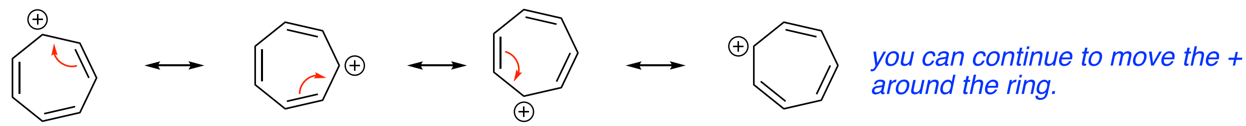
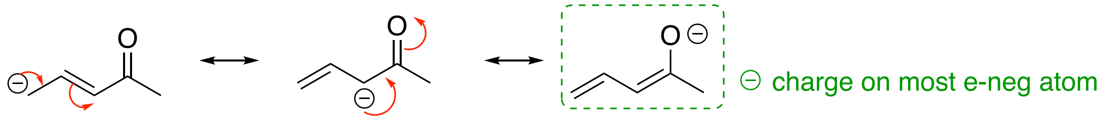
## Resonance and Conjugation

1) For each of the structures below, draw all other possible resonance structures. Use curved arrow to show the flow of electrons. For b, c, d, f, and g circle the structure that you would expect to be the major contributor to the resonance hybrid. *Hint: It helps to draw in lone pairs.*

