Homework 7
Organic Chemistry I (CHM 221/223) • Prof. Chad Landrie
Score (4 pts)
Lectures
14-18
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 $S_{N} 2$ with sodium cyanide $\left(1=\right.$ slowest $S_{*} 2 ; 5=$ fastest $\left.S_{\vee} 2\right)$.





$\square$

$\square$

B. Rank in order of increasing nucleophilicity ( $1=$ least nucleophilic; $4=$ most nucleophilic $)$.
$\mathrm{H}_{3} \mathrm{C}-\mathrm{SNa}$

$\mathrm{H}_{3} \mathrm{C}-\mathrm{ONa}$





C. 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 $S_{N} 1$ processes.





D. Rank in order of increasing rate of $\mathrm{S}_{\mathrm{N}} 2(1=$ slowest rate; $4=$ fastest rate $)$. Hint: Also consider the nucleophilicity of cyanide in the solvents listed below the reaction arrow.




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E. Rank each compound in order of increasing rate of $S_{N} 1$ reaction $(1=$ slowest rate; $5=$ fastest rate $)$.







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2. (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.
a

b


C

(
3. Draw four resonance structures for the carbocation formed following the heterolysis of the $\mathrm{C}-\mathrm{Br}$ bond.

4. Draw the transition states represented by $\mathbf{A}, \mathbf{B}$, and $\mathbf{C}$ for the reaction of 2-methyl-2-butanol with HCl . Draw partial bonds as dotted lines. Be sure to show all partial charges ( $\delta+$ or $\delta-$ ) if they exist on the correct atoms.


| A | B | C |
| :--- | :--- | :--- |
|  |  |  |
|  |  |  |

5. Circle the compounds below that could be considered a polar aprotic solvent.








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6. 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.

7. 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 $(\mathrm{X}=\mathrm{Cl})$ and bromination $(\mathrm{X}=\mathrm{Br})$ of the compound shown.


8. Write IUPAC names for each structure. Be sure to include stereodescriptors for chirality centers.



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


$\mathrm{HCl}, \mathrm{CHCl}_{3}$

$\xrightarrow[\text { 2. } \mathrm{NaSH}]{\text { 1. } \mathrm{MsCl}, \mathrm{K}_{2} \mathrm{CO}_{3}}$

a. NaH (a strong base)
$\overrightarrow{\text { b. then methyl iodide }}$





a. $\mathrm{Et}_{3} \mathrm{~N}$ (amine base) b. propyl triflate


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





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


13. Consider the carbocations that could be formed from the compounds below through substitution reactions and assuming no rearrangements. Circle the compounds whose carbocations would be stabilized by resonance.










14. The alcohol below was optically pure (i.e. one enantiomer). After treating with dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ in water the optical rotation changed as shown in the graph. NMR and IR spectra confirm that the compound after this treatment had the same constitution as before. Explain this observation. Draw a mechanism to support your explanation and draw all reaction products.

15. Write the missing conditions ( $a, b, c$ ) and draw the missing structures ( $A, B, C$ ) in the synthesis below. The H-NMR spectrum is given for the final product, C .



