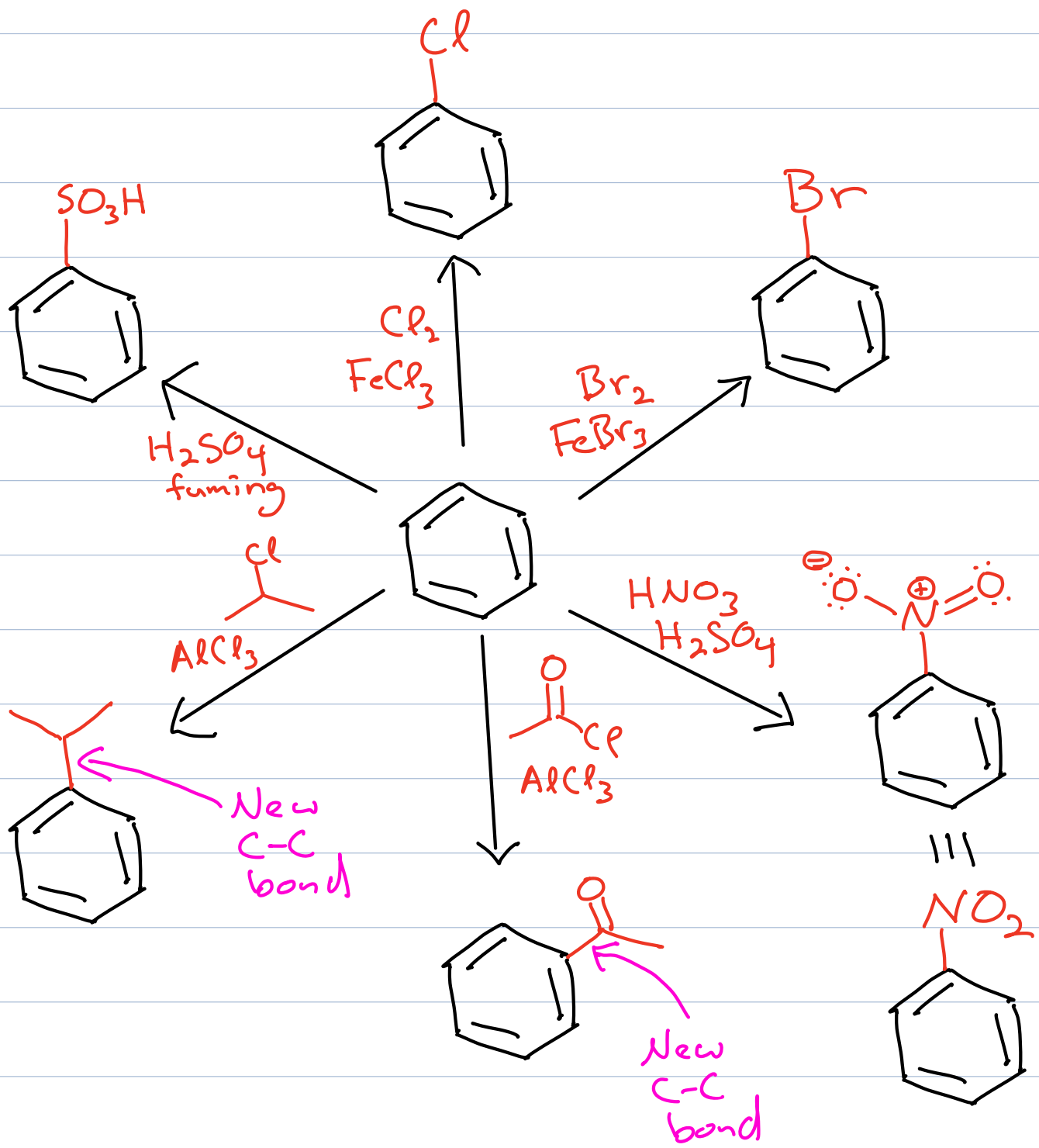


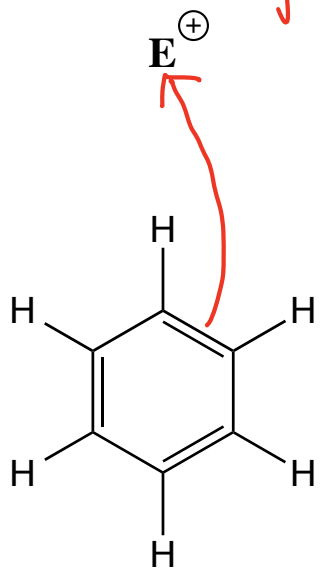


THE GOOD, THE BAD AND THE UGLY (1966)