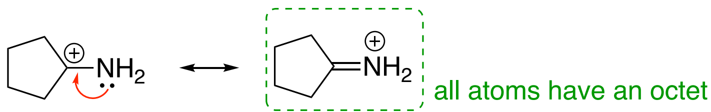
**a**



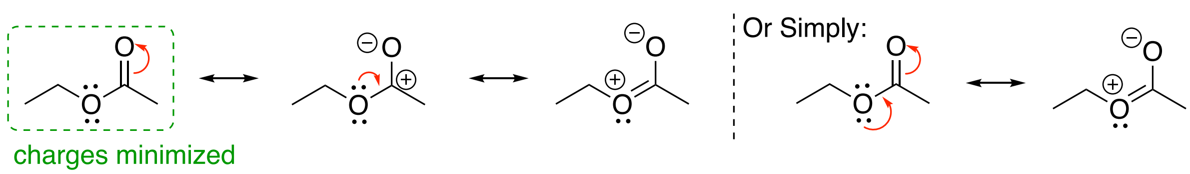

**b**



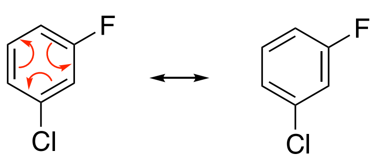

**c.**



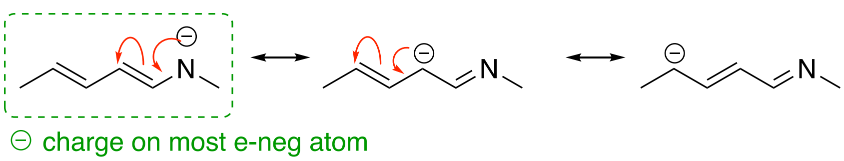

**d.**



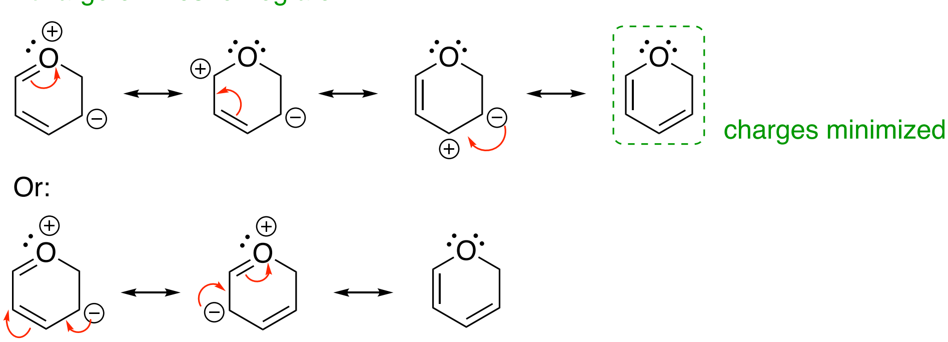

**e.**



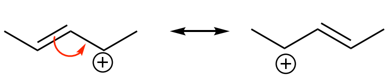

**f.**



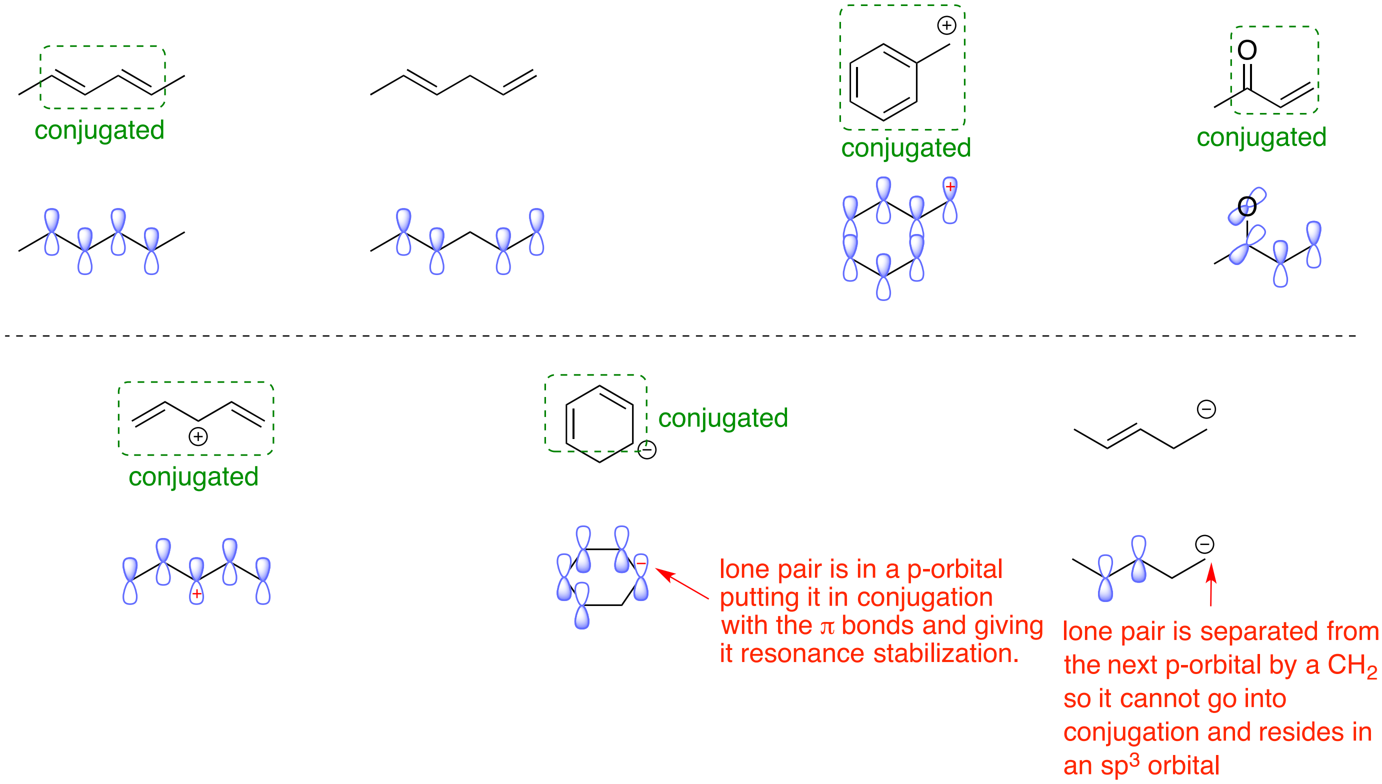

**g.**




**h.**

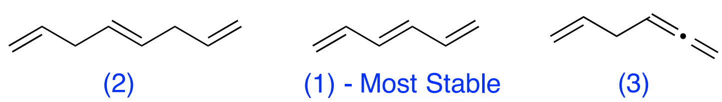


2) For each of the compounds below, draw a representation showing all of the p-orbitals. Determine if each compound is conjugated. For the conjugated compounds, circle the atoms involved in conjugation.

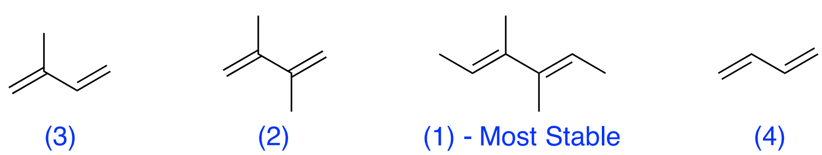



3) For each of the following sets of compounds, rank the series in order of increasing stability

