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

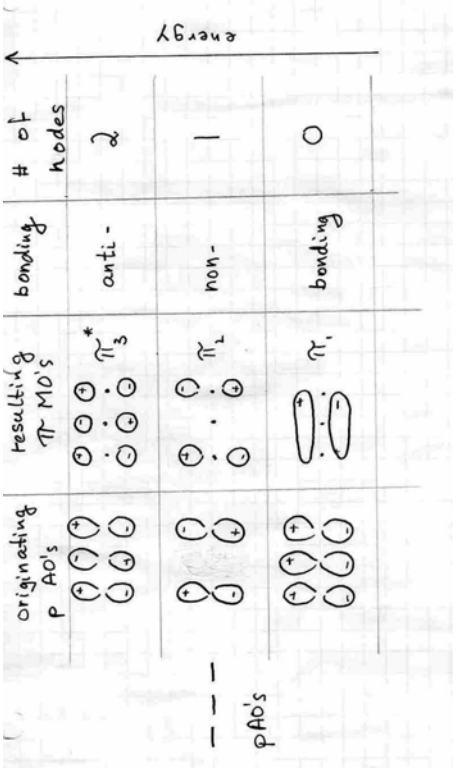
For conjugated dienes; e.g. 1,3-butadiene,
in the 1st step only the 2^{o} allylic cation forms
b/c it is resonance stabilized

Allylic Cation

• explained by resonance

Allylic Cation

• expained by MO Theory



Comments on Allylic Cation

Overall Result

1,2 - add^n product

low temp.

kinetic product

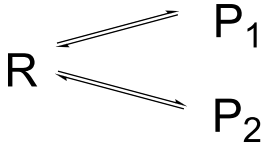
predominant at

1,4 - add^n product

high temp.

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

$\therefore$ 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)

Diels-Alder Rxn (D-A)

conj. diene + – ene (dienophile) → D-A product

Simplest Ex.

Remarkable:

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

} **all formed in 1 step**

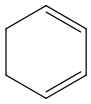
Requirements for D-A Rxn

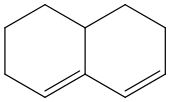
1.) Diene (conjugated)

must be able to assume

s – cis conformation

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





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:

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:

Example Reaction: