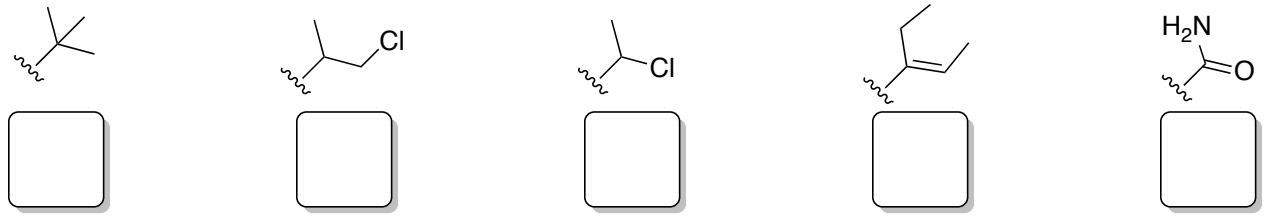
Homework 8
Organic Chemistry I (CHM 221/223) • Prof. Chad Landrie

Score (4 pts)		Lectures	18-21	Name	

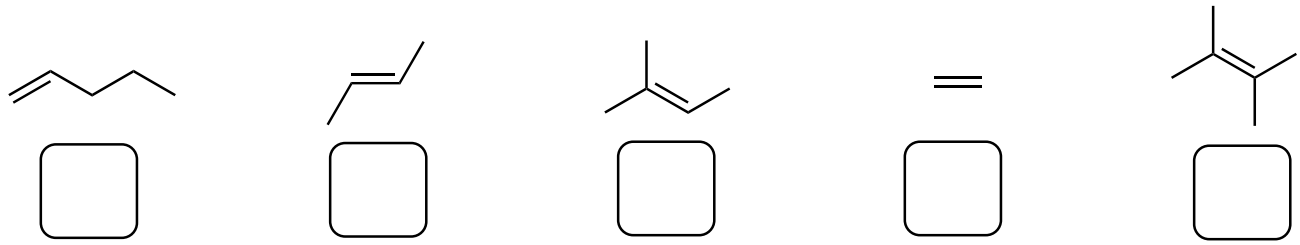
1. Rank the molecules in each set below according to the trends observed for the physical and chemical properties indicated.

A. Rank in order of increasing rate of chlorination (Cl_2, no light) (1 = slowest rate; 4 = fastest rate). *Hint: More nucleophilic alkenes react with Cl_2 faster*.

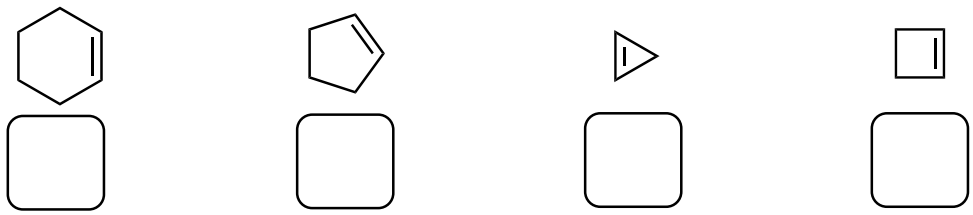
B. Rank in order of increasing CIP priority. The squiggly line represents the point of attachment to another group (e.g., an alkene). (1 = lowest CIP priority; 5 = highest CIP priority)



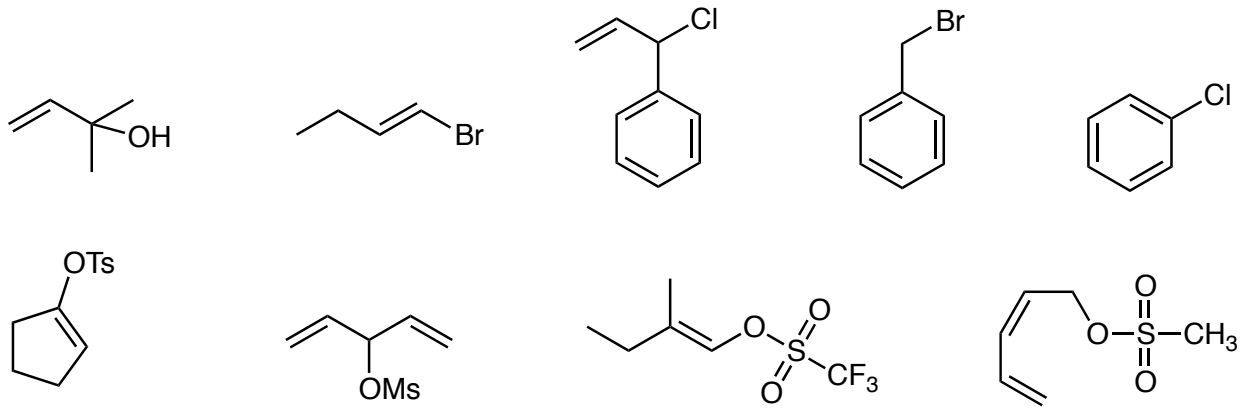
C. Rank in order of increasing heat of hydrogenation (1 = lowest; least heat released; 5 = highest; most heat released).



