(29) **Today**

Chap 16.1 - 16.5: Electrophilic Aromatic Substitution

Substituent Effects

Next Class (30)

Substituent Effects

Friday

(31) **Second Class from Today**

Substituent Effects

Back to Ketones and Aldehydes?

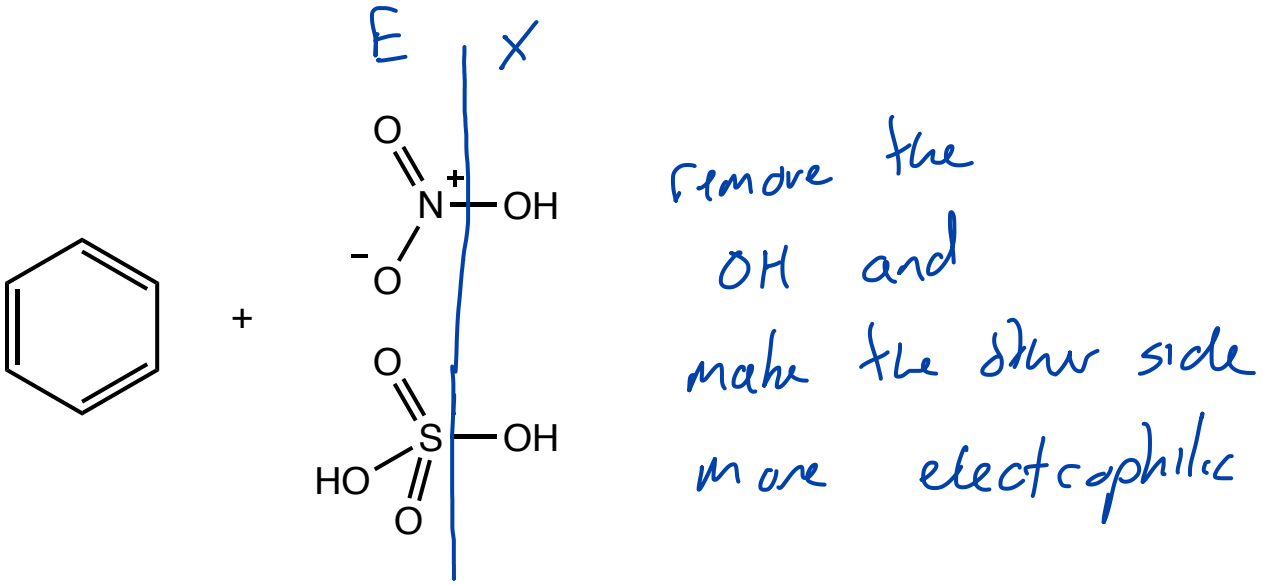
Wednesday

Third Class from Today (32)

