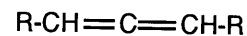
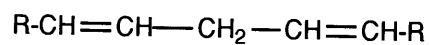
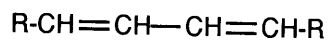


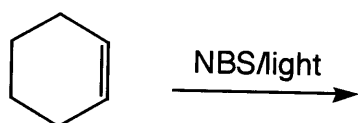
CHAPTER 15: Conjugated Systems, Orbital Symmetry, UV Spectroscopy

Types of Dienes:



Nomenclature: review alkenes - diene

Preparation of Conjugated diene: elimination of HX from allylic halide



Stability of Conjugated Dienes

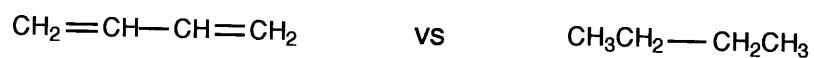
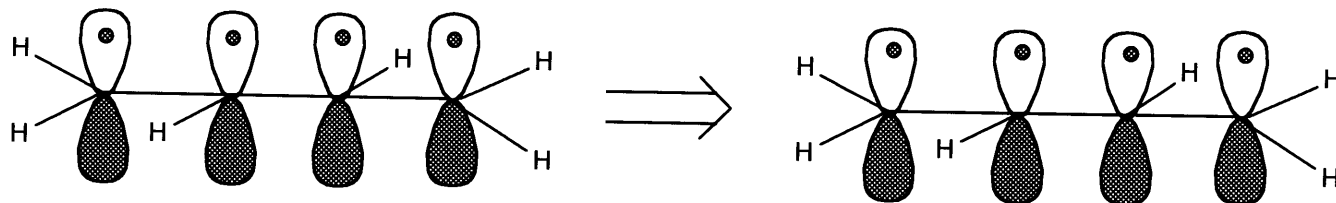
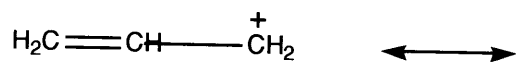
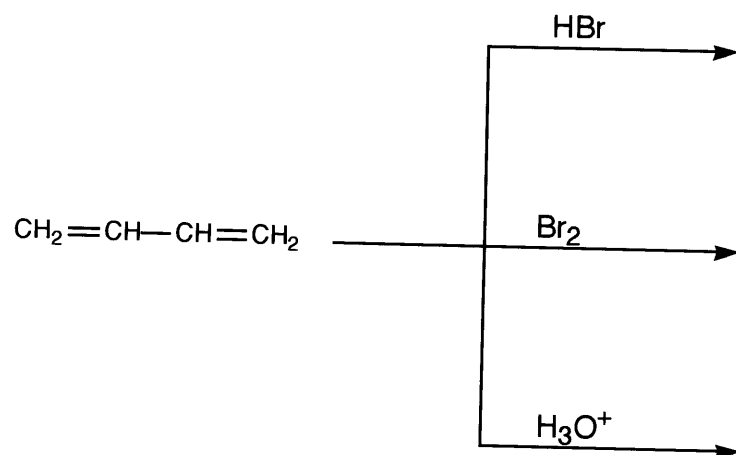
Compare heats of hydrogenation:

1. $CH_2=CH-CH_2CH_3 \xrightarrow{H_2/Pd}$ $\Delta H^\circ_{\text{hydrog}} = 30.3 \text{ kcal/mol}$
2. $CH_2=CH-CH_2-CH=CH_2 \xrightarrow{2 H_2/Pd}$