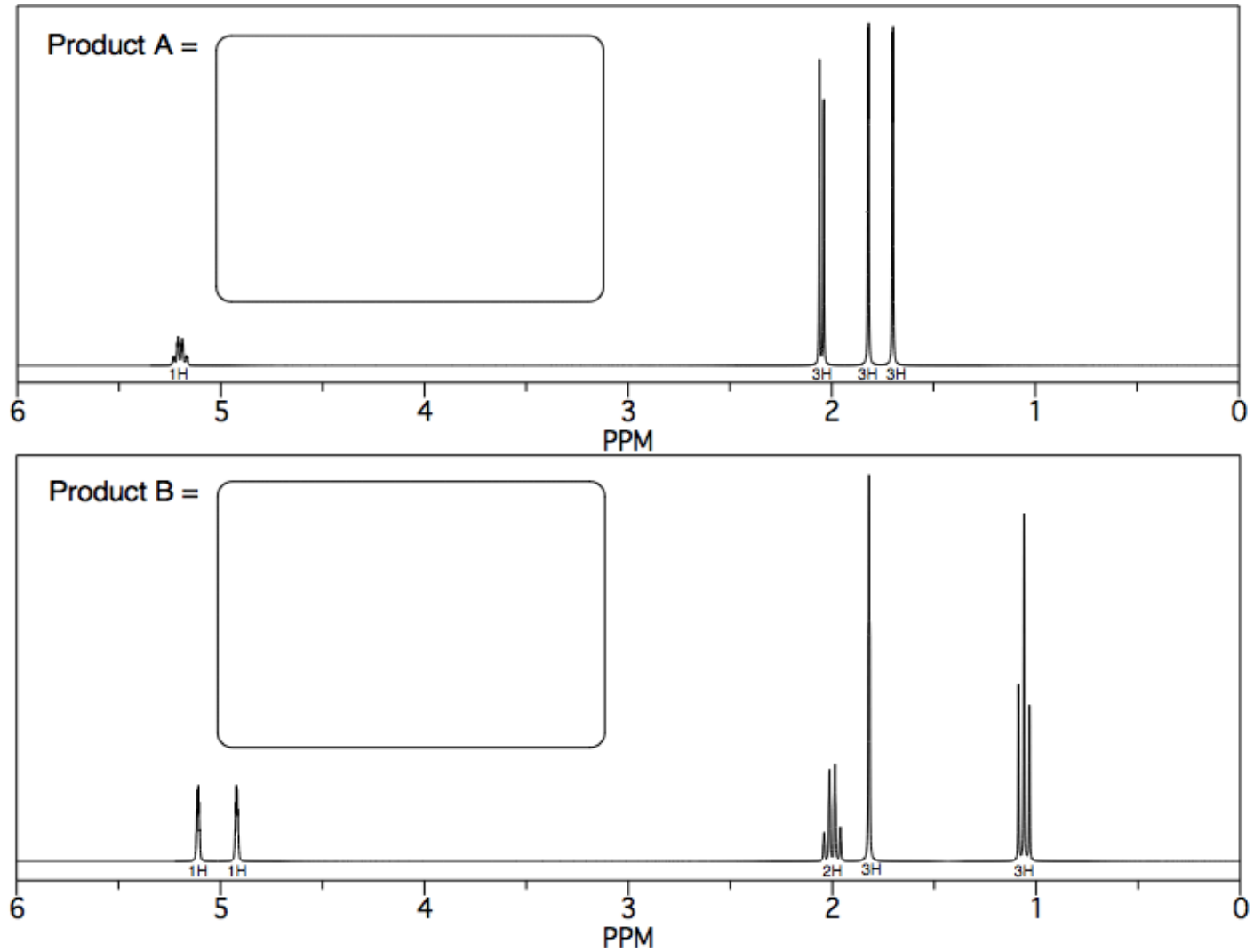
D. Rank in order of increasing heat of hydrogenation (1 = lowest; least heat released; 4 = highest; most heat released).