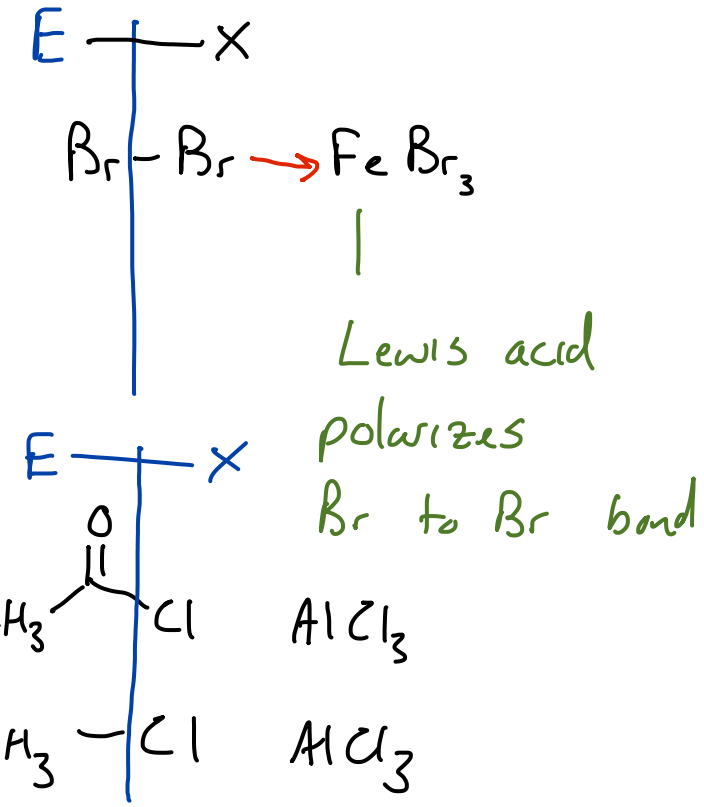
Test 3

Friday

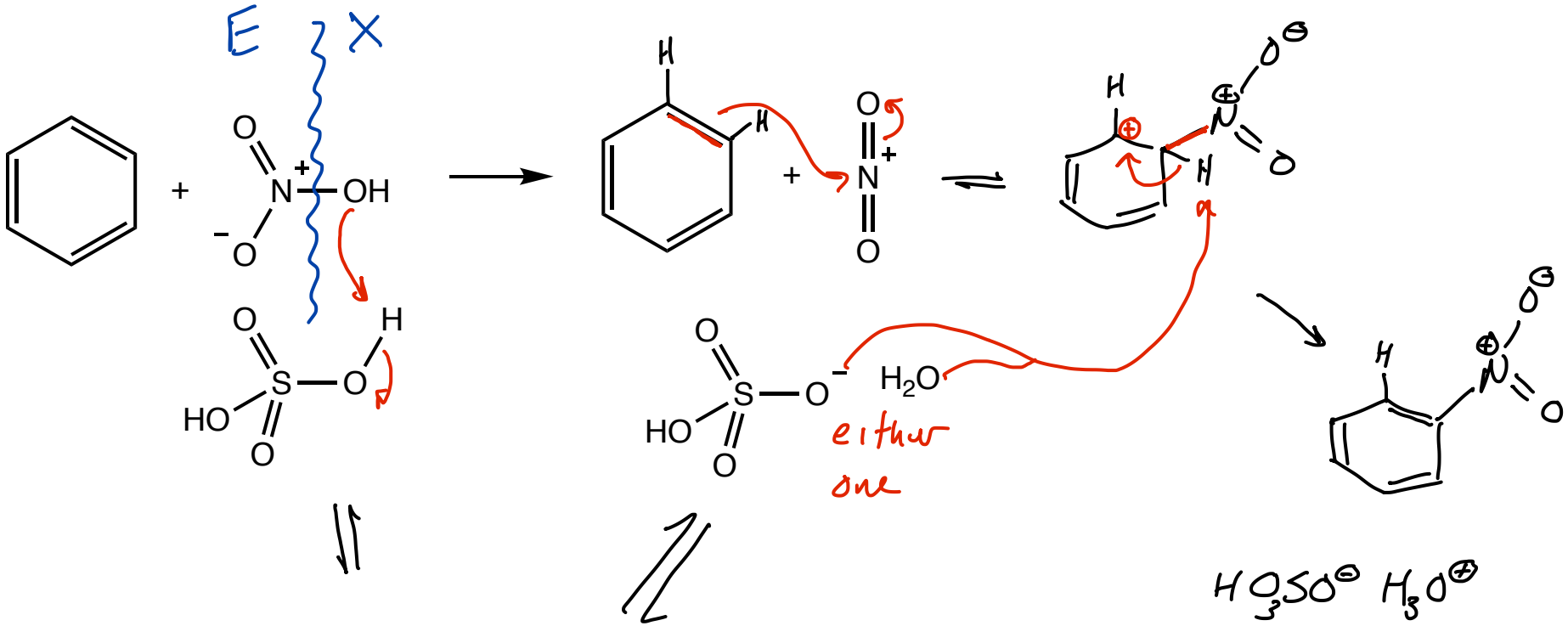
No classes on Monday, April 21

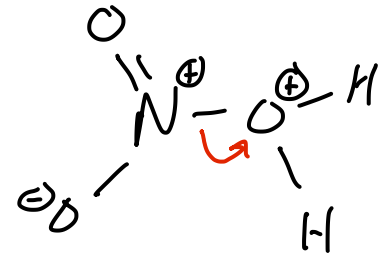


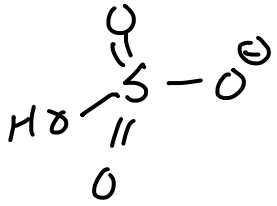
remove the OH and make the other side more electrophilic



