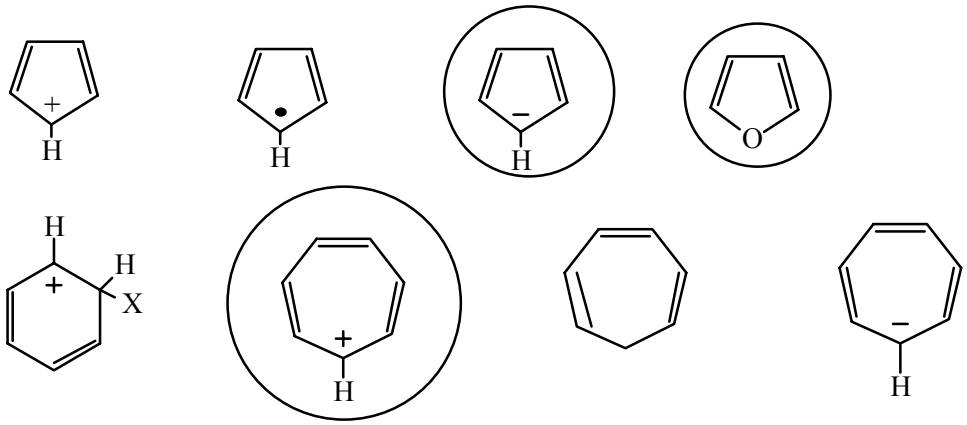
1. (5 marks) Aromaticity

Circle those of the following structures which you would expect to show aromaticity:



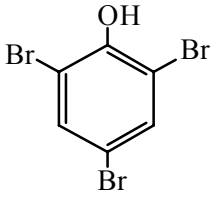
2. (12 marks) Structure and Nomenclature

(2 marks each)

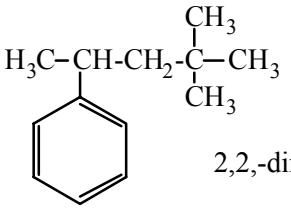
Draw structures for which names are given and name the given structures by any accepted system

a) CH_2CH_2OH (with C_6H_5 below) 1-(2-hydroxyethyl)benzene or 2-phenylethanol

b) 2,4,6-tribromophenol

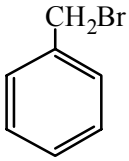


c)



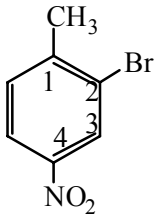
2,2,-dimethyl-4-phenylpentane

d) benzyl bromide



e) $CH_2OHCHOHCH_2OH$ 1,2,3-propantriol or glycerol

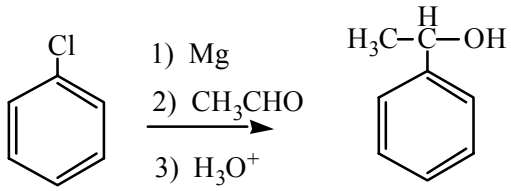
f)

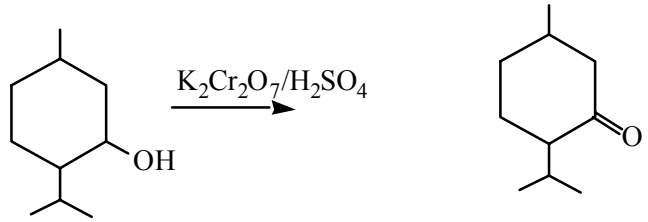


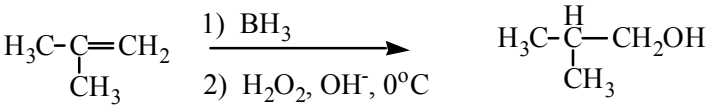
2-bromo-4-nitrotoluene
or 2-bromo-1-methyl-4-nitrobenzene

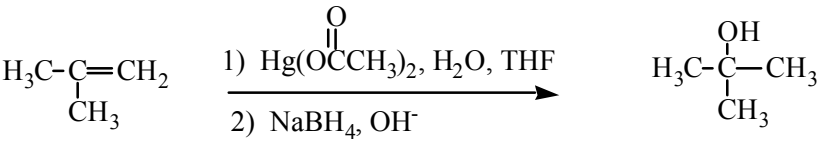
3. (34 marks) Reactions

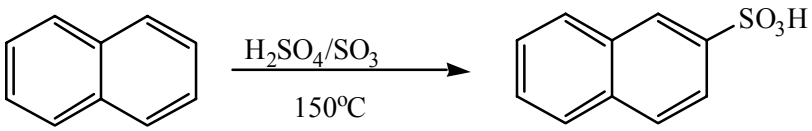
A. (3 marks each) Draw the structure of the major organic product(s) of the following reactions

