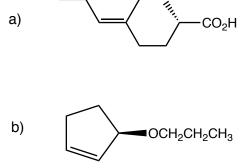
CHEM 234	Final E	xam		Ian R. Gould	
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K Ca Sc Ti V Cr Mn Fe Co	Ni Cu Zn Ga Ge	As Se Br Kr	H/Me ~1.4	Et/Me ~0.95	
Rb Sr Y Zr Nb Mo Tc Ru Rh	Pd Ag Cd In Sn	Sb Te I Xe	Me/Me ~2.6	i-Pr/Me ~1.1	
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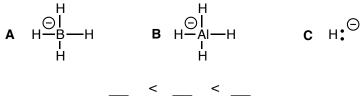
NAME

Question Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

- 2 -



Question 2) Rank the following in order of Lewis base strength, and give a BRIEF explanation



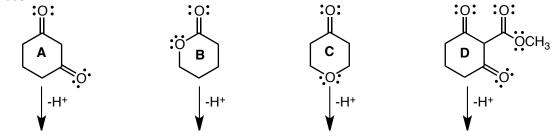
Question 3) Indficate which of the following two structures A or B would react fastest with a diene in a Diels-Alder reaction. Give an explanation that includes the following terms: "energy of the HOMO", "energy of the LUMO", and also "withdrawing substituent" and "donating substituent", you should also identify and withdrawing and donating substituents

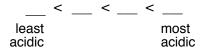


NAME

Question 4) Rank the following in order of increasing Bronsted acidity. For each, ADD THE MISSING MOST ACIDIC HYDROGEN ATOM to the provided structure and draw the conjugate base anion, include any important resonance contributors and give a brief explnanation for your choices

-3 -

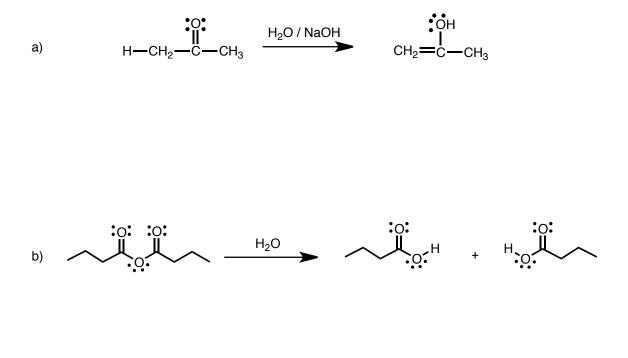


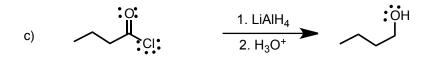


- 4 - NAME

Question 5 (Give a curved arrow pushing mechanism for the following reactions • AS APROPRIATE, SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no +H<sup>+</sup>/-H<sup>+</sup>) • DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate • At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and

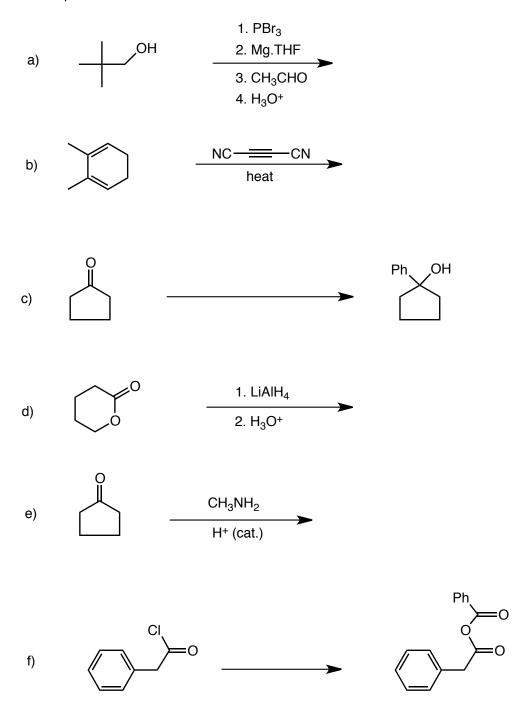
whether they are also Bronsted acids and bases (BA or BB) as appropriate





