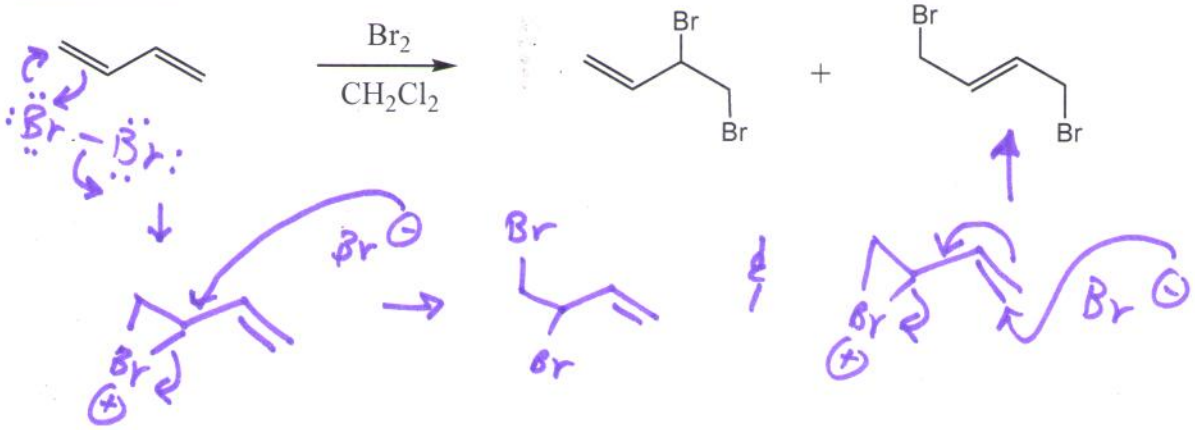
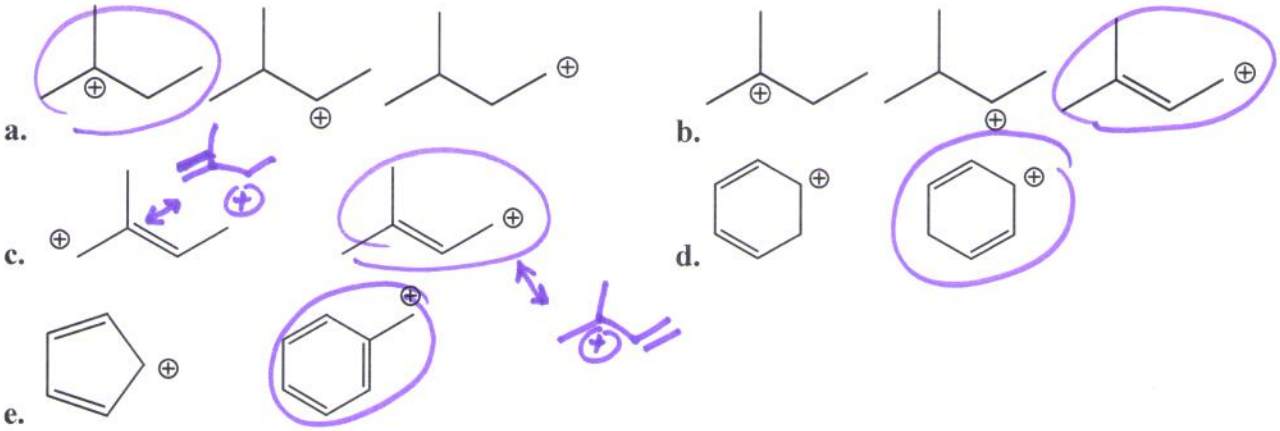
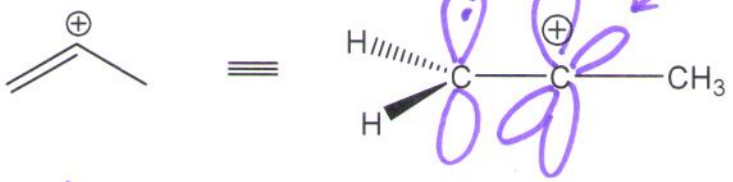
1. Draw the complete mechanism which illustrates formation of both products and circle the more stable isomer.



