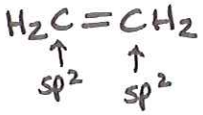
① **WEEK 1**

- Welcome! (Introductions)
- Review Syllabus
- Ch. 12: Dienes

Announcements: Labs start next week.

②

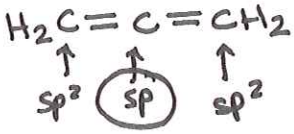
Recall: Alkene (olefin)



π-bond:

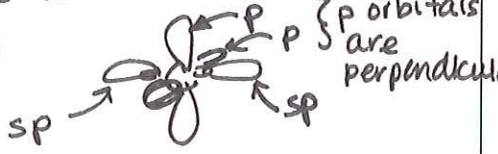
③ Dienes = Compounds w/ 2-π-bonds

Simplest: Allene (reactive)



Where are π-bonds in space?

Central C:



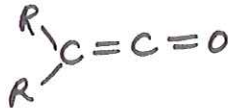
π-bonds are perpendicular!

Build yourself a model.

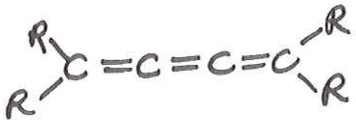
④

Related compounds:

carbon dioxide



ketenes



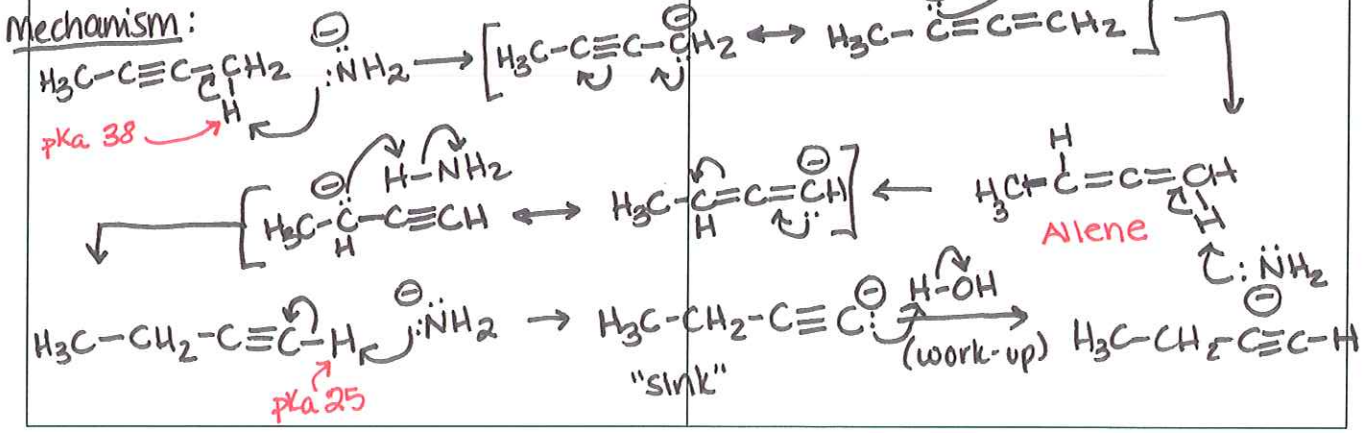
cumulenes

(What does this molecule look like in 3-D?)

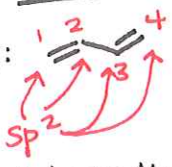
⑤ Allenes = intermediates in Alkyne isomerization

ex: $H_3C-C\equiv C-CH_3 \xrightarrow[2)\,H_2O]{1)\,K^{\oplus}\,{}^{\ominus}NH_2} H_3CCH_2C\equiv CH$

Mechanism:



(7) 1,3-Dienes

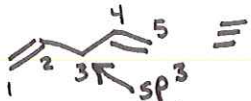
ex: 

1,3-butadiene

Conjugated π-bonds

Overlap between
C1-C2
C2-C3
C3-C4
} 2p orbitals

Contrast w/ unconjugated diene:



1,4-pentadiene

sp^3 C insulates π-bonds from each other.

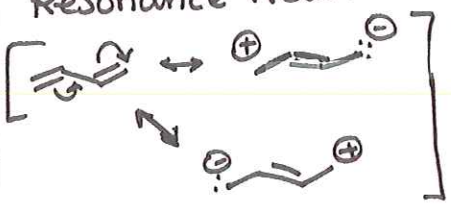
∴ 2 Dbl bonds behave independently.

(8) Physical Consequences of Conjugation

Molecular Orbital Diagram:

Suggests dbl bond character btwn C2-C3.

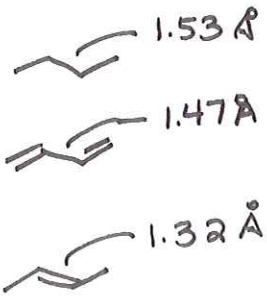
Resonance View:



Also: dbl bond character btwn C2-C3.

(9)

Bond lengths:

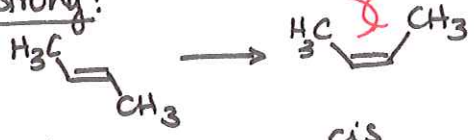


Some dbl bond character (but not as strong as a full dbl bond).

(10) How Strong?

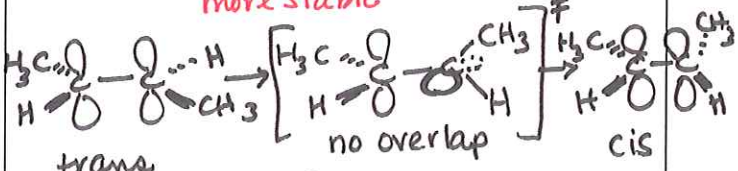
steric repulsion

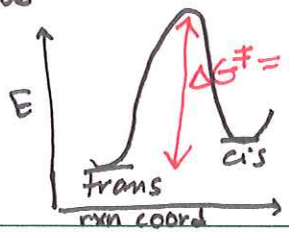
Recall:



trans — cis

favored / more stable





HUGE!! No rotation occurs.

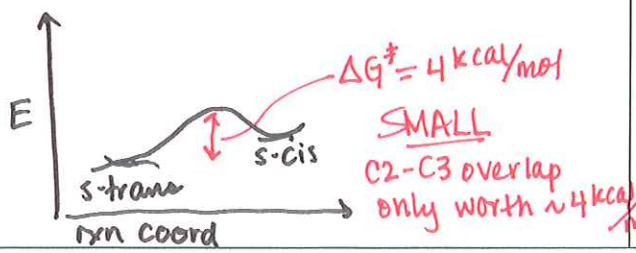
(11)

rotation abt single bond →

s-trans — more stable (a lot)

Both species @ equilibrium

s-cis (a little) — steric repulsion



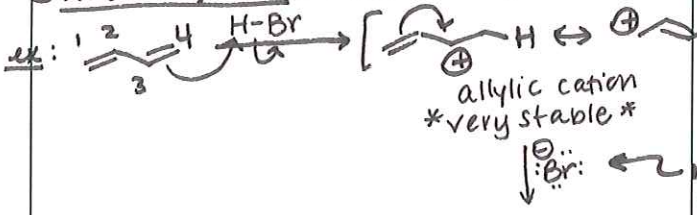
SMALL

C2-C3 overlap only worth ~4 kcal/mol.