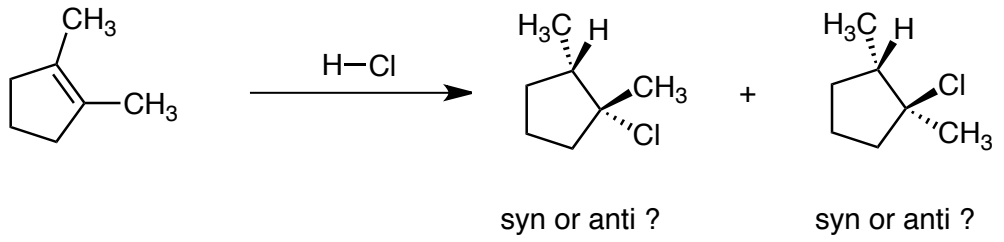
2. Circle the compounds below that would not participate in S_N1 or S_N2 reactions.



3. A compound with a broad band at 3400 cm^{-1} in the IR spectrum was treated with H_2SO4/H_2O. Two products were isolated with the 1H-NMR spectra below. Draw the structure of product A and B.

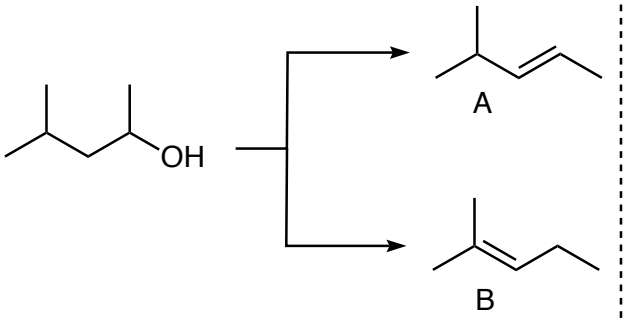


4. The addition of HCl across the alkene results in approximately equal amount of products A and B. **First**, under each product, circle whether it represents a syn-addition or an anti-addition. **Second**, draw a mechanism that shows how each product is formed. **Third**, explain why a mixture of both products is formed.



syn or anti ? syn or anti ?

5. The dehydration of alcohols can in some cases result in carbocation rearrangements. In the boxes, write whether each set of conditions will result in product A or product B as the major product.



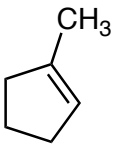
$POCl_3$, pyridine ☐ H_3PO_4 ☐

H_2SO_4 ☐ 1. TsCl 2. $NaOCH_3$ ☐

6. Choose one set of conditions that would provide products A as the major product in the question above and draw the mechanism.

7. Choose one set of conditions that would provide products B as the major product in the question above and draw the mechanism.

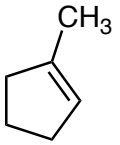
8. **First**, draw the major organic product for each reaction below. **Second**, circle whether the reactions proceeds primarily by syn-addition, anti-addition or no preference/neither.



a. B_2H_6, diglyme

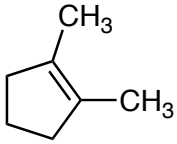
b. H_2O_2/NaOH then H_3O^+/H_2O

syn, anti or neither?



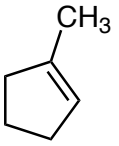
Br_2, CH_2Cl_2

syn, anti or neither?



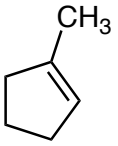
H_2, Pd/C, CH_3CH_2OH

syn, anti or neither?



HBr, CCl_4

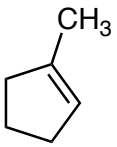
syn, anti or neither?



OsO_4,

$(CH_3)_3COOH$, $(CH_3)_3COH$

syn, anti or neither?

