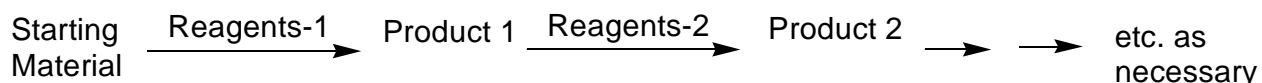


Chemistry 35

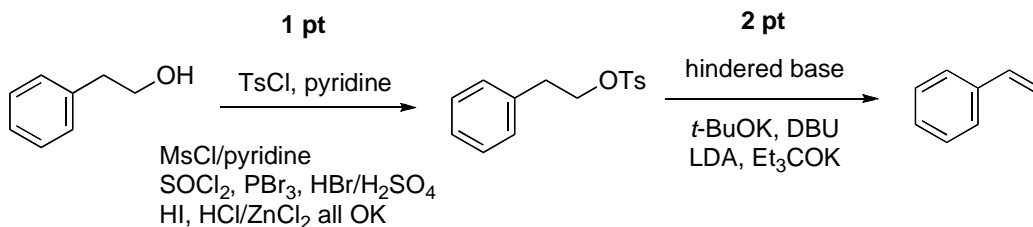
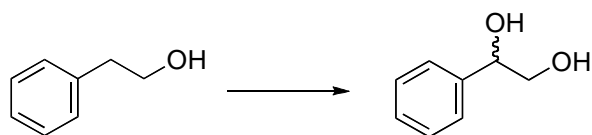
Exam 3 Answers – May 2, 2007

Problem 1. (24 points) Synthesis: Propose a series of reactions (reagents and conditions) that convert the Starting Material into the Product. **You do NOT need to draw mechanisms for each reaction.**

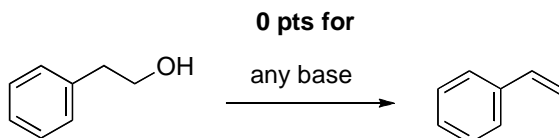
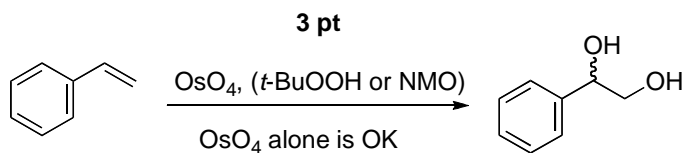
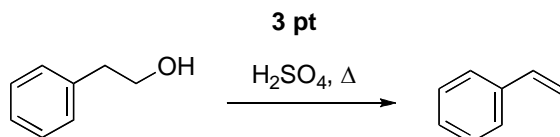
Structure your answer as follows:



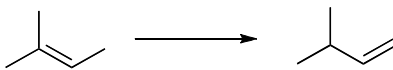
A) (6 points)



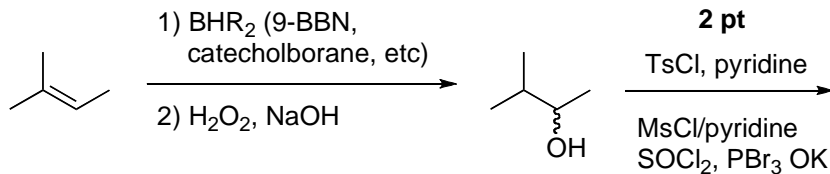
OR



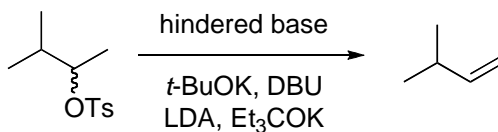
B) (6 points)



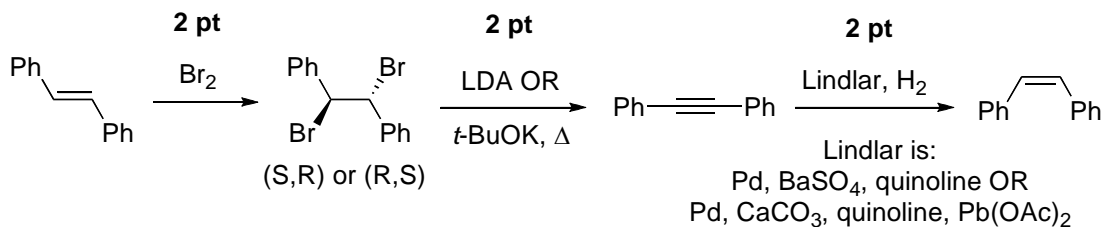
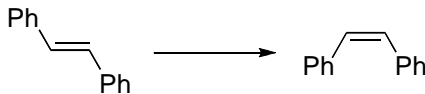
2 pt



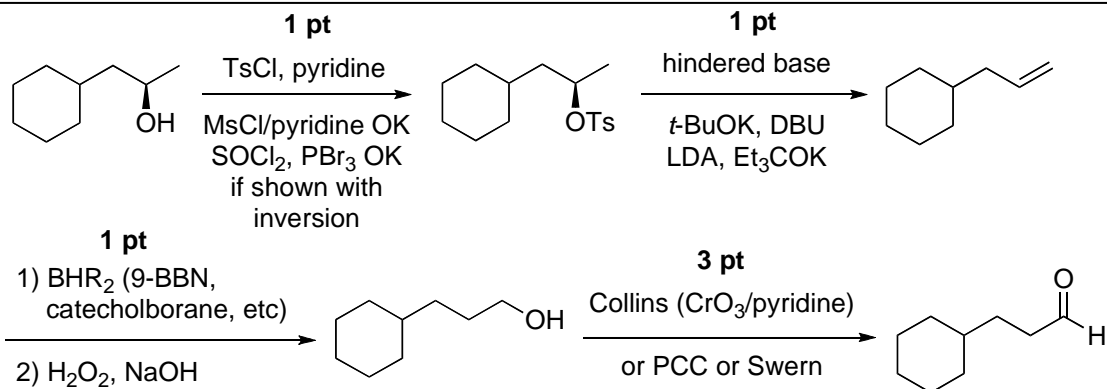
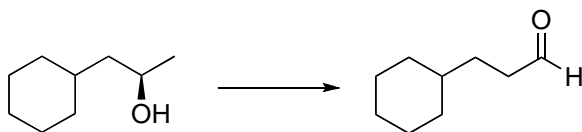
2 pt



C) (6 points)



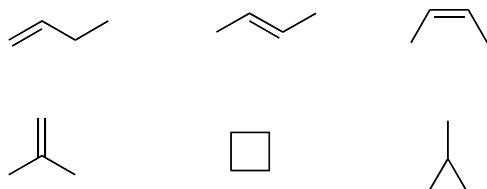
D) (6 points)



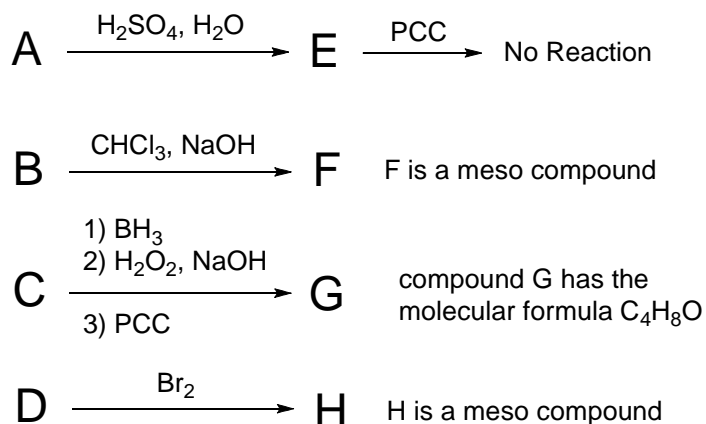
Problem 2. (18 points)

A) (6 points) Draw out all of the isomers, including stereoisomers, that have the formula C_4H_8 . Include only structures with complete octets and zero formal charges. There may be more or fewer boxes than isomers.

