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CHM 1321

Final Exam

Review Package

ANSWER KEY

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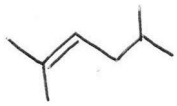
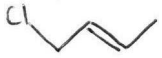
University of Ottawa

Winter 2013

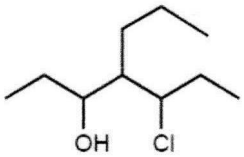
ORGANIC MOLECULAR STRUCTURE

1. Draw the line (zig-zag) structure for the following compounds: **(6 points)**
   (a) 2,5-dimethyl-2-hexene
   (b) 1-chloro-2-butene
   (c) 2-methyl-2-cyclohexen-1-ol

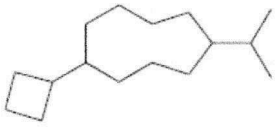
(a) 

(b) 

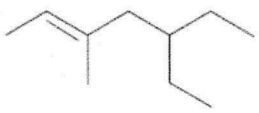
2. Give the IUPAC name for the following compounds: **(9 points)**

(a) 

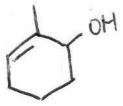
5-chloro-4-propyl-3-heptanol

(b) 

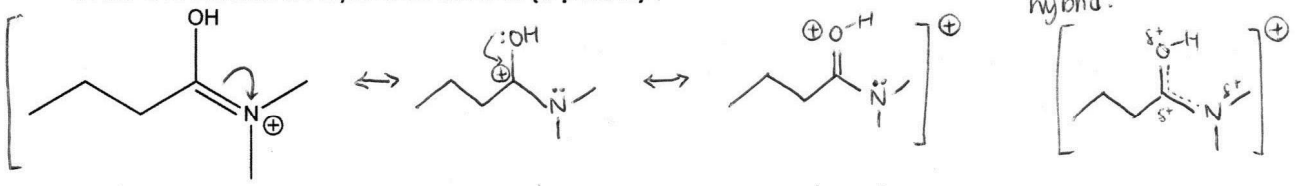
1-cyclobutyl-5-(1-methylethyl)cyclononane

(c) 

(E)-5-ethyl-3-methyl-hept-2-ene

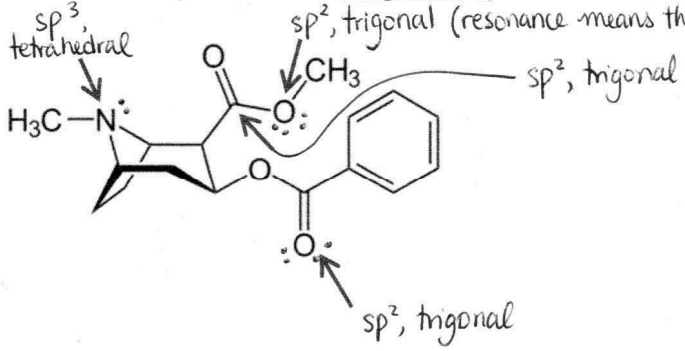
(c) 

3. For the molecule shown below:
   - Draw all of the resonance structures of the compound, using curved arrows to show the movement of electrons. **(5 points)**
   - Rank the resonance structures from best to worst. **(2 points)**
   - Draw the resonance hybrid structure. **(3 points)**



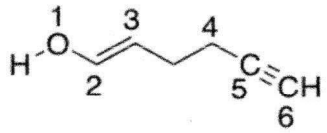
best worst 2nd best

4. Below is the structure of cocaine. Give the hybridization and geometry of the indicated atoms. **(8 points)**



(Fun fact: Although cocaine was first isolated in 1855 by Friedrich Gaedcke, and first synthesized in 1898 by Richard Willstätter, coca leaves were being chewed in South America hundreds or thousands of years earlier!)

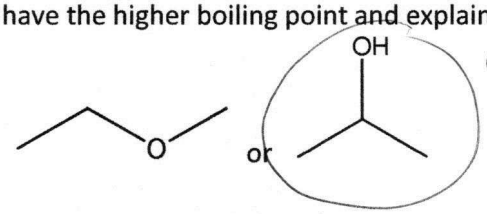
5. For the molecule shown, which molecular orbitals join the following atoms together? **(3 points)**



(a) O1 and H: σ
(b) C2 and C3: $\sigma + \pi$
(c) C5 and C6: $\sigma + \pi + \pi$

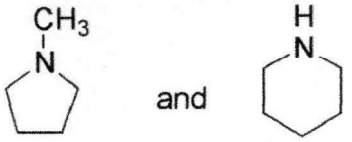
6. Draw CH_3COH using the LCAO method, and label the atomic orbitals used to make each bond, the type of each bond, and the hybridization states. **(10 points)** (see next page)

7. Circle the compound that will have the higher boiling point and explain your reasoning. **(3 points)**



Compound on right has stronger H-bonds, while the compound on left has only dipole-dipole intermolecular forces.

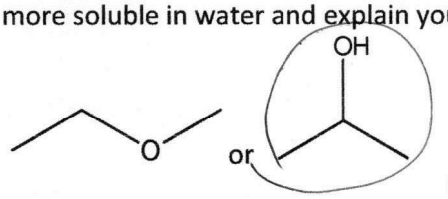
8. Explain the difference in boiling point for the following pair of compounds. **(3 points)**



bp 81 °C bp 106 °C

~ same VdW
- Compound on left has dipole-dipole interactions.
- Compound on right is capable of H-bonding (stronger) with itself (due to $\ddot{N}$-H), therefore it has the higher b.p.

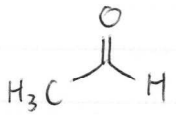
9. Circle the compound that will be more soluble in water and explain your reasoning. **(3 points)**

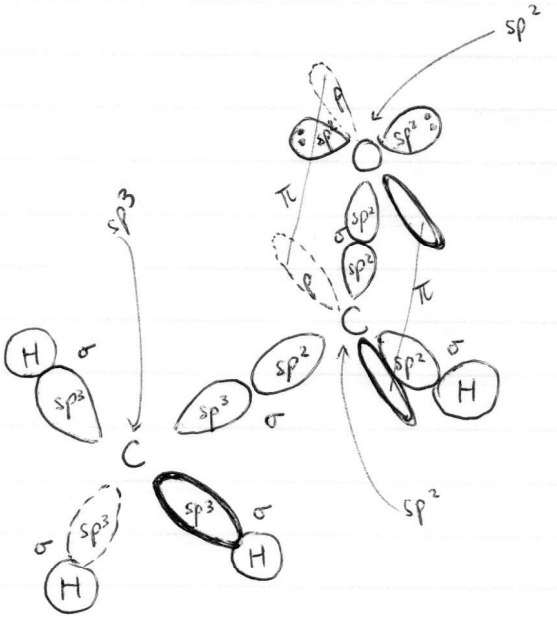


"Like dissolves like"
Compound on right is capable of H-bonding with H_2O as both an H-bond acceptor and donor, thus can interact to a greater degree than compound on the left (only H-bond acceptor)

6. CH_3COH

(acetaldehyde)

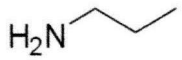




(Fun fact: Acetaldehyde, a metabolite of ethanol, is a suspected cause of hangovers!)