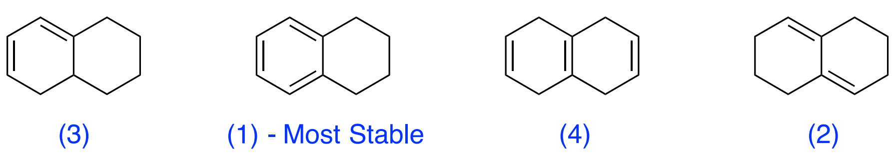
**a.**




**b.**



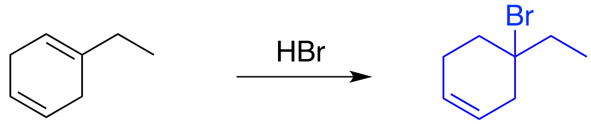

**c.**

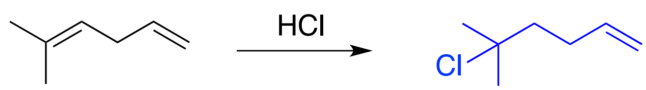


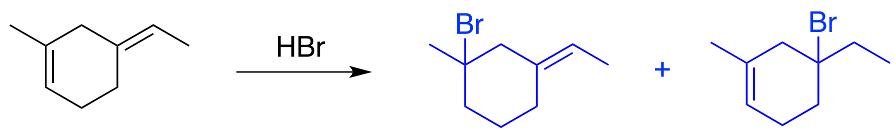
## Electrophilic Addition to Dienes

4) Predict the major product(s) for each of the reactions below. Unless otherwise specified, assume 1 equivalent of reagent is added. *rt stands for room temperature (where you have the potential of both the 1,2 and 1,4 products.

