Homework Eight
Organic Chemistry I (223) • Prof. Chad Landrie
Spring 2013

Completion (6 pts)		**Name**	
Random Sample(s) (4 pts)		**BID**	
Total (10 pts)		**Section-CRN**	

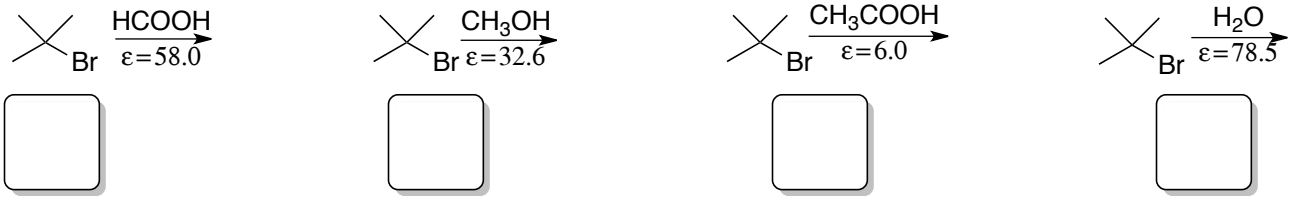
Additional Recommended Problems from McMurray (8th Ed.)	7.29, 7.30, 7.31, 7.37, 7.38, 7.40, 7.45, 7.46, 7.47, 7.48, 7.55, 7.58, 7.59, 8.26, 8.27, 8.28, 8.29, 8.31, 8.32, 8.34, 8.35, 8.38, 8.58, 8.61, 10.17, 10.37, 11.45, 11.46, 11.50, 11.52, 11.53, 11.56, 11.58, 11.64, 11.67, 11.71

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

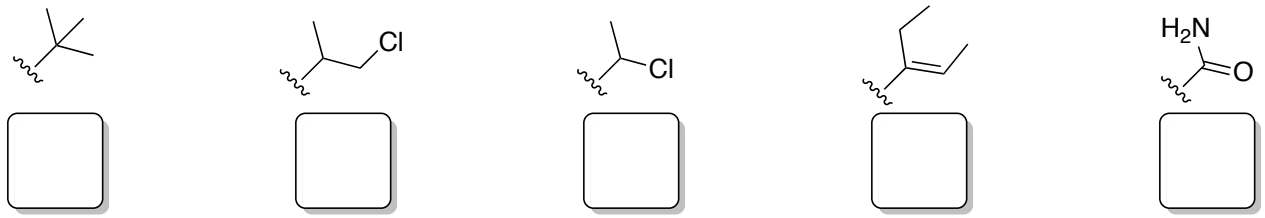
A. (4 pts) Rank in order of increasing rate of chlorination (Cl_2, no light) (1 = slowest rate; 4 = fastest rate). *Hint: More nucleophilic alkenes react with Cl_2 faster.*

B. (4 pts) Rank in order of increasing nucleophilicity (1 = least nucleophilic; 4 = most nucleophilic).

C. (4 pts) Rank in order of increasing rate of solvolysis. *The dielectric constant is written below each solvent.* (1 = slowest rate; 4 = fastest rate). *Hint: Each of these solvoylses are S_N1 processes.*



D. (4 pts) 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)



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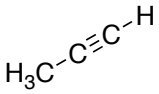
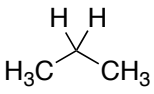
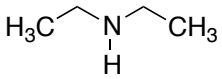
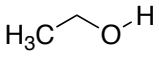
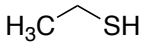
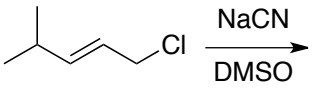
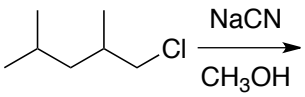
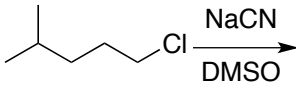
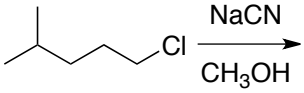
E. (4 pts) Rank in order of increasing acidity (1 = least acidic, highest pK_a; 5 = most acidic, lowest pK_a).

