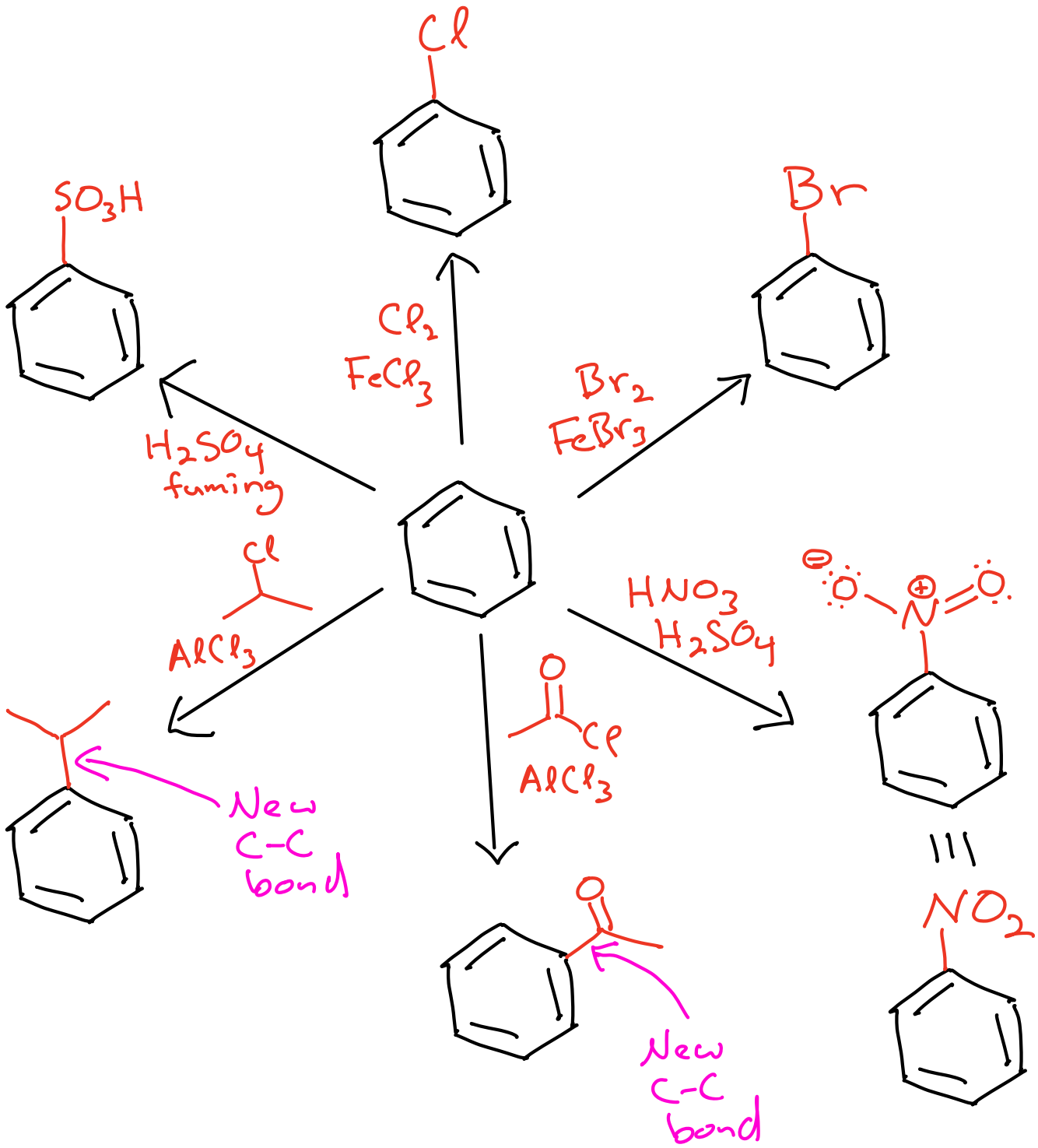
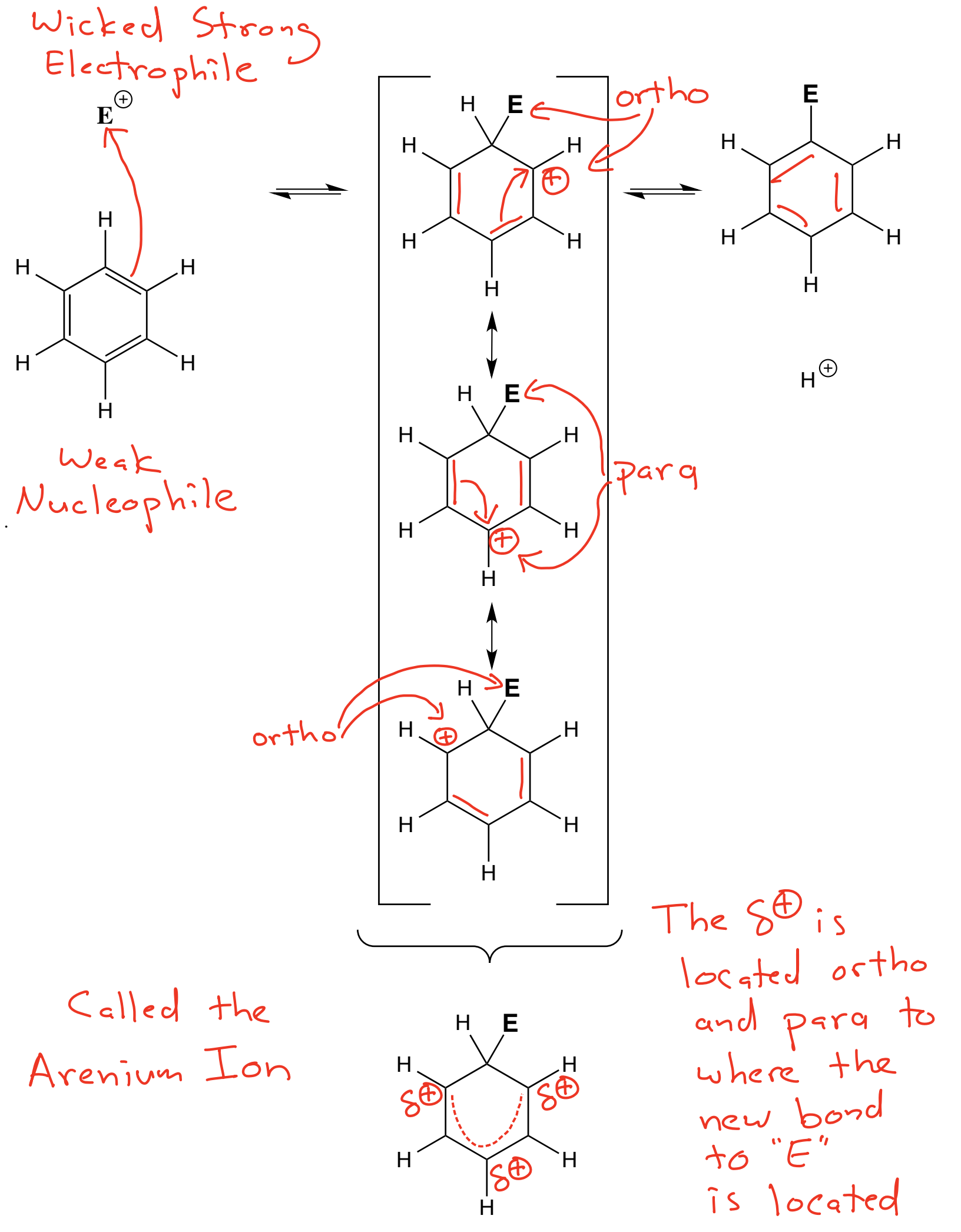
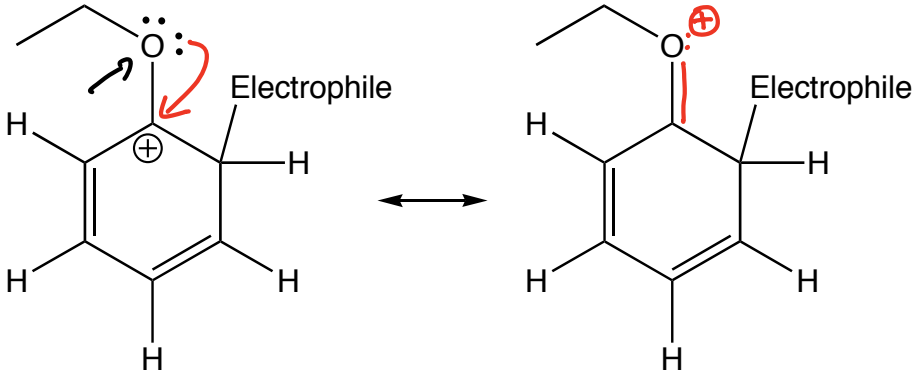
THE GOOD, THE BAD AND THE UGLY (1966)


