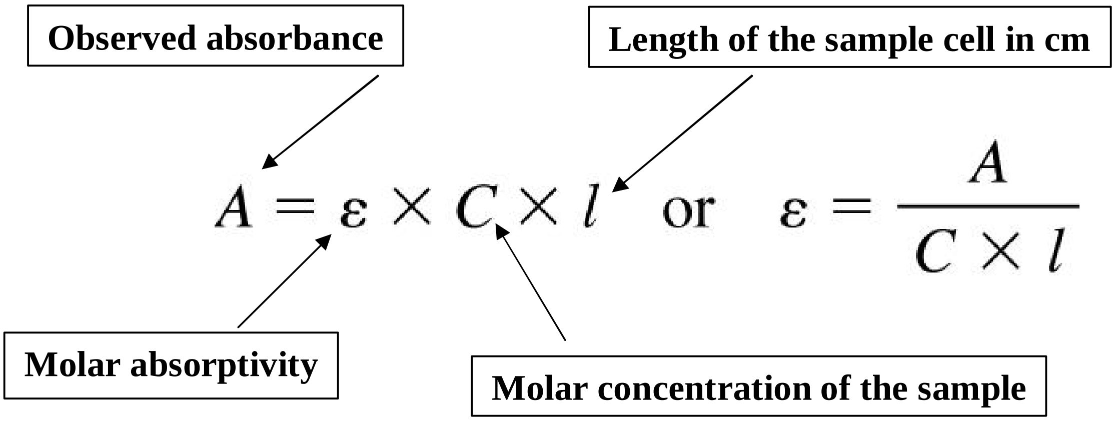
- **The wavelength of maximum absorption (λmax) is reported in units of nanometers (nm)**



Observed absorbance

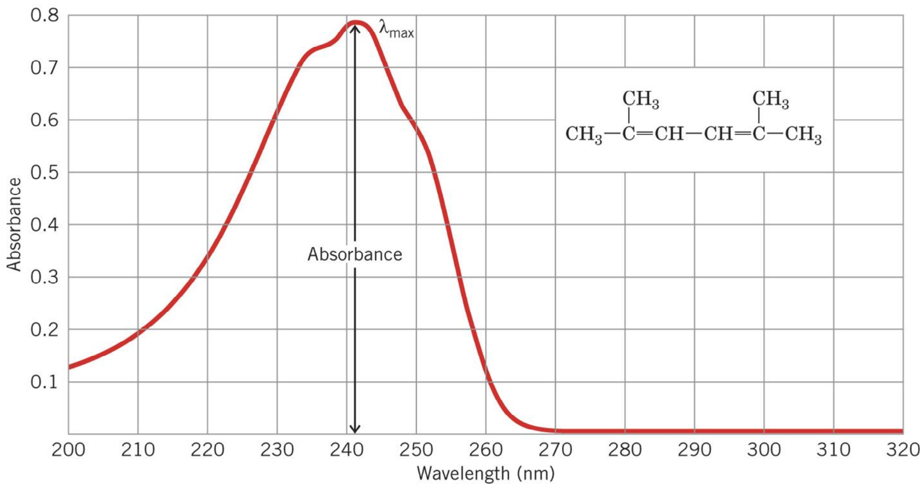
Length of the sample cell in cm

$$A = \varepsilon \times C \times l \quad \text{or} \quad \varepsilon = \frac{A}{C \times l}$$

