Oakton Community College

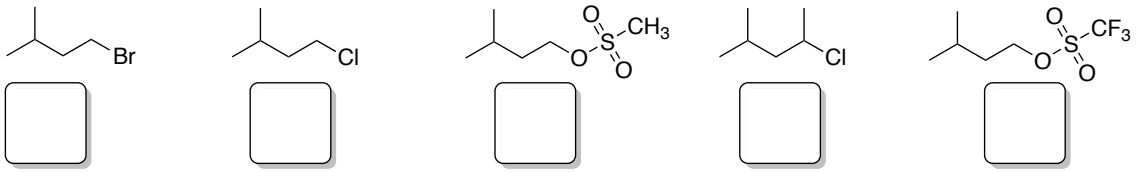
Homework Seven
Organic Chemistry I (223) • Prof. Chad Landrie
Spring 2013

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

Additional Recommended Problems from McMurray (8th Ed.)	11.25-11.31; 11.32; 11.33; 11.34; 11.36; 11.38; 11.41; 11.42; 11.43; 11.44; 7.27; 7.29; 7.30; 7.31; 7.38; 7.40

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

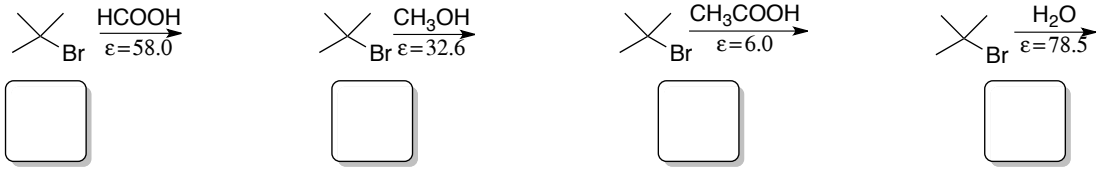
A. (4 pts) Rank in order of increasing rate of S_N2 with sodium cyanide (1 = slowest S_N2; 5 = fastest S_N2).



B. (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*.

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

D. (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*.



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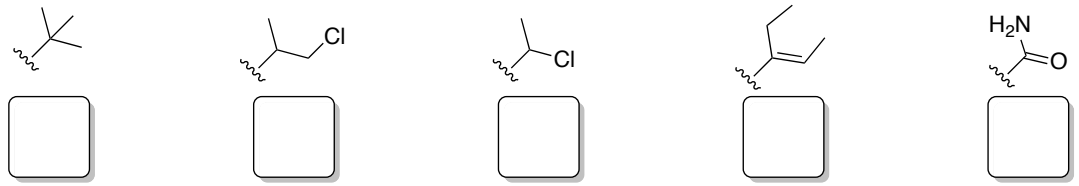
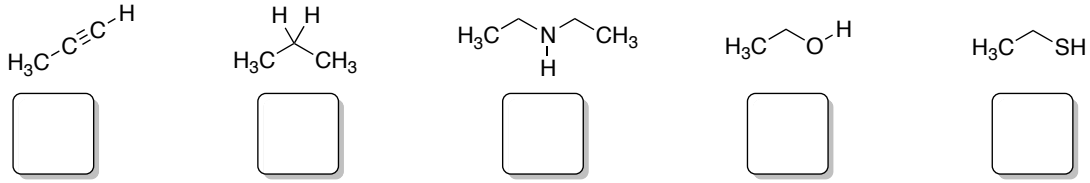
E. (4 pts) Rank in order of increasing CIP priority. The squiggly line represents the point of attachment to another group (e.g., an alkene). (1 = lowest CIP priority; 5 = highest CIP priority)

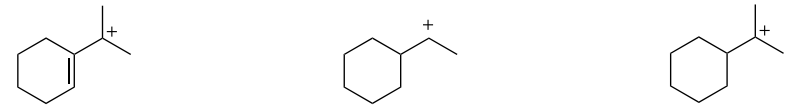


F. (4 pts) Rank in order of increasing bond dissociation energy for the circled C-H bond (1 = lowest BDE, least energy required to break bond; 4 = most energy required to break bond). *Hint: Consider the stability of radical intermediates formed upon homolysis.*

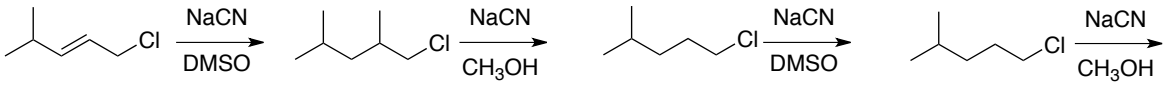
G. (4 pts) Rank in order of increasing acidity (1 = least acidic, highest pK_a; 5 = most acidic, lowest pK_a).



