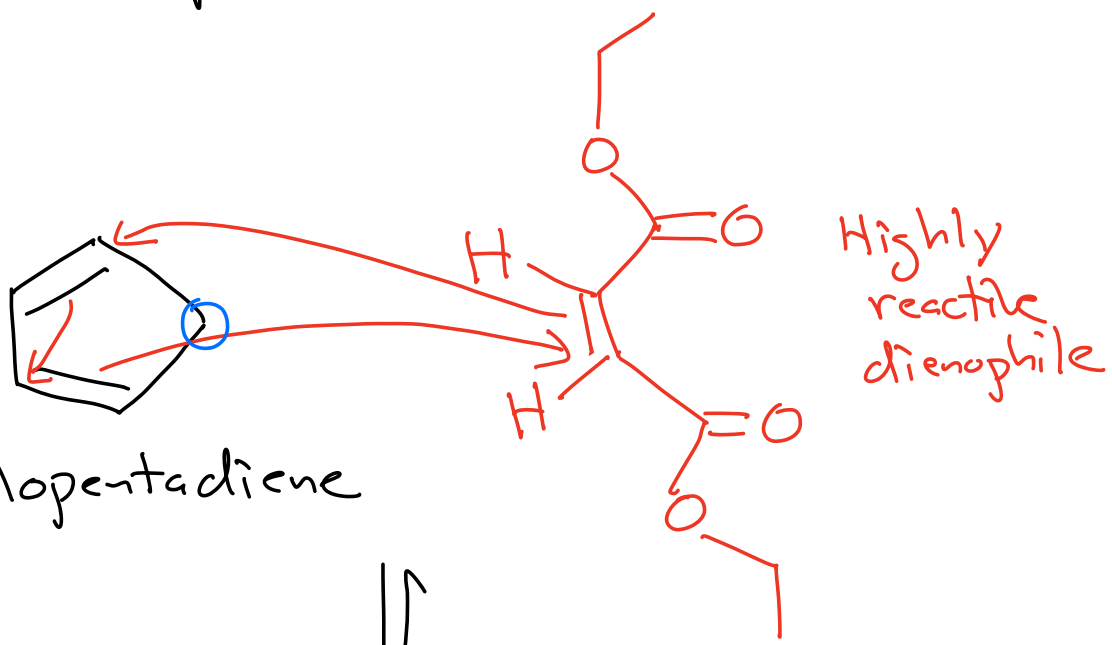
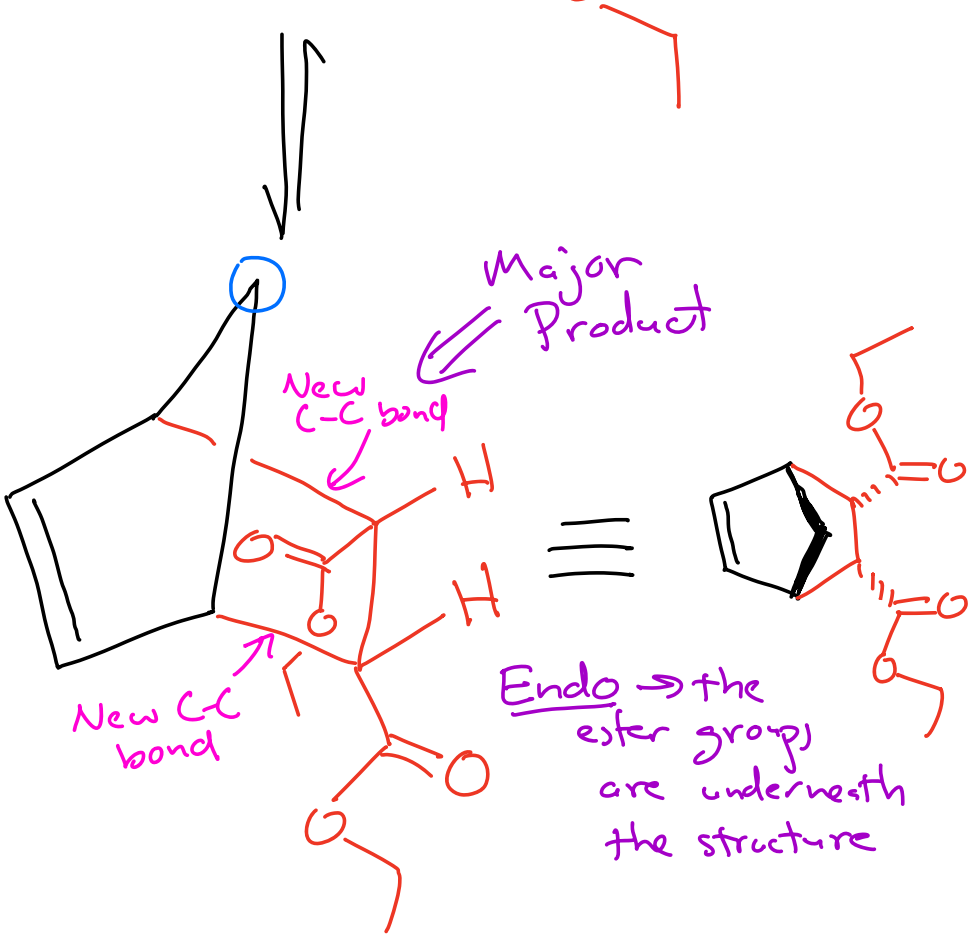
The following is the only Diels-Alder reaction you are responsible for in this class

