Chemistry 218, Winter 2008 **Exam 1** **Name:**

1. _____

2. _____

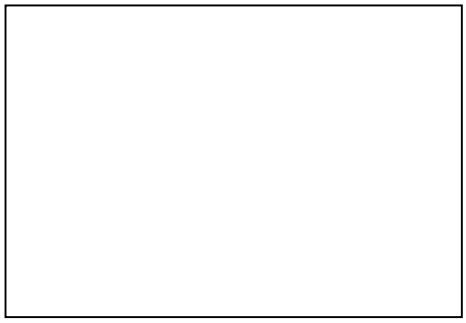
3. _____

4. _____

5. _____

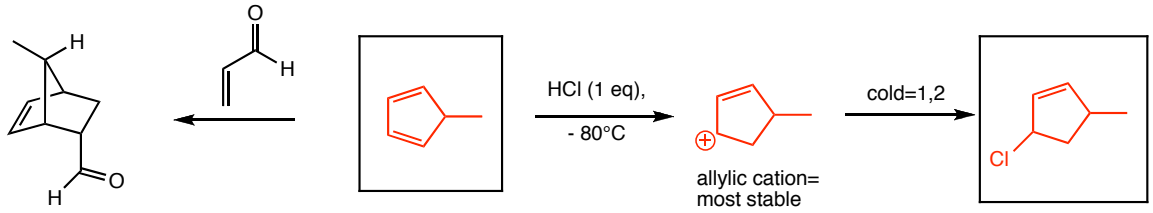
6. _____

7. _____

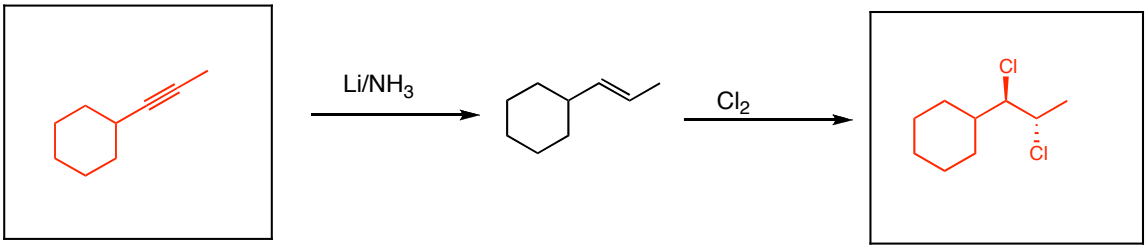


1. Fill in the blanks. (5 pts ea.)

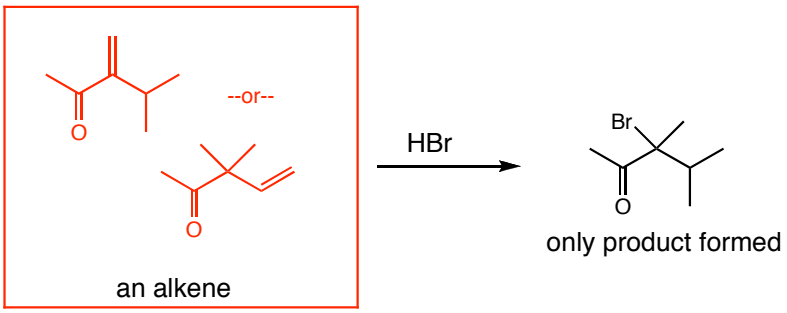
(a)



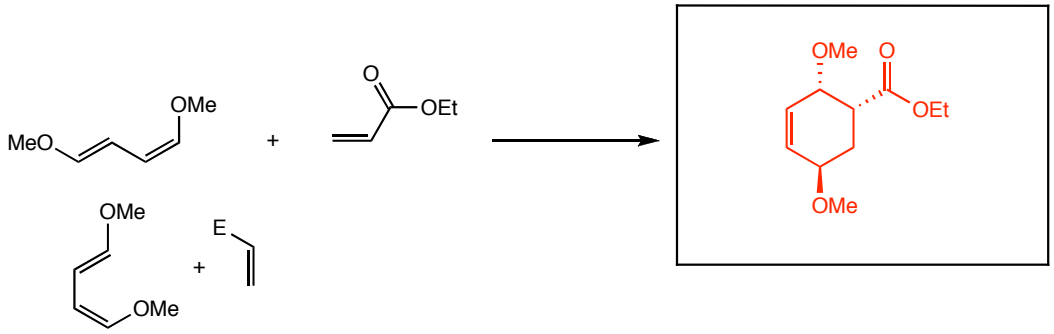
(b)



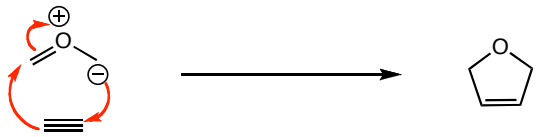
(c)



(d)