H. (4 pts) Rank in order of increasing carbocation stability (1 = least stable; 5 = most stable).



I. (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.*



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

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2. Circle the *best* answer. Your understanding of the explanation is more important than getting the correct answer. There is no multiple choice on exam 3.

A. Which solvent would provide the *slowest* S_N2 reaction of 1-bromobutane with sodium cyanide?
   a. acetonitrile
   b. *N*,*N*-dimethylformamide
   c. dimethyl sulfoxide
   d. dichloromethane
   e. methanol

B. Which stereoisomer is a *meso* form?
   a. *cis*-1,3-dimethylcyclohexane
   b. *trans*-2-chloropent-3-ene
   c. (+)-carvone
   d. (2*R*, 3*R*)-2,3-dibromobutane
   e. All of the above are meso.

C. Which statement is *false* concerning nucleophiles?
   a. For atoms in the same row and with the same charge, nucleophilicity descreases left to right across the periodic table.
   b. For identical atoms: the more basic, the more nucleophilic.
   c. Nucleophilicity decreases for halides down group 7 since larger halides are better solvated.
   d. Nucleophilicity decreases as the size of the nucleophile increases.
   e. All of the above are true statements.

D. Which reaction below is stereospecific?
   a. S_N1 solvolysis of 2-bromobutane with CH_3OH
   b. Markovnikov addition of HCl to *E*-2-pentene
   c. Addition of Br_2 *Z*-2-pentene
   d. S_N2 of 2-bromobutane with NaCN
   e. None of the above.

E. S_N2 of 2-bromobutane with NaCN is faster in polar aprotic solvents than in polar protic solvents. Why?
   a. Polar protic solvents are acids, which may protonate the carbocation intermediate.
   b. Polar protic solvents raise the potential energy of *tert*-butyl chloride.
   c. Polar aprotic solvents lower the potential energy of the carbocation intermediate and transition state through electrostatic attractions.
   d. Polar aprotic lower the potential energy of the product.
   e. Cyanide is more nucleophilic in polar aprotic solvents than polar protic solvents.

F. Which reagent(s) could be used to produce an "Anti-Markovnikov" product?
   a. B_2H_6, diglyme
   b. Br_2 (no light), CH_2Cl_2
   c. HBr, CH_2Cl_2
   d. H_2SO_4/H_2O
   e. Cl_2, H_2O

G. Which best explains Markovnikov's predictive rule that the most substituted products are formed through addition of hydrogen halides across alkenes?
   a. More substituted products are more stable.
   b. Halides add to the least sterically hindered carbon of the alkene.
   c. Protonation of the alkene occurs at the least substituted carbon since steric hinderance is the lowest.
   d. Addition proceeds through the most stable carbocation intermediate.
   e. None of the above.

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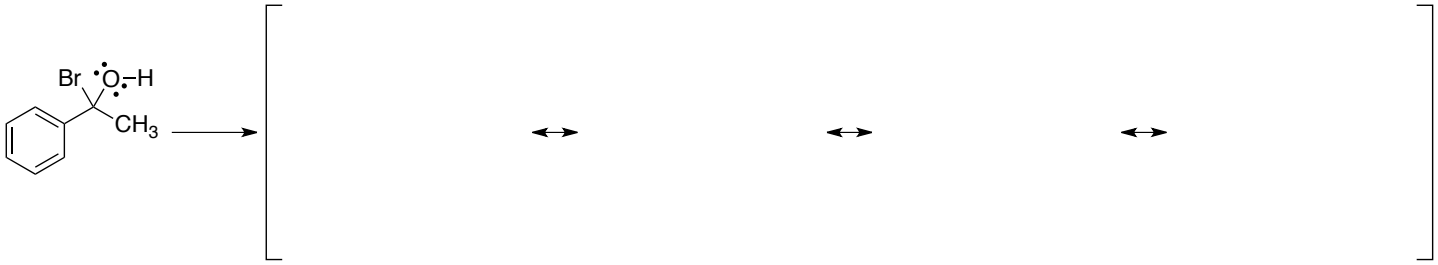
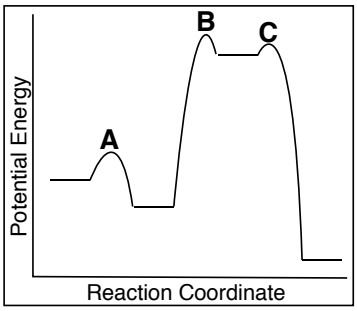
3. 4 pts) Draw four resonance structures for the carbocation formed following the heterolysis of the C-Br bond.