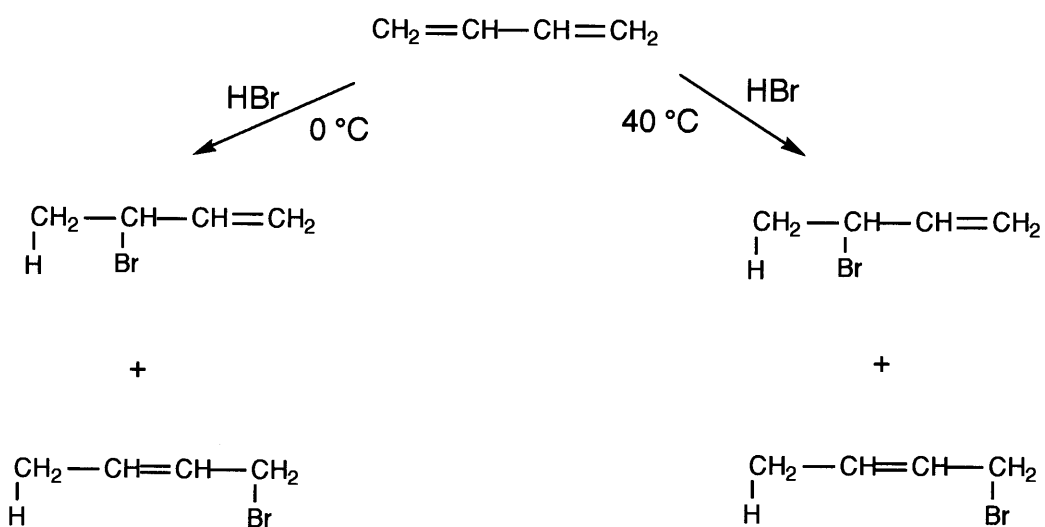
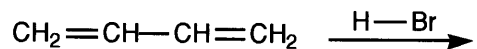
expect:
observe:
3. $CH_2=CH-CH=CH_2 \xrightarrow{2 H_2/Pd}$

expect:
observe:
4. $CH_2=CH-CH=CH-CH_3 \xrightarrow{2 H_2/Pd}$

expect:
observe:

Explanation of Stability:**Allyl Cation:****C⁺ Stability:****How does conjugation affect reactivity?**

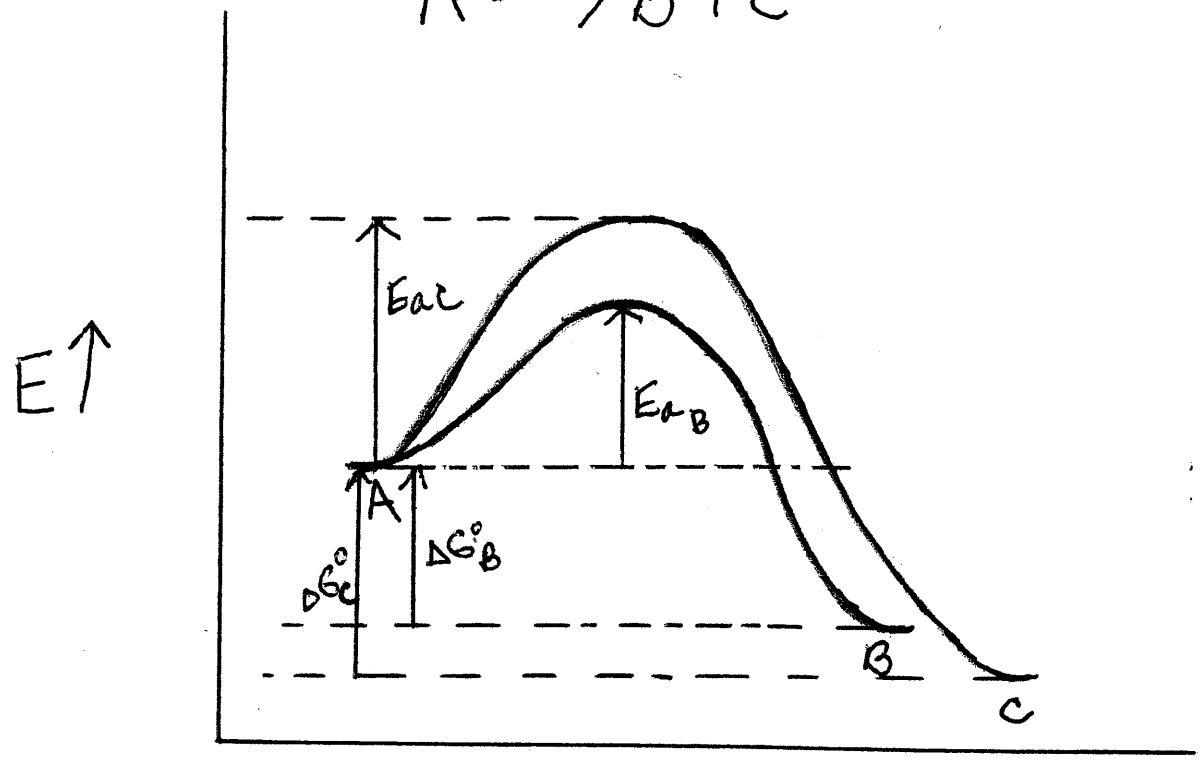
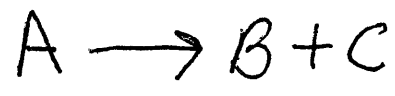
Mechanism of addition of HBr



