

No Quiz or recitation today

Office hours until 12:30pm

Diels-Alder: Regiochemistry

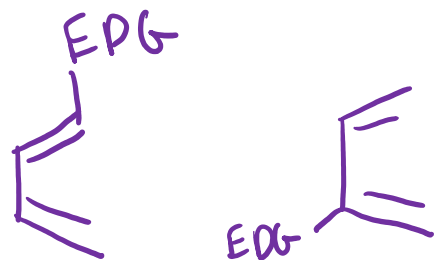


4/7/2023

1950 Nobel Prize

Electronics of Diels Alder

Need one e^- rich partner (Nucleophile) (the diene) and one e^- deficient partner (Electrophile) (dienophile)



EDG: e^- donating group

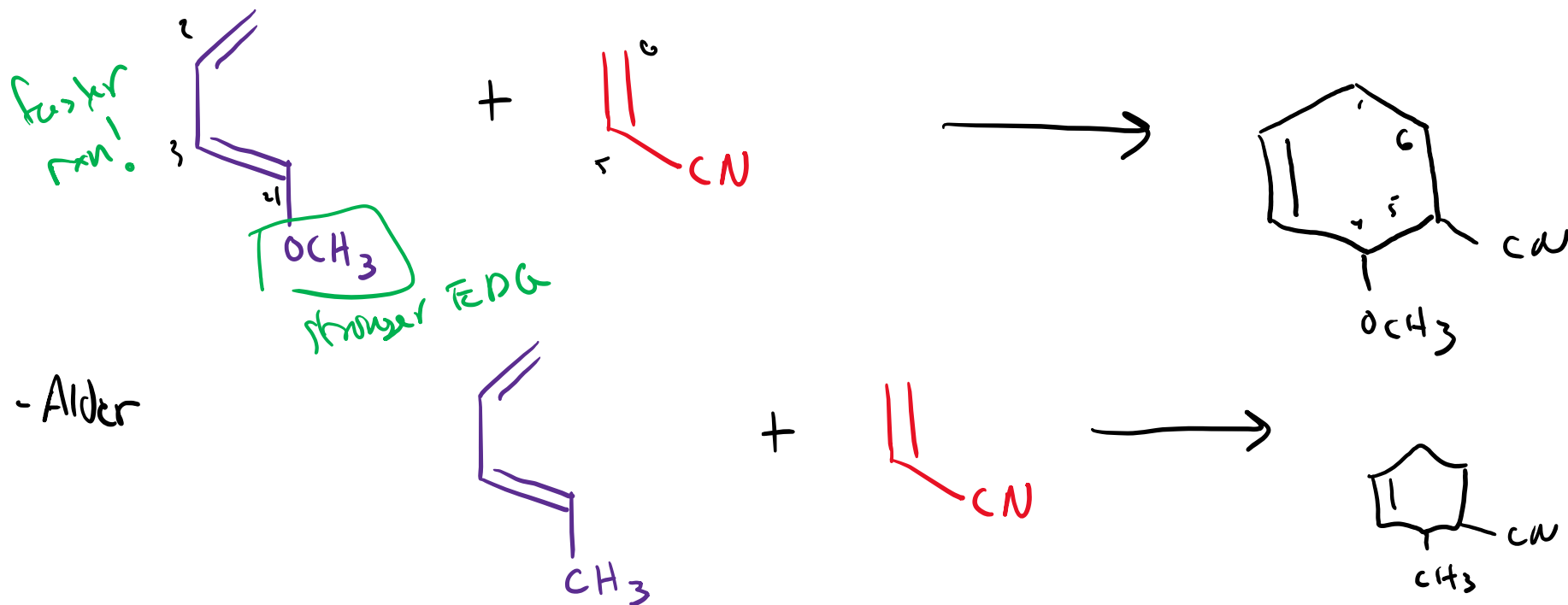


EWG: e^- withdrawing group

more e^- rich diene / e^-

poor diene

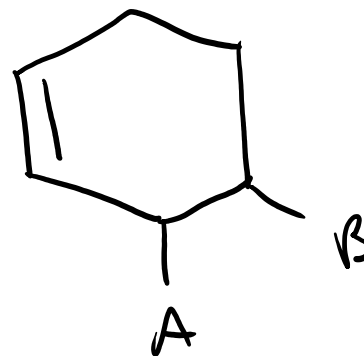
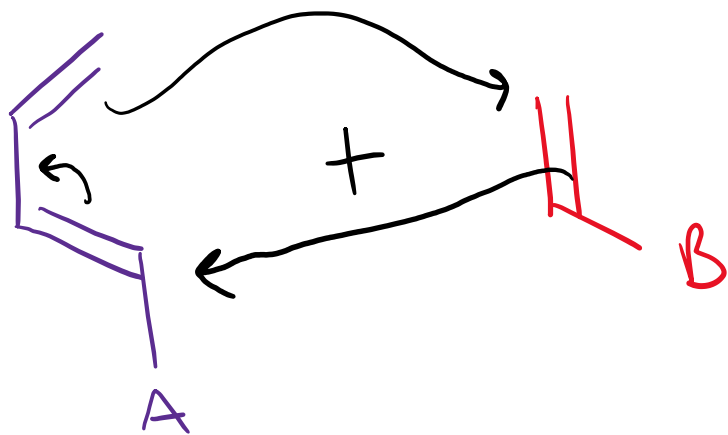
↳ faster Diels-Alder Reaction



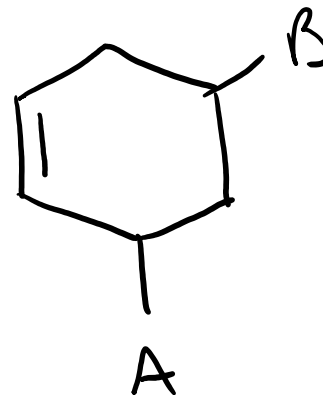
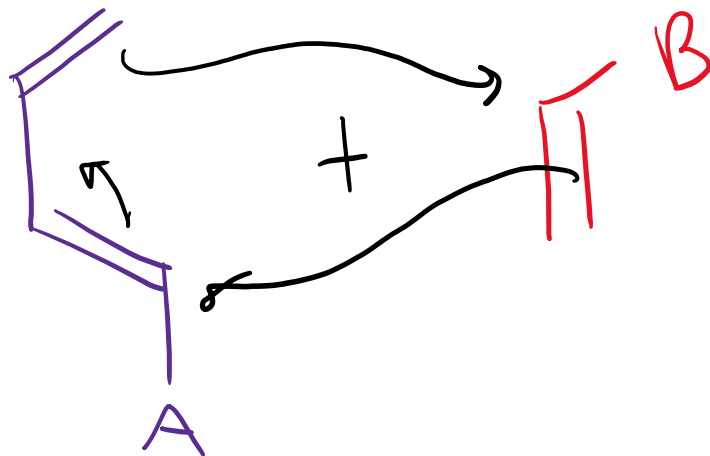
Regiochemistry of Diels-Alder

How do we predict which isomer???