CHM 234, FINAL EXAM PRACTICE TEST #1 - 5 - NAME

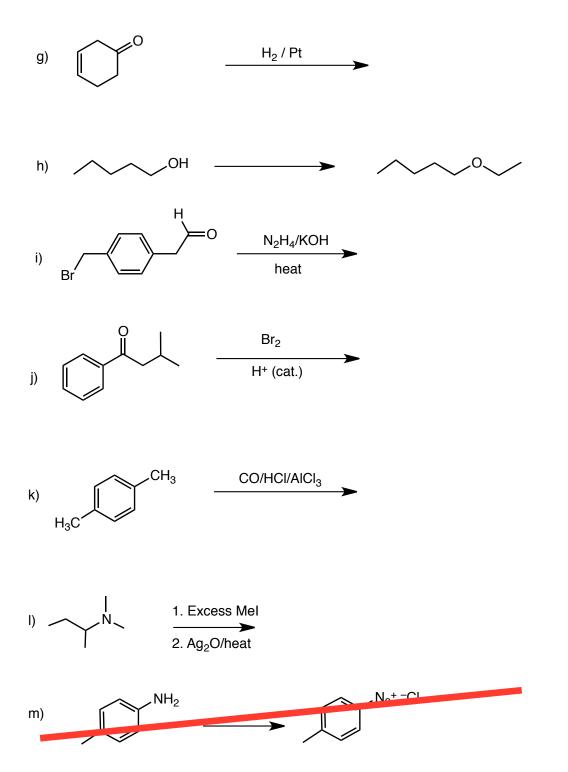
Question 6 Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



NAME

- 6 -

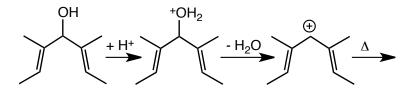
Question 6, contd.



NAME

Question 7) Protonation of the alcohol below results in loss of water as a leaving group to generate a cation that undergoes an electrocyclic ring closing reaction

- 7 -



a) give the curved arrow-pushing that accounts for electrocyclic reaction

b) draw the electrocyclic product, paying special attention to relative stereochemistry of any substituents

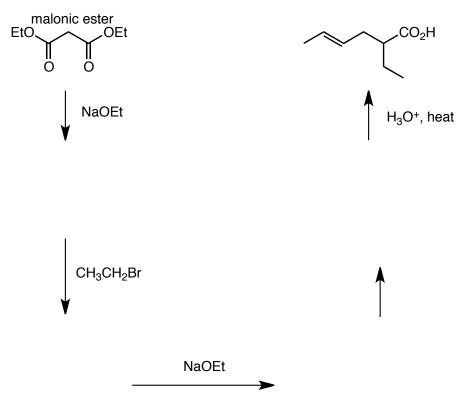
c) in the product(s), indicate the locations of any chiral (asymmetric) carborts atoms with the\* symbol, and state whether the product(s) are racemic, a meso compound or achiral

d) ON TOP OF THE CATION STRUCTURE, give a drawing of the HOMO

e) state the number of vertical nodes and clearly indicate their positions

f) state whether the allowed reaction proceeds via a conrotatory or a disrotatory ring closing

Question 8) Provide the missign structures in the following malonic ester synthesis of a carboxylic acid



- 8 -

NAME

Question 9) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. If necessary, you must indicate steps that require separation of isomers

`\_C<sup>- NH</sup>2 0 a) 0<sub>2</sub>N b)

CHM 234, FINAL EXAM PRACTICE TEST #1 -9- NAME\_

Question 10) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

## THESE SYNTHESIS PROBLEMS USE ONLY REACTIONS FROM THE "MINIMAL SET OF REACTIONS" PROVIDED ON THE CLASS WEB PAGE!

OН a) OH

Br b)

Question 11) Give a curved arrow pushing mechanism for the following reactions

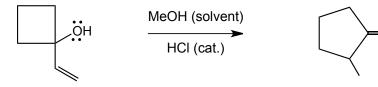
• SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no +H+/-H+) (assuem that H-Cl is completely dissociated in methanol

DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate

• At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate

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· Add hydrogen atoms and non-bonding electrons where appropriate



CHM 234, FINAL EXAM PRACTICE TEST #1 - 10 - NAME

Question 12) Disconnect the indicated bond according to the method of retrosynthetic analysis, generate the synthons and convert these into "real reagents", or "synthetic equivalents".



Question 13) For the Bronsted acid/base reaction below, label the acids/bases and which are stronger and give a brief explanation, give the curved arrow-pushing in both directions, draw a reaction energy diagram and include a drawing of the transition state, indicate which reaction is faster (left to right or vica versa) and on which side the equilibrium lies

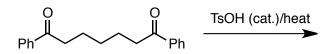


CHM 234, FINAL EXAM PRACTICE TEST #1 - 11 - NAME

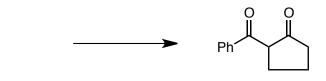
Question 13) Synthesize the (target) molecule on the right from the starting molecule on the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.



Question 14) Provide the major organic product of the following reaction and classify it as an Aldol or a Claisen reaction



Question 15) Provide the reactants/reagents/conditions to for the provided product and state whether the reaction is an Aldol condensation or a Claisen reaction



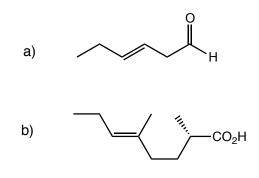
Question 16) Explain why electron donating substituents on a benzene ring increase reactivity in electrophilic aromatioc substitution, whereas electron donating groups on a C=O gewnerally decrease reactivity in nucleophilic addition, e.g. reaction with Grignards.

NAME

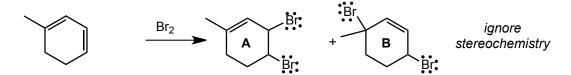
## **START OF PRACTICE TEST #2**

Question 1) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

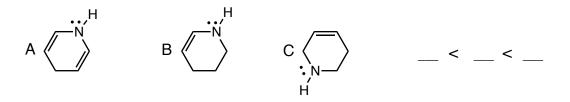
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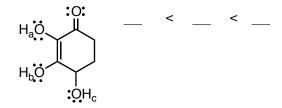
Question 2) Provide a curved arrow pushing mechanism for the following reactions (indicate LB/LA and BB/BA as appropriate). For any resonance stabilized intermediates, include all relevant resonance contributors, INDICATE WHICH IS THE MAJOR CONTRIBUTOR and explain WHY, and draw an "actual" structure using the "delta" notation to indicate partial charges. Indicate which would be the major product under conditions of **kinetic control** and which under thermodynamic control, give a BRIEF explanation for your choice that metions temperature.



CHM 234, FINAL EXAM **PRACTICE TEST #2** -3 - NAME Question 3) Rank in order of increasing basicity and give a brief explanation



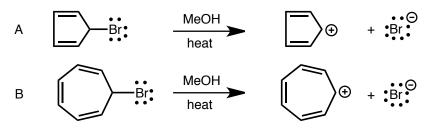
Question 4) Rank the following hydrogens Ha, Hb and Hc in order of increasing Bronsted acidity, draw structures of the relevant conjugate base anions to support your reasoning andfgive a brief explanation



Question 5) In what way is the Lewis acid/base description of reactions idifferent from the nucleophile/electrophile description?

- 4 - NAME

Question 6) Indicate which of the following two reactions, A or B would be faster. **GIVE AN EXPLANATION THAT INCLUDES A DISCUSSION OF THE EXOTHERMICITY OR ENDOTHERMICITIES OF THE REACTIONS** (only 1 point for the correct answer, 9 pts for the explanation, include the term "energy of the electrons" in your explanation)



Question 7)

a) Give the structures of the best anion and alkyl halide pair that can be used to form the provided ether (this is a Williamson ether synthesis).



b) Give the structures of the amine and the carbonyl compound that can be used to make the provided amine in a reductive amination, you should also add the reagents/conditions to the reaction arrow (you can specify reagents for either an indirect or a direct reductive amination)

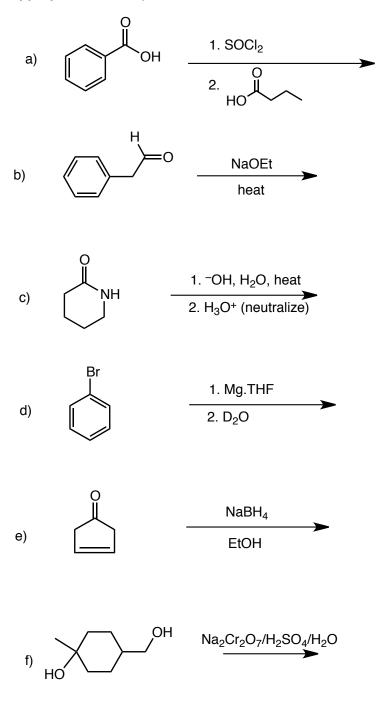


c) Give the structures of carbonyl compounds which could be used to prepare the following using an Aldol or Claisen type reaction and also provide example reagents and conditions O O