CONFORMATIONAL ANALYSIS

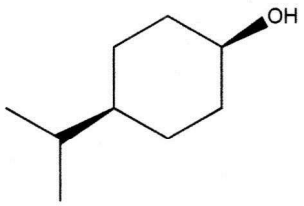
1. For the molecule shown below:



(Fun fact: The Newman-Kwart rearrangement is also named after Melvin Spencer Newman, who introduced the Newman projection in 1952.)

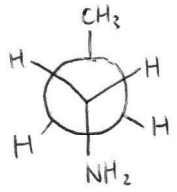
   (a) Draw and name the Newman projection down the C1-C2 bond of the most stable conformation. **(3 points)**
   (b) Draw and name the Newman projection down the C1-C2 bond of the least stable conformation. **(3 points)**

2. (a) Draw the two chair conformations of the molecule below. Note: you do not have to draw the H's. **(5 points)**
   (b) For each structure, label the substituents as being axial or equatorial. **(2 points)**
   (c) Identify the most stable conformation. **(1 point)**
   (d) Are the substituents on the ring cis or trans? **(1 point)**



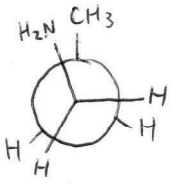
1.

(a)



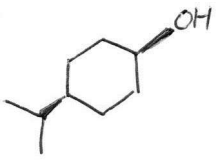
anti-staggered

(b)



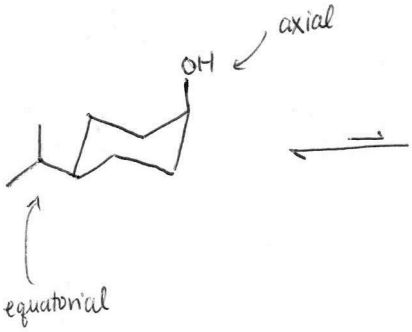
eclipsed

2.

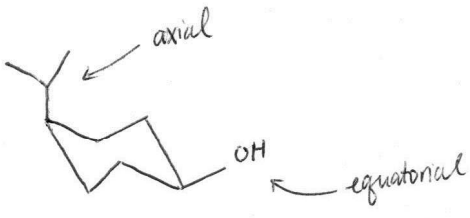


cis

≡



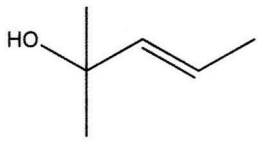
most stable

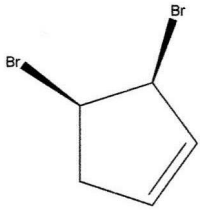


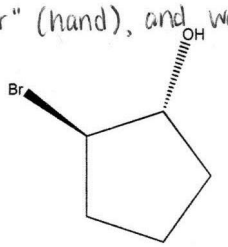
STEREOCHEMISTRY

1. Circle the molecules that are chiral. **(3 points)**

(Fun fact: The word "chiral" comes from the Greek "kheir" (hand), and was first coined by Lord Kelvin!)

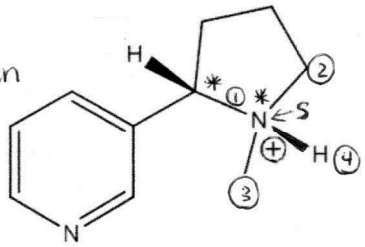


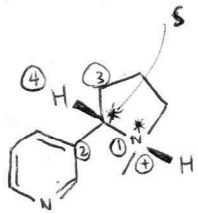




2. Below is the structure of nicotine (protonated).
   - Label all of the stereocentres with a star (*). **(2 points)**
   - Determine the priorities of the substituents around each stereocentre. **(4 points)**
   - Assign each stereocentre an R/S configuration. **(2 points)**
   - What is the maximum number of stereoisomers of this molecule? Show your calculation. **(2 points)** 2 stereogenic centres ∴ max. # stereoisomers $= 2^2 = 4$

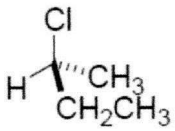
(Fun fact: Nicotine was named after Jean Nicot, French embassador to Portugal, who sent tobacco and seeds back to France in 1561.)



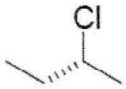


3. What is the isomeric or stereochemical relationship (enantiomers, diastereomers, etc.) between the following pairs of molecules? **(3 points)**

(a)

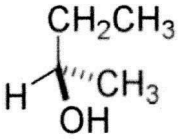


and

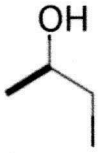


enantiomers

(b)

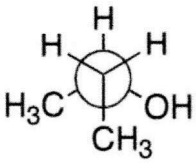


and

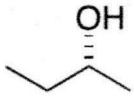


same

(c)



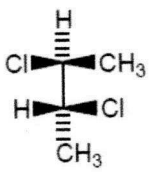
and



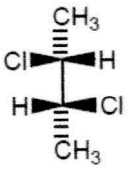
enantiomers

(Fun fact: (S)-(+)-amphetamine is a much more potent psychoactive drug than its enantiomer, (R)-amphetamine!)

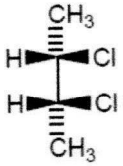
4. Which of the following is/are *meso* compounds?



I



II



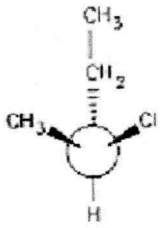
III

A) I
B) II
C) III
D) Both II and III
E) Both I and III

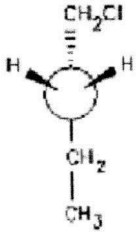
5. (2R,4S) -2,4-Dichloropentane and (2S,4R)-2,4-dichloropentane are:

- conformational isomers
- constitutional isomers
- diastereomers
- enantiomers
- identical

6. I and II are:



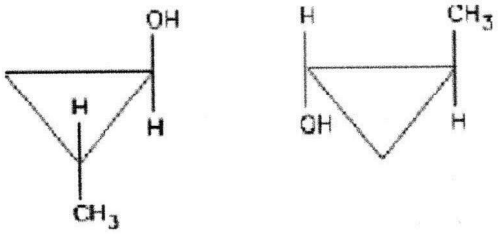
I



II

A) constitutional isomers.
B) enantiomers.
C) non-superposable mirror images.
D) diastereomers.
E) not isomeric.