Molar absorptivity

Molar concentration of the sample

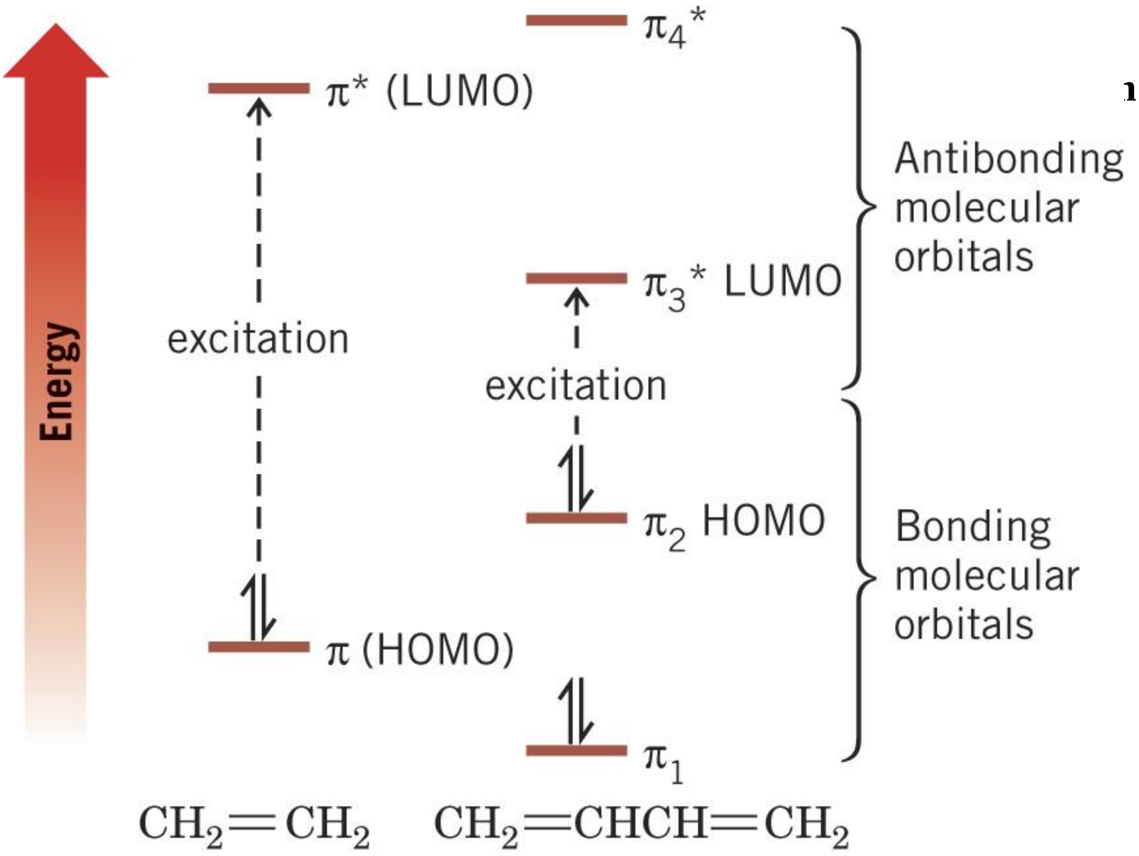
<u>Example:</u> UV absorption spectrum of 2,5-dimethyl-2,4-hexadiene in methanol at a concentration of 5.95 x 10^{-5} M in a 1.0 cm cell



2,5 Dimethyl 2,4 hexadiene, $\lambda_{\max}^{\text{methanol}}$ 242.5 nm ($\varepsilon = 13{,}100$)

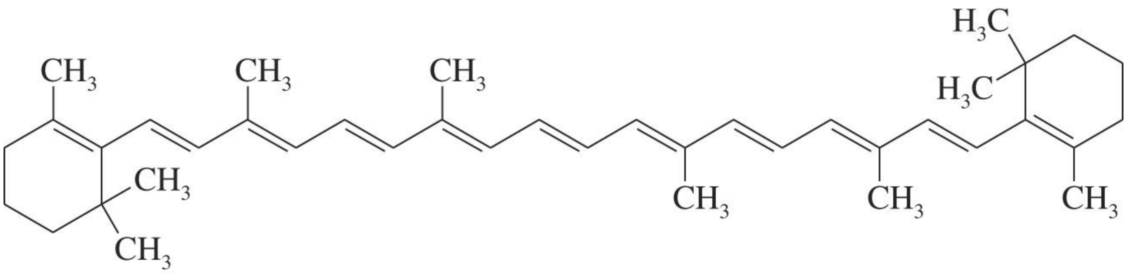
- **<u>Absorption Maxima for Nonconjugated and Conjugated Dienes:</u>**
  - **In UV-Vis spectroscopy, the electrons are excited from lower energy levels to higher ones**

- The electron is generally excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)
- Alkenes and nonconjugated dienes have absorptions below 200 nm because the energy difference between the HOMO and LUMO is large
- In conjugated dienes these energy levels are much closer together



§The longer the conjugated system, the smaller the energy difference between the HOMO and the LUMO.

