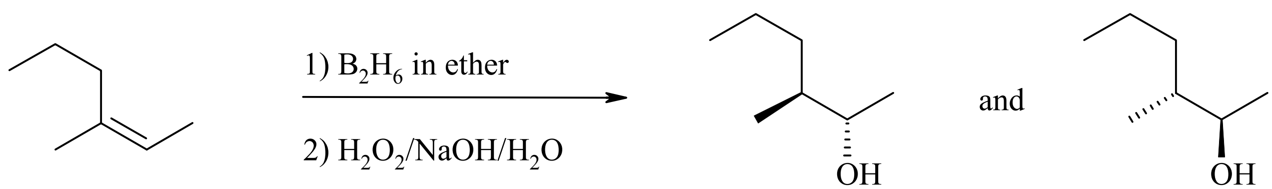
Chem 2P20 Assignment 4
Due Monday Dec. 2, 5 pm

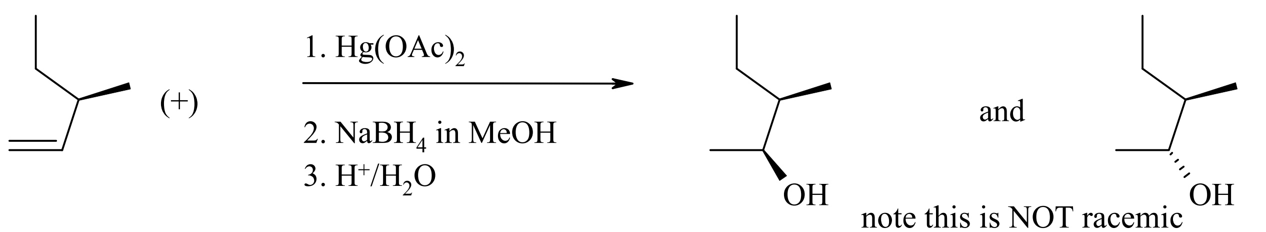
Name: ____________________
ID Number: ____________________

1. Draw the *MAJOR* organic product for each reaction, paying attention to stereoisomerism where appropriate. Pick the name that best applies to each reaction from the following list, and write that name underneath the product (12 marks)

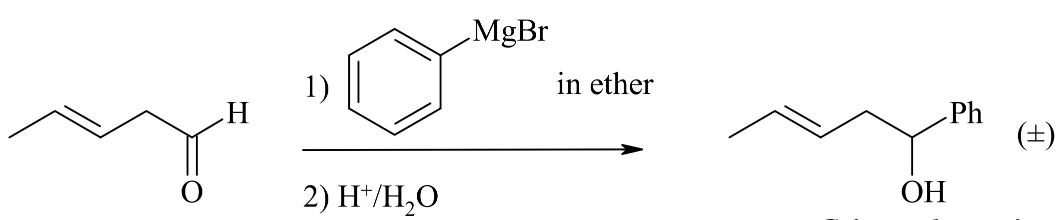
Grignard reaction	hydride reduction
halogenation	esterification
chromic acid oxidation	epoxidation
syn-dihydroxylation	ozonolysis
hydroboration/oxidation	oxymercuration/demercuration



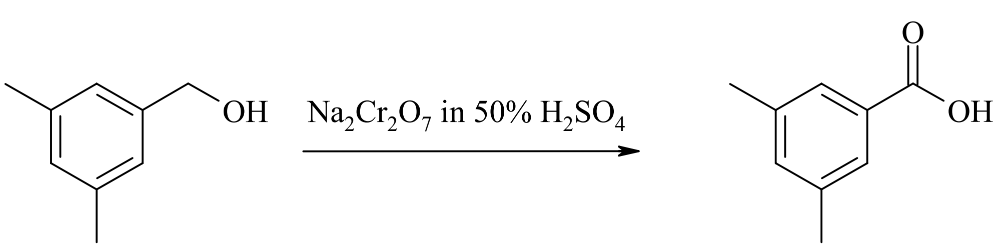
Hydroboration/Oxidation



Oxymercuration/Demercuration

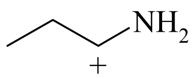


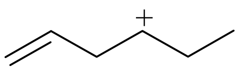
Grignard reaction

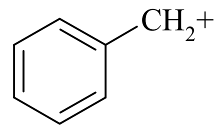


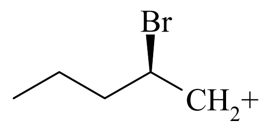
Chromic Acid Oxidation

2. a) Rank the following carbocations in order of stability (using "1", "2", "3", "4", with "1" the most stable, and "4" the least stable. (4 marks)