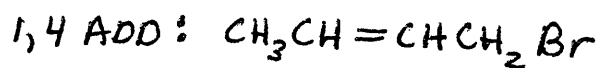
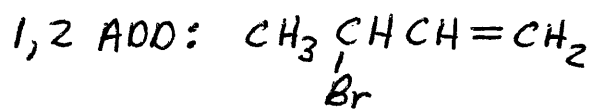
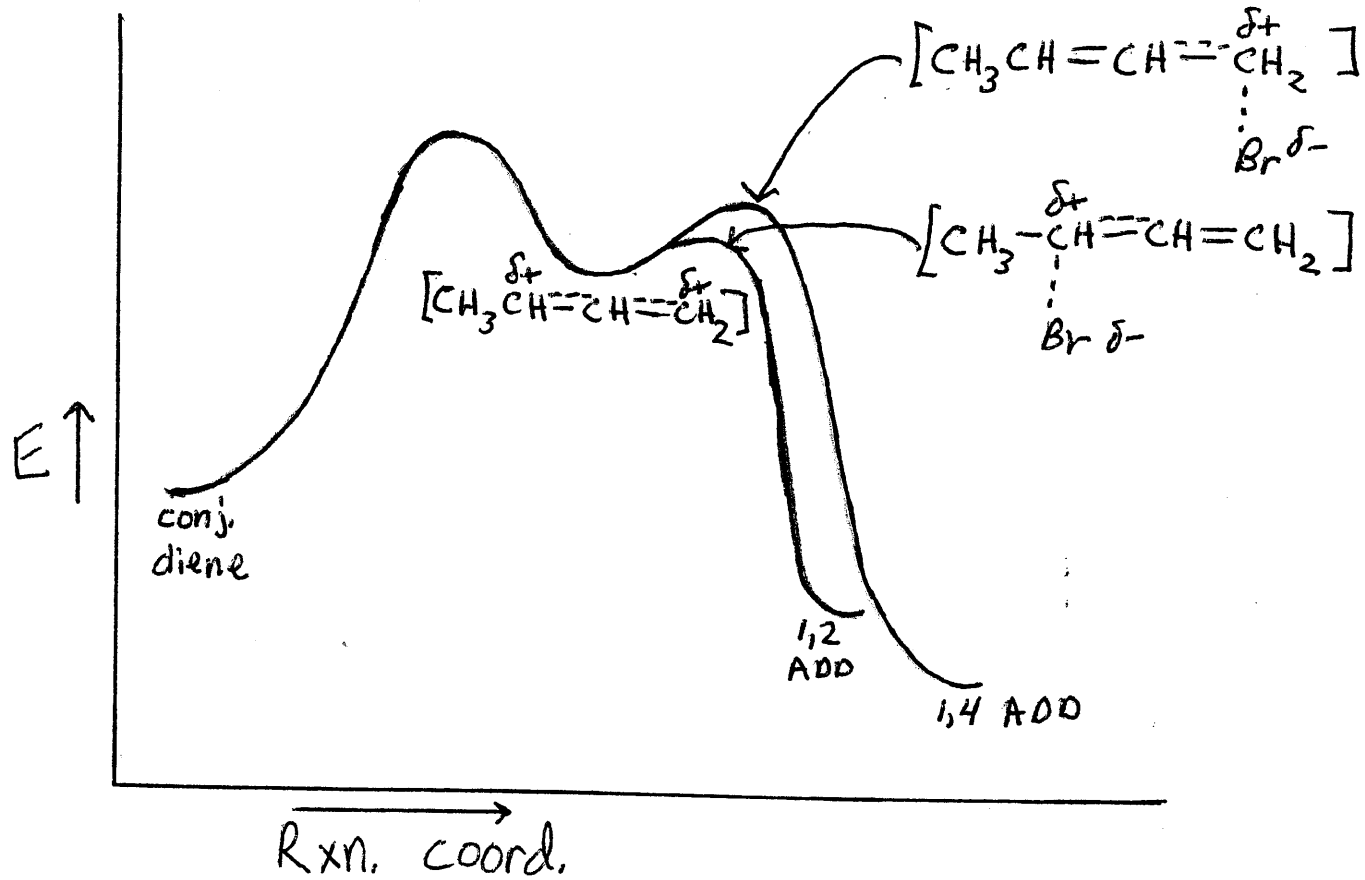
ratio of products: at low temperature

