pts) When the following alkyl halide is reacted with NaOH product A is produced. However, when it is reacted with $(\text{CH}_3)_3\text{COH}$ product B is produced. How do you explain the difference in product formation?



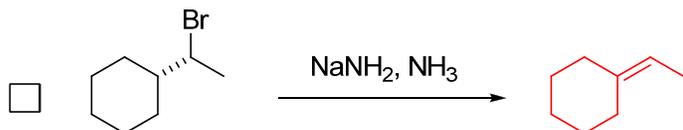
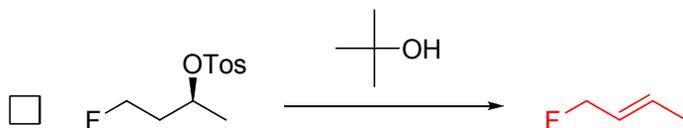
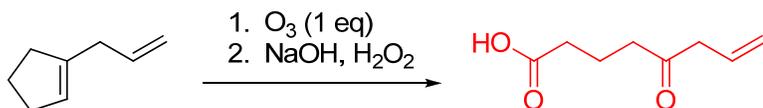
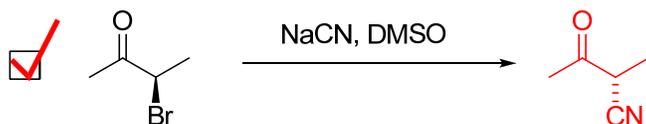
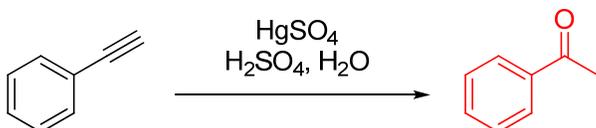
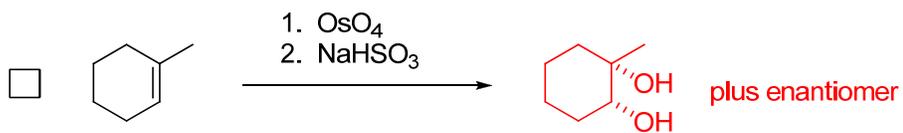
Product A is formed by an E2 elimination while Product B is formed by an E1 elimination.

With NaOH used as the nucleophile/base, since it is a strong base reacting with a hindered substrate an elimination will occur. Since it is a strong base, an E2 elimination will occur. For E2, the hydrogen that is lost must be anti to the Br - only the carbon to the left of the C-Br has an anti hydrogen.

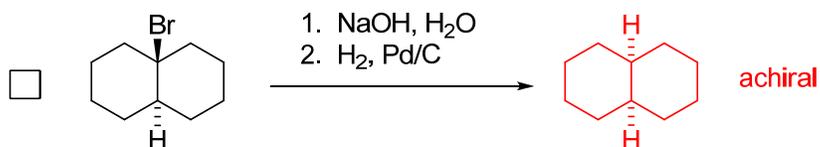
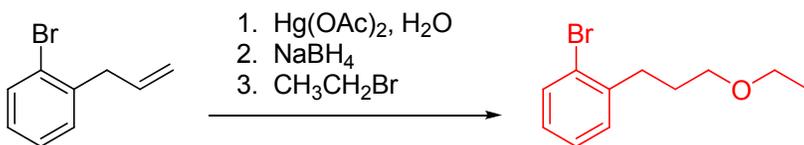
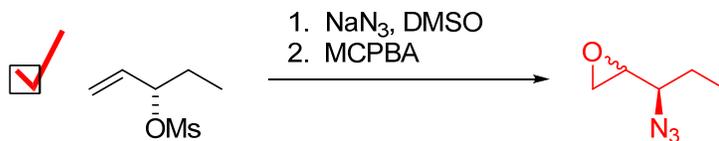
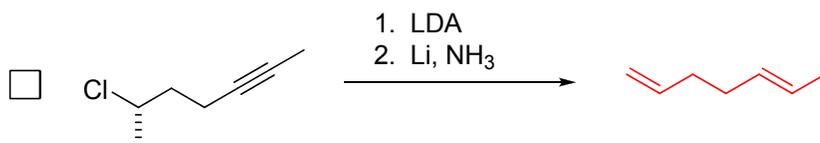
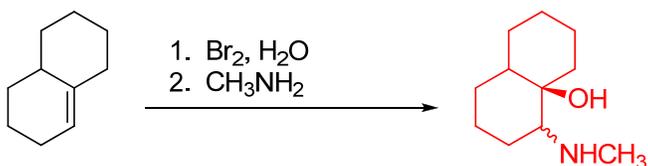
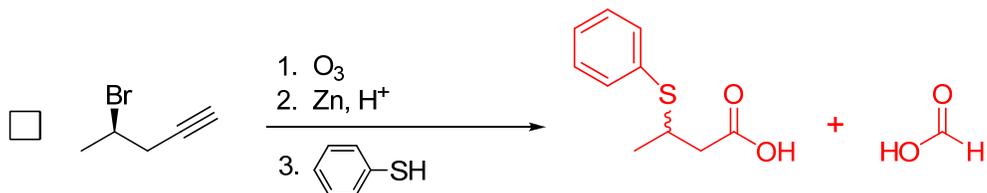
With $(\text{CH}_3)_3\text{COH}$ a hindered substrate reacting with a hindered weak base will give E1. This produces a secondary carbocation that will rearrange to the tertiary carbocation and eliminate to the most substituted alkene.



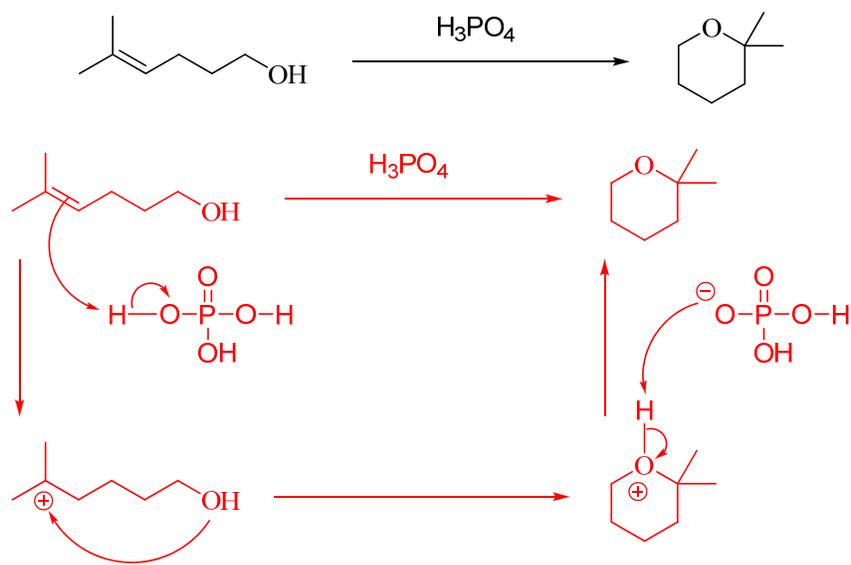
8. (28 pts) Provide the major product(s) for each of the following reactions. Be sure to include appropriate stereochemistry where necessary. For reactions with a box in front, check the box if the product is predicted to be optically active.



9. (30 pts) Provide the major product(s) for each of the following reactions. Be sure to include appropriate stereochemistry where necessary. For reactions with a box in front, check the box if the product is predicted to be optically active.



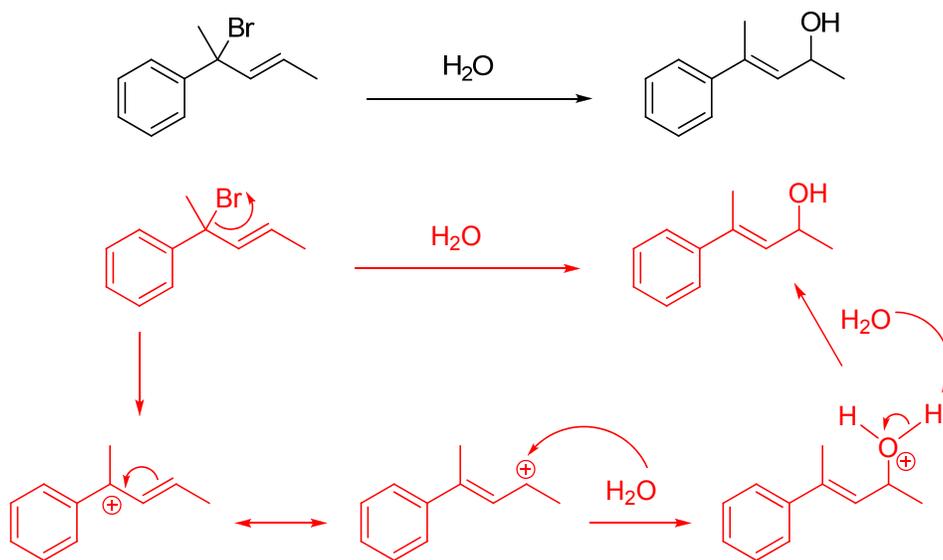
10. (14 pts) (a) In an attempt to dehydrate the following alcohol, the cyclic product shown below was obtained. Propose a mechanism to explain how this product is produced.



