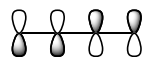
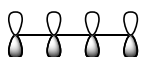


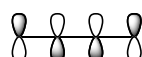
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| Score (4 pts) | | Lectures | 22-28 | Name | |
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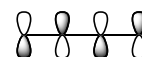
1. Rank the molecules in each set below according to the trends observed for the physical and chemical properties indicated.

A. Rank in order of increasing amount of net bonding interactions (1 = least bonding/most antibonding; 4 = most net bonding).

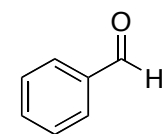


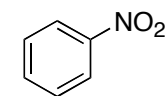


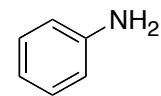


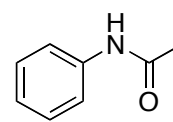


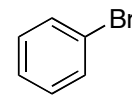
B. Rank in order of increasing rate of electrophilic aromatic substitution (S_EAr) (1 = slowest rate; 5 = fastest rate).



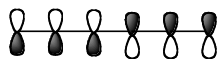


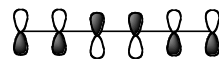


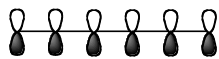


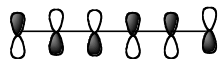


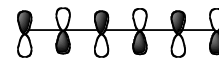
C. Rank each symbolic MO representation in order of increasing potential energy (1 = lowest PE; 5 = highest PE).



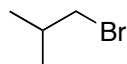


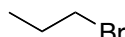


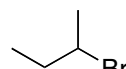


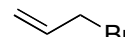


D. Rank in order of increasing rate of S_N2 (1 = slowest rate; 4 = fastest rate).

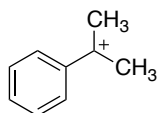


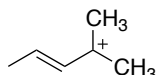


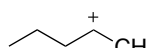


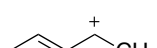


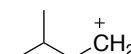
E. Rank in order of increasing stability (1 = least stable, highest potential energy; 5 = most stable, lowest potential energy).



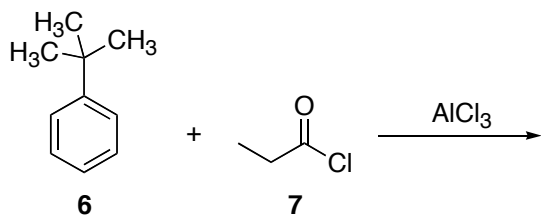








2. *tert*-Butyl benzene (**6**) undergoes Friedel-Crafts acylation in the presence of AlCl_3 . Not surprisingly, this reaction is highly regioselective. **First**, draw the *major* product for this reaction. **Second**, draw the mechanism for the formation of the acylium ion when propanoyl chloride (**7**) reacts with AlCl_3 ; show both resonance structures for the acylium ion. **Third**, draw the mechanism for the reaction of toluene with the acylium ion to give the final product. Draw all resonance structures for the arenium ion intermediate.