+ OCH<sub>3</sub> Ph

CHM 234, FINAL EXAM PRACTICE TEST #2 - 5 - NAME

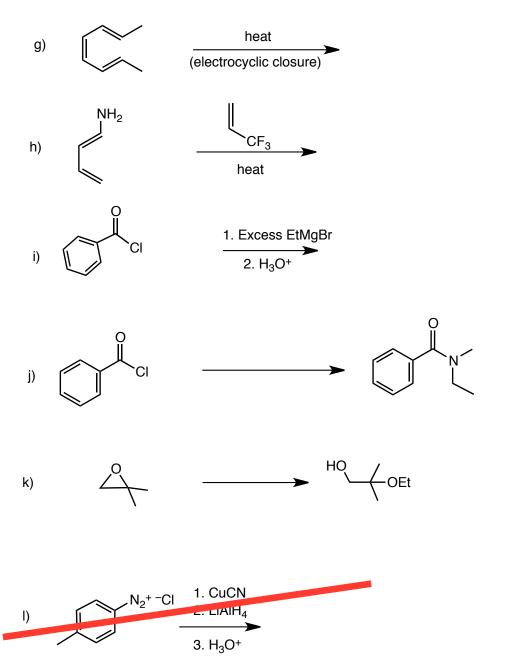
Question 8) Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



NAME

- 6 -

Question 8, contd.



Question 9) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers** 

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.CO<sub>2</sub>H

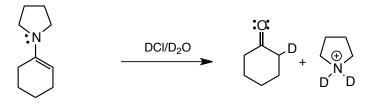


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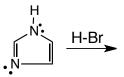
NAME

Question 10) Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structure of the intermediates

 $DCI/D_2O$  = deuterated HCl in heavy water,  $D_2O$ , acts just like any acid in water, but shows you which protons come from the aqueous acid medium



Question 11) Give the product of the following Bronsted acid/base reaction, give the curved arrow pushing and give a BRIEF explanation for your choice of reaction product

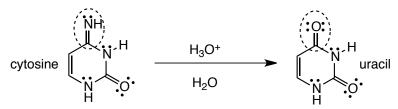


CHM 234, FINAL EXAM PRACTICE TEST #2 -9- NAME

Question 12) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

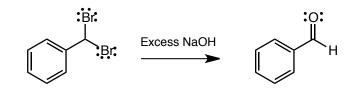
THESE SYNTHESIS PROBLEMS USE ONLY REACTIONS FROM THE "MINIMAL SET OF REACTIONS" PROVIDED ON THE CLASS WEB PAGE!

CO<sub>2</sub>H a) b) Ph Question 13) Draw the complete arrow pushing mechanism for deamination of cytosine to give uracil. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structure of the intermediates. This is an acid hydrolysis mechanism that is veryt similar to many we covered in class



CHM 234, FINAL EXAM PRACTICE TEST #2 - 10 - NAME

Question 14) Draw the complete arrow pushing mechanism for the following reaction. Even though we have not seen this one it just uses principles that we have seen. (hint: start by doing two consecutive  $S_N 2$  reactions at the benzylic carbon)



Question 15) For the following cation, draw all reasonable additional resonance contributors including appropriate curved arrow pushing, and on TOP of the provided structure, draw the HOMO using "p A.O." notation we used in class and CLEARLY INDICATE ANY VERTICAL NODES, AND state the number of p A.O.s involved, the TOTAL number of pi-molecular orbitals that are possible and the number of electrons in the pi-system

**(**+)

Question 16) Assign the following structures as aromatic, non-aromatic or anti-aromatic andf give the number of electrons associated with the conjugated systems, assume that the structures are as planar as possible

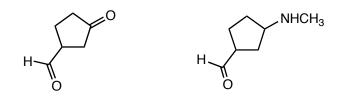




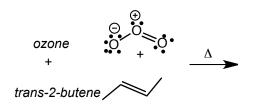


CHM 234, FINAL EXAM PRACTICE TEST #2 - 11 - NAME

Question 17) Synthesize the (target) molecule on the right from the starting molecule on the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.



