

Chemistry 2420 S10 Spring 2005 Final Exam 180 Minutes

Name: Student Number

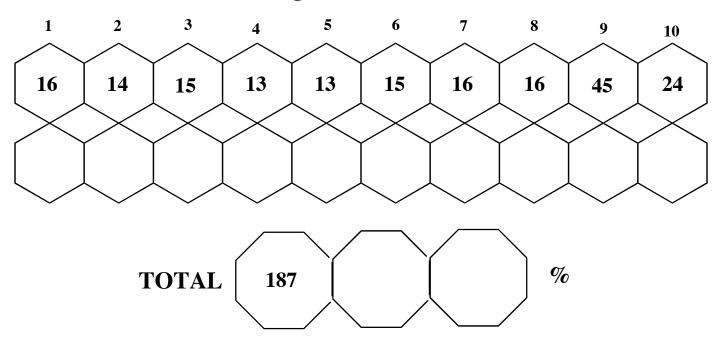
This paper consists of 14 pages (10 questions) including this title page.

Ensure that you have a complete paper (a data page will also be provided).

Molecular models may be used during this examination.

Marking Scheme For The Exam

QUESTION

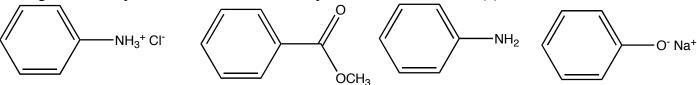


All the best for the future.

I hope you enjoyed the course!!

Question 1. (16 Marks) Provide the correct answer for each of the following.

a) Place **G** (for good) in the ring for the compound that will have the most pleasant aroma and **B** (for bad) in the ring for the compound that will have the least pleasant aroma. (2)



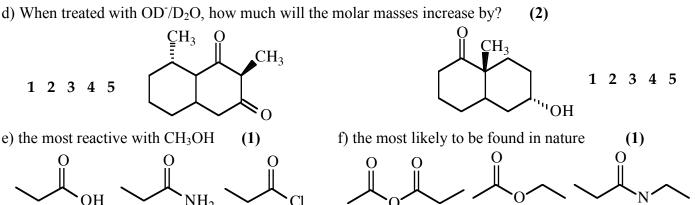
b) Place S (for strong) in the ring for the compound that will be the strongest base and W (for weak) in the ring for the compound that will be the weakest base. (2)



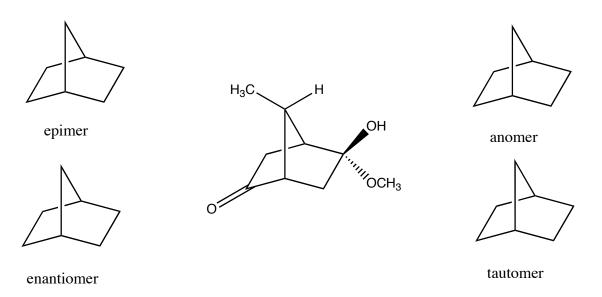
c) Circle the **two** structures that are significantly more stable than expected because of resonance.



(2)



g) Using the following compound as a guide, provide the structures of suitable isomeric compounds to illustrate that you understand the meaning of each listed term. (6)



Question 2. (14 Marks) Match each of the entries A through N with the number of one term chosen from the following list that best describes or defines that entry. Place your answers in the boxes below.

1. Carbinolamine

13. Hemiacetal

- 2. Oil
- 3. Fat
- 4. Fatty Acid
- 5. Soap
- 6. Imine

- 7. Enamine
- 8. Lactam

14. Cyanohydrin

- 9. Lactone
- 10. Betaine
- 11. Ylide

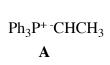
16. Steroid

12. Acetal17. Alkaloid

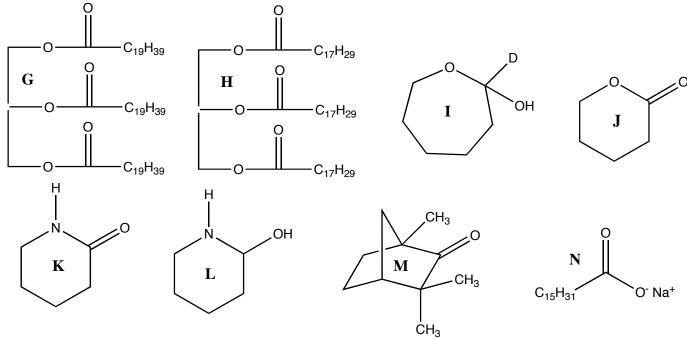
- 18. Resonance Effect
- 19. Inductive Effect

15. Terpene

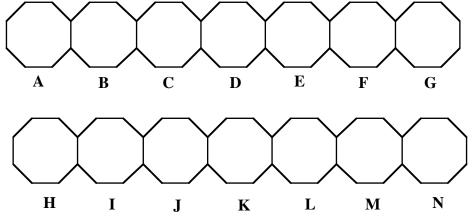
20. Isotope effect



- **E.** Phenol is a stronger acid than cyclohexanol.
- **F.** 2-chloropropanoic acid is a stronger acid than 2-methoxypropanoic acid.