Cl
SO3H
Br
Cl2
FeCl3
Br2
FeBr3
H2SO4
fuming
Cl
AlCl3
HNO3
H2SO4
O
Cl
AlCl3
New
C-C
bond
NO2
New
C-C
bond


Wicked Strong Electrophile
E⊕
Weak Nucleophile
ortho
para
ortho
H⊕
Called the Arenium Ion
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

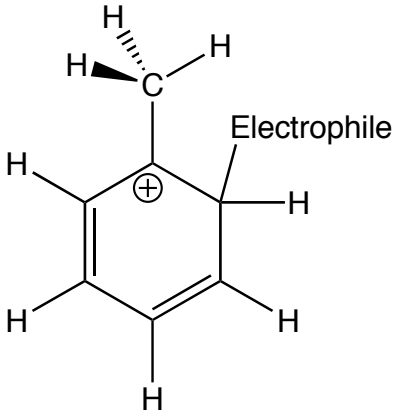


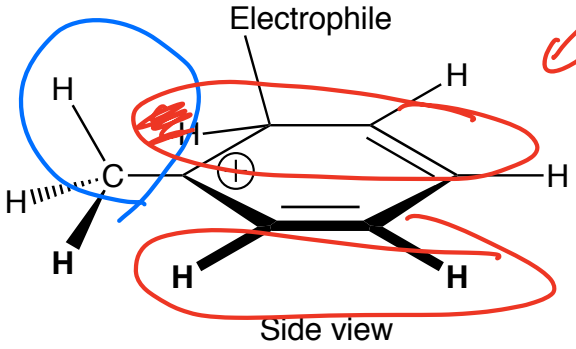
← "pi-pi"

The "Greek interactions"

"sigma-pi"

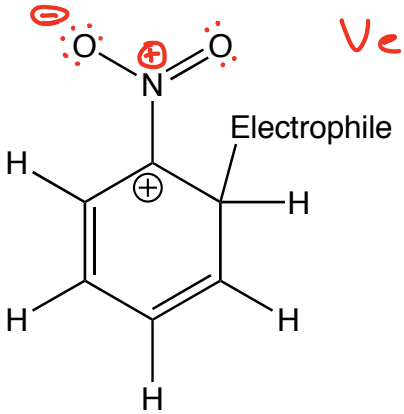
B) **Hyperconjugation** for alkyl groups attached to the ring