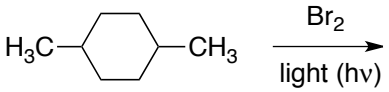


4. (6 pts) Draw the transition states represented by **A**, **B**, and **C** for the reaction of 2-methyl-2-butanol with HCl. Draw partial bonds as dotted lines. Be sure to show all formal charges (+ or –) and all partial charges (δ+ or δ–) if they exist on the correct atoms.

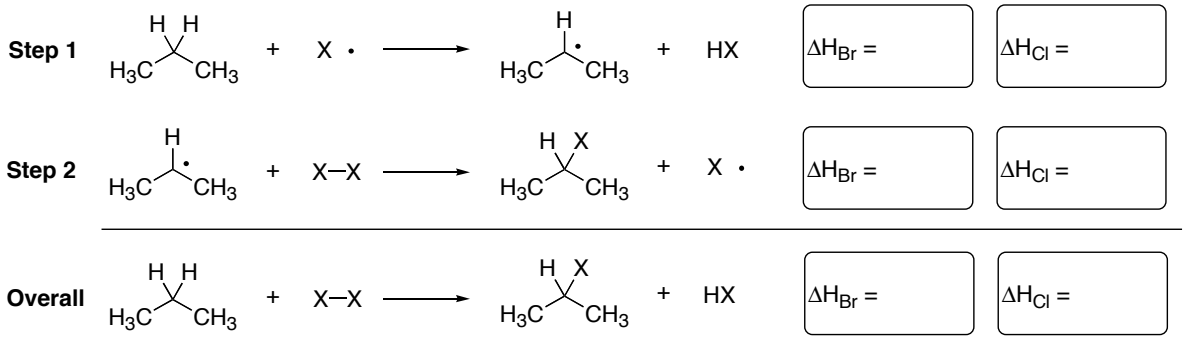


A	B	C

5. (4 pts) First, draw all three monobromination products for the reaction below. Second, using the relative rates of halogenation in the lecture notes, determine the product distribution (percentage of each product). Show all work.



6. Using the table of bond dissociation energies in your textbook (pg. 204), calculate the enthalpy of each step and the enthalpy of the overall reaction for both chlorination (X = Cl) and bromination (X = Br) of the compound shown.



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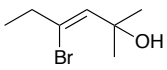
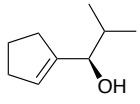
7. First, explain why carbocations are higher in energy than oxonium ions, despite oxygen being more electronegative than carbon. Second, state four factors that account for the relative stabilities of carbocations.

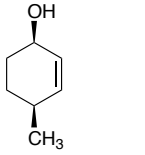
8. Draw the complete Lewis structure for three polar aprotic solvents commonly employed in S_N reactions. Below each structure, write the full name and the abbreviation (e.g. dichloromethane, DCM).

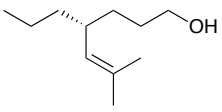
9. More substituted alkenes are lower in potential energy than less substituted alkenes do to increased hyperconjugation. Draw the the hyperconjugation model that shows the overlap between an antiperiplanar C-H bond and a p-orbital of an alkenes.

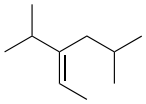
10. Provide IUPAC names for each of the following structures. Be sure to include stereodescriptors (e.g., *E/Z and R/S*) where appropriate.