Provide the numbers corresponding to the terms listed above to describe entries A through N.

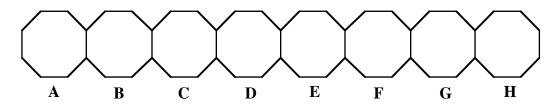


Question 3. (15 Marks)

A. During this semester we have used many different words to describe the inter-conversion of chemical structures. Match each of the following terms with **one** of the processes listed below (the letter of the process is shown below the arrow). (12)

1. Tautomerization 2. Racemization 3. Mutarotation 4. Saponification 7. Oxidation 5. Epimerization 6. Reduction 8. Resonance OH В OH OH НО H₃C,,,,,,, CH_3 CH_3 H_2O -OH OH. .OH D C \mathbf{E} HO' -OH CH_2O CH₃OH C₁₅H₃₁ F

Provide the numbers corresponding to the terms listed above to describe entries A through H.



B. Provide suitable arrows representing the movement of electrons to show how the following molecule will react upon heating and give the structure of the product before and after tautomerism. (3)

What is the name of the process that occurred when the original molecule was heated?

Question 4. (13 Marks) A. Provide the IUPAC names for the following compounds (under the structures) as well as completing structure C for a congener of compound B. (3)

B. The following biologically active compound can be found in the Merck Index under two different names: **ibuprofen** and **Advil**. Briefly explain the difference between the two names and why the IUPAC name for the compound would likely not appear on a bottle of the compound in the drug store. (2)

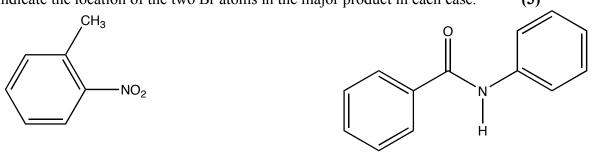
C. The following compound can be acetylated (with difficulty) with propanoyl chloride in the presence of AlCl₃. The major product from the reaction is the meta-substituted compound. Provide a localized resonance structure for the starting material that would support these experimental observations. Make certain that you indicate the location of any lone pairs of electrons and any formal charges. (2)

D. Complete the structures of the products isolated (including the location of any charges) when the following $\{D/L\}$ amino acid undergoes the following reactions. (3)

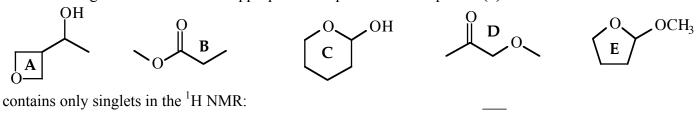
E. Complete the structure of compounds B and C (isomers of A) such that compound B would undergo a faster reaction than A and compound C would undergo a slower reaction than A with Br₂/Fe . (3)

$$egin{picture}(10,0) \put(0,0){\line(0,0){100}} \put(0,0){\line(0,0){100}$$

Question 5. (13 Marks) A. The following two compounds are each subjected to dibromination with Br₂/Fe. Indicate the location of the two Br atoms in the major product in each case. (3)