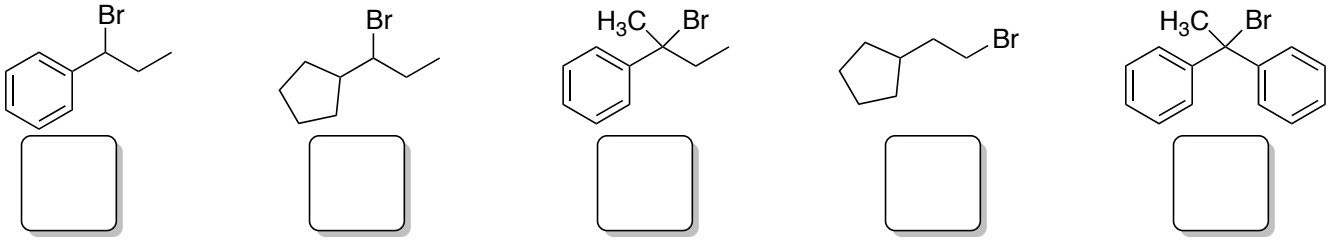






F. (4 pts) Rank in order of increasing rate of S_N2 (1 = slowest rate; 4 = fastest rate). *Hint: Also consider the nucleophilicity of cyanide in the solvents listed below the reaction arrow.*

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

H. Rank each alkene in order of increasing rate of S_N1 reaction (1 = slowest rate; 5 = fastest rate).



2. We have learned three ways to prepare alkyl halides. Draw a specific example of each method.

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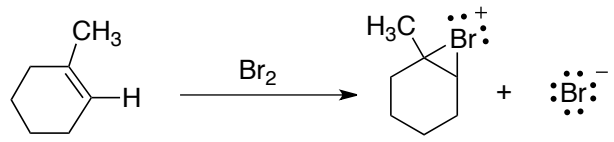
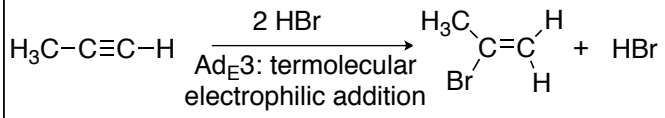
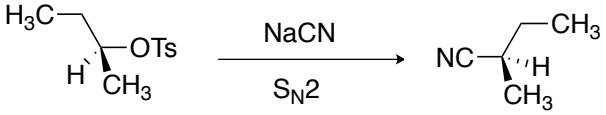
3. Draw the transition state (TS) for each elementary step below. Be sure to include all formal charges, partial charges, lone-pairs of electrons and use dotted lines to represent partial bonds.







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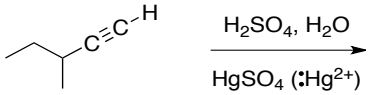
4. **First**, draw the *major* product of the reaction below. **Second**, draw a mechanism for this transformation. Draw one elementary step per reaction arrow. Be sure to draw all electron lone-pairs and radicals; show all formal charges; and use curved-arrow notation to show the movement of electrons. **Third**, label the mercuronium ion intermediate and the enol intermediate. **Fourth**, using your mechanism, briefly explain the observed regioselectivity for the reaction.



Final Product

Mechanism

Explanantion

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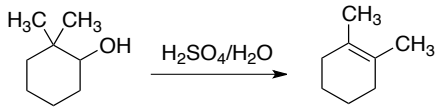
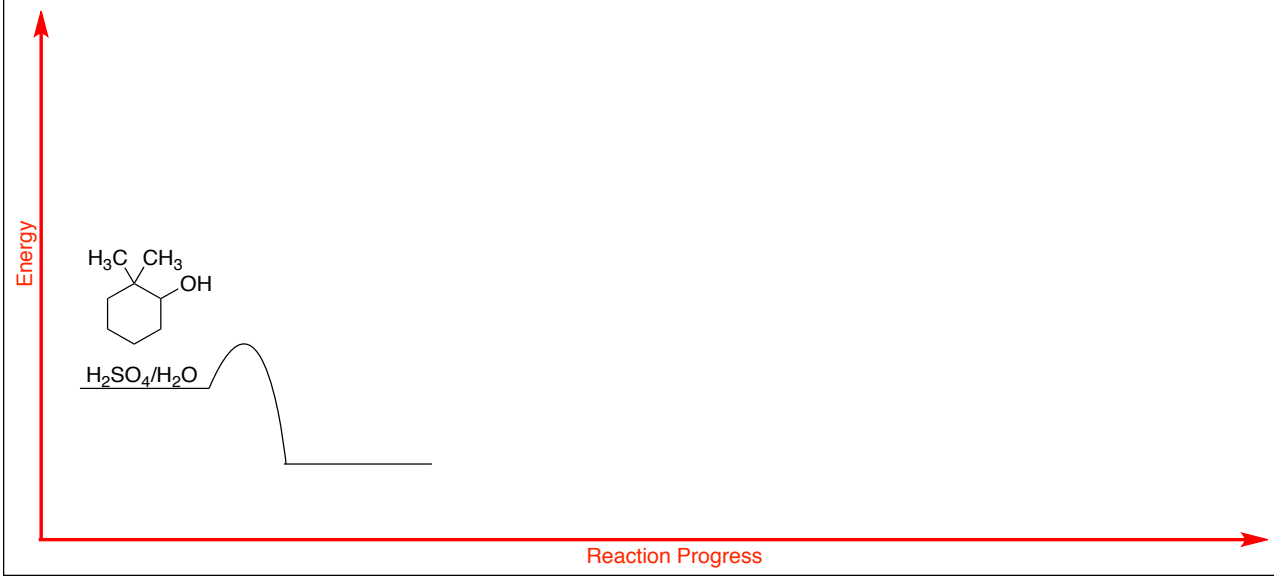
5. **First**, draw a mechanism that accounts for the E1 reaction below. Draw one elementary step per reaction arrow. Be sure to draw all electron lone-pairs and radicals; show all formal charges; and use curved-arrow notation to show the movement of electrons. **Second**, finish the potential energy diagram that has been started for you by using the intermediates and final product in your mechanism. Draw each intermediate above a horizontal line that represents its relative potential energy. **Third**, label the activation energy for the rate-determining step.