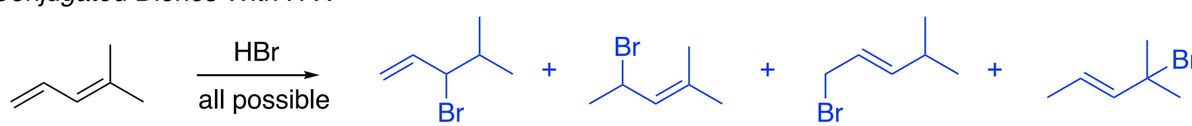
*Isolated Dienes*

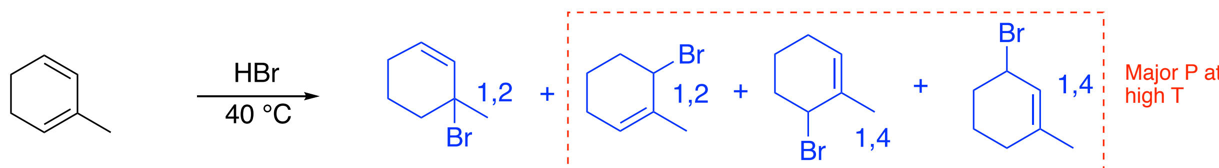


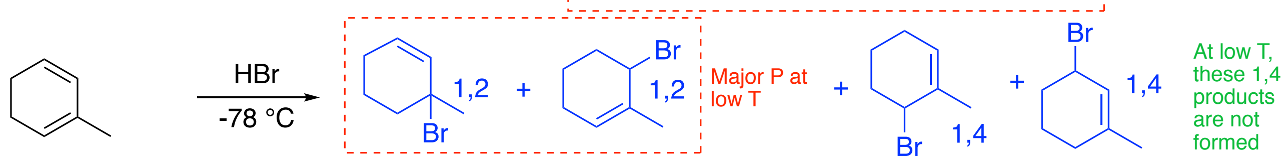



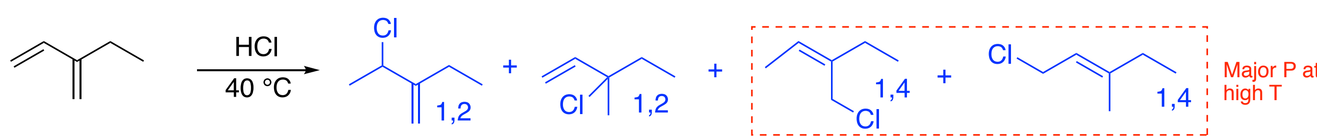



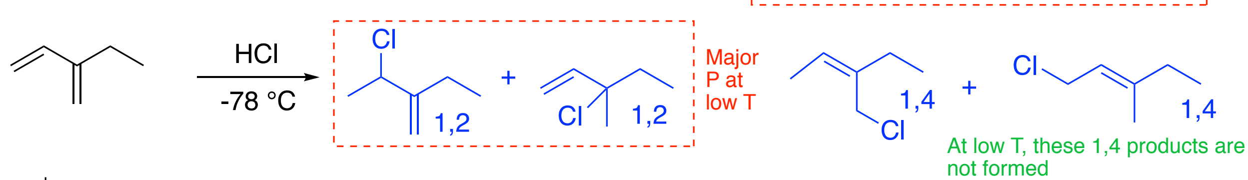

*Conjugated Dienes With H-X*

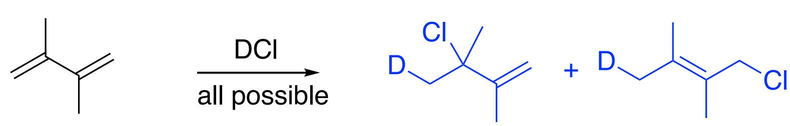


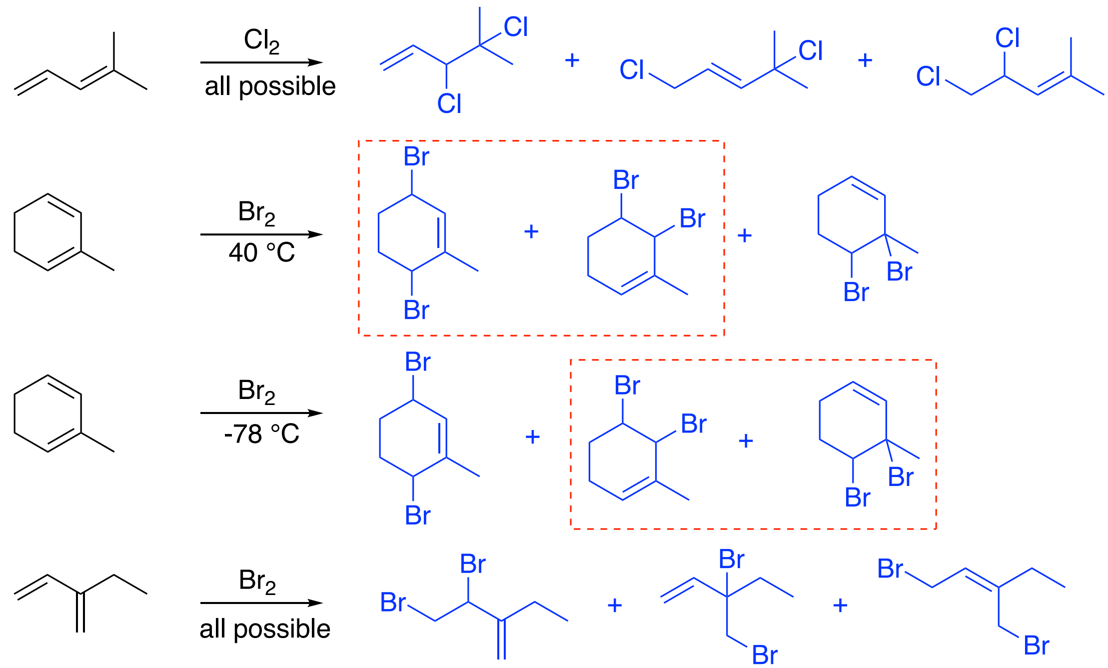



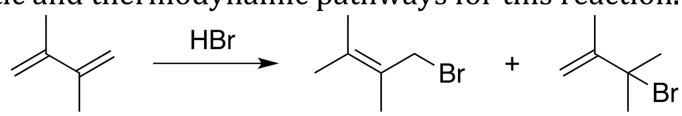

*D = deuterium, which reacts similarly to H*

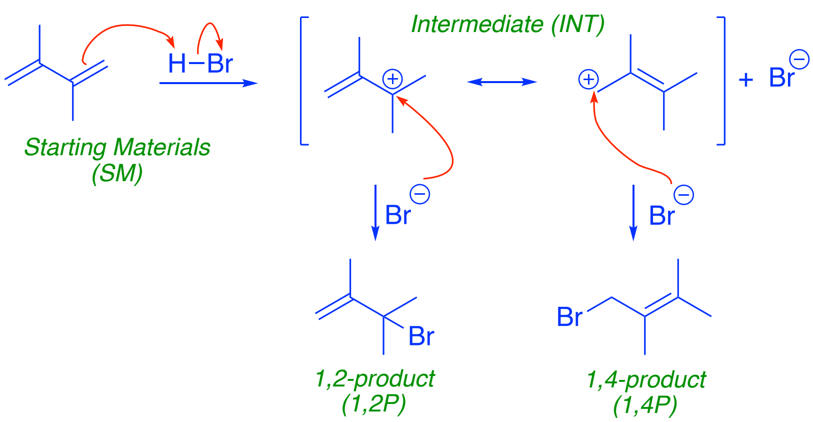
*Conjugated Dienes With $X_2$*

For the temp controlled reactions, I drew all products and then boxed the ones that you actually get from the reaction.

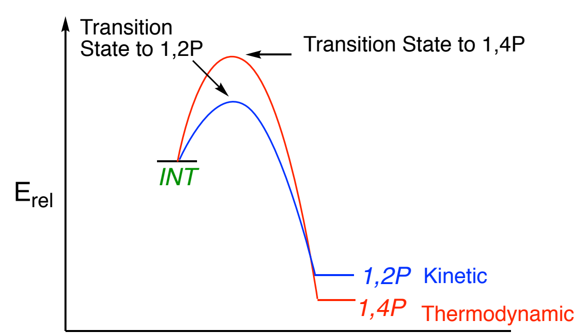



5) Provide a full electron pushing mechanism for the reaction below. Draw a reaction energy diagram that illustrates the kinetic and thermodynamic pathways for this reaction.