7. The molecules shown are:



A) constitutional isomers.
(B) enantiomers.
C) diastereomers.
D) identical.
E) None of these

8. Calculate the ee and specific rotation of a mixture containing 7 g of (+)-glucose and 3 g of (-)-glucose. The specific rotation of pure (-)-glucose is -17.6°. **(7 points)**

(Fun fact: optical rotation was first observed in 1811 by François Jean Dominique Arago, who constructed a polariscope to gather evidence supporting the wave theory of light.)

8.

$$ee = \frac{|d-l|}{d+l} \times 100\% \quad \text{and} \quad d = 7g, \; l = 3g$$ (remember: d isomer has + rotation)

$$\therefore ee = \frac{|7g-3g|}{7g+3g} \times 100\% = \boxed{40\%}$$

$$\text{optical purity} = ee = \frac{\text{specific rotation of mixture}}{\text{specific rotation of pure}} \times 100\%$$

$$0.40 = \frac{\text{specific rotation of mixture}}{17.6^\circ}$$

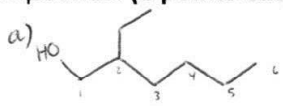
$\therefore$ specific rotation of mixture = 7.04°

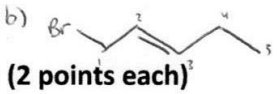
Since the (+) isomer is in excess, the sign of the rotation will be positive.

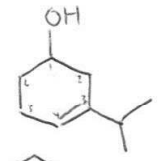
$\therefore$ specific rotation of mixture = $\boxed{+7.04^\circ}$

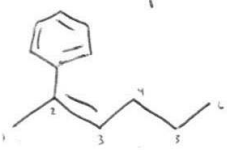
NOMENCLATURE REVIEW

1. Draw the line (zig-zag) structure for the following compounds: **(2 points each)**
   (a) 2-ethyl-1-hexanol
   (b) 1-bromo-2-pentene
   (c) 3-isopropyl-3-cyclohexen-1-ol
   (d) (Z)-2-phenylhex-2-ene

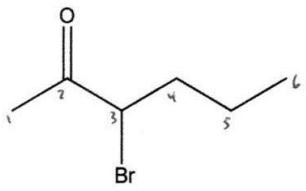
a) 

b) 

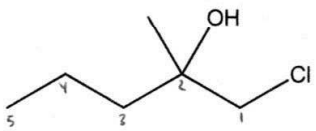
c) 

d) 

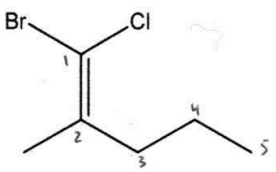
2. Give the IUPAC name for the following compounds: **(2 points each)**

(a) 

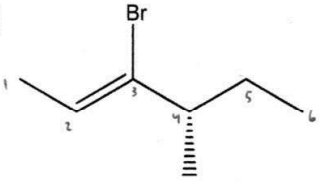
3-bromohexan-2-one

(b) 

1-chloro-2-methylpentan-2-ol

(c) 

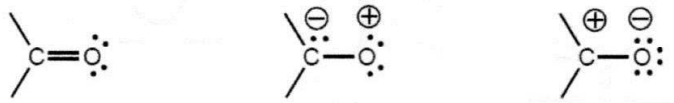
(E)-1-bromo-1-chloro-2-methyl-1-pentene

(d) 

(S, Z)-3-bromo-4-methylhex-2-ene

ACID/BASE REACTIONS

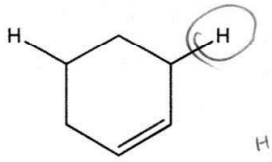
1. Which of the following resonance structures isn't a significant contributor to the hybrid for the carbonyl group? **(1 point)**



I II III

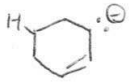
a) I
b) II
c) III
d) Neither II nor II is significant
e) All are significant contributors

2. (a) Compare the two hydrogens shown and circle the one that is more acidic. **(1 point)**

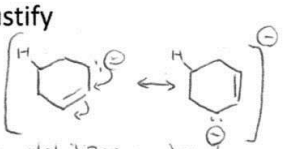


(b) Draw the 2 possible conjugate bases. **(2 points)**

(c) For your answer above, identify which of the conjugate bases is more stable and briefly justify your answer. **(4 points)**



is more stable because resonance is possible:



Resonance stabilizes conjugate bases by spreading out the charge.

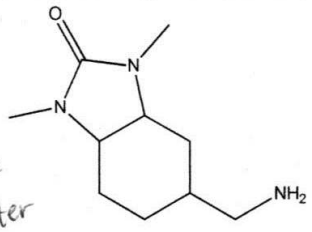
3. Predict which will be the stronger acid and briefly justify your answer. **(4 points)**

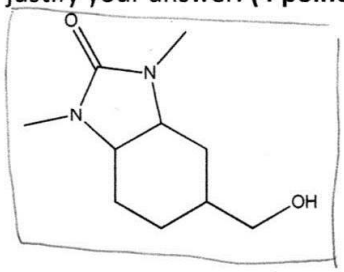
Look at conj. bases:

$R-NH_2 \rightleftharpoons R-NH^{\ominus} + H^{\oplus}$

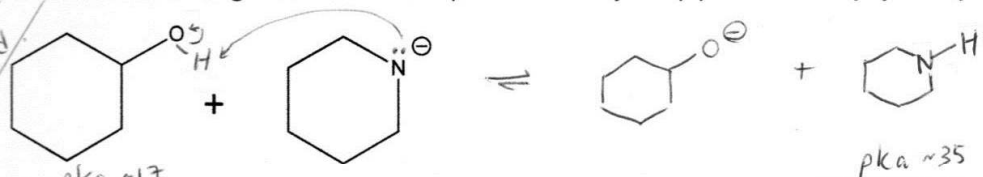
$R-OH \rightleftharpoons R-O^{\ominus} + H^{\oplus}$

O is to right of N on per. table
-O is more electronegative
-O stabilizes the $\ominus$ charge better
- $R-O^{\ominus}$ is more stable (weaker) base
- thus, R-OH is stronger acid.