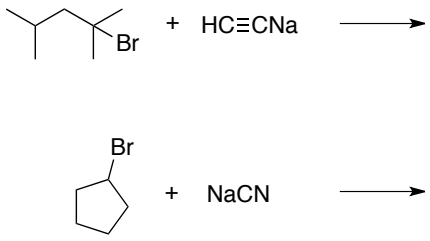


mCPBA, CH_2Cl_2

$NaHCO_3$

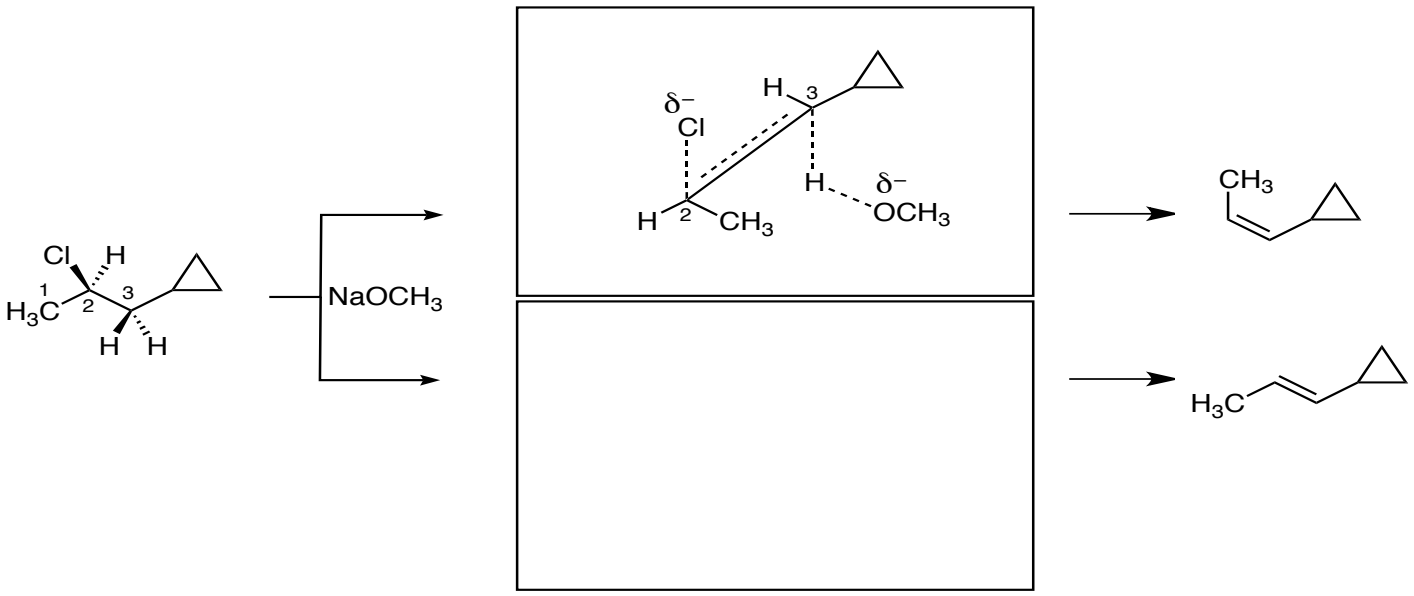
syn, anti or neither?

9. In each reaction below, substitution and elimination compete with one another. **First**, draw the *major* product expected for each reaction. **Second**, list three conditions favoring nucleophilic substitution over elimination.