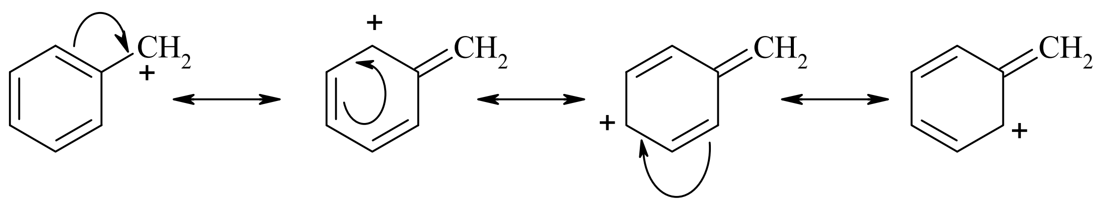




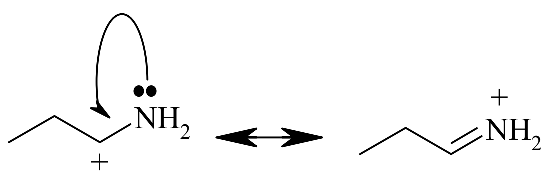


______2_____ ______3_____ ______1_______ ________4______

#1 is the BENZYL CATION and is stabilised due to resonance (4 resonance structures:



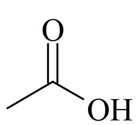
#2 is an alpha-amino cation that has two resonance structures:

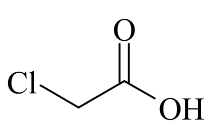


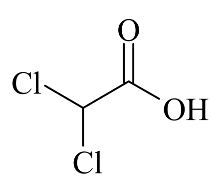
#3 is 2° carbocation that is NOT stabilised by resonance

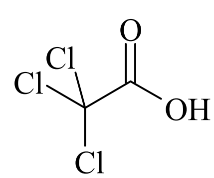
#4 is a 1° carbocation that is destabilised by the nearby proximity of an electron-withdrawing Br atom

2. b) Rationalise the following trend in acidity: (1 marks)









pK_A 4.76 pK_A 2.86 pK_A 1.48 pK_A 0.70

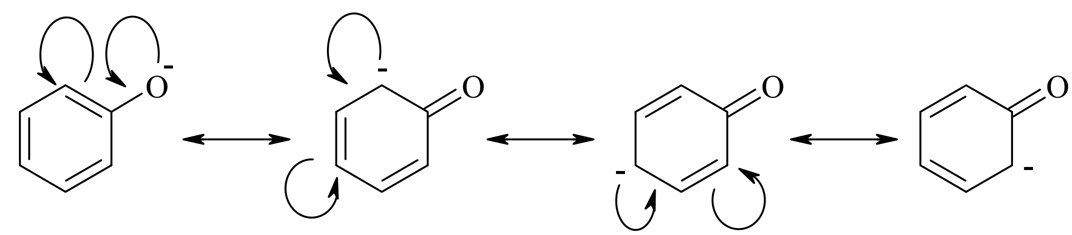
Answer: Each chlorine atom is highly electronegative and withdraws electron density from the carboxyl group. This helps stabilise the CARBOXYLATE ANION that results from deprotonation; thus the more Cl atoms, the more stable the anion and the more acidic the acid.

2. c) Use resonance to explain why alcohols are much weaker acids (pK_A 16) than phenols (pK_A 10) (3 marks)

Alcohols ROH have one resonance structure upon deprotonation:

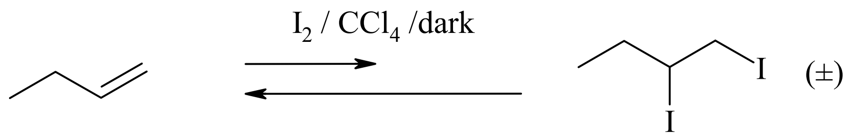
$$RO{-}H \longrightarrow RO^{-} \quad H^{+}$$

Phenols PhOH have at least FOUR resonance structures that stabilise the negative charge. With a more stable anion, the acidity (ease of removing the proton) inceases by a factor of $10^{(16\text{-}10)} = 10^{6} =$ 1 million!



