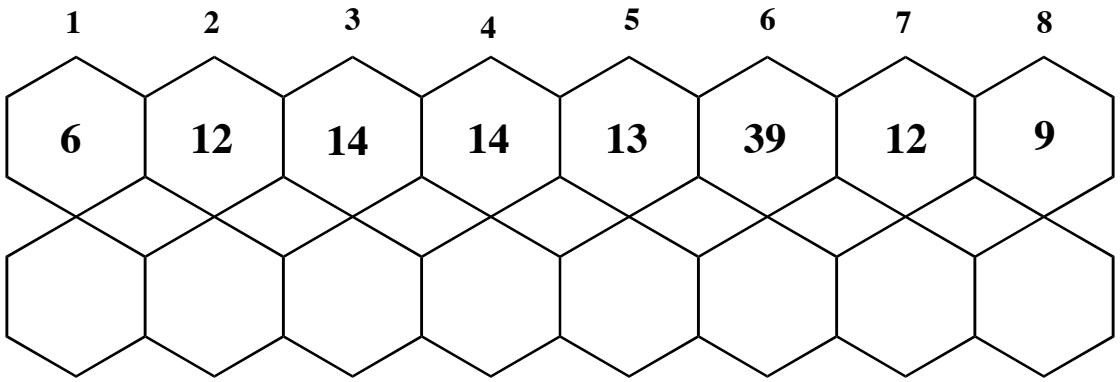
Kwantlen UNIVERSITY COLLEGE

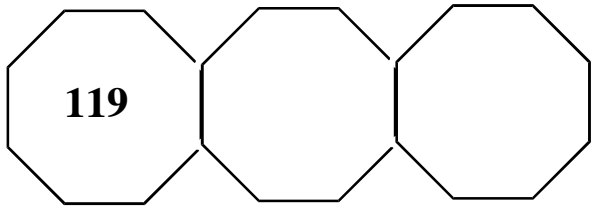
Chemistry 2420 S10 Spring 2005
Term Exam #1
110 Minutes

Name: _____ **Student Number**_____

Marking Scheme For The Exam

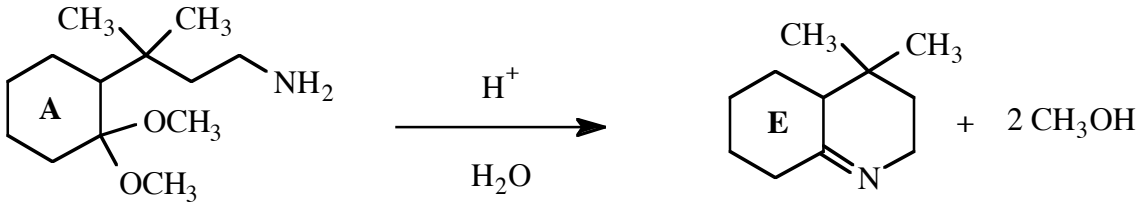
QUESTION





Question 1. (6 Marks) Under mildly acidic conditions, compound A reacts to produce compound E plus two equivalents of methanol.

Identify the main functional group present in: **A**: _____ **E:** _____

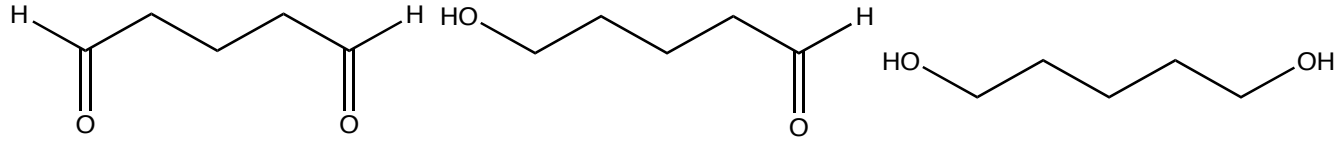


Provide the structures of the three additional neutral molecules (B, C and D) that are formed during the conversion. Identify the major functional group present in each of the molecules you have drawn.

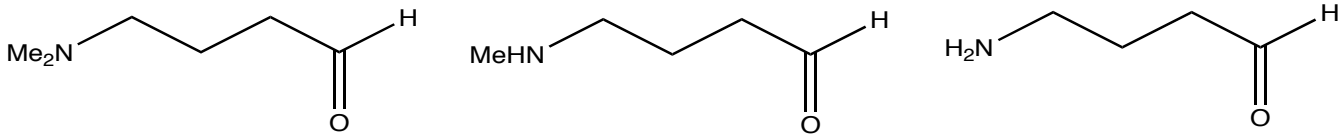
A ⟶ **B** ⟶ **C** ⟶ **D** ⟶ **E**

Question 2. (12 Marks) Circle the structure that will best satisfy the given information.

- the compound able to undergo an intramolecular cyclization to form a hemiacetal

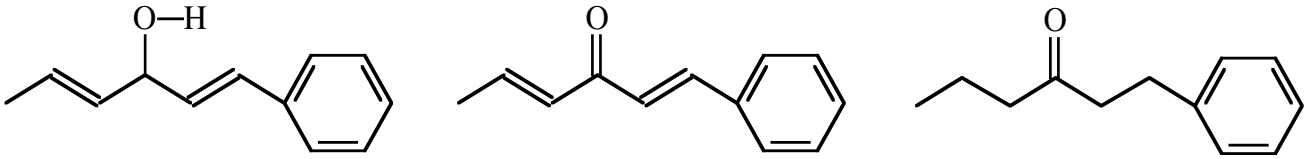


- the compound able to undergo an intramolecular cyclization to form an enamine

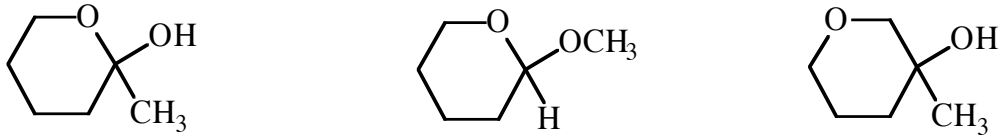


- the product formed from treatment of 2-butanone with $NaBD_4$ followed by a H_3O^+ work-up

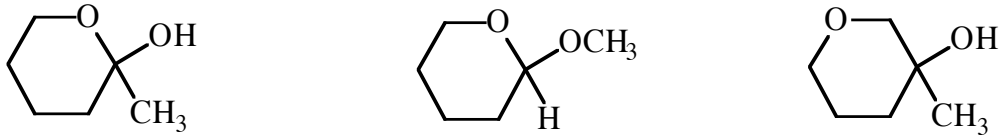
- the compound that would most likely be coloured



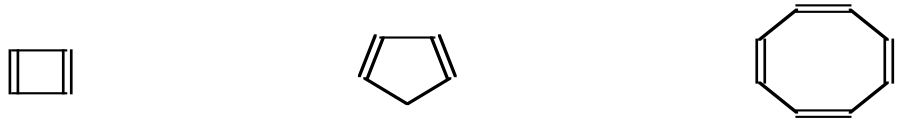
- the compound capable of undergoing mutarotation



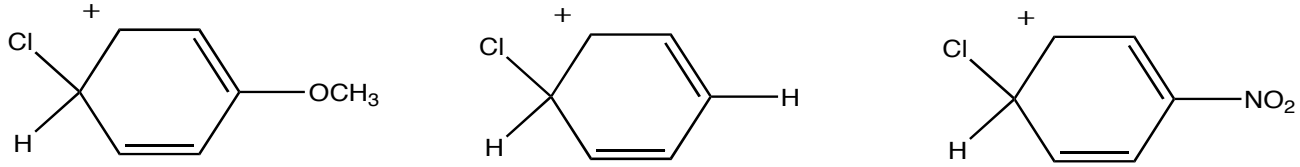
- the compound that would not react with MeMgBr



- the compound best described as "anti-aromatic":