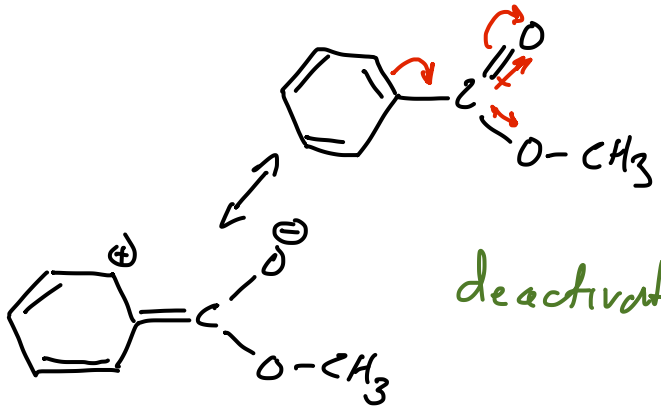
Nitroso ion





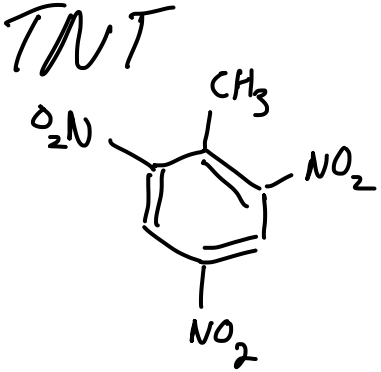


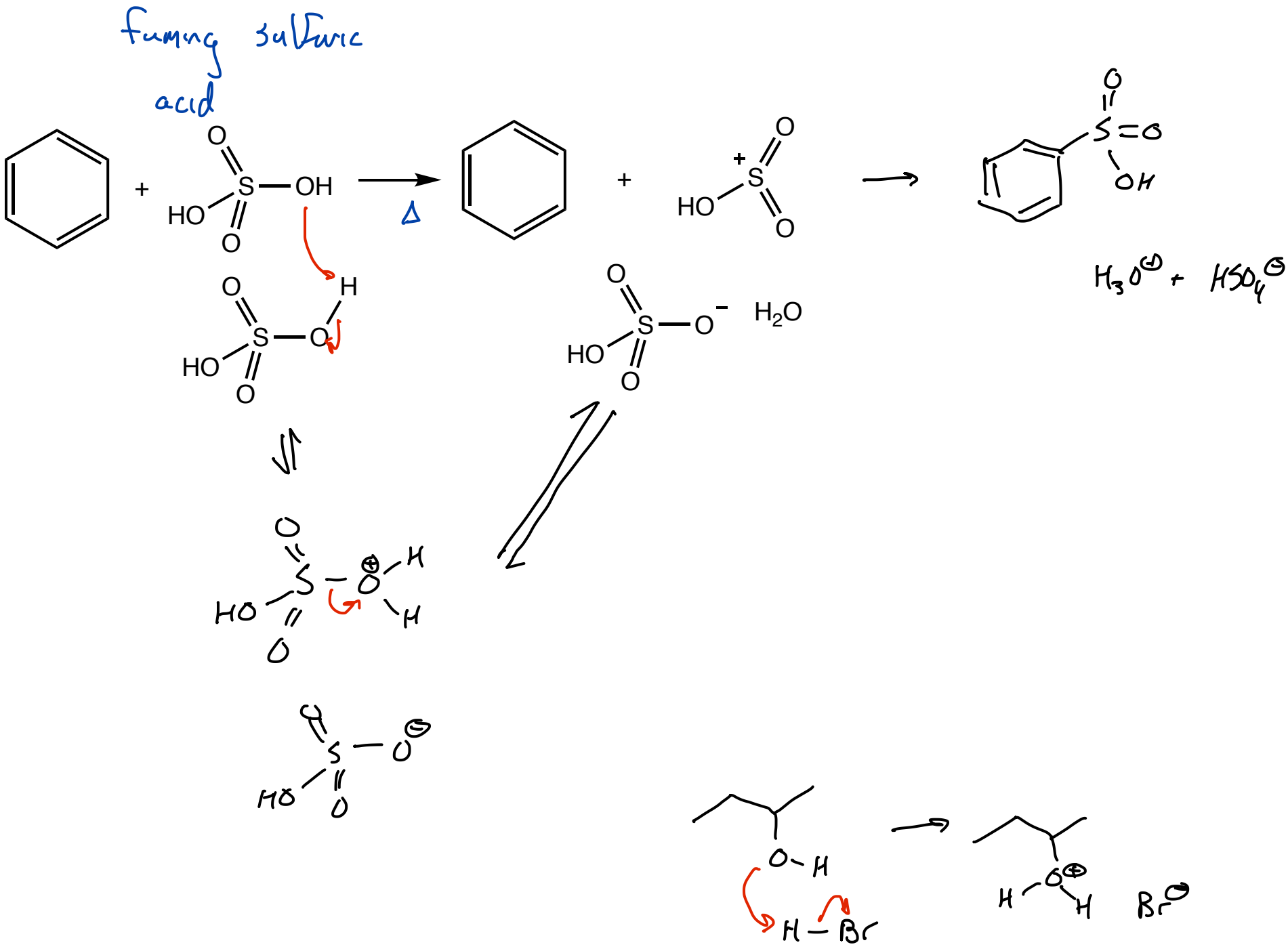
In lab

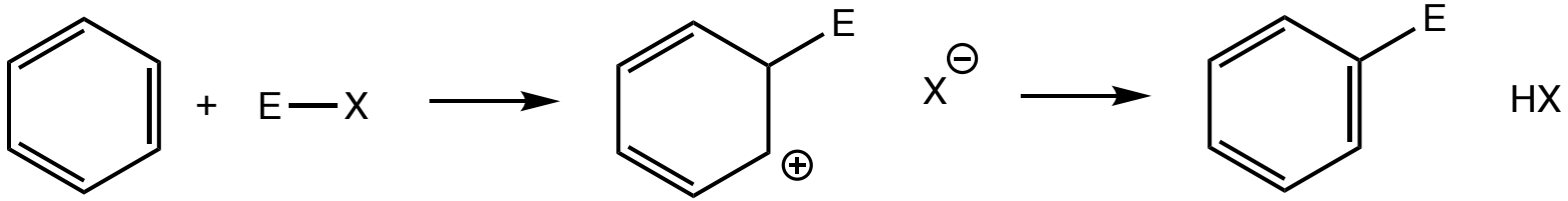


deactivates benzene ring

TNT




fuming sulfuric acid
Δ
H_2O
$H_3O^{\oplus}$ + $HSO_4^{\ominus}$



Increase election density to make the benzene ring more reactive toward electrophiles

Stabilize the intermediate to make the reaction go faster

Move Electron Density Around Using....