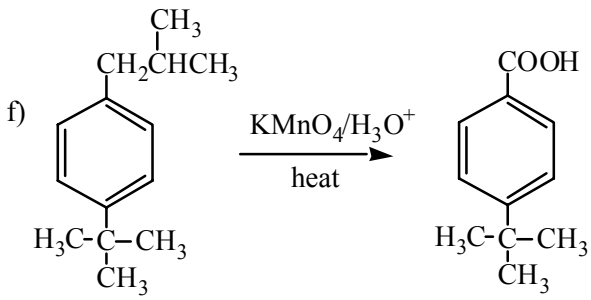
a) 

b) 

c) 

d) 

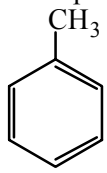
e) 

f) 

no proton on the carbon attached to the benzene ring (the benzylic carbon) in this group, so oxidation cannot occur

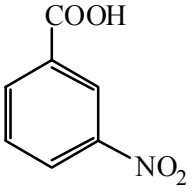
B. (4 marks each) List the reagents which will accomplish the following transformations. In all cases, more than one step is required

a)



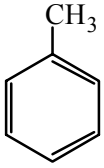
1) $KMnO_4$, H_2SO_4

2) HNO_3, H_2SO_4



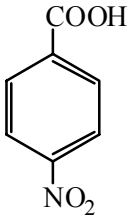
oxidize the methyl group first to give the carboxylic acid which is meta directing, then nitrate

b)



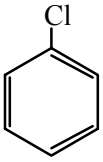
1) HNO_3, H_2SO_4

2) $KMnO_4$, H_2SO_4



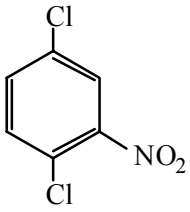
nitrate first so that the nitro group goes into the para position since methyl is o, p directing, then oxidize the methyl to the carboxylic acid

c)



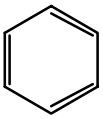
1) $FeCl_3$, Cl_2

2) HNO_3, H_2SO_4



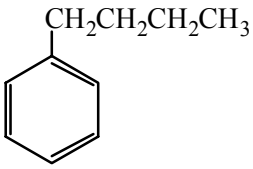
chlorinate first so that the chlorine goes into the para position, then nitrate; note that all four remaining positions are identical, so it does not matter where the NO_2 substitutes,

d)



$CH_3CH_2CH_2COCl$, $AlCl_3$

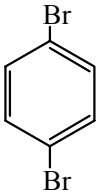
NH_2NH_2 or Sn,/HCl



must do Friedel Crafts acylation and reduce the resulting ketone since Friedel Crafts alkylation with $CH_3CH_2CH_2CH_2Cl$ and $AlCl_3$ will yield a primary carbocation which will rearrange

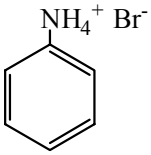
4. (5 marks) Reactivity

a) (2 marks) Rank the following compounds according to their reactivity towards electrophilic aromatic substitution by numbering them from 1 to 4 where 1 is the most reactive and 4 is the least reactive.



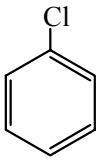
3

more deactivating than chlorobenzene since there are two electron-withdrawing groups in the ring instead of 1.

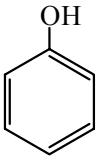


4

strongly deactivating to electrophilic substitution due to the positive charge on the nitrogen



2

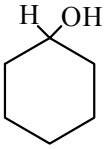


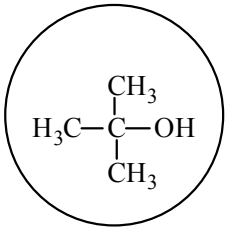
1

activating towards electrophilic substitution

b) (3 marks) Circle the one of the following alcohols which will most readily undergo acid-catalyzed dehydration to the corresponding alkene and provide a brief explanation to justify your answer.