 at high temperature

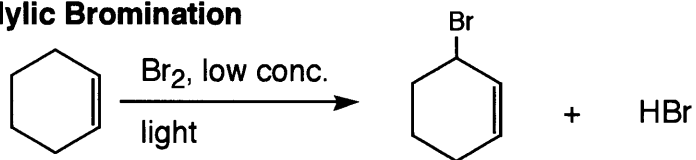
The process above is an example of Rate (Kinetic) versus Equilibrium (Thermodynamic) Control.



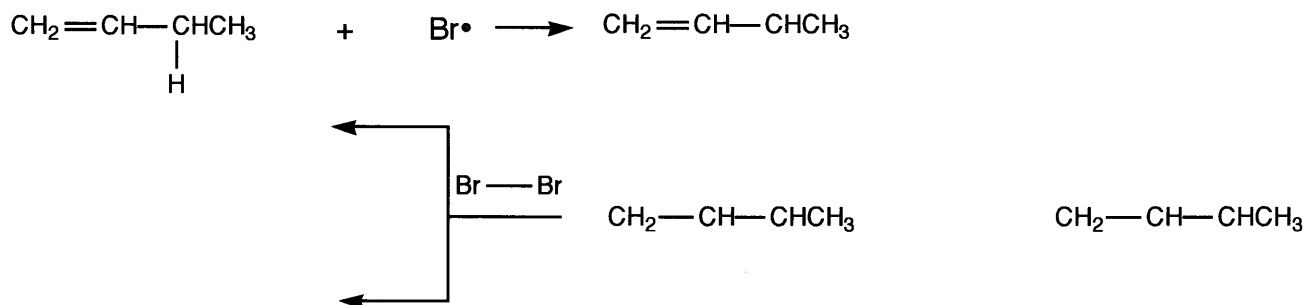
Rxn. coord.



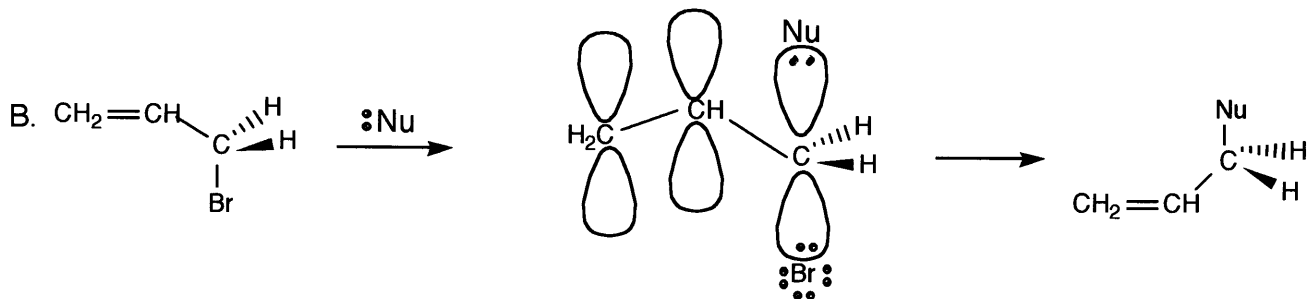
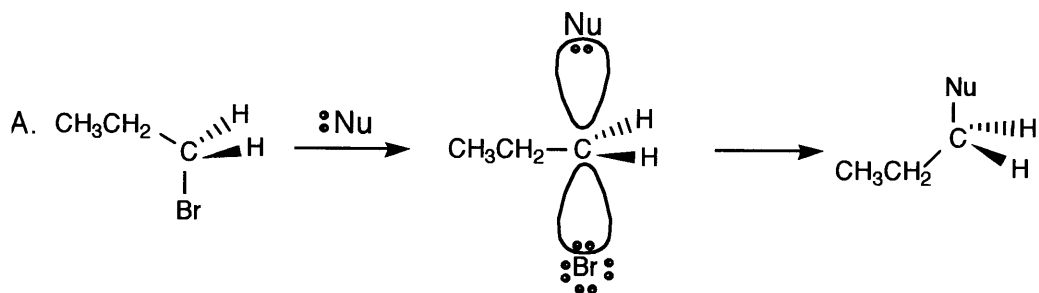
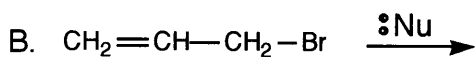
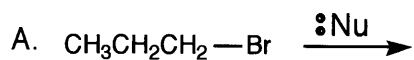
Allylic Bromination



