



CHEMISTRY 2600

Topic #5: Addition Reactions of Conjugated Dienes

Fall 2018

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Different Kinds of Dienes

- When a molecule contains multiple π -bonds, their reactivity is dictated in part by their relative locations in the molecule:
 - An **isolated double bond** is separated from all other π -bonds by at least one tetrahedral carbon atom. It is its own π -system and reacts independently of any other π -systems in the molecule.
 - A **conjugated double bond** is part of an extended π -system which reacts as a single entity. This is usually characterized by alternating single and double bonds.
 - A **cumulated double bond** is one of two double bonds involving the same carbon atom. The two π -systems are perpendicular and react completely independently.



Different Kinds of Dienes

- According to molecular orbital (MO) theory^{*}, all π -symmetric orbitals in a π -system combine to give a set of π -MOs in which:
 - The number of π -MOs is equal to the number of p orbitals which combined to make them. This means you have one π -MO per atom in the pi system.
 - In a linear π -system, # energy levels = # π -MOs.
 - In a cyclic π -system, use a Frost circle to predict energy levels; the polygon should always point down.
 - The number of delocalized π -electrons is equal to 2 electrons per double bond + 2 electrons per **lone pair that is part of the π -system**. *We are primarily interested in the HOMO and LUMO of any given π -system, so make sure you count your electrons carefully to correctly identify the HOMO and LUMO!*

^{*} Sorrell implies that MOs can be made from hybridized orbitals. This is a case of mixing two different (and largely incompatible) bonding theories and drives the physical chemists nuts! ☺
The σ (and σ^*) MOs of any nonlinear molecule are not trivial to predict and do **not** resemble what you'd predict using hybridization and VB theory. Fortunately, we rarely need to know what they look like – and, if we do, we just ask HyperChem!
All we need to know is how the energies of the σ - and π -MOs generally compare: σ , π , nonbonding, π^* , σ^*



Different Kinds of Dienes

- The shape of each MO can be predicted using symmetry and nodes:
 - The lowest energy π -MO has all p orbitals aligned in phase, giving no nodes perpendicular to the plane of the π -system.
 - The next π -MO will have one node perpendicular to the plane of the π -system, the next π -MO will have two such nodes, etc.
 - The highest energy π -MO will have every p orbital out-of-phase with the p orbitals on both neighbouring atoms.
 - As long as the π -system is symmetric, every MO will be either **symmetric** or **antisymmetric** (lobes are symmetric in shape, but phases are opposite).
 - It's usually easiest to
 - 1) Draw the highest and lowest energy π -MOs
 - 2) Count the perpendicular nodes in those π -MOs.
 - 3) Determine how many perpendicular nodes ought to be in each other π -MO.
 - 4) Draw the remaining π -MOs, remembering that the nodes must be spaced evenly if the π -system is symmetric.

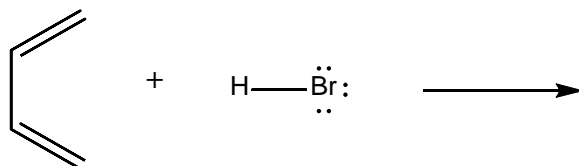


Different Kinds of Dienes

- Draw a valence π -MO energy level diagram and the π -MOs for 1,3-butadiene.

Electrophilic Addition Reactions of Dienes

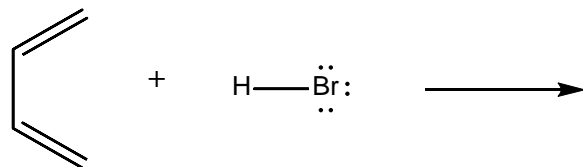
- When an electrophilic addition reaction is performed on a diene, the electrons are donated from the HOMO. As we saw on the previous page, that's a pi bonding MO involving all four atoms in the diene.
- The resulting carbocation has a positive charge that is delocalized over two carbon atoms. We can show this by drawing two resonance structures:



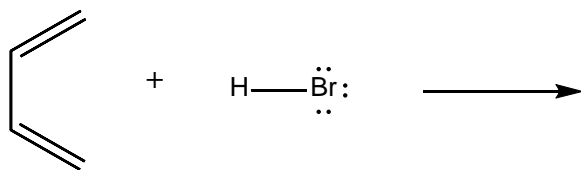
- This is referred to as an **allylic carbocation**, and the nucleophile can attack **either** of the two positively charged carbon atoms. 6

Electrophilic Addition Reactions of Dienes

- Since the carbocation will more closely resemble the better resonance structure, attack of the nucleophile at that atom is faster. This gives the kinetic product:



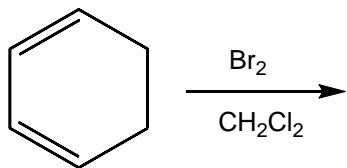
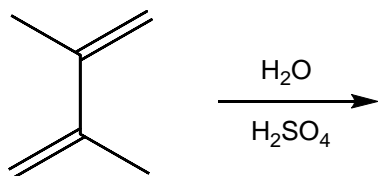
- The product with the more substituted double bond is the thermodynamic product:



- If the same product is both kinetic and thermodynamic, it will be the major product. If the kinetic and thermodynamic products are different, how do we favour each?