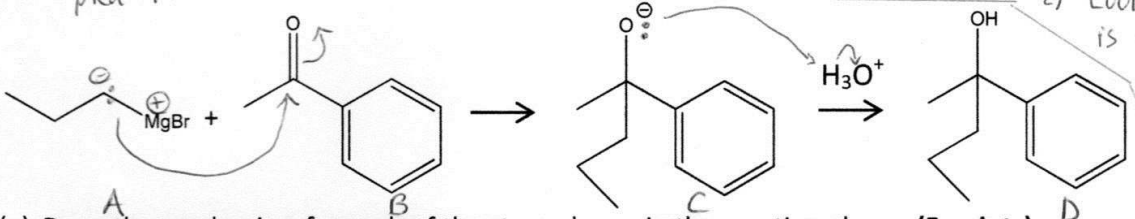
4. Write an equation for the following using arrow notation. **(2 points)** Predict whether the reaction will favor the starting materials or the products and justify your choice. **(3 points)**



pka ~17 pka ~35

Reaction will favor products.
1) O is more EN than N, so $R-O^{\ominus}$ is weaker base, so reaction will favor that side.
2) Look at pka's: R-OH is a stronger acid (ROH has lower pka), so reaction will favor products.

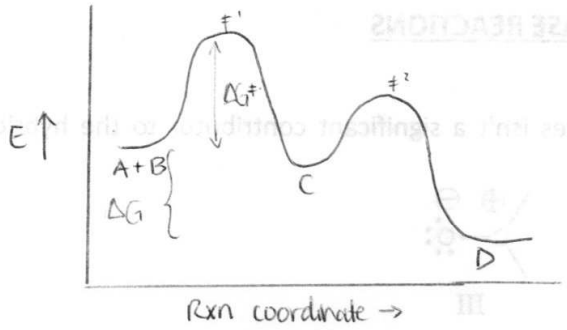
5.

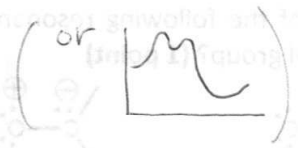


A B C D

(a) Draw the mechanism for each of the steps shown in the reaction above. **(5 points)**
(b) Draw and label the reaction coordinate diagram for this reaction (exothermic overall). **(5 points)**

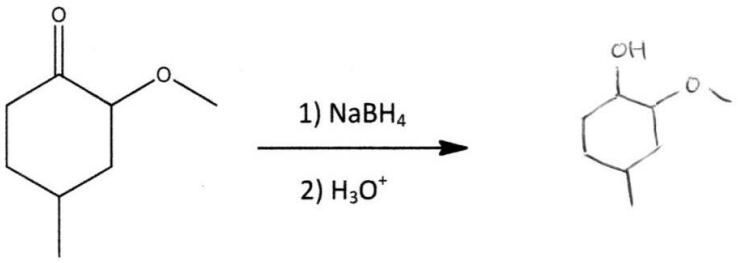
5. b)



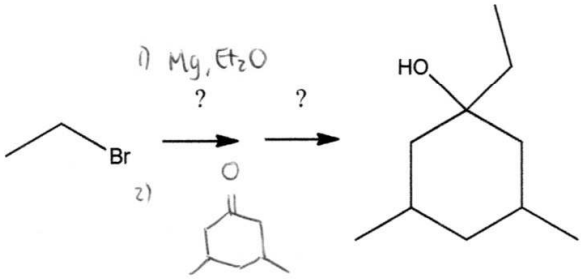


π BONDS AS ELECTROPHILES (CARBONYLS)

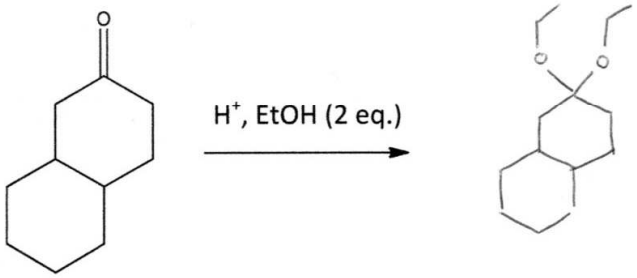
1. What is the product of the following reaction?



2. Fill in the missing reagents.

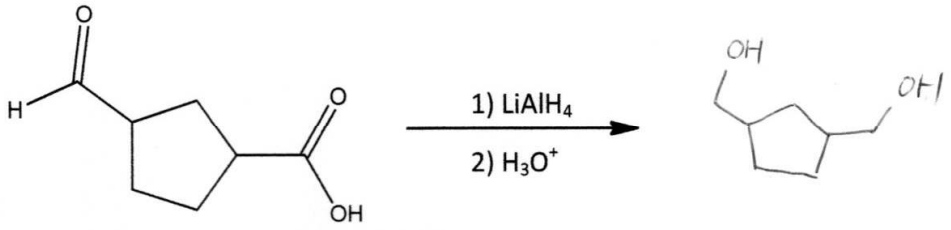


3. What is the product of the following reaction? Draw the mechanism with proper arrows.



See mechanism for acid-catalyzed acetal (ketal) formation.

4. What is the product of the following reaction?



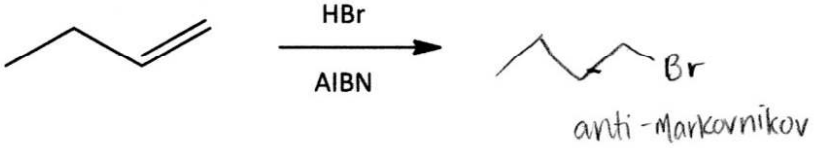
5. What are two different ways to make a new carbon-carbon bond?

organometallics (e.g., Grignard) and cyanohydrins (with NaCN)

π BONDS AS NUCLEOPHILES (ALKENES)

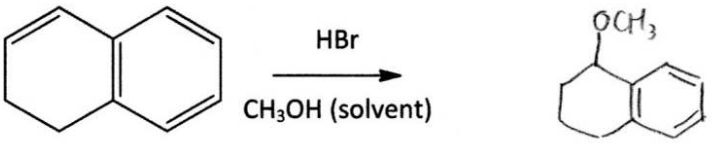
1. Give the products of the following transformations **(2 points each)**

(a)

