CHM 3150 - Organic Chemistry - Dr. Starkey

Ch 16 - Conjugated Dienes

Recall: Conjugated π bonds (16.1-16.2) (eg. 1,3-butadiene)

*aligned sets of p-orbitals can interact/delocalize

Resonance!

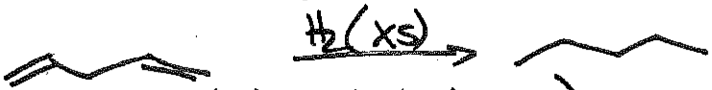
"trans" about a single bond → s-trans, more stable

s-cis, less stable

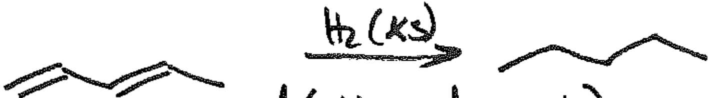
Diene Stability ΔH~~hydrogenation~~ (kcal/mol)

Ⓐ


cumulated (⊥ p orbitals) −70.3

Ⓑ


Isolated (unrelated p orb.) −60.7 (ΔH alkene x2)

Ⓒ


conjugated (aligned p orb.) −54.1

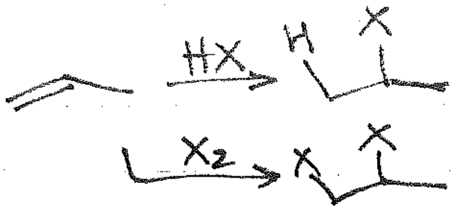
Allylic carbocations, ...) + radicals

$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2$ $\quad CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$

* both are resonance stabilized (delocalized e^- in p orbitals)

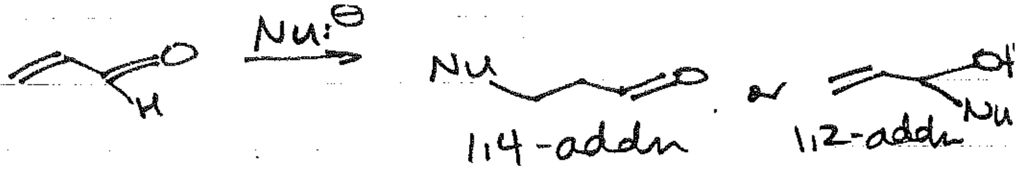
Electrophilic Additions to Dienes (16.4)

Recall: alkenes (8.2, 8-3, 8-8)

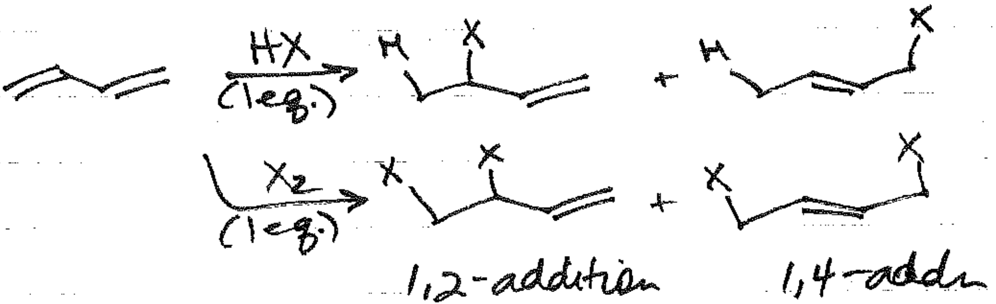


Markovnikov Addn

α,β-unsatd ketone (22-18)

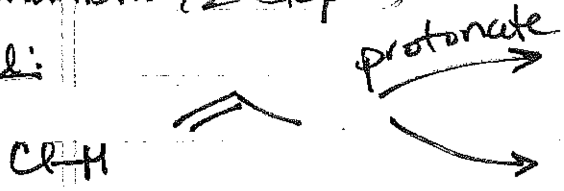


conj. dienes (15-5)