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

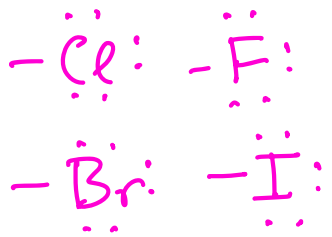
→ Both GOOD and BAD at the same time

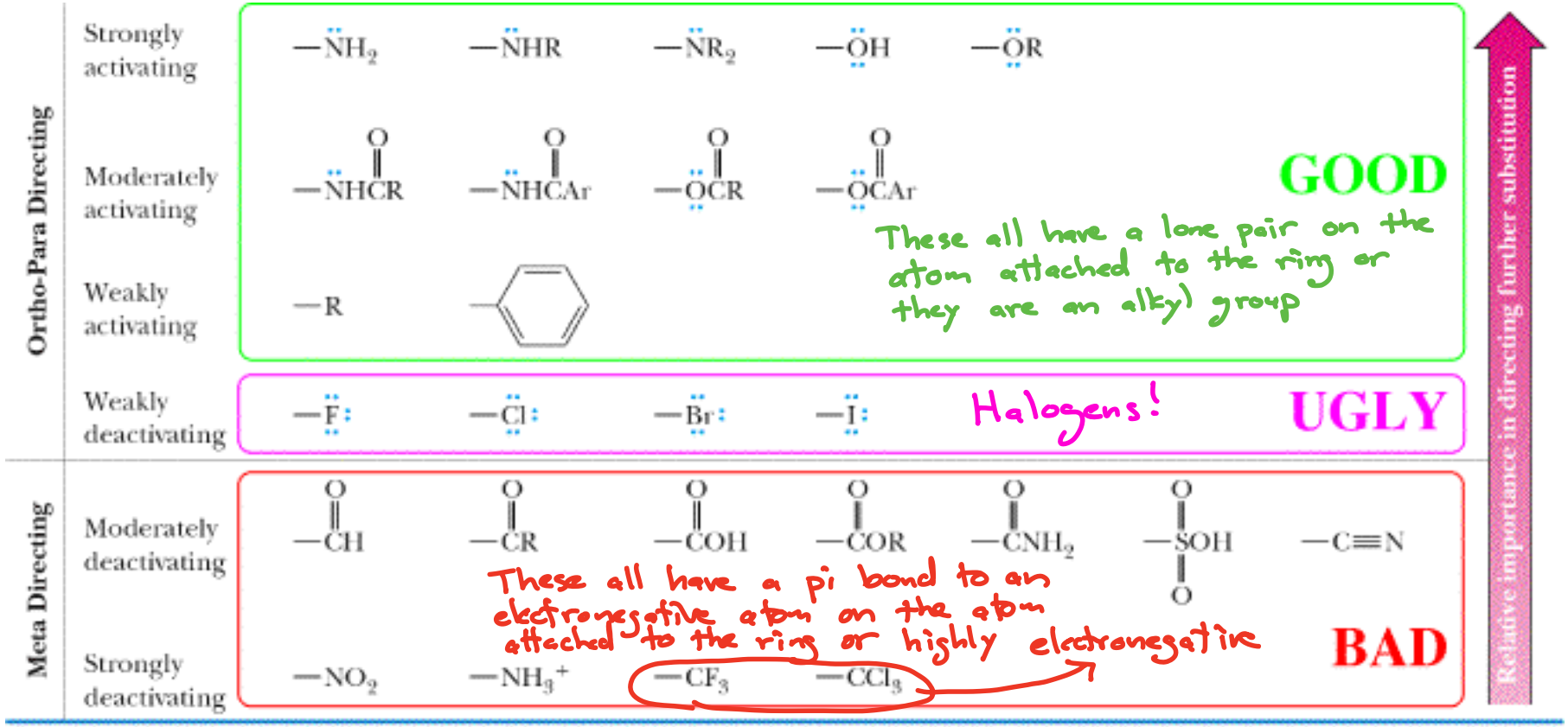
→ Through pi donation or hyperconjugation the arenium ion is stabilized