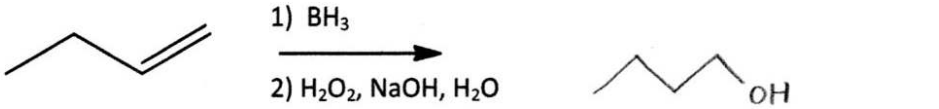


anti-Markovnikov

(b)

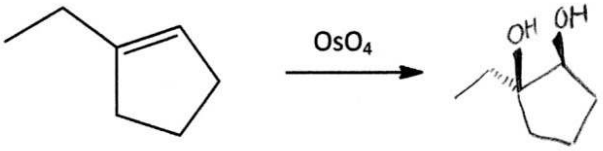


(c)

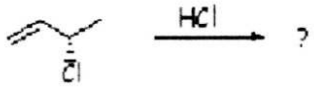


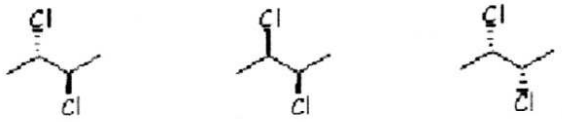
anti-Markovnikov

(d)



2. Addition of hydrogen chloride to the following molecule would produce

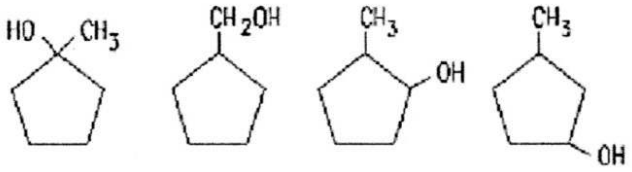




I II III

A) I and II
B) I and III
C) II and III
D) I, II and III
E) III

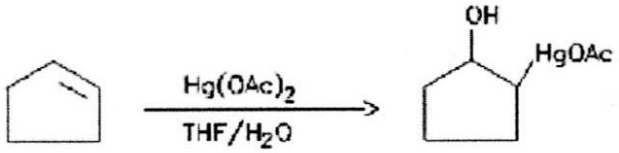
3. Oxymercuration-demercuration of 3-methylcyclopentene produces



I II III IV

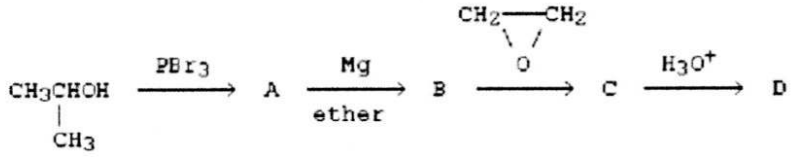
A) I
B) II
C) III
D) IV
E) Both III and IV

4. What is the electrophilic species involved in the initial step of the reaction below?



A) ^{+}OH
B) $^{+}HgOAc$
C) H_3O^{+}
D) THF
E) the THF/H_2O complex

5. The final product, D, in the following reaction sequence



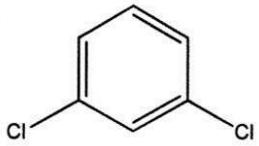
would be

A. $CH_3CHOCH_2CH_2OH$ (CH_3 branch)
B. $CH_3CHCH_2CH_2Br$ (CH_3 branch)
C. $CH_3CHCH_2CH_2OH$ (CH_3 branch)
D. $CH_3CHOCH_2CH_3$ (CH_3 branch)
E. $CH_3CHCH_2CH_3$ (CH_3 branch)

AROMATIC COMPOUNDS

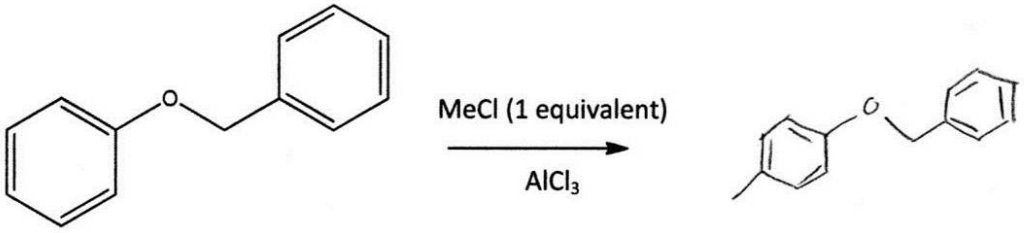
1. What are the three criteria/rules for a compound to be aromatic? **(3 points)**
   1) must be a flat ring
   2) must have p orbitals at each atom in ring
   3) must have $(4n+2)e^-$ in p orbitals