electron delocalization can move e⁻ density around

π donors increase e⁻ density through resonance

π withdrawing decrease e⁻ density

inductive effects based on the presence of

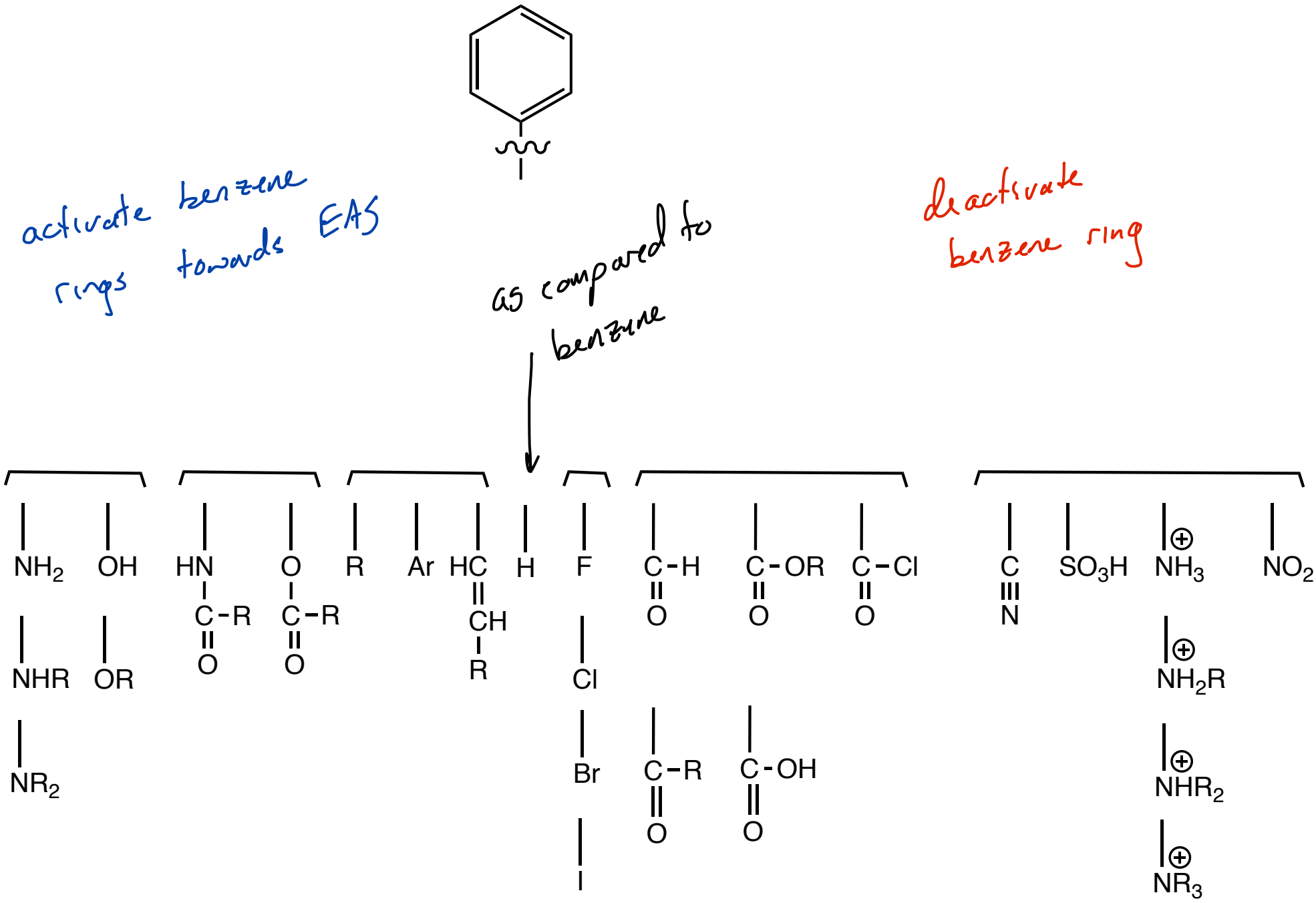
electronegative or electropositive atoms