Mechanism

Reaction Potential Energy Diagram



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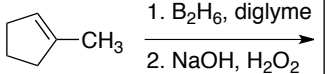
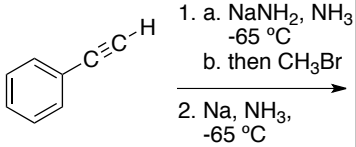
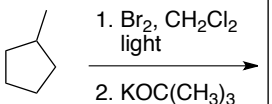
6. Draw the *major* organic product after each series of reactions. You must draw the correct regioisomer and/or stereoisomer for full credit. Some schemes contain more than one step; you do not need to draw the product after each step. Only the final products drawn in the boxes provided will be graded.



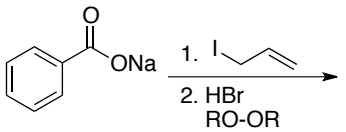
regioselectivity & stereoselectivity?



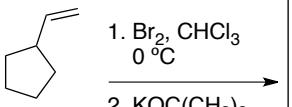
stereoselectivity?

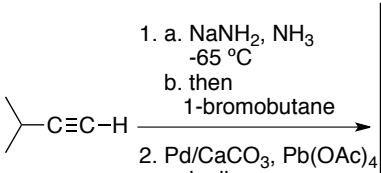


regioselectivity?

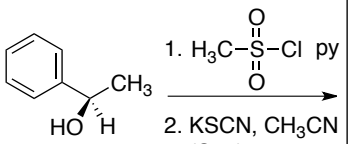


regioselectivity?

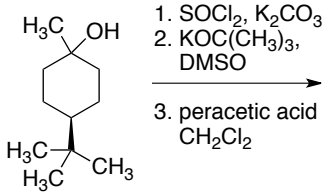




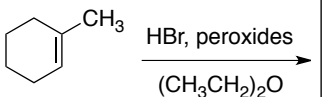
stereoselectivity?



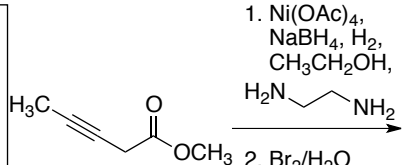
stereoselectivity?



regioselectivity & stereoselectivity?



regioselectivity?



regioselectivity & stereoselectivity?

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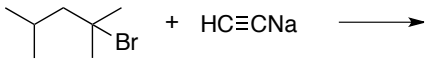
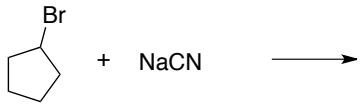
7. In each reaction below, substitution and elimination compete with one another. **First**, draw the *major* product expected for each reaction. **Second**, list four conditions favoring nucleophilic substitution over elimination.