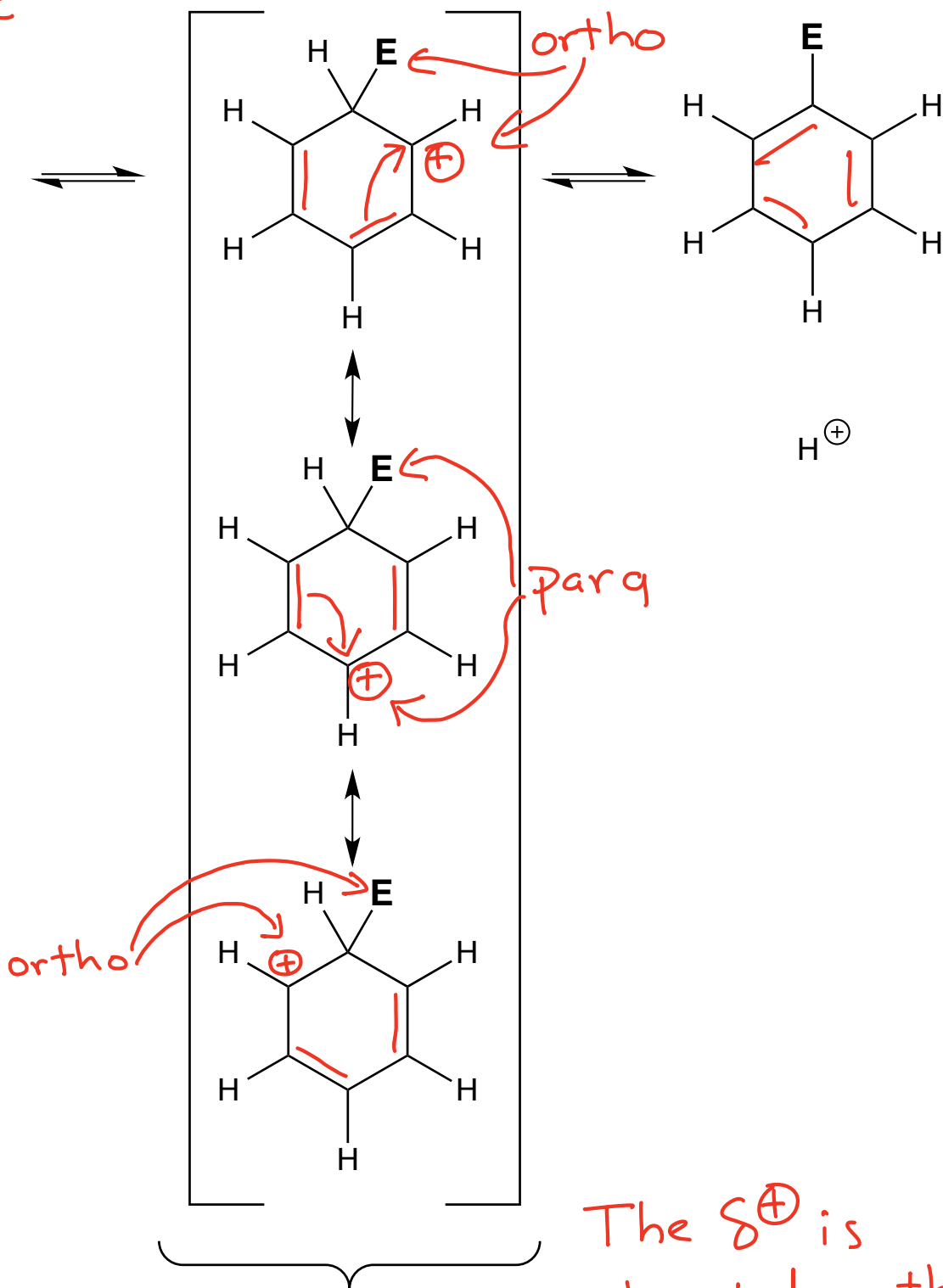
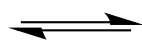




