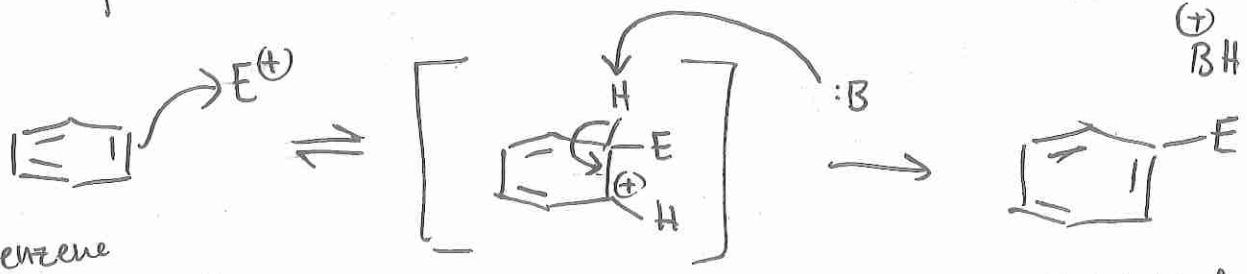
MTW 5/1/2017

Electrophilic Aromatic Substitution → "EAS"



Benzene
Weakly Nucleophilic

Arenium Ion
Intermediate

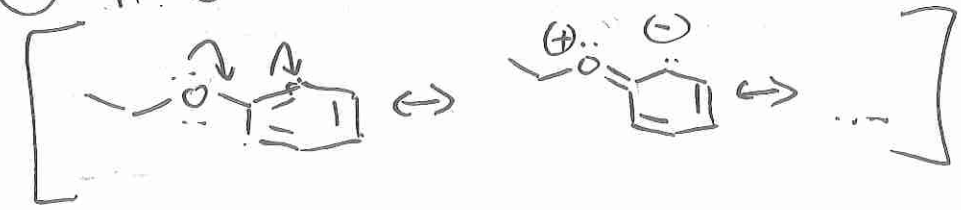
Substituted
Benzene
Ring

Reactivity:

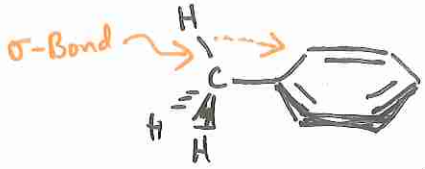
Activating Groups: → Reacts faster than Benzene

makes aromatic ring more reactive, gives it more e⊖ density → Better Nucleophile compared to Benzene