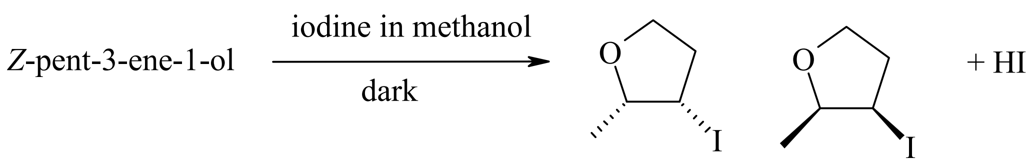
3. Electrophilic iodination, in theory, proceeds along the same lines as bromination or chlorination. However, in practise, most 1,2-diiodides are unstable to reverting back.

In chemical terms, it is an equilibrium that lies on the side of reactants, i.e.,

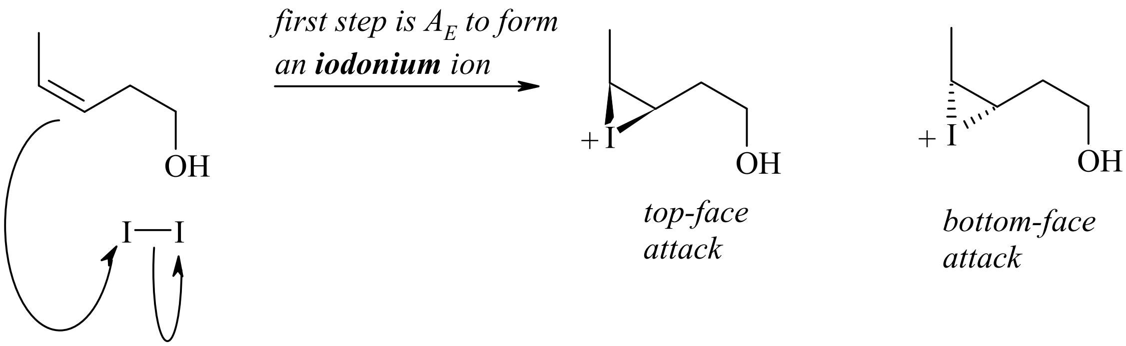


However, the intermediate iodonium ion can still be trapped by nucleophiles to give useful products in high yield ...

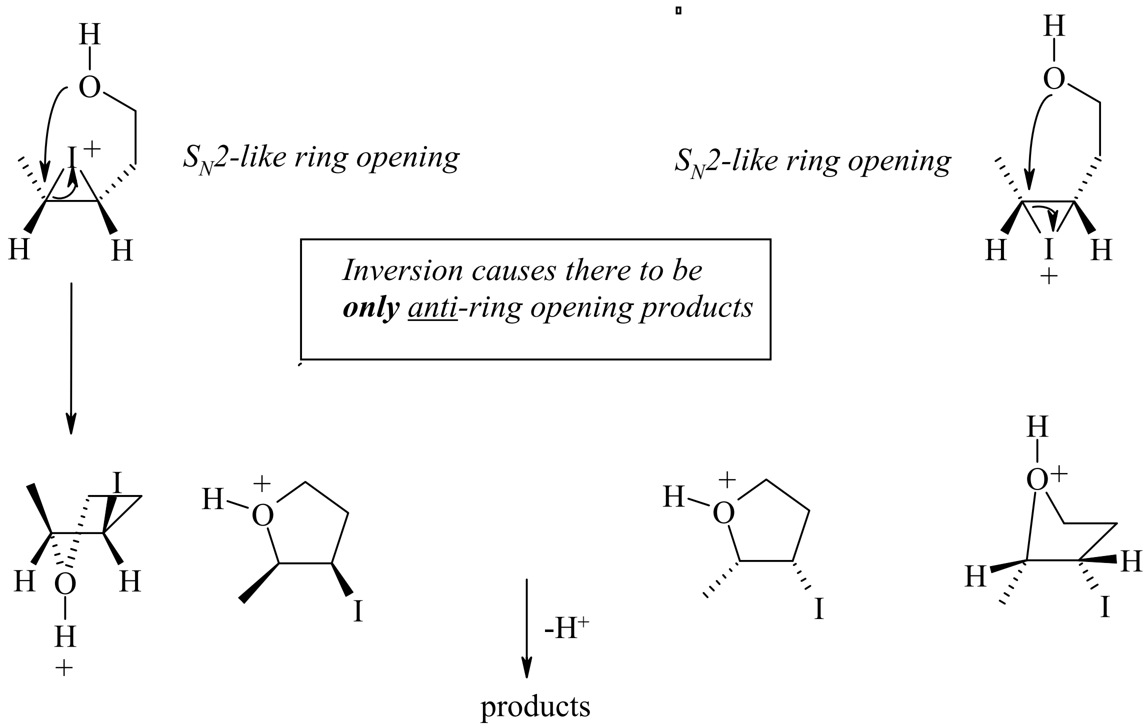
Provide a mechanism for the following reaction. Show all steps; and show all electron movement in all steps with curly arrows. Make sure your mechanism explains the *stereoselectivity* of the reaction. (10 marks)