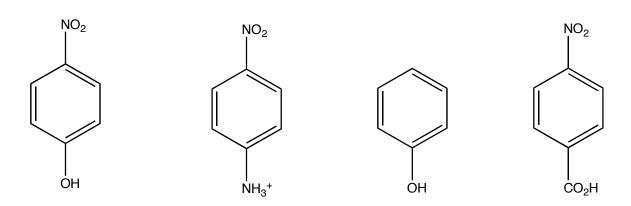


B. Place a single letter for the most appropriate compound in each space. (3)



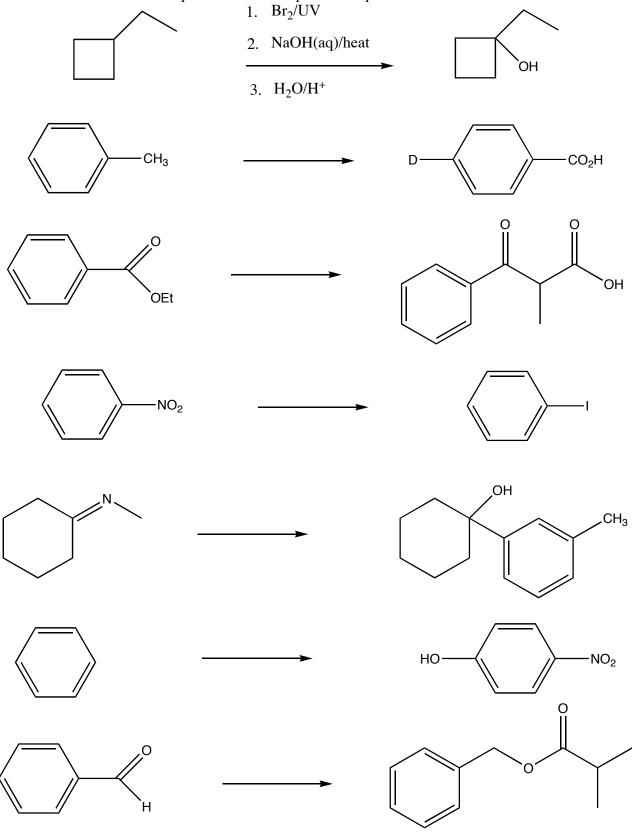
C. During this course you have been introduced to a number of concepts that may be used to describe trends in a series of related compounds. For the following set of acidic compounds, place the correct pK_a value inside the aromatic ring.

(4) pK_a values = 1.0 3.4 7.1 10.0

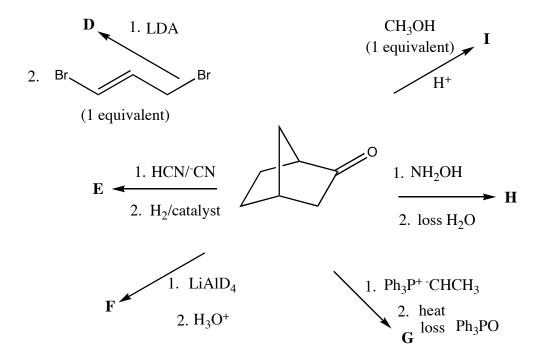


D. Provide an additional resonance structure for the following cation (A) and the following anion (B), showing the location of all lone pairs of electrons and charges. (3)

Question 6. (15 Marks) You have been exposed to a large number of reagents in CHEM 2320/2420 to convert one functional group into another. Provide the identity of the reagents necessary for the sequence of reactions shown below. Each synthesis will require only **three steps and the order of reactions may be important in some cases**. I have provided an example of a sequence below:



Question 7. (16 Marks) A. Provide the structures of the major products D, E, F, G, H and I formed in the reaction of the bicyclic ketone shown below. (9)

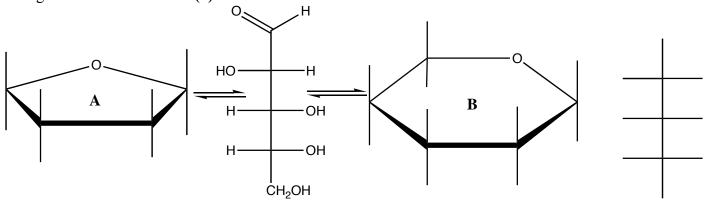


B. Complete the following mechanism by using electron-shift arrows and show the positions of any charges present in the reaction intermediates. (4)

C. Provide the structure of the **major product** formed in each of the following reactions. (3)

$$\begin{array}{c|c} CH_3OD \\ \hline \\ warm \end{array} \begin{array}{c|c} + & PhN(CH_3)_2 \\ \hline \\ warm \end{array}$$

Question 8. (16 Marks) A. Complete the Haworth structures for two of the cyclic compounds A and B that are in equilibrium with the monosaccharide D-arabinose. Complete the Fischer Projection formula on the right for L-arabinose. (4)



D-arabinose L-arabinose

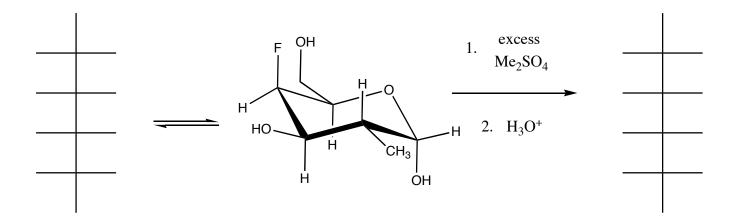
Provide the full IUPAC name for your compound A. (1)