(1) π-Donation

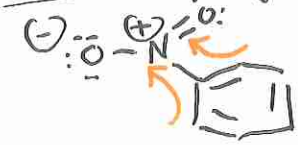


(2) Hyperconjugation



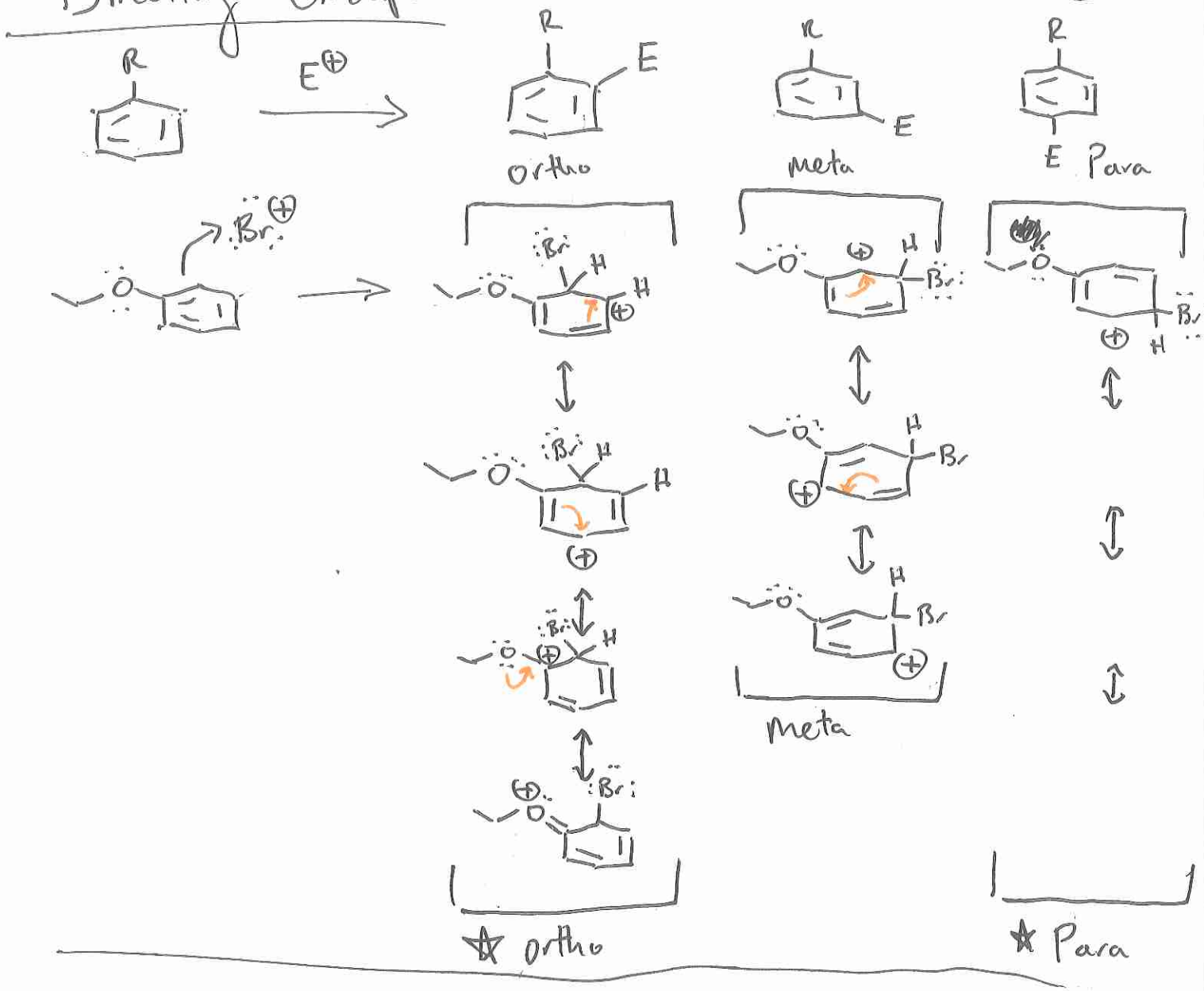
Deactivating Groups: → Reacts slower than Benzene

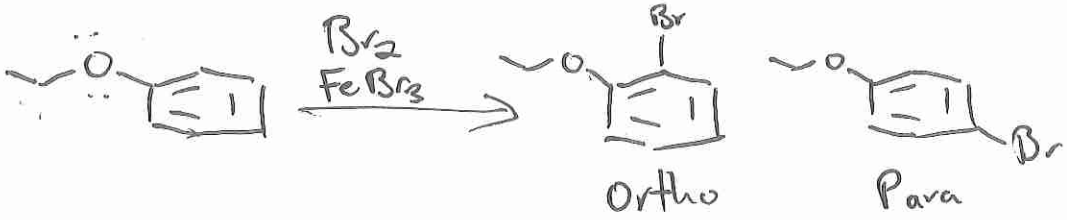
less reactive, less e⊖ density in ring ↓ Worse Nucleophile compared to benzene