1 pt each

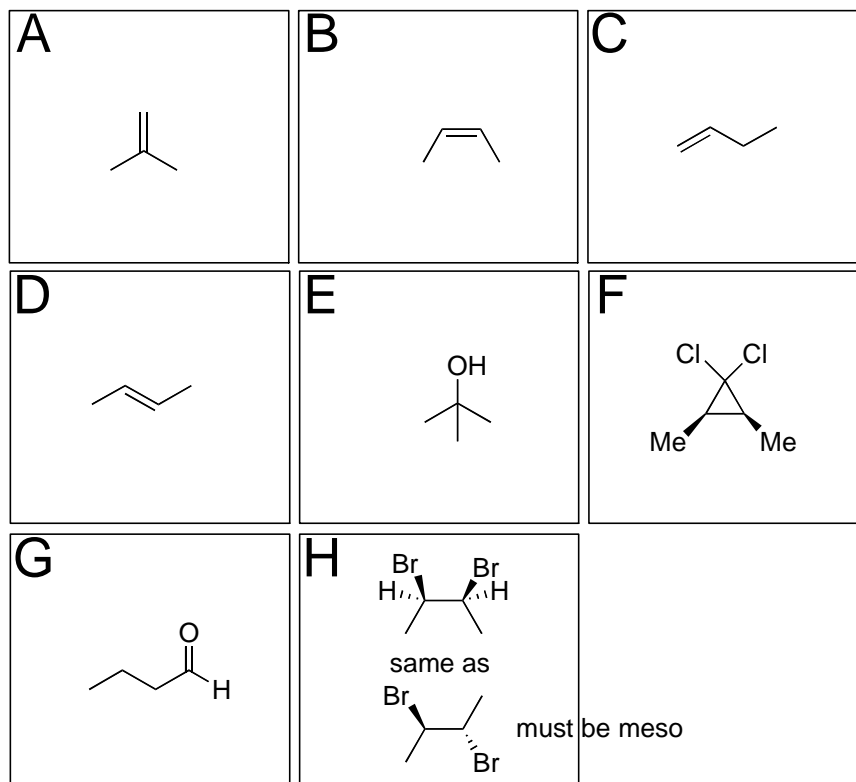


B) (12 points) Compounds A-D are four of the possible isomers or stereoisomers that have the formula C_4H_8 . Compounds E-H are the major products from the reactions shown below.



Based upon the information that you can infer from these reactions, and the other information that is provided, draw the correct structures for compounds A-H in the boxes provided below. Be sure to show stereochemistry where necessary.

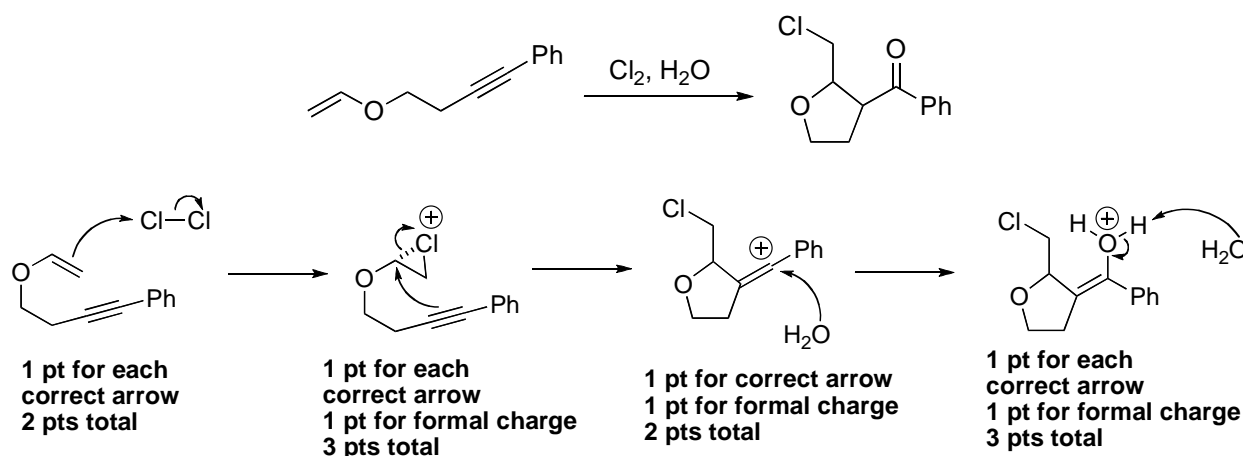
1 pt each for A-D
2 pt each for E-H – No partial credit