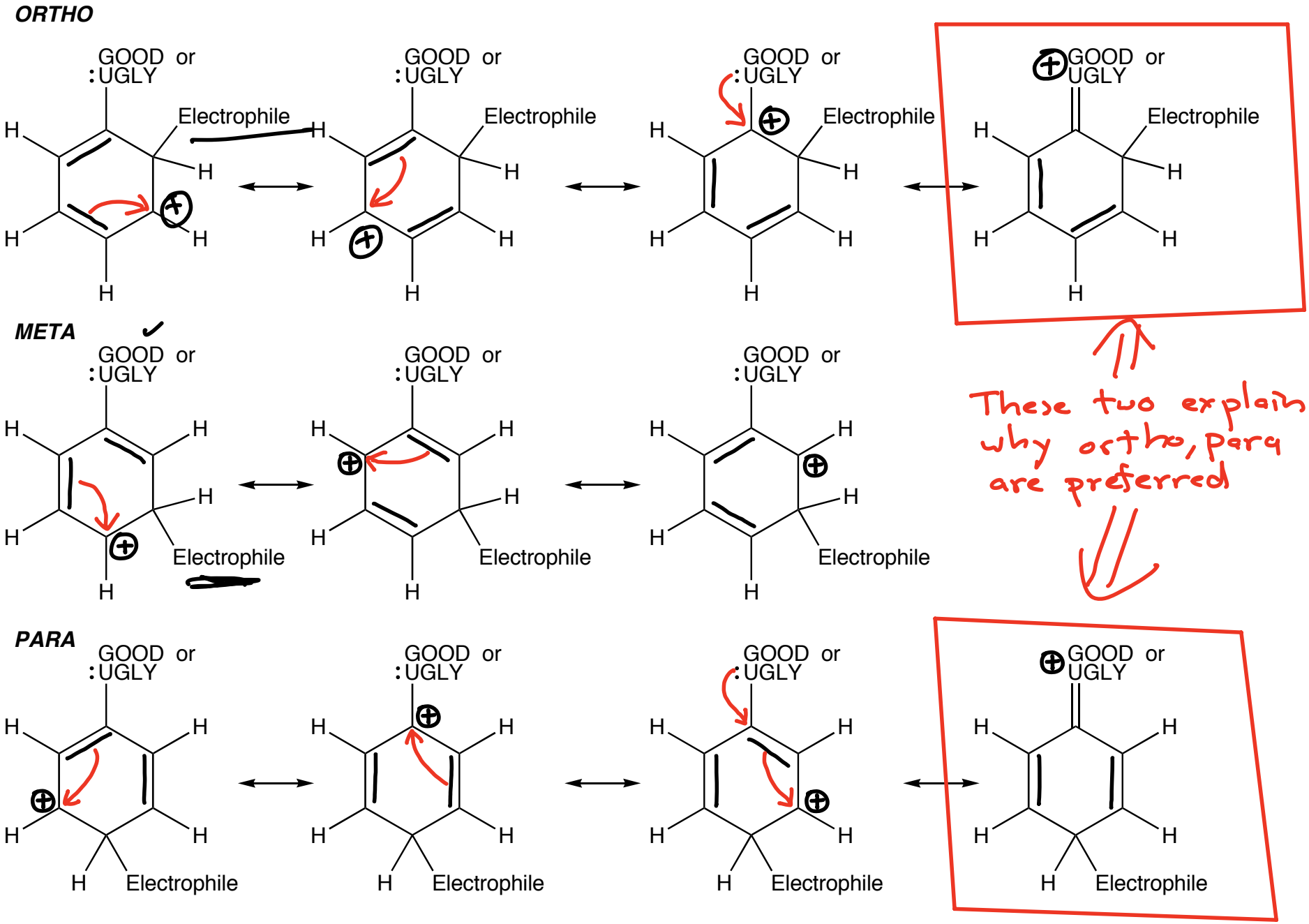
Most effective ortho and para

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

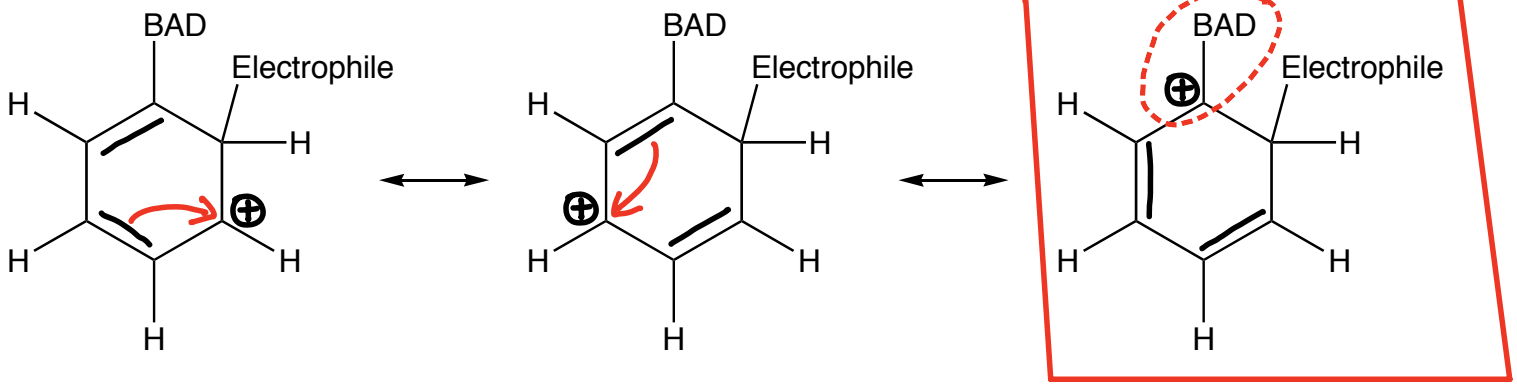
Halogens



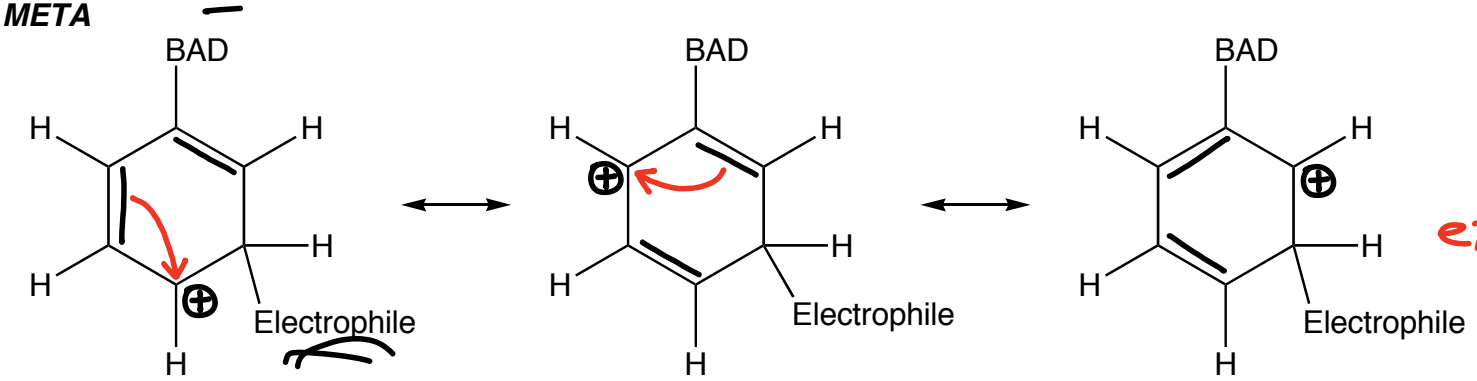

Ortho-Para Directing
Strongly activating
—NH2
—NHR
—NR2
—OH
—OR
Moderately activating
—NHCR
—NHCAr
—OCR
—OCAr
Weakly activating
—R
GOOD
These all have a lone pair on the atom attached to the ring or they are an alkyl group
Weakly deactivating
—F:
—Cl:
—Br:
—I:
Halogens!
UGLY
Meta Directing
Moderately 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

