KWANTLEN UNIVERSITY COLLEGE

CHEMISTRY 2420 R10 - ORGANIC CHEMISTRY II

Term Exam 1 - February 13, 2002 **NAME: _____**

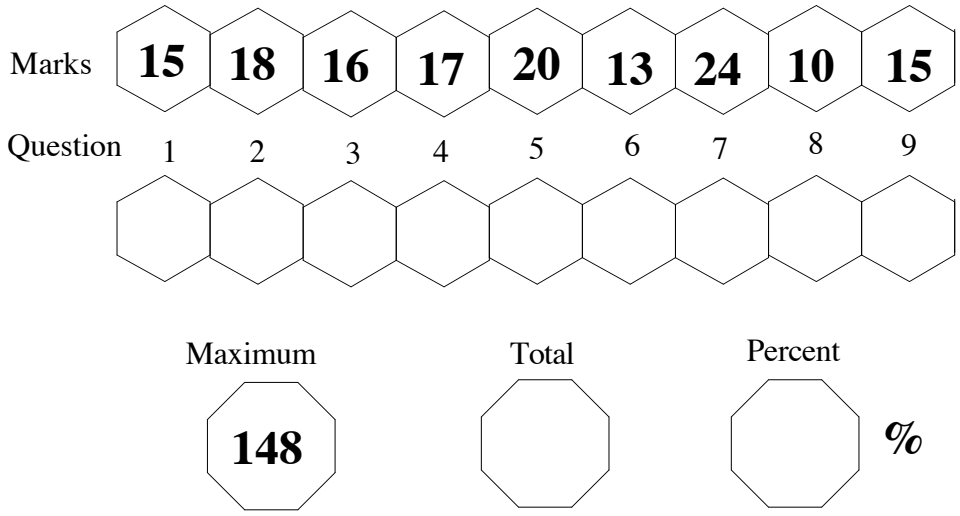
Time: 110 minutes **Budget your time carefully and good luck!!!**

This paper consists of **10 pages** (**9 questions**) including this title page.

Molecular models may be used during this examination.

Place all your answers on this examination paper.

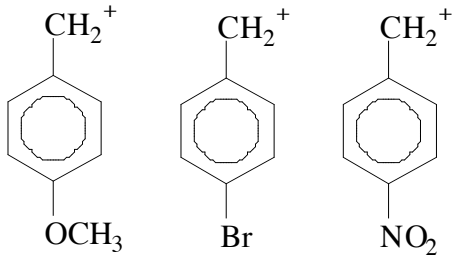
Grading Scheme For The Exam



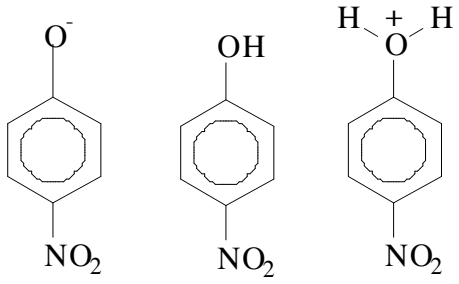
Maximum	Total	Percent
148		%

Question 1. **(15 Marks)** Circle the structure that **best satisfies** the information presented in each of the following cases.