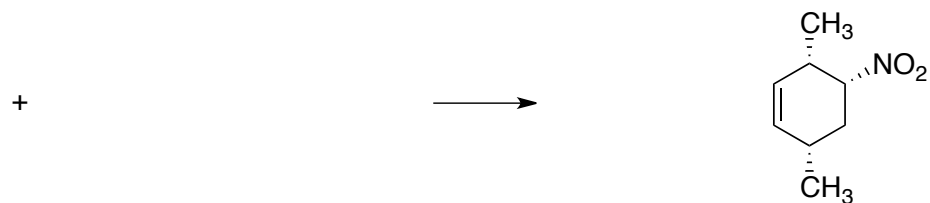
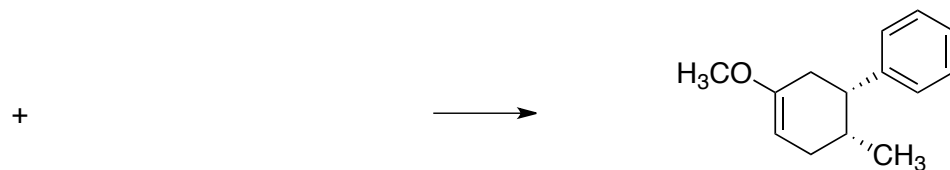
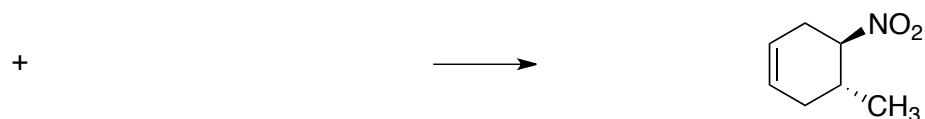
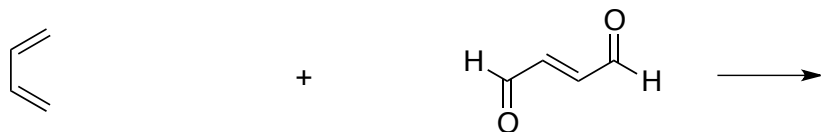


3. **First**, draw the symbolic representations for each π -molecular orbital (MO) of 1,3-butadiene. Use shading to indicate the location of nodes in each MO. **Second**, use up or down arrows to represent the electrons in each MO. **Third**, label the HOMO and LUMO. **Fourth**, write the net amount of bonding or antibonding for each MO (e.g., "2 net bonding" or "1 net antibonding").

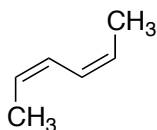
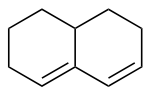
| net bonding or antibonding | | symbolic representations |
|----------------------------|--|--------------------------|
| | | |

4. **First**, using the Frost Circle mnemonic, draw the molecular orbital diagram for the conjugate base of cyclopentadiene (energy levels only; symbolic representations not needed). **Second**, label each MO as bonding, non-bonding or antibonding. **Third**, use up and down arrows to represent the electrons present in each orbital. **Fourth**, state whether the conjugate base of cyclopentadiene is aromatic, antiaromatic or neither. Use your diagram to **explain**.

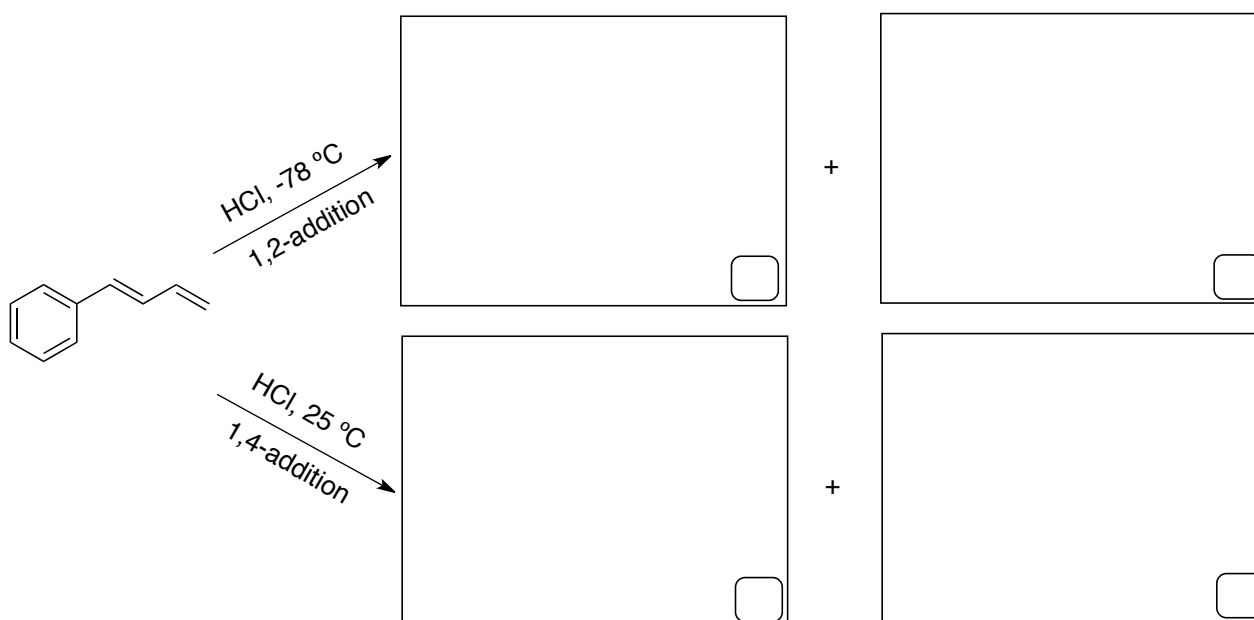
5. Draw the Diels-Alder adduct for the first five reactions and the diene and dienophile for the last five reactions. Be sure to draw the *major* stereoisomer where applicable.