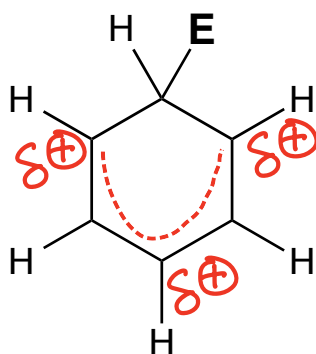
Wicked Strong Electrophile



Weak Nucleophile



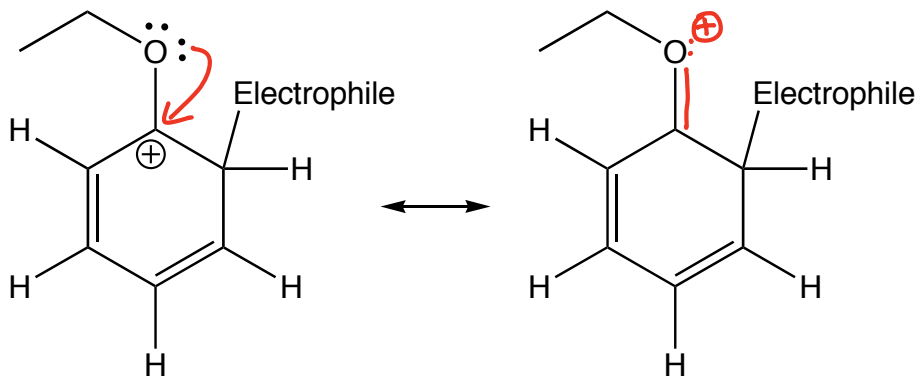
Called the Arenium Ion



The δ^+ is located ortho and para to where the new bond to "E" is located

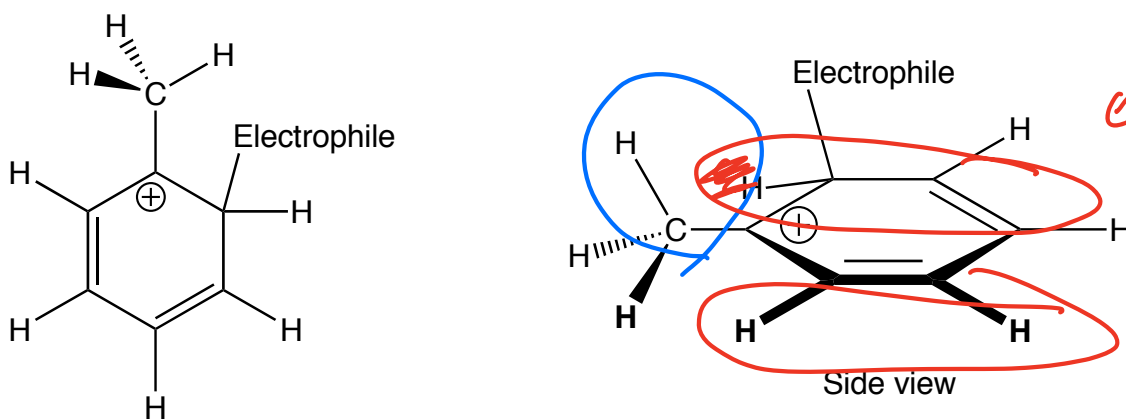
Arenium ion *stabilizing* interactions ← GOOD

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



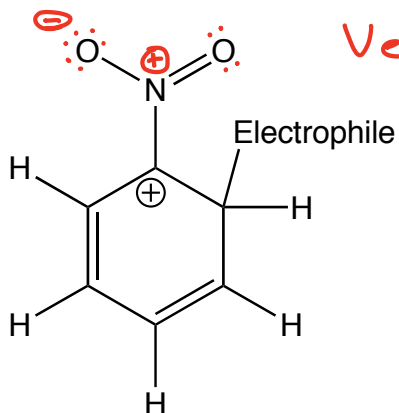
← "pi-pi"
✓ ↑↑
The "Greek interactions"
↓
"sigma-pi"

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 π 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



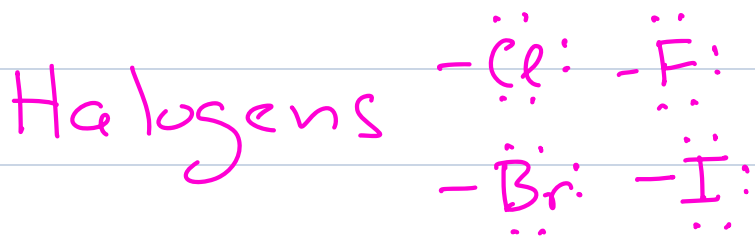
Deactivating
Ortho-Para
Directing

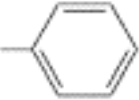
→ Both GOOD and BAD
at the same time

→ Through π donation
or hyperconjugation
the arenium ion
is stabilized

Most effective ortho
and para

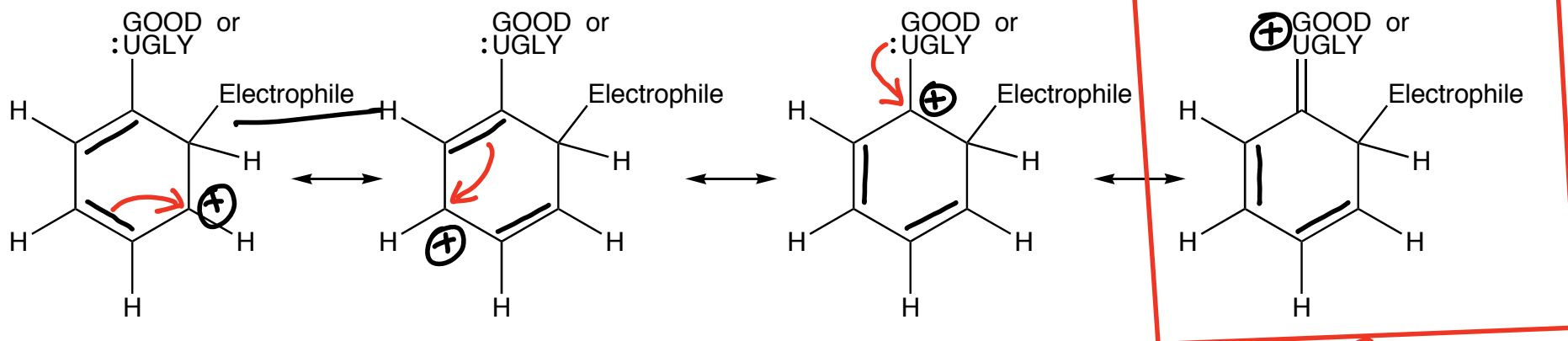
→ Through the
inductive effect -
electron withdrawing
groups - the arenium
ion is destabilized



