

CHEM 222 section 01

LECTURE #15

Tues., Oct.23, 2007

Lecture topics & readings

Today's class

- diene reactivity: Diels-Alder reactions

Before next class

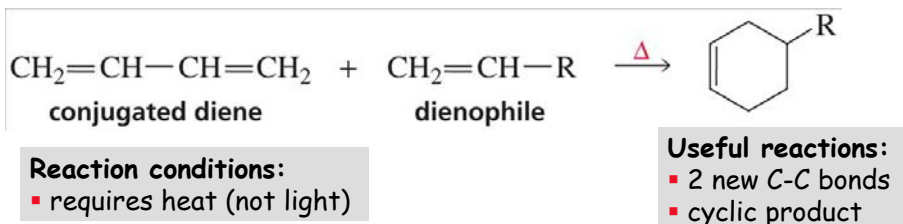
- build molecular models \Rightarrow visualize Diels-Alder rxns
- read & review all Ch.7 topics

Next class

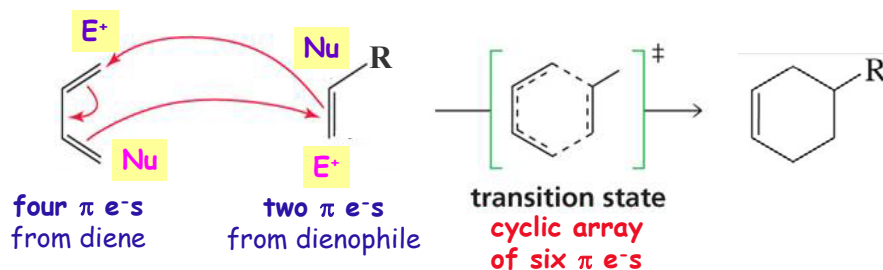
- rxns of benzene: Ch. 14.1-...

- (1) Midterm exam: Tues. Oct. 30 (some mult.choice, some written)
everything to end of NMR...

Classic diene rxn: Diels-Alder 1,4-cycloadditions (7.12)



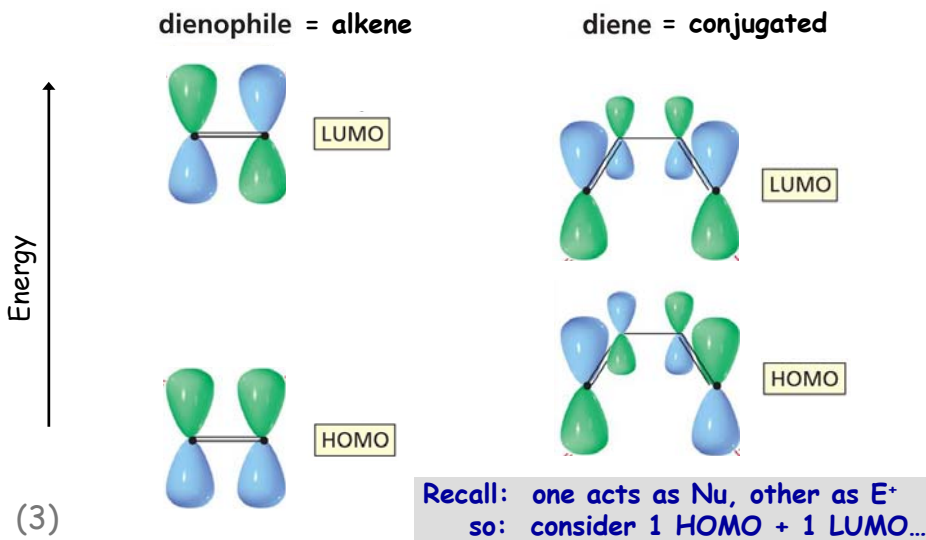
*Mechanism: concerted, via cyclic shift of e⁻s = a pericyclic rxn
[4+2] cycloaddition*



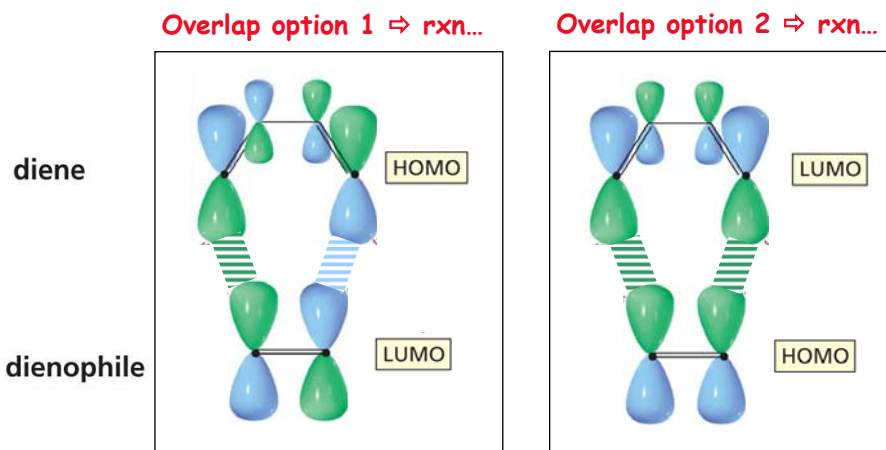
Use molecular orbitals to understand pericyclic rxns

Pericyclic reactions: obey **conservation of orbital symmetry**

- rxn occurs because of **overlap of in-phase orbitals**
- consider the HOMO & LUMO of each reactant:



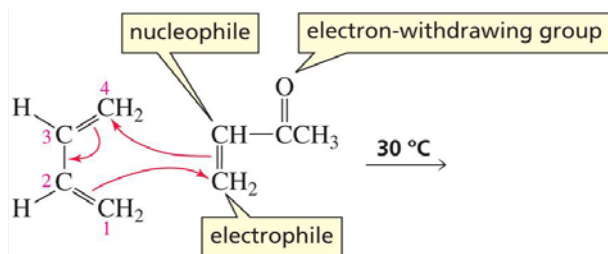
Diels-Alder rxn due to in-phase overlap of HOMO & LUMO



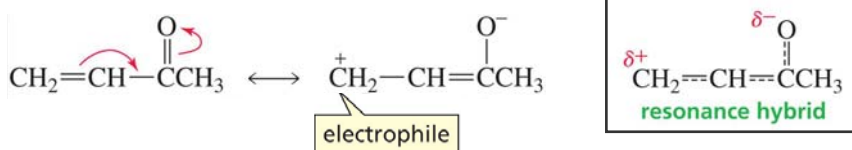
Notice:

- one molecule "lands on" the other ⇒ **syn addition** wrt to both reactants
- both options lead to **in-phase, end-on orbital overlap** ⇒ 2 σ -bonds form
- π -e⁻s in diene rearrange simultaneously (not shown) ⇒ 1 new π -bond

Diels-Alder rxn: [4+2] cycloaddition with 1,4- regiochem.

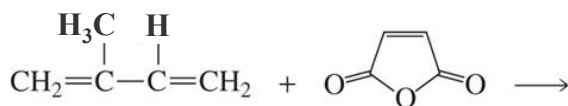


resonance contributors of the dienophile



Dienophiles = more reactive with EWG substituents

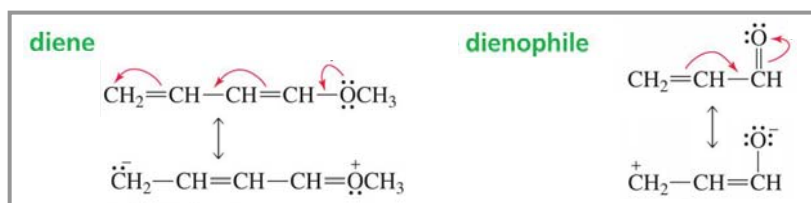
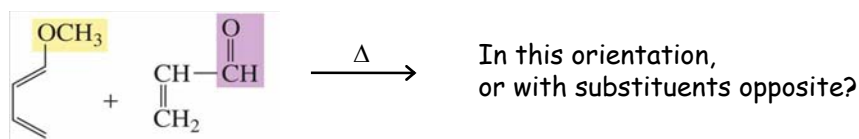
Maleic anhydride - a reactive dienophile



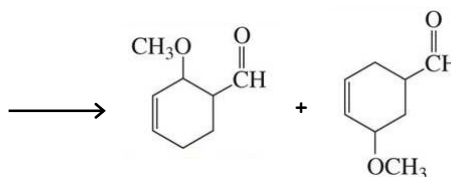
Stereochem.: configuration of reactants does not change during rxn