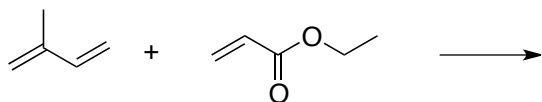
6. Both of the dienes below are activated by electron donating alkyl groups. However, neither undergoes Diels-Alder reactions with dienophiles. Explain why. Hint: Draw each in the conformation required to undergo a Diels-Alder cycloaddition.



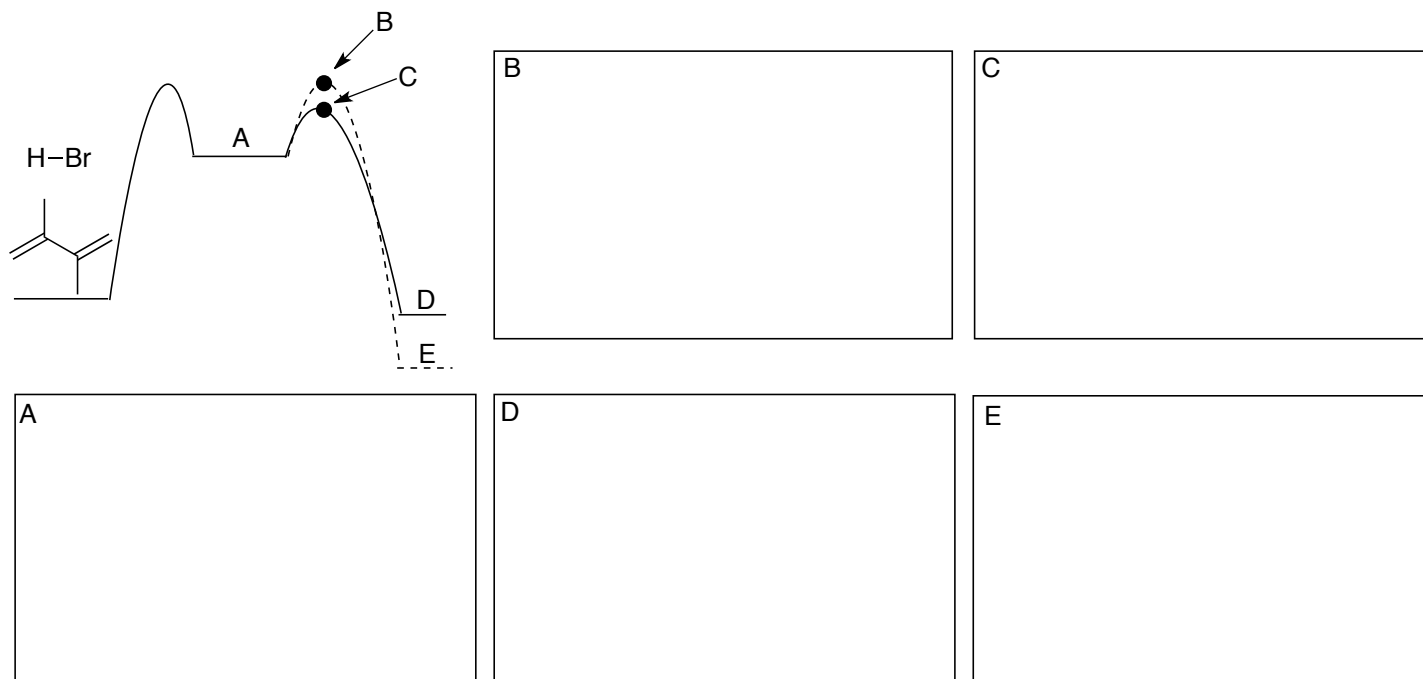
7. **First**, draw all four possible products (two 1,2-addition and two 1,4-addition) of HCl addition to the diene below. **Second**, place a check mark in the box for the major product in each category. **Third**, explain your choice.