2. Give the IUPAC name for the following compound. **(2 points)**

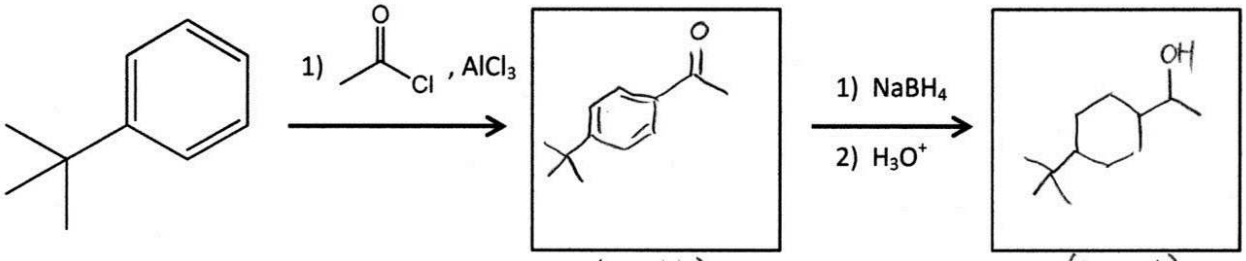


1,3-dichlorobenzene
or
m-dichlorobenzene

3. Give the major product(s) of the following transformation **(2 points)**

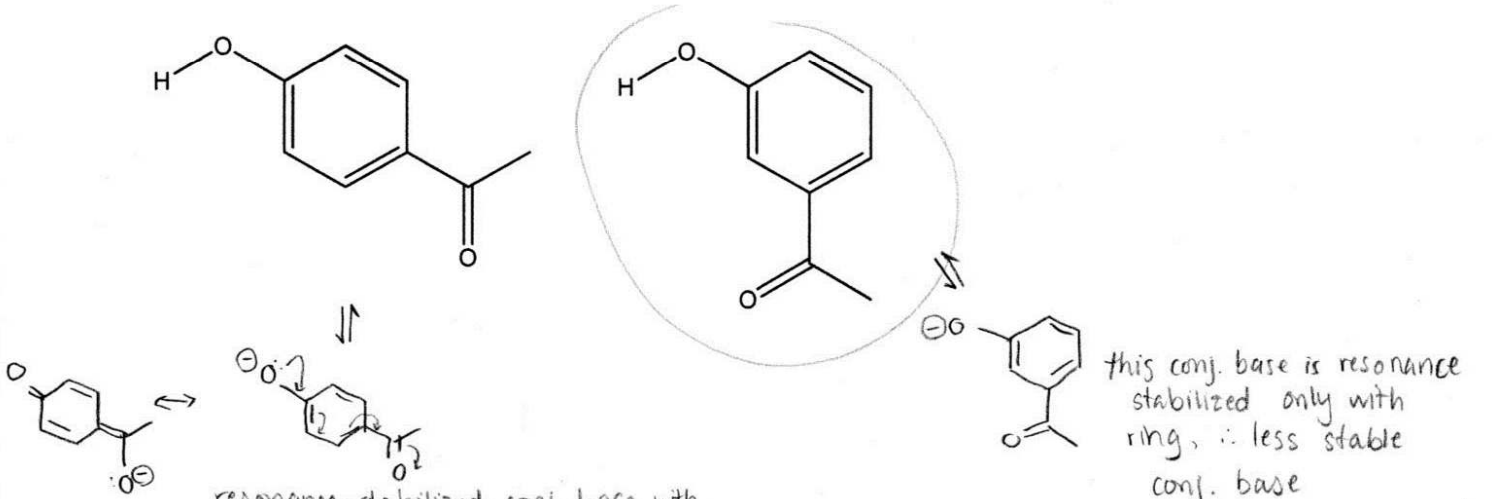


4. Give the major product after each transformation **(3 points)**



(2 points) (1 point)

5. (a) Circle the weakest acid of the pair. **(1 point)**
   (b) Clearly justify your answer and include the key structures that support your answer. **(5 points)**

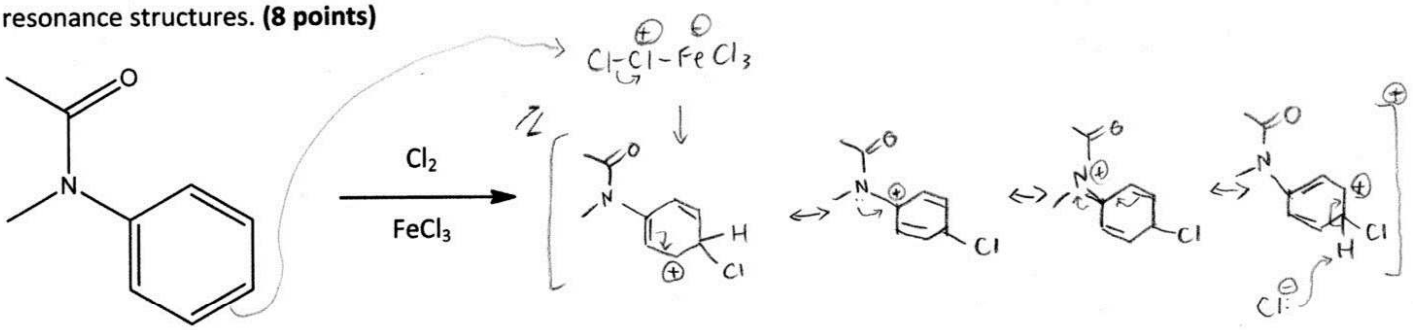


ketone + ring

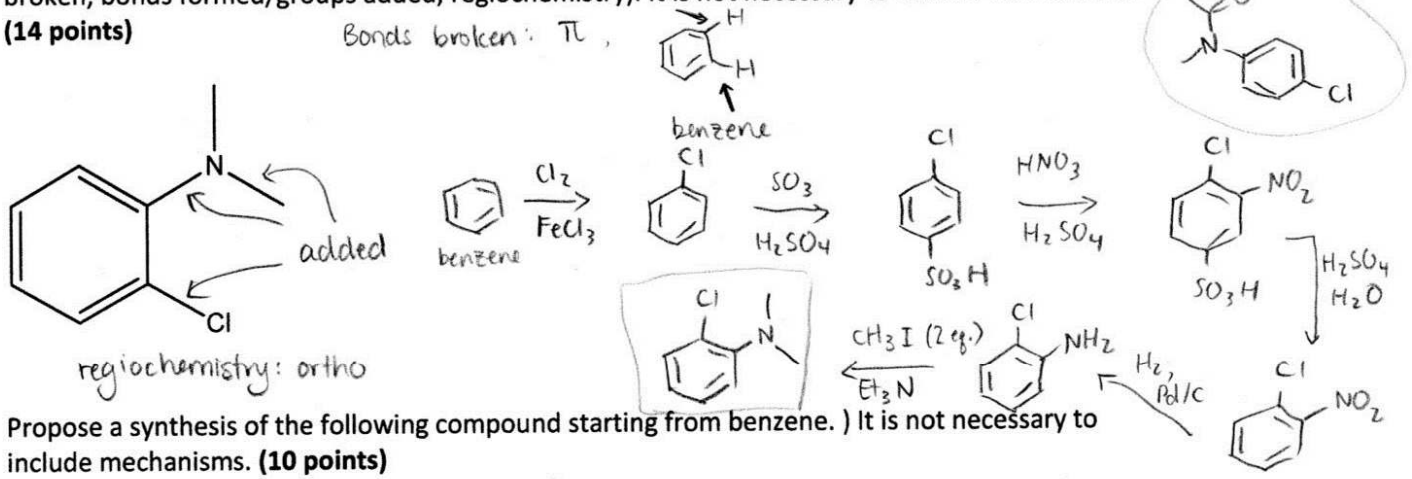
resonance stabilized conj. base with ring is more stable

this conj. base is resonance stabilized only with ring, ∴ less stable conj. base
∴ weaker corresponding acid