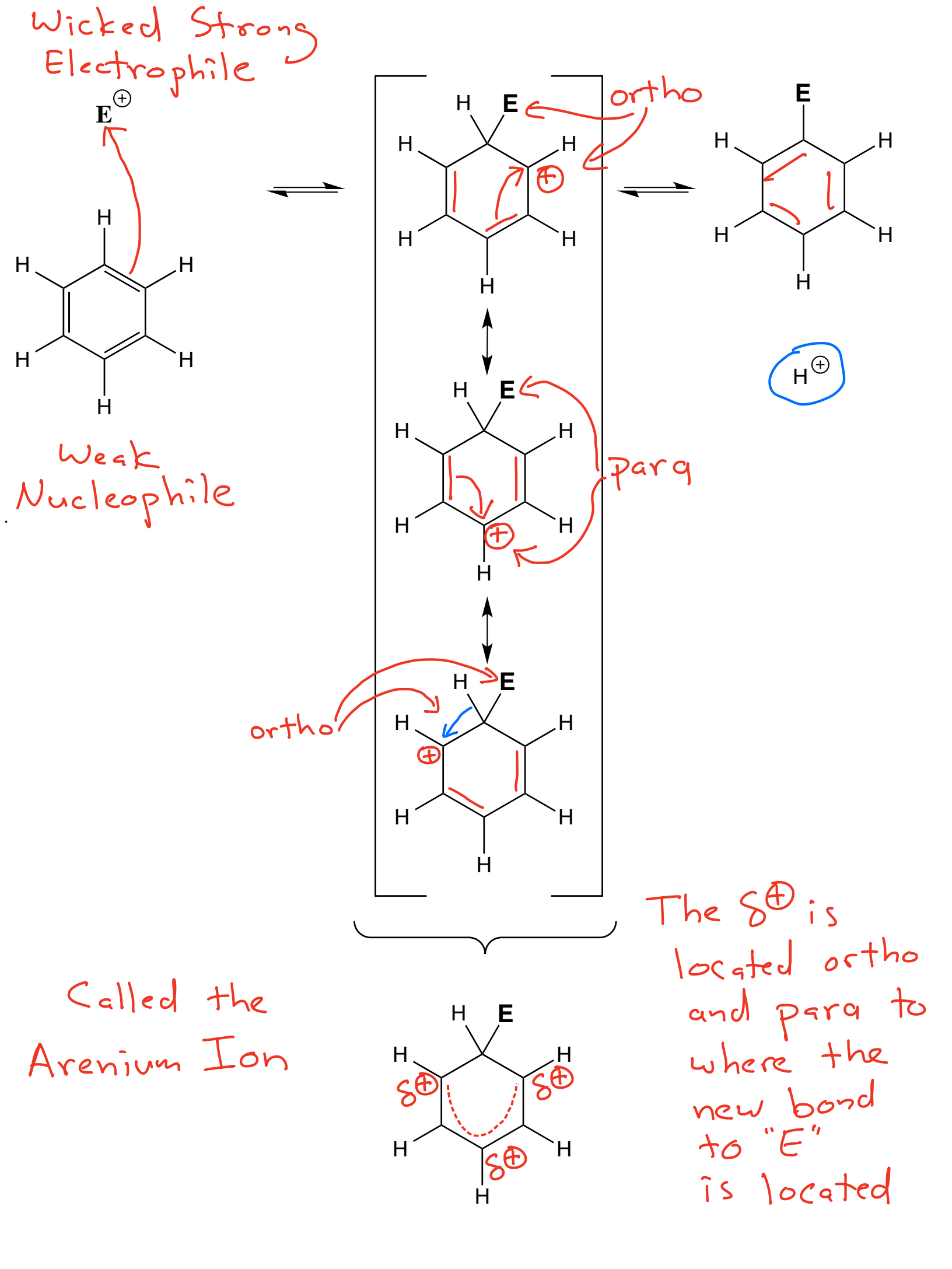


Highly reactive dienophile

Cyclopentadiene

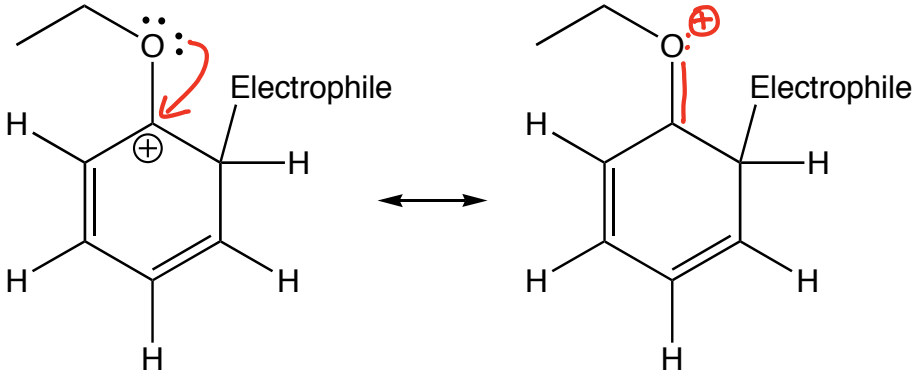


Endo → the ester groups are underneath the structure


Wicked Strong Electrophile
E⊕
H
H
H
H
H
H
Weak Nucleophile
ortho
para
ortho
H E
H⊕
Called the Arenium Ion
δ⊕
δ⊕
δ⊕
The δ⊕ is located ortho and para to where the new bond to "E" is located

Arenium ion ***stabilizing*** interactions ← GOOD

A) **Pi donation**, a resonance effect for atoms with lone pairs attached to the ring

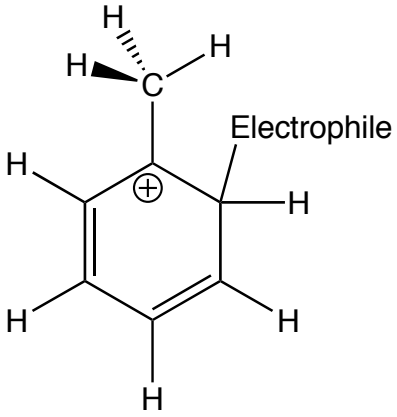


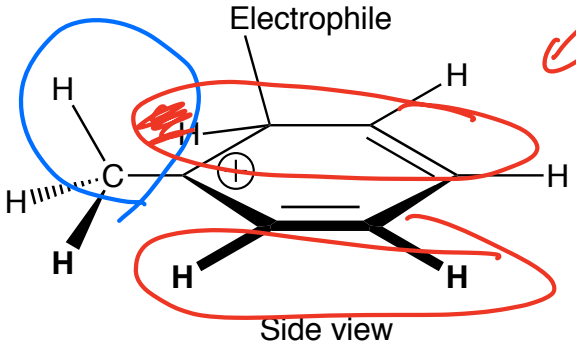
← "pi-pi"