8. Isoprene (2-methyl-1,3-butadiene) reacts with ethyl propenoate to provide two regioisomers. Draw the structure of each and explain why a mixture is formed (how does each arise?).



9. Consider the addition of HBr to 2,3-dimethyl-1,3-butadiene. Draw each intermediate, transition state or product indicated in the potential energy diagram.



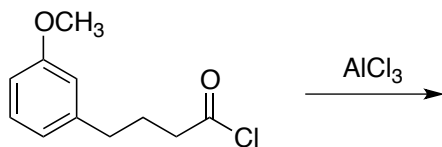
A. Draw both resonance structures of intermediate **A**.

B. Explain why transition states **B** and **C** are different in energy.

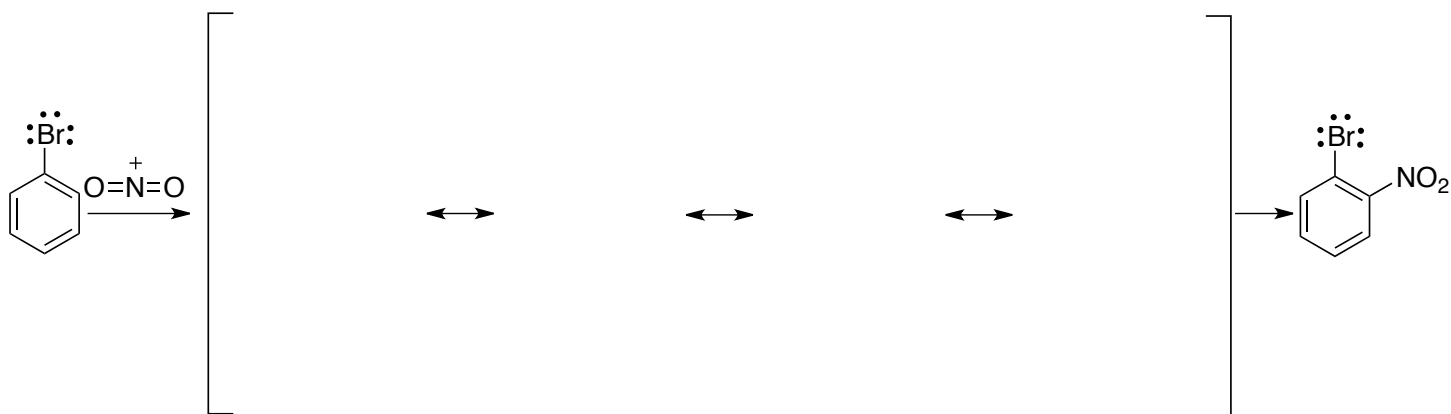
C. Explain why products **D** and **E** are difference in energy.

D. What reactions conditions favor product **D** and what conditions favor product **E**? Label each as kinetic control or thermodynamic control and explain why different products are obtained for each.