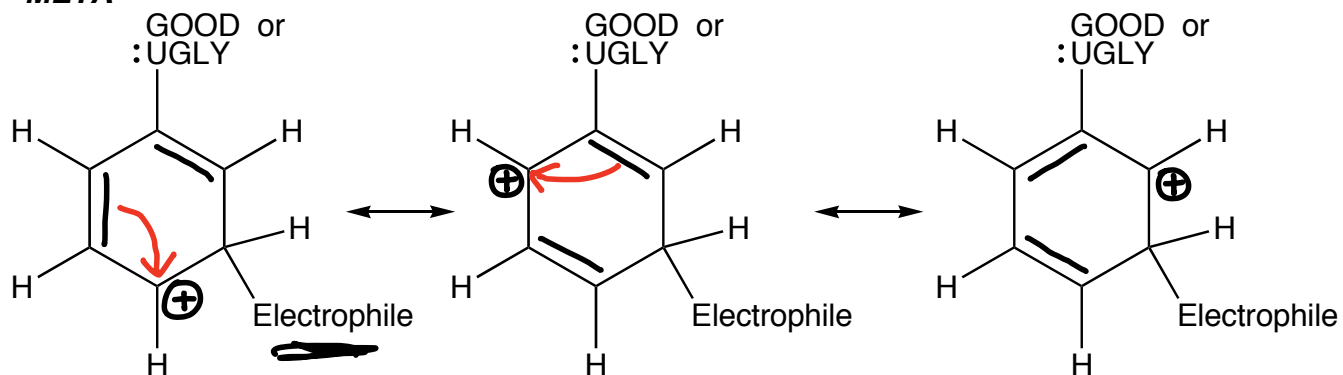
Ortho-Para Directing	Strongly activating	$\text{--}\ddot{\text{N}}\text{H}_2$ $\text{--}\ddot{\text{N}}\text{HR}$ $\text{--}\ddot{\text{N}}\text{R}_2$ $\text{--}\ddot{\text{O}}\text{H}$ $\text{--}\ddot{\text{O}}\text{R}$	
	Moderately activating	$\text{--}\ddot{\text{N}}\text{H}\overset{\text{O}}{\parallel}\text{CR}$ $\text{--}\ddot{\text{N}}\text{H}\overset{\text{O}}{\parallel}\text{CAr}$ $\text{--}\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{CR}$ $\text{--}\ddot{\text{O}}\overset{\text{O}}{\parallel}\text{CAr}$	GOOD
	Weakly activating	--R 	<p>These all have a lone pair on the atom attached to the ring or they are an alkyl group</p>
	Weakly deactivating	$\text{--}\ddot{\text{F}}:$ $\text{--}\ddot{\text{Cl}}:$ $\text{--}\ddot{\text{Br}}:$ $\text{--}\ddot{\text{I}}:$	<p>Halogens!</p> <p>UGLY</p>
Meta Directing	Moderately deactivating	$\text{--}\overset{\text{O}}{\parallel}\text{CH}$ $\text{--}\overset{\text{O}}{\parallel}\text{CR}$ $\text{--}\overset{\text{O}}{\parallel}\text{COH}$ $\text{--}\overset{\text{O}}{\parallel}\text{COR}$ $\text{--}\overset{\text{O}}{\parallel}\text{CNH}_2$ $\text{--}\overset{\text{O}}{\parallel}\text{SOH}$ $\text{--C}\equiv\text{N}$	
	Strongly deactivating	--NO_2 --NH_3^+ --CF_3 --CCl_3	<p>These all have a pi bond to an electronegative atom on the atom attached to the ring or highly electronegative</p> <p>BAD</p>