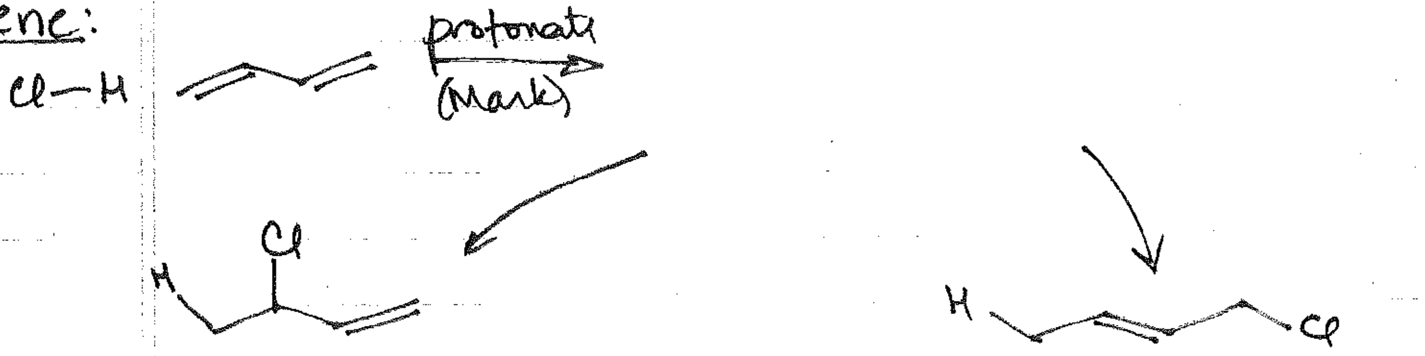
Mechanism (2-steps)

<u>Alkene:</u>



* the reason behind Markovnikov's Rule

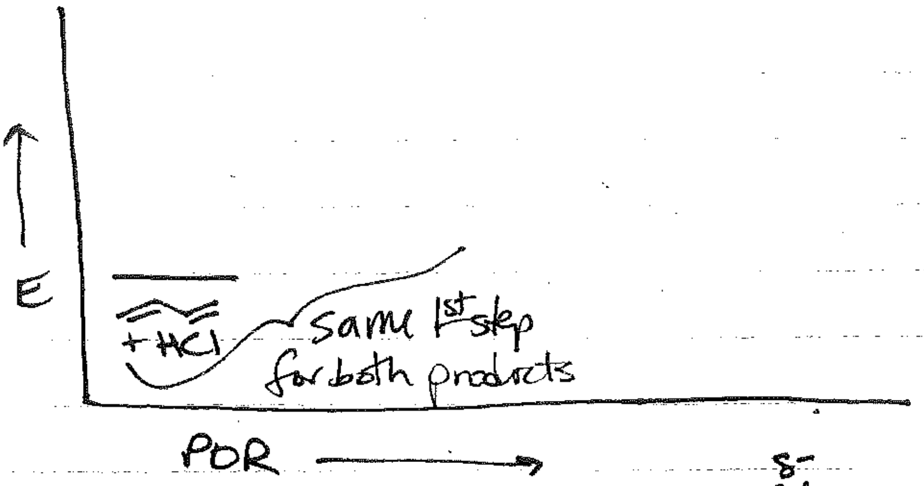
<u>Diene:</u>



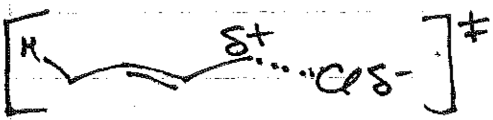
1,2 "kinetic" product
→ favored in <u>cold</u> rxn conditions

1,4 "thermodynamic" product
→ favored in <u>hot</u> rxn. cond.

