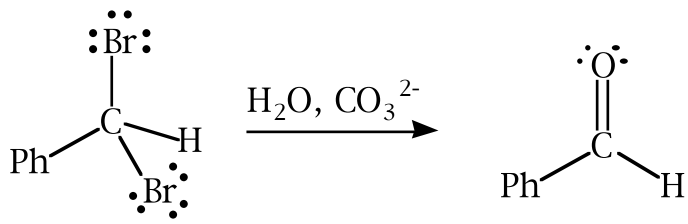
Chem 2600 Final Exam 2003, April 16th, 9:00 am to 12:00 am

You are permitted the use of a model kit. No other aids, including a periodic table are allowed. A periodic table and a table of pKas appears at the end of this paper. Answer all questions in this booklet. Print and sign your name below. Your signature indicates that you agree not to divulge or discuss the contents of this exam in any way until the final marks have been released.

Name:_______________ Signature:_______________

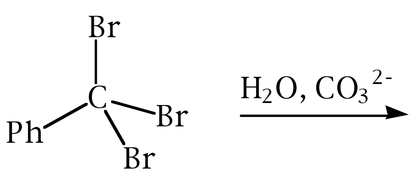
Question One (4 marks)

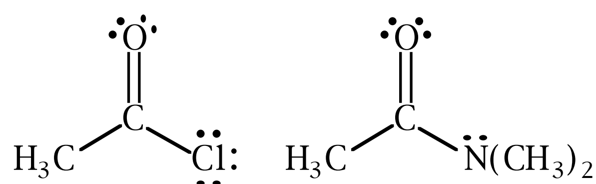
i) Benzylic geminal dibromides are easily prepared and can be hydrolyzed to aldehydes under S_N1 conditions. Propose a mechanism for the hydrolysis.



ii) Trihalides also react under these conditions. What is the product? (No mechanism required.)

Question Two (3 marks)





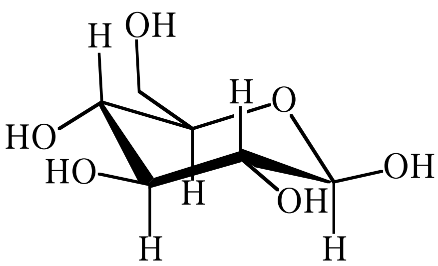
i) One of the carboxylic acid derivatives shown to the right can be prepared from the other. Give the mechanism of this reaction using the appropriate nucleophile.

ii) Which of these two molecules is more reactive? Explain.

iii) Aldehydes and ketones do not undergo acyl substitution reactions. Why not?

Question Three (3 marks)

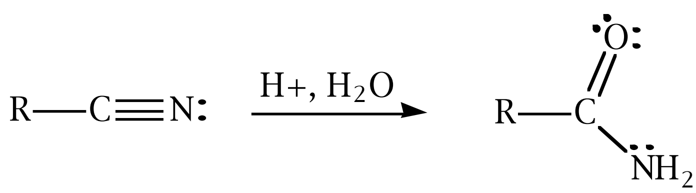
When crystals of the optically pure sugar molecule below are freshly dissolved in water, the resulting solution rotates plane polarized light by 18.7°. Over time, this rotation increases to a value of 56.8°. Explain what is happening and include the relevant structures.



β-D-glucopyranose

Question Four (4 marks)

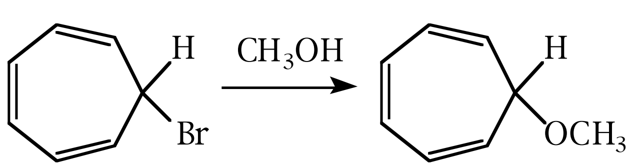
Propose a mechanism for the following transformation.



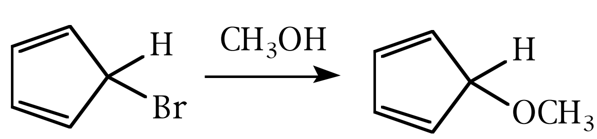
Question Five (6 marks)

Of the following solvolysis reactions (S_N1, you will recall), Reaction 1 occurs much faster than Reaction 2. Making reference to the mechanism and intermediates involved in both cases, rationalize the difference in the

Reaction 1



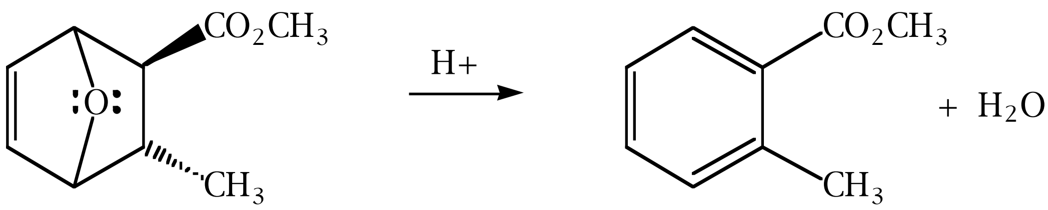
Reaction 2



rate of these reactions.

Question Six (3 marks)

i) Propose a mechanism for the following acid-catalyzed reaction.



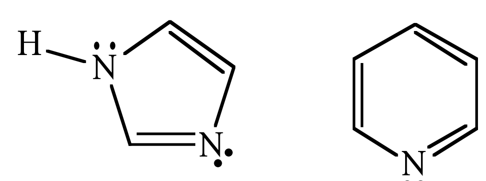
ii) What factor(s) drive this reaction to the product side?

iii) If the reactant of the above reaction is heated to a sufficiently high temperature, it undergoes a retro (i.e. reverse) Diels-Alder reaction. Give the structure of the products.

iv) Why does high temperature bring about retro Diels-Alder reaction?

Question Seven (4 marks)

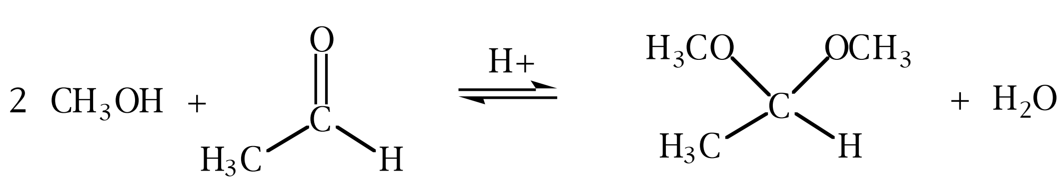
The molecules to the right are imidazole (the business end of the amino acid histidine) and pyridine. One of them is 100 times more basic than the other. Which one, and why?



Would imidazole be expected to display aromatic character? Why or why not?

Question Eight (9 marks)

The following reaction shows the equilibrium between an aldehyde, methanol and an acetal.



i) This equilibrium is reactant favoured. Why?

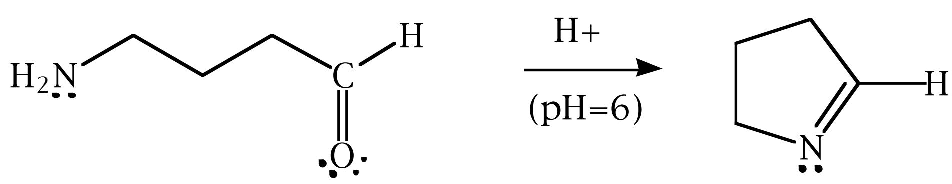
ii) Why is acid (H+) added to this reaction and how does it affect the equilibrium position?

iii) Give two ways in which this reaction can be driven to the product side. Be specific as to how this accomplished.

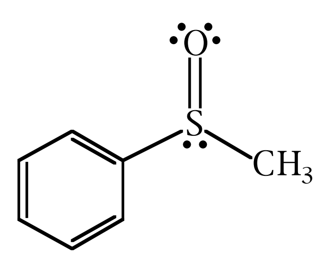
iv) Give an example of how an acetal can be used as a protecting group.

Question Nine (5 marks)

Give a mechanism for the following reaction.



Question Ten (6 marks)



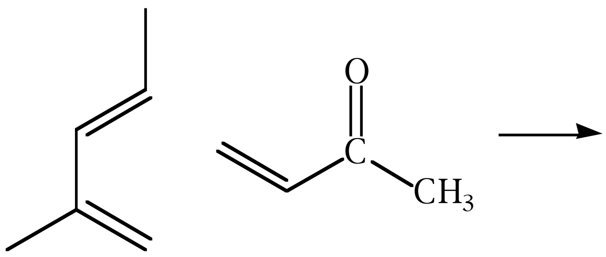
The benzene ring of the molecule on the right has a sulfoxide substituent. The following questions deal with the directing properties that you might expect such a functional group to have.

i) Give the mechanism for electrophilic aromatic substitution of this compound (para, with the generic E+ electrophile) and make a case for this substituent as an ortho/para directing group. Draw all resonance structures that are relevant to your case.

ii) Make a case for this substituent as a meta-directing group.

Question Eleven (8 marks)

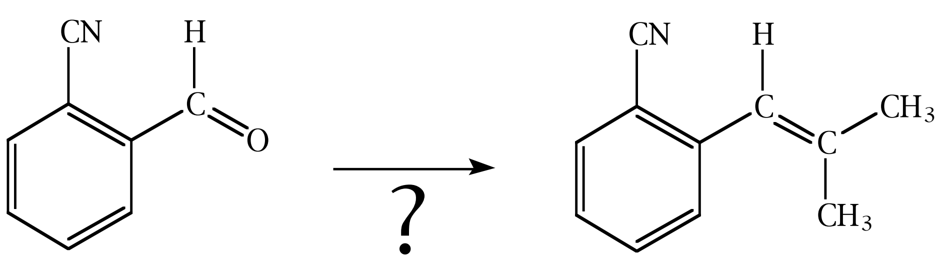
Give the structure of the major product of the following Diels-Alder reaction and indicate whether it is the endo or exo adduct.

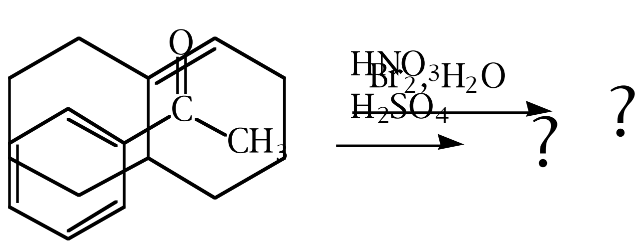


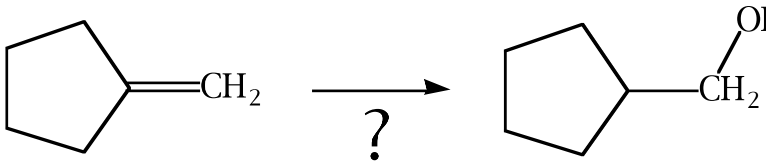
Show that with respect to the HOMO of the diene and LUMOof the dienophile, this reaction is a thermally allowed process.

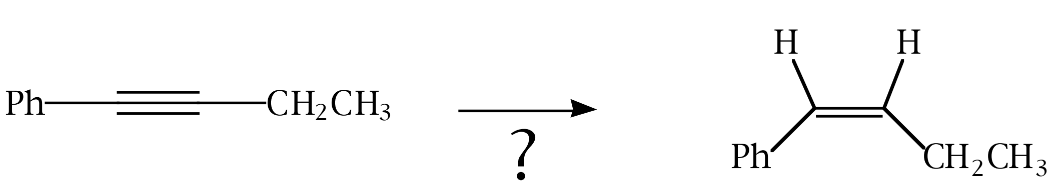
Question Twelve (3 marks)

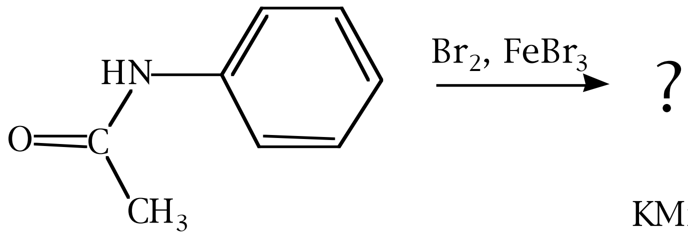
Fill in the missing component of the following reactions.

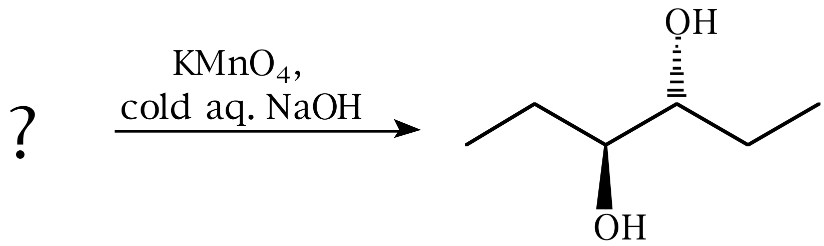


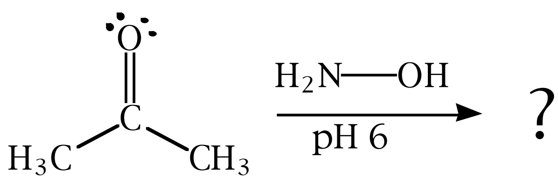


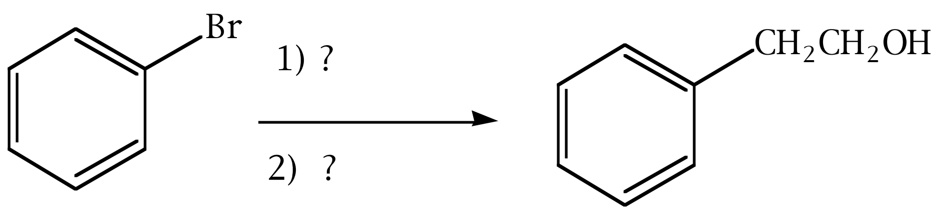





HN
O
C
CH3
Br2, FeBr3
?

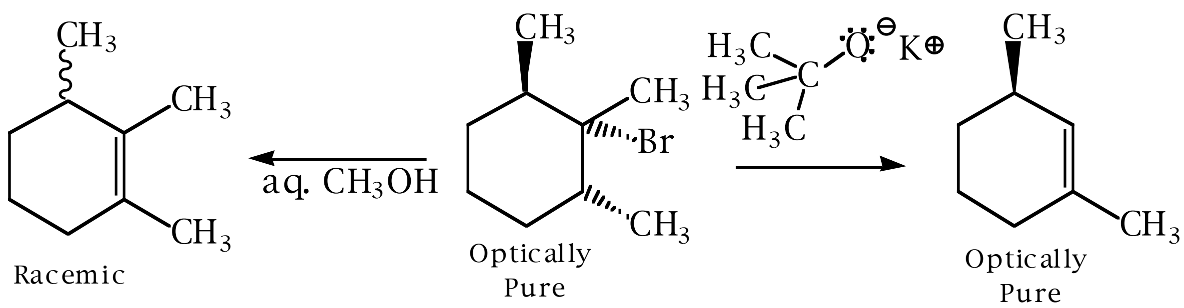

?
KMnO4,
cold aq. NaOH
OH
OH


O
C
H3C
CH3
H2N—OH
pH 6
?


Br
1) ?
2) ?
CH2CH2OH

Question Thirteen (5 marks)

Reaction of the optically pure material (of given absolute configuration, middle below) with potassium t-butoxide gives only the optically pure product on the right. When reacted in aqueous methanol, all of the corresponding elimination product (obtained with SN1 product) is racemic. Explain the reason behind the differing stereochemical outcomes.



Question Fourteen: Syntheses
DO FOUR OF THE FOLLOWING SEVEN.
INDICATE CLEARLY WHICH FOUR YOU WISH TO BE MARKED.

Answer these questions in the booklets provided. Provide a synthesis of four of the following seven molecules. You may use any stable organic molecule containing four carbons or less, benzene and cyclohexanone -- note that if you use a Grignard or alkyllithium you must show how it is prepared. If you attempt more than four, be sure to clearly indicate which you want marked. Be as complete with reaction conditions as possible. You may use common acronyms for reagents rather than formulae.

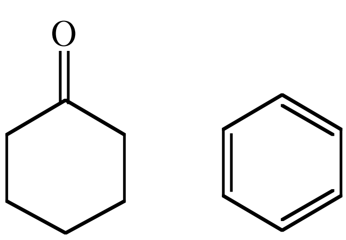


Table 6.3
Acidities of molecules and ions commonly encountered in organic chemistry.[a]