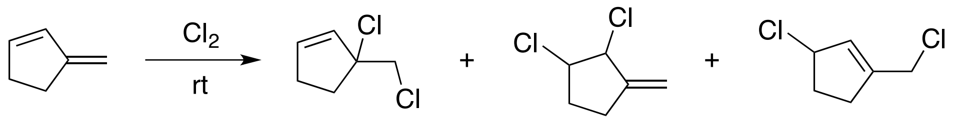


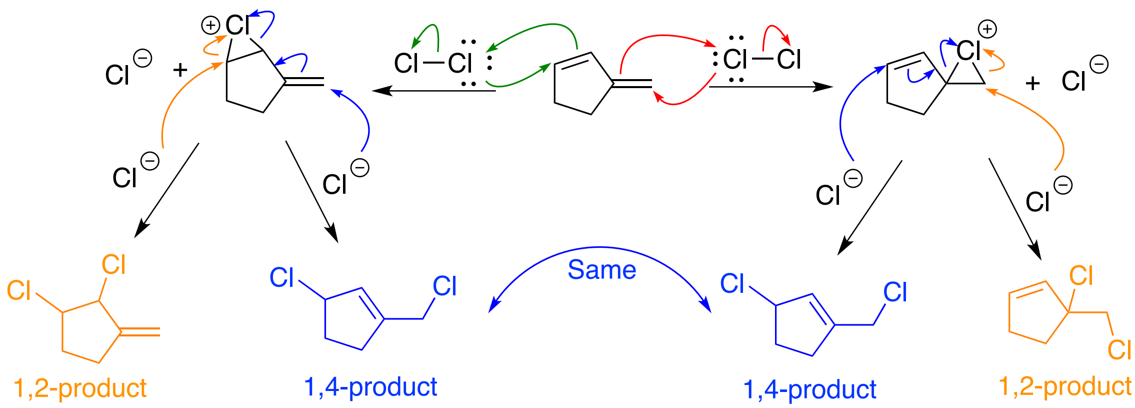




**Energy Diagram**

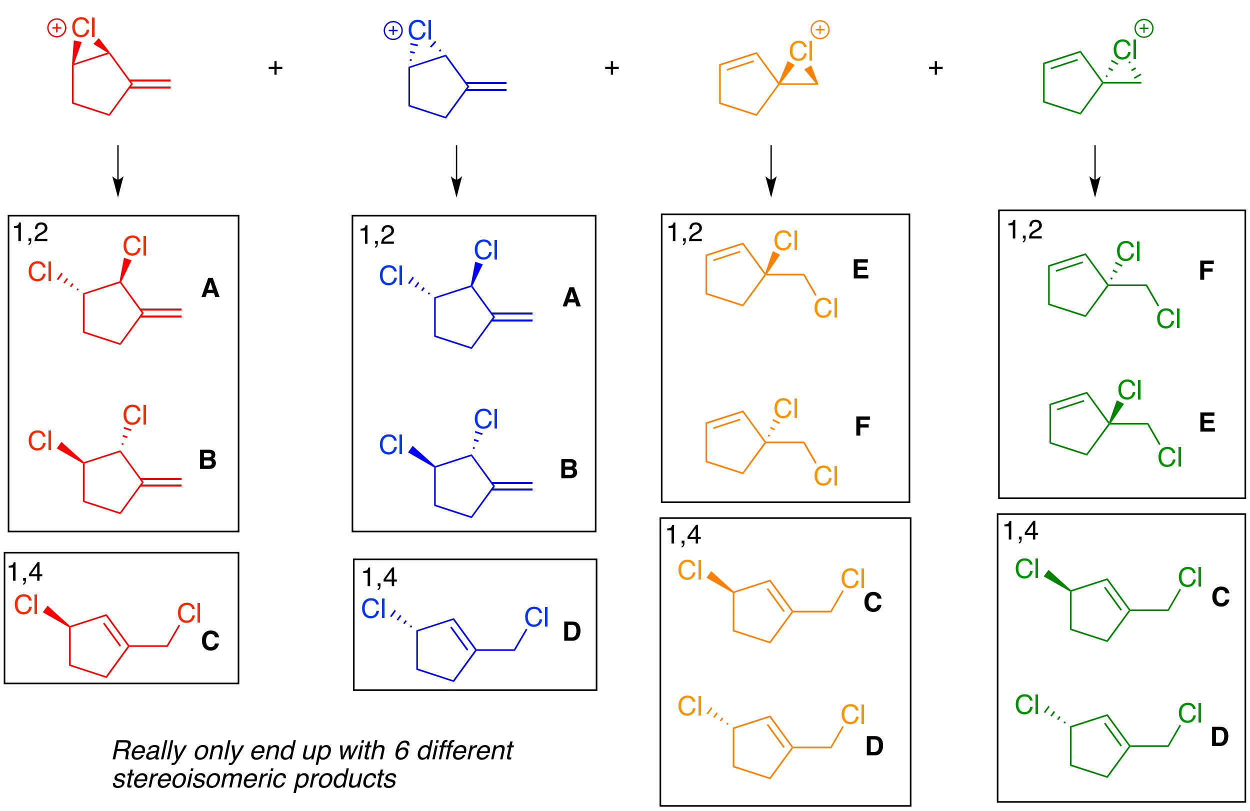


6) Provide a full electron pushing mechanism for the reaction below. Label the 1,2- and 1,4-products.



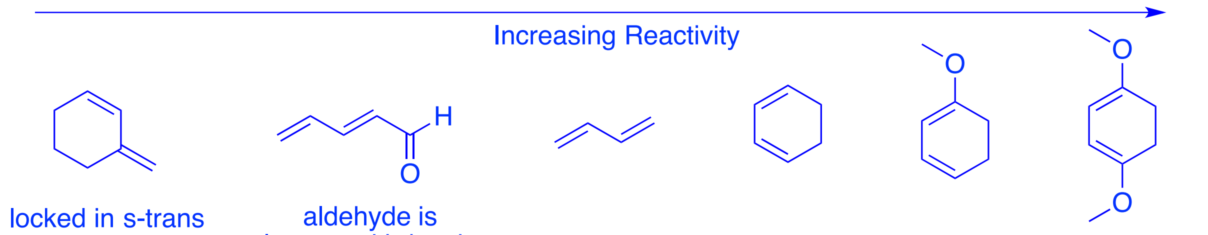

7) Challenge Problem: If you dare, determine all of the possible stereoisomers that could be formed in the reaction above. *Don't worry, I would not put this on an exam.*



## **The Diels-Alder Reaction**

8) Rank the dienes below in order of increasing reactivity in a normal Diels-Alder reaction.