The "Greek interactions"

"sigma-pi"

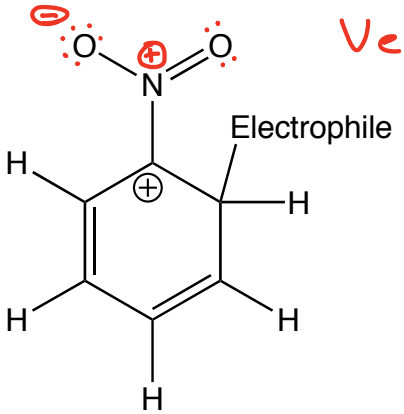
B) **Hyperconjugation** for alkyl groups attached to the ring





Arenium ion ***destabilizing*** interaction ← BAD

A) **Inductive effect** of electronegative atoms or groups attached to the ring



Very electron withdrawing

GOOD → Through pi donation or hyperconjugation the arenium ion is stabilized

↓

Activating
Ortho-Para
Directing

Most effective ortho and para

Atoms attached to the ring have a lone pair of electrons or alkyl groups

BAD → Through the inductive effect – electron withdrawing groups – the arenium ion is destabilized

↓

Deactivating
Meta directing

"Least bad" meta

Mostly when the atom attached to the ring has a π bond or $-CX_3$ in which X is halogen