The sugar that is epimeric to D-arabinose at C#2 contains { 2 / 3 / 4 } stereogenic carbon atoms and would be a { non-reducing / reducing } { aldo / keto } { pentose / hexose }. This { chiral / achiral } compound would { undergo / not undergo } mutarotation and would give a { positive / negative } Tollens test. The osazones formed from this sugar and L-arabinose would be { enantiomers / identical / diastereomers }. (6)

What reagents would be necessary to convert D-arabinose to: (1)

D-arabinitol: _____ D-arabinaric acid: _____

B. Complete the Fischer Projection formula on the left for the sugar derivative shown below and the Fischer Projection formula on the right for the reaction product under the conditions indicated. (3)



At which carbon atom is this sugar epimeric with D-glucose? (1)

Question 9. (45 Marks) Provide the structures of all carbon-containing products formed in the following reactions. You may assume that each reaction goes to completion and that you have excess reagent unless otherwise specified. Be careful with the possibility of acid/base transfer in the products.

$$\begin{array}{c|c}
\hline
0 \\
NH_2
\end{array}$$

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

HO-/
$$H_2O$$
Ho-/ H_2O
CN
catalyst
dropwise
(loss H_2O)

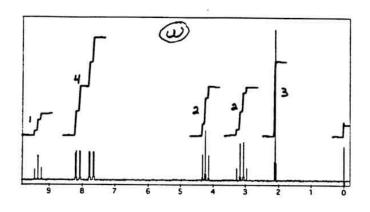
$$\begin{array}{c} D \\ \hline \\ D \\ \hline \\ N_2^+ \end{array} \qquad \begin{array}{c} D \\ \hline \\ D \\ \end{array} \qquad \begin{array}{c} D \\ \\ D \\ \end{array} \qquad \begin{array}{c} D \\$$

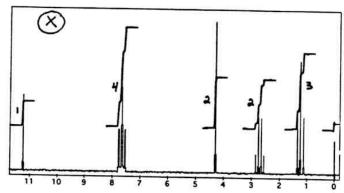
$$\begin{array}{c|c} O & OH & excess \\ I_2 & \\ \hline & KOH(aq) & \end{array}$$

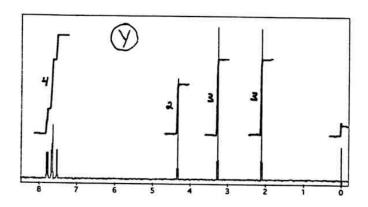
EtO
$$\stackrel{\text{a}}{\longrightarrow}$$
 $1. \text{ LiAlD}_4$ $2. \text{ H}_3\text{O}^+$

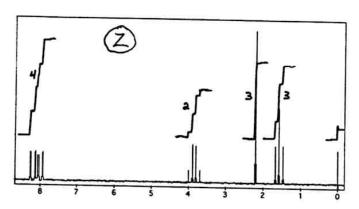
$$CH_3$$
 H_3O^+

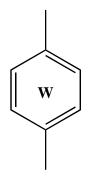
Question 10. (24 Marks) A. Compounds W, X, Y and Z (all para-disubstituted benzenes) have the same molecular formula $(C_{10}H_{12}O_2)$ and all have a strong band near 1700 cm⁻¹ in the IR (compound X also has a broad band from 2500 to 3300 cm⁻¹). Compounds W and Z are the only ones to give a positive 2,4-DNP test. The ¹H NMR spectra of all four compounds are shown below. Complete the structures of compounds W, X, Y and Z. (12)



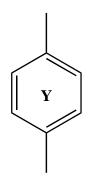


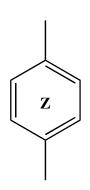












B. Poor CHEM 2420 graduate I.M. Confused is having trouble with his new job at ACME Pharmaceuticals. He has come across 3 unlabelled bottles (containing compounds A, B and C) and has managed to deduce that A is a mono-substituted benzene. Compound A was used to prepare compound B, a para-substituted benzene. Mass spectral analysis of compound C (also a para-substituted benzene, formed in a reaction of compound B) indicated that it had the molecular formula $C_{10}H_{11}BrO$. The IR spectrum of compound C showed a strong band near 1700 cm⁻¹ and its ¹H NMR spectrum is shown below. As I.M. Confused cannot remember how to analyze the spectra, it is up to you to complete the structures of compounds A, B and C, as well as providing the reagents used to prepare compound A from benzene as well as to convert compound A to B and compound B to compound C. (12)