Consider allylic bromination in an asymmetric alkene:



S_N2 Displacement Reactions of Allylic Halides (and Tosylates)



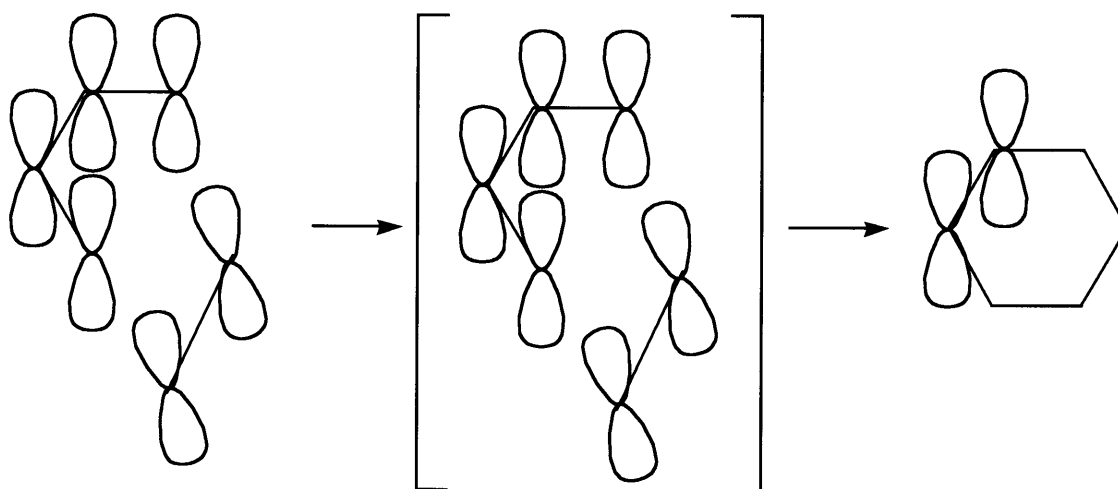
Example:



The Diels - Alder Reaction: a [4 + 2] cycloaddition and a Nobel Prize winning reaction

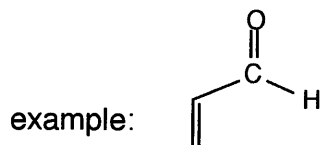
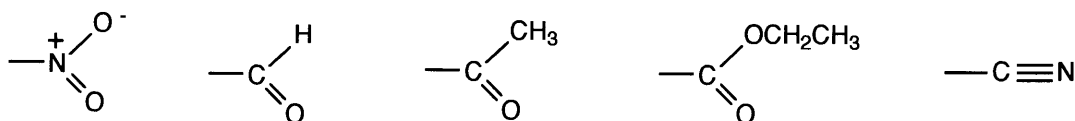


Mechanism:

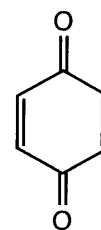
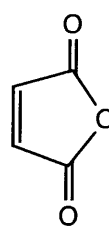
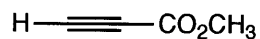


The dienophile:

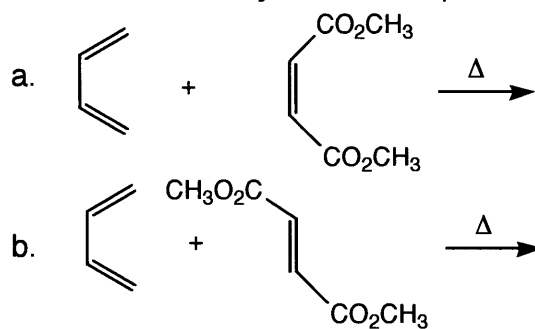
1. Must have at least one good electron withdrawing group to be reactive (electron withdrawal by resonance is best)



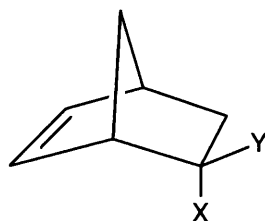
other dienophiles:



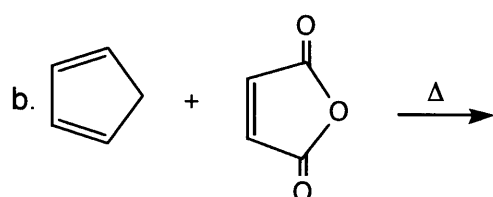
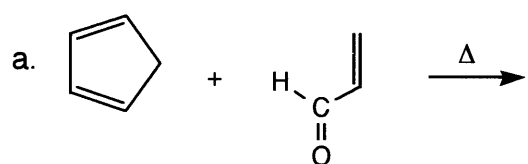
2. Stereochemistry of the dienophile is maintained.