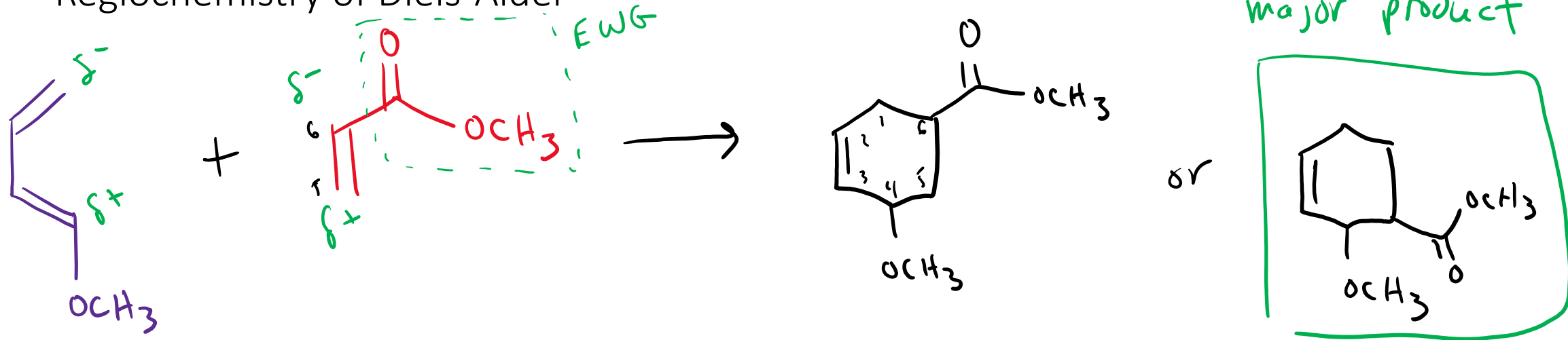
→ label partial charges. (w/o stereochem... for now)