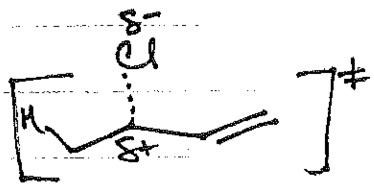
E vs POR Diagram



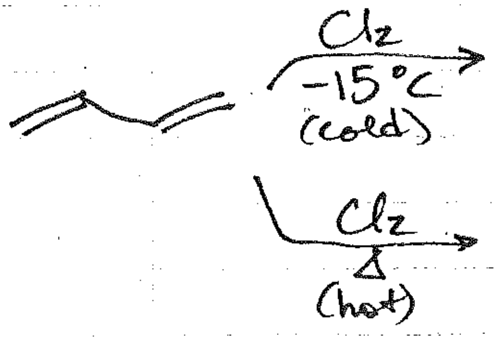
1,4 TS



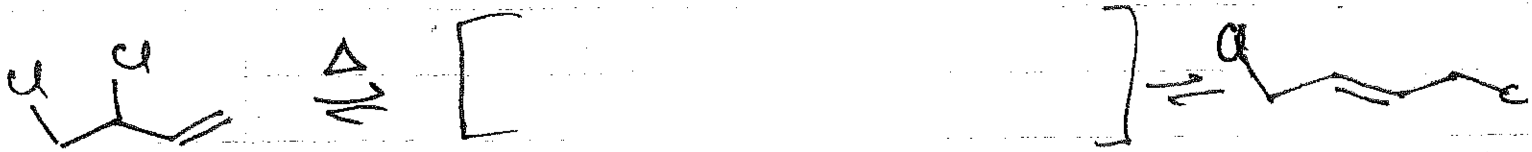
1,2-TS



Kinetic vs. Thermodynamic Control (16.5)



✓predict
✓major?



1,2 (less stable product)

1,4 (more stable produc

Diels Alder Reaction (16.7)

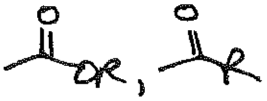
* Diels-Alder is a concertd, pericyclic reaction called a [4+2] cycloaddition

Dienophiles (E+)

→ alkene or alkyne

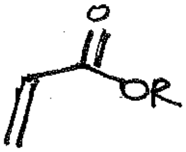
→ best if e⁻ poor (typically has EWG)

EWG = −CN,

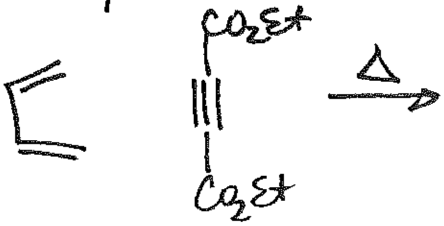


, ~~$-NO_2$~~

Why are these good E+?



Alkyne Example



Dienes (nu:)

* best if e−rich (often has EDG: −R, −OR, ~~−OH~~)

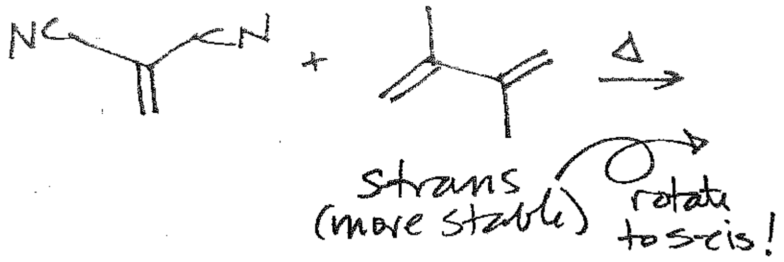
consider:

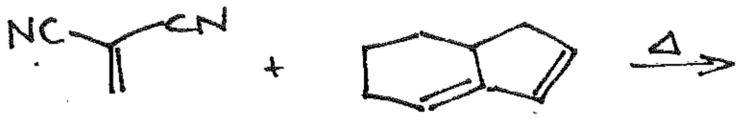
Why are these good nu:?

stable?

Diels-Alder rxn...