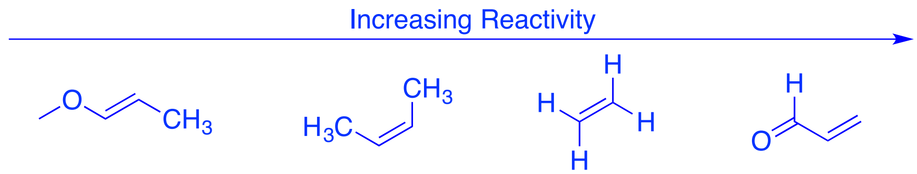
Electron donating groups like methyl (weakly) and methoxy (strongly) on the diene increase the rate of the D-A Rxn. Also, s-cis is more reactive than s-trans.




locked in s-trans (can not react) | aldehyde is electron withdrawing | These three are locked in s-cis. Adding $OCH_3$ groups increases the reactivity

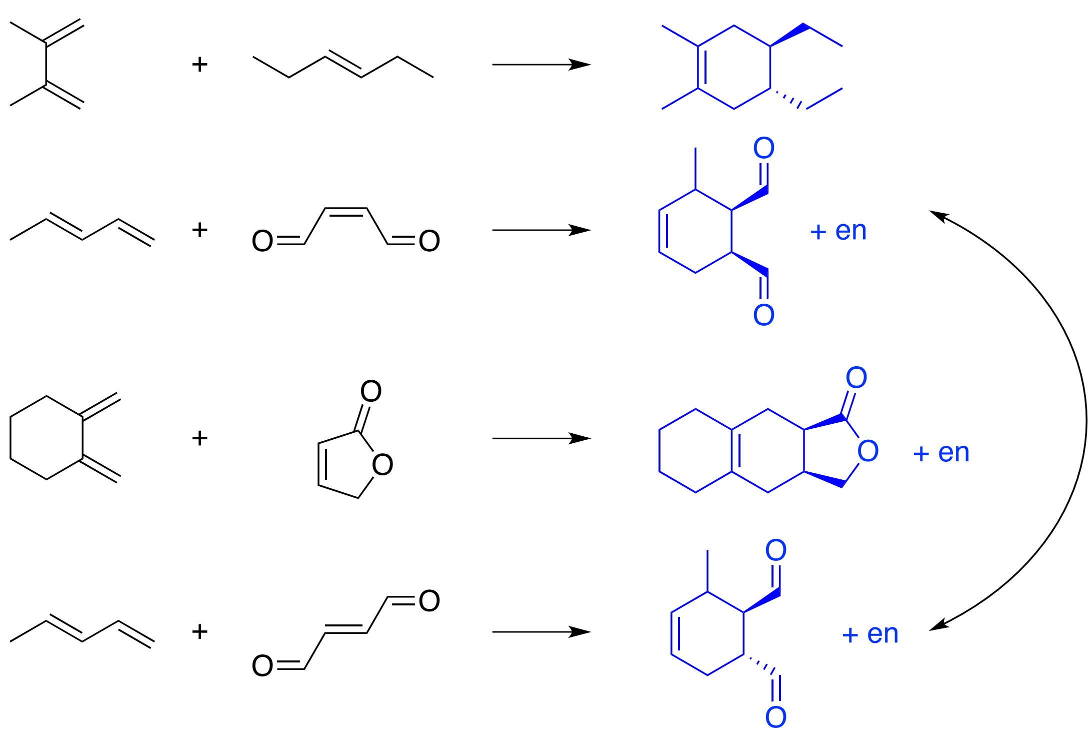
9) Rank the dienophiles below in order of increasing reactivity in a normal Diels-Alder reaction.