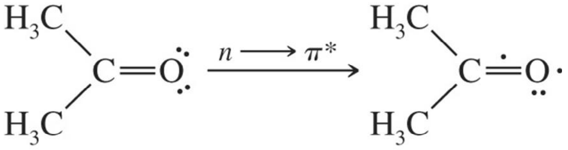
- A smaller energy gap results in longer λmax in the ultraviolet - visible spectrum
- β-Carotene has 11 conjugated double bonds and an absorbance maximum at 497 nm which is in the blue-green region of the visible spectrum
- β-Carotene is perceived as red-orange, the complementary color of blue-green



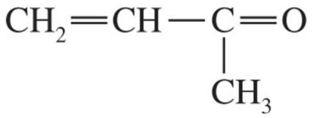
β-Carotene

§**<u>Carbonyl compounds also absorb light in the UV region:</u>**

- **An unshared (n) electron on oxygen is promoted to a π* orbital**



Acetone
λ_{max} = 280 nm
ε_{max} = 15

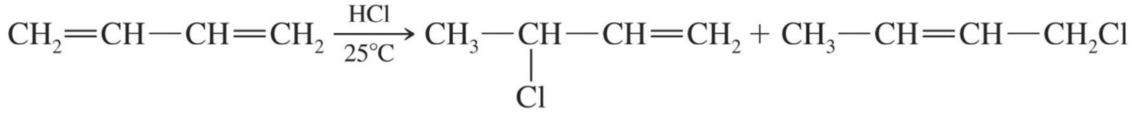


$$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O$$

$n \longrightarrow \pi^*$ λ_{max} = 324 nm, ε_{max} = 24
$\pi \longrightarrow \pi^*$ λ_{max} = 219 nm, ε_{max} = 3600

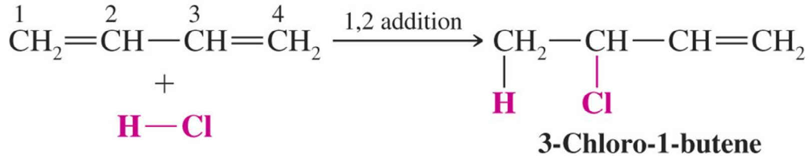
13.11) Electrophilic Attack on Conjugated Dienes: 1,4 Addition:

§ **When 1,3-butadiene reacts with one equivalent of HCl at room temperature 78% of the 1,2 addition product and 22% of the 1,4 addition product are obtained**



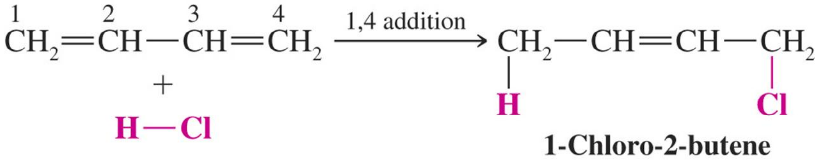
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[25^\circ C]{HCl} CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH{=}CH_2 + CH_3{-}CH{=}CH{-}CH_2Cl$$

1,3-Butadiene **3-Chloro-1-butene (78%)** **1-Chloro-2-butene (22%)**



$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} + H{-}Cl \xrightarrow{1,2\ addition} \underset{\displaystyle H}{\underset{|}{CH_2}}{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH{=}CH_2$$

3-Chloro-1-butene

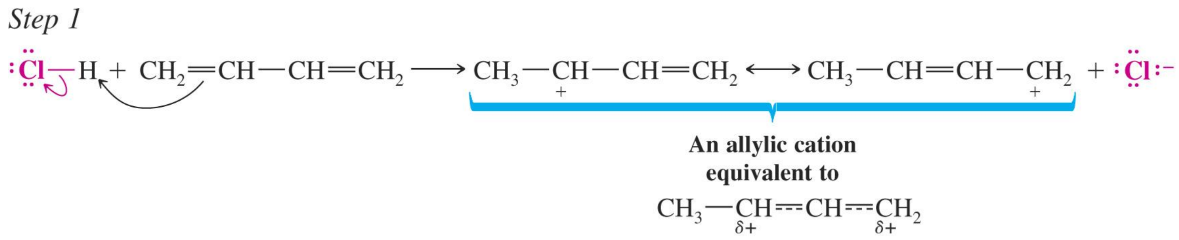


$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} + H{-}Cl \xrightarrow{1,4\ addition} \underset{\displaystyle H}{\underset{|}{CH_2}}{-}CH{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

1-Chloro-2-butene

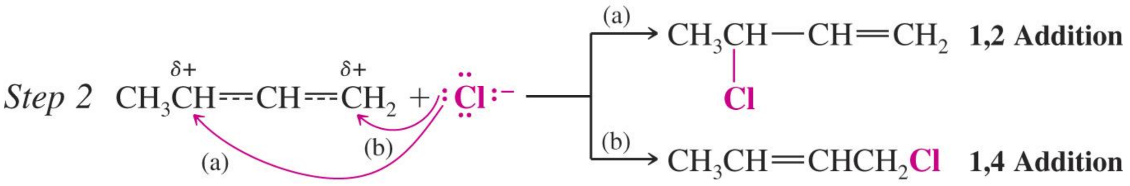
§ In step 1 hydrogen chloride reacts to add hydrogen to a terminal carbon which gives a stable allyl cation intermediate.