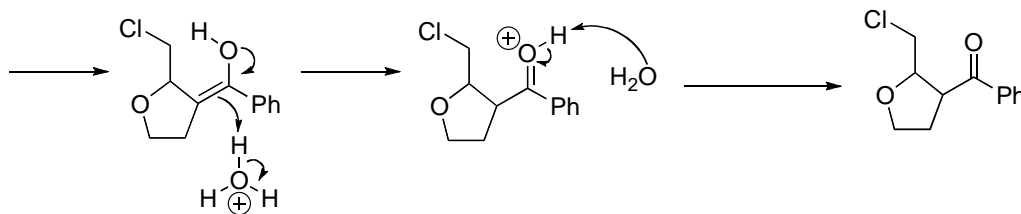
Problem 3. (12 points) Provide a detailed, step-by-step mechanism for the following reaction. In this question, we provide the reactants, products and reaction conditions. **YOUR JOB IS TO:**

- 1) Show the individual chemical steps and all intermediates formed in the process of converting the reactant to the product.
- 2) Use curved arrows to show all changes in bonding and lone pair electrons.
- 3) Show all formal charges and all contributing resonance structures.

Remember, the sequence of steps you propose must convert the reactant into the product using only the starting material and reagents provided. You may not use additional acids or bases, since they are not present in the reaction mixture.



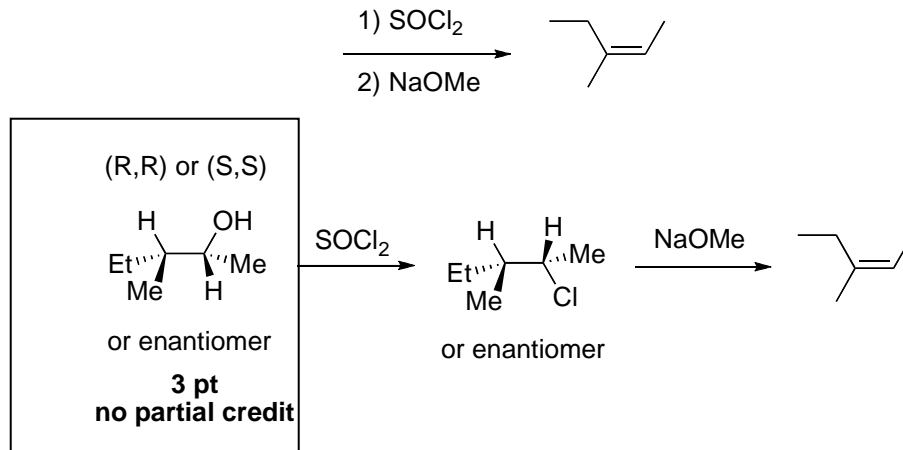
2 additional pts if all 4 structures above are drawn completely correctly



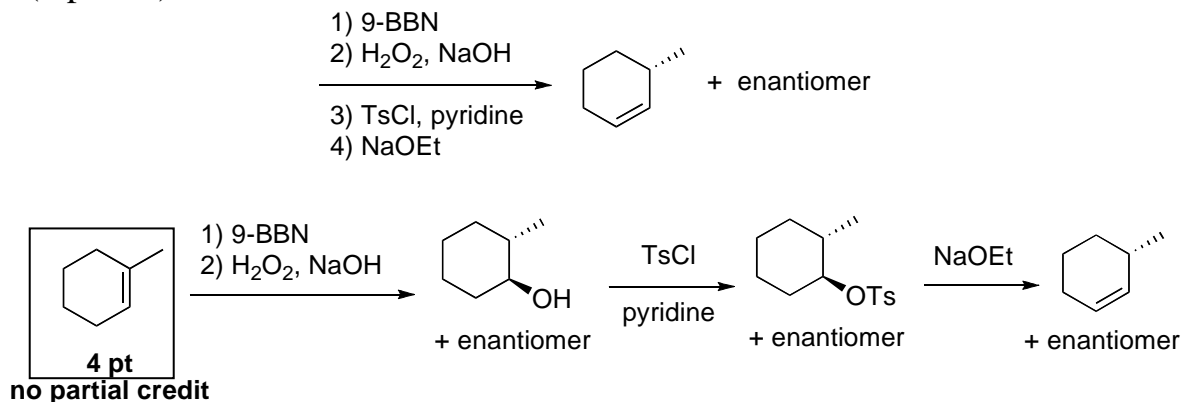
No points are associated with these three structures since identical steps are assigned points in Problem 6.