$CH_3CH_2CH_2CH_2OH$

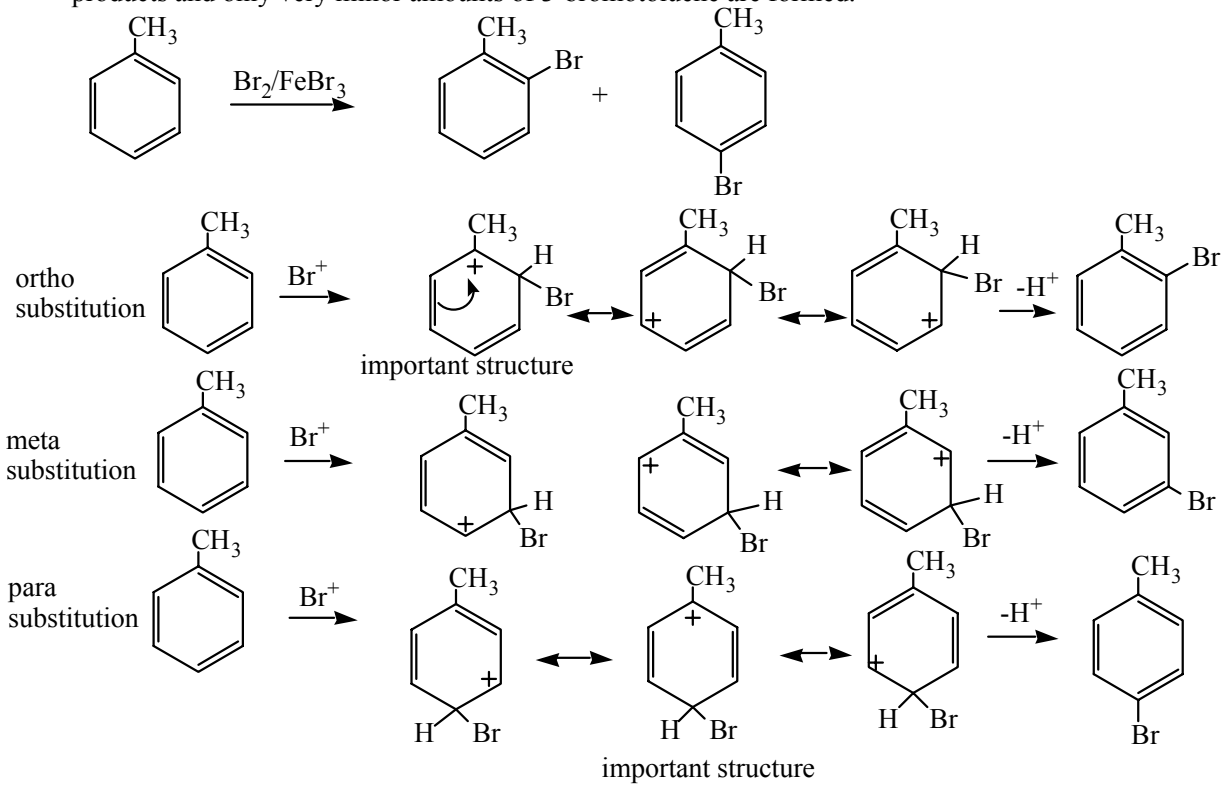




Protonation by acid yields a tertiary carbocation which can readily lose a proton to yield an alkene.

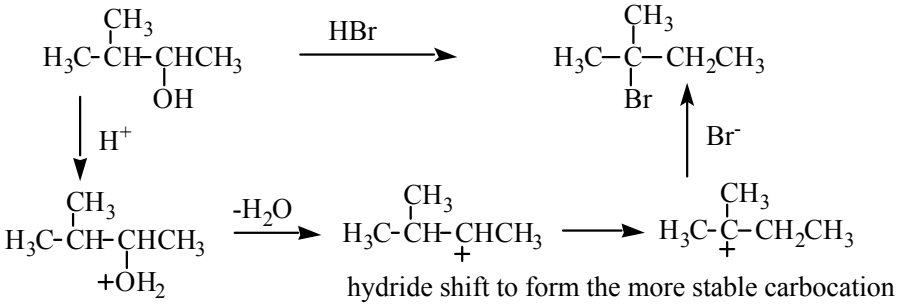
5. (16 marks) Reaction Mechanisms

a) (8 marks) The bromination of toluene with bromine and ferric bromide results in the formation of two major products, 2-bromotoluene and 4-bromotoluene. Indicate the intermediates in this reaction and show, using resonance structures, why these are the major products and only very minor amounts of 3-bromotoluene are formed.