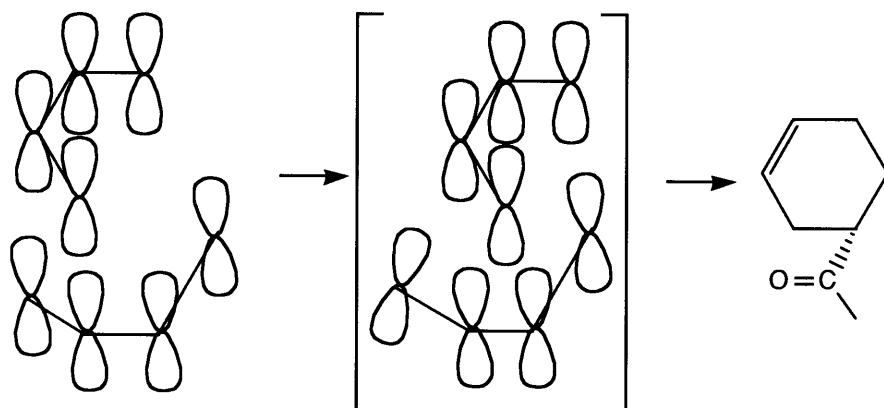
3. The Endo Rule: The electron withdrawing substituent of the dienophile prefers to occupy the endo position on the new ring system.



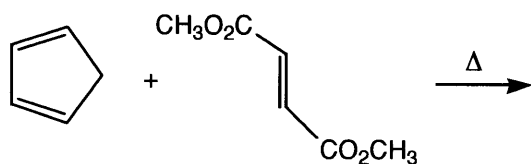
Example:



Explanation:

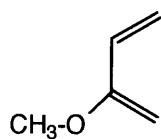


One more "endo" example:

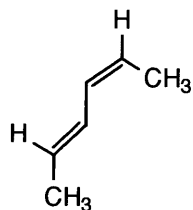
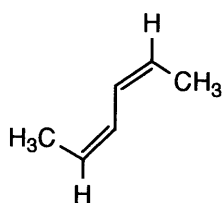
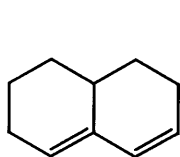
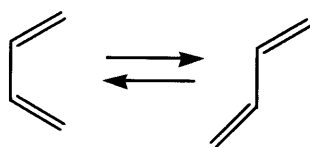


The Diene

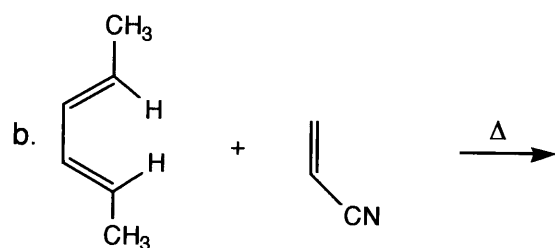
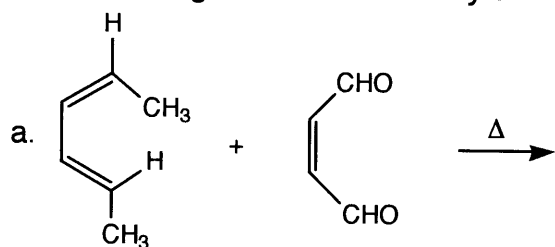
1. Electron donating groups enhance reactivity, but are not required. Examples - alkyl groups (R-), alkoxy groups (RO-)



2. Conformation:



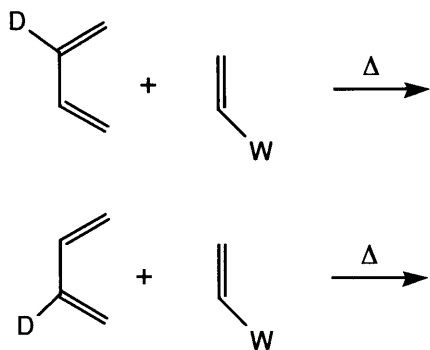
3. Translating the stereochemistry of the diene to the product:



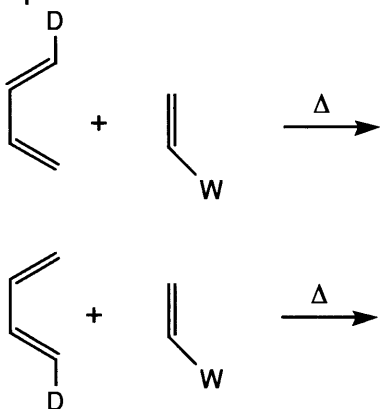
Diels-Alder Reactions Using Unsymmetrical Reagents

Two possible orientations for reagents in the transition state:

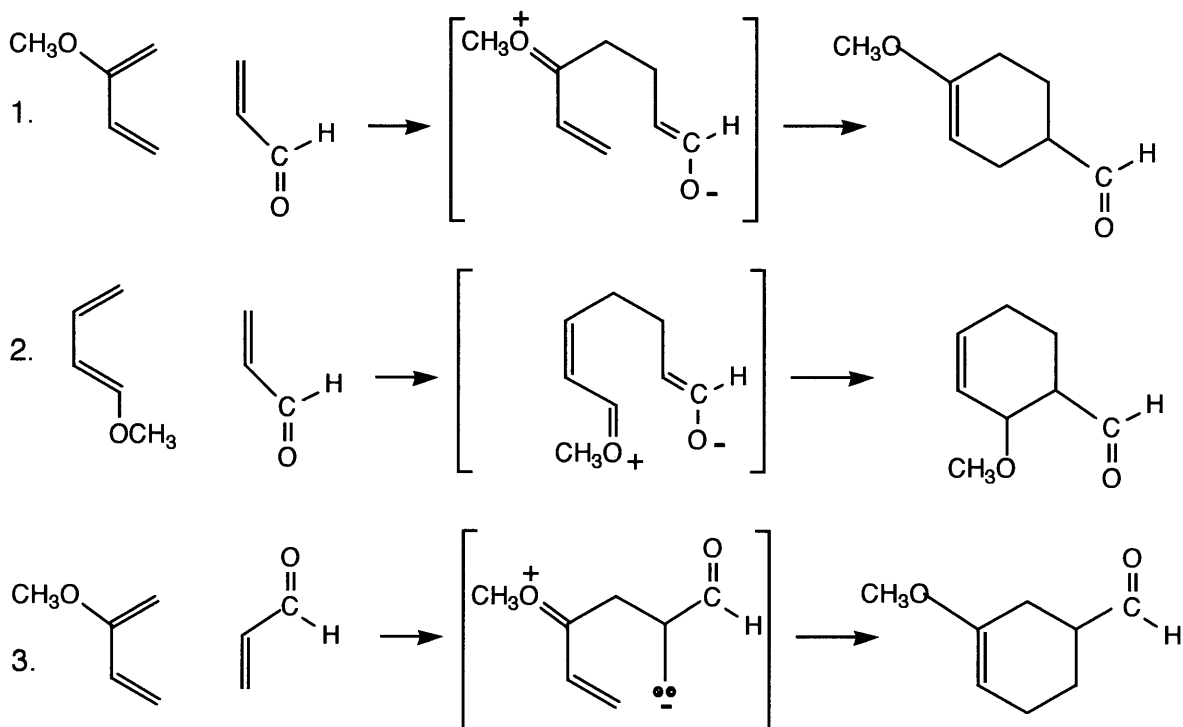
Example 1:



Example 2:

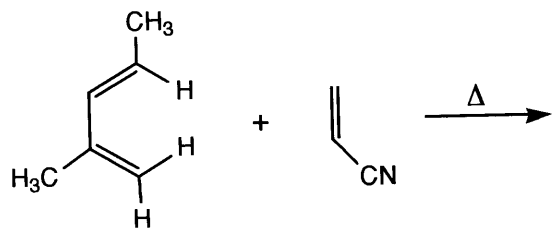


Explanation: Stability of imaginary intermediate that results from imaginary electron flow from donating to withdrawing group or the "push - pull" mechanism.





Unsymmetrical Example:



UV- VIS Spectroscopy - our most "exciting" technique

Pi molecular orbitals of:

