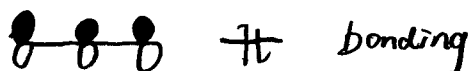
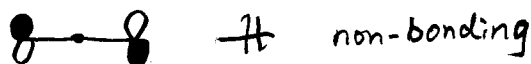
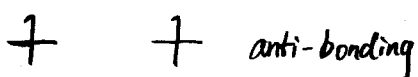
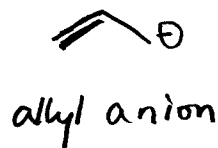
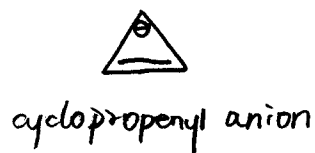


Answer key for Exam 1, Feb. 1 2007
CHM 172 Q

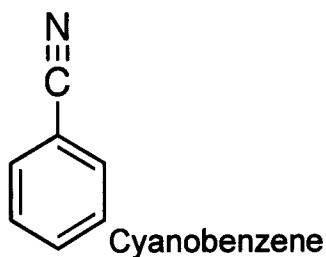
1. Consider cyclopropenyl anion. Discuss its stability relative to allyl anion, with the help of an MO diagram and a Hückel electronic energy diagram.



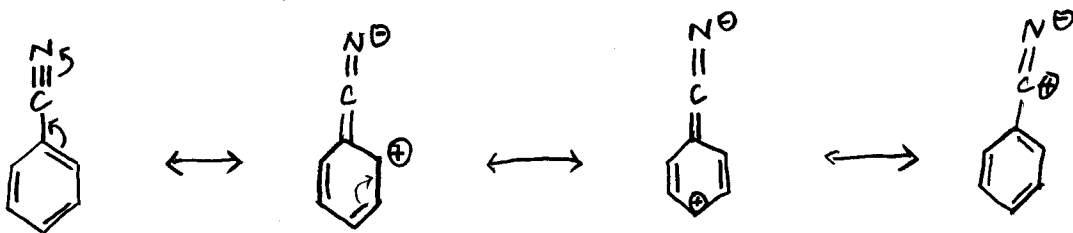
From the MO diagram drawn above, we can see the cyclopropenyl anion has two unpaired electrons in its anti bonding orbital, whereas the allyl anion has two paired electrons in its nonbonding orbital, and there are 4 electrons in the cyclopropenyl ring system, which makes this ring antiaromatic, therefore, the allyl anion is more stable than cyclopropenyl anion.

(25 points)

2. Consider the reactivity of cyanobenzene relative to benzene. Will it be more or less reactive? What product do you expect when cyanobenzene is treated with $\text{Br}_2/\text{FeBr}_3$? Explain your answers with the help of drawings.

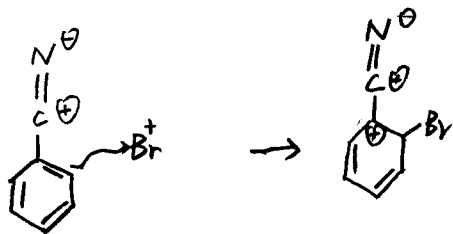


Cyanobenzene is less reactive because the cyano group withdraws electron density from the ring due to the high electronegativity of N via σ -induction effect. as illustrated below:

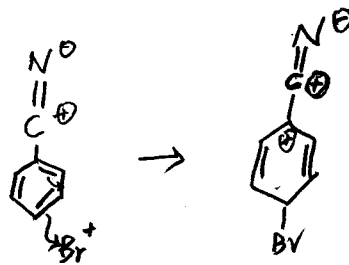


when reacting with Br_2 , there would be 3 possible products:

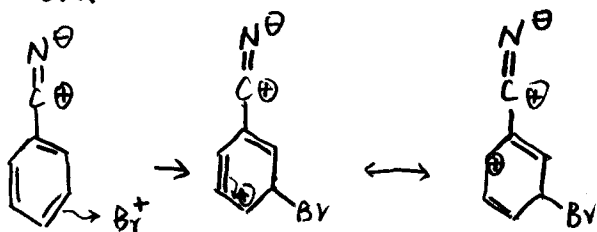
Ortho:



Para:



Meta:

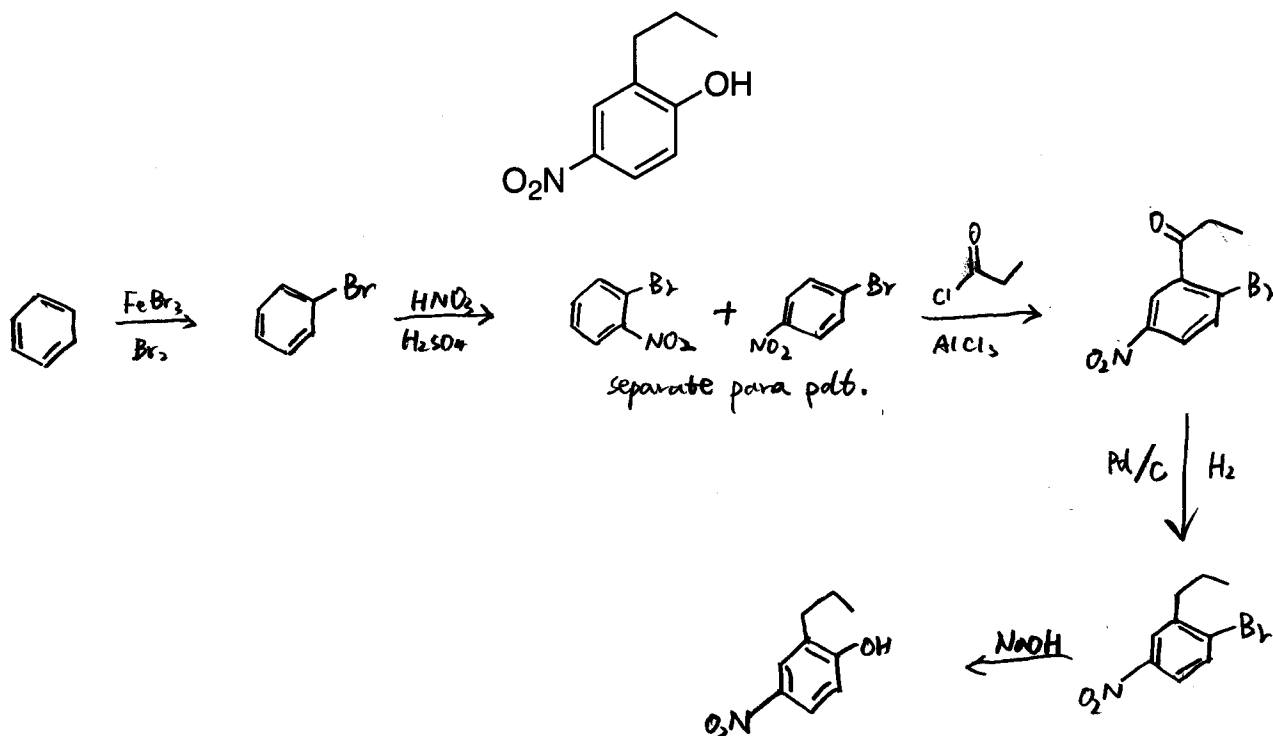


As we can see, in ortho and para products there are positive charged C atoms next to each other, which is very destabilizing, while in meta product we don't have this destabilizing effect.

(20 points)

So we will have meta-brominated cyanobenzene as our product.

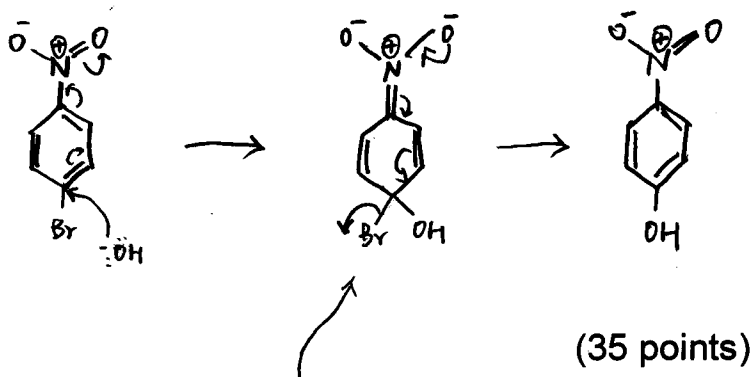
3. a. Propose a synthesis for compound B. You will need to separate ortho and para isomers once- indicate that step in your proposed route.