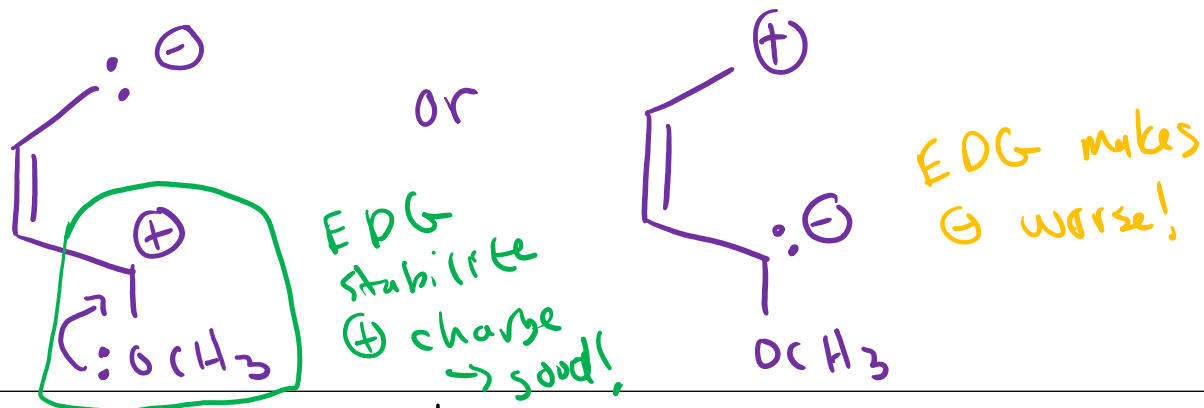
Constitutional Isomers



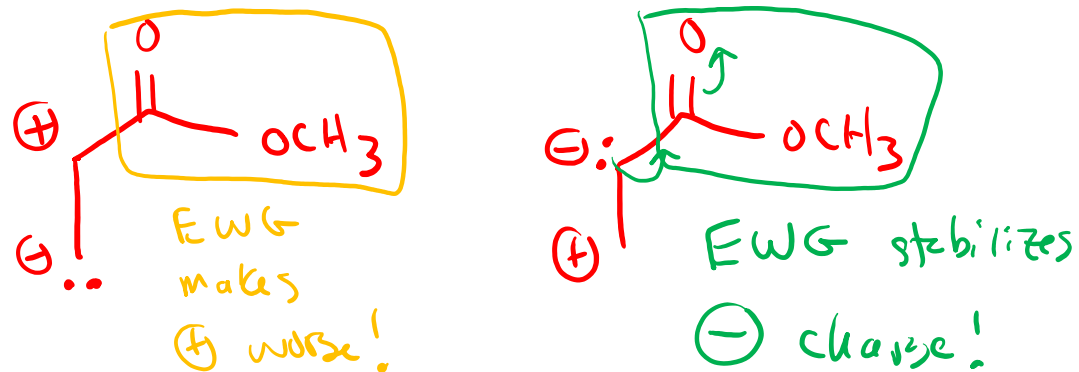
Regiochemistry of Diels-Alder