Electrophilic Addition Reactions of Dienes

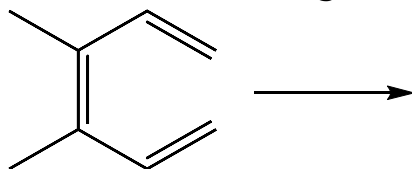
- For each of the following reactions, predict the 1,2-addition product and the 1,4-addition product. Also, indicate which you would expect to be kinetically favoured and which would be thermodynamically favoured.



Pericyclic Reactions

- Polyenes (including dienes) can also undergo a variety of **pericyclic reactions** in which the π -electrons rearrange to form new bonds:

- In an **electrocyclic reaction**, a single conjugated π -system is used to form a σ -bond connecting the two ends of the former π -system:



- In a **sigmatropic rearrangement**, two π -systems on the same molecule are used to "migrate" a C-C σ -bond:

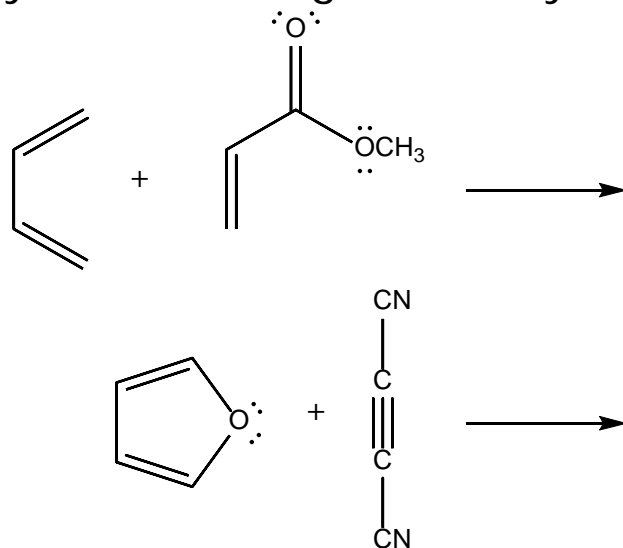


- In a **cycloaddition**, one π -system is "added across" another π -system (often on a different molecule), creating a ring:



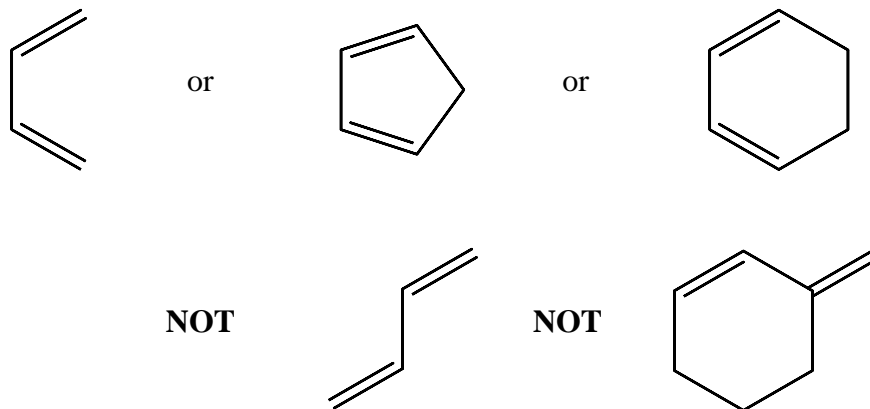
Diels-Alder Reactions

- One of the most important pericyclic reactions is a type of cycloaddition called the **Diels-Alder reaction**:
 - This is a [4+2] cycloaddition, meaning that one reactant contributes 4 π -electrons while the other contributes 2 π -electrons.
 - A Diels-Alder reaction therefore must involve a **diene** and an alkene (or alkyne), typically referred to as a **dienophile**.
 - The reaction is concerted. All 6 electrons move at once.
 - A Diels-Alder adduct (addition product) always contains a cyclohexene ring formed by addition of the dienophile to the diene:



Diels-Alder Reactions: Dienes and Dienophiles

- In order for a diene to react in a Diels-Alder reaction, it must adopt an *s-cis* (short for “sigma cisoid”) conformation:



- Many dienes can also act as dienophiles. You can't buy a bottle of pure 1,3-cyclopentadiene; you buy dicyclopentadiene which must be “cracked” to generate the diene via a retro-Diels-Alder reaction:



Diels-Alder Reactions: Dienes and Dienophiles

- As seen on the previous pages, one new cyclohexene ring is formed in a Diels-Alder reaction; however, all pre-existing rings are preserved.
 - If the diene is cyclic, the Diels-Alder adduct will be bicyclic:

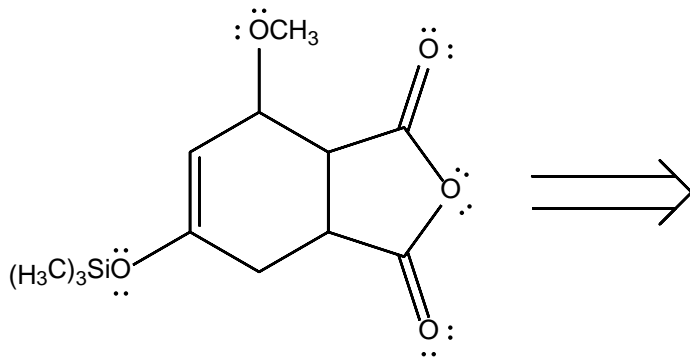
 - If the dienophile is cyclic, the Diels-Alder adduct will be bicyclic:

 - If both diene and dienophile are cyclic, the adduct will be tricyclic:

- In this way, the Diels-Alder reaction can be used to quickly assemble relatively complex molecules.

Diels-Alder Reactions: Dienes and Dienophiles

- Dienophiles are usually alkenes; however, they may also be alkynes. When the dienophile is an alkyne, only one π -system is involved in the reaction, so only one π bond is broken. In this case, the newly formed ring is a 1,4-cyclohexadiene ring (*instead of a cyclohexene*).
- To determine what diene and what dienophile reacted to give a Diels-Alder adduct, find the cyclohexene ring and work out which bonds were formed in the reaction:





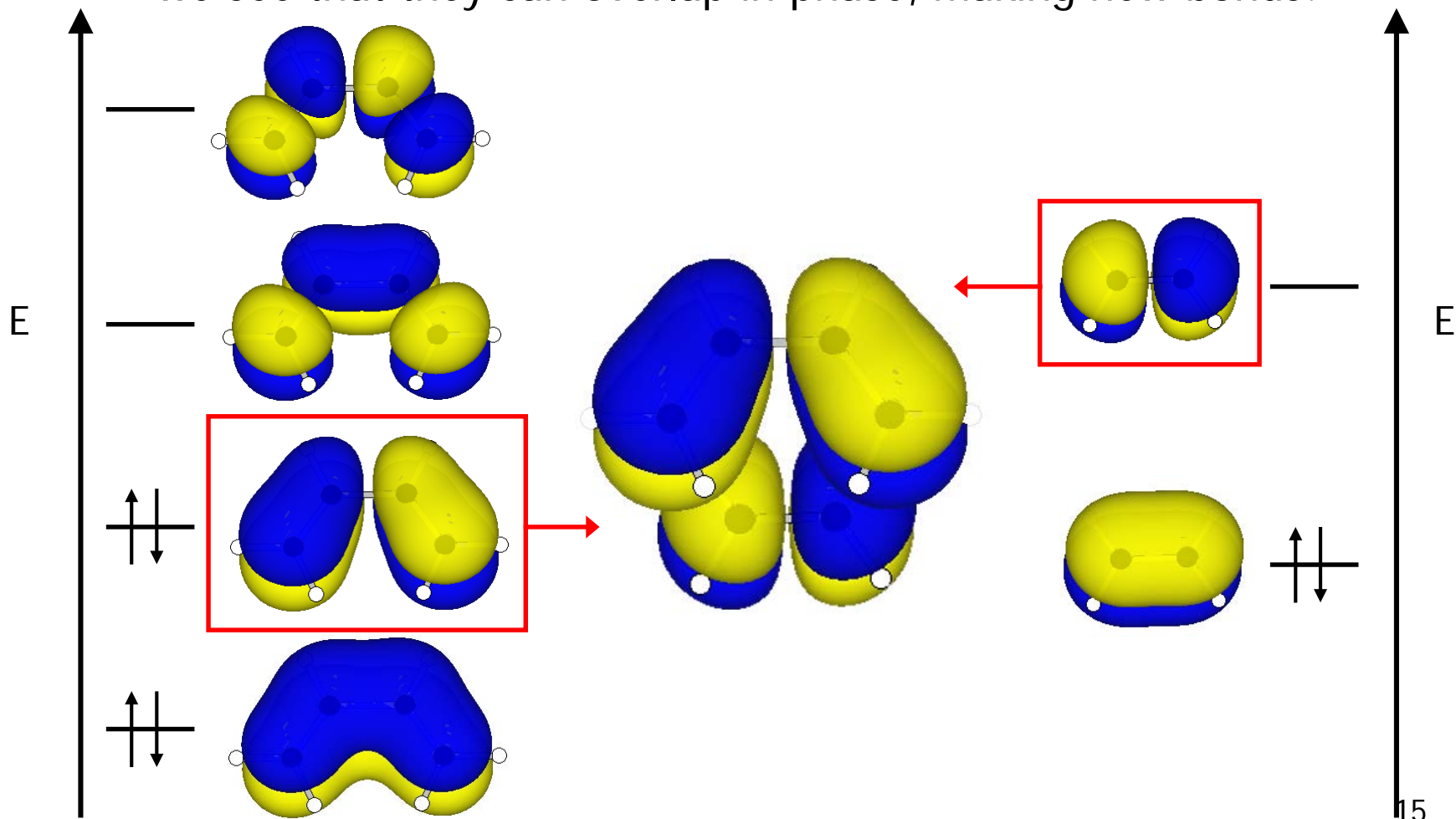
Diels-Alder Reactions: Substituent Effects