a) the least stable intermediate

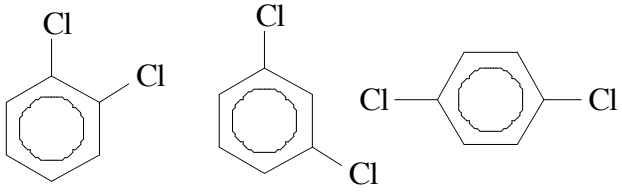


b) will most likely form a coloured solution

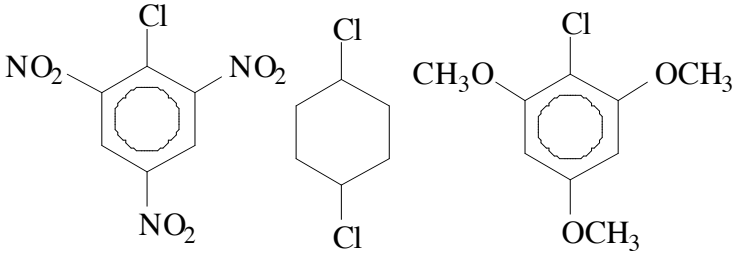


c) the least stable intermediate

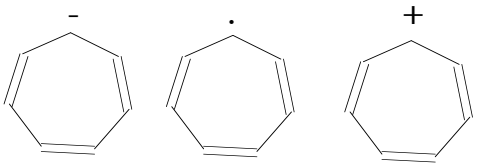
d) the highest melting point



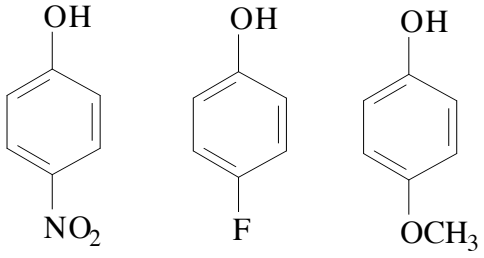
e) most persistent in the environment



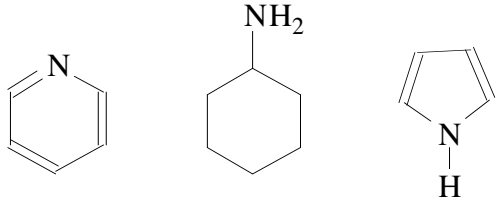
f) the most stable intermediate



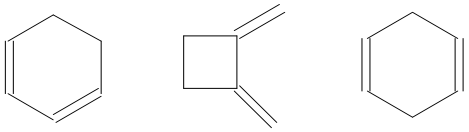
g) the weakest acid



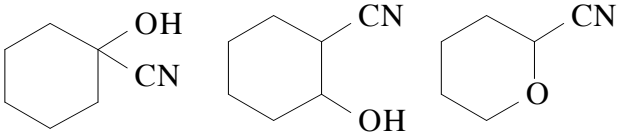
h) the strongest base



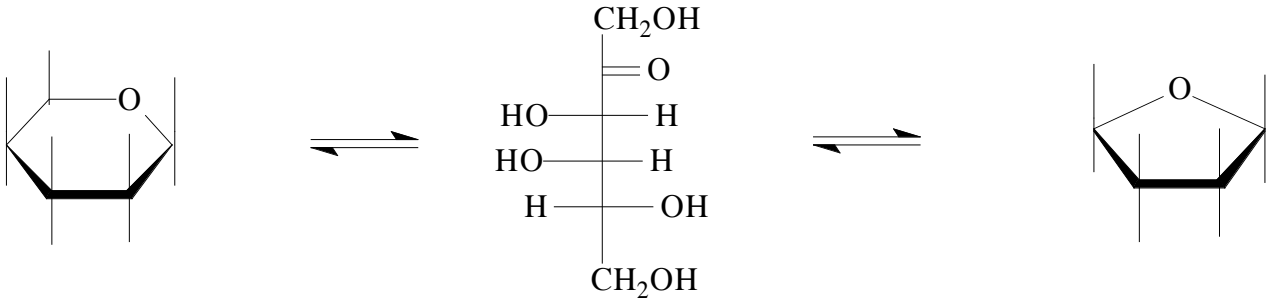
i) could function as a dienophile



j) is a cyanohydrin

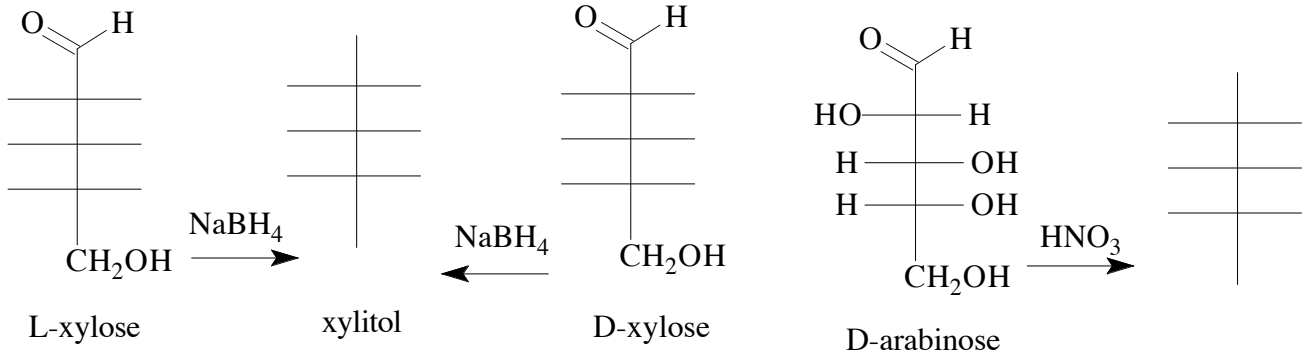


Question 2. (18 Marks) The compound **D-tagatose** is shown below in the open-chain Fischer Projection. When **D-tagatose** is dissolved in water, an equilibrating mixture of four possible cyclic structures forms. Complete the Haworth structures for two of the cyclic compounds. **(4)**