2. Circle the more stable carbocation in a-e:



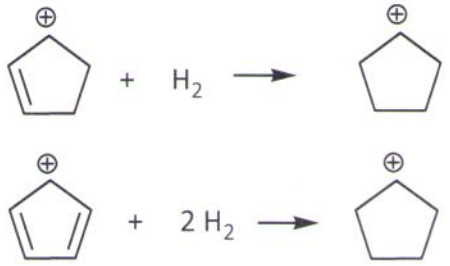
3. Vinyl cations are not as stable as alkyl, benzylic or allylic carbocations since the vinyl cation is located on an sp hybridized carbon. Draw all p-orbitals on the partial structure below to illustrate why delocalization of the positive charge does not occur and include a brief explanation.



empty p-orbital is perpendicular (orthogonal) to π bon

π bond cannot delocalize e's into empty p orbital

4. Calculate the resonance energy of the cyclopentadienyl cation:

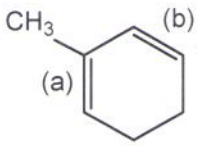


2 × 15 = 3 kcal for 2 dbl bonds

73
− 30
43 kcal is resonance energy

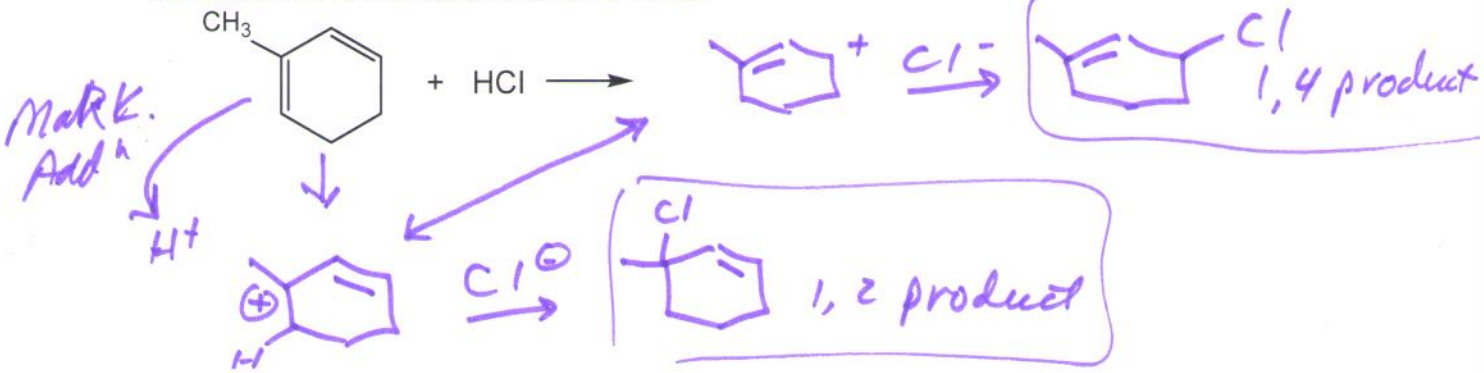
5. Addition of HCl to an alkene involves nucleophilic attack of a pi bond to the electrophile, H^+.

a. Which double bond is more reactive, a or b? A one sentence explanation is required.

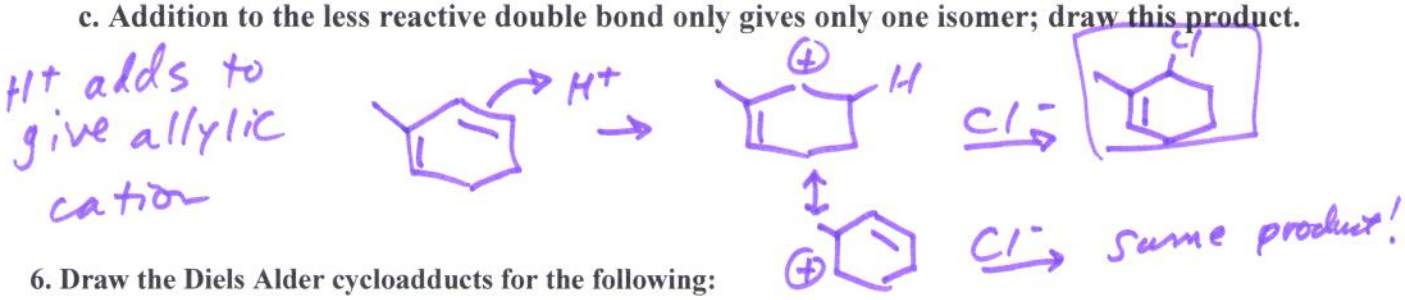


(a) is more reactive nucleophile due to e⁻ donating group (CH_3)

b. Based on your answer above, draw both 1,2- and 1,4-addition products when addition occurs at the more reactive double bond.