* Dienes must have "s-cis" conformation **16.5**

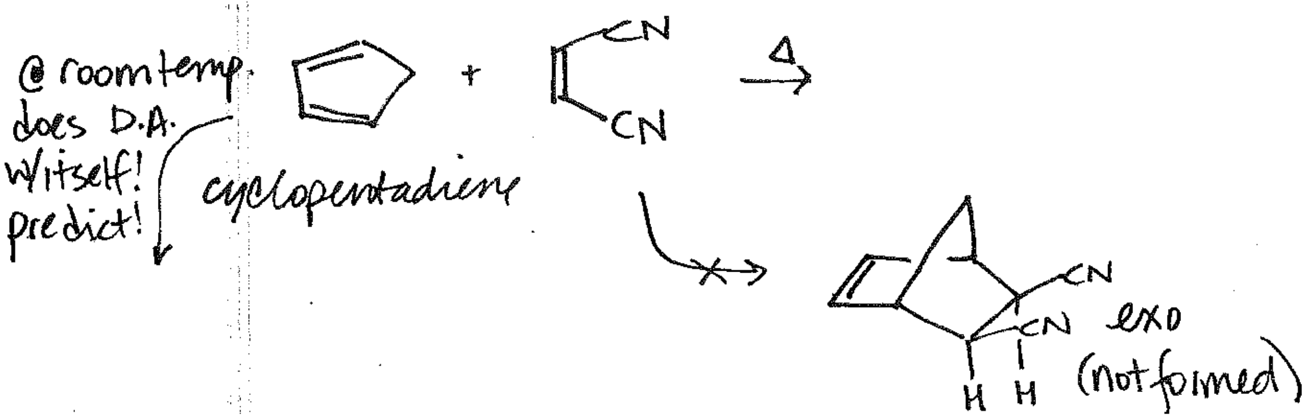


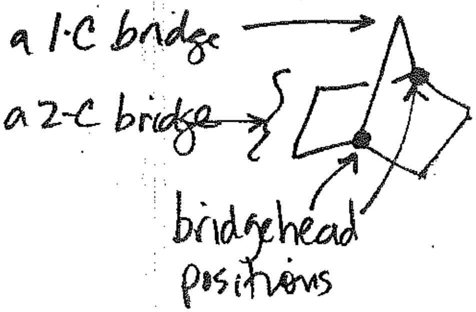


* cyclic dienes are great for Diels Alder Rxn.

→ perfect for D.A. because locked in s-cis conf.

→ stereochemistry: gives "endo" product





norbornane (common name)

IUPAC(FYI) bicyclo$[2.2.1]$ heptan

list bridg sizes in decreasin order

IUPAC?

Ex.

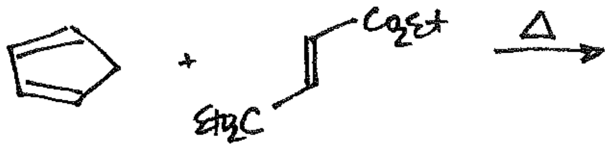
Stereochemistry of the Diels Alder Rxn

16.6

→ endo is major product if bicyclic
→ stereochem. of dienophile is retained
→ chiral products are formed as racemate

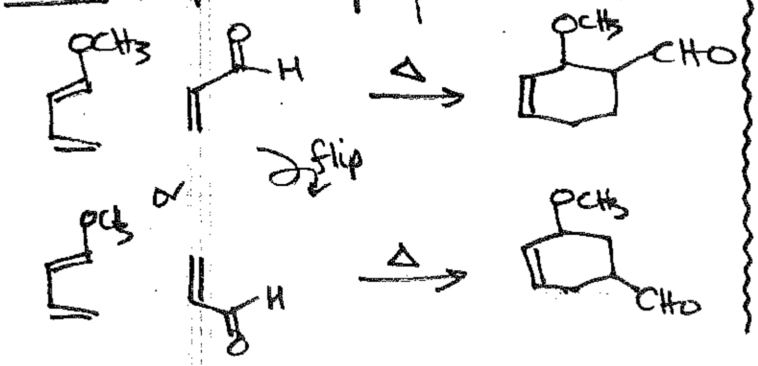
Ex.

Ex.