(12)

(13) REACTIONS OF 1,3-BUTADIENES

① Add'n of H-X (Should look familiar)

ex: 

Both products observed!

kinetically favored

	1,2-add'n	1,4-add'n
−78°C	81	18
25°C (r.t.)	44	56

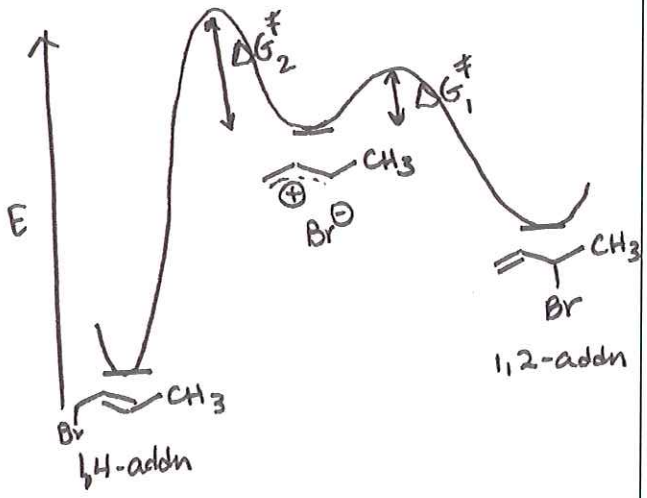
thermodynamically favored

(14)

Overall electronic character:

(Why isn't  observed?)

(15)



(16)

② The Diels-Alder Reaction

Form'n of cyclohexenes

ex: 

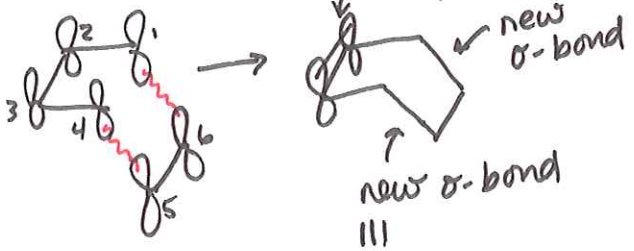
DIENE (s-cis) + alkene DIENOPHILE → cyclohexene (Diels-Alder "adduct")

Mechanism:

concerted (Bonds form at the same time)

(17)

Molecular Orbitals:

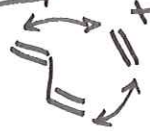


III

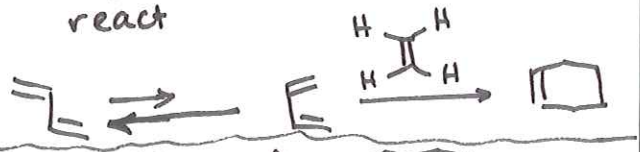
always s-cis

(18)

Only s-cis conformation reacts:



s-trans cannot react



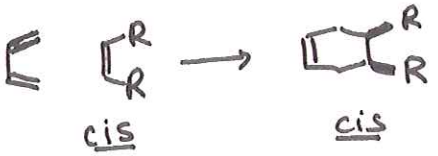
ex: 

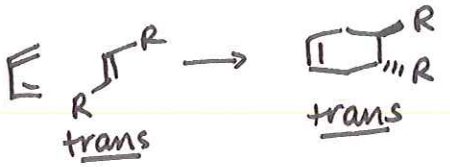
always s-cis

always s-trans

(19) Stereochemical Considerations:

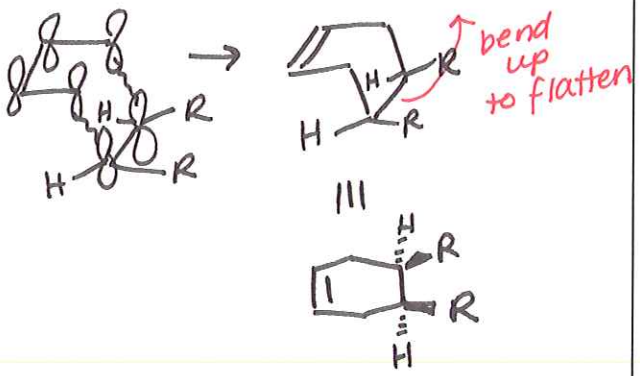
① Concerning the dienophile (alkene):





ex: 

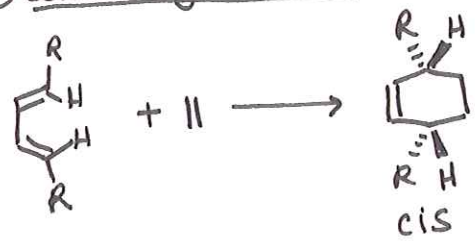
(20) Why?



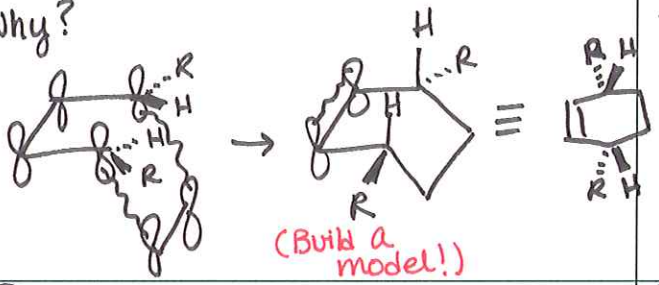
(Build a model)

(21)

② Concerning the diene



Why?



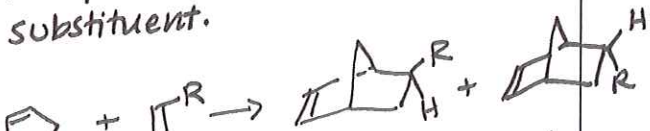
(Build a model!)

(22)

③ The "Alder" Rule

Generally needs to be applied if
1) Diene is cyclic (some exceptions where diene is acyclic)

2) Dienophile has unsaturated substituent.

ex: 

R = unsaturated substituent

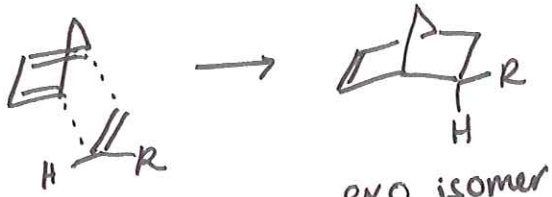
exo-isomer (R) points away from alkene

endo-isomer (R) toward alkene

FAVORED

(23)

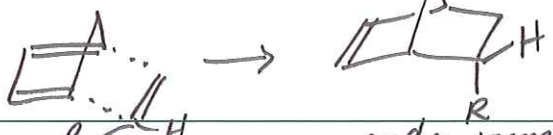
Exo-approach:



R away from diene

exo isomer

Endo-approach:



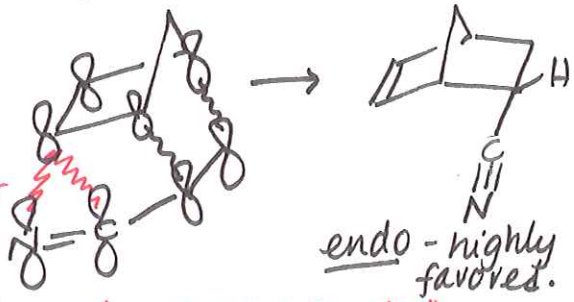
R toward diene.

endo isomer

(24) Why is endo approach favored for unsaturated substituents?

Consider: 

Endo Approach:

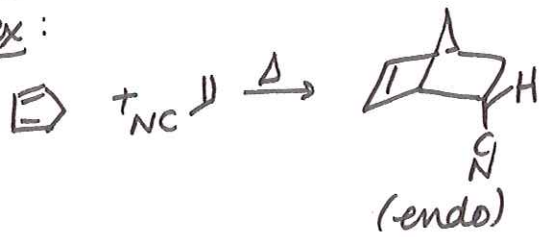


endo - highly favored.

Favorable

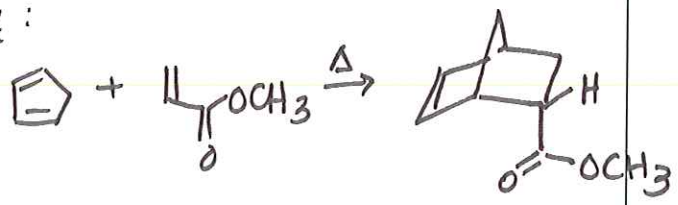
(25)

ex :



(endo)

ex :



(endo)