

The Diels-Alder Reaction

Synthetic method for preparing compounds containing a cyclohexene ring

In general...



conjugated diene

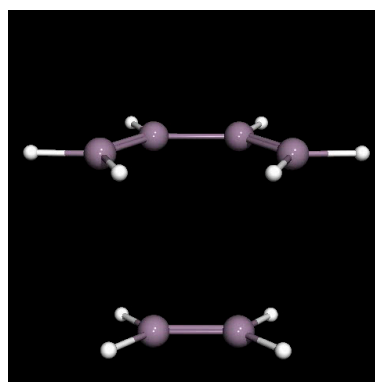
alkene (dienophile)

cyclohexene

via



transition state



Mechanistic features

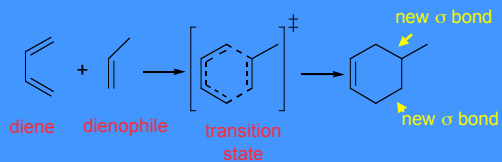
concerted mechanism

[4+2] cycloaddition

pericyclic reaction

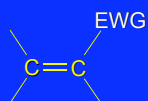
a concerted reaction that proceeds through a cyclic transition state

Only the s-cis conformation of the diene can react

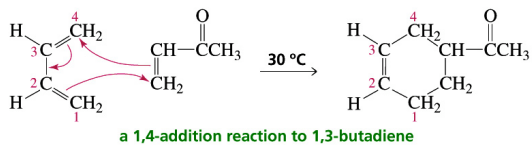
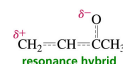
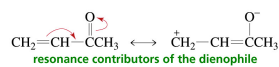
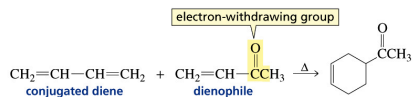


What makes a reactive dienophile?

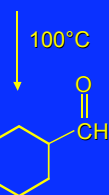
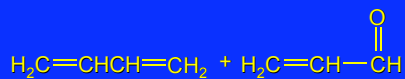
The most reactive dienophiles have an electron-withdrawing group (EWG) directly attached to the double bond.



Typical EWGs

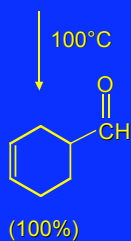
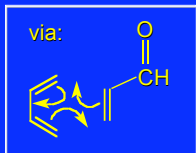
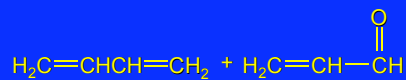


Example

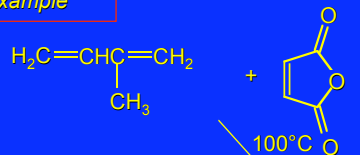


(100%)

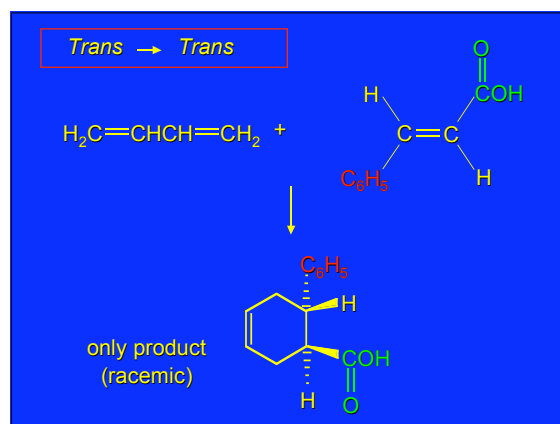
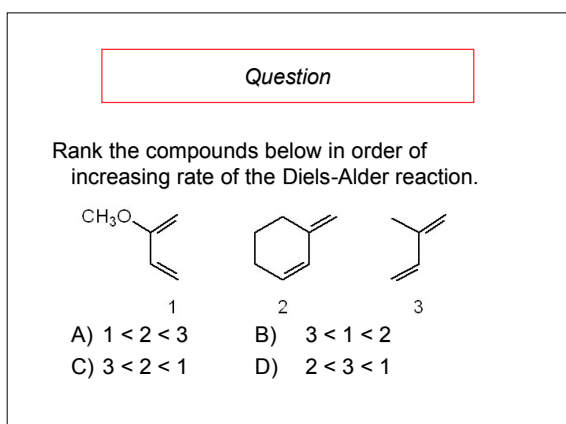
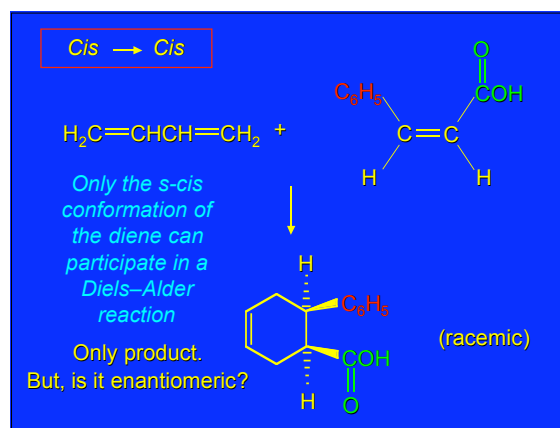
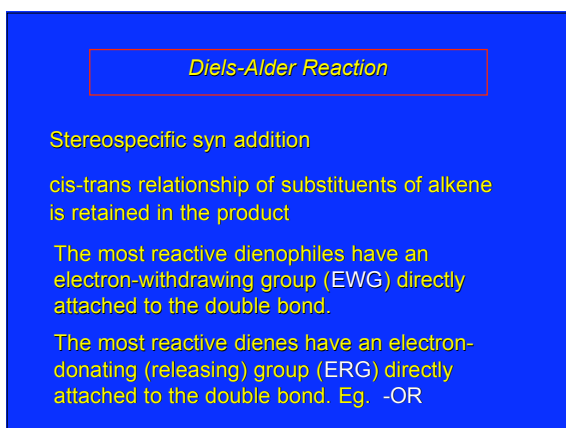
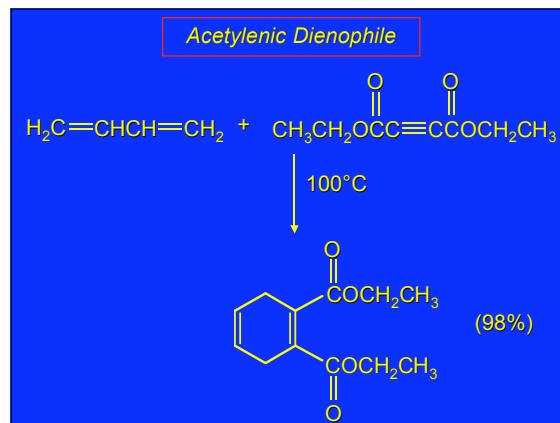
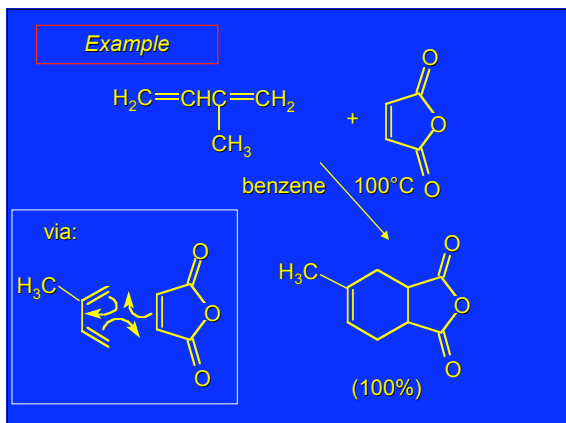
Example



Example

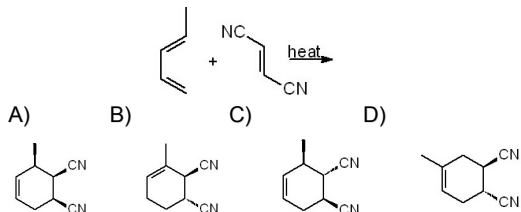


(100%)

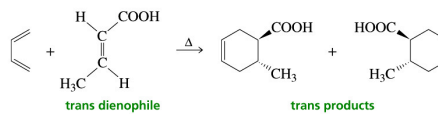
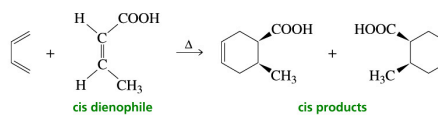


Question

What is the product of the Diels-Alder reaction that occurs between the reactants shown here?

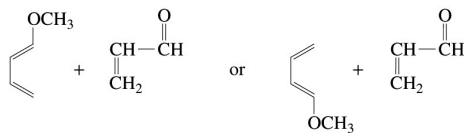


Stereospecific, concerted, syn addition:

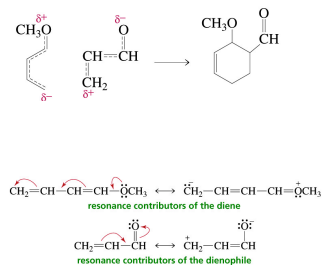


Predict the reaction products:

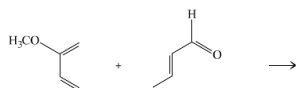
1. Consider the alignment of the reactants



2. Consider the charge distribution in each of the reactants



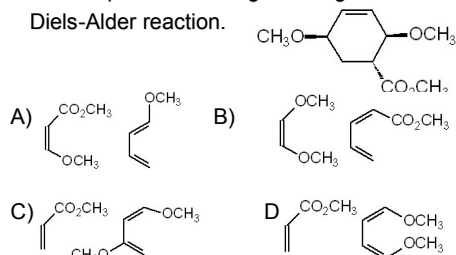
Click on all of the atoms that have an unhybridized p-orbital, and then click "Done."



Done

Question

Select the correct starting materials to make the compound at the right through the Diels-Alder reaction.

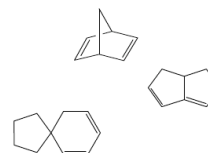


Cyclic dienes yield bridged bicyclic Diels-Alder adducts.

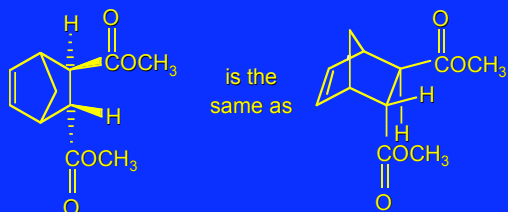
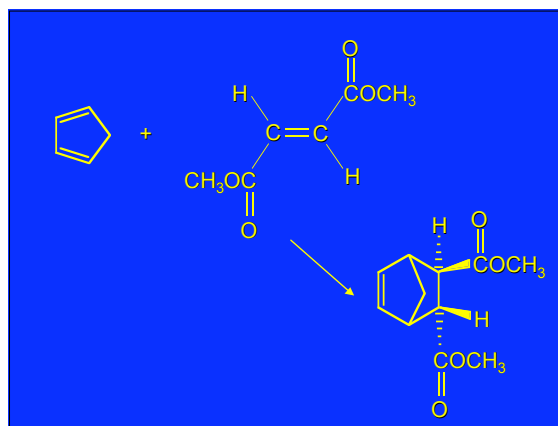
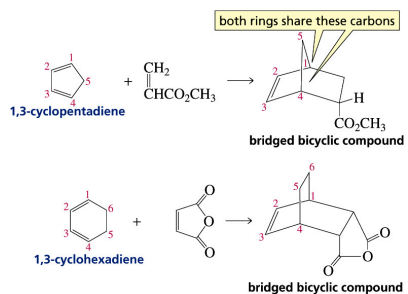


☉ Touch a label on the left to see the corresponding atoms, groups, or molecules.

bicyclic compounds
 bridged bicyclic compound
 fused bicyclic compound
 spirocyclic compound
 isolated double bonds
 conjugated double bonds
s-cis conformation
s-trans conformation



Since only cis dienes can participate in Diels-Alder reactions: 5- & 6- membered rings are ideal



The π Molecular Orbitals
 of
 Ethylene and 1,3-Butadiene

Orbitals and Chemical Reactions

A deeper understanding of chemical reactivity can be modeled using *frontier orbitals* of the reactants.

Electrons flow from the highest occupied molecular orbital (HOMO) of one reactant to the lowest unoccupied molecular orbital (LUMO) of the other.

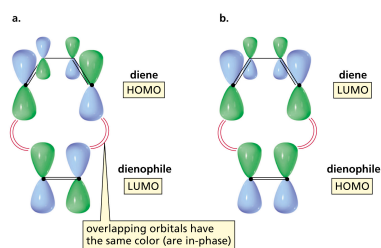
Orbitals and Chemical Reactions



We can illustrate HOMO-LUMO interactions by way of the Diels-Alder reaction between ethylene and 1,3-butadiene.

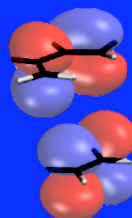
We need only consider only the π electrons of ethylene and 1,3-butadiene. We can ignore the framework of σ bonds in each molecule.

Reactants' HOMO and LUMO



MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene

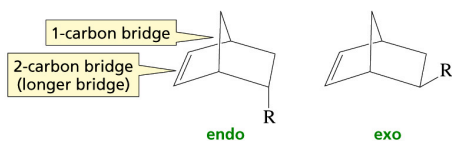


HOMO of 1,3-butadiene and LUMO of ethylene are in phase with one another

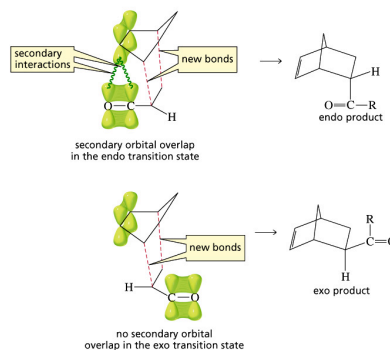
allows σ bond formation between the alkene and the diene

LUMO of ethylene (dienophile)

Two Possible Configurations of Bridged Bicyclic Compounds



Secondary orbital overlap favors the endo product formation



A π Molecular Orbital Analysis
of the
Diels-Alder Reaction

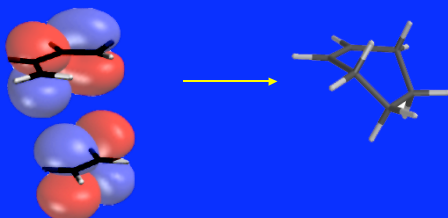
MO Analysis of Diels-Alder Reaction



Inasmuch as electron-withdrawing groups increase the reactivity of a dienophile, we assume electrons flow from the HOMO of the diene to the LUMO of the dienophile.

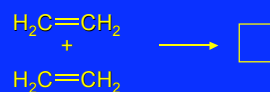
MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene



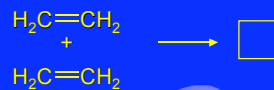
LUMO of ethylene (dienophile)

A "forbidden" reaction

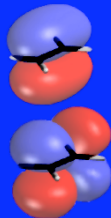


The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions.

A "forbidden" reaction



HOMO-LUMO mismatch of two ethylene molecules precludes single-step formation of two new σ bonds



HOMO of one ethylene molecule

LUMO of other ethylene molecule

Click on a button to indicate whether the following [4+2] cycloaddition reaction occurs under thermal or photochemical conditions.

