Conjugated Systems II

Rxns

HX Addition

Diels Alder Rxn

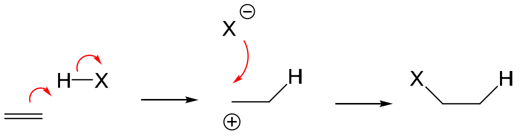
Ref 13: 10, 11 (both ed^{ns})

Prob 13: 10 - 15, 23 - 27, 33, 42 (both ed^{ns})

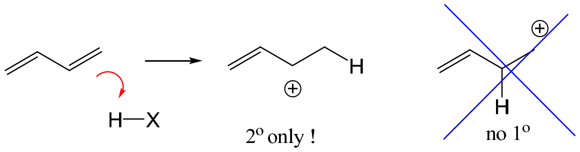
Adv Rdg 14: 1 – 4 (both ed^{ns})

Add^{n} of H–X

recall:
electrophilic rxns for isolated –enes,
goes in 2 steps

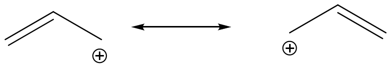


For conjugated dienes; e.g. 1,3-butadiene,
in the 1st step only the 2^{o} allylic cation forms
b/c it is resonance stabilized

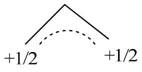


Allylic Cation

- explained by resonance

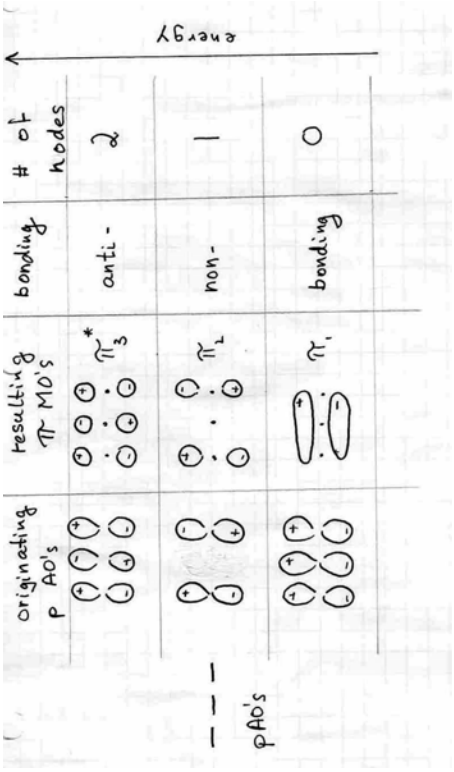


or

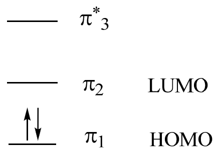


Allylic Cation

- expained by MO Theory



Comments on Allylic Cation



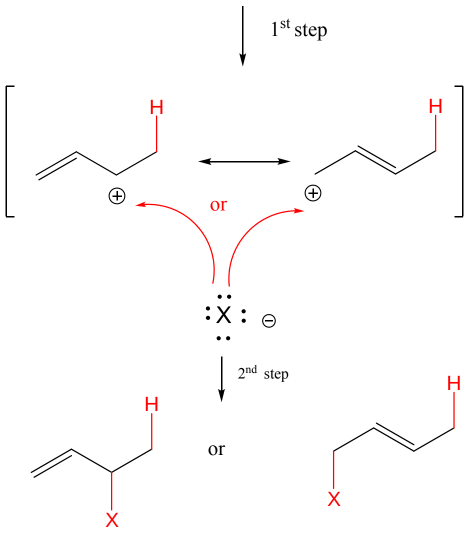
π_2 is empty MO

mostly located at end C's

e$^-$'s from X$^-$ go there

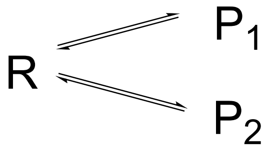
explains attack of X$^-$ at outer C's

Overall Result

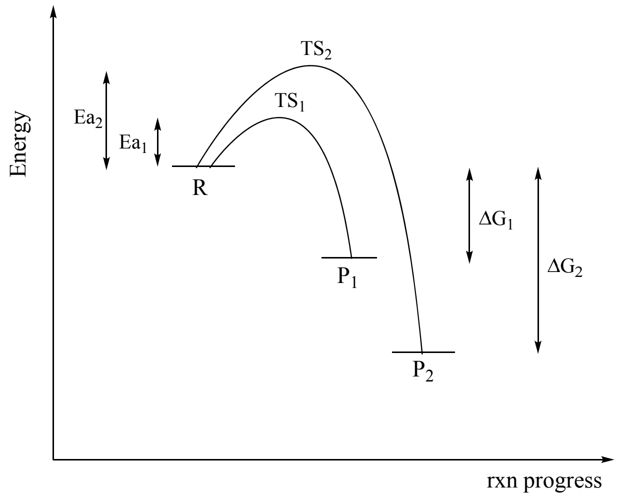


1,2 - add^n product		1,4 - add^n product
low temp.	predominant at	high temp.
kinetic product		thermodynamic product

Kinetic vs. Thermodynamic Control



Rxn Profile



---

kin./thermodyn. control

At **low** temp.