- A normal Diels-Alder reaction involves the HOMO of the diene and the LUMO of the dienophile. Since a reaction is easiest when electrons are donated from a high energy MO (HOMO) into a low energy MO (LUMO), we want:
 - A diene with a high-energy HOMO. This means electron-donating groups to make the diene electron-rich!
 - A dienophile with a low-energy LUMO. This means electron-withdrawing groups to make the dienophile electron-poor!

It is possible to perform an "inverse electron demand" Diels-Alder reaction where the dienophile donates electrons to the diene. In this case, the dienophile would have to be electron-rich while the diene would be electron-poor. This is not the norm.

Diels-Alder Reactions: Substituent Effects

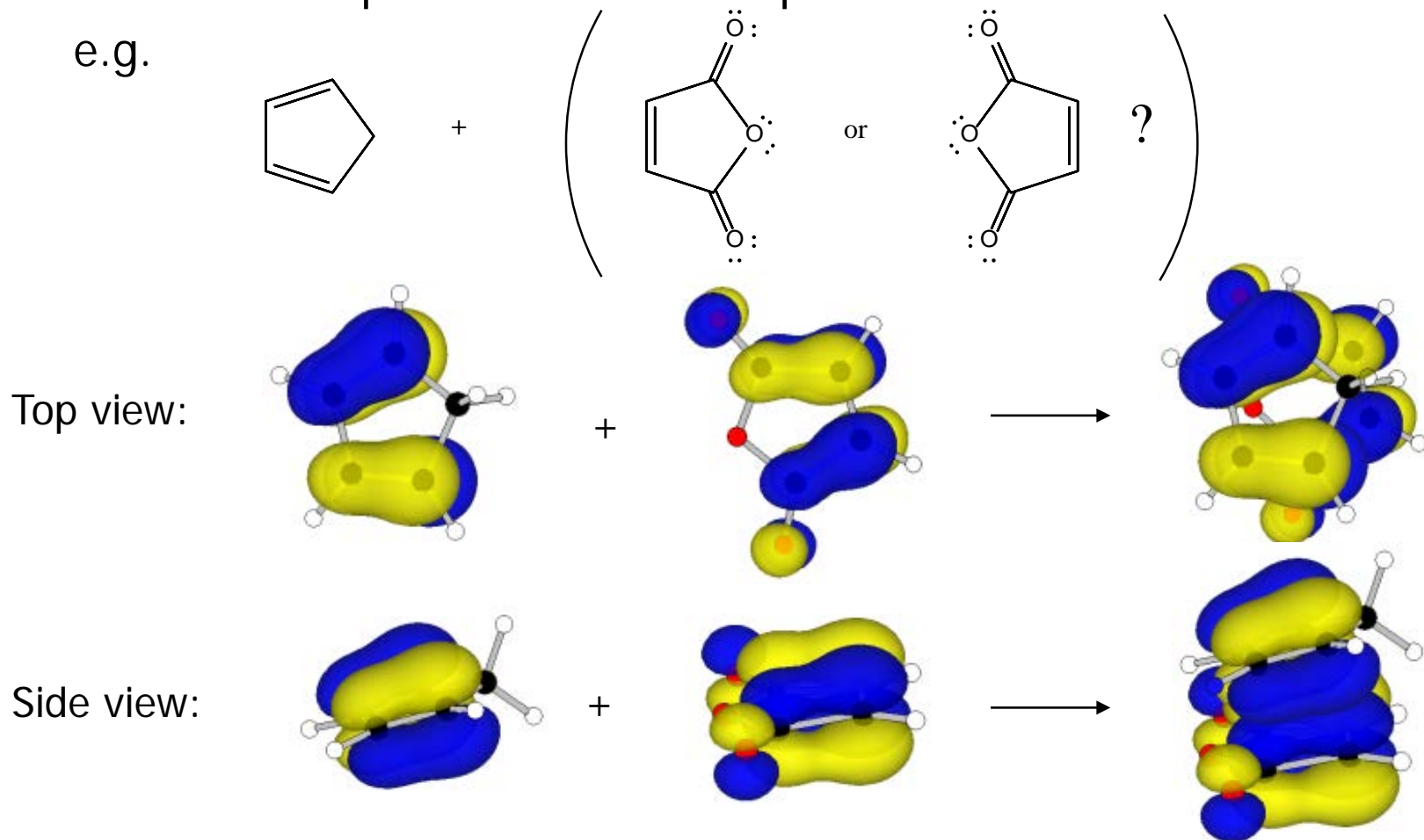
- Looking at the HOMO of a diene and the LUMO of a dienophile, we see that they can overlap in phase, making new bonds:



Diels-Alder Reactions: Stereochemistry

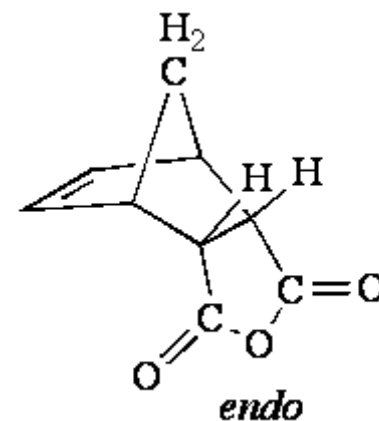
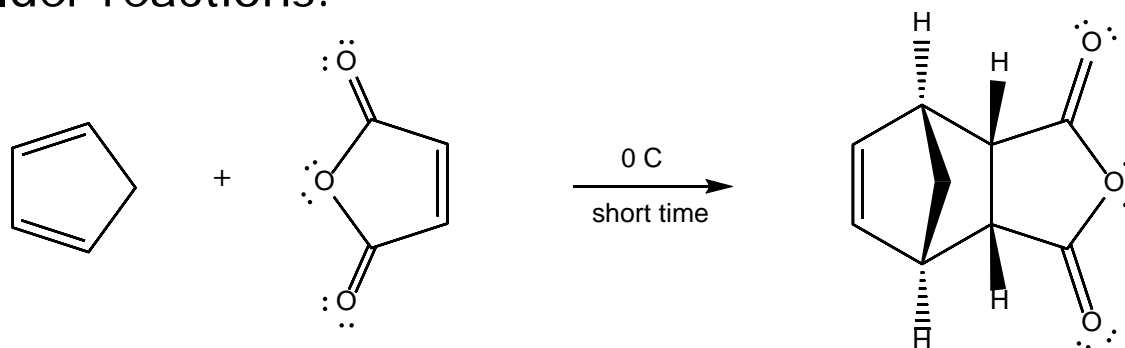
- π orbitals are stabilized by "stacking". If the dienophile has any substituents with double (or triple) bonds, it tends to orient itself such that the pi bond stacks on top of the back of the diene.

e.g.



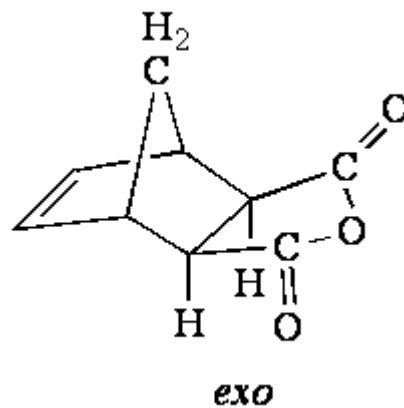
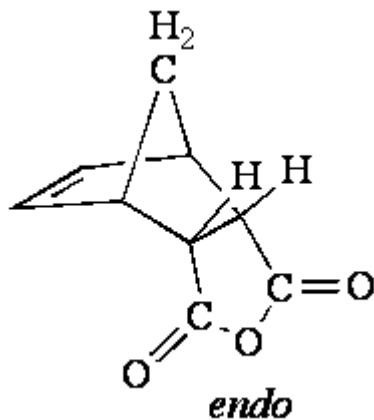
Diels-Alder Reactions: Stereochemistry

- This gives the *endo* adduct, which is the kinetic product of most Diels-Alder reactions.



Diels-Alder Reactions: Stereochemistry

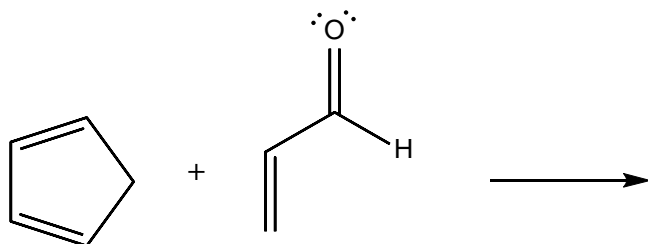
- The alternative to the *endo* product is the *exo* adduct (which happens to be the thermodynamic product). Since Diels-Alder reactions are reversible, the *exo* adduct can be favoured by _____ while the *endo* adduct can be favoured by _____.
- What is the stereochemical relationship between the *exo* and *endo* adducts which can be produced from the same Diels-Alder reaction?