- the most stable carbocation

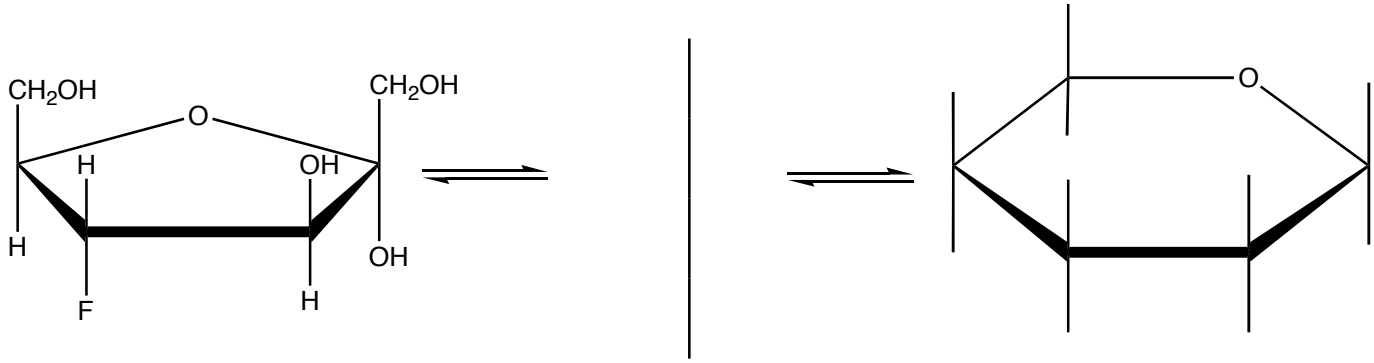


Question 3. (14 Marks)

a) Circle the terms that best apply to the sugar below on the left that has an optical rotation of - 24°. **(3)**

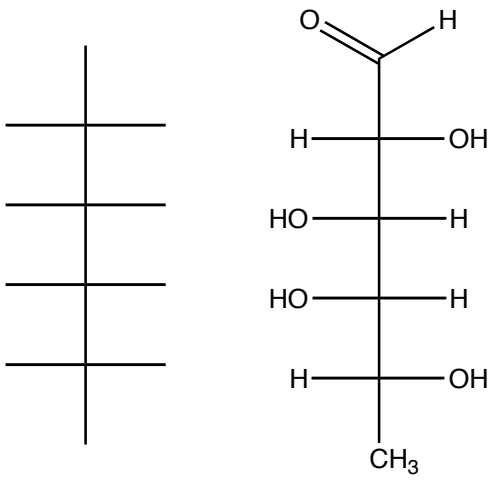
Aldose or Ketose **d or l** **α or β** **D or L**

Pyranose or Furanose **Hexose or Pentose**



b) Complete the Fischer Projection and the Haworth Projection of the sugar above. **(3)**

c) The Fischer Projection of the deoxy-sugar D-fucose (**a deoxygalactose**) is shown below. Complete the Fischer Projection for L-fucose, the product of the reaction of D-fucose with $NaBH_4$ (after acid work-up) and a sugar (**not an epimer**) that would produce the same osazone as D-fucose. **(5)**

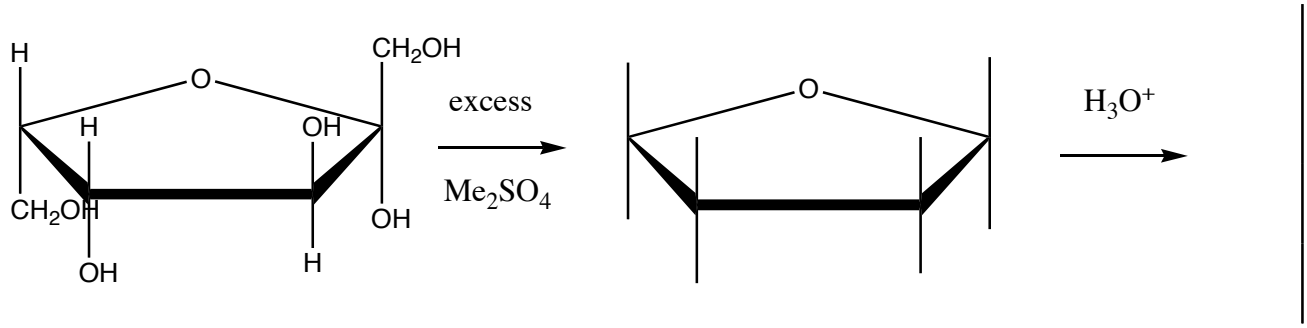


L-fucose D-fucose $NaBH_4$ product osazone sugar

The systematic name of this deoxygalactose would be require the number (n): **1 2 3 4 5 6**