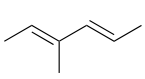












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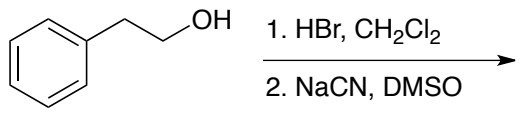
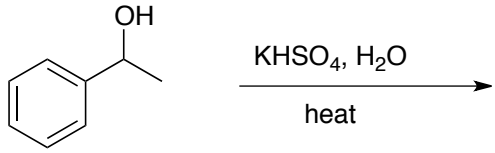
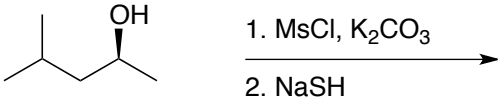
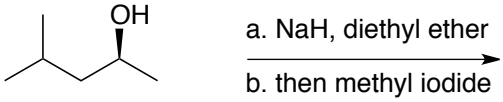
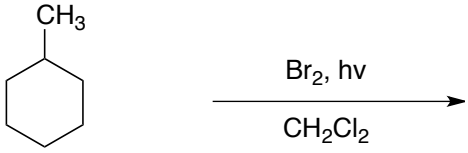
11. Draw the *major* product for each of the following reactions. Be sure to indicate the correct stereochemistry where appropriate.

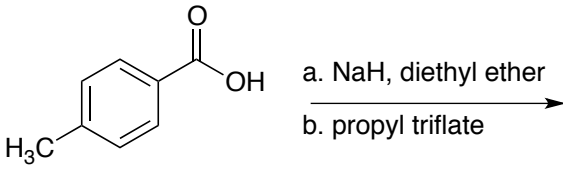


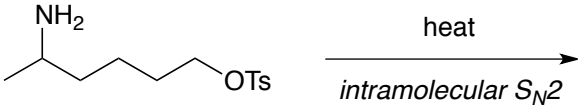












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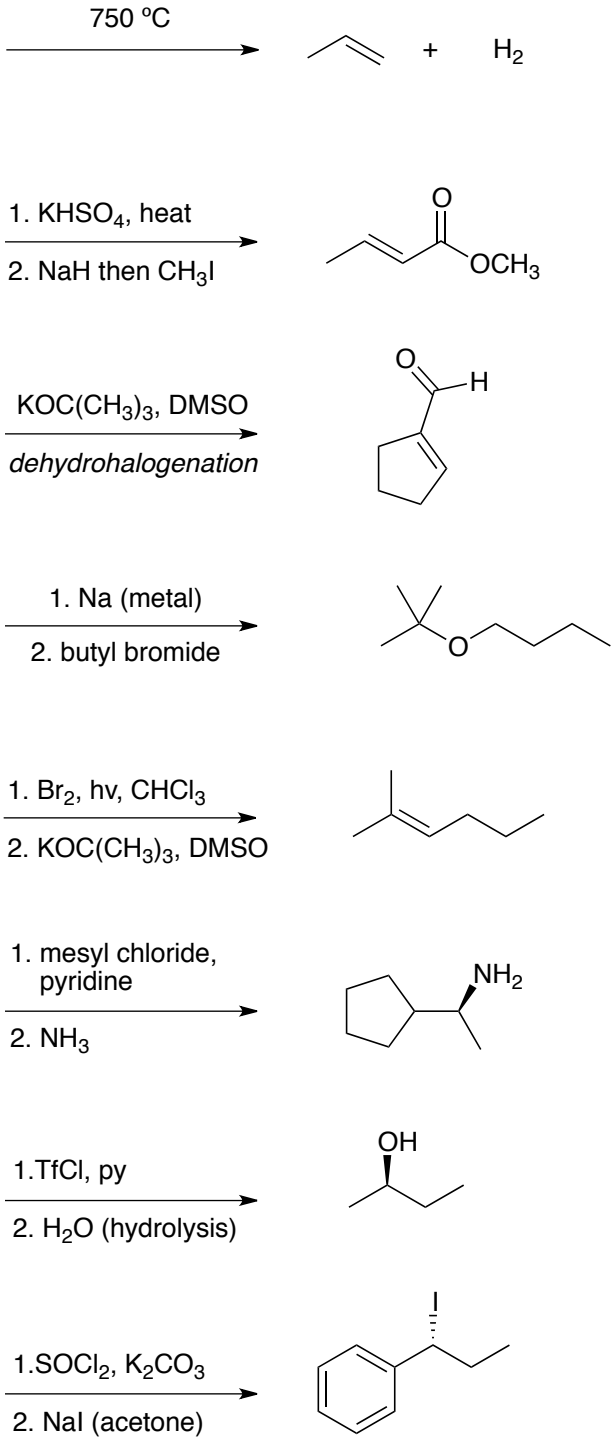
12. Draw the reactant required to produce each *major* product. Be sure to indicate the correct stereochemistry where appropriate.