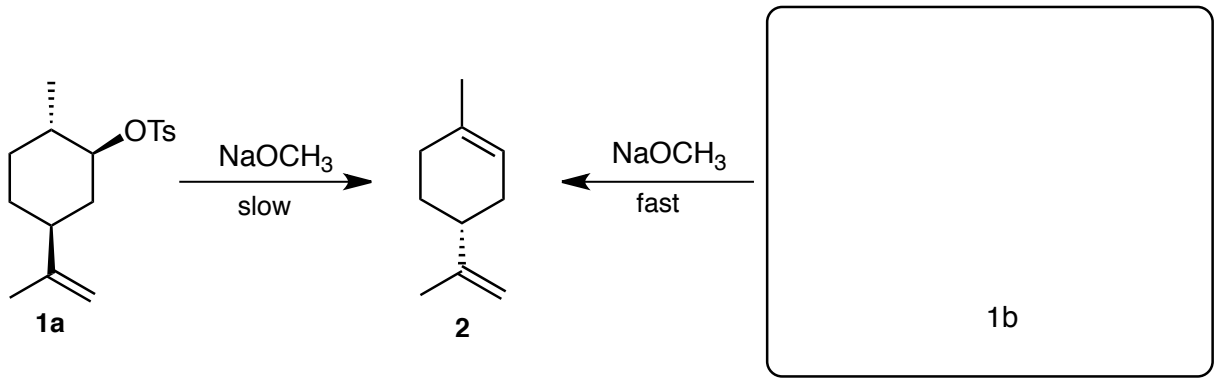


Conditions favoring substitution:

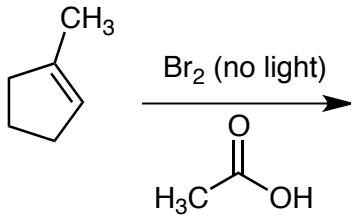
10. Dehydrohalogenation (E2) is stereoselective. **First**, circle the in the reaction below. **Second**, using the top transition state as an example, draw a transition state using a sawhorse projection that sites down the C2-C3 bond (drawn for you) leading to the *trans* product that illustrates *anti*-elimination. Your transition state should include dashed lines for partial bonds as well as partial charges. **Third**, explain why the transition state leading to the major product you circled is lower in energy.



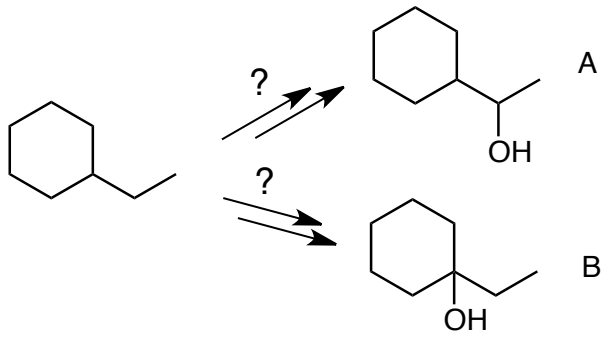
11. Compound 1a does not undergo E2 reaction readily to provide alkene 2. Compound 1b, however, does and is an isomer of 1a. Draw the structure of compound 1b. Be sure to include correct stereochemistry at relevant carbon atoms.



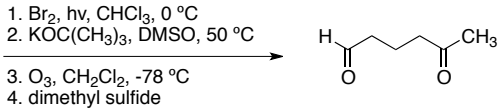
12. The alkene below reacts with Br_2 and acetic acid to form a vicinal haloester. The reaction is both stereoselective and regioselective. **First**, draw the *major* product you would expect including correct regiochemistry and stereochemical notation (i.e. dashes and wedges). **Second**, draw a complete mechanism that includes curved arrow notation to show electron flow, shows all electron pairs being used in your mechanism and indicates charges where appropriate. Your mechanism should account for the fact that this reaction is both stereospecific and regioselective. *Hint: show the correct stereochemistry of the bromonium ion intermediate*.

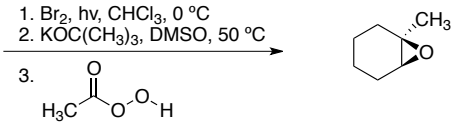


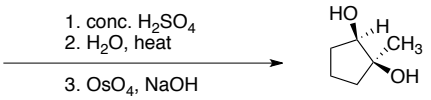
13. Outline a separate synthesis for alcohols A and B shown below. Each synthesis must proceed through an alkene.

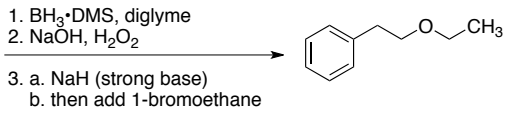


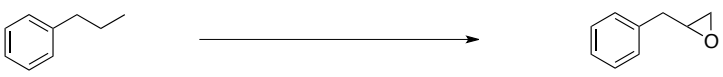
14. Fill in the missing reactant or reagents for each transformation. Two or more steps may be needed.











15. Provide an IUPAC name for each. Be sure to use stereodescriptors such as *R*, *S*, *E*, *Z* when appropriate.