Galactose must be epimeric to glucose at carbon: **1 2 3 4 5 6**

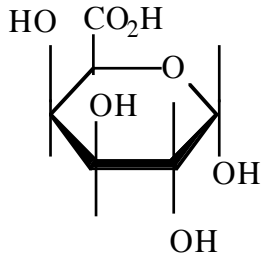
d) Complete the structures of the compounds formed in the following reactions. **(3)**

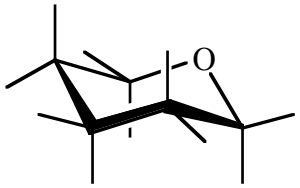


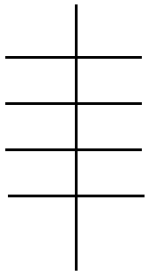
Question 4. (14 Marks)

a) The monosaccharide shown below on the far left can be isolated from the hydrolysis of pectin. **(4)**

The compound is best described as an **aldonic** **aldaric** **uronic** acid.



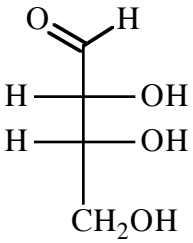




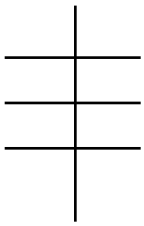
Complete the chair conformer of the sugar as well as its Fischer Projection formula.

This sugar would give a positive Tollens test: **T** **F**

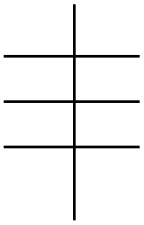
c) When D-erythrose is subjected to the series of reactions involved in the Kiliani-Fischer synthesis, the compounds D-ribose and D-arabinose are isolated. **Reaction of only D-arabinose** with HNO_3 produces a product that is optically pure. Reaction of D-ribose with Br_2/H_2O also gives a product that is optically pure. Complete the Fischer Projection formulas below for D-ribose and D-arabinose and the product from the HNO_3 reaction of D-arabinose and the product from the Br_2/H_2O reaction of D-ribose. **(6)**



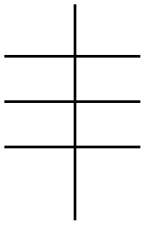
D-erythrose



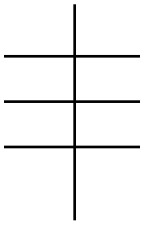
D-ribose



Br_2/H_2O product



D-arabinose

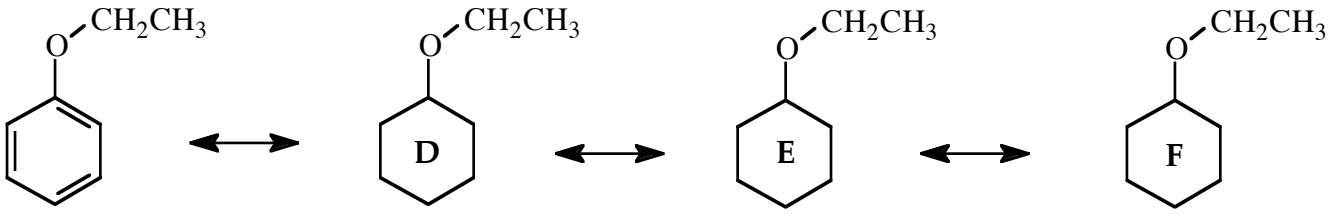


HNO_3 product

d) Briefly describe how it would be possible for a disaccharide made up 2 units of D-glucose to be either reducing or non-reducing. **Your answer must include at least one chemical structure. (4)**