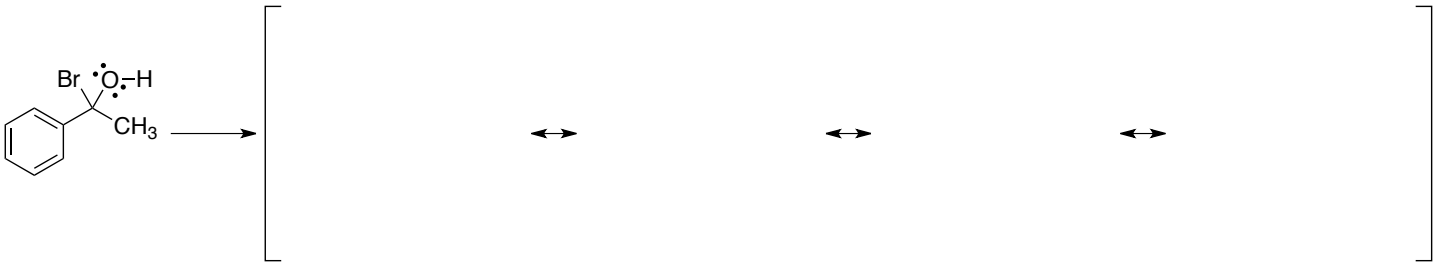
Conditions favoring substitution:

8. (4 pts) **First**, draw an example of a reaction that is stereospecific. Include the reactant, conditions and product. **Second**, draw an example of a reaction that is stereoselective, but not stereospecific. In both, use dash-and-wedge notation to indicate the configuration of both reactants and products.

Stereospecific

Stereoselective but not stereospecific

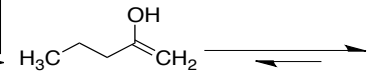
9. (4 pts) Draw four resonance structure for the carbocation formed following the heterolysis of the C-Br bond.



10. (8 pts) Hydration of an alkyne gives an enol as the initial product, which subsequently undergoes tautomerization to give the final product. Fill in the boxes below to illustrate

starting alkyne

conditions



enol

tautomer

functional group name

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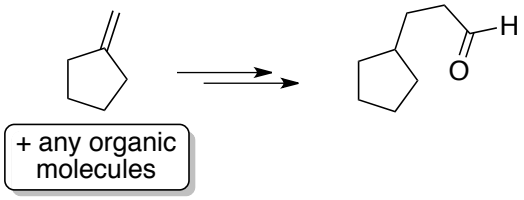
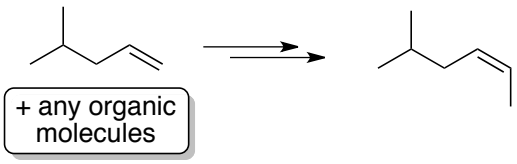
11. **First,** write a forward synthesis for each transformation below. Each reaction arrow should represent *one* synthetic step. Draw the *major* product after each step. Include all essential reagents above the reaction arrow; solvents, temperature and other "non-essential" conditions are not required. Draw every product after each step. You may also write out a retrosynthesis; however, only the forward synthesis will be graded. **Second**, label all substitution and elimination reactions as S_N1, S_N2, E1 or E2 below the reaction arrow.





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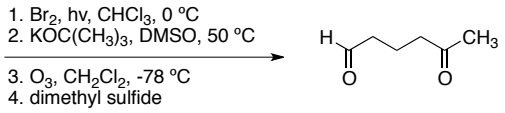
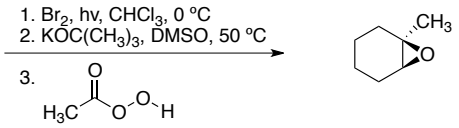
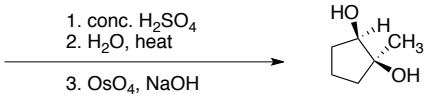
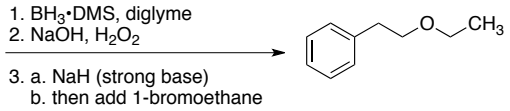
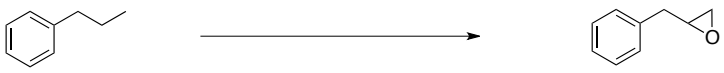
12. Fill in the missing reactant or reagents for each transformation. Two or more steps are needed for every reaction.