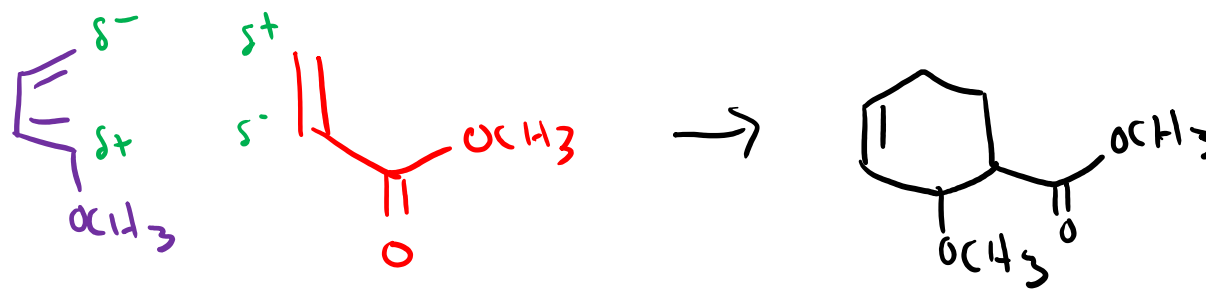
Diene:



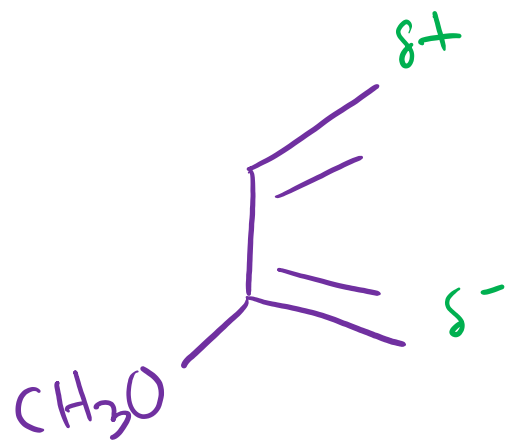
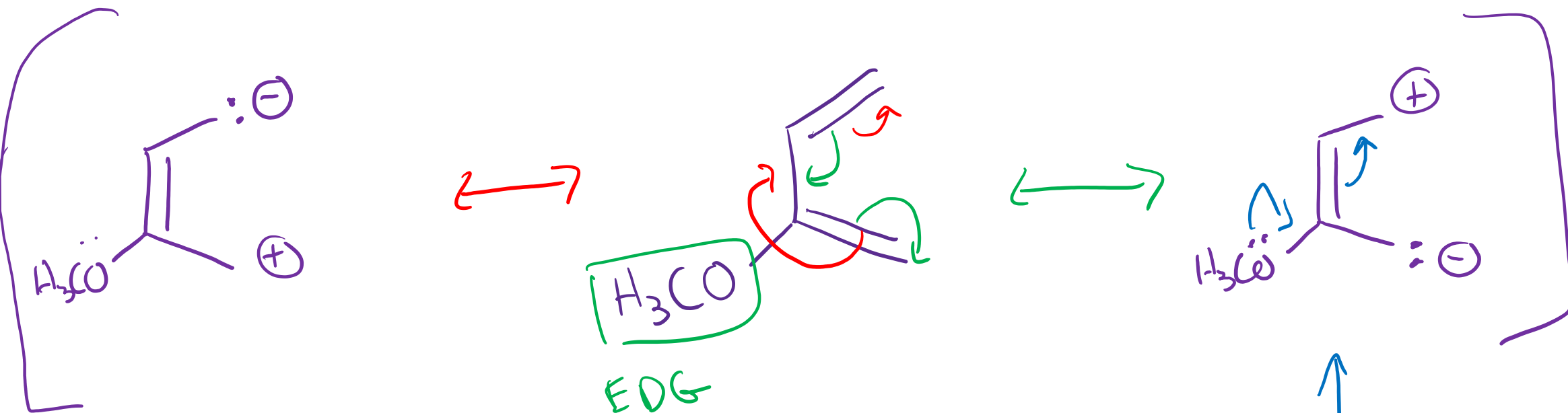
Dienophile:



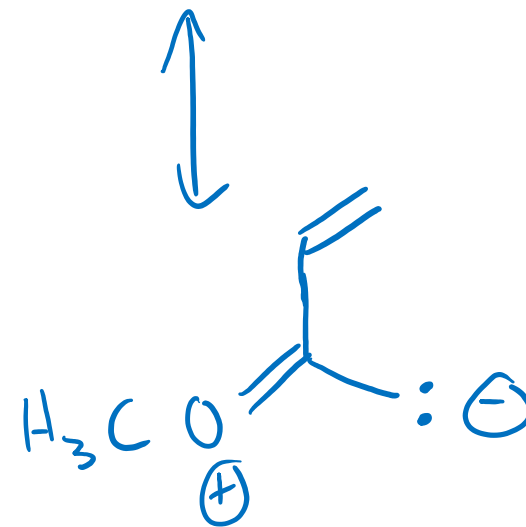
Put them together:
(line up δ^+ w/ δ^-)



Changing Position of Electron Donating Group (EDG) on Diene



★ here, EDG stabilizes δ^+ in less obvious way than before ★

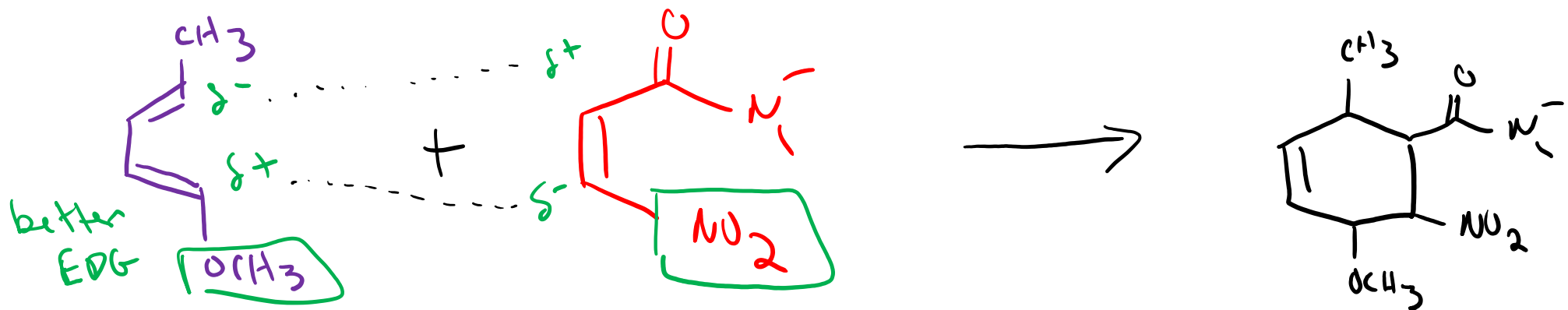


Diels-Alder Regiochemistry: Other Notes

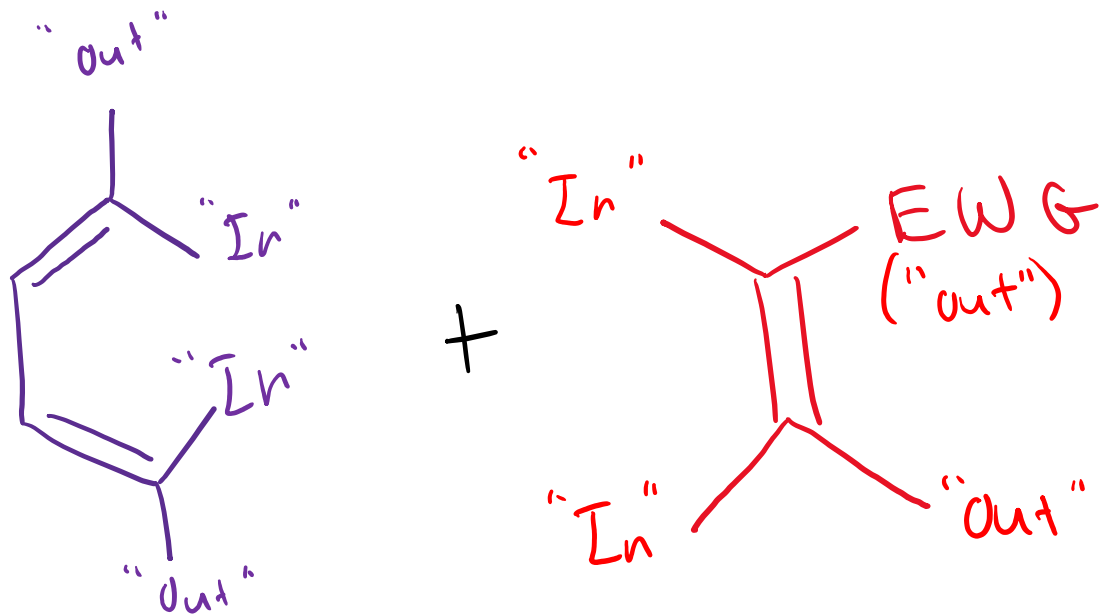
- a) EDG + EWG strengths are the same as in Chapter 18 (EAS)
- alkyls ($-\text{CH}_3$, $-\text{Et}$, $-\text{R}$) are weak EDG (induction)
 - halogens ($-\text{X}$) are weak EWG (induction only)