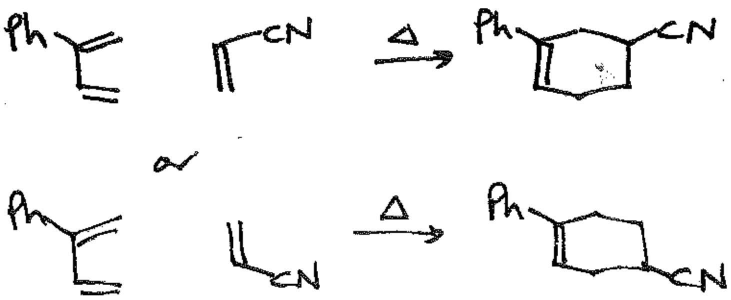


Regiochemistry of the Diels-Alder Rxn

Rule: 1,2-product preferred over 1,3-

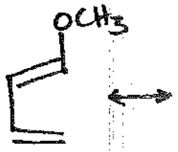


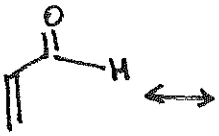
Rule: 1,4-product preferred over 1,3-



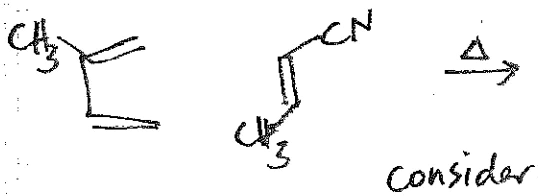
Why? See discussion of MO Theory: highest occupied MO (HOMO) + lowest unoccupied (LU
↳ best nu: + ↳ best E^+

Ex.





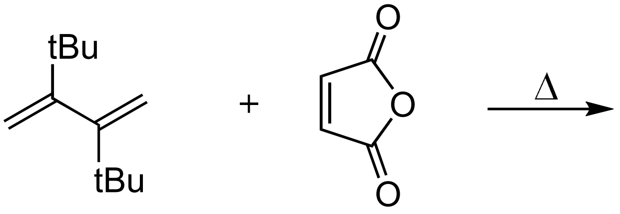
predict:



consider: regiochemistry + stereochemistry!

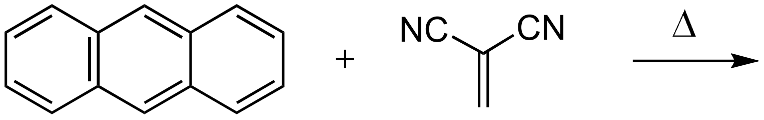
Diels-Alder Practice Problems

A)



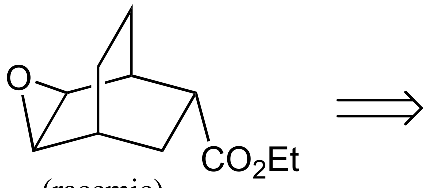
No Reaction
(explain)

B)



(why is it okay to do a Diels-Alder
on anthracene, an aromatic compound?)

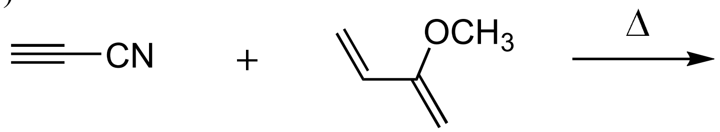
C)



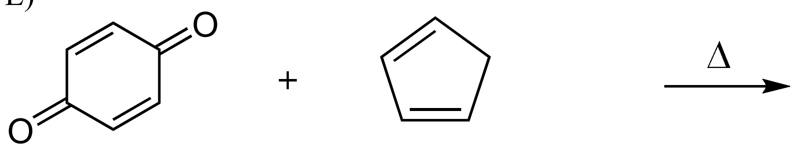
(racemic)

synthesize the above TM from
starting materials containing no
more than six carbon atoms
(first, consider retrosynthesis)

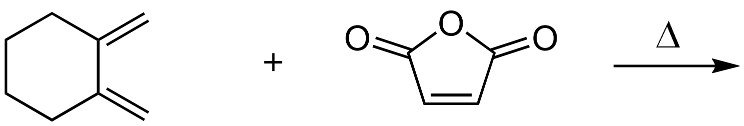
D)



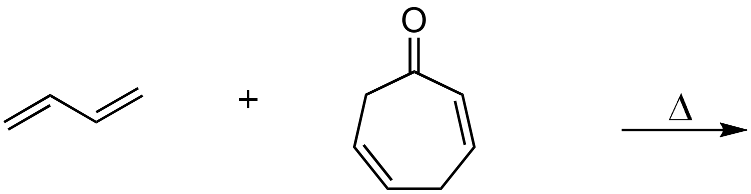
E)



F)