these *cis*-isomers only



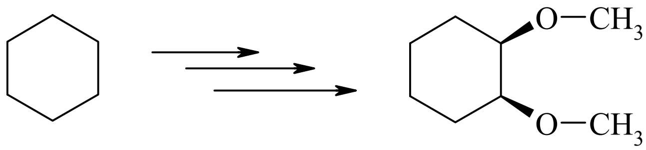
Second step is an INTRA-molecular capture of the iodonium ion by the internal nucleophilic OH-group:

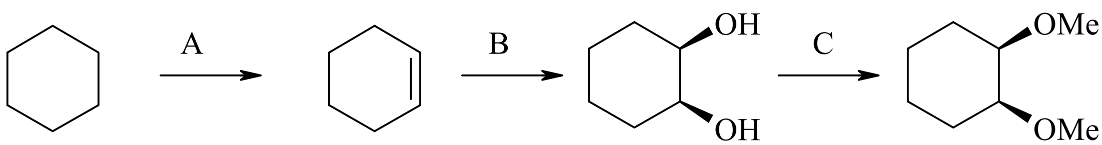


4. Show how to transform the starting material at the left into the product at the right *in high yield* using any other reagents. If multiple reactions are required, make sure to separate the steps. Be sure to list appropriate solvents and conditions such as heat.

(15 marks)

a)



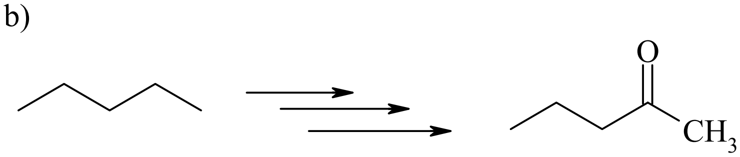


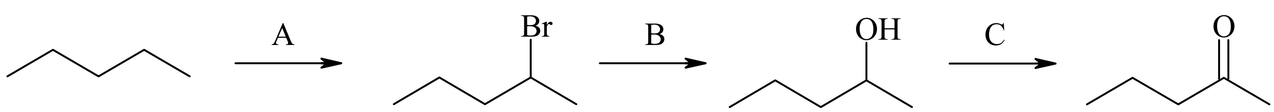
A = 1) Br_2/ Heat
2) LDA/THF

B = 1) OsO_4 / py
2) $NaHSO_3$ / water

C = 1) Na metal
2) 2 mols CH_3I in THF

b)



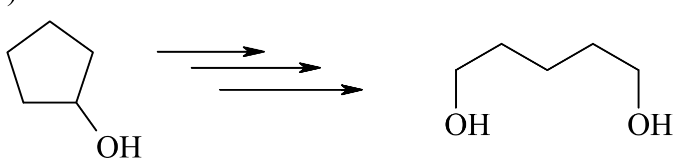


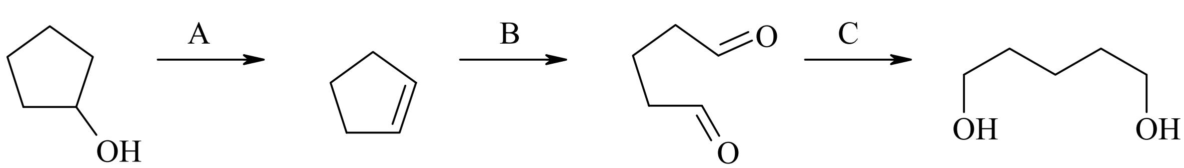
A = Br_2 / heat

B = dilute KOH in cold THF

C = H_2CrO_4 / 50% H_2SO_4

c)





A = 85% phosphoric acid / heat

B = 1) O_3 in CH_2Cl_2
2) Zn dust in acetic acid

C = 1) $NaBH_4$ in MeOH
2) H^+ / H_2O