Note that both adducts are racemic! There is no reason why the dienophile couldn't have approached the diene from above!^{1,8}

Diels-Alder Reactions: Stereochemistry

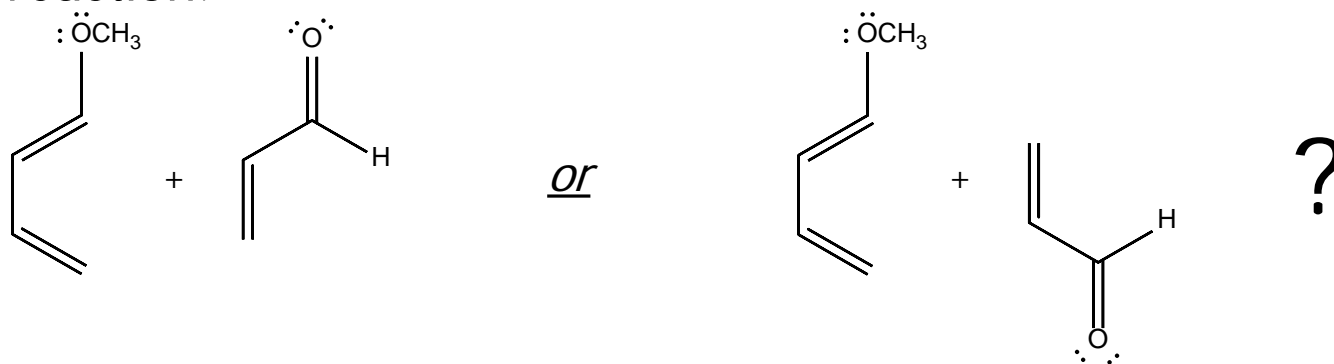
- Draw the *endo* and *exo* products for the following reaction:



- In which Diels-Alder reactions would the adducts **not** be classified as *endo* or *exo*?

Diels-Alder Reactions: Regiochemistry

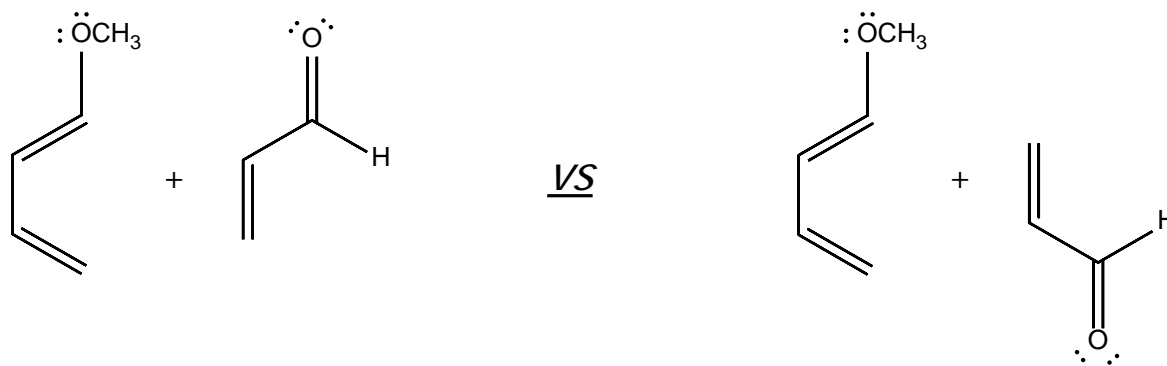
- When both the diene and dienophile in a Diels-Alder reaction are unsymmetrical, we must also consider the regiochemistry of the reaction.



- The rule of thumb is that the strongest EWG on the dienophile and the strongest EDG on the diene will be either 1,2- or 1,4-disubstituted. *You may hear this referred to as the "ortho or para rule" – even though that terminology isn't really appropriate given that the product is not a benzene ring.*