- syn addition from top *OR* bottom \Rightarrow new asymmetric centres = racemic
- dienophile: if substituents are cis \Rightarrow will remain cis in product
- diene: if substituents are s-cis \Rightarrow will remain cis in product

Predicting products with asymmetric dienes & dienophiles

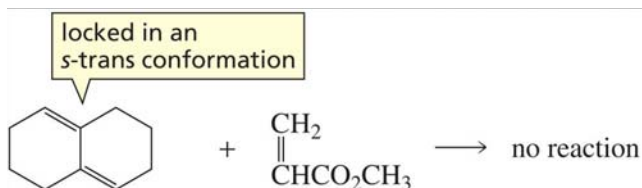


So: which is the major product?

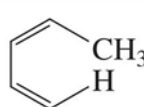
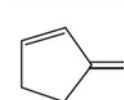
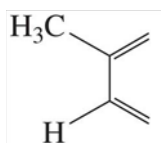


Hint: draw resonance structures to reveal electrostatic steering

Diels-Alder rxn requires diene in s-cis conformation

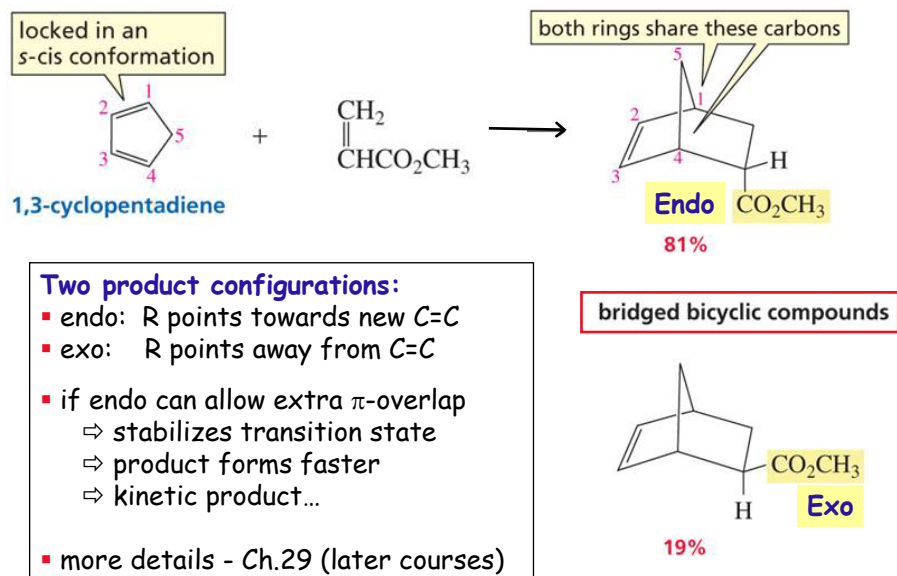


Rank these dienes in order of increasing reactivity to a dienophile:



Diene = more reactive if more s-cis conformation (usually more s-trans...) e.g., locked in place OR small substituents pointing "in"...

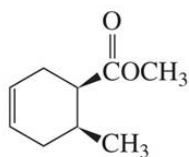
Locked s-cis dienes yield bicyclic products: endo vs exo



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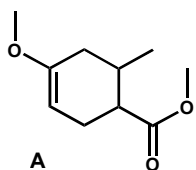
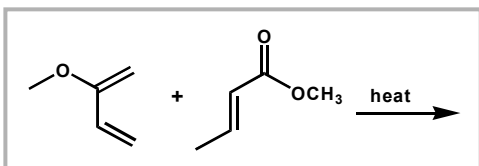
Retrosynthetic analysis of Diels-Alder 1,4-cycloadditions

What diene and what dienophile were used to synthesize the following compound?

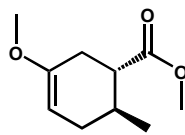


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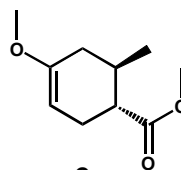
Which compound is the expected product of this rxn?



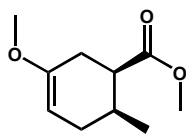
A



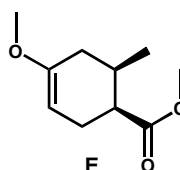
B



C



D



E

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