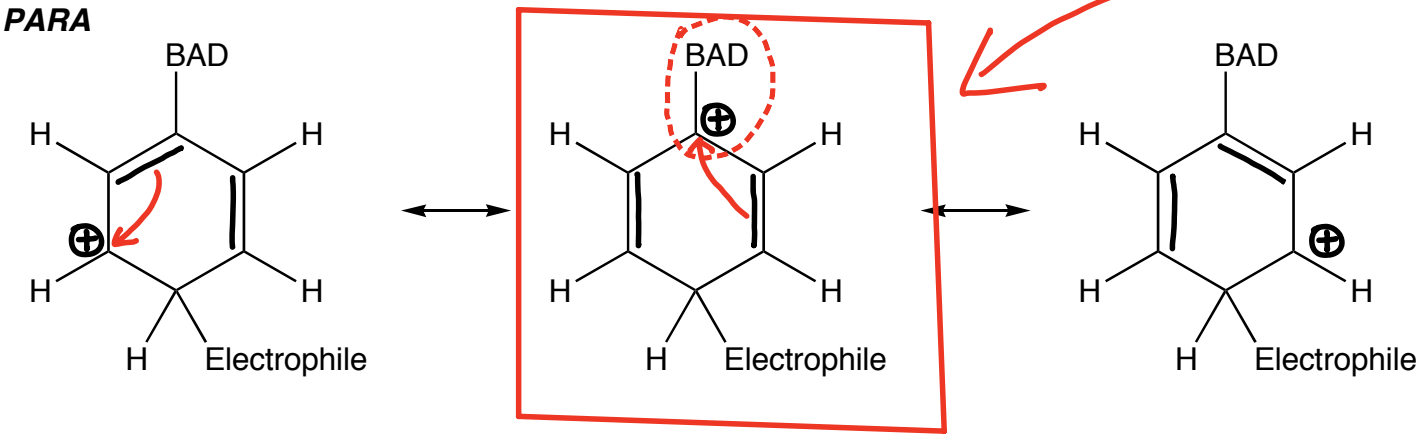
ORTHO



META



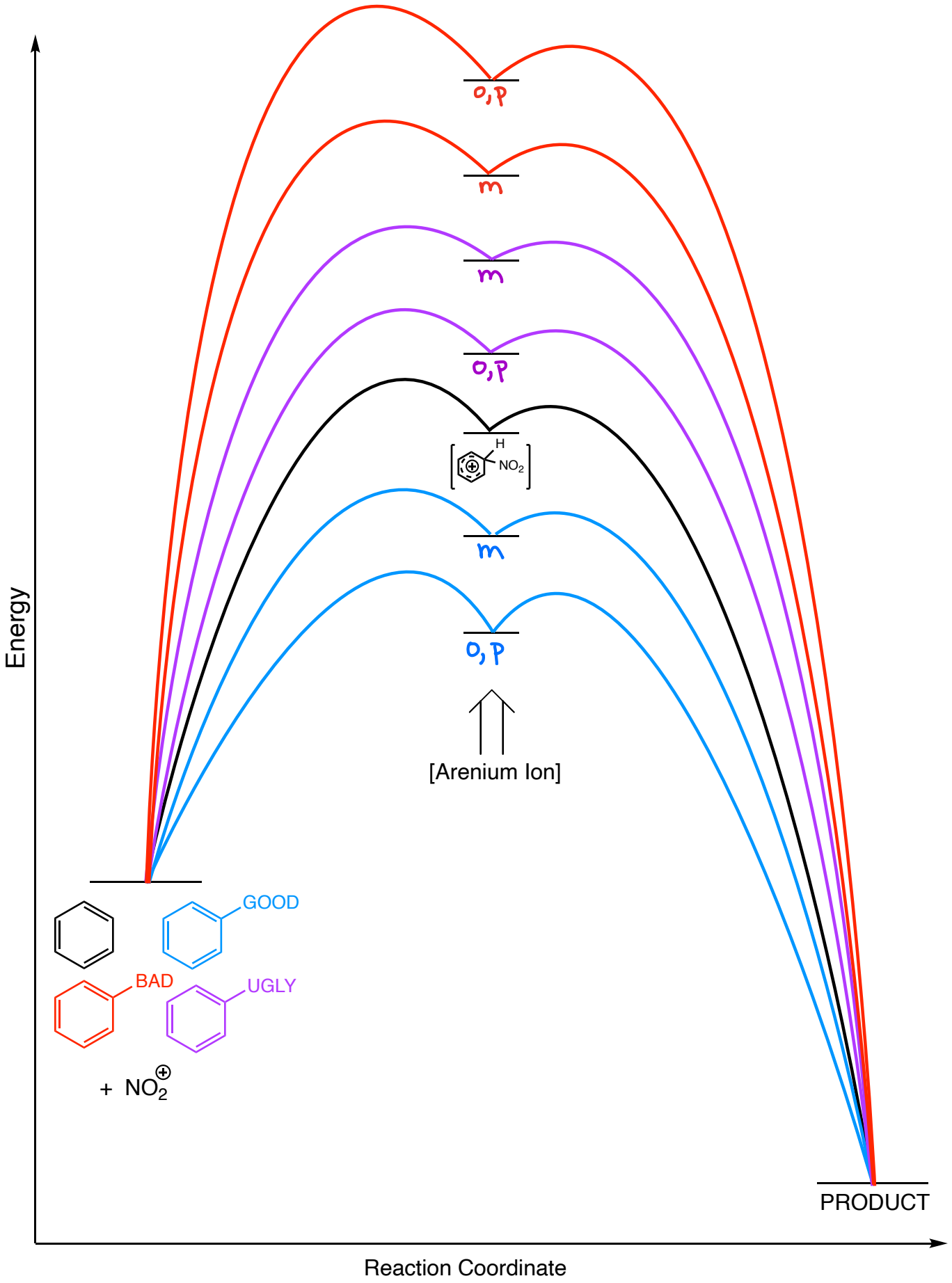
PARA



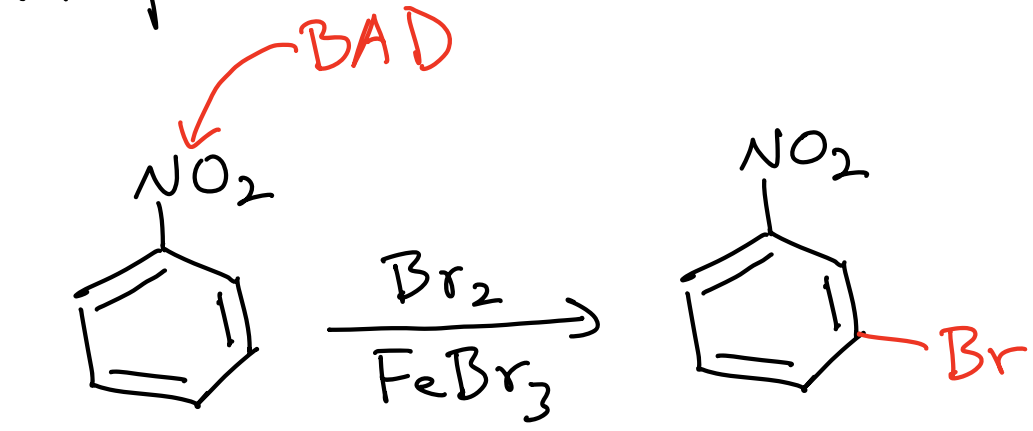