UGLY

↓

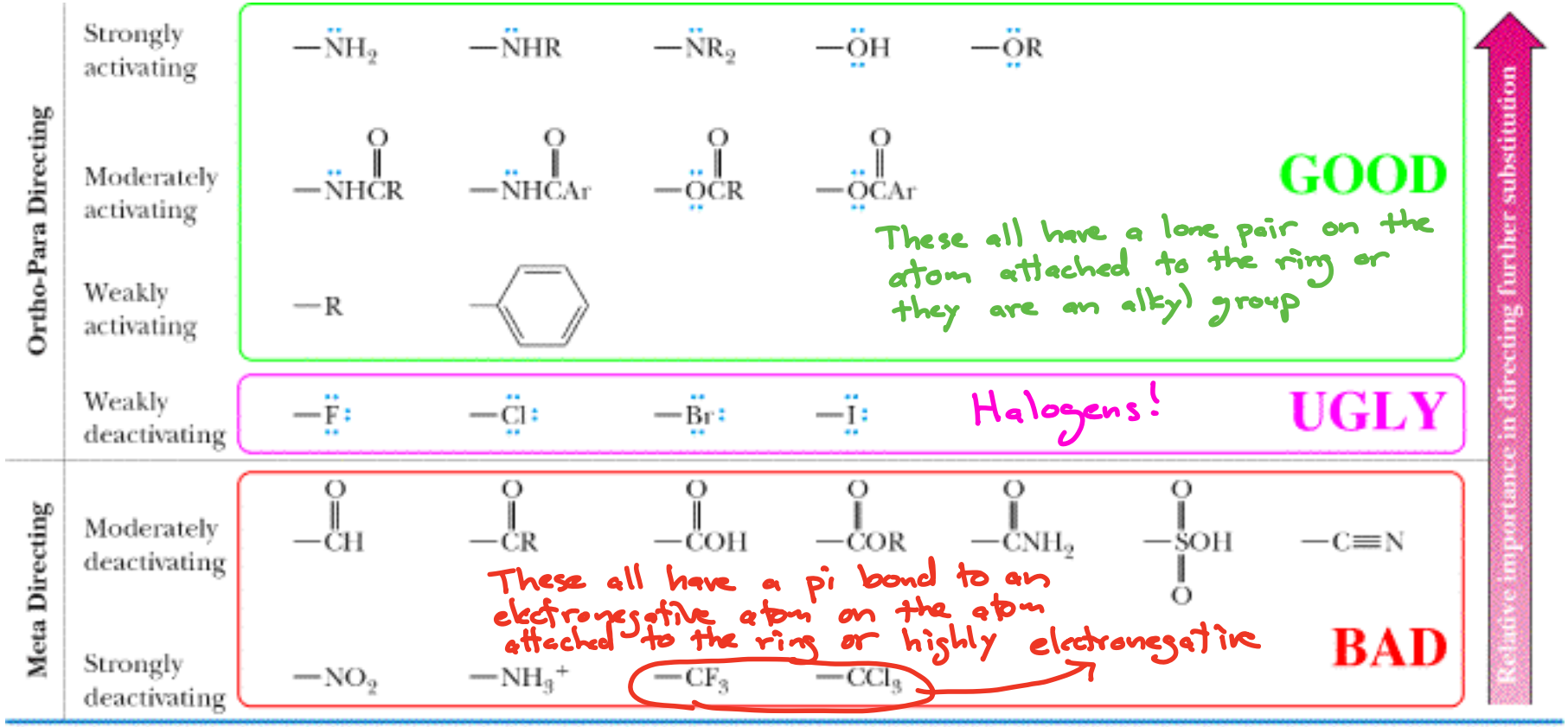
Deactivating
Ortho-Para
Directing

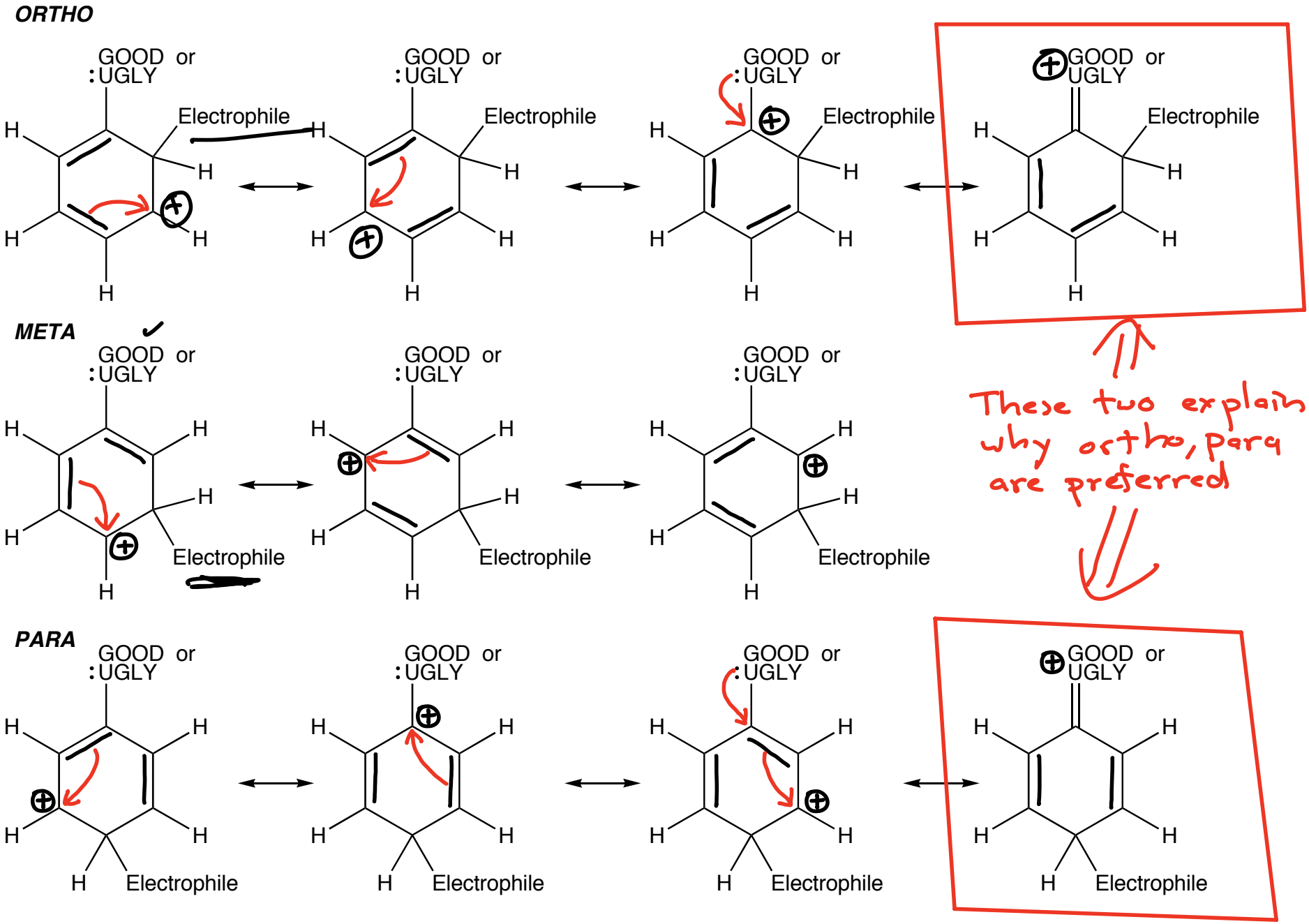
→ Both GOOD and BAD at the same time

→ Through pi donation or hyperconjugation the arenium ion is stabilized
Most effective ortho and para

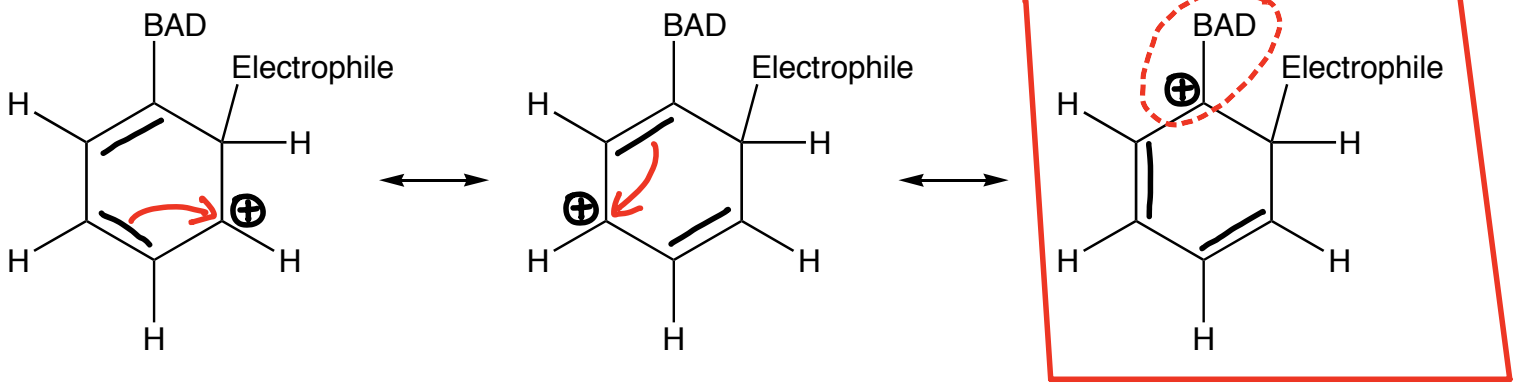
→ Through the inductive effect- electron withdrawing groups- the arenium ion is destabilized

Halogens -Cl: -F:
-Br: -I:

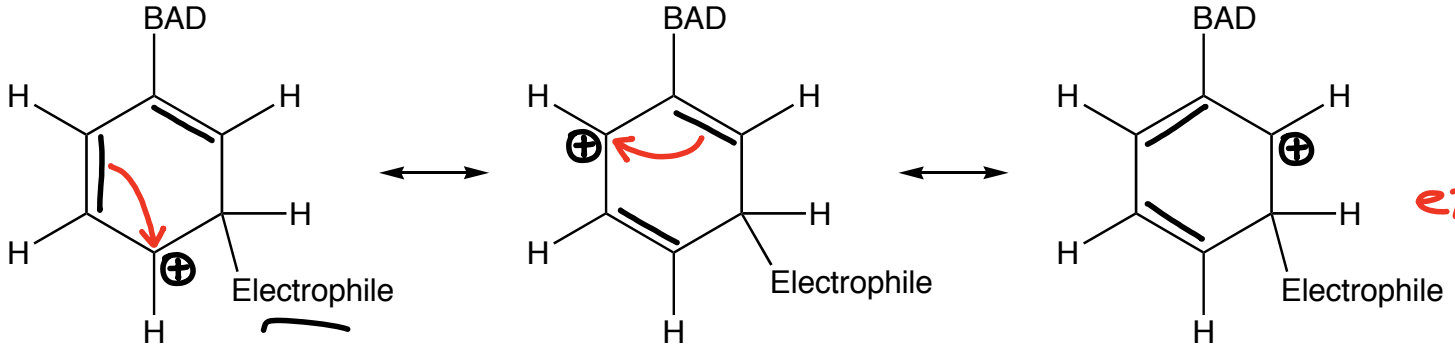

Ortho-Para Directing
Strongly activating
—NH2
—NHR
—NR2
—OH
—OR
Moderately activating
—NHCR
—NHCAr
—OCR
—OCAr
Weakly activating
—R
These all have a lone pair on the atom attached to the ring or they are an alkyl group
GOOD
Weakly deactivating
—F:
—Cl:
—Br:
—I:
Halogens!
UGLY
Meta Directing
Moderately deactivating
—CH
—CR
—COH
—COR
—CNH2
—SOH
—C≡N
These all have a pi bond to an electronegative atom on the atom attached to the ring or highly electronegative
Strongly deactivating
—NO2
—NH3+
—CF3
—CCl3
BAD
Relative importance in directing further substitution


ORTHO
GOOD or
:UGLY
Electrophile
META
PARA
These two explain why ortho, para are preferred