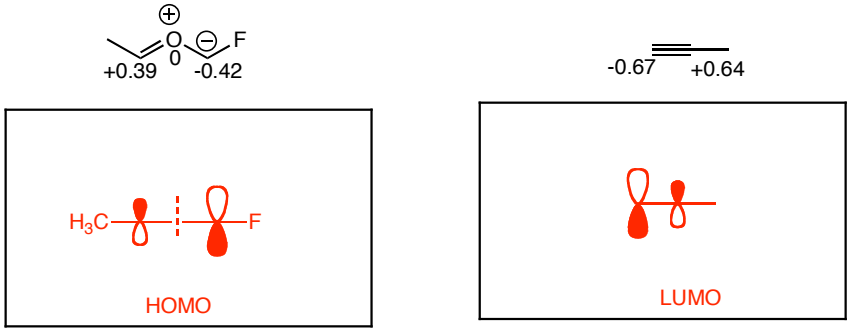


2. The following reaction is called a dipolar cycloaddition, and involves a dipolar species and a dipolarophile. It is concerted, and is very similar to the Diels-Alder reaction.



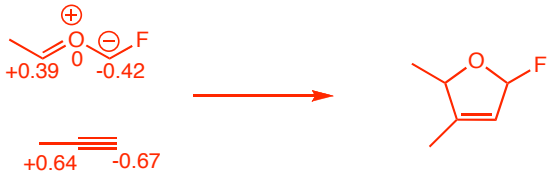
(a) Draw a mechanism on the structures above that shows how the product is formed. (4 pts)

(b) The coefficients of the $2p_y$ orbitals for the reactive molecular orbitals for a dipolar compound and a dipolarophile are shown below. For each, sketch the molecular orbital that is described by the coefficients. Be sure that your sketch takes both the sign and the magnitude of the coefficient into consideration. (5 pts ea.)

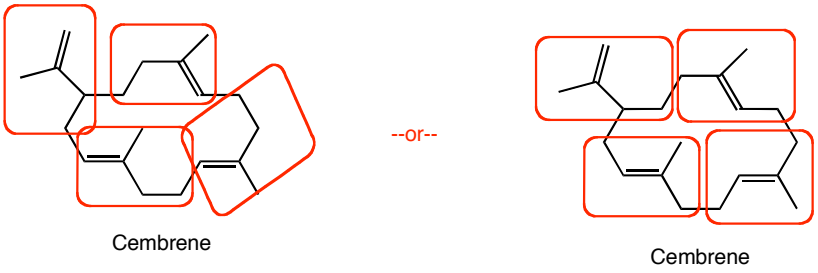


(c) Label each orbital above as the HOMO or LUMO. (5 pts. ea.)

(d) Draw the product that arises when the two compounds above are allowed to react (pay attention to regioselectivity, but do not worry about stereochemistry). (5 pts)
Match up small coefficients with small coefficients:



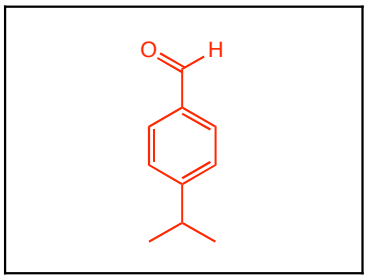
3. The terpene cembrene is a termite trail pheromone. Circle the isoprene units present in cembrene. (5 pts)



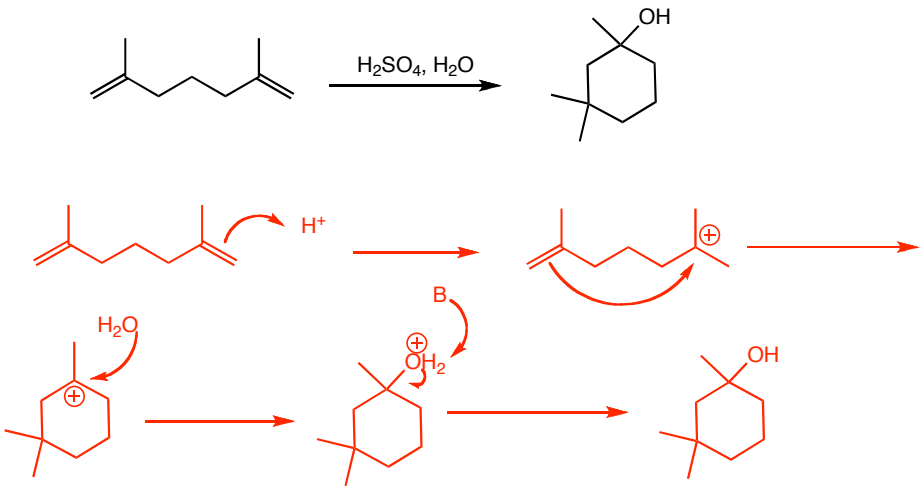
4. Cuminaldehyde is a constituent of the essential oils of eucalyptus, myrrh, cassia, and cumin, and is an ingredient in many perfumes. The ^{13}C data and some of the important peaks from the mass spectrum are given below. Part of the structure of cuminaldehyde is given. Fill in the missing parts. (6 pts)