- (b) Why did the initially planned alcohol dehydration not work (1-2 sentences)?

Cannot dehydrate a primary alcohol, only secondary and tertiary. So the only thing left to do is to protonate the alkene with phosphoric acid leading to the tertiary carbocation.

11. (14 pts) (a) Propose a mechanism for the following reaction.

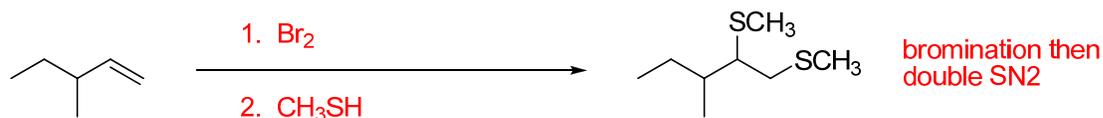
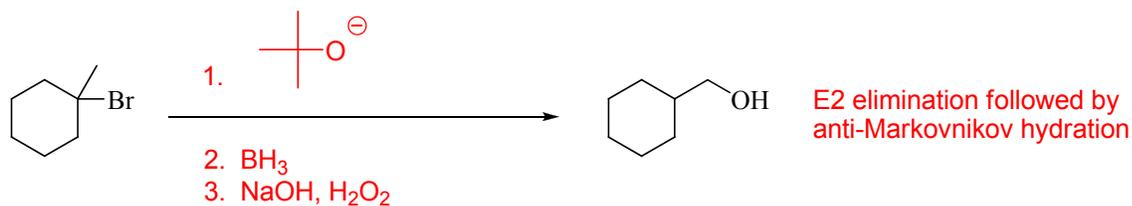


SN1 substitution where you must consider resonance structure for carbocation

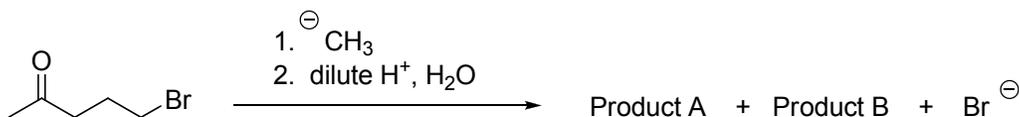
- (b) Why is the given product thermodynamically favored (1-2 sentences)?

Substitution is favorable as we convert a weaker C-Br bond into a stronger C-O bond. Water attacks 2° carbon to form more substituted (stable) alkene final product

12. (14 pts) Propose a sequence of steps to synthesize the following product from the given starting material.



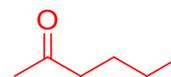
13. (14 pts) The following reaction produces two organic products, product A and B, along with a bromide anion (note step 2 just neutralizes charge). Using the following data for product A and B, along with your understanding of organic reactions, what are the structures of A and B?



Product A: Degree of unsaturation = 1
 ^{13}C spectrum = 6 signals
 (one above 200 ppm)

Draw Product A Below

IR spectrum on following page:



Product B: Degree of unsaturation = 0
 ^{13}C spectrum = 5 signals
 (all below 90 ppm)