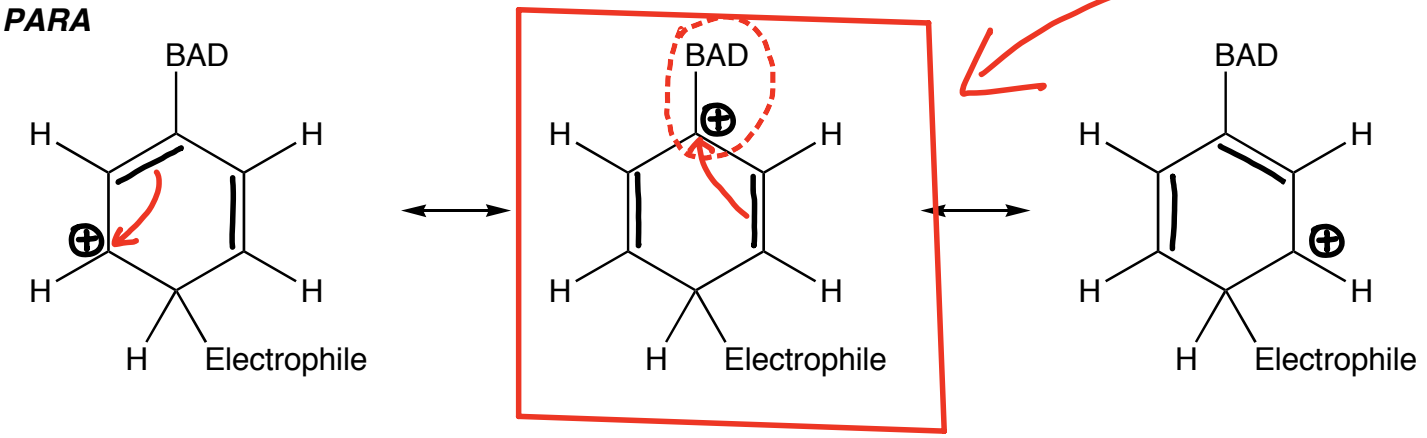
ORTHO



META



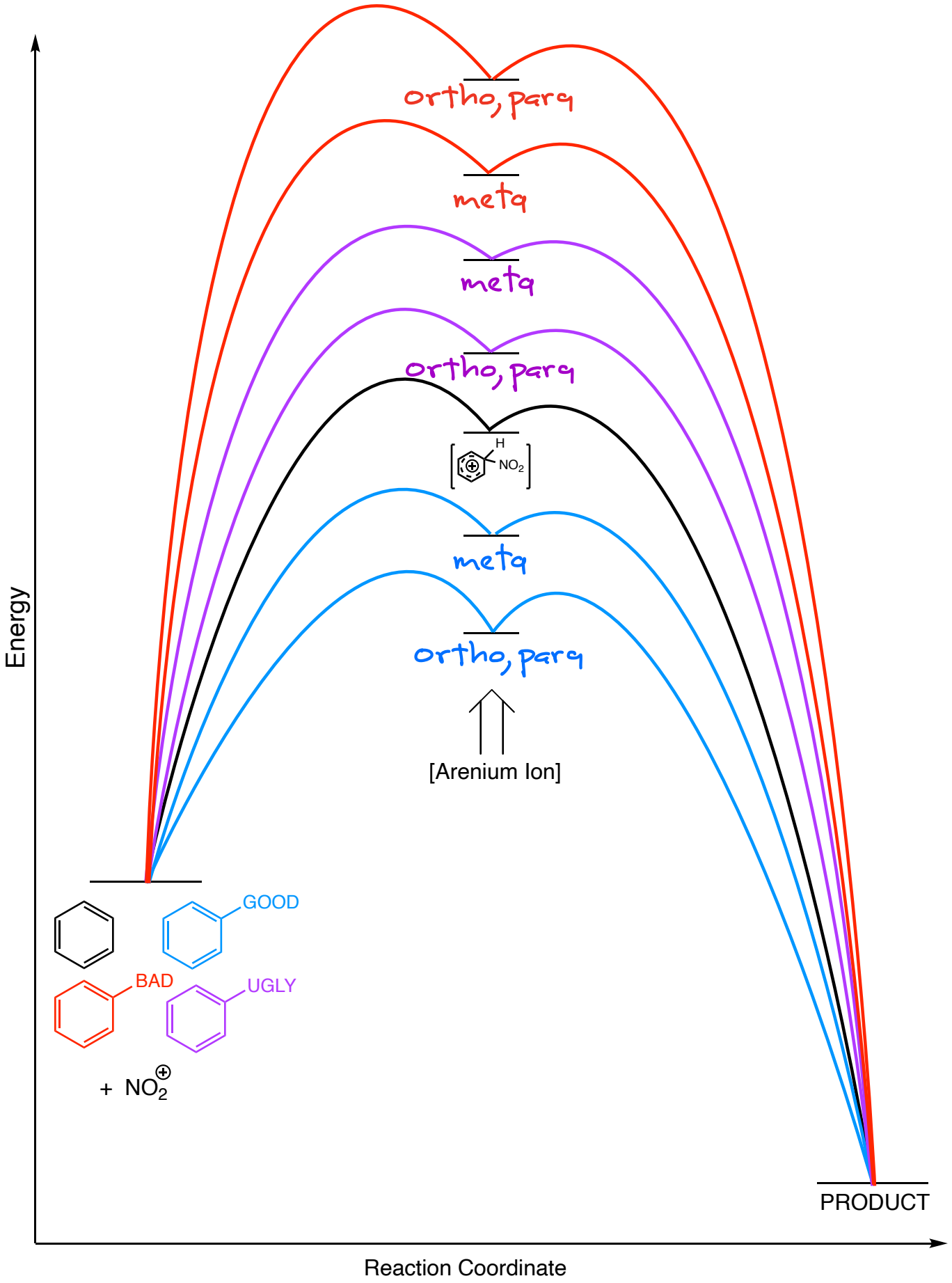
PARA



Very destabilizing explaining why for BAD groups

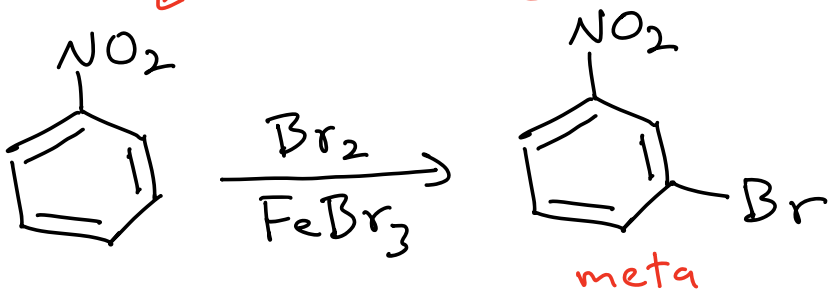
"meta is betta"

No terrible interaction meta like there is ortho, para


ortho, para
meta
meta
ortho, para
H
NO2
meta
ortho, para
[Arenium Ion]
GOOD
BAD
UGLY
+ NO2
PRODUCT
Energy
Reaction Coordinate