★ Can't do Friedel Crafts when deactivating groups are already on the ring

Directing Groups





Either ⇒ ortho/para directing

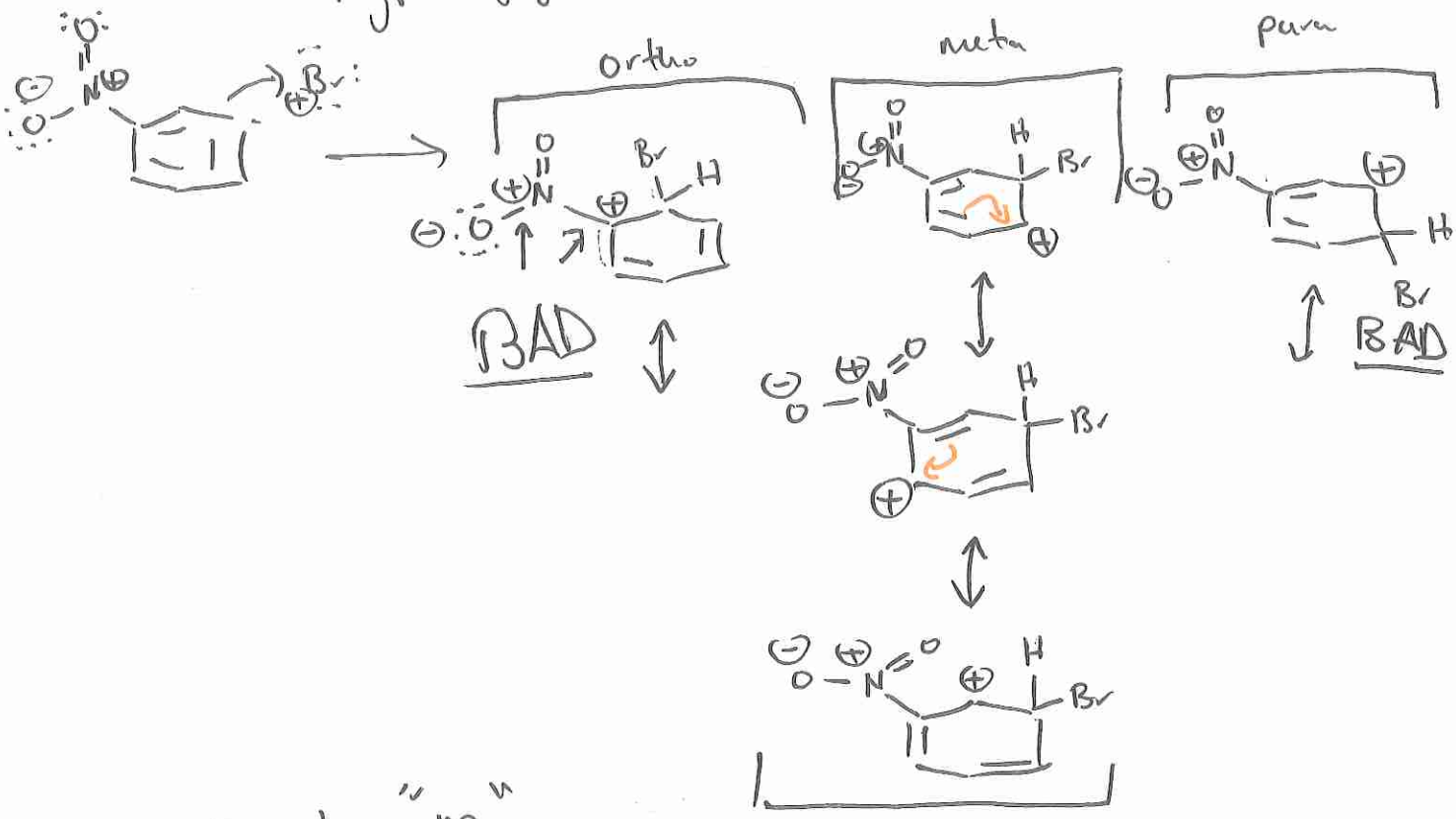
OR

meta directing

Ortho/Para Directing → "o/p"

Stabilizes the carbocation intermediate by

- π-Donation
- Hyperconjugation



Meta Directing "m"

↳ I extra contributing structure if $E^{\oplus}$ is added ortho/para

↳ "Bad" aka High energy

⇓

Destabilizes ⊕ charge of Arenium Ion Intermediate

(1) Good Groups ⇒ Activating, stabilizes the arenium cation, o/p director

Have lone pair on atom attached to ring OR alkyl groups

(2) Bad Groups ⇒ Deactivating, introduce a destabilized resonance contributing structure if $E^{\oplus}$ adds o/p → meta director