Question 18) Alkenes react with ozone,  $O_3$ , to form an ozonide, an example reaction with trans-2-butene is shown below.



a) give the curved arrow-pushing that accounts for formation of the ozonide

b) draw the ozonide, paying special attention to relative stereochemistry of any substituents

c) indicate the locations of any chiral (asymmetric) carbons atoms with the \* symbol, and state whether the ozonide is racemic, a meso compound or achiral

d) give drawings of the HOMO and LUMO, ON TOP OF OZONE and trans-2-BUTENE, respectively

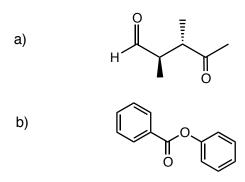
e) state the number of vertical nodes for each MO and clearly indicate their positions

f) state whether the allowed reaction is suprafacial/suprafacial or suprafacial/antarafacial and give a brief explanation

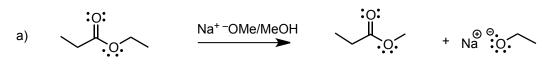
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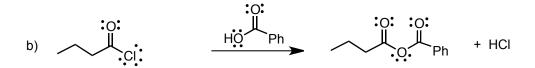
## **START OF PRACTICE TEST #3**

Question 1) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.



Question 2) Give curved arrow-pushing mechanisms for the following reactions. Indicate the Lewis acid and base and Bronsted acid and base at each step as appropriate. Show where every proton comes from and goes to (i.e. no +H+ and -H+). The first reaction is a transesterification (we mentioned this in class but did not really cover it properly, until now!). Transesterification transforms one ester into another, as shown.



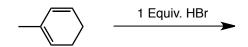


NAME

Question 3)

a) Give a curved arrow-pusing mechanism that describes formation of the two reaction products, indicate the Lewis and Bronsted acids and bases at each step as appropriate and identify which product is more likely to be formed under kinetic control conditions and which under thermodynamic control conditions and WHY!

-3 -



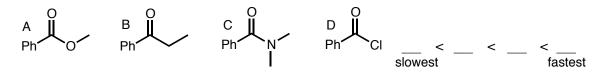
b) Include resonance contributors for intermediates as appropriate, and indicate the MAJOR CONTRIBUTOR and WHY it is the major contributor

Indicate which would be the major product at high and low temperature conditions and state WHY

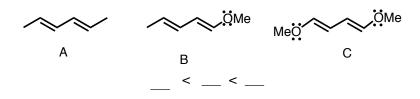
c) Draw a properly labelled reaction energy diagram for these reactions ON THE SAME DIAGRAM identify the positions of the starting structure, the intermediates, locate the positions of the transition states but do not draw them and indicate the rate determining step

- 4 - NAME

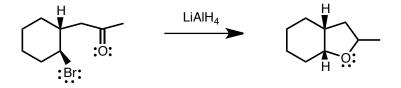
Question 4) Rank in order of increasing rate of reaction with a Grignard reagent and give a brief explanation, AND ASSIGN EACH FUNCTIONAL GROUP



Question 5) Rank in order of increasing rate of reaction in a Diels-Alder reaction and give an explanation that includes the terms HOMO and LUMO

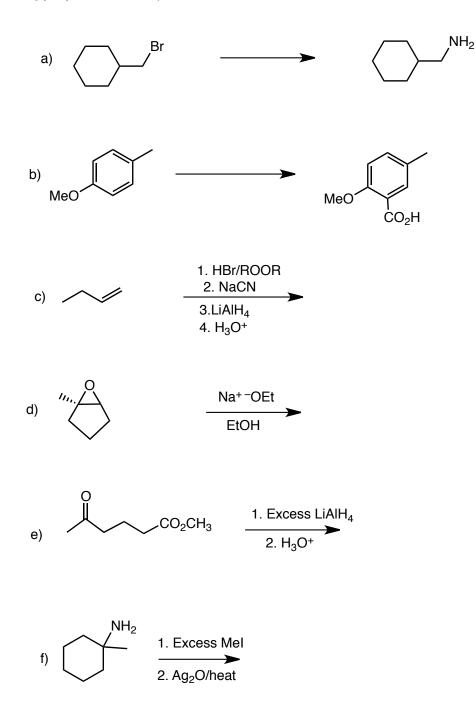


Question 6) Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base for each INTERMOLECULAR step, and if they are also Brønsted acids bases. Add non-bonding electrons as necessary.