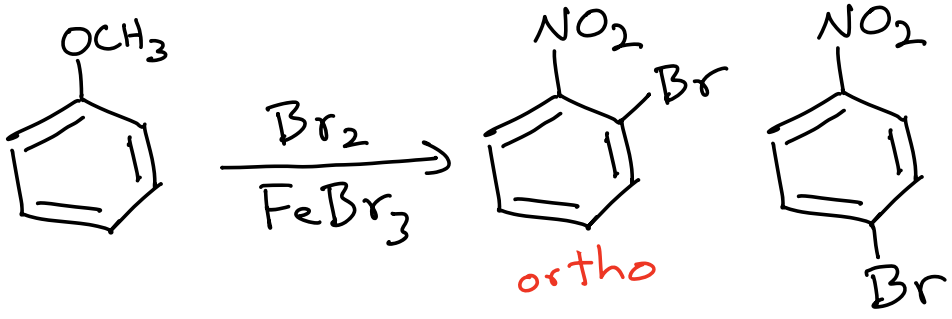
Examples

BAD, meta directing



meta

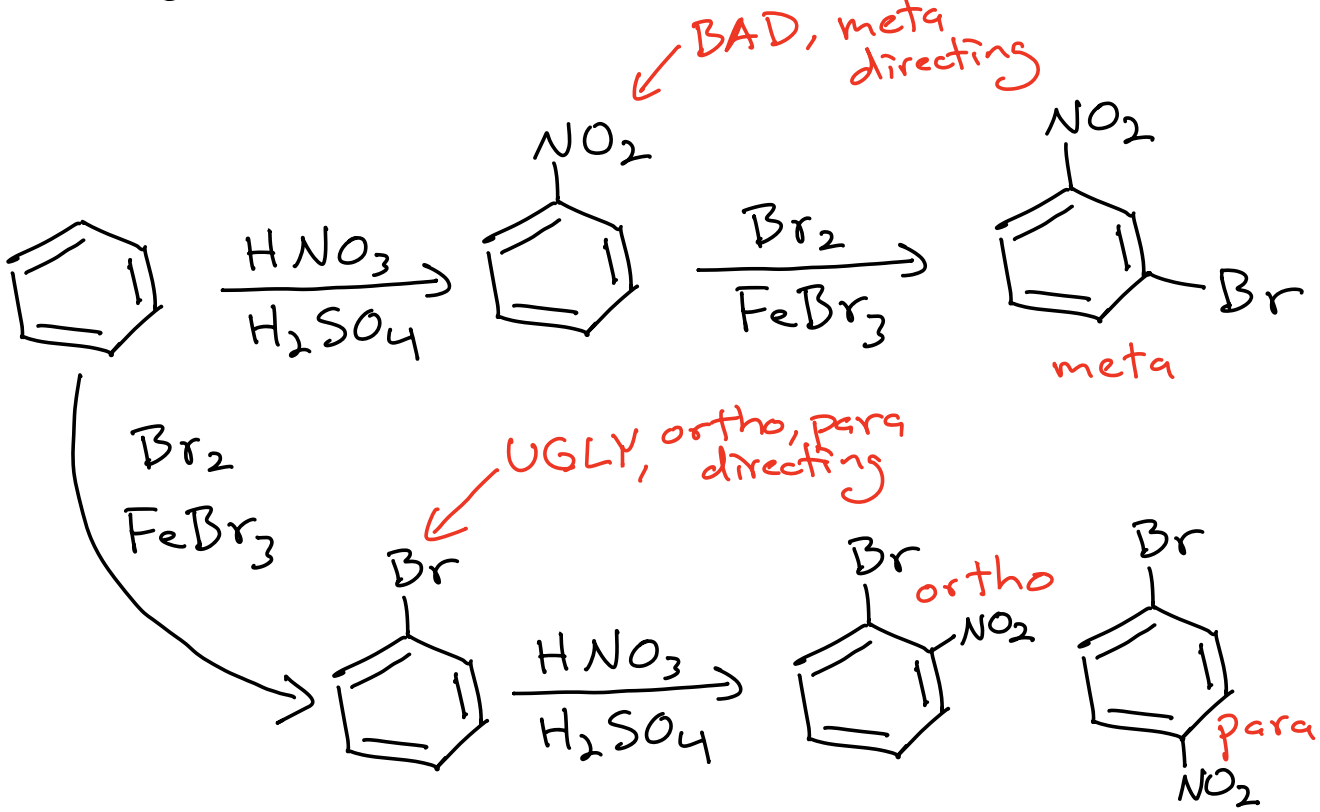
GOOD, ortho, para directing



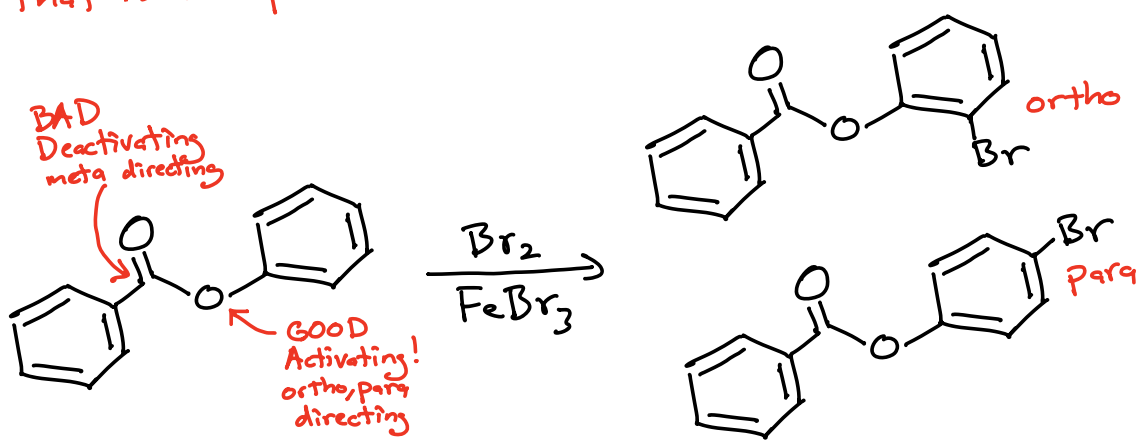
ortho

para

The order in which you add groups matters!



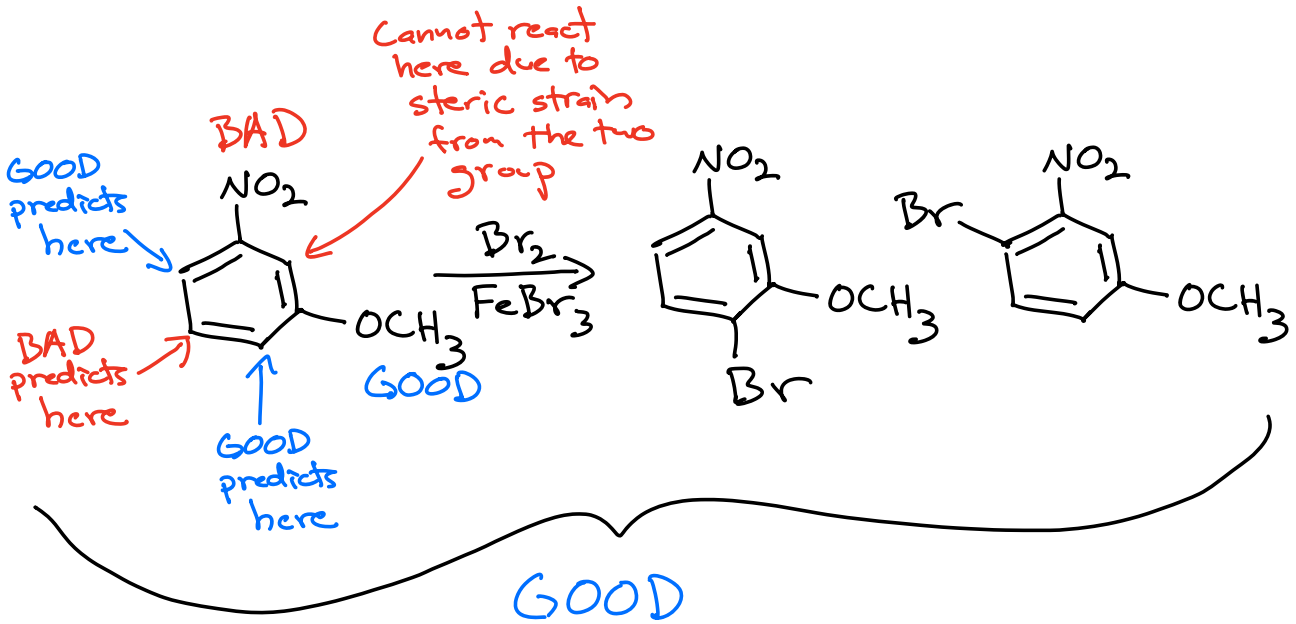
Classic Question → As you can see in the energy diagrams, the ring with the GOOD group has a lower energy barrier so that is the product we see → ortho, para