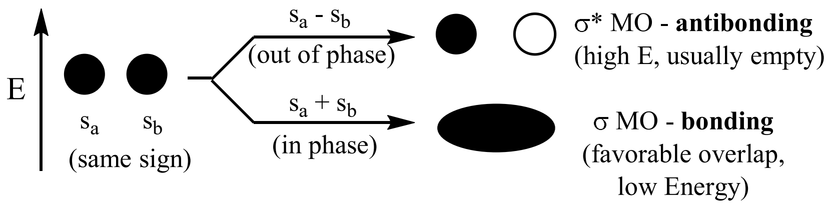
G)



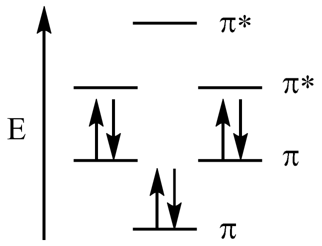
which pi bond reacts? (explain)

MO Theory of Chemical Reactions

Molecular Orbital theory of bonding

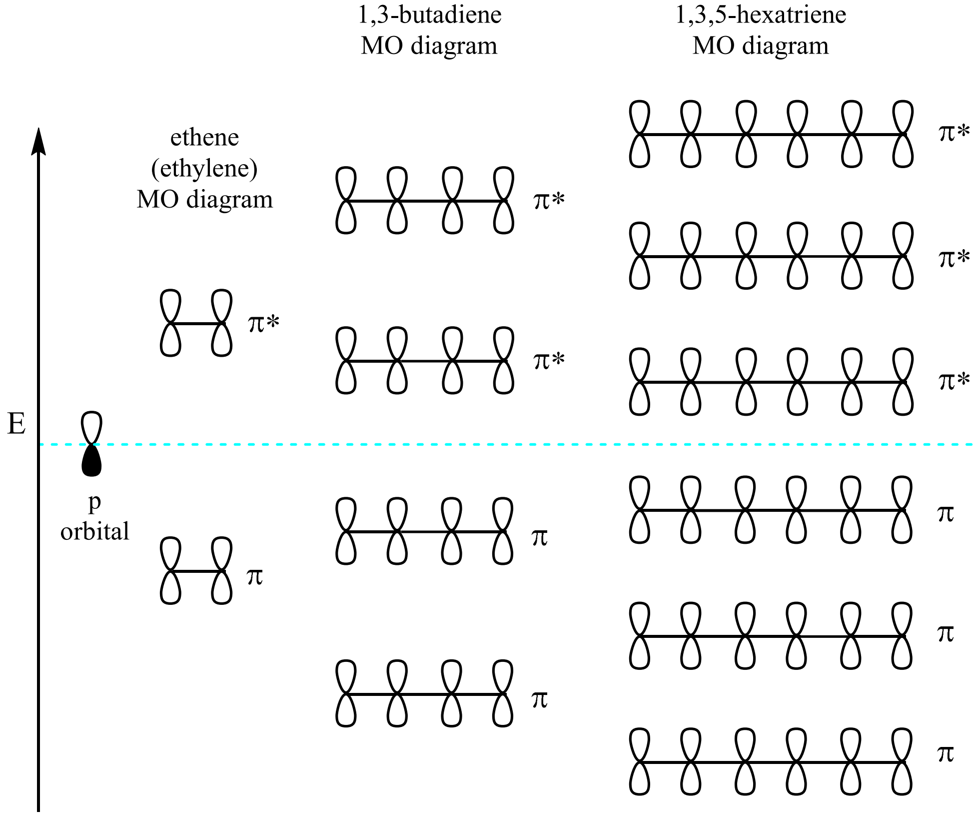


MO theory of aromaticity

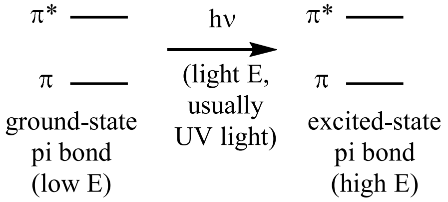


4n + 2
electrons
needed for
aromatic
resonance
(Huckel's Rule)