- Addition of hydrogen to in internal carbon leads to an unstable 1o carbocation



§In step 2 chloride can react at either end of the allyl cation.

- This leads to either 1,2 or 1,4 product



§Other electrophilic reagents add to conjugated dienes in similar fashion

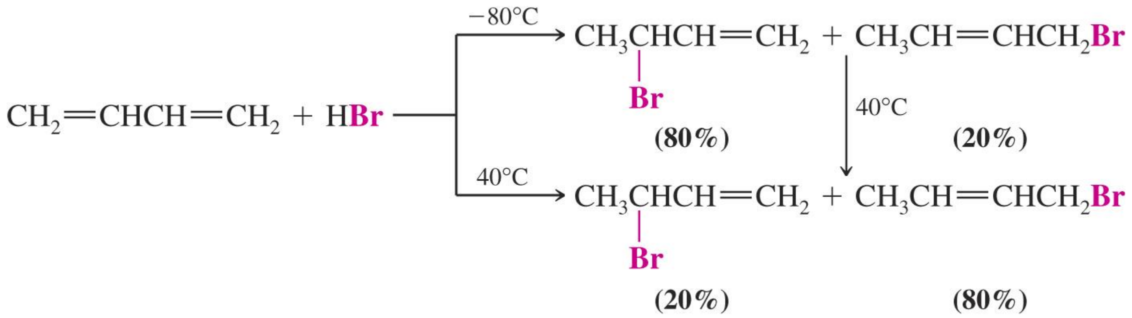
$$CH_2{=}CHCH{=}CH_2 \xrightarrow[40^\circ C]{HBr} \underset{(20\%)}{CH_3CHBrCH{=}CH_2} + \underset{(80\%)}{CH_3CH{=}CHCH_2Br}$$

$$CH_2{=}CHCH{=}CH_2 \xrightarrow[-15^\circ C]{Br_2} \underset{(54\%)}{CH_2BrCHBrCH{=}CH_2} + \underset{(46\%)}{CH_2BrCH{=}CHCH_2Br}$$

l Kinetic Control versus Thermodynamic Control of a Chemical Reaction:

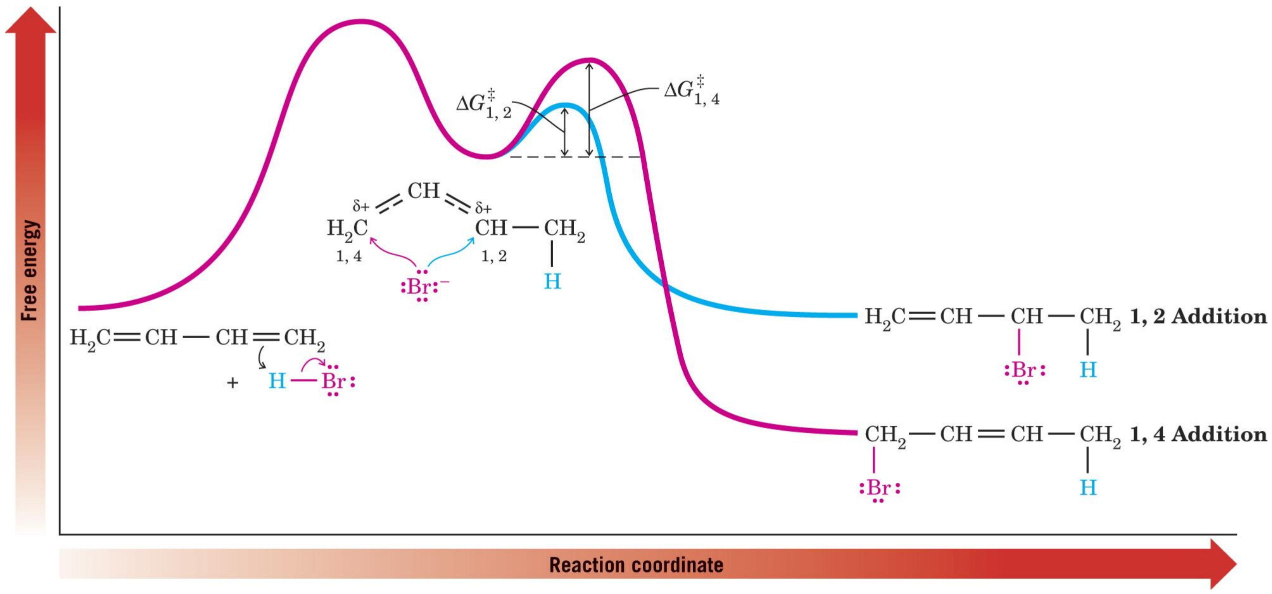
§When HBr adds to 1,3-butadiene the reaction temperature greatly affects the distribution of 1,2 and 1,4 products .