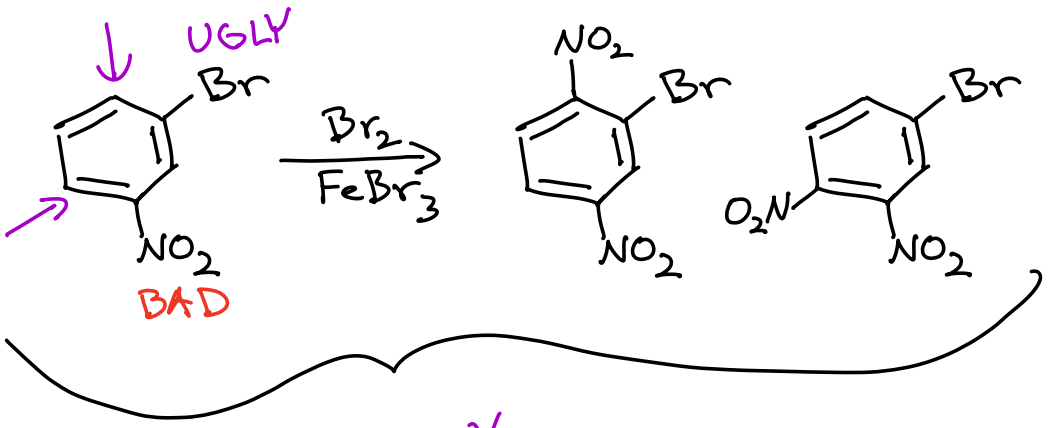
What if there are two groups already on the ring and they predict different products? It is a duel → the movie got it right!

GOOD beats BAD and UGLY

UGLY beats BAD

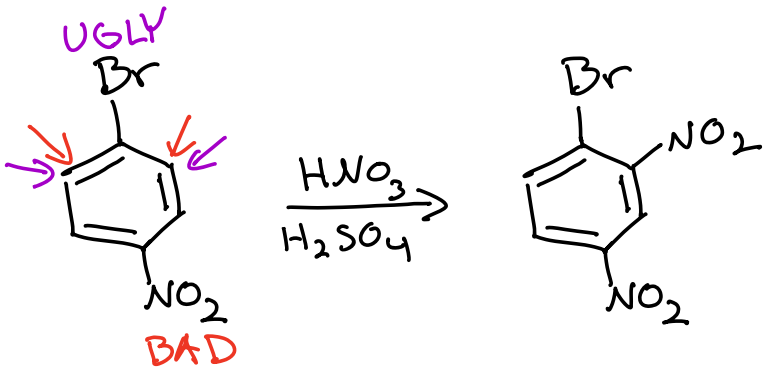


GOOD beats BAD!

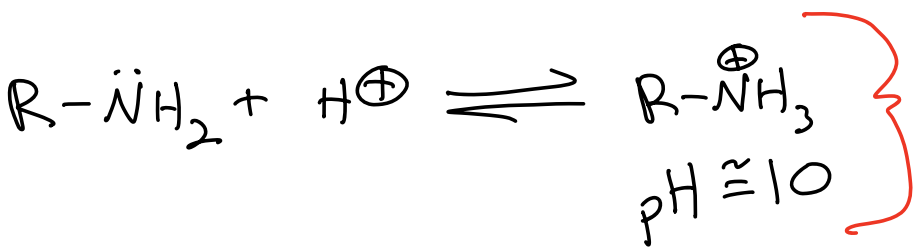


UGLY beats BAD!

Sometimes two groups will predict the same outcome



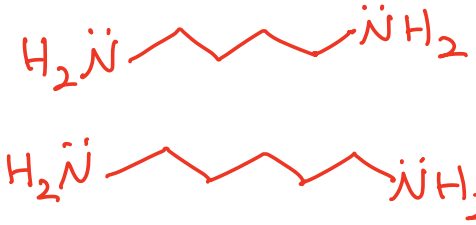
Amines → Relatively strong bases and relatively strong nucleophiles



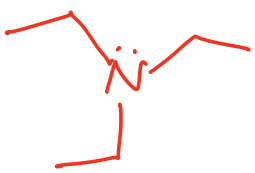
Major form present at neutral pH!

Amines are protonated and positively-charged at neutral pH ⇒ Very important in biochemistry!

Our sense of smell is highly sensitive to certain molecules that are the result of decomposition of mammal and fish flesh among other things. Not only can we detect very small amounts of these "signal" molecules, we are hard wired to be highly nauseated when we smell them → evolutionary protection to keep us from eating what might look OK, yet would make us sick.

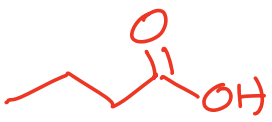


Rotten Mammal



Rotten Fish

H_2S Rotten Eggs



Barf