π-Bonds or ⊕ charge attached to ring

(3) Ugly Groups ⇒ Halogens (F, Cl, Br, I), deactivating

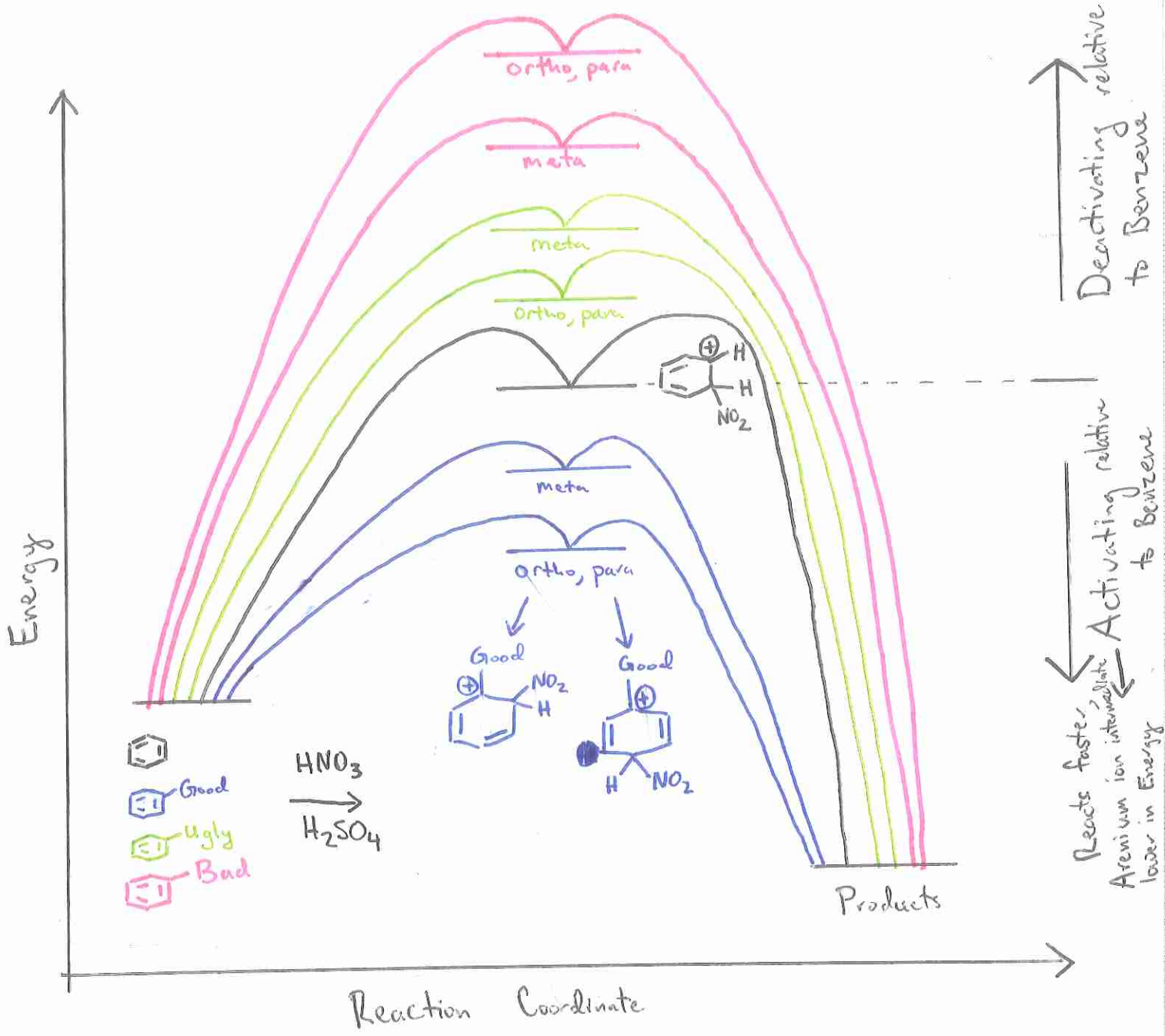
Halogen

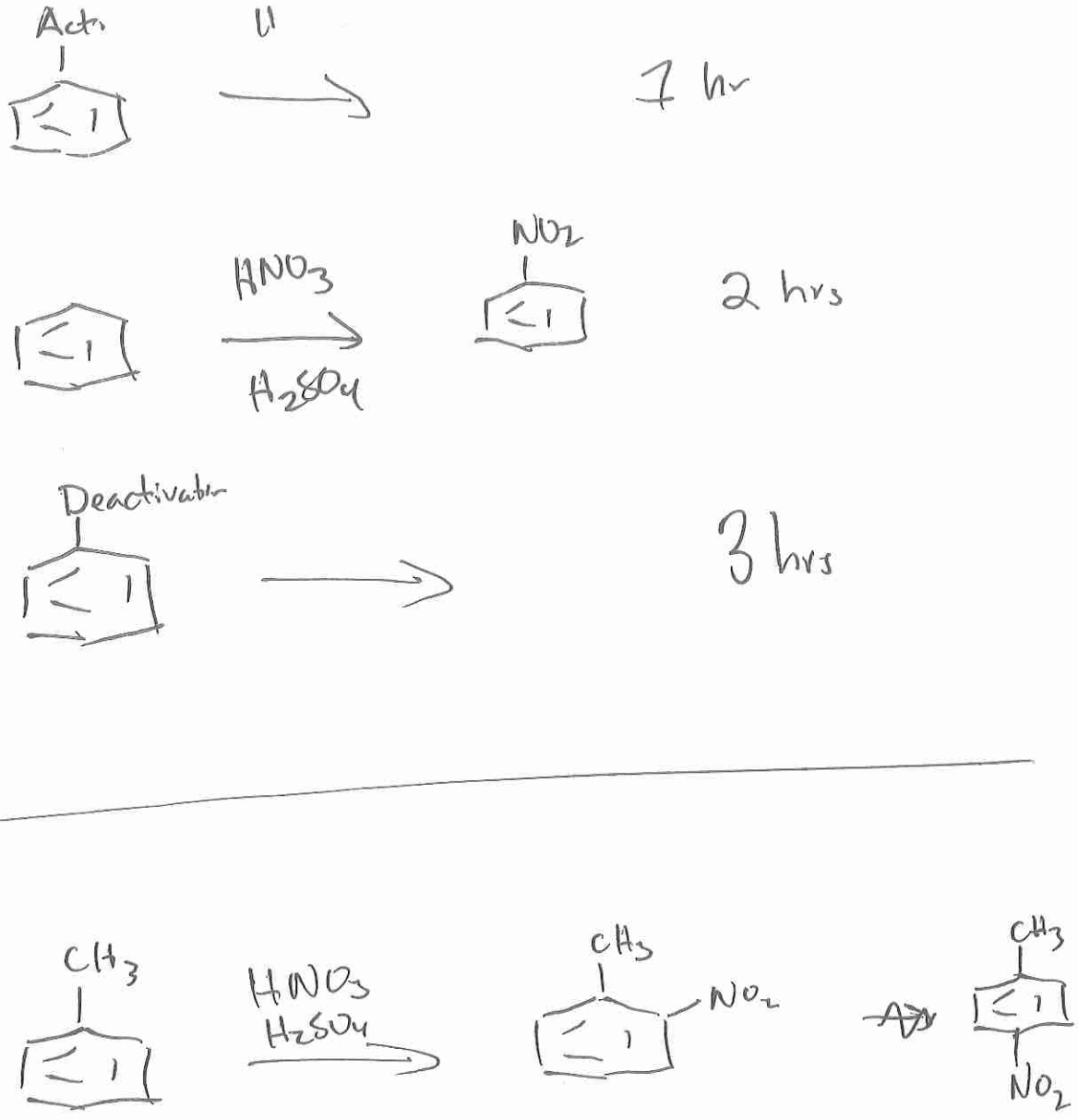
But o/p directors

Good always wins

Ugly Beats Bad

Bad always loses


Energy
Reaction Coordinate
ortho, para
meta
meta
ortho, para
meta
ortho, para
Good
Good
Ugly
Bad
HNO_3
H_2SO_4
NO_2
H
Products
Deactivating relative to Benzene
Activating relative to Benzene
Reacts faster, Arenium ion intermediate lower in Energy


Activator
1
7 hr
HNO_3
H_2SO_4
NO_2
2 hrs
Deactivator
3 hrs
CH_3
HNO_3
H_2SO_4
CH_3
NO_2
CH_3
NO_2