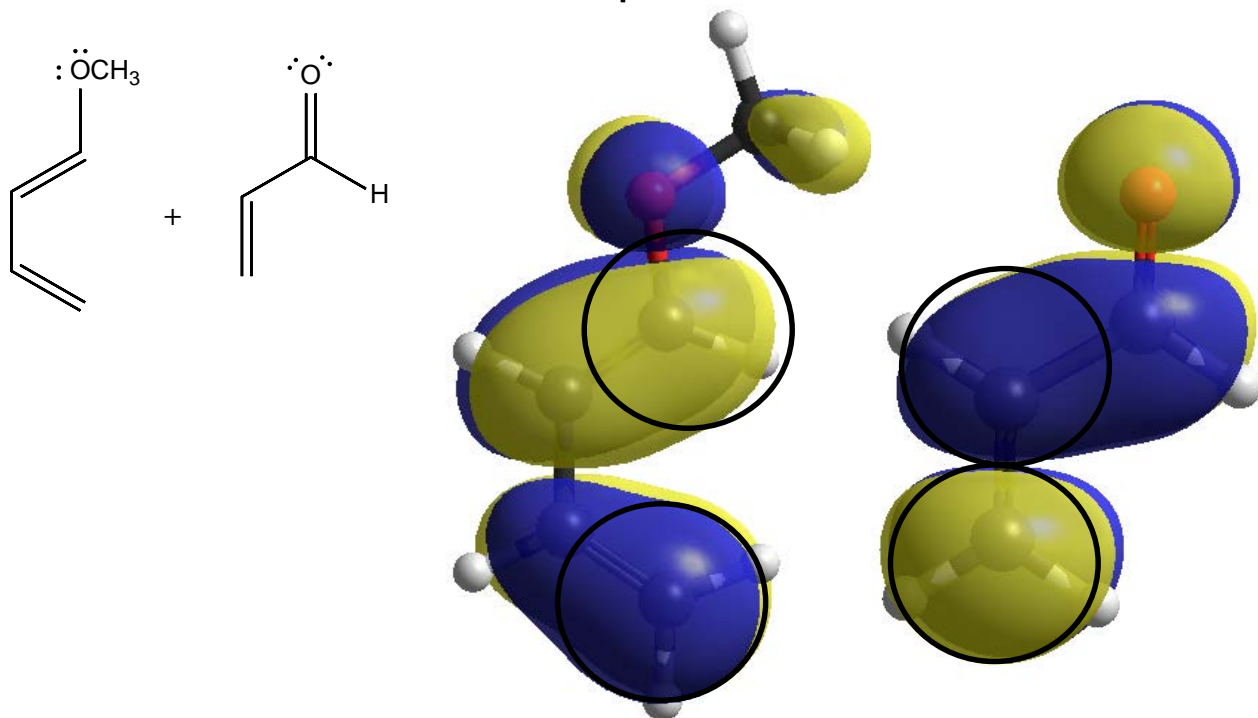
Diels-Alder Reactions: Regiochemistry

- We can use resonance structures to rationalise the preference for the 1,2-regioisomer over the 1,3-regioisomer:



Diels-Alder Reactions: Regiochemistry

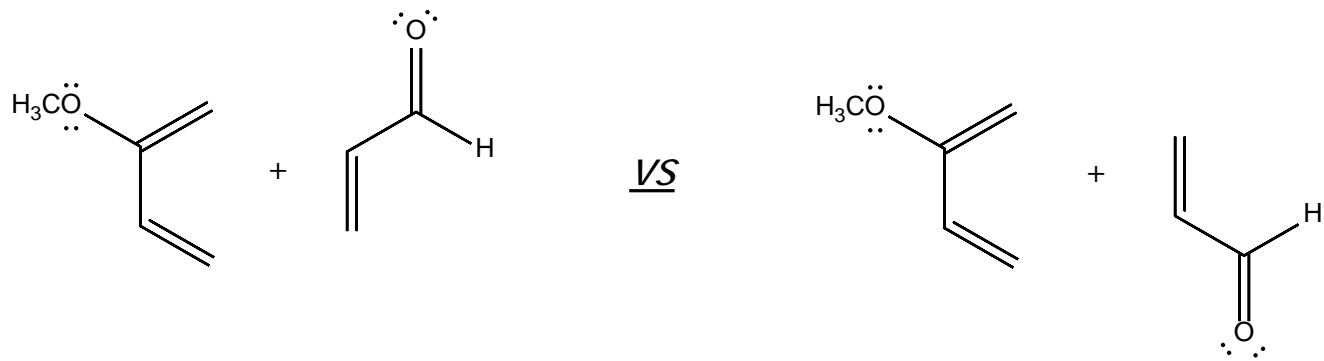
- We can also look at the molecular orbitals to see how to get the largest lobe on the diene's HOMO to overlap with the largest lobe on the dienophile's LUMO:



- The black circles are all the same size – which helps us see which lobes are larger – but it's certainly not immediately obvious. That's why the resonance arguments are still useful. 23