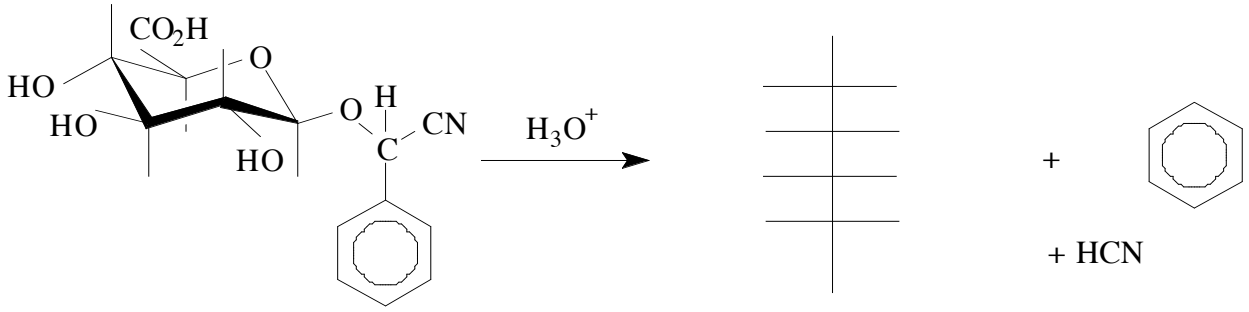


b) The deoxy-sugar **fucose** is shown below in its cyclic Haworth Projection. Complete its chair conformation on the right and provide its Fischer Projection on the left. **(4)**

c) **L-xylose is an epimer of D-arabinose**. Reaction of either L-xylose or D-xylose with $NaBH_4$ gives (after acidic work-up) the same compound, xylitol. Complete the Fischer formulas for L-xylose, D-xylose, xylitol and the structure of the product of the reaction of D-arabinose with HNO_3. **(6)**



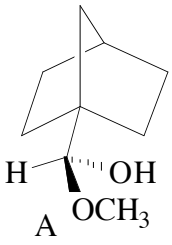
d) The following compound has been studied for the treatment of some cancers. Complete the Fischer Projection formula of the sugar derivative and the aromatic compound isolated (along with one molecule of HCN) from the hydrolysis. **(3)**



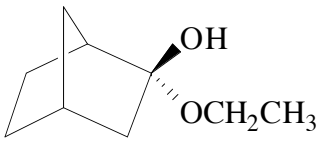
The sugar derivative is an: **(1)** **aldonic acid** **aldaric acid** **uronic acid**

Question 3. **(16 Marks)** As you saw in Chem 2320, learning organic chemistry is very much like learning a new language. By carefully considering the isomeric bicyclic structures below (all $C_9H_{16}O_2$), circle the letter(s) which illustrate(s) each of the listed terms. **NOTE:** This question will be marked by subtracting one-half the incorrect answers from the correct answers.

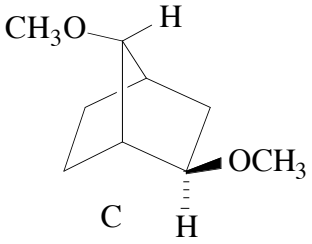
One term has three correct structures; all the others have one or two.