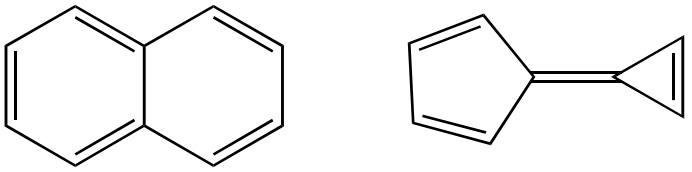
Question 5. (13 Marks) One way of rationalizing the directing effects of the various substituents on an aromatic ring is to consider the resonance structures of the starting material.

a) Complete the resonance structures D, E and F for **ethoxybenzene** by indicating the location of any lone pairs of electrons and any formal charges. **(3)**



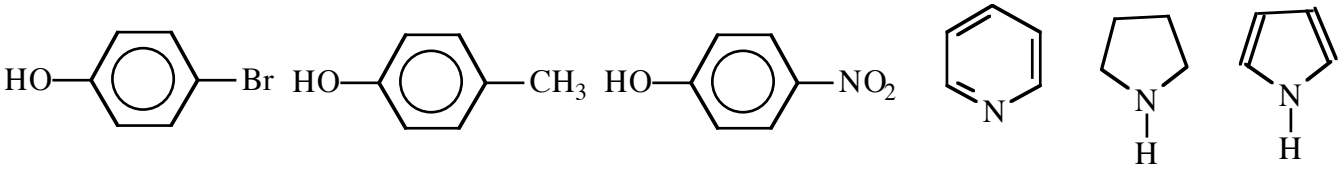
b) The ethoxy group will **{ activate / deactivate }** the benzene ring for **{ electrophilic / nucleophilic }** **{ substitution / addition }** reactions and will be **{ ortho&para / meta }** directing. The inductive effect of the ethoxy group is best considered as **{ electron-donating / electron-withdrawing }** while the resonance effect of the ethoxy group is best considered as **{ electron-donating / electron-withdrawing }**. The Friedel-Crafts reaction of ethoxybenzene with CH_3Cl /$AlCl_3$ will be **{ slower / faster** } than benzene as the inductive effect of the ethoxy group is **{ greater / less }** than the resonance effect of the ethoxy group. **(4**

c) The non-polar molecule naphthalene is aromatic while the aromatic molecule calicene is a polar molecule. Provide a brief explanation of these observations by considering resonance structures in light of Huckel Theory. Your answer should also include the direction of the dipole moment in calicene. **(3)**



naphthalene calicene

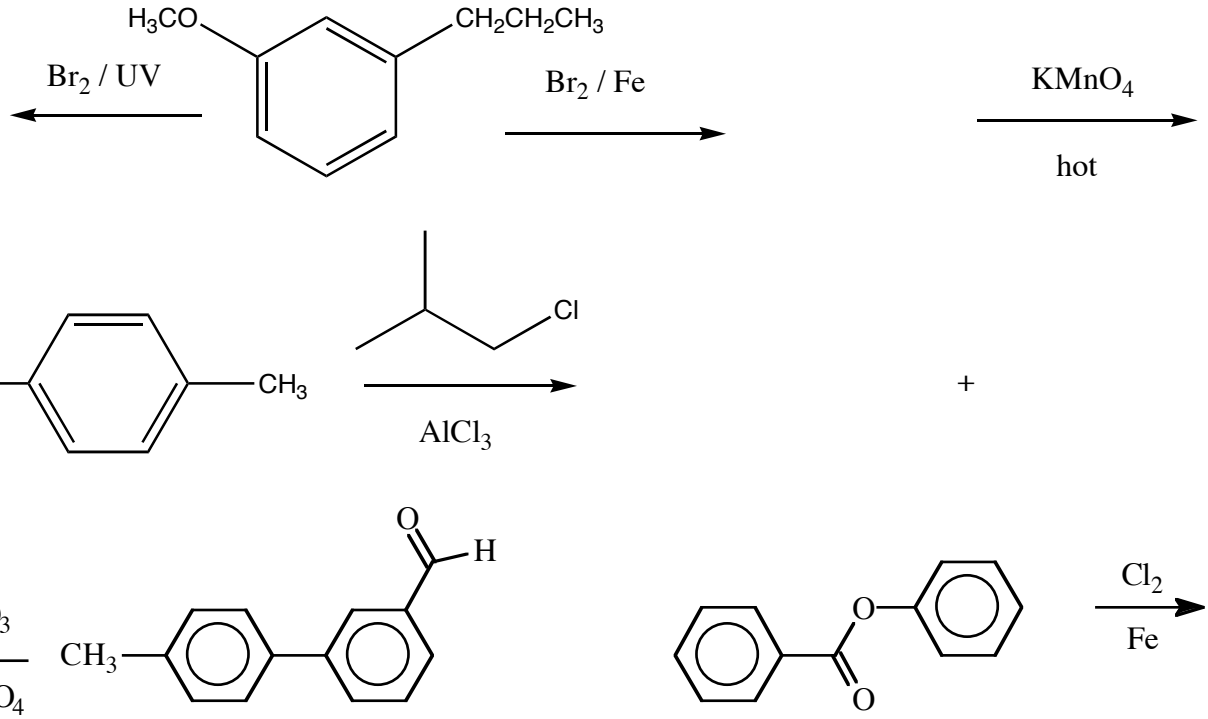
d) Match the pK_a (10.2, 9.4, 7.2) and pK_b (14, 8.8, 3.7) values with the correct structures: **(3)**