Electron withdrawing groups on the dienophile increase the reaction rate. Aldehyde is a strong electron withdrawing group. H is a very weak electron withdrawing group.



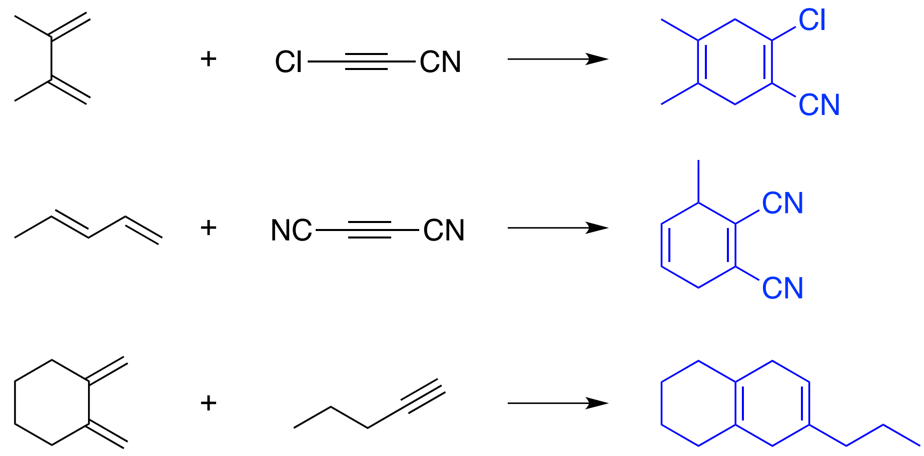

10) Predict the product for each of the Diels-Alder Reactions shown below.