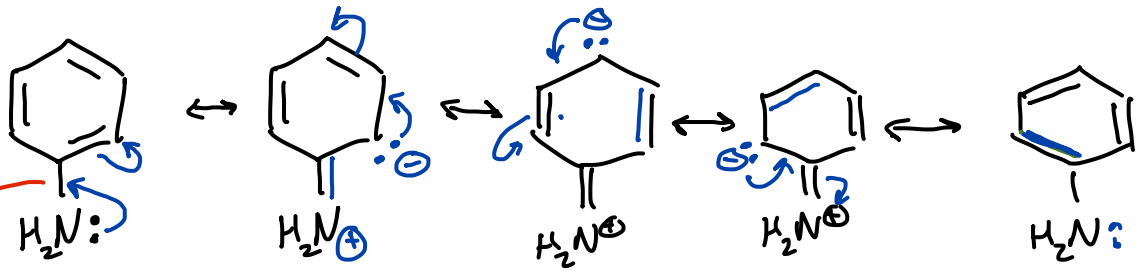
attract electrons in a bond to themselves

σ withdrawing

donate electrons in a bond to the other atom

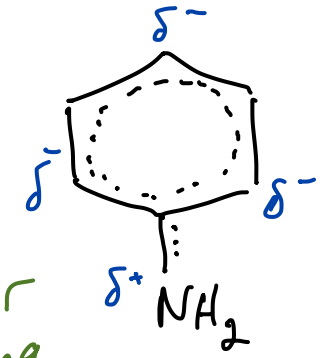
σ donor

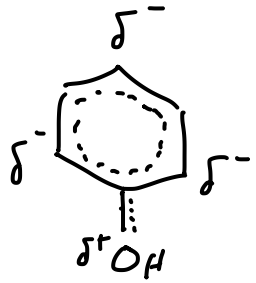

activate benzene rings towards EAS
as compared to benzene
deactivate benzene ring
NH2
OH
NHR
OR
NR2
HN
C-R
O
O
C-R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C-H
O
C-OR
O
C-Cl
O
C-R
O
C-OH
O
C
N
SO3H
NH3
NH2R
NHR2
NR3
NO2



σ withdrawing group

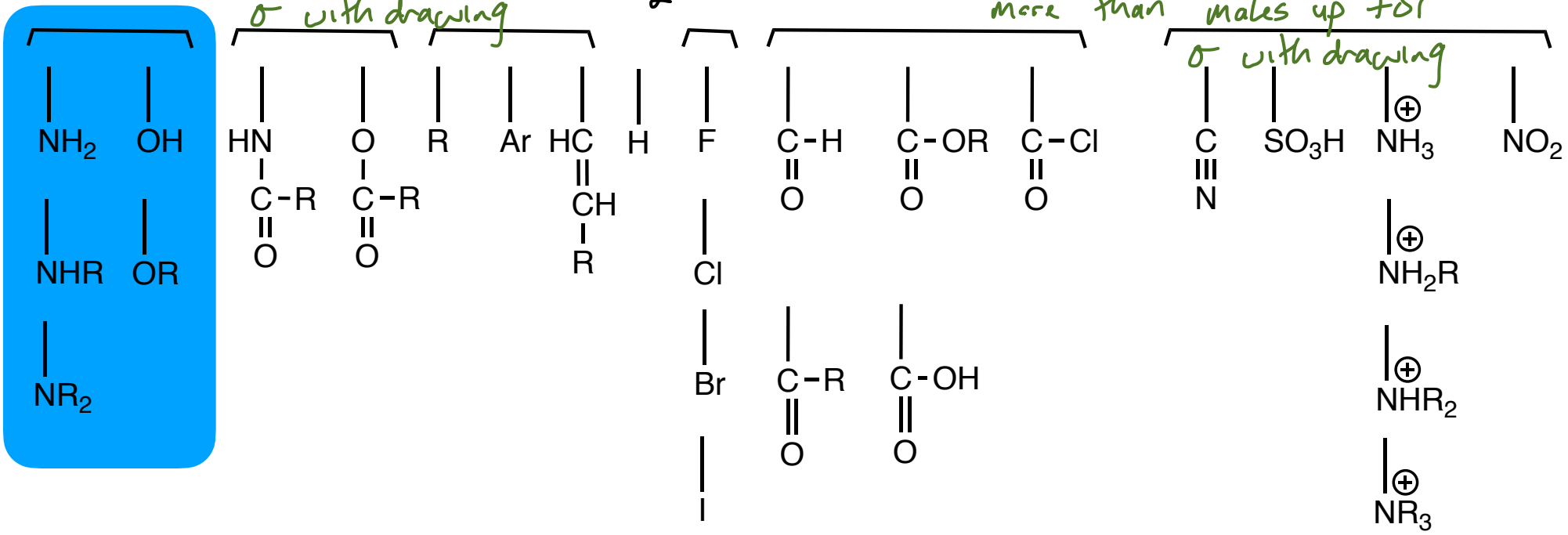
π donating great more than makes up for σ withdrawing