Relative importance in directing further substitution

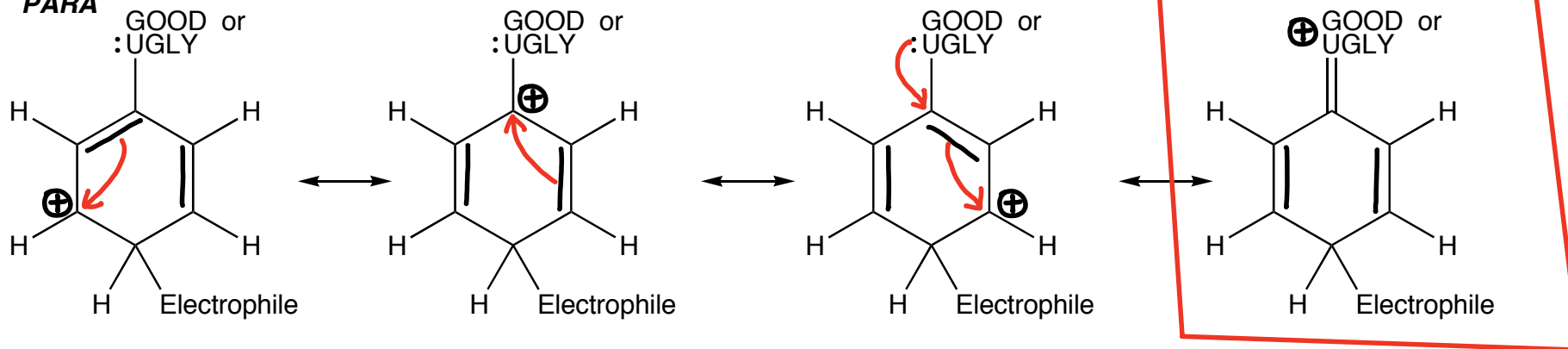
ORTHO



META

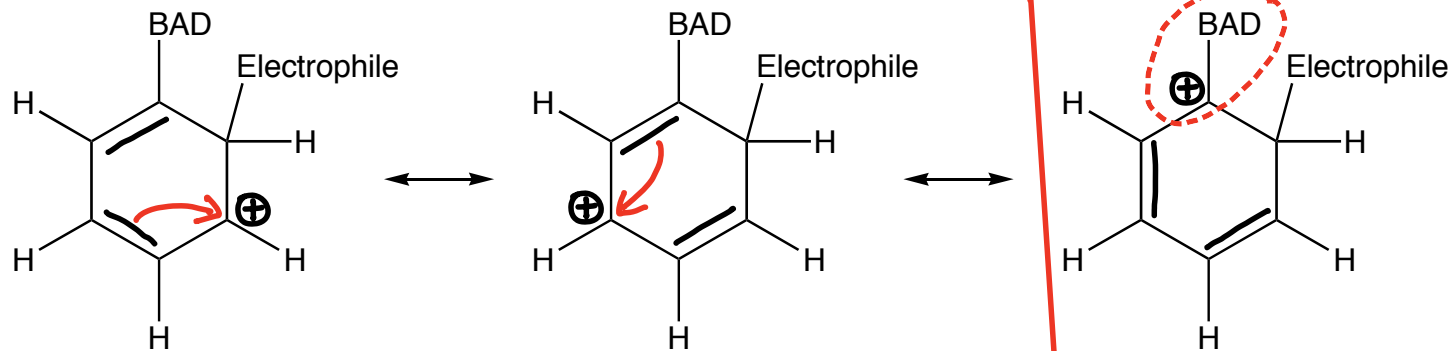


PARA

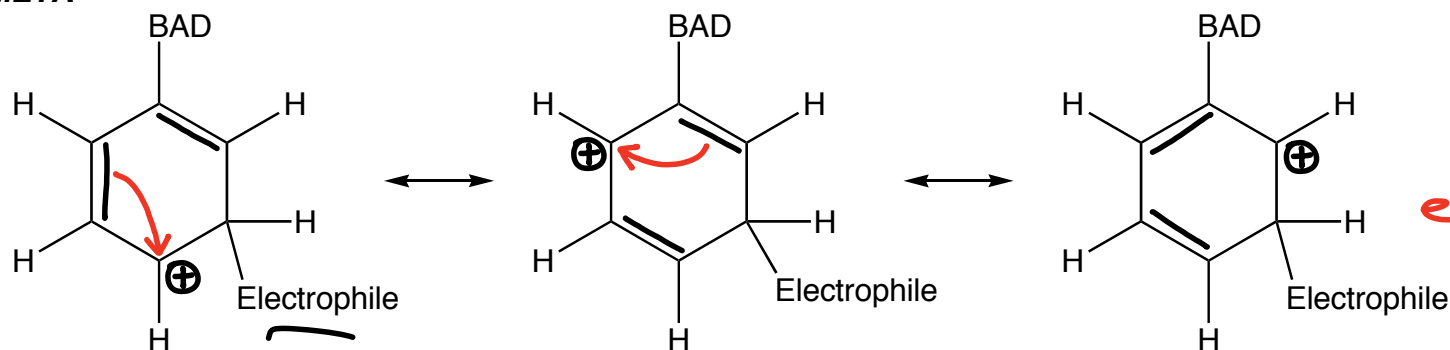


↑↑