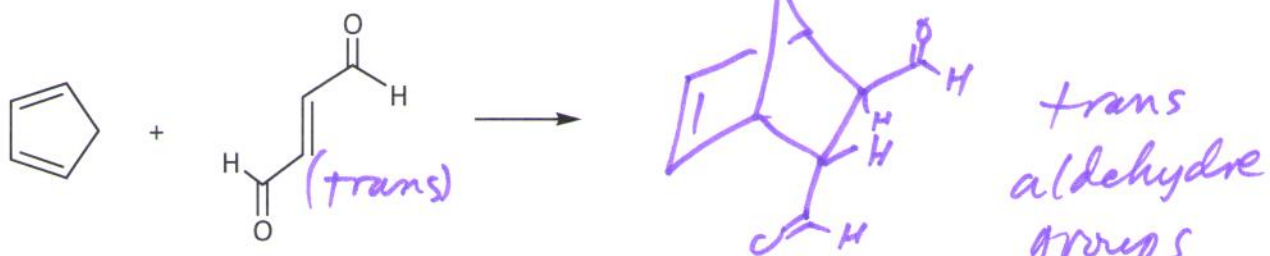


c. Addition to the less reactive double bond only gives only one isomer; draw this product.

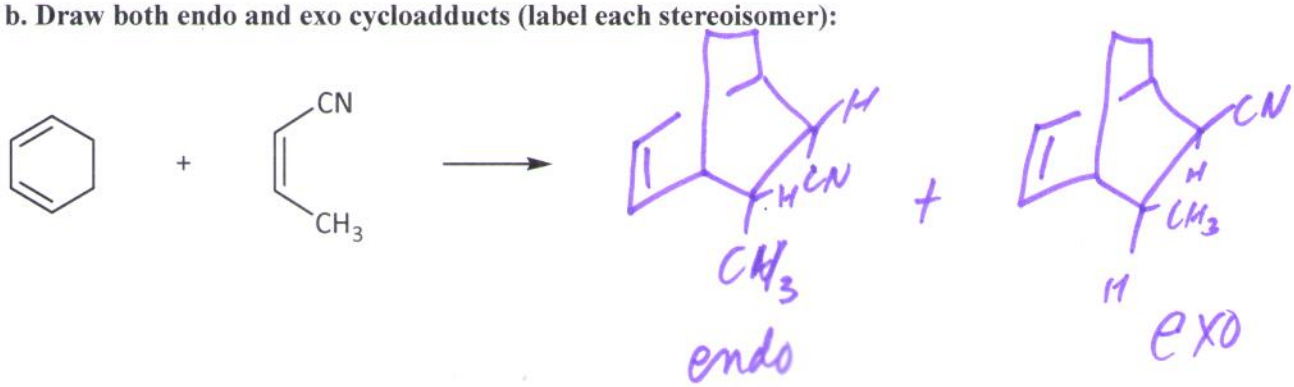


6. Draw the Diels Alder cycloadducts for the following:

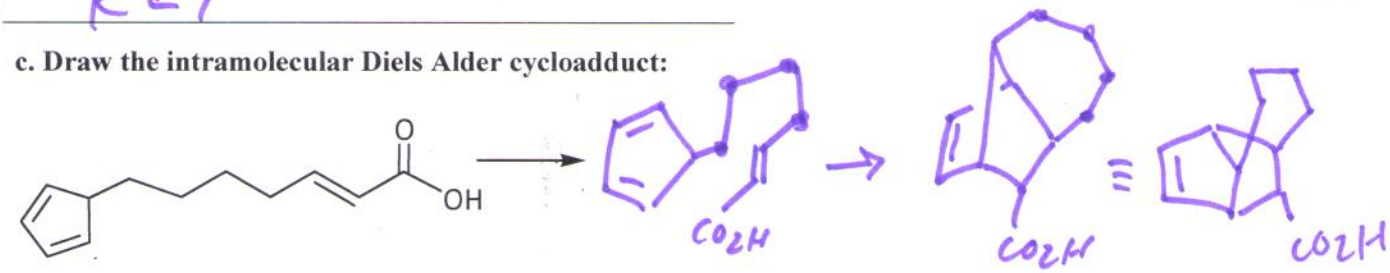
a. Show stereochemistry in the Diels Alder cycloadduct:



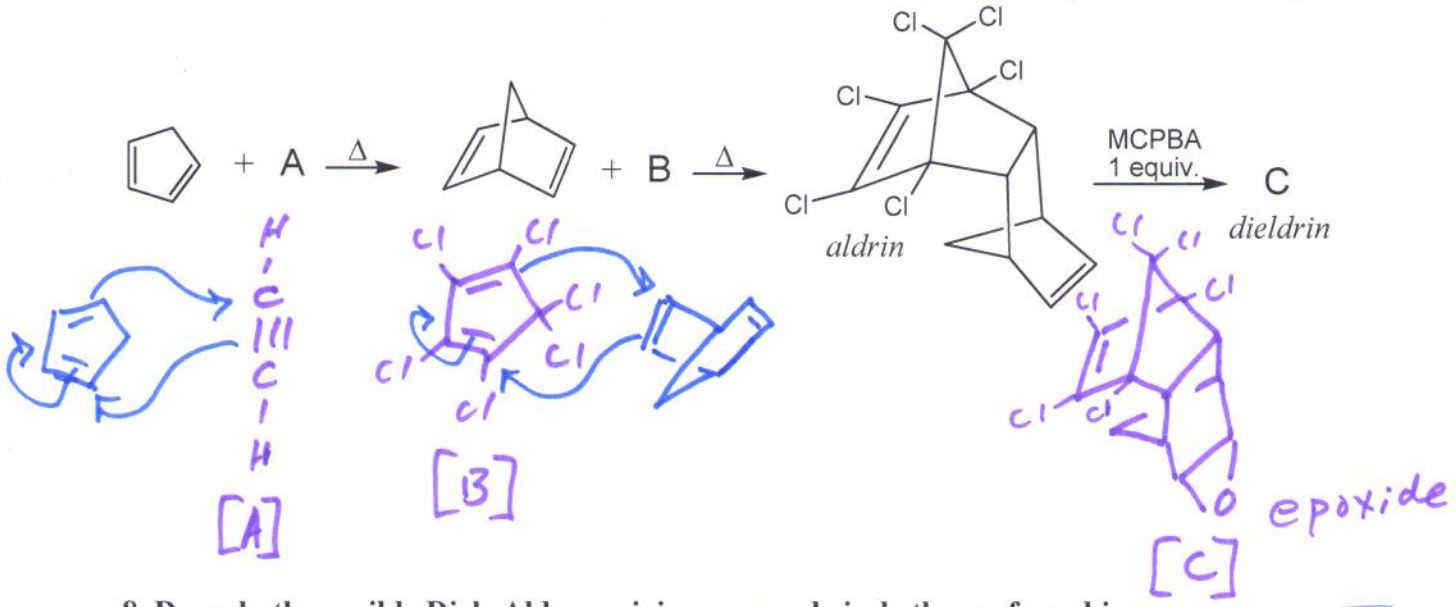
b. Draw both endo and exo cycloadducts (label each stereoisomer):



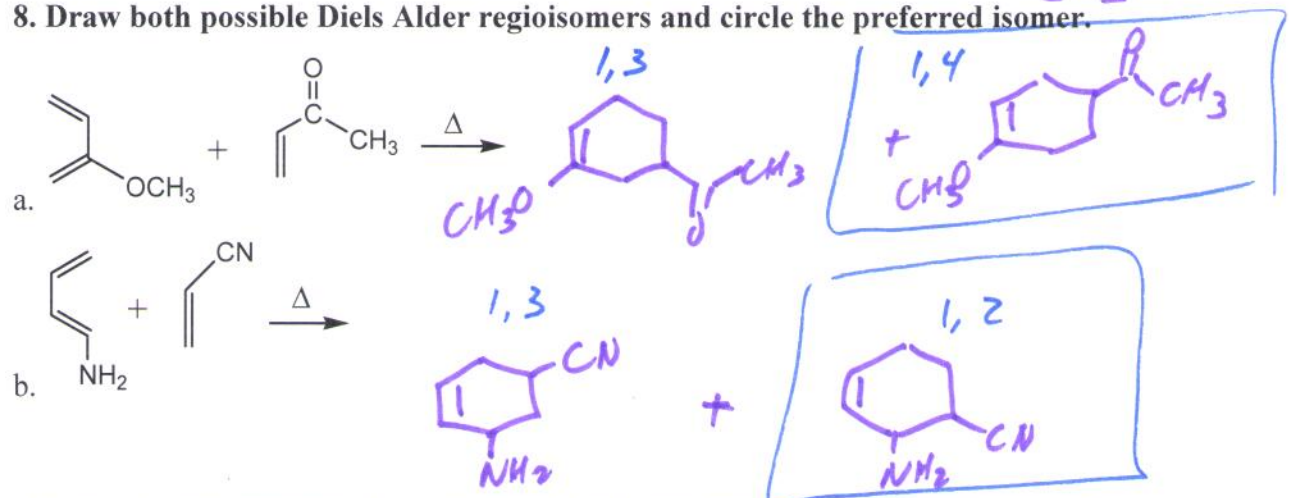
c. Draw the intramolecular Diels Alder cycloadduct:



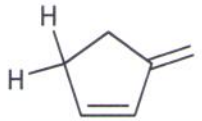
7. Some interesting history … Two pesticides, dieldrin and aldrin were actually named after Diels and Alder. Shown below is a reaction scheme used to make these compounds. Draw A, B and C.