- Low temperature (e.g., -80^{o}C) favors 1,2-addition product
- High temperature (e.g., 40^{o}C) favors 1,4-addition product
- When the mixture of products formed at low temperature is heated, the product ratios change to favor 1,4-addition product



§ Heating the 1,2-addition product leads to an equilibrium which favors the 1,4-addition product.

- Because equilibrium conditions favor the 1,4-addition product it must be the most stable



§ **At <u>lower temperatures</u> the proportion of products is determined by the relative rates of formation of product.**

- **At low Temp., 1,2-addition product is formed faster (the major product)**
- **The $\Delta G^{\ddagger}$ for formation of 1,2-addition product is lower than for 1,4-addition product**
- **At low temperatures fewer molecules have enough energy to overcome the higher $\Delta G^{\ddagger}$ for formation of the 1,4-addition product.**
- **<u>The reaction is said to be under kinetic control</u>**

§ **At <u>higher temperatures</u> when an equilibrium is established, the most stable product predominates.**

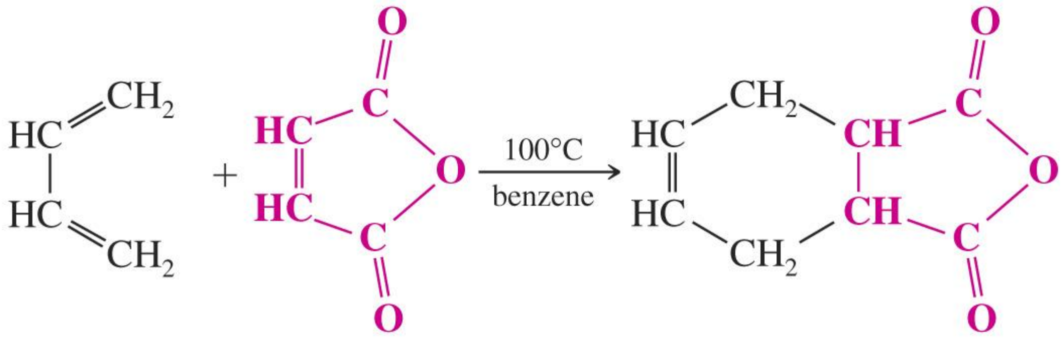
- **Enough energy is available to overcome $\Delta G^{\ddagger}$ barriers for formation of 1,2- and 1,4-addition products <u>and</u> for the reverse reactions**
- **The most stable product is the major one**
- **1,4-addition product is more stable and is the major product at high temperatures**
- **<u>The reaction is said to be under thermodynamic control</u>**

§ **The 1,4 product is most stable because it leads to a disubstituted double bond, while the 1,2 addition product is less stable because it has a monosubstituted double bond.**

§ **The 1,2-addition product is formed faster because the allyl cation has more $\delta+$ charge density at the 2^{o} rather than the 1^{o} carbon**

13.12) The Diels-Alder Reaction: A 1,4-Cycloaddition Reaction of Dienes:

§Heating 1,3-butadiene and maleic anhydride gives a 6-membered ring product in 100% yield



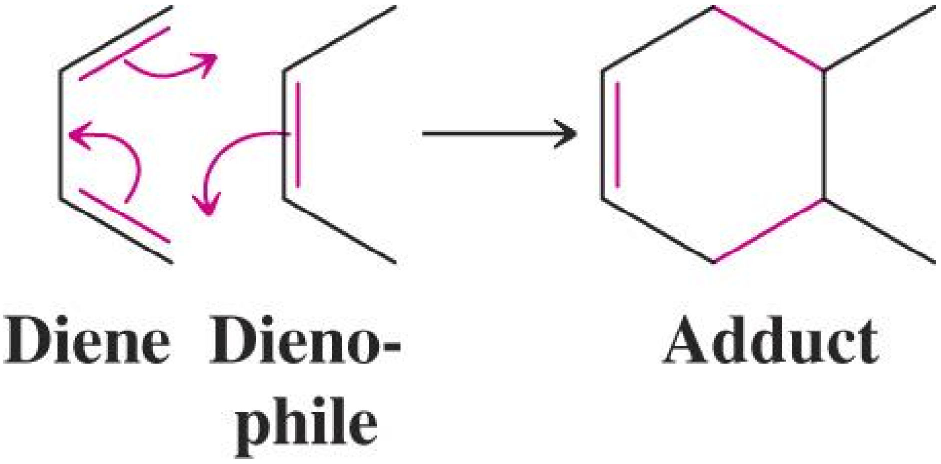
1,3-Butadiene **(diene)**

Maleic anhydride **(dienophile)**

Adduct **(100%)**

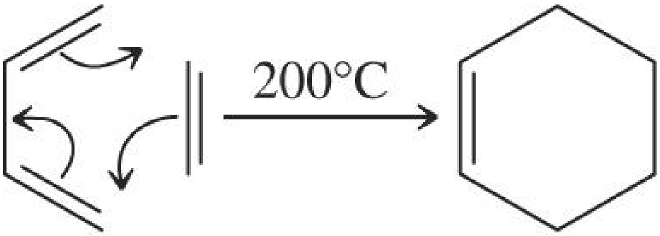
§The general Diels-Alder reaction forms a <u>cylohexene</u> product.

- Overall, two new s bonds are formed at the expense of two π bonds
- The conjugated diene is a 4π-electron system
- The dienophile (“diene lover”) is a 2π-electron system
- The product is called an adduct



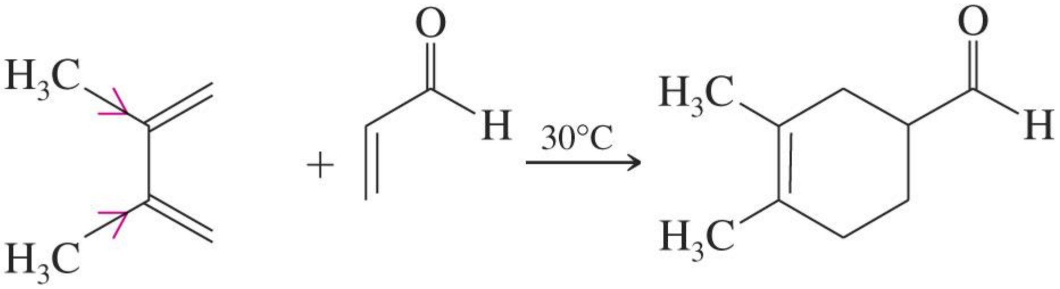
Factors Favoring the Diels-Alder Reaction:

- **The simplest possible example of a Diels-Alder reaction goes at very low yield and requires high temperatures**



(20%)

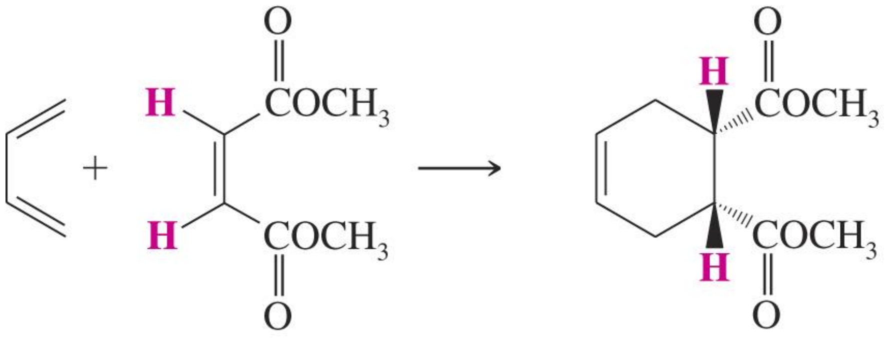
- **To proceed in good yield and at low temperature the dienophile should have <u>electron-withdrawing groups</u>.**
  - **It also helps if the *diene has electron-releasing groups***
  - **Dienes with electron-donating groups and dienophiles with electron-withdrawing group can also react well together**