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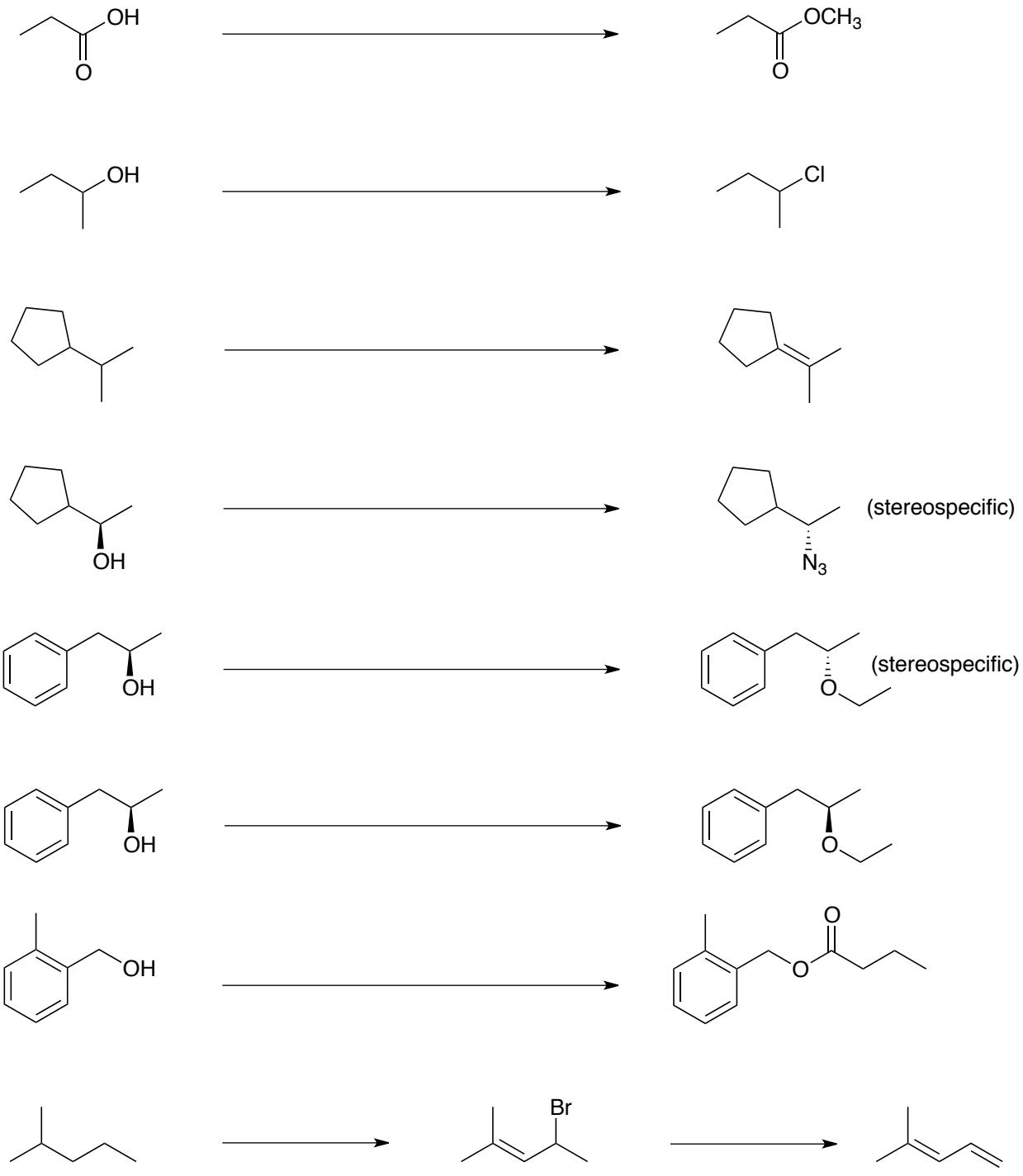
13. Fill in the reagents and conditions necessary to effect each transformation. More than one step may be required. Number separate steps.



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14. Draw a mechanism that accounts for each transformation using curved arrow notation. Include all electron lone-pairs on all atoms and formal charges.