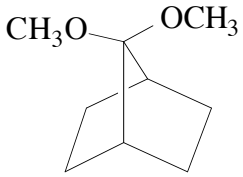
A



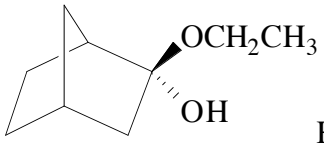
B



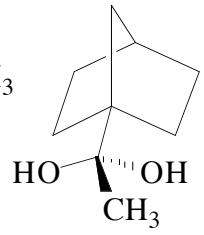
C



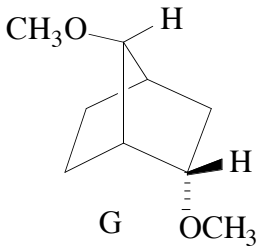
D



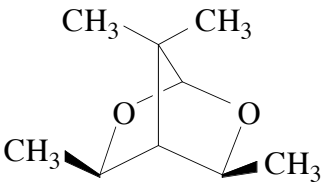
E



F



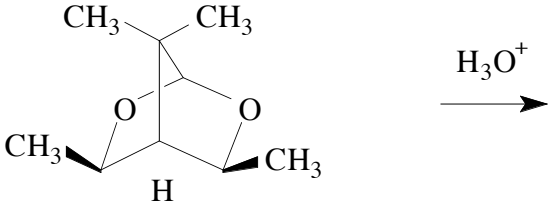
G



H

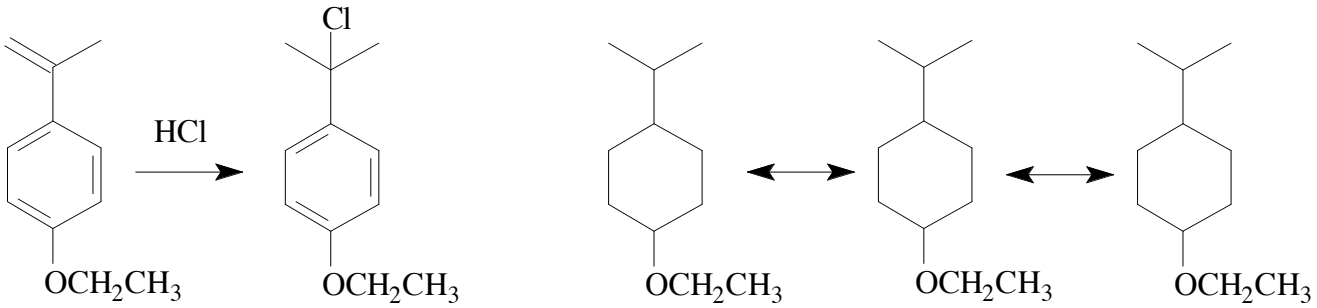
Can undergo mutarotation:	A	B	C	D	E	F	G	H
Meso compound:	A	B	C	D	E	F	G	H
Hydrate:	A	B	C	D	E	F	G	H
Hemiacetal:	A	B	C	D	E	F	G	H
Acetal:	A	B	C	D	E	F	G	H
Hemiketal:	A	B	C	D	E	F	G	H
Ketal:	A	B	C	D	E	F	G	H
Epimers:	A	B	C	D	E	F	G	H
Anomers:	A	B	C	D	E	F	G	H

Give the structure of the carbonyl compound formed when compound H is dissolved in dilute aqueous acid. **(2)**



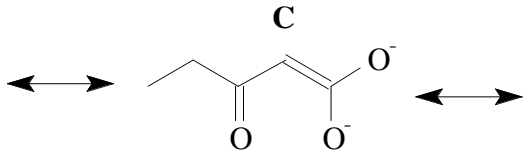
Question 4. (17 Marks)

a) The reaction of the alkene below with HCl forms the corresponding benzylic chloride. Complete the three localized resonance structures on the right for the carbocation reactive intermediate for the process. **(4)**

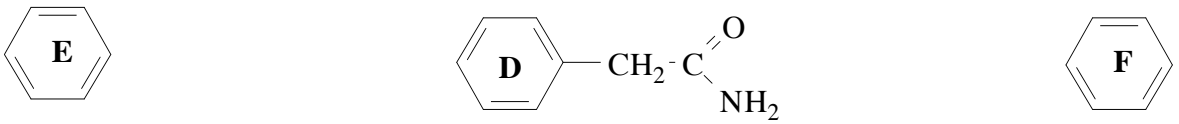


The p-ethoxy group will { **speed up / slow down** } the rate of the reaction relative to the unsubstituted compound; i.e., where a H atom is bonded to the benzene ring instead of the p-ethoxy group. **(1)**

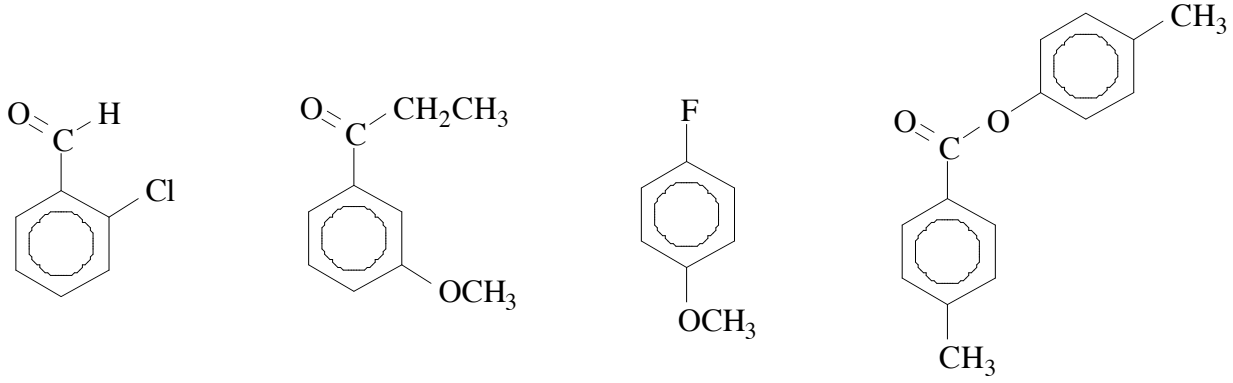
b) For the dianion C, give two additional localized resonance structures. **(3)**