^{13}C (ppm): 190, 155, 135, 130, 127, 36, 22

MS (m/z): 148, 119, 105

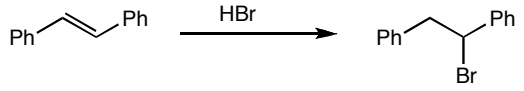


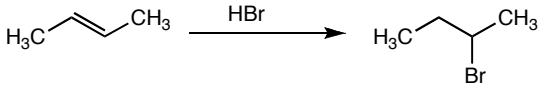
5. Propose a mechanism for the following transformation. (8 pts)



6. Briefly explain why reaction **A** is faster than reaction **B** in both examples shown below. (6 pts. ea.)

(a)

(**A**) 

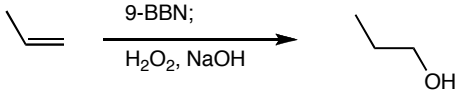
(**B**) 

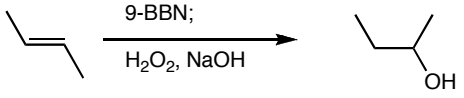
Cation formed from **A**:

Cation formed from **B**:

The carbocation formed in reaction **A** is stabilized by conjugation with the phenyl ring. By the Hammond postulate, if the cation is stabilized, the transition state is stabilized, the activation energy is lower, and the rate increases.

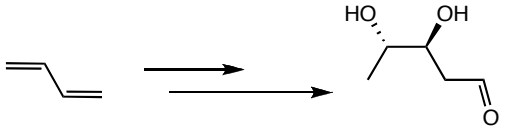
(b)

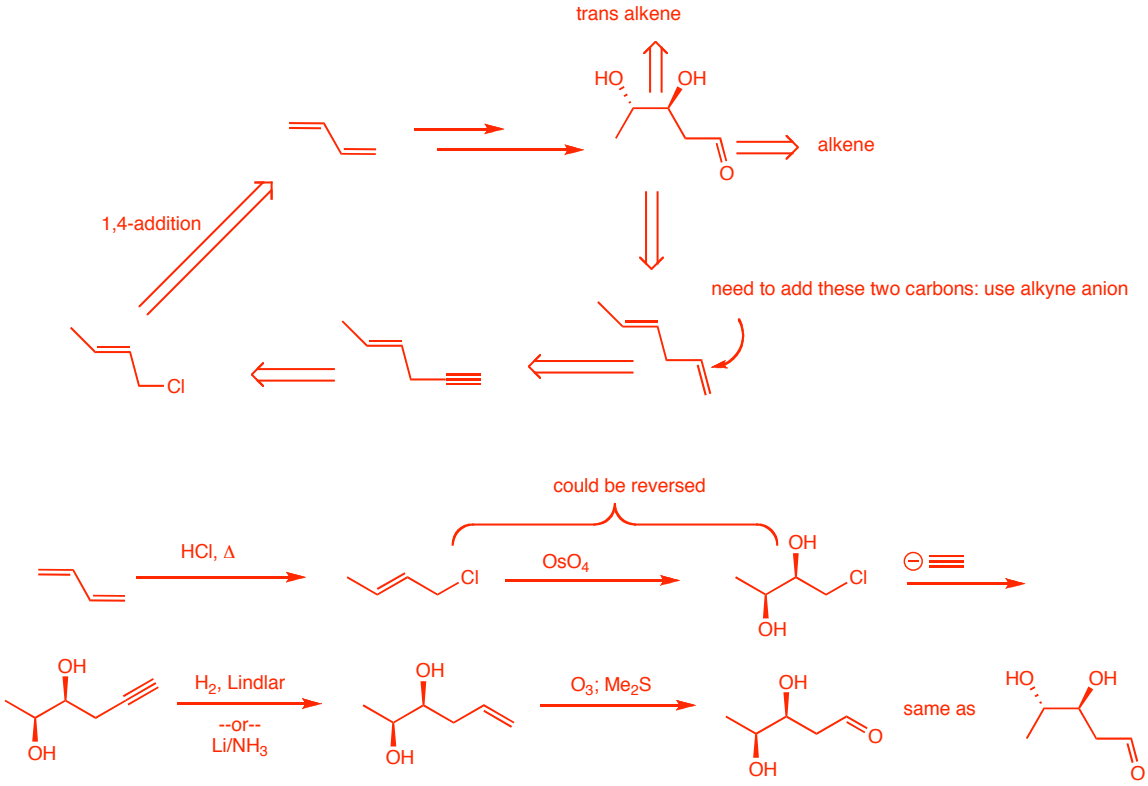
(**A**) 

(**B**) 

9-BBN is a very large reagent, and will approach the least sterically hindered alkened fastest.

7. Propose a synthesis of the following molecule from the starting material given. You may use any other organic or inorganic compound or reagent you need. No mechanisms necessary. (10 pts)





Extra credit: Draw the structure of (2*Z*,4*E*,6*Z*,8*E*)-deca-2,4,6,8-tetraene