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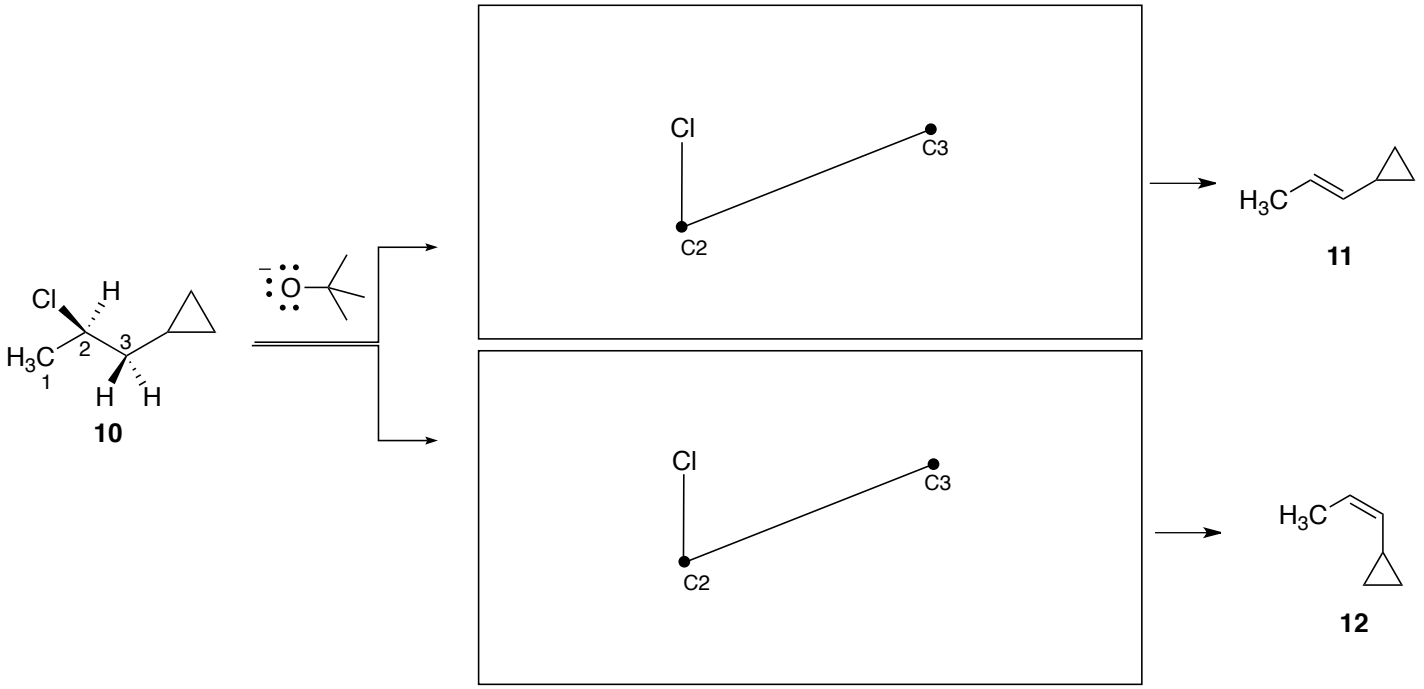
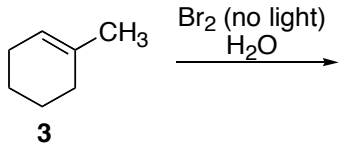
13. The dehydrohalogenation of **10** is stereoselective. **First**, circle the number corresponding to the *major* alkene product in the reaction below. **Second**, draw a transition state using a sawhorse projection that sites down the C2-C3 bond (drawn for you) leading to each product and that illustrates *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.



Explanation:

14. Methylcyclohexene (**3**) reacts with Br_2 and H_2O to form a vicinal halohydrin. 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.*



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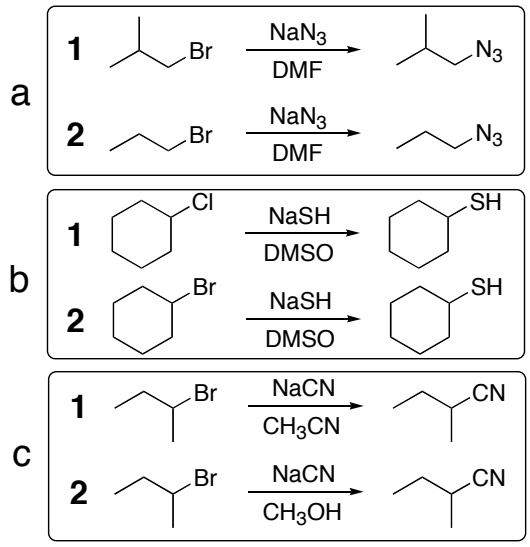
15. **First**, determine the fastest reaction in each pair. **Second**, write a short essay explaining your choices. Your essay should include considerations of mechanism, nucleophile, leaving group and solvent.



16. Predict the products from the reaction of 1-hexyne with the following reagents:

a. 1 equivalent of HBr

b. 1 equivalent of Cl_2

c. H_2, Lindlar catalyst

d. $NaNH_2$ in NH_3, then CH_3Br

e. H_2O, H_2SO_4, $HgSO_4$

f. 2 equivalents of HCl

17. Predict the products from the reaction of 2-hexyne with the following reagents:

a. 2 equivalents of Br_2

b. 1 equivalent of HBr

c. Li in NH_3

d. excess H_2, Pd/C catalyst