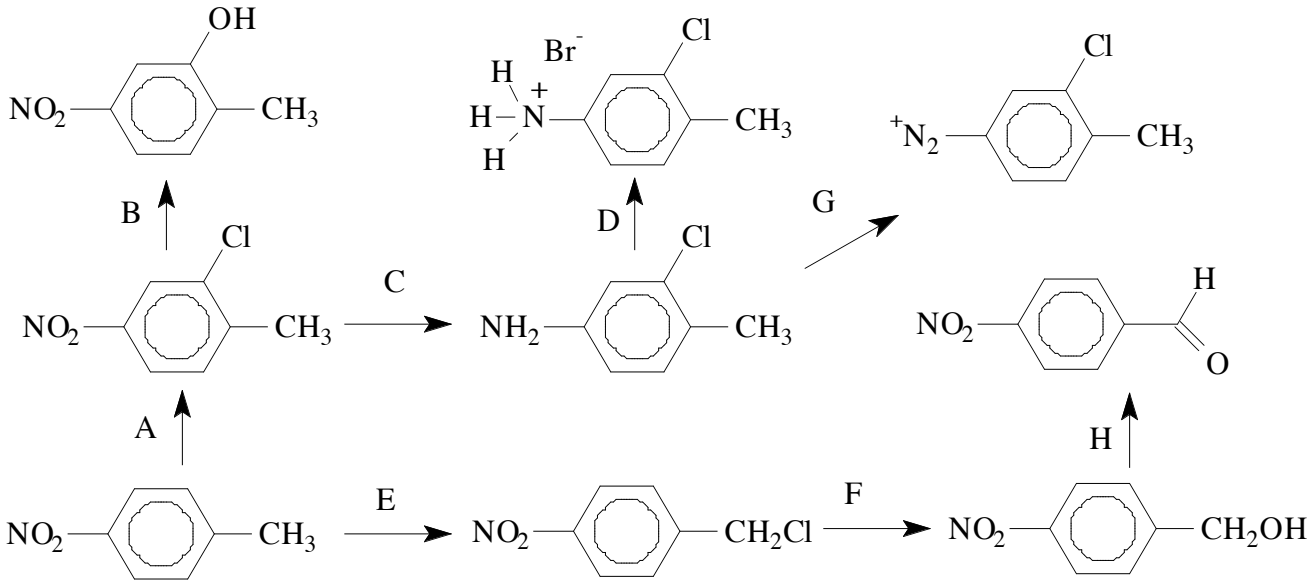
c) Complete the structure of an isomer E that will undergo electrophilic aromatic substitution **much faster** than compound D and an isomer F which will undergo electrophilic aromatic substitution **much slower** than compound D. **(3)**



d) Each of the following aromatic compounds is subjected to electrophilic monobromination. Indicate where the Br atom will be attached in the major product isolated in each reaction. **(6)**



Question 5. **(20 Marks)** Provide the identity of the unknown reagents in the following sequence of reactions. Indicate if a letter represents reagents that need to be used in 2 steps.



A	B	C	D

E	F	G	H

Give the **single letter** of the reagent which represents the reaction best described as:

electrophilic aromatic substitution ___

free radical substitution ___

nucleophilic aliphatic substitution ___

nucleophilic aromatic substitution ___

acid-base reaction ___

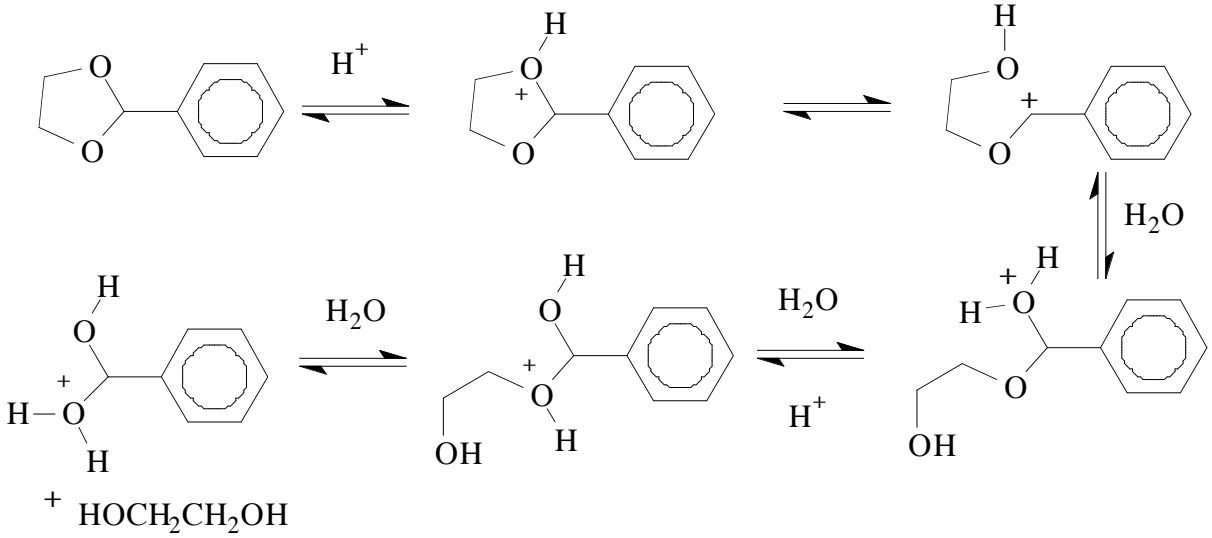
oxidation ___

diazotization ___

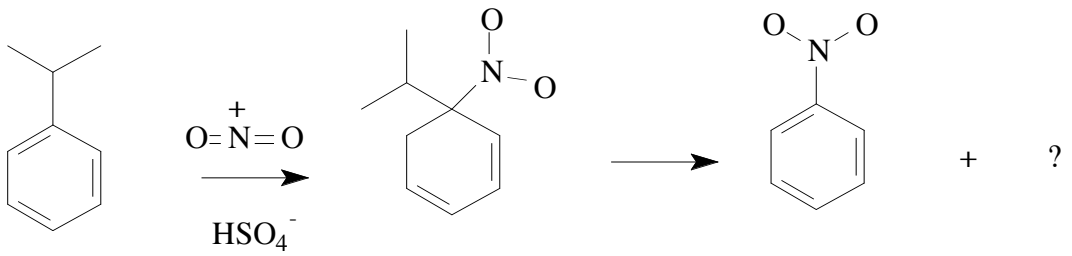
reduction ___

Question 6. (13 Marks)

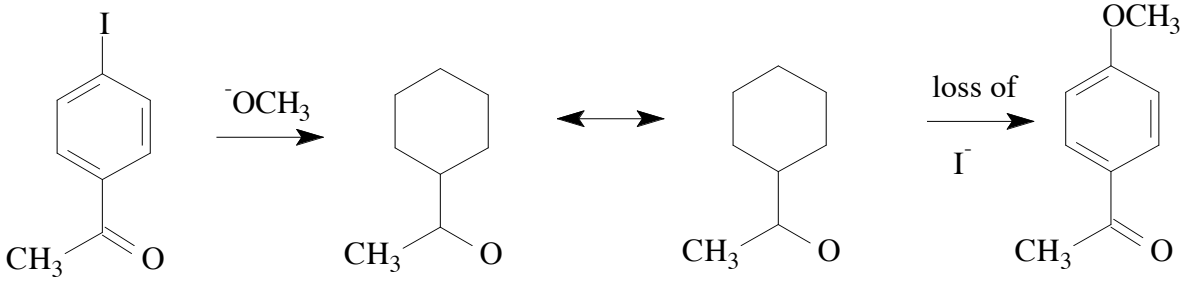
a) Provide the correct electron movement arrows to complete the following partial mechanism. Include any necessary lone pairs of electrons. **(5)**



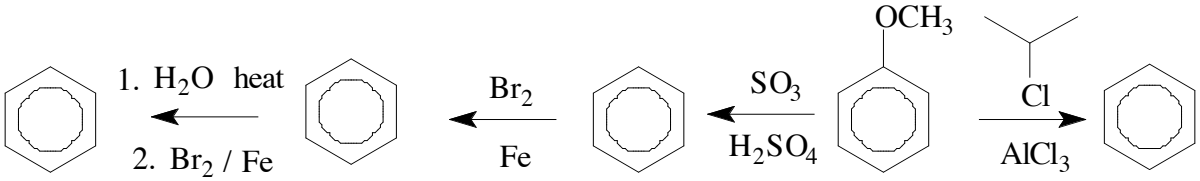
b) In some electrophilic aromatic substitution reactions, the group originally on the benzene ring can be replaced. This process is known to as **ipso substitution**. Provide the correct electron movement arrows to account for the formation of nitrobenzene in the following reaction. Include any pertinent formal charges and also provide the identity of the other organic compound formed. **(4)**