Molecular Orbital theory of conjugated systems (UV-Vis Spectroscopy) (Klein 16.11)



this Energy gap gets
smaller as conjugated
system gets larger



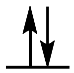
if...**increase** – # of conjugated pi bonds
then...**increase** – resonance stabilization
and...**decrease** ↓ E needed for π ⟶ π*

lower Energy **visible light**
is absorbed so these
compounds are **COLORED!**

Molecular Orbital theory of chemical reactions

Nucleophile (electron donor) uses electrons in the highest occupied molecular orbiral (HOMO)

Electrophile (electron acceptor) has a vacancy in the lowest unoccupied molecular orbiral (LUMO)



HOMO of
Nucleophile

LUMO of
Electrophile

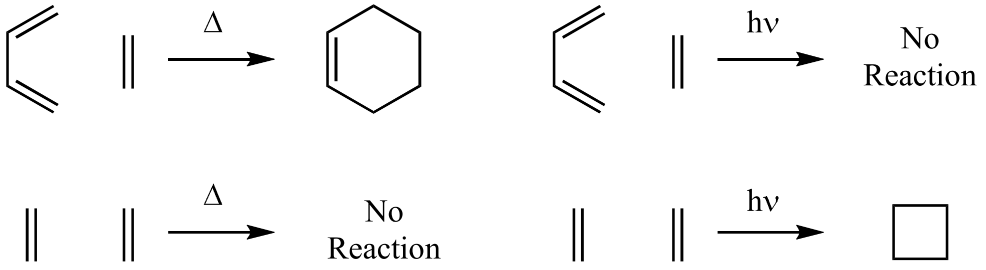
Examples:	B:	H−A	:Nu	R−X
	base	acid	Nu:	E^+

HOMO = n orbital (filled nonbonding orbital)

LUMO = σ* orbital (empty orbital can accept electrons)

MO theory of pericyclic reactions (the Woodward-Hoffmann rules) (Klein 16.8)

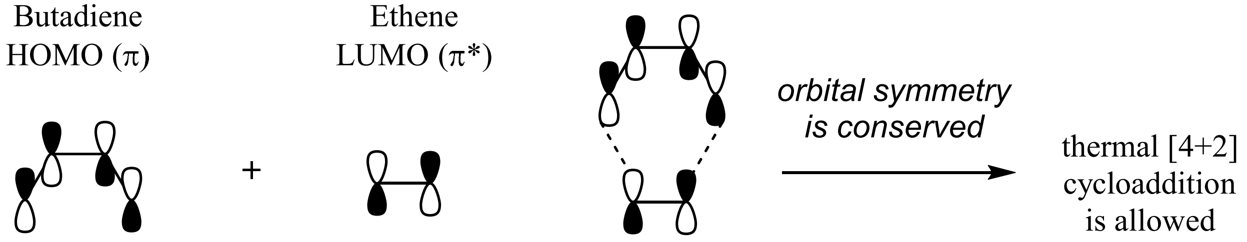
Heat-promoted pericyclic reactions   Light-promoted pericyclic reactions

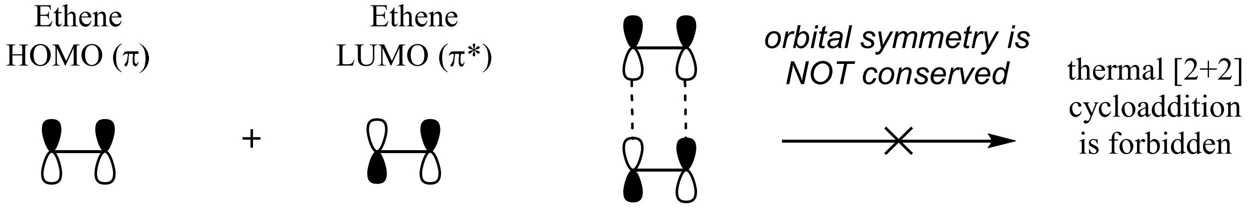


4+2 cycloadditions are thermally/photochemically allowed

2+2 cycloadditions are thermally/photochemically allowed

Why is a [4+2] cycloaddition thermally allowed while the [2+2] is not?





Why is a [2+2] cycloaddition photochemically allowed?