2,3-Dimethyl-1,3-butadiene **Propenal** **(100%)**

Stereochemistry of the Diels-Alder Reaction:

- **The Diels-Alder reaction is stereospecific *i.e.* the reaction is a syn addition, and the configuration of the dienophile is retained in the product**

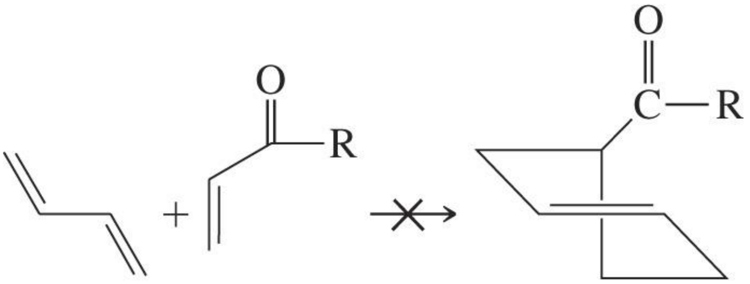


Dimethyl maleate
(a *cis*-dienophile)

Dimethyl cyclohex-4-ene-*cis*-
1,2-dicarboxylate

§The diene must be in the *s*-cis conformation to react

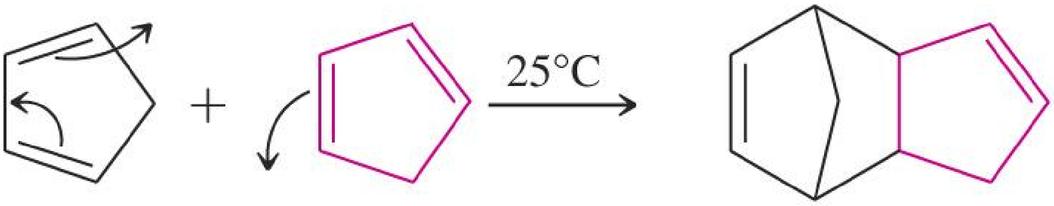
- ***s*-Trans conformation would lead to formation of a highly unstable trans bond in a 6-membered ring**
- **Cyclic dienes which must be in the *s*-cis conformation are highly reactive**



Highly strained

§Cyclopentadiene is so reactive it spontaneously undergoes Diels-Alder reaction with itself at room temperature.

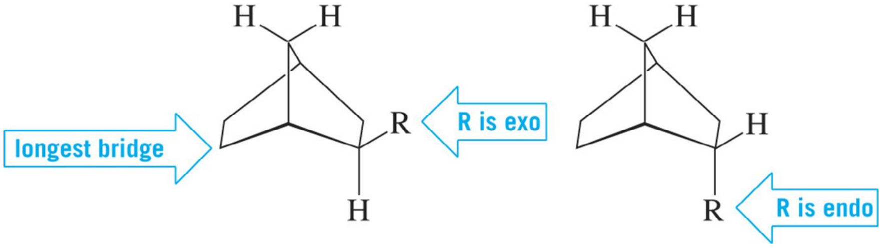
- **This dimer can be “cracked” (undergo retro-Diels-Alder reaction) by heating and the cyclopentadiene product isolated by distillation.**

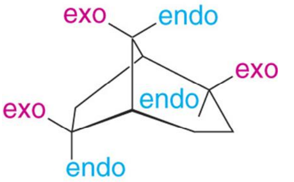


"Dicyclopentadiene"