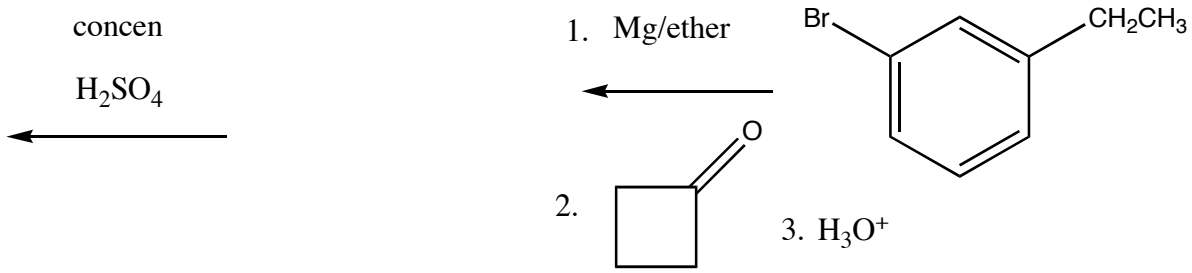
_____ _____ _____ _____ _____ _____

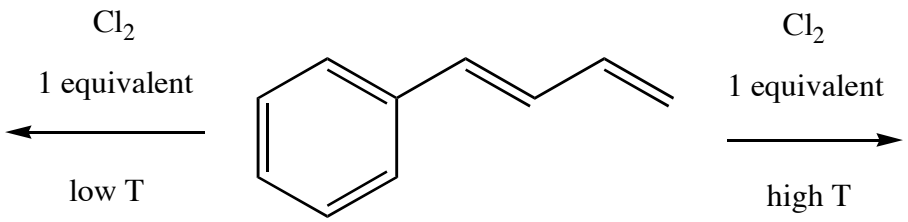
pK_a values pK_b values

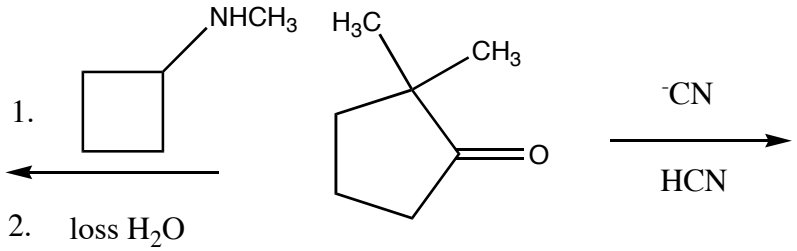
Question 6. (39 Marks) Provide the structure of the **major product(s)** in each of the following reactions. You can represent stereoisomers with a single structure.