Several of those steps above are interchangeable as long as the synthetic pathway is reasonable.

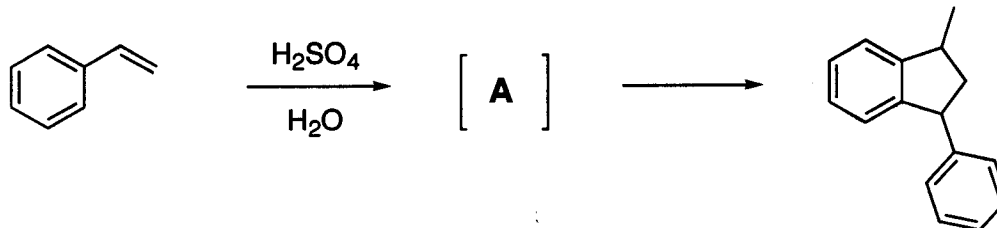
Note: The aromatic substitution of Br for OH only occurs when there is electro-withdrawing group on the ring; and the introduction of $\text{CH}_2\text{CH}_2\text{CH}_3$ is not likely to happen unless you make it more electron-withdrawing by introducing $\text{C}=\text{O}$.

b. Draw a mechanism for the C-O bond-forming reaction.

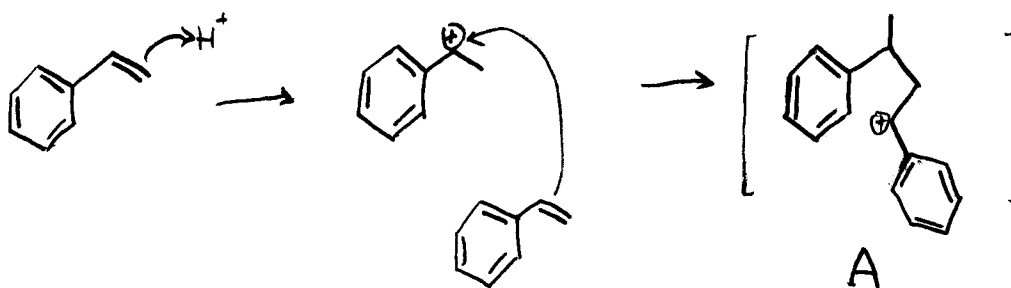


the negative charge on oxygen could also be on any other position on the ring as long as it is right resonance structure and the ring bears a electron-withdrawing group.

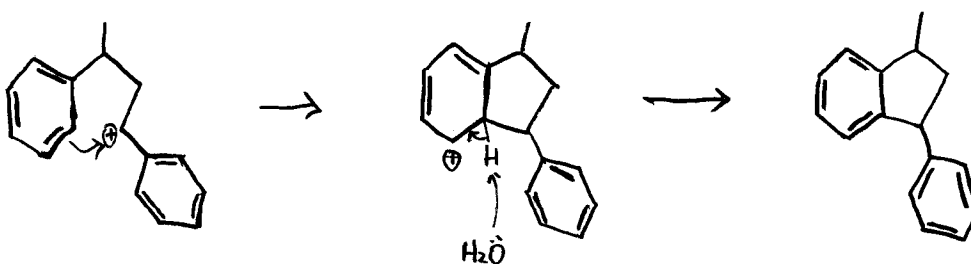
4. Consider the two-step reaction sequence shown below. Intermediate **A** is a charged dimeric intermediate that undergoes an electrophilic aromatic substitution to give the product dimer.



- a. Give the structure of the charged dimeric intermediate **A**.



- b. Provide a mechanism for the second step of the reaction sequence.



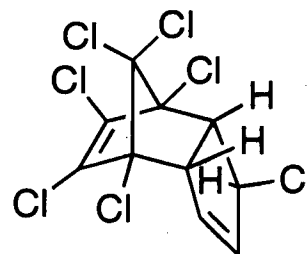
- c. Name the electrophilic aromatic substitution process.