- only E_{a1} is available from kinetic motion
- can reach only TS_1
- only P_1 is formed

∴ kinetic control gives “kinetic product” kin./thermodyn. control

At **high** temp.

- sufficient energy (E_{a2}) is available
- to reach TS_2
- P_1 and P2 can be formed

- also can go back from P_1 to R
- ultimately, P_2 is dominant
  b/c it has lower energy
  (the system “equilibrates”, see Chem 102)
- system reaches equilibrium

∴ product with lower energy is the major one

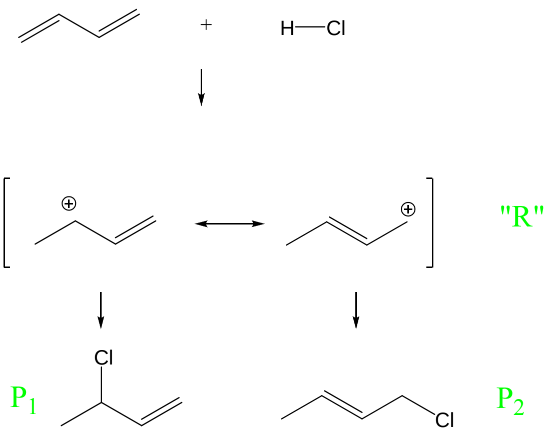
∴ thermodynamic control gives
“thermodynamic product”

Note

- could also start with P_1,
- under the same rxn conditions
  P_1 will equilibrate with P2 via R,
  see rxn profile

Application

(HX add^n to conjugated dienes)



1,2 - adduct

kinetic control

reason:
proximity effect,
less E_a required

1,4 - adduct

thermodynamic control

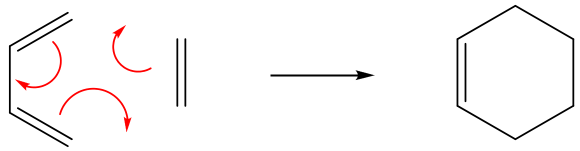
reason:
more stable
b/c di-substituted double bond

Diels-Alder Rxn (D-A)

conj. diene + – ene → D-A product

(dienophile)

Simplest Ex.



Remarkable:

- 2 new C-C bonds
- 1 π bond
- 6-membered ring

all formed in 1 step

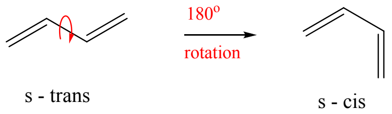
Requirements for D-A Rxn

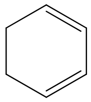
1.) Diene (conjugated)

must be able to assume

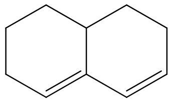
s – cis conformation

(*s means "cis at single bond"*)





s - cis preformed;
reacts well !



s - trans fixed;
cannot be diene in D-A

---

requirements ...

2.) Dienophile

- most –enes / -ynes are feasible
- if diene has only (or no) alkyl substituents

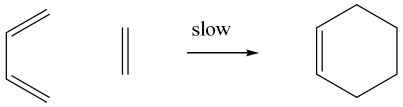
  then –enes w/ conjugated

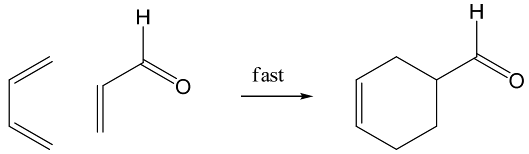
  e^- withdrawing groups (EWG's) react faster

Illustration:

good dienophiles:

$C{=}C{-}C{=}O$, $C{\equiv}C{-}C{\equiv}N$ ......



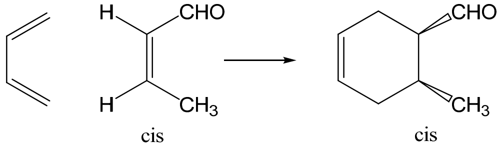


Stereochemistry

1.) cis / trans configuration of dienophile

is retained in rxn.

Ex.



2.) endo/exo preference

important for bicyclic dienes:

"the π system of the
EWG (s) of the dienophile interact
w/ the π system of the diene"

therefore EWG's remain in
close proximity of the diene system

this is the "endo" configuration;

the opposite is the "exo" configuration.

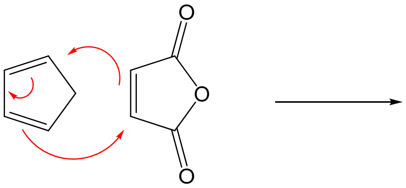
---

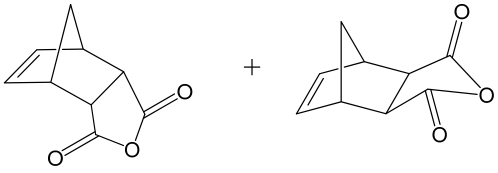
description of endo/exo:

R's occupying

endo positions exo

Example Reaction:





endo product,
major

exo product,
minor