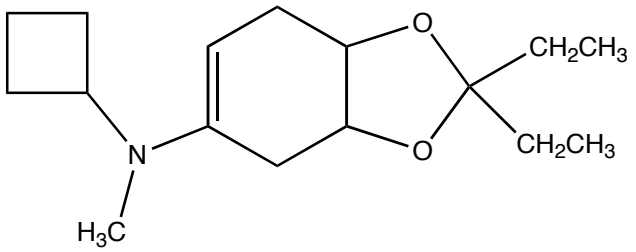


(designate the product by putting a group on each starting material molecule above)



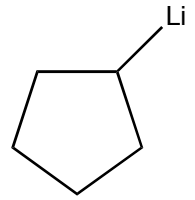






H_3O^+

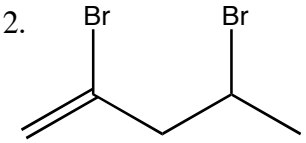
(3 products)



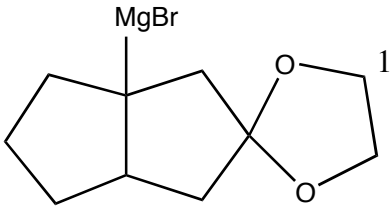
D_2O

1. CuI

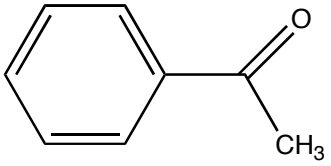
2.



(1 equivalent)



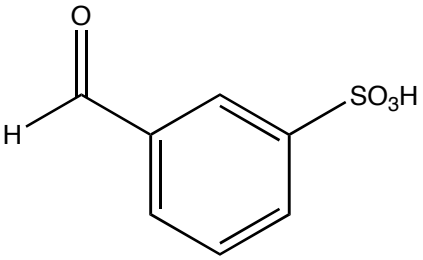
1.



2. NH_4Cl

H_3O^+

(2 products)

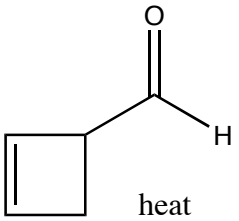


HNO_3

H_2SO_4

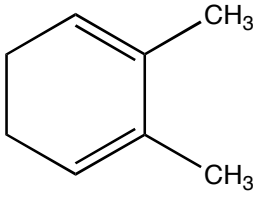
D_2O

heat



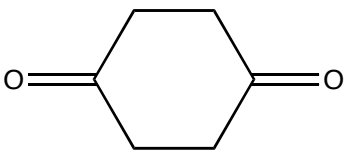
heat

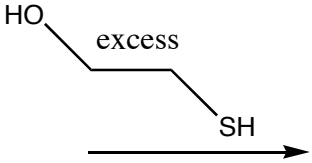
(Diels Alder)



heat

(Diels Alder)



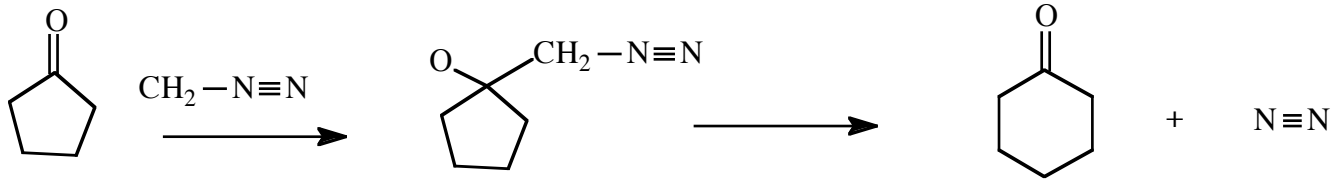


excess

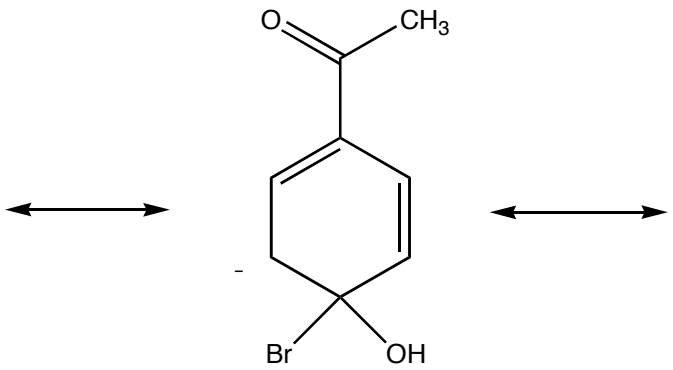
(loss H_2O)