Very destabilizing explaining why for BAD groups

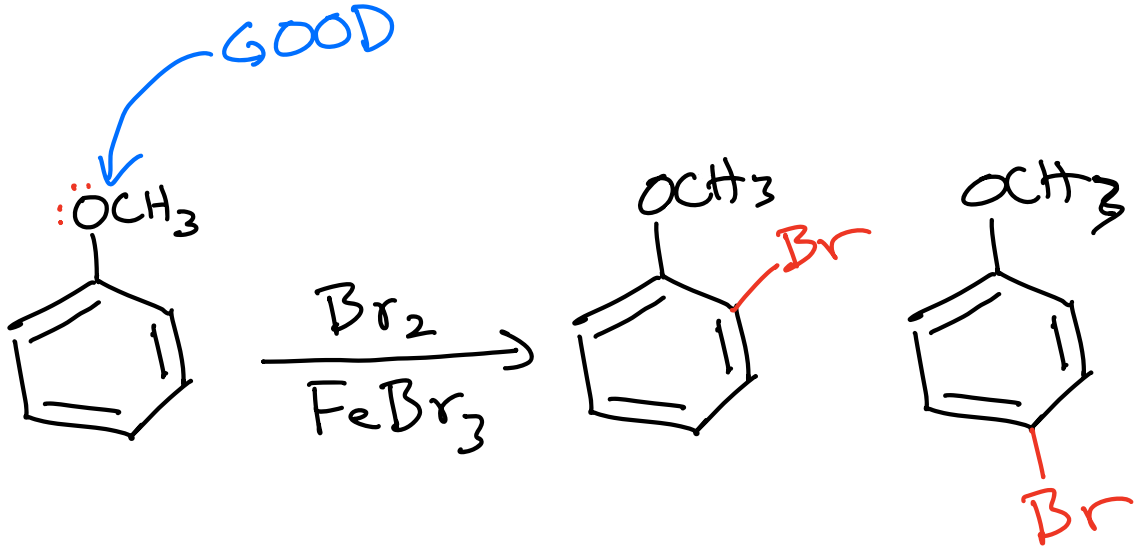
"meta is betta"