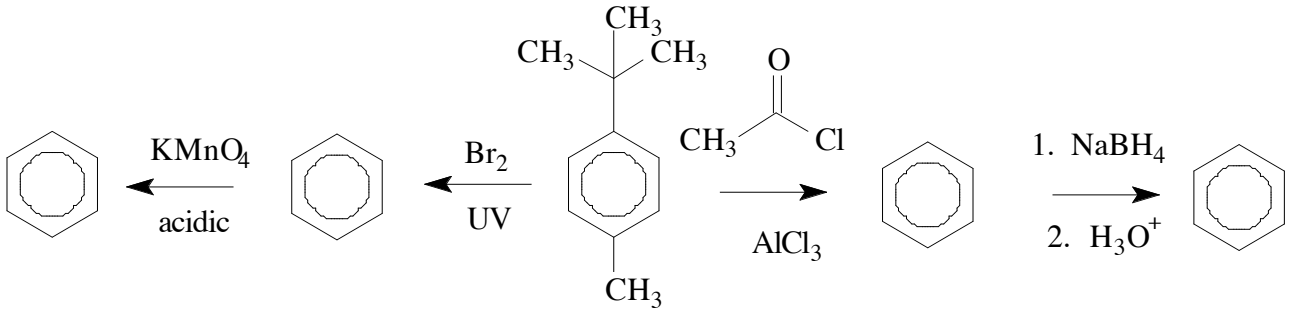


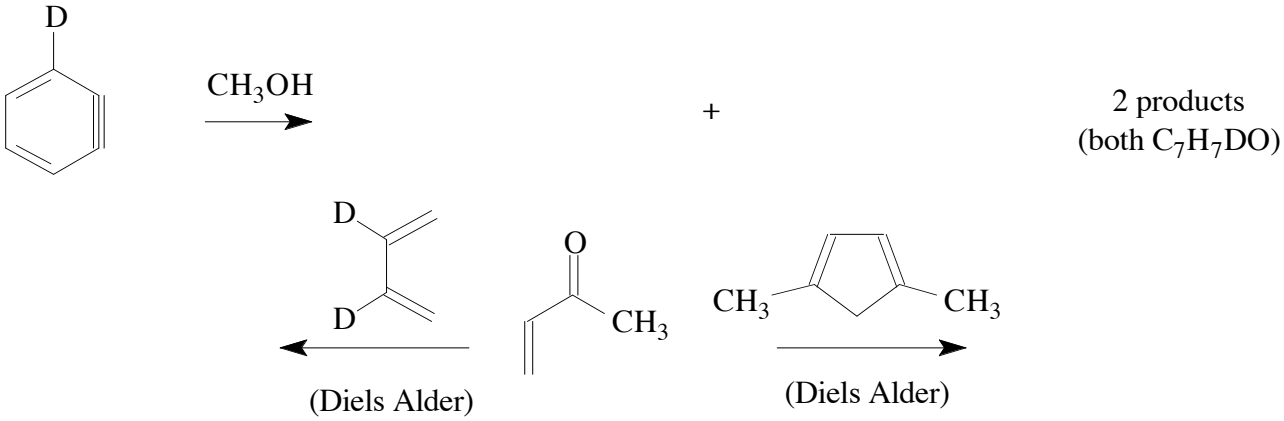
c) Provide two different localized resonance structures (showing the location of all atoms, bonds, lone pairs of electrons and charges) of the intermediate formed in the following reaction. **(4)**

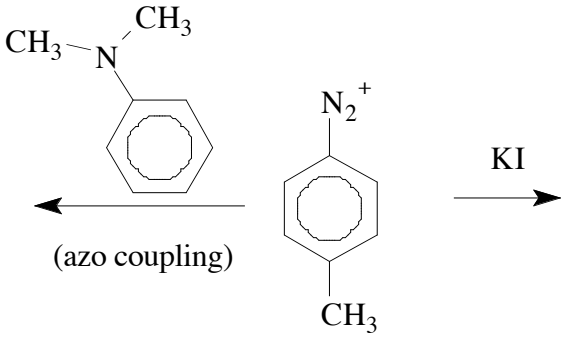


Question 7. **(24 Marks)** Complete the structure of the major product for each of the following reactions.





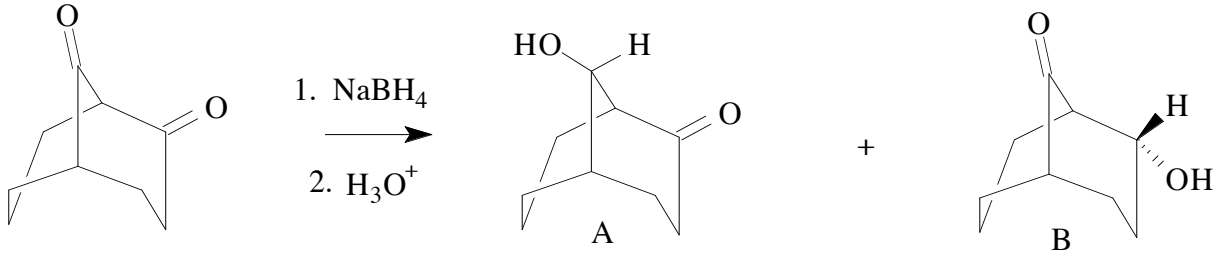




Question 8. (10 Marks)

a) Starting with benzene (plus any other one or two carbon compound), provide the suitable reagents and conditions to prepare the following compound. You should show the structure of the major product isolated after each step, and you may assume that you can separate para compounds from ortho compounds. **(5)**

b) The two alcohols A and B have recently been prepared in a 1:1 ratio from the diketone. **(5)**

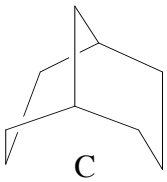


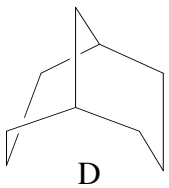
Both compounds have the same generic name: hydroxybicyclo[3.3.1]nonanone