Resonance >>>> induction alwaysTM for electronic stability

- b) Strongest EDG / EWG takes priority when assigning partial charges

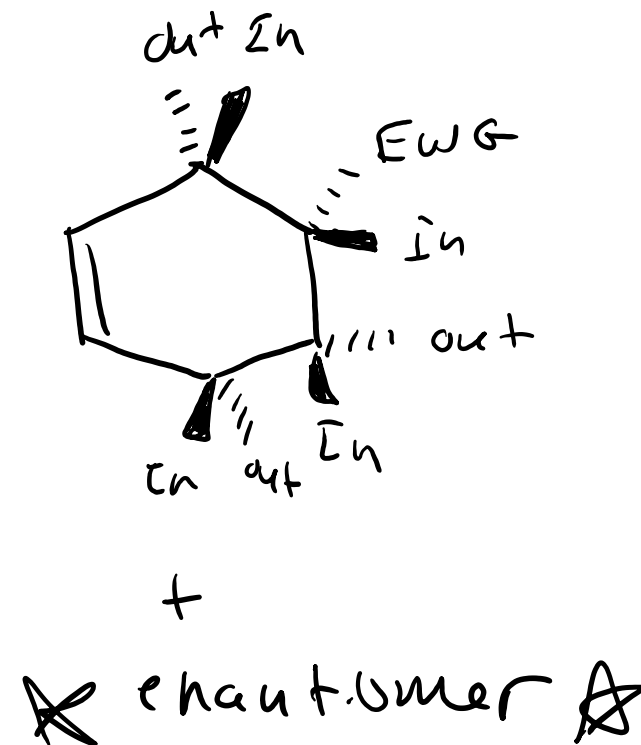


Stereochemistry of Diels-Alder



all "In" go to wedge (▴)
all "out" go to dash (▾)

always face
EWG "out"



Drawing Diels-Alder Products: Strategy

- ① Rotate *diene* to s-cis conformation
- ② Label partial charges & line up regiochemistry
- ③ Use "In/out" to determine stereochemistry (wedges + dashes)