These two explain why ortho, para are preferred
↓↓

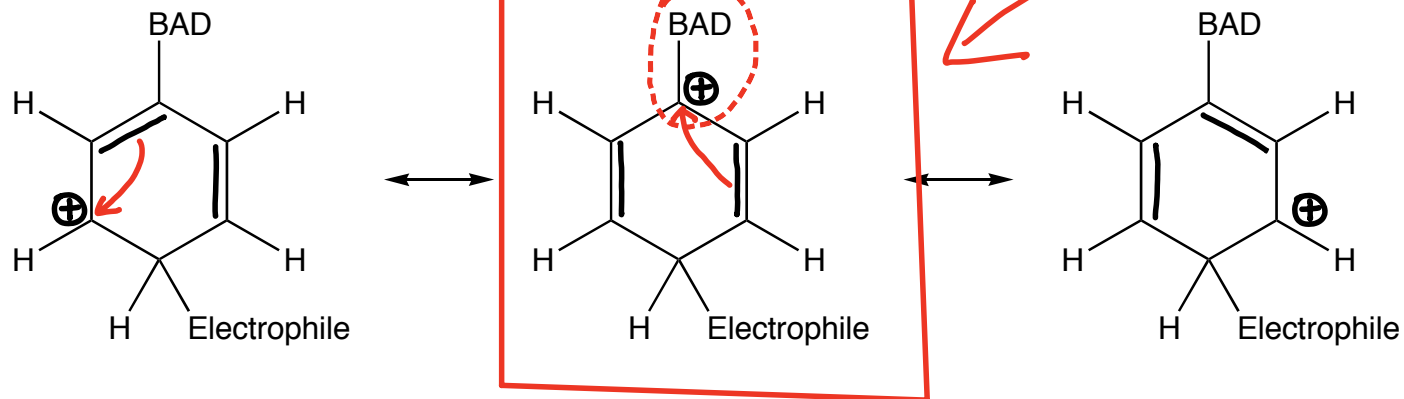
ORTHO



META

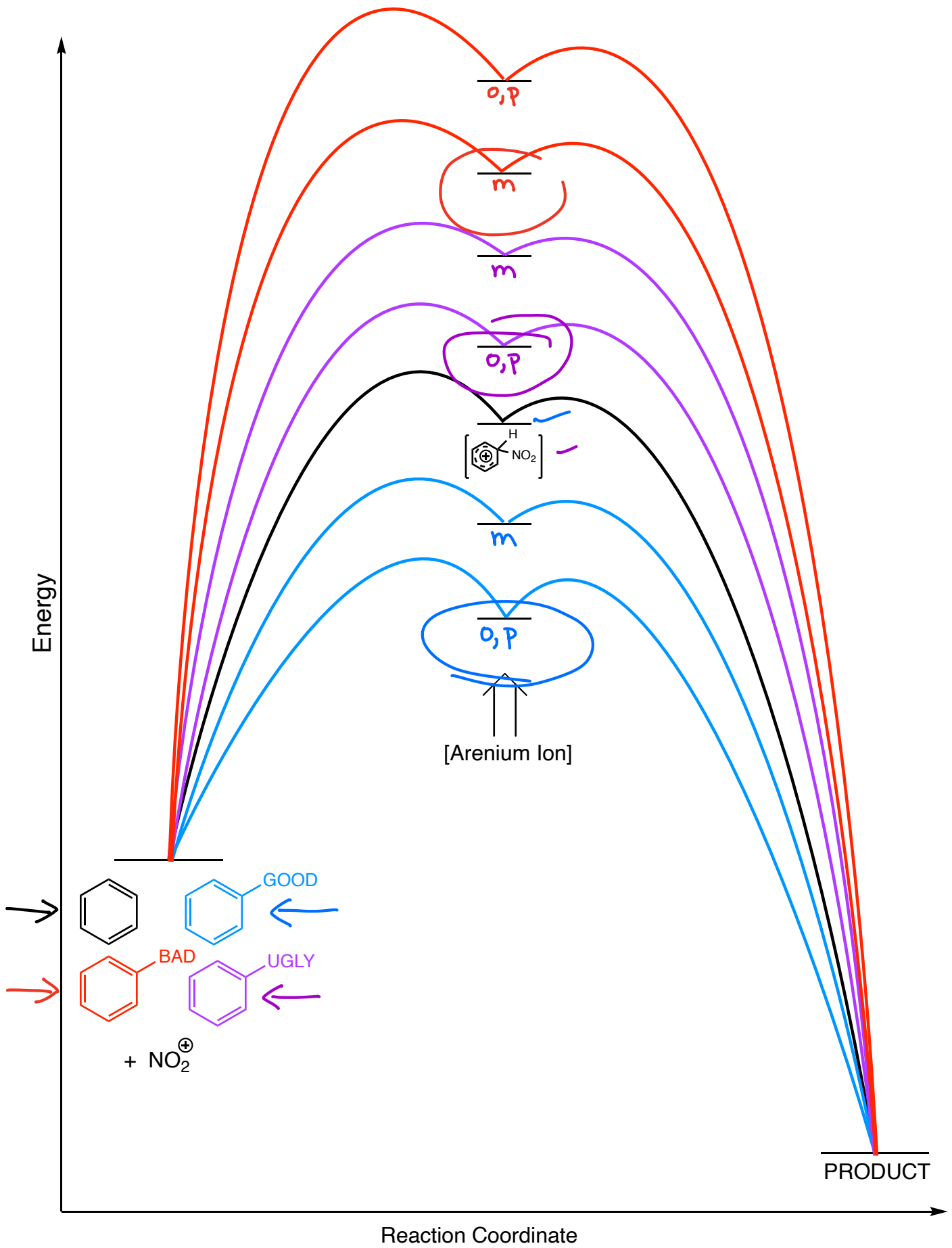


PARA

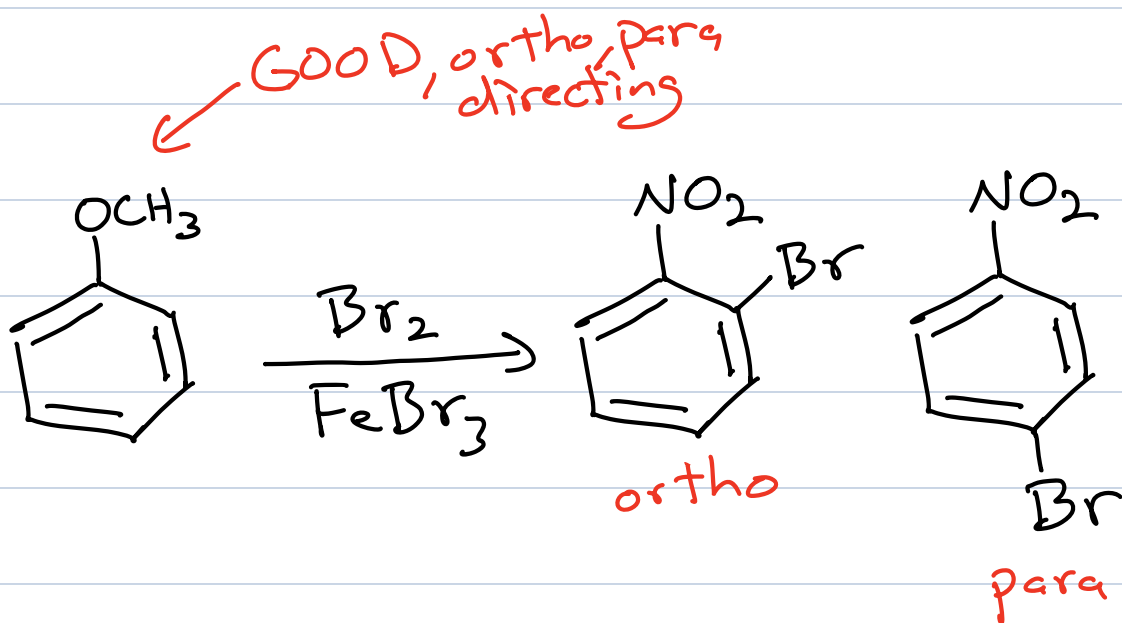
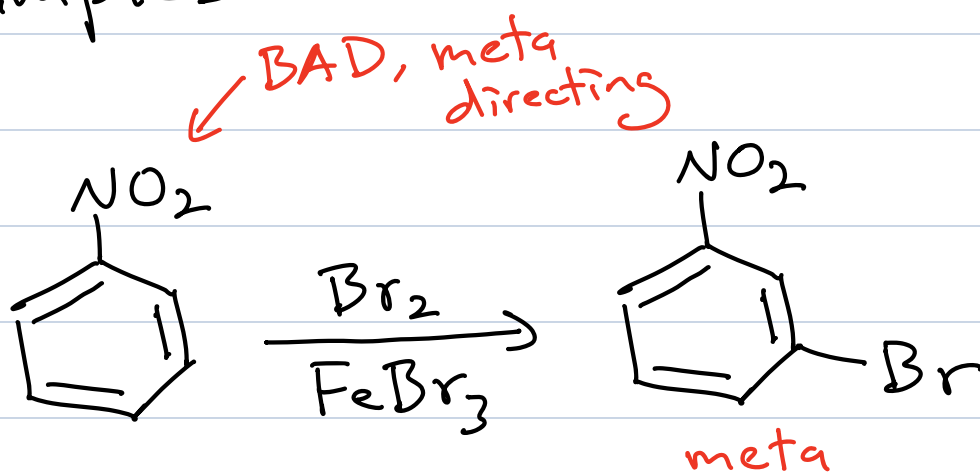