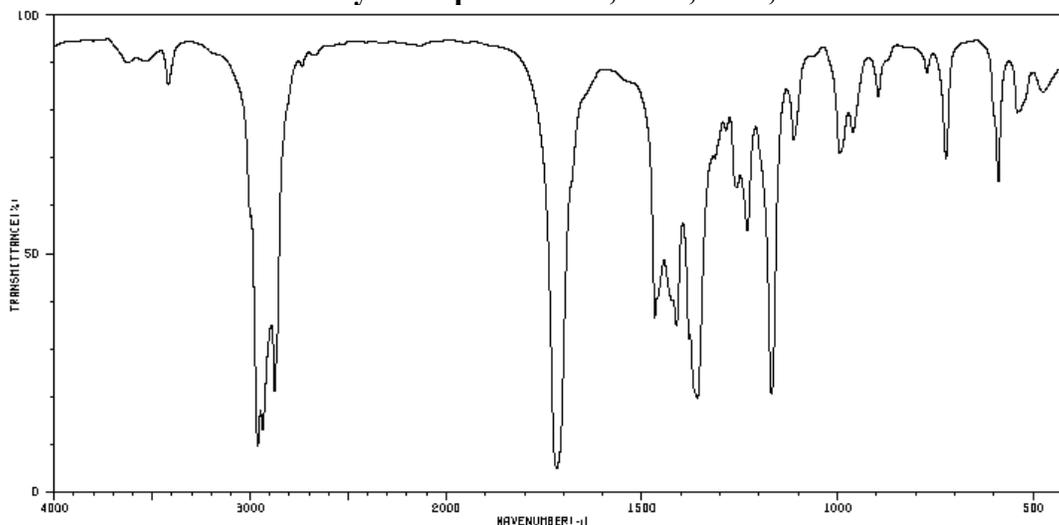
Draw Product B Below

IR spectrum on following page:

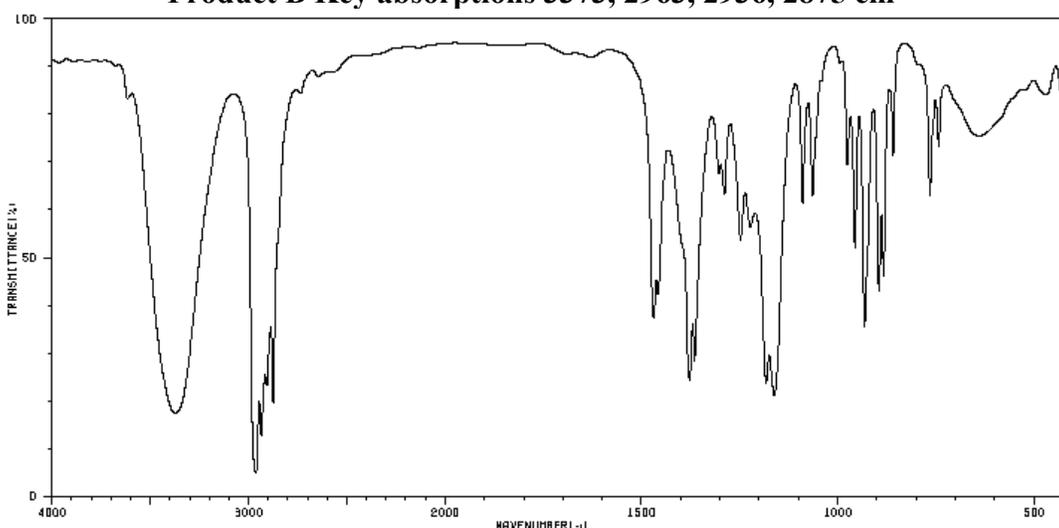


C=O

Product A Key absorptions 2962, 2936, 2875, 1718 cm^{-1}



Product B Key absorptions 3373, 2963, 2936, 2875 cm^{-1}



OH

Table 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity	Functional Group	Absorption (cm^{-1})	Intensity
Alkane			Amine		
C-H	2850-2960	Medium	N-H	3300-3500	Medium
Alkene			C-N	1030-1230	Medium
=C-H	3020-3100	Medium	Carbonyl compound		
C=C	1640-1680	Medium	C=O	1670-1780	Strong
Alkyne			Carboxylic acid		
\equiv C-H	3300	Strong	O-H	2500-3100	Strong, broad
C \equiv C	2100-2260	Medium	Nitrile		
Alkyl halide			C=N	2210-2260	Medium
C-Cl	600-800	Strong	Nitro		
C-Br	500-600	Strong	NO ₂	1540	Strong
Alcohol			Aldehyde		
O-H	3400-3650	Strong, broad	C-H	2800 - 2700	Medium
C-O	1050-1150	Strong			
Arene					
C-H	3030	Weak			
Aromatic ring	1660-2000	Weak			
	1450-1600	Medium			