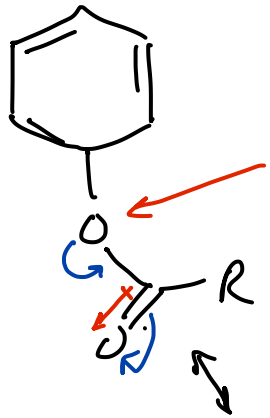




Stronger σ withdrawing group

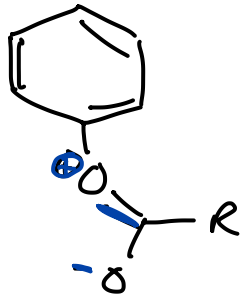
π donating more than makes up for σ withdrawing

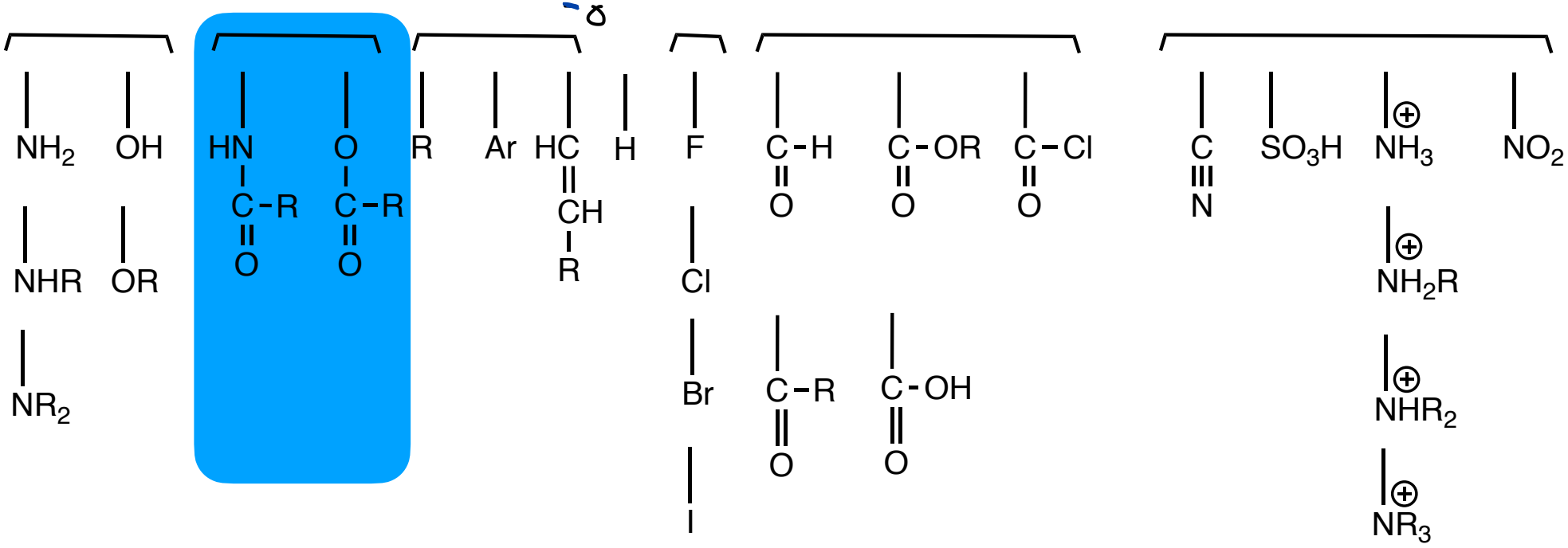


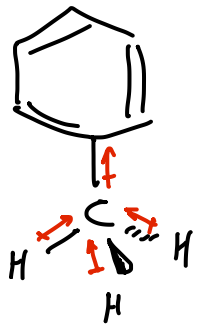


σ withdrawing a bit better than just O or N because C=O

