

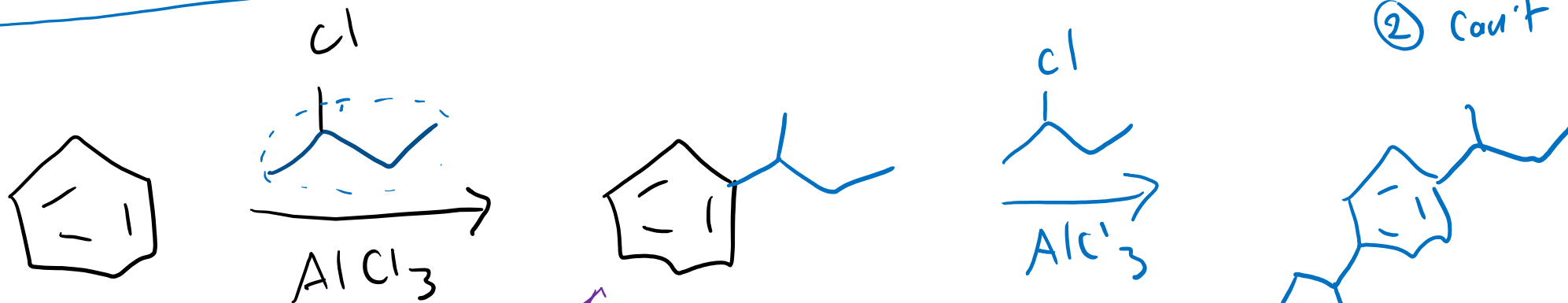
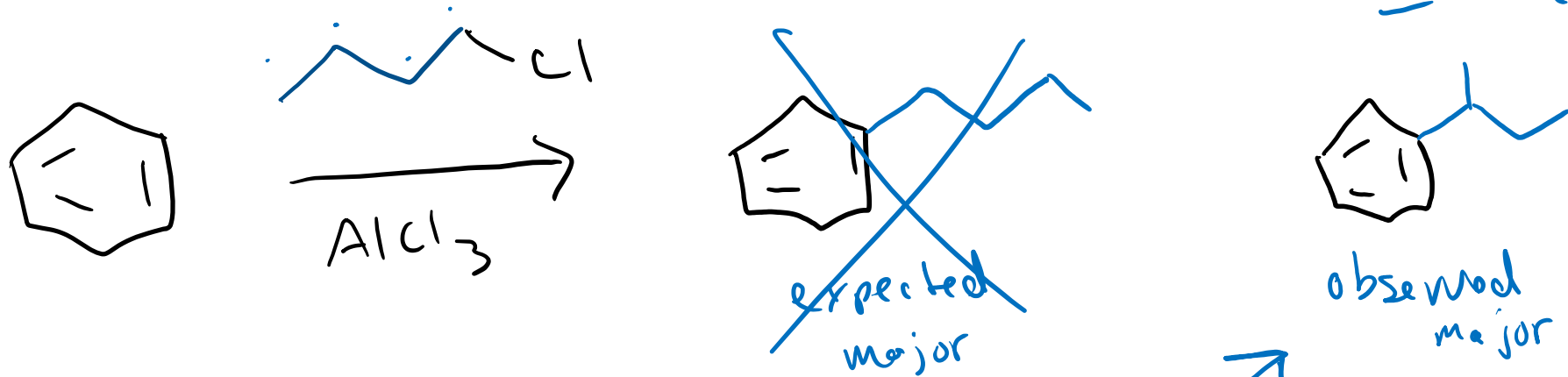
Friedel-Crafts Acylation

Substituted Benzenes and EAS

1/23/2023

Friedel-Crafts Alkylation: Limitations

① C^+ shifts can + will occur!
(1° alkyl halide no good!)



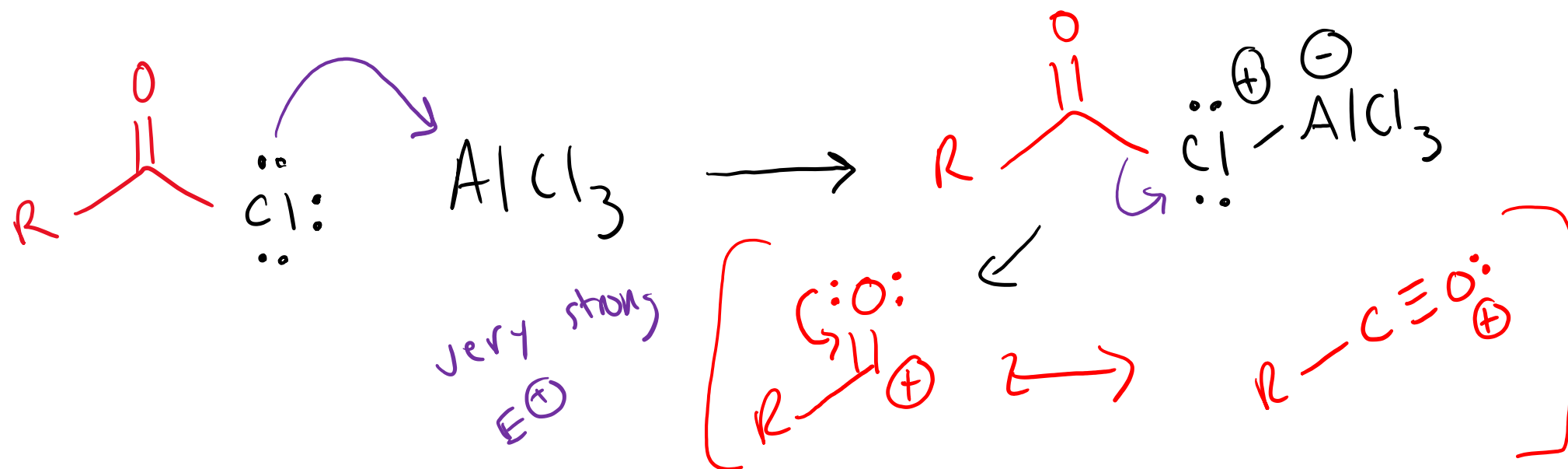