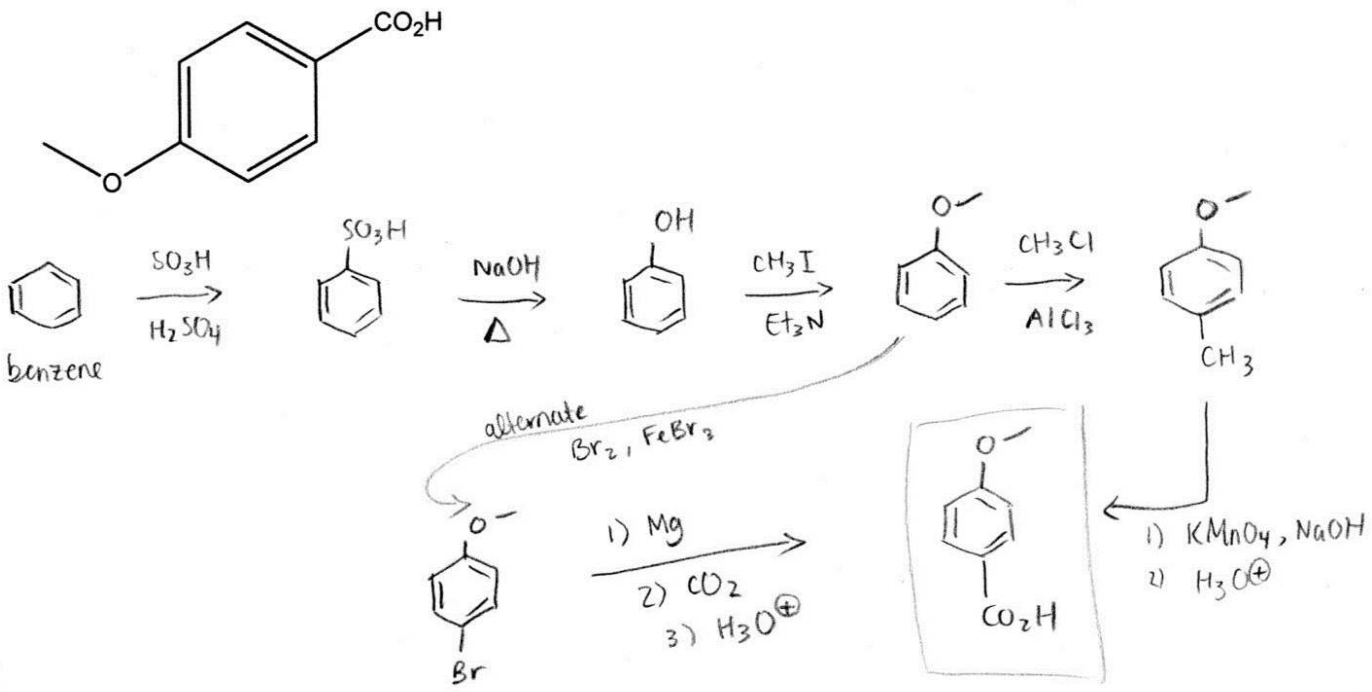
6. Propose a mechanism for the formation of the major product of the following reaction. Include resonance structures. **(8 points)**



7. Propose a synthesis of the following compound starting from benzene. Include an analysis (bonds broken, bonds formed/groups added, regiochemistry). It is not necessary to include mechanisms. **(14 points)**



8. Propose a synthesis of the following compound starting from benzene.) It is not necessary to include mechanisms. **(10 points)**



LABS

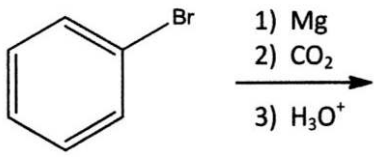
TYPES OF QUESTIONS YOU MAY SEE ON THE FINAL EXAM

- **Describe how to separate a mixture of two types of compounds, using a flowchart. Hint: use acid/base properties.**

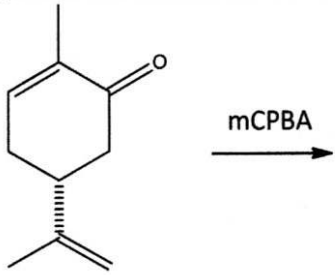
1. ▪ e.g., Describe how you would separate a mixture of benzyl amine and benzophenone. Both compounds are soluble in EtOAc. BE SPECIFIC – a first year student should be able to perform the separation following your instructions. **(10 points)**

- **Give a mechanism for one of the reactions you performed.**

2. ▪ e.g., Give a mechanism for the following reaction. **(11 points)**



3. ▪ e.g., Draw the mechanism for the reaction of carvone with *m*CPBA. **(8 points)**



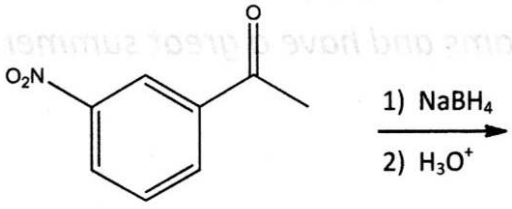
- **Explain the importance of a given step in the experimental procedure.**

4. ▪ e.g., Why is it important to obtain dry ice *immediately before* using it in experiment 4? **(2 points)**

- **Explain the purpose of a given reagent in the experimental procedure.**

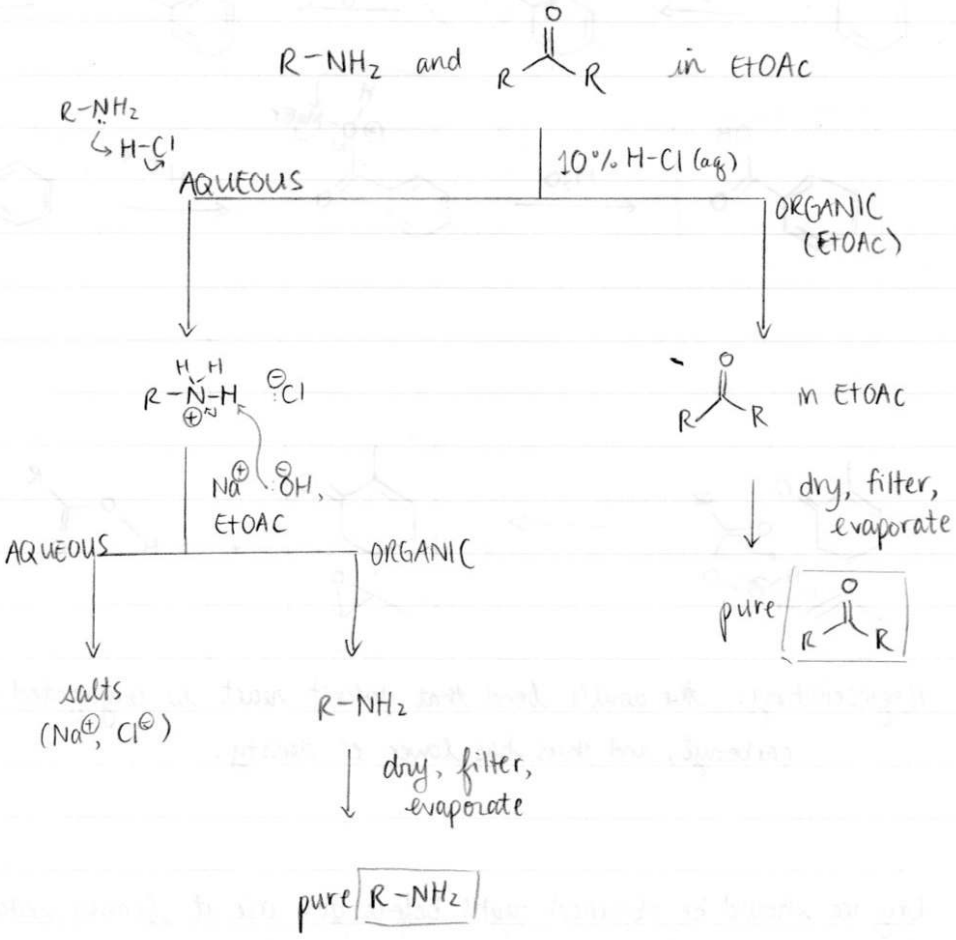
5. ▪ e.g., When you did a TLC of the epoxidation reaction mixture in experiment 5, you dipped the TLC plate in a solution of potassium permanganate (the purple solution). Why did the spots on the TLC change colour? **(1 point)**