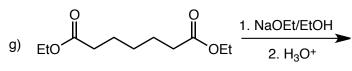
CHM 234, FINAL EXAM PRACTICE TEST #3 - 5 - NAME

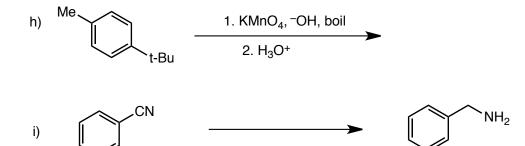
Question 7) Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



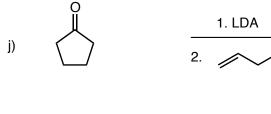
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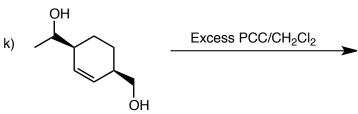
Question 7, contd.





Br





NAME

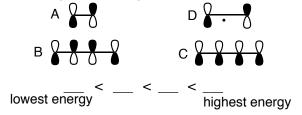
Question 8) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers** 

a)	tt	nis problem involves a diaze dam salt	OH Br

b) Ph OH Ph C C C II II O O

Question 9.) Rank the energies of an electron in each of the following  $\pi$ -molecular orbitals. Give a BRIEF explanation for your choice.

- 8 -



Question 10) On each side of the following equilibrium, identify the stronger and weaker acid and base, identify which acid would have the LOWER pKa, indicate on which side the equilibrium would lie, and give a brief explanation for your choices.



Question 11) Why do two hydrogen atoms react to make a hydrogen molecule? This is one of my favorite questions to ask at a chemistry PhD oral defence you would be surprised how few satisfactory answers I get!

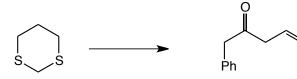
CHM 234, FINAL EXAM PRACTICE TEST #3 - 9 - NAME

Question 12) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

THESE SYNTHESIS PROBLEMS USE ONLY REACTIONS FROM THE "MINIMAL SET OF REACTIONS" PROVIDED ON THE CLASS WEB PAGE!

a) HO Ph ∵Br OH b)

Question 13) Give the reagents/conditions you would use to make the following ketone using a dithiane synthesis

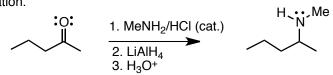


Question 14) Give the reagents/conditions you would use perform the following eraction using the Stork enamine method

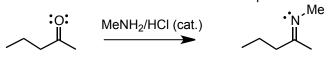


CHM 234, FINAL EXAM **PRACTICE TEST #3** - 10 - NAME

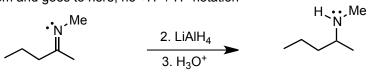
Question 15) Give a curved arrow-pushing mechanism for the two parts of the following indirect reductive amination.



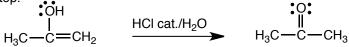
a) First, the mechanism of formation of the imine intermediate structure (i.e. the reaction below), you can use the abbreviated  $+H^+$  and  $-H^+$  notation for this part of the mechanism



b) Second, the reduction to the amine, shown below, you MUST show exactly where each proton comes from and goes to here, no  $+H^+$  /- $H^+$  notation



Question 16) Give a curved arrow-pushing mechanism for the following reaction, show where every proton comes from and goes to, no +H+/-H+, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step.



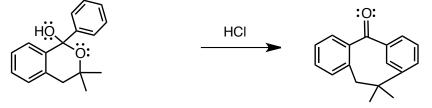
Question 17) For the following elimination reactions a) Indicate which is the major and which the minor alkene product

 $H_2O$ OH NMe<sub>3</sub> NMea

b) State whether the major product is formed as a result of kinetic control or thermodynamic control, give a BRIEF one-sentance explanation

c) Draw a reaction energy diagram for formation of both products on the SAME diagram

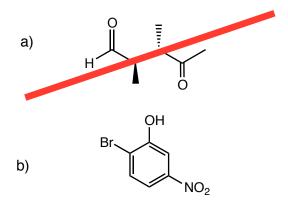
Question 18) Draw the complete arrow pushing mechanism for the following reaction.Add non-bonding electrons as necessary. Draw the resonance structures as appropriate



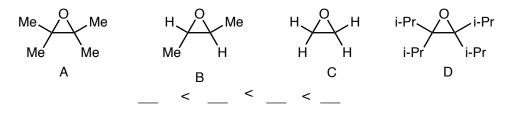
CHM 234, FINAL EXAM PRACTICE TEST #4 - 2 - NAME

## **START OF PRACTICE TEST #4**

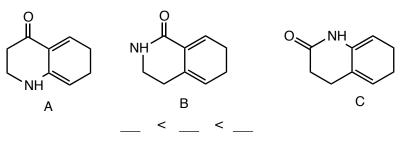
Question 1) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.