Question 7. (12 Marks)

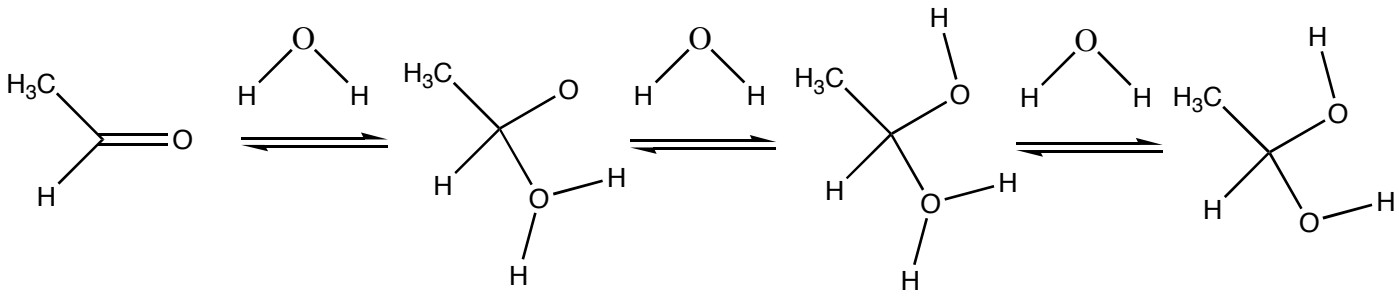
a) For the following reaction, provide any necessary lone pairs of electrons, charges and reaction arrows to represent the movement of electrons from starting material to final product. **NOTE:** All atoms have a filled outer shell of electrons in all the structures. **(2)**



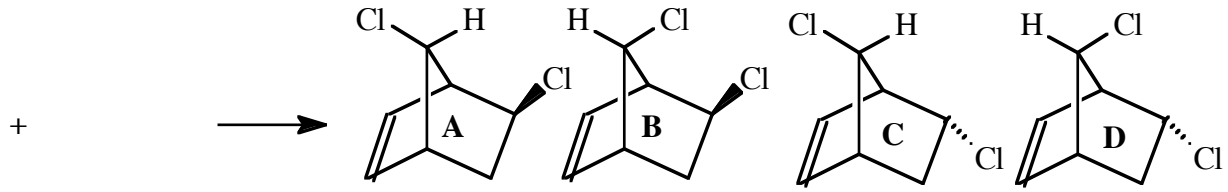
b) Provide two localized resonance structures for the following carbanion intermediate. One of them must show how the ketone group will **stabilize** **destabilize** the intermediate. **(3)**



c) The following steps are some of those involved in the conversion (using an aqueous oxidizing agent) of a primary alcohol to the corresponding carboxylic acid. Provide any necessary lone pairs of electrons, charges and reaction arrows to represent the movement of electrons. **(3)**



d) The following four compounds were isolated from a Diels Alder process. Give the structures of the diene and dienophile used in the reaction. **(4)**



What is the relationship between A and D? **enantiomers** **epimers** **diastereomers**

Which compound should be the major product in the reaction? **A** **B** **C** **D**

Question 8. (9 Marks) I.M. Confused is having trouble in his new research position at ACME Pharmaceuticals. He has found three unlabelled bottles (A, B and C) left behind by Clever Clyde, a former employee of the company, who had prepared all three compounds using benzene as a starting material. I.M. Confused has managed to determine that all three compounds have the same molecular formula ($C_{10}H_{11}BrO$) and are **all disubstituted benzene derivatives (A and C – para, B – meta)**. He has also obtained the ^1H NMR spectra for the three compounds (shown below), and has also found that the IR spectra of all three compounds contain a strong band around 1700 cm^{-1}. He cannot remember how to analyze these spectra. Help him out and provide the complete structures of compounds A, B and C.