Acid	Conjugate base	pK_a
$HClO_4$	ClO_4^-	−10
HI	I^-	−10
$R{-}C({=}\overset{+}{O}H){-}H$	$R{-}C({=}O){-}H$	−10
H_2SO_4	HSO_4^-	−10
HBr	Br^-	−9
HCl	Cl^-	−7
$R{-}C({=}\overset{+}{O}H){-}R$	$R{-}C({=}O){-}R$	−7
$ArSO_3H$	$ArSO_3^-$	−6.5
$R{-}C({=}\overset{+}{O}H){-}OR'$	$R{-}C({=}O){-}OR'$	−6
$R{-}\overset{+}{O}(H){-}R'$	$R{-}O{-}R'$	−3.5
$R{-}\overset{+}{O}(H){-}H$	$R{-}O{-}H$	−2
H_3O^+	H_2O	−1.7
HNO_3	NO_3^-	−1.4
HSO_4^-	SO_4^{2-}	2
HF	F^-	3.1
$ArNH_3^+$	$ArNH_2$	4
RCOOH	$RCOO^-$	5
H_2CO_3	HCO_3^-	6.4
H_2S	HS^-	7
ArSH	ArS^-	7
$CH_3C({=}O)CH_2C({=}O)CH_3$	$CH_3C({=}O)\overset{-}{C}HC({=}O)CH_3$	9
HCN	CN^-	9.2
NH_4^+	NH_3	9.2
ArOH	ArO^-	10
$R{-}CH_2NO_2$	$R{-}\overset{-}{C}H{-}NO_2$	10
RNH_3^+	RNH_2	11
RSH	RS^-	11
$CH_3C({=}O)CH_2C({=}O)OR$	$CH_3C({=}O)\overset{-}{C}HC({=}O)OR$	11
CH_3OH	CH_3O^-	15.2
H_2O	HO^-	15.7
RCH_2OH	RCH_2O^-	16
$R_2CH{-}OH$	$R_2CH{-}O^-$	17
$R_3C{-}OH$	$R_3C{-}O^-$	17
$R{-}C({=}O){-}NH_2$	$R{-}C({=}O){-}NH^-$	17
$R{-}C({=}O){-}CH_3$	$R{-}C({=}O){-}CH_2^-$	20
$RO{-}C({=}O){-}CH_3$	$RO{-}C({=}O){-}CH_2^-$	24
$R{-}CH_2CN$	$R{-}\overset{-}{C}H{-}CN$	25
$H{-}C{\equiv}C{-}H$	$H{-}C{\equiv}C^-$	25
H_2	H^-	35
NH_3	NH_2^-	38
$Ph{-}CH_3$	$Ph{-}CH_2^-$	40
$C_6H_5{-}H$ (benzene)	$C_6H_5^-$	43
$CH_2{=}CH_2$	$CH_2{=}CH^-$	44
CH_4	CH_3^-	48

1A	2A											3A	4A	5A	6A	7A	8A
1.008 **H** 1 2.1																	4.003 **He** 2
6.939 **Li** 3 1.0	9.012 **Be** 4 1.5											10.811 **B** 5 2.0	12.011 **C** 6 2.5	14.007 **N** 7 3.0	15.999 **O** 8 3.5	18.998 **F** 9 4.0	20.183 **Ne** 10
22.990 **Na** 11 1.0	24.312 **Mg** 12 1.2											26.982 **Al** 13 1.5	28.086 **Si** 14 1.8	30.974 **P** 15 2.1	32.064 **S** 16 2.5	35.453 **Cl** 17 3.0	39.948 **Ar** 18
39.102 **K** 19 0.9	40.08 **Ca** 20	44.956 **Sc** 21	47.90 **Ti** 22	50.942 **V** 23	51.996 **Cr** 24	54.938 **Mn** 25	55.847 **Fe** 26	58.93 **Co** 27	58.71 **Ni** 28	63.546 **Cu** 29	65.37 **Zn** 30	69.72 **Ga** 31	72.59 **Ge** 32	74.922 **As** 33	78.96 **Se** 34	79.904 **Br** 35 2.8	83.80 **Kr** 36
85.47 **Rb** 37	87.62 **Sr** 38	88.905 **Y** 39	91.22 **Zr** 40	92.906 **Nb** 41	95.94 **Mo** 42	(99) **Tc** 43	101.07 **Ru** 44	102.9 **Rh** 45	106.4 **Pd** 46	107.86 **Ag** 47	112.40 **Cd** 48	114.82 **In** 49	118.69 **Sn** 50	121.75 **Sb** 51	127.60 **Te** 52	126.90 **I** 53 2.5	131.30 **Xe** 54
132.90 **Cs** 55	137.34 **Ba** 56	138.91 **La** 57	178.49 **Hf** 72	180.94 **Ta** 73	183.85 **W** 74	186.2 **Re** 75	190.2 **Os** 76	192.2 **Ir** 77	195.09 **Pt** 78	196.96 **Au** 79	200.59 **Hg** 80	204.37 **Tl** 81	207.19 **Pb** 82	208.98 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86