No terrible interaction meta like there is ortho, para

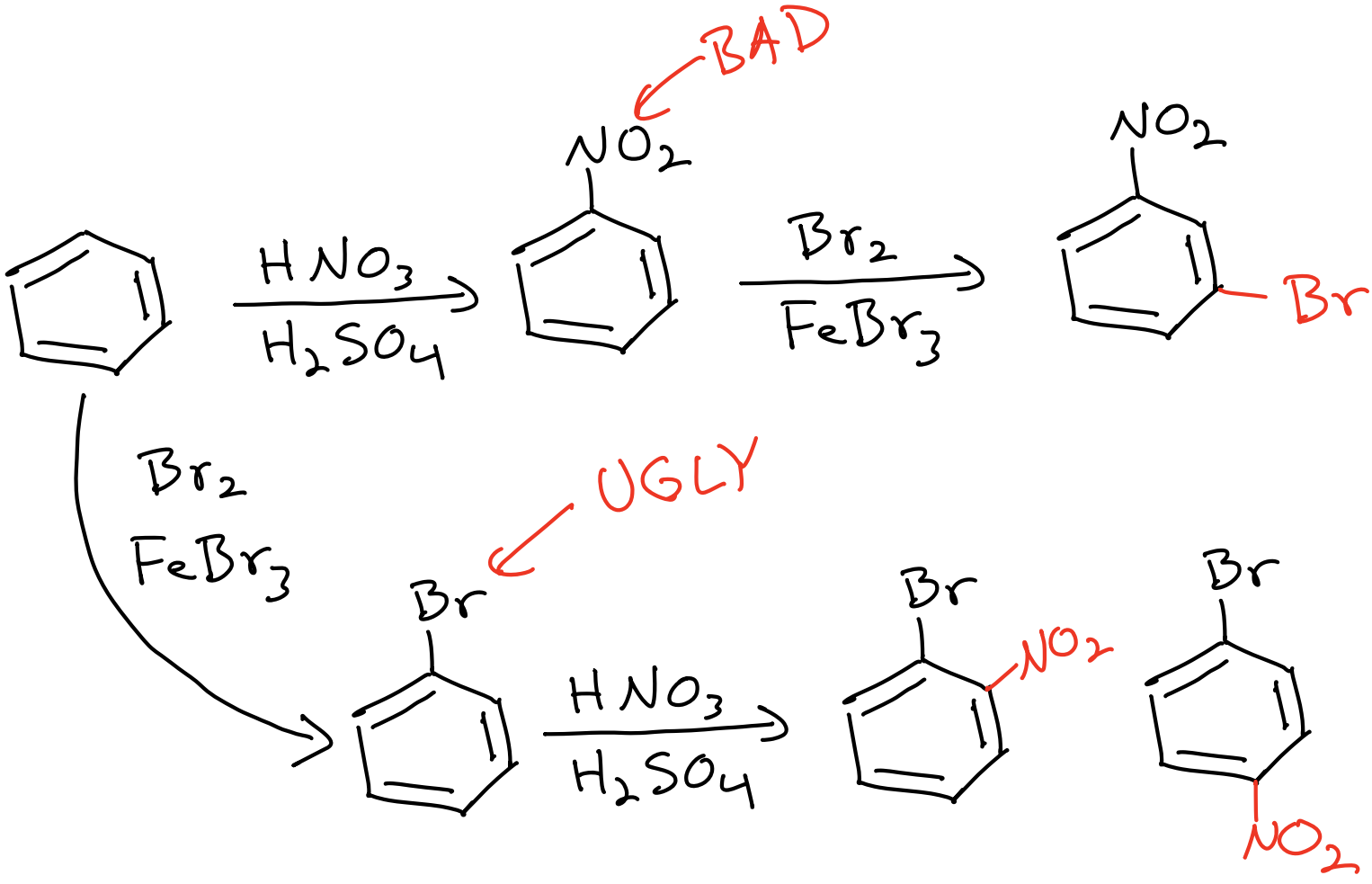

o,p
m
m
o,p
H
NO2
m
o,p
[Arenium Ion]
GOOD
BAD
UGLY
+ NO2⊕
PRODUCT
Energy
Reaction Coordinate

Examples



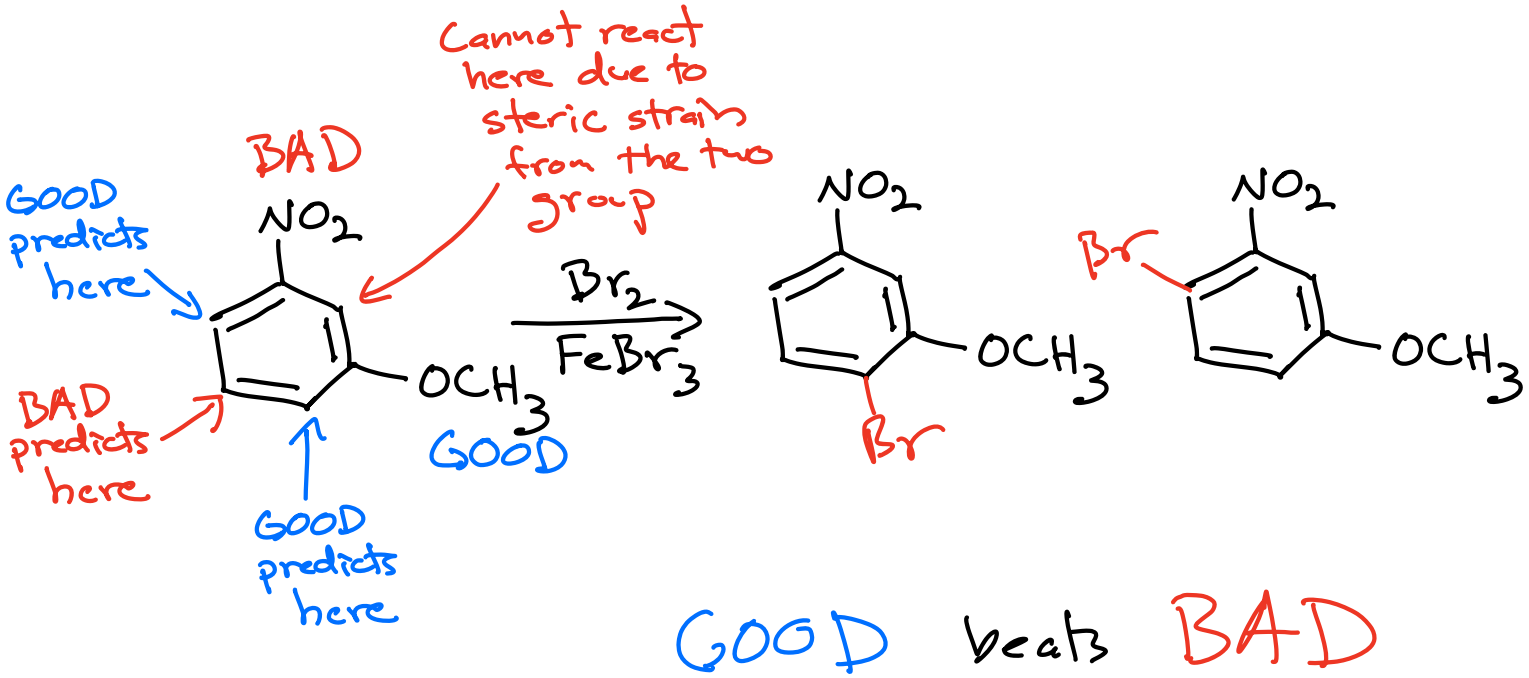


The order in which you add groups matters!

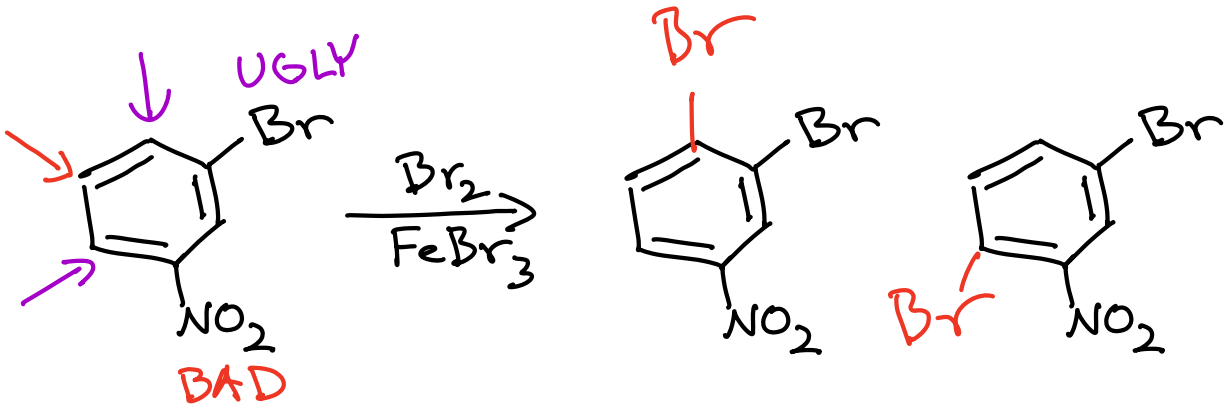


What if there are two groups already on the ring and they predict different products? It is a duel → the movie got it right!