Question 2) Rank the following in terms of increasing rate of reaction in a base catalyzed hydrolysis reaction (addition of water in the presence of hydroxide) and give a brief explanation

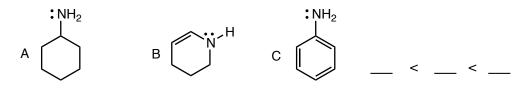


Question 3) Rank the following in terms of increasing energy of an electron in the HOMO of the following dienes. Give an explanation which also states which would react faster in a Diels-Alder reaction

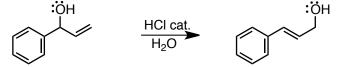


-3 - NAME

Question 4) Rank in order of increasing rate of reaction with an acid chloride to make an amide, give a brief explanation.



Question 5) Give a curved arrow-pushing mechanism for the following reaction, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step, include all important resonance contributors for intermediates and give the number of steps in your mechanism:



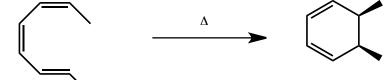
b) Is this reaction exothermic? Give a brief explanation

Draw a properly labelled reaction energy diagram for this reaction, identify the locations of the transition states (do not draw them) and the locations of the various intermediates in your mechanism

NAME

Question 6) The purpose of this question is to determine whether the provided product is allowed or forbidden.

- 4 -



1) draw the arrow-pushing that describes formation of the product

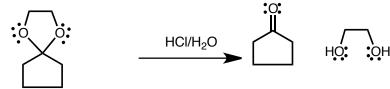
2) How many electrons are involved in the reaction?

3) FOR THE REACTION SHOWN (which may or may not be allowed), would the ring closing be disrotatory or conrotatory?

4) FOR THE REACTION SHOWN (which may or may not be allowed), would the transition state be Hückel or Möbius?

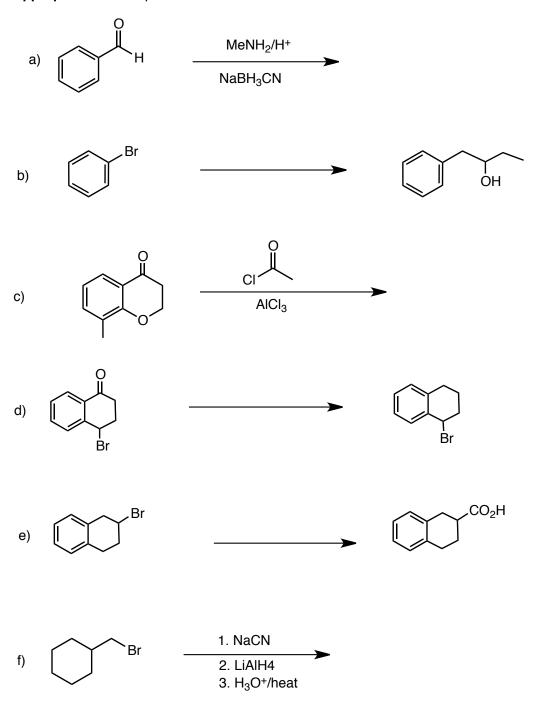
5) Is THE REACTION SHOWN allowed or forbidden?