*Basic Reactions*

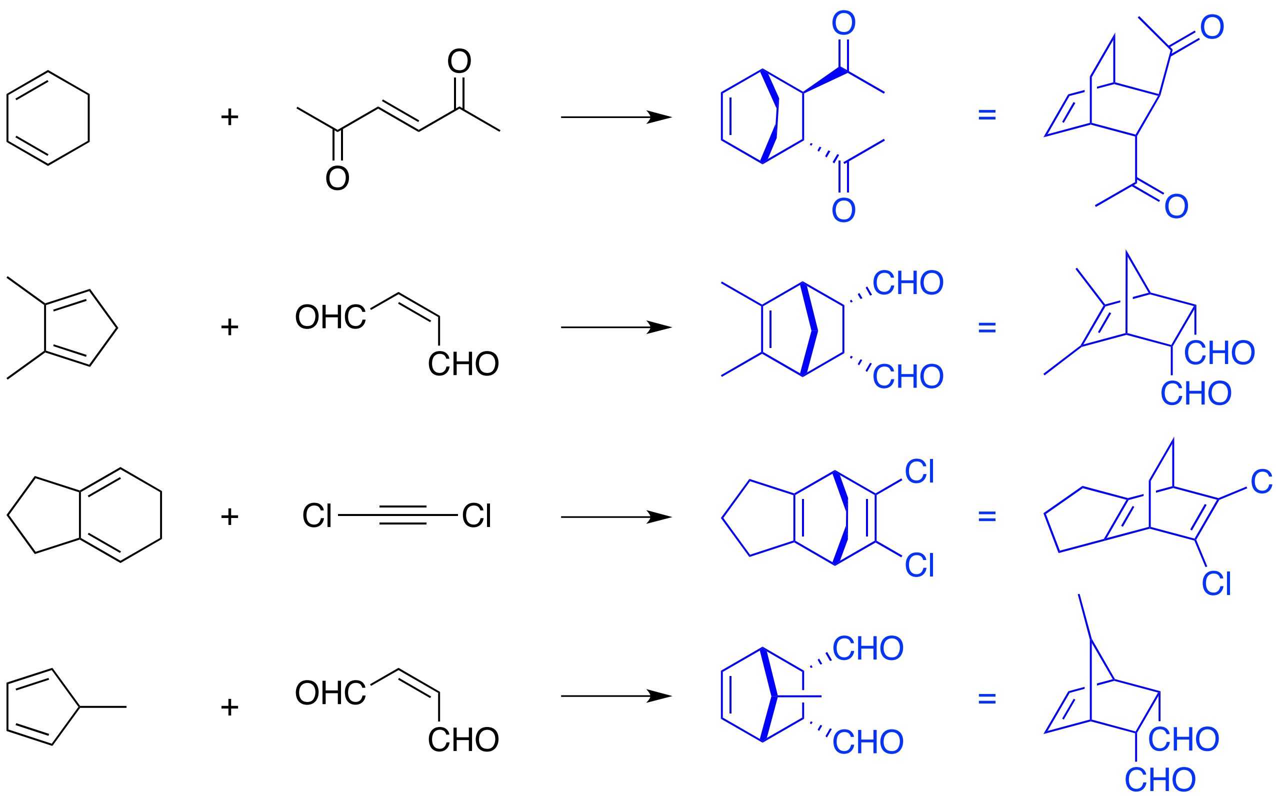



These actually have another stereocenter formed at the top carbon of the ring, but determining the stereochemistry at that position is beyond the scope of the course.

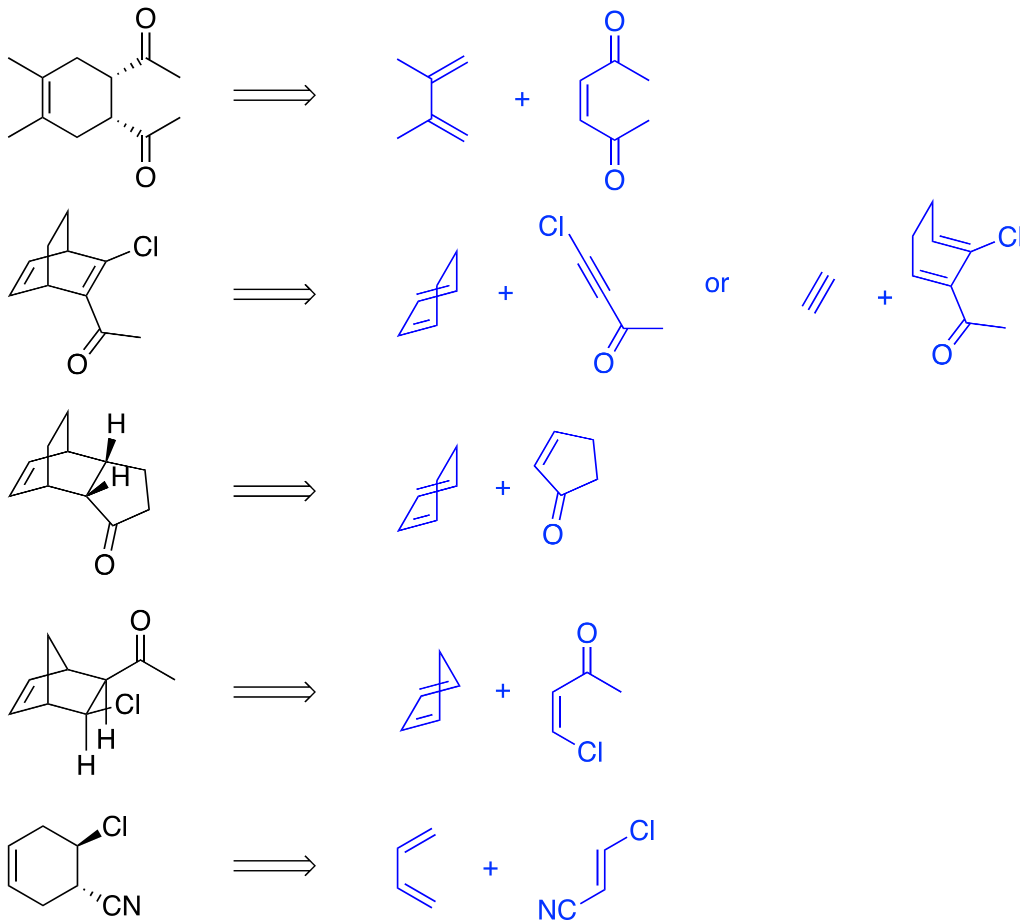
*Reactions with an Alkyne Dienophile*




*Reactions Involving Cyclic Dienes*



11) Determine the starting materials that could have been used to synthesize each of the Diels-Alder adducts shown below.



12) Fill in the empty boxes in the synthetic scheme below. Yes, I have thrown in some organic I reactions. Remember, you will be taking the ACS final exam, which includes both organic I and II material.