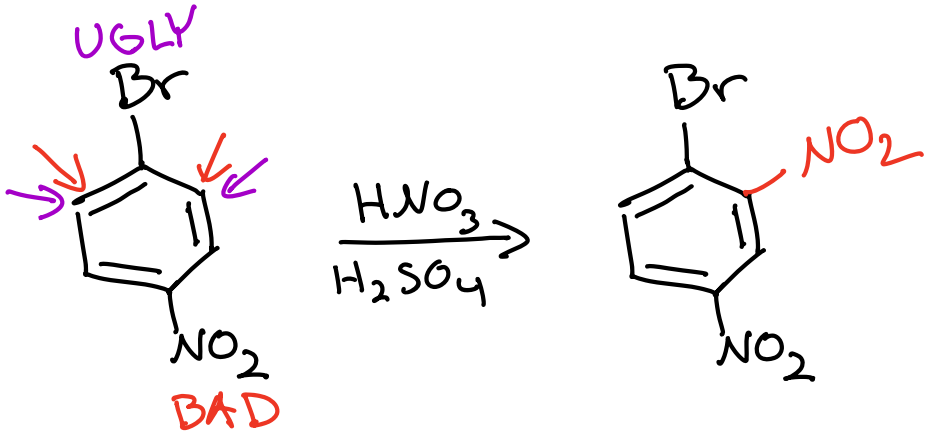
Just like in the movie: GOOD beats BAD and UGLY, UGLY beats BAD!



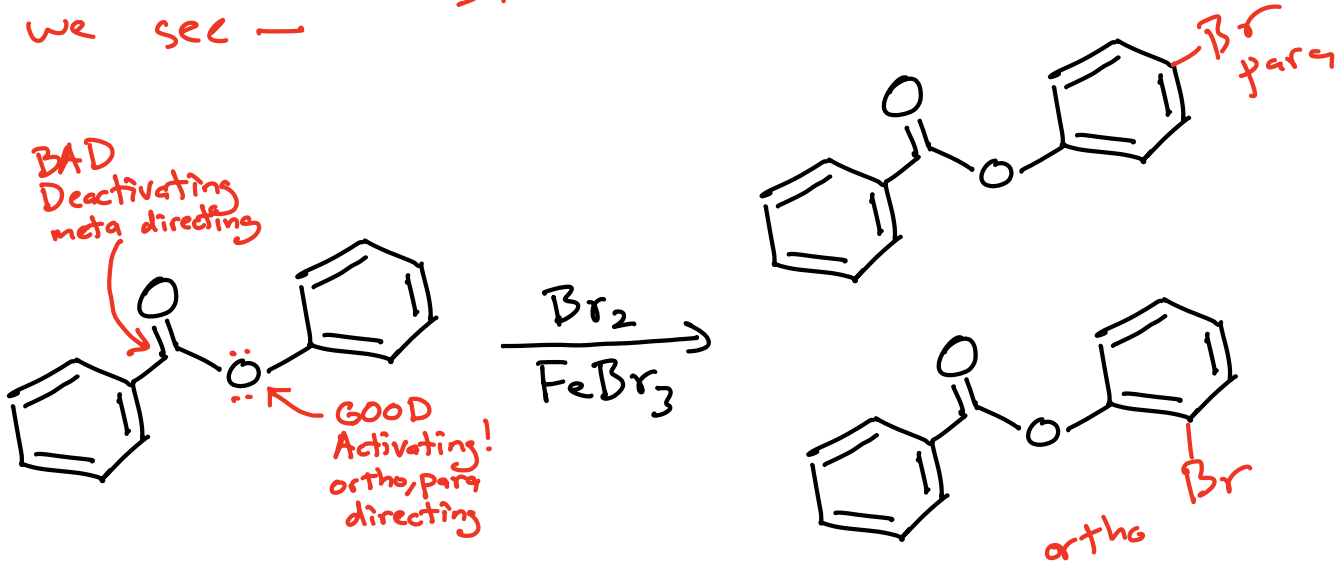
GOOD beats BAD



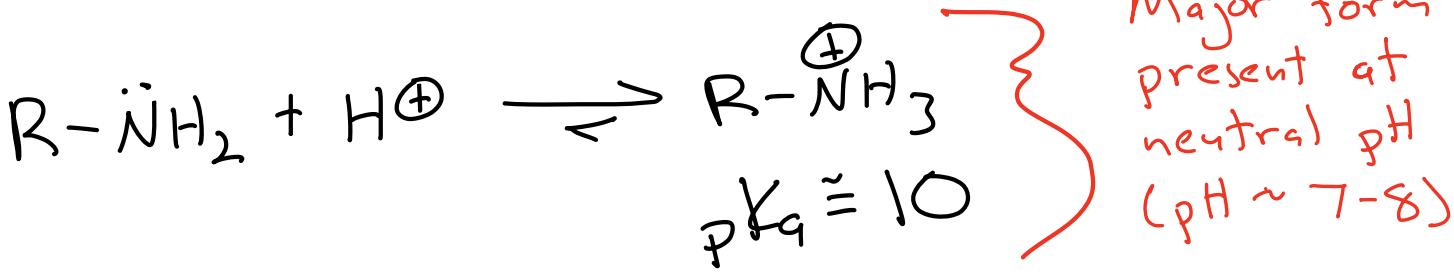
Sometimes two groups will predict the same outcome



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



Amines → Relatively strong bases and relatively strong nucleophiles



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