Problem 4. (10 points) Provide the structure of the starting material for each of the following reaction sequences. Your starting material must yield the indicated product as the **major product** from the transformations.

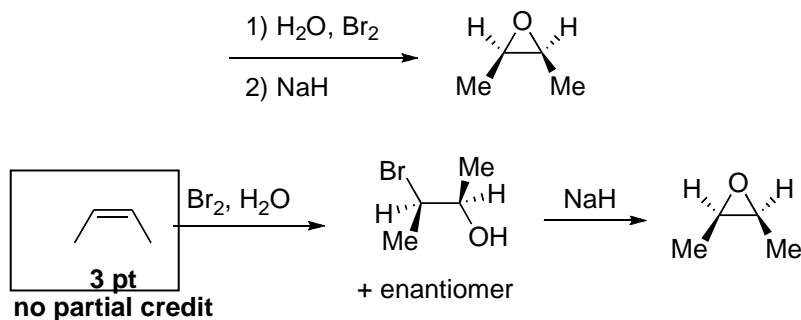
A) (3 points)



B) (4 points)

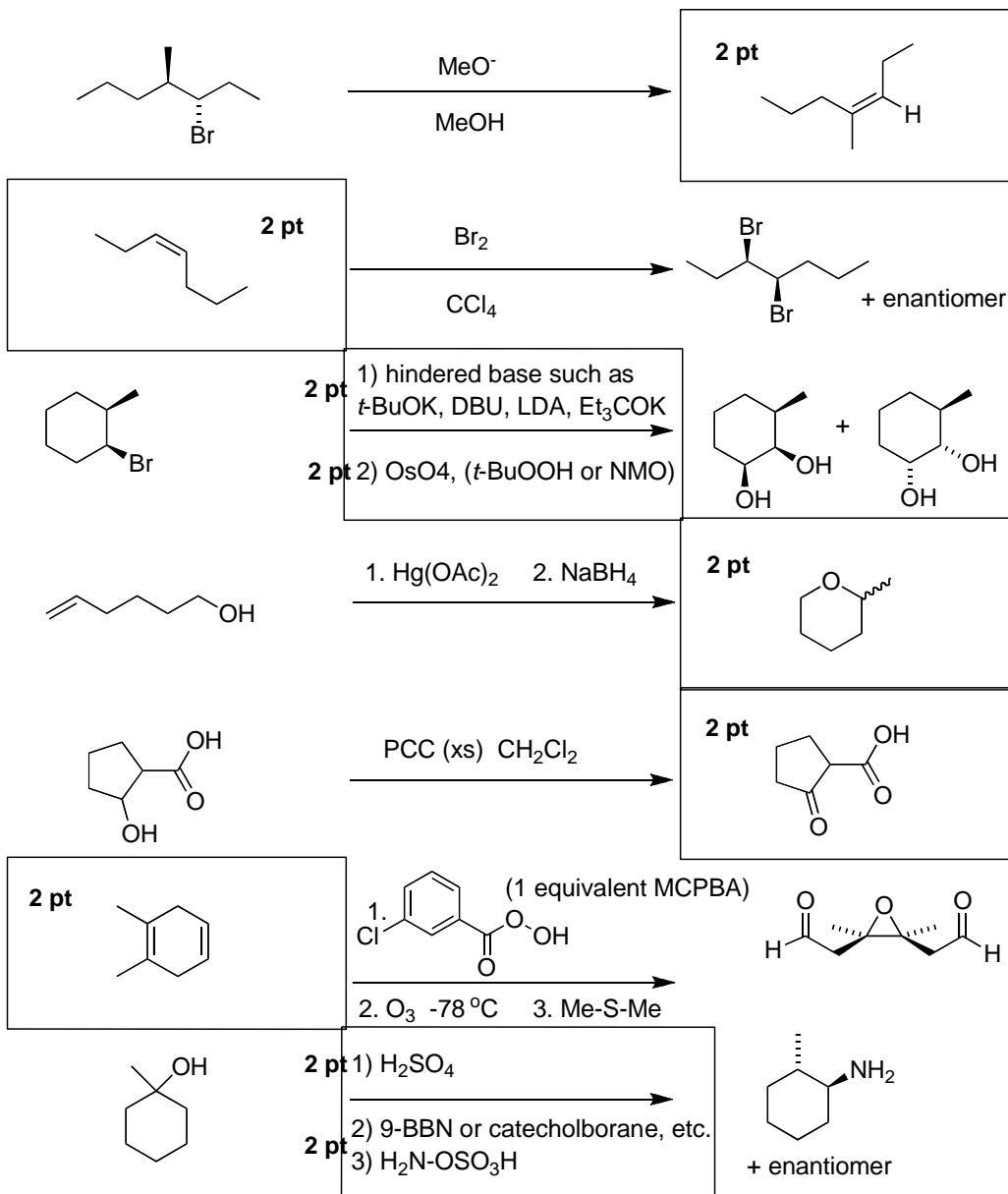


C) (3 points)

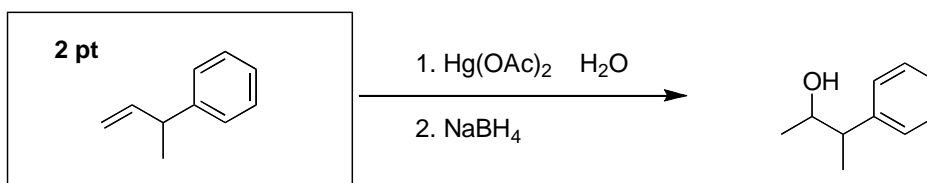