6. ▪ e.g., Consider the reduction of nitroacetophenone in experiment 3 (shown below). Explain the role of the workup step. **(2 points)**



LABS

1.



1 - dissolve both in EtOAc

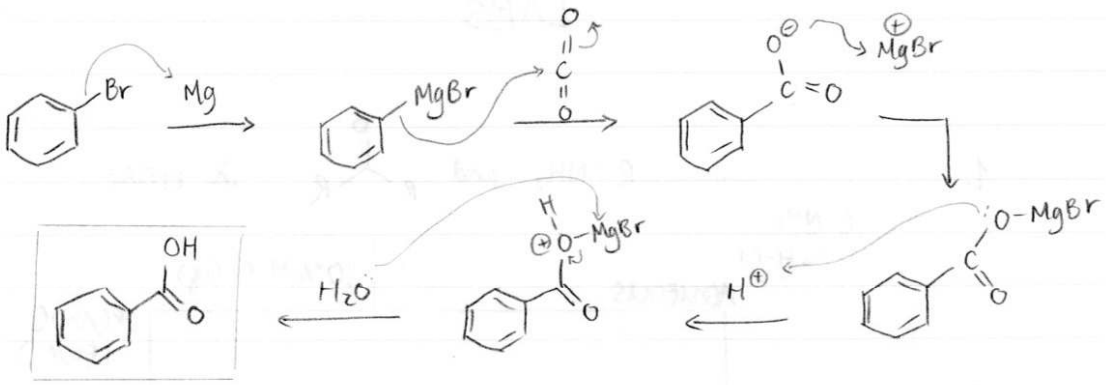
2 - add 10% HCl (aqueous), shake and separate the layers.

3 - Evaporate the organic layer → get pure ketone.

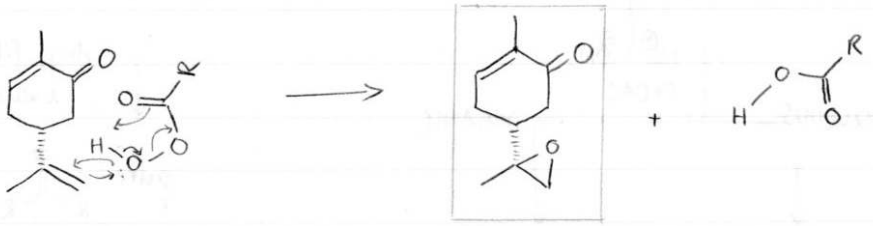
4 - Add EtOAc (solvent) to the aqueous layer, shake and separate the layers.

5 - Evaporate the organic layer → get pure amine.

2.



3.



Regioselectivity: the double bond that doesn't react is conjugated with the carbonyl, and thus has lower e^- density.

4. Dry ice should be obtained right before you use it because water vapour from the air condenses on it if it sits out for long. We want to minimize the water present when the Grignard reacts with CO_2 because water protonates and "kills" the Grignard, which would reduce the yield.

5. The $KMnO_4$ reacts with the unreacted double bond in carvone, oxidizing it and therefore causing its colour to change from purple to brown.

6. Hydrolysis of borate ester: see scheme 2 (p. 31) in the lab manual for the mechanism.

- **Calculate the yield, given the mass and molar mass of the starting material and product.**
  7. ▪ e.g., Calculate the yield if a student began experiment 4 with 3.0 mL of bromobenzene (density = 1.5 g/mL, molar mass = 157 g/mol) and obtained 2.9 g of white crystals at the end of the reaction (molar mass of product = 122 g/mol). Please clearly show your calculations. **(3 points)**
- **Explain the regioselectivity of a reaction.**
  8. ▪ e.g., Explain the regioselectivity of the epoxidation in experiment 5 with *m*CPBA (i.e., why does one π bond react preferentially over the other?) **(4 points)**

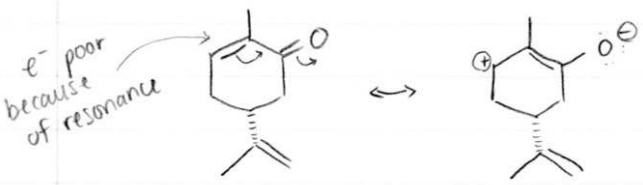
Best of luck for all your exams and have a great summer!

7. $\%\ \text{yield} = \frac{\text{actual}}{\text{theoretical}} \times 100\%$

$$\text{theoretical} = 3.0\ \text{mL bromobenzene} \times 1.5\ \frac{\text{g}}{\text{mL}} \times \frac{1\ \text{mol}}{157\ \text{g}} \times \frac{1\ \text{mol benzoic acid}}{1\ \text{mol bromobenzene}} \times \frac{122\ \text{g}}{\text{mol}} = 3.497\ \text{g}$$

$$\%\ \text{yield} = \frac{2.9\ \text{g}}{3.497\ \text{g}} \times 100\% = \boxed{82.9\%}$$

8. See p. 47 of lab manual.



The reaction rate is higher for the double bond that is more e⁻ rich. In this case, the double bond at the top is conjugated with the carbonyl, causing e⁻ density to be drawn away, and therefore it is e⁻ poor compared to the double bond at the bottom.