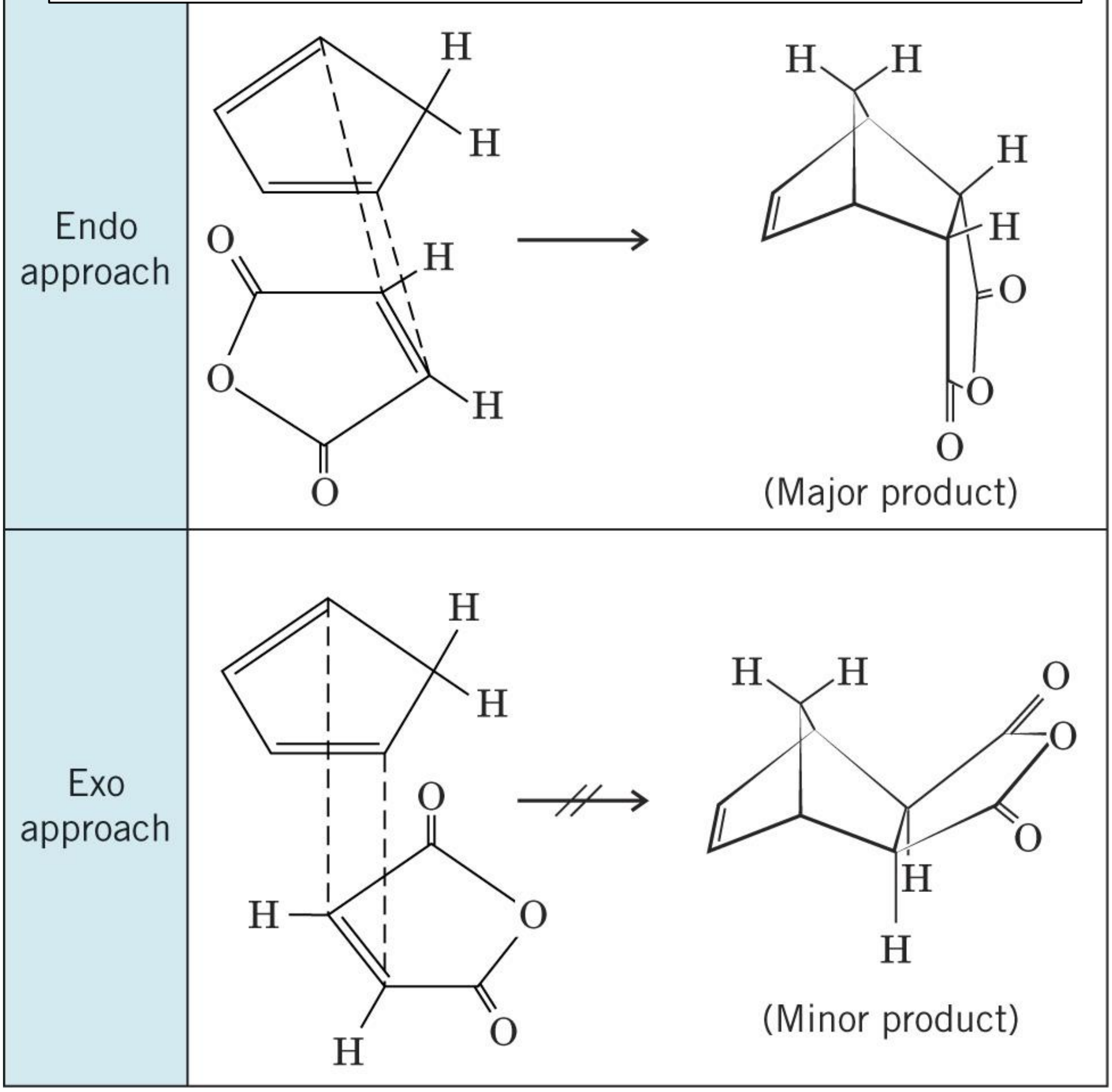
§The Diels-Alder reaction occurs primarily in an endo rather than an exo fashion when the reaction is kinetically controlled.

A group is anti to the longest bridge

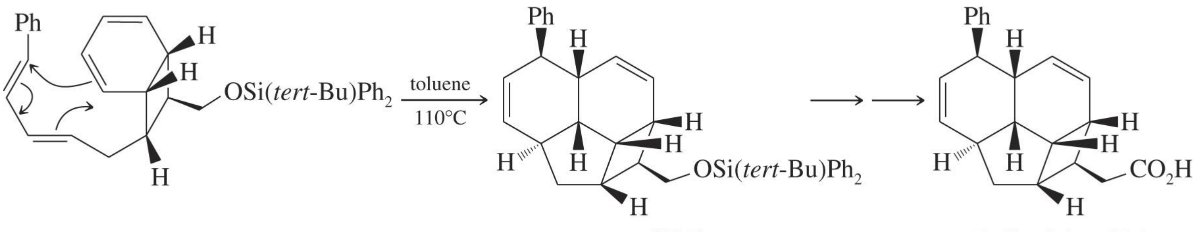




A group that is endo is on the same side as the longest bridge



- **Intramolecular Diels-Alder Reactions:**
  - §**Intramolecular reactions are those in which the reacting groups are part of the same molecule**



100%

Endiandric acid A