Problem 5. (20 points) Provide the missing starting material, reagent(s) or major product(s).

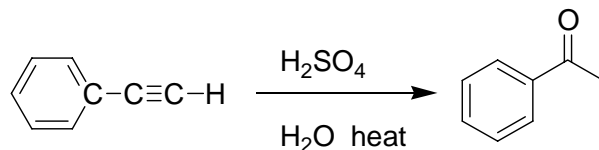
No Partial Credit



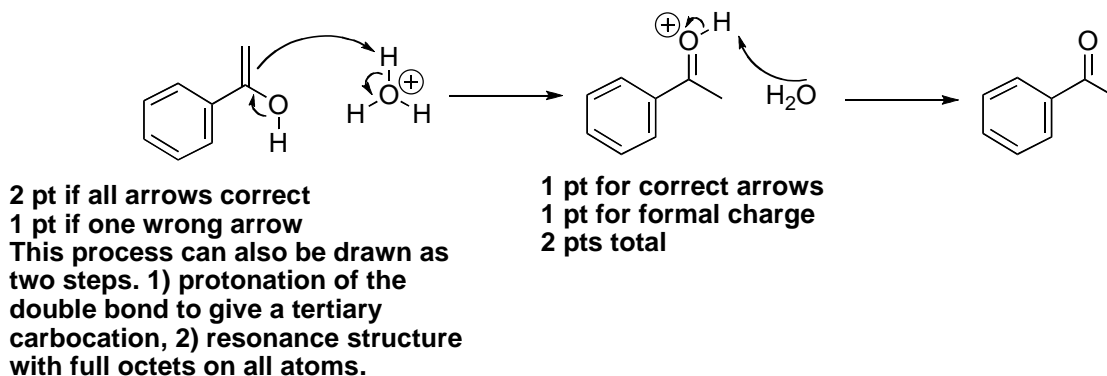
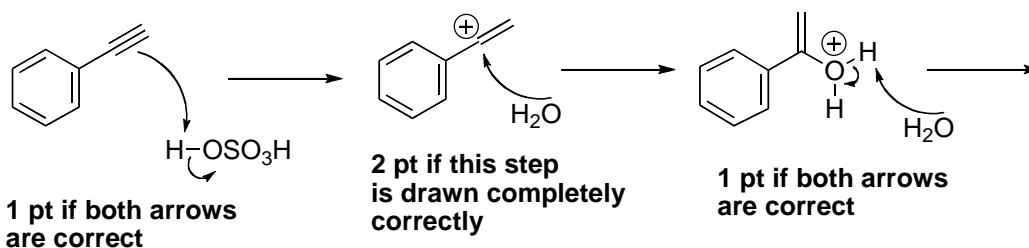
A variety of other reagents can be used in the first step of this synthesis including TsOH, TsCl/pyridine followed by Δ , SOCl_2 followed by Δ , or PBr_3 followed by Δ .