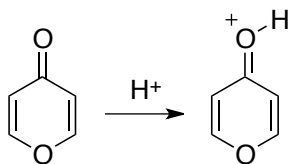
10. (2 pts) The acid chloride below undergoes intramolecular Friedel-Crafts acylation when treated with AlCl_3 . Draw both potential regioisomers of the product.



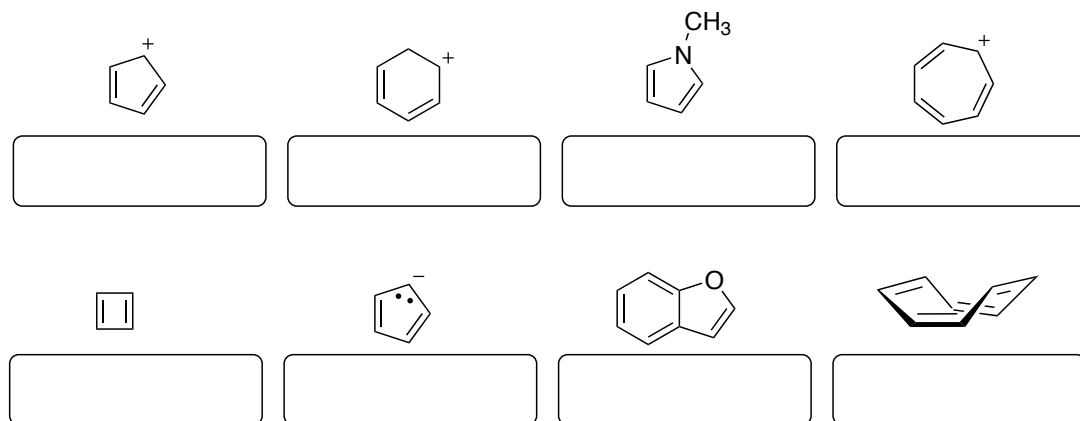
11. (4 pts) Draw four resonance structures for the arenium ion formed by ortho nitration of bromobenzene. Include all electron lone-pairs and formal charges on all atoms.



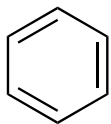
12. On reaction with acid, 4-pyrone is protonated on the carbonyl-group oxygen to give a stable oxonium ion. Using resonance structures and the Huckel $4n+2$ rule, explain why the conjugate acid is so stable.



13. (4 pts) Classify each structure as aromatic, antiaromatic or neither.



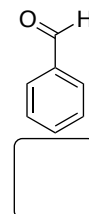
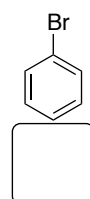
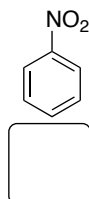
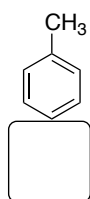
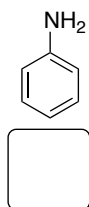
14. Use the Frost circle mnemonic to draw the MO orbital diagram (including electrons) for each system below. Draw a dotted line between bonding and anti-bonding MOs.



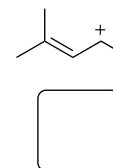
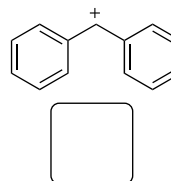
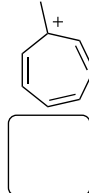
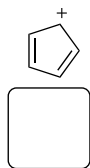
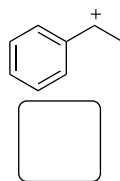
15. Draw the HOMO for the left-hand reactant above the LUMO for the right-hand reactant. Draw dashed lines between the interacting orbitals in each pair. Using your diagram, state whether each cycloaddition is symmetry-allowed or symmetry-forbidden. Explain.



16. Rank in order of increasing rate of Friedel-Crafts Acylation (1 = slowest; 5 = fastest).



17. Rank the carbocations in order of increasing stability (1 = least stable; highest potential energy; 5 = most stable; lowest potential energy). Be sure to consider whether any are aromatic or antiaromatic.



18. Draw the *major* product for each reaction. Be sure to draw the *major* regioisomer where applicable.