Very destabilizing explaining why for BAD groups

"meta is better"
No terrible interaction meta like there is ortho, para

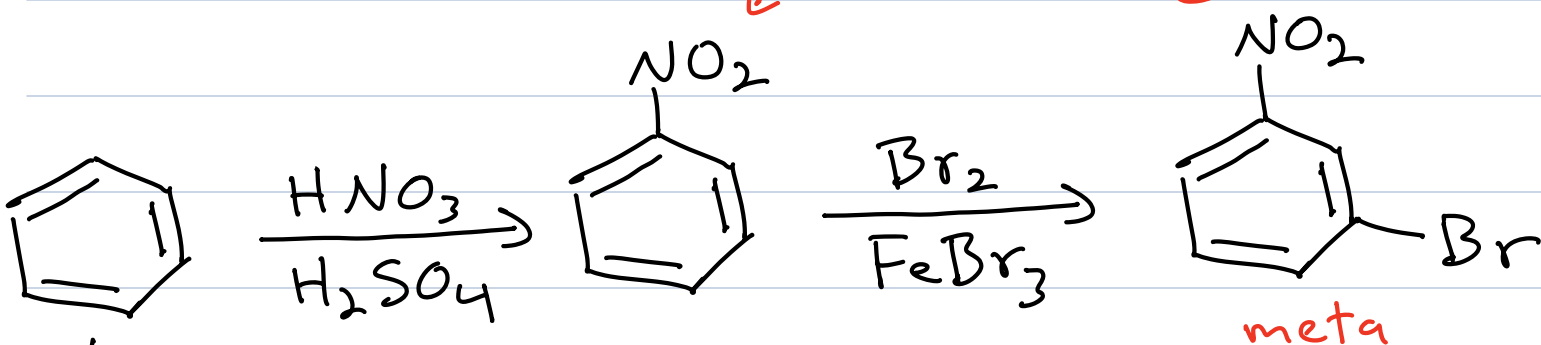


Examples



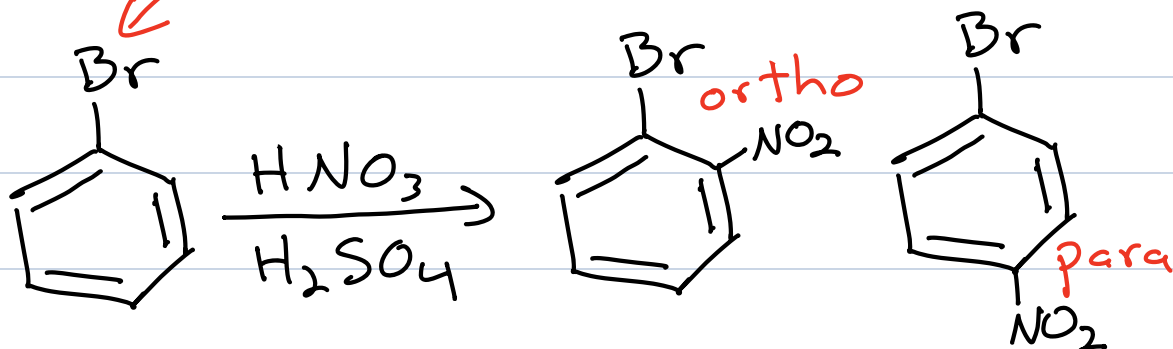
The order in which you add groups matters!