Problem 6. (16 points) A vinyl carbocation is formed as an intermediate during the acid catalyzed electrophilic addition of water to an alkyne (shown below). While this reaction is often catalyzed by metals such as HgSO_4 and PtCl_2 , the reaction can also occur in the absence of metals at elevated temperatures.



A. (8 points) Provide a detailed, step-by-step mechanism for the reaction shown above. Do not use metals in your mechanism.



B. (6 points) The carbocation center of the vinyl cation formed as an intermediate in this reaction could be either sp or sp^2 hybridized.

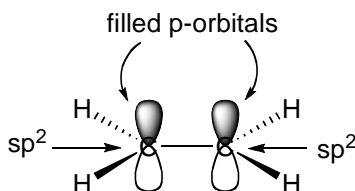
Provide 3D-sketches of the atomic / hybridized orbitals of the vinyl cation carbons indicated with a "C" in the alkyne (shown above part A) formed by protonation if you assume that

(a) the cationic carbon is sp hybridized, or (b) the cationic carbon is sp^2 hybridized.

Your drawings should:

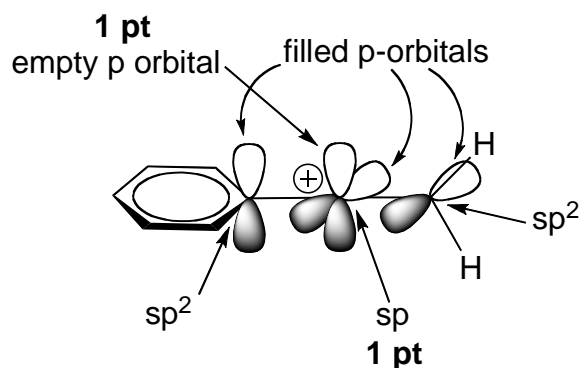
- Show all sigma bonds as lines between atoms.
- Draw in the orbitals for all pi-bonds, all p-orbitals, and all empty orbitals.
- Label each orbital as s, sp , sp^2 , sp^3 or p. Also indicate if the orbital is empty or filled.
- Label the hybridization of the vinyl cation carbons indicated with a "C."
- Be sure that the geometry of your structure is clearly drawn.

We have provided a drawing of ethylene as an example of what your structure should look like.

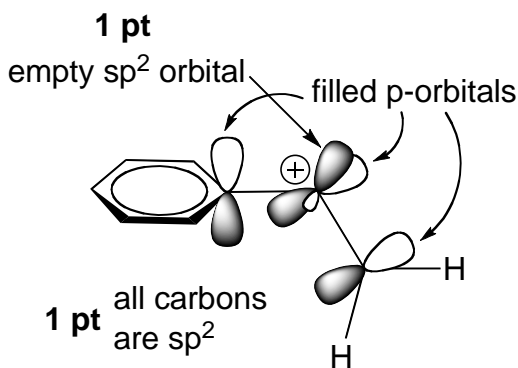


(a) cationic carbon is sp hybridized

(b) cationic carbon is sp^2 hybridized



1 pt if structure is linear



1 pt if structure is bent

C. (2 points) In reality, the vinyl cation carbon is sp hybridized. Briefly explain why the vinyl cation prefers sp hybridization over sp^2 hybridization.

1 pt - The sp hybridization results in an empty p-orbital, which can be aligned parallel with the pi system of the benzene ring. Thus, the cation can be stabilized by resonance interactions with the benzene ring.

1 pt - The sp^2 hybridization results in an empty sp^2 orbital, which is unfavorable because of its greater s-character.

In addition, the empty sp^2 orbital does not have as effective overlap with the pi system of the benzene ring.