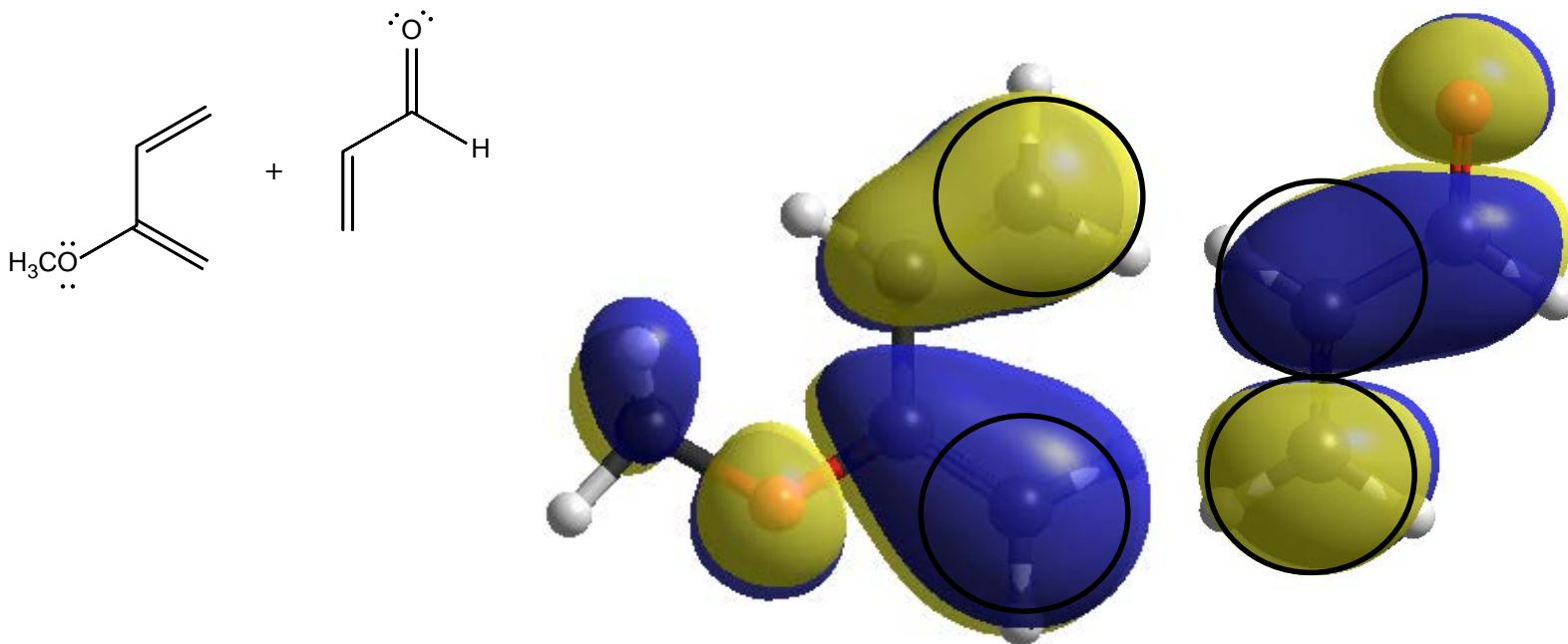
Diels-Alder Reactions: Regiochemistry

- The same type of resonance argument works to rationalise the preference for the 1,4-regioisomer over the 1,3-regioisomer:



Diels-Alder Reactions: Regiochemistry

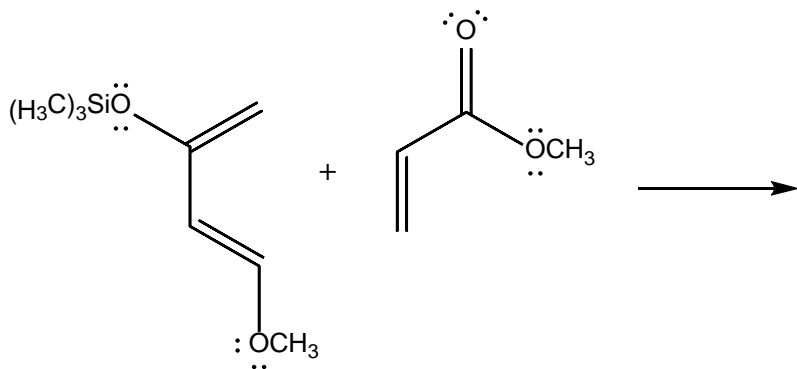
- Again, we can look at the molecular orbitals to see how to get the largest lobe on the diene's HOMO to overlap with the largest lobe on the dienophile's LUMO:



- Again, the black circles are all the same size to help us see which lobes are larger. It's a little more obvious in this case than the last one.

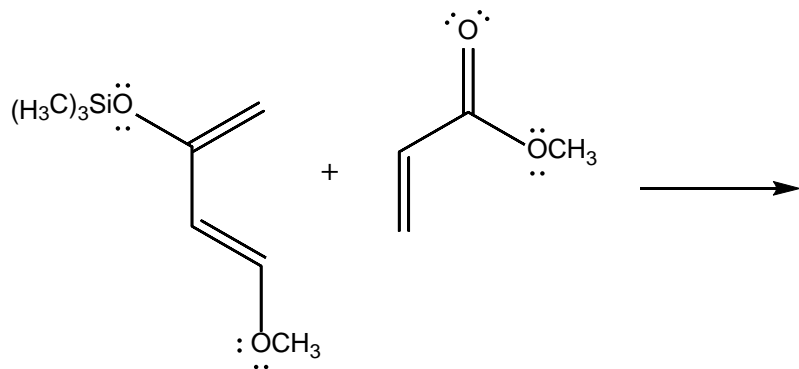
Diels-Alder Reactions: Putting It All Together

- Considering all stereochemical and regiochemical factors, what is the major product of the reaction below at low temperature?



Diels-Alder Reactions: Putting It All Together

- What is the major product of the same reaction performed at high temperature?



Diels-Alder Reactions: Putting It All Together

- Which of the compounds below could you prepare via a Diels-Alder reaction? For those that could be made this way, identify the diene and dienophile.