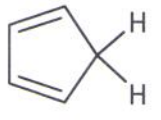
8. Draw both possible Diels Alder regioisomers and circle the preferred isomer.



9. Explain the difference in acid strength for these two conjugated hydrocarbons:



3-methylenecyclopent-1-ene
pKa > 50

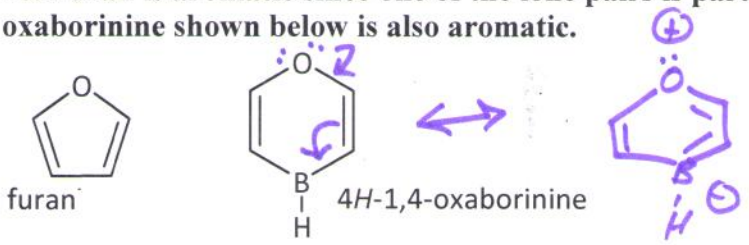


cyclopenta-1,3-diene
pKa = 16

reaction with base gives aromatic cyclopentadienyl anion - a very stable conj. base. weaker base means stronger acid

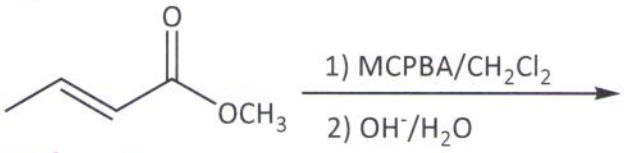
reaction with base gives resonance stabilized anion but not aromatic

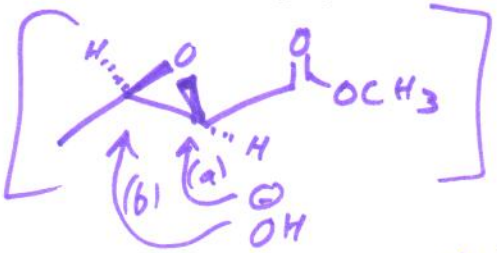
10. Furan is aromatic since one of the lone pairs is part of the pi system. Explain why the oxaborinine shown below is also aromatic.

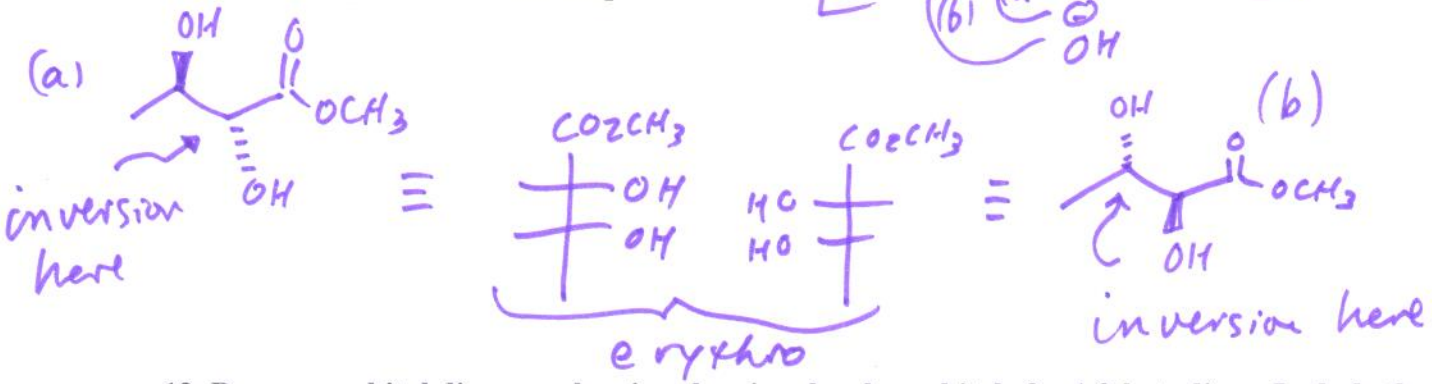


resonance structure creates aromatic system of 6 π e's

11. Draw the final product and illustrate the product with a Fischer projection and label as erythro or threo.







12. Draw an orbital diagram showing the pi molecular orbitals for 1,3-butadiene. Include these four labels where appropriate: bonding M.Os; antibonding M.Os.; HOMO; LUMO