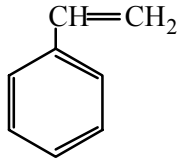
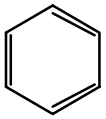
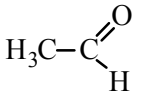
There are three resonance structures for the intermediate formed in the substitution of Br^+ into the aromatic ring of toluene for ortho, meta, or para substitution. However, in meta substitution, it is not possible to draw a resonance structure in which the positive charge is on the carbon carrying the methyl group. This is an important contributor to the resonance hybrid since the methyl group is electron donating.Therefore, the intermediates formed in the ortho or para substitution are of lower energy than than for meta substition and so meta substitution is unfavored.

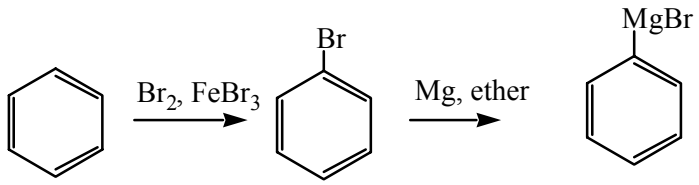
b) (8 marks) Treating 3-methyl-2-butanol with HBr yields 2-bromo-2-methylbutane as the major product. Indicate how this product arises by showing the mechanism of the reaction.

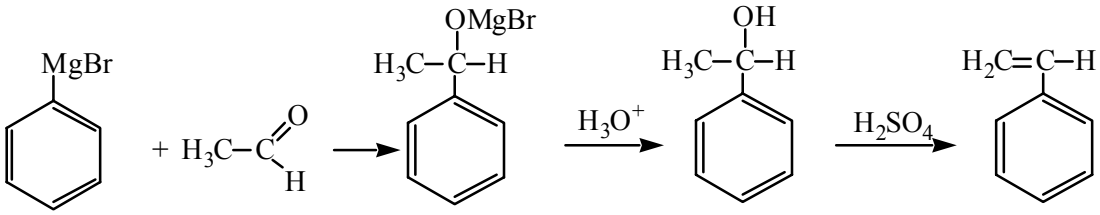


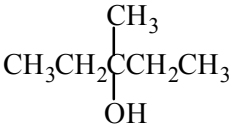
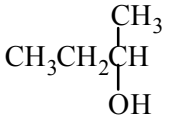
6. (16 pts) Synthesis

Write reactions by which you could synthesize the following compounds from the indicated starting materials and any inorganic reagents required.

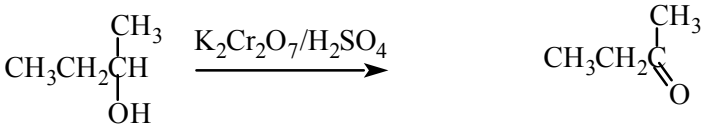
a) (8 marks)  from  and 

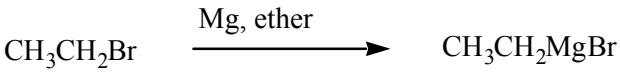


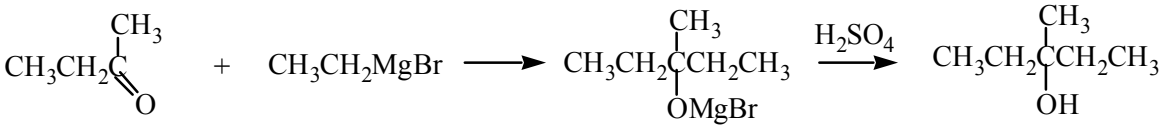


b) (8 marks)  from  and CH_3CH_2Br

(hint: one of the inorganic reagents required is $K_2Cr_2O_7/H_2SO_4$

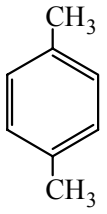


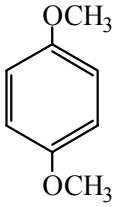


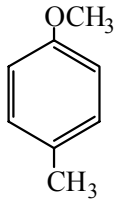


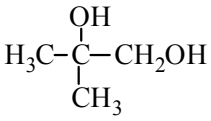
7. (12 marks) NMR Spectroscopy

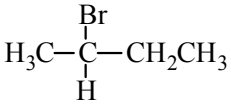
The NMR spectra shown are of two of the following compounds:

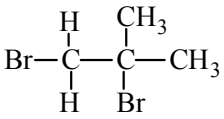










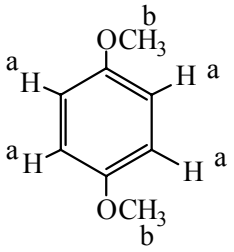


a) (6 marks) Draw the appropriate structure on each spectrum

b) (6 marks) Assign the signals in the spectrum to the protons they represent

(A table of chemical shifts of hydrogens attached to various functional groups is provided)

First NMR is of

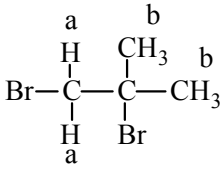


a protons absorb at about 6.8
b protons absorb at about 3.7

Signals are both singlets
Notice that the four aromatic protons are equivalent, therefore the signals are not split

The b protons are too far downfield to be of methyl groups on the aromatic ring

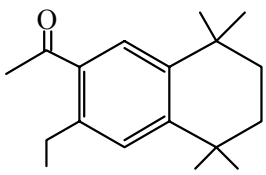
Second NMR is of



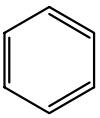
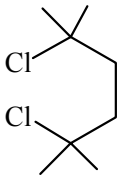
a protons absorb at about 3.9
b protons absorb at about 1.8

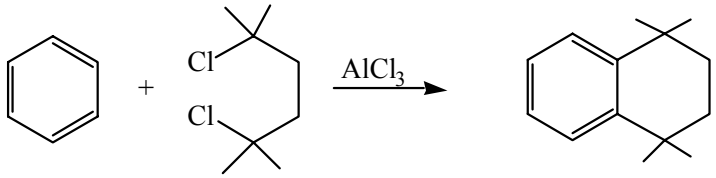
Both signals are singlets

8. (12 marks) Versalide has a strong musk odor and is commercially synthesised for use in perfumes. Indicate the reactions by which it could be synthesized from the reagents shown and any other inorganic compounds required.

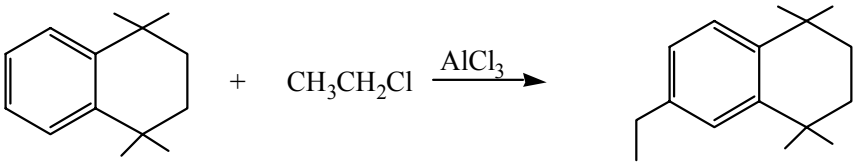


Versalide

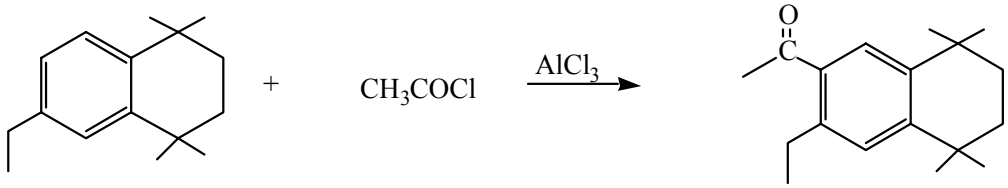
Synthesize from CH_3COCl, CH_3CH_2Cl,  and 



Friedel Crafts alkylation is possible with this bulky group. There are only two products which can be formed, the other would have a second tetramethylcyclohexane fused to the other side of the bezene ring. These would be very easily separated. Putting the bulky group in first ensures that the substituents in the next two reactions can be substituted in the desired positions.



This Friedel Crafts acylation will give only one product. The positions on the benzene ring ortho to a ring junction with the cyclohexane ring are too sterically hindered for the ethyl group to enter.



This step has to be done last since the carbonyl group deactivates the ring and Friedel Crafts reactions will not proceed on deactivated rings. The acetyl group enters ortho to the ethyl group since the positions ortho to the ring junction with the cyclohexane ring are more sterically hindered.