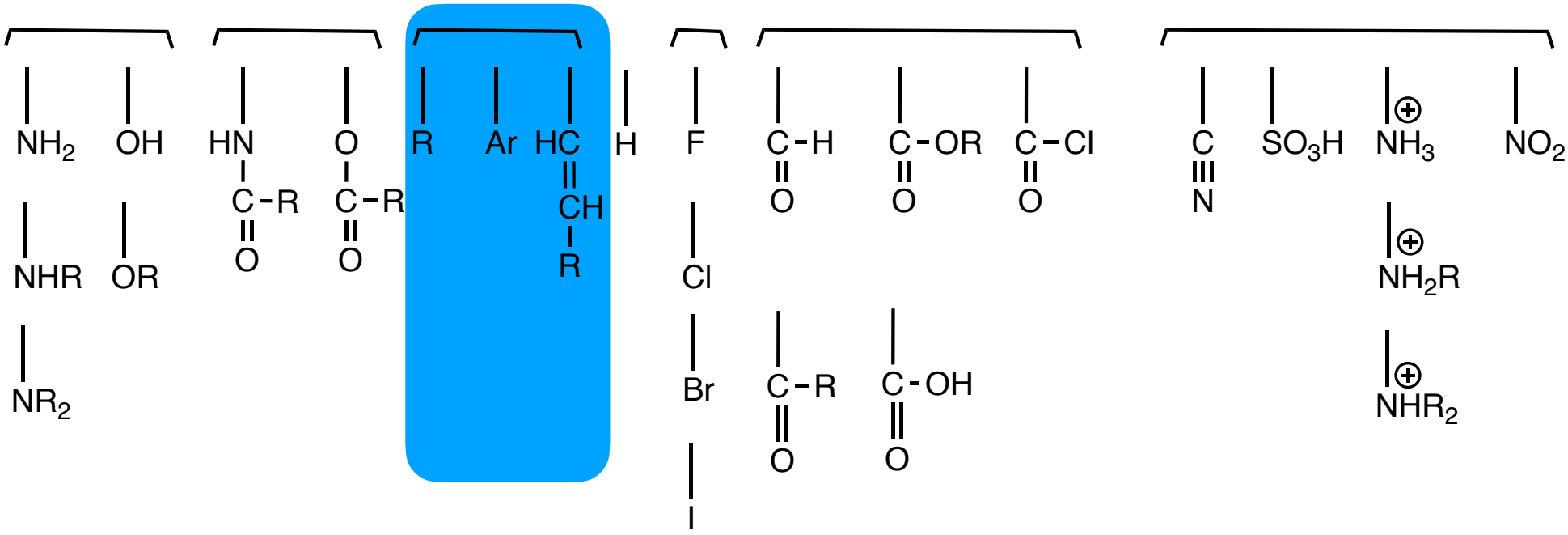
π donor but not as good because e⁻'s are also delocalized into C=O π system







σ ··· donor


NH2
OH
NHR
OR
NR2
HN
C–R
O
O
C–R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C–H
O
C–OR
O
C–Cl
O
C–R
O
C–OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2