Friedel-Crafts alkylation

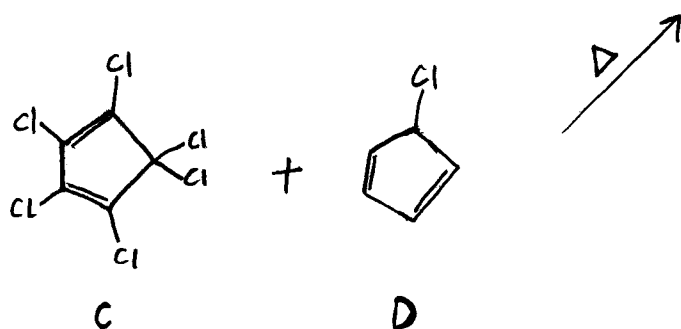
(25 points)

5. Provide structures for C, D and E.

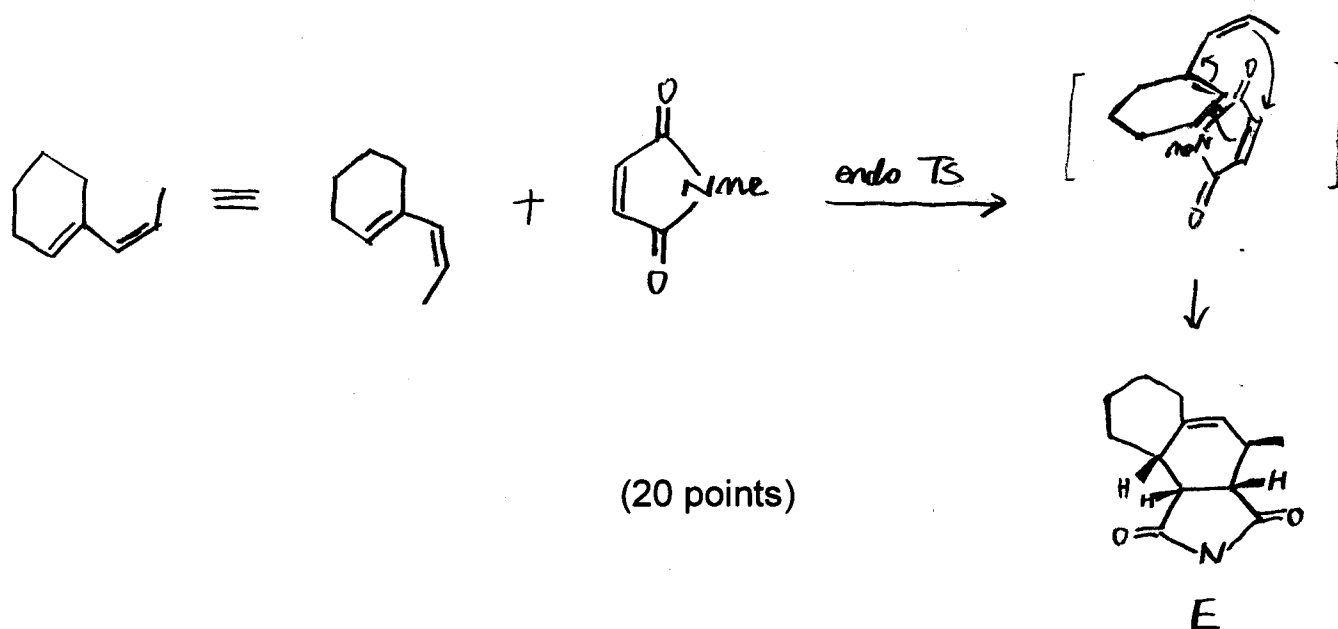
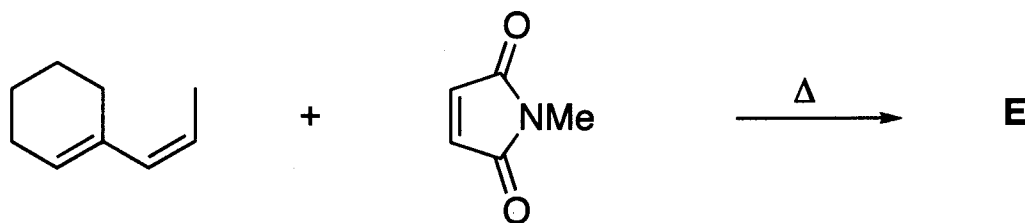
a.



Heptachlor (an insecticide)



b.



(20 points)