← BAD, meta directing



← UGLY, ortho, para directing

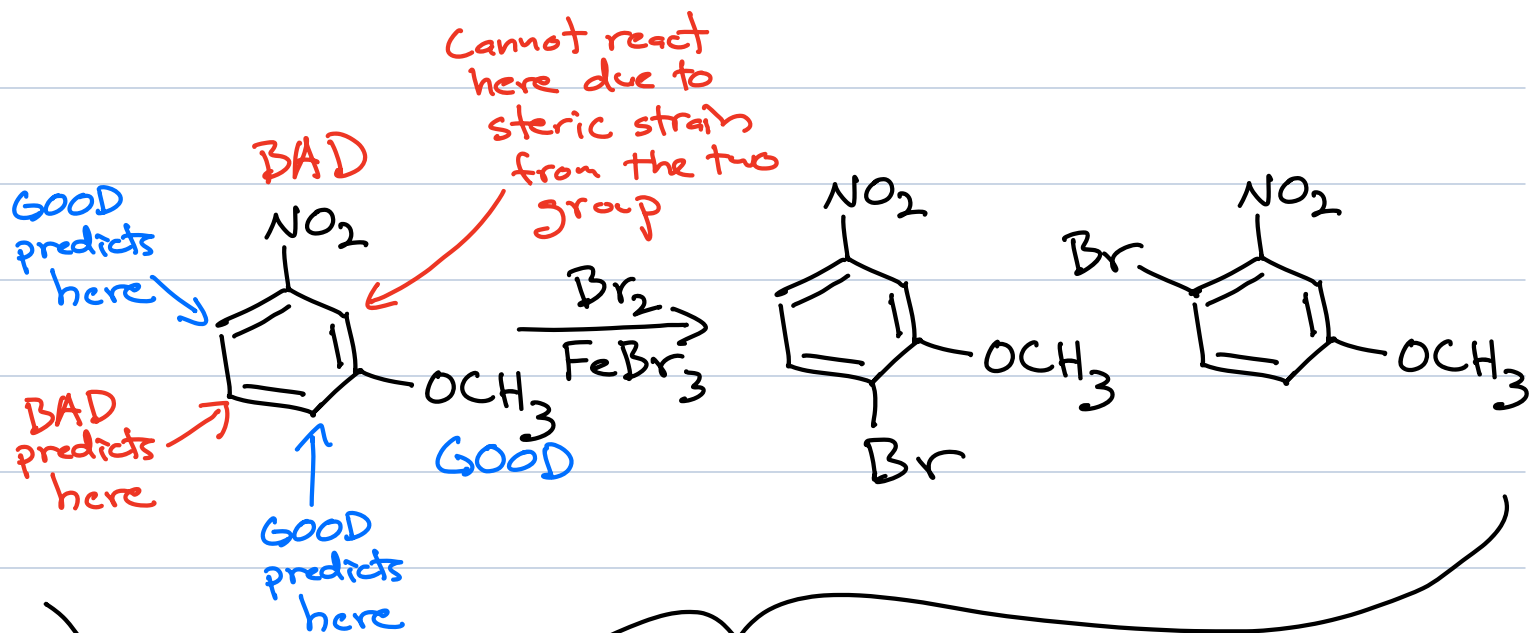
Br_2
 FeBr_3



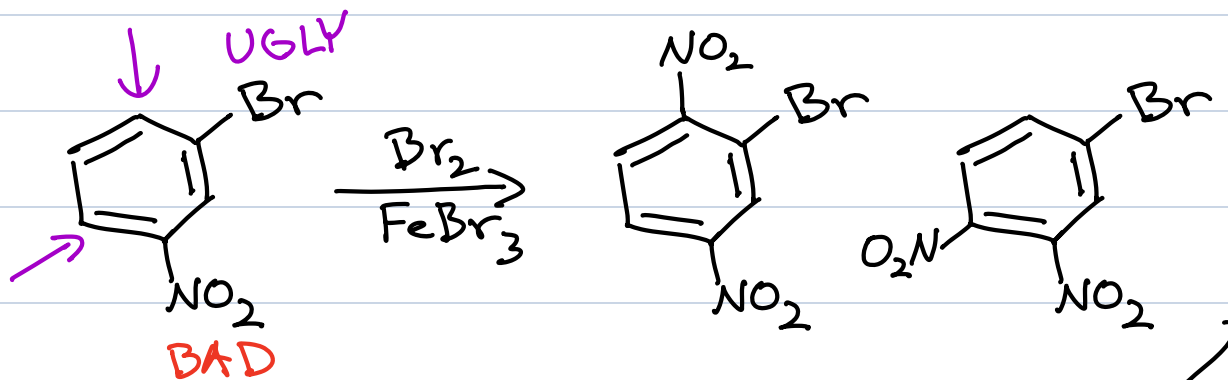
What if there are two groups already on the ring and they predict different products?

It is a duel → the movie got it right!

GOOD beats BAD and UGLY
UGLY beats BAD

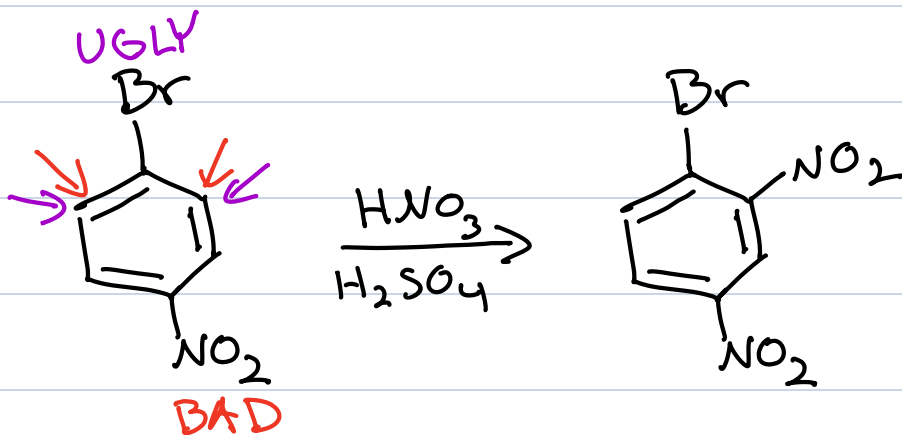


GOOD
beats BAD!



UGLY
beats BAD!

Sometimes two groups will predict the same outcome



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