Question 7) Draw the complete arrow pushing mechanism for the following reaction. Indicate the Lewis acid/base at each step, and if they are also Brønsted acids bases. Add non-bonding electrons as necessary. Draw the **ALL important** resonance structure of the intermediates and do NOT use the abbreviated  $+H^+/-H^+$  notation



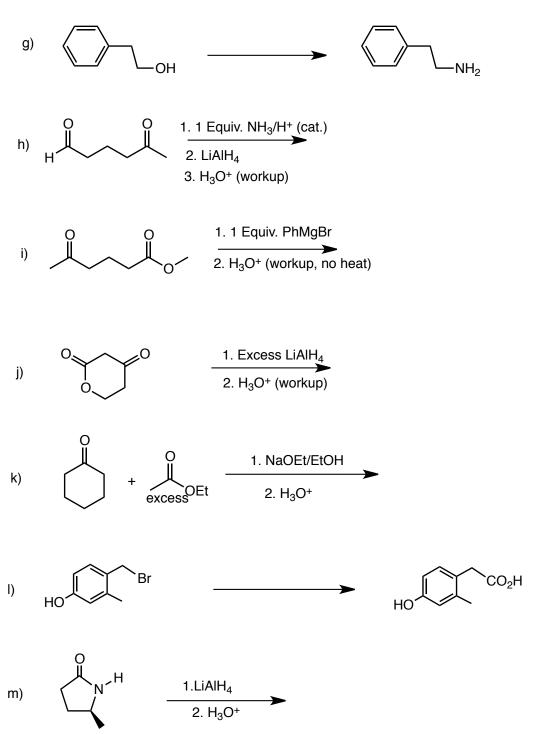
CHM 234, FINAL EXAM PRACTICE TEST #4 - 5 - NAME

Question 8) Provide the missing major organic products, or reagents/conditions, or organic reactants, as appropriate. **Do not forget to include stereochemistry as appropriate** unless specified otherwise.



- 6 -

Question 8) contd.

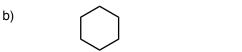


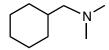
NAME

Question 9) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers** 

- 7 -

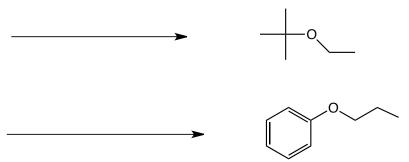
a) CI



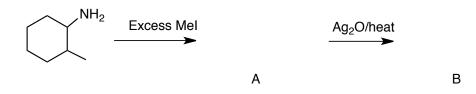


-8- NAME

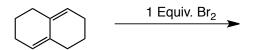
Question 10) Provide the ALCOHOL and the bromide and all other reagents/reactants in proper sequence to synthesize the following ethers using a Williamson ether synthesis



Question 11) The following reaction sequence represents a Hofmann elimination, give the missing organic structures A and B.



Question 12) Give the major organic product of the folloiwng reaction, assume THERMODYNAMIC CONTROL (ignore stereoisomers)



Question 13) When we say that reactions are controlled mainly by the energy of the electrons, how do we understand this statement in terms of reaction free energy?

NAME

Question 14) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

- 9 -

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# THESE SYNTHESIS PROBLEMS USE ONLY REACTIONS FROM THE "MINIMAL SET OF REACTIONS" PROVIDED ON THE CLASS WEB PAGE!

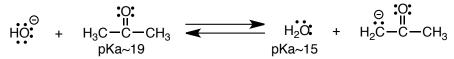


CHM 234, FINAL EXAM PRACTICE TEST #4 - 10 - NAME

Question 15) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



Question 6) For the following equilibrium, indicate the strongest acid and base on EACH side (use the provided pKa values), indicate which reaction is faster and which slower, and draw a reaction energy diagram for the equilibrium, include a drawing of the transition state

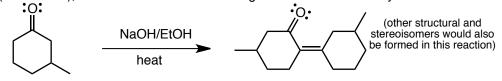


Question 17) Give the major organci product of teh following reaction. Remember that deuterium (D) is an isotope of hydrogen that can be used to track what happens to specific hydrogens in a reaction, you can assume that it reacts exactly the same as hydrogen for this problem

$$\begin{array}{c} 0 \\ 1. \text{ LiAlH}_4 \\ 2. \text{ D}_3 \text{O}^+ \end{array}$$

CHM 234, FINAL EXAM PRACTICE TEST #4 - 11 - NAME

Question 18) Give a curved arrow-pushing mechanism for the following reaction, indicate the Lewis and Bronsted acids/bases for each INTERmolecular step, include all important resonance contributors for intermediates, give the number of steps in your mechanism, indicate the Lewis and Brionsted acids/bases for each INTERmolecular step, show where every proton comes from and goes to (no +H<sup>+</sup>/-H<sup>+</sup>), add H atoms and non-bonding electrons as necessary



for the mechanism below you can use the +H+/-H+ abbreviated notation