What prefix would be required for compound A? exo endo syn anti

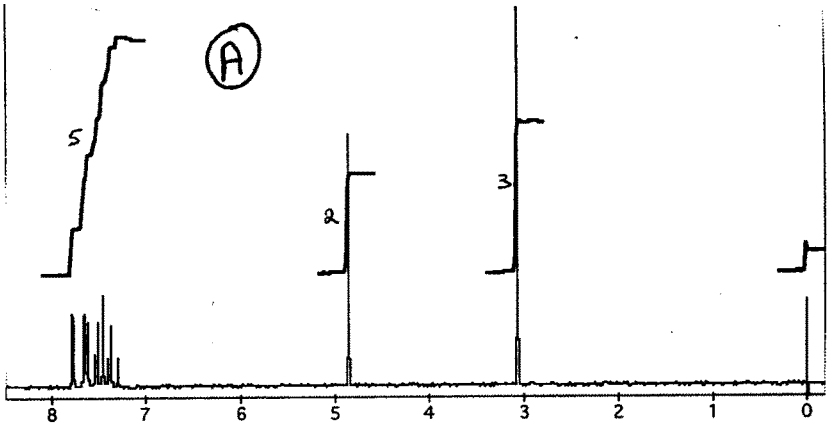
What prefix would be required for compound B? exo endo syn anti

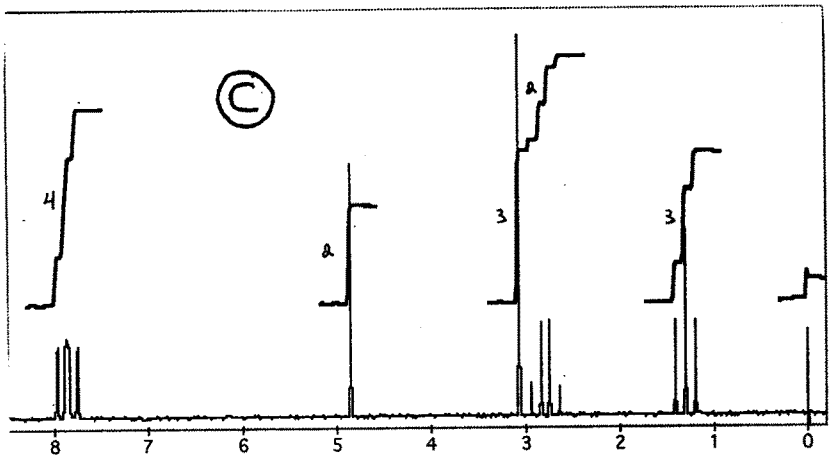
Complete structure C so that it is an epimer of compound A. Complete structure D so that it is the enantiomer of compound B.

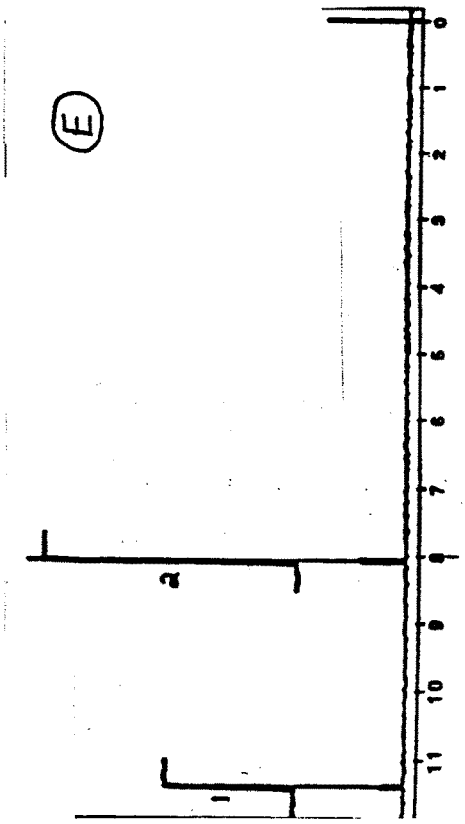

C


D

Question 9. **(15 Marks)** I.M. Confused is having trouble at ACME Pharmaceuticals. He has performed a Friedel Crafts reaction between compound A ($C_8H_{10}O$) and compound B (C_3H_5ClO) in the presence of an $AlCl_3$ catalyst and isolates compound C ($C_{11}H_{14}O_2$). He treats compound C with $NaBH_4$ and isolates (after hydrolyzing the intermediate boron complex) compound D ($C_{11}H_{16}O_2$). He then realizes that he has made an error and proceeds to boil compound D with acidic $KMnO_4$ solution to try and recover compound C. Unfortunately for him, the IR and NMR spectra indicate that the white solid he has isolated is a new substance, compound E ($C_8H_6O_4$). The NMR spectra are shown below for compounds A, C and E, but he cannot remember how to analyze them. The IR spectrum of compound A is pretty dull (no exciting bands), but the IR spectra for compounds B, C and E show a strong band around 1700 cm^{-1}, while a strong band near 3400 cm^{-1} is found for compound D and a broad band from ~ 2500 to 3100 cm^{-1} for compound E. As you can probably guess, his memory of IR is also gone. Help him out and provide the structures of compounds A, B, C, D and E.







A: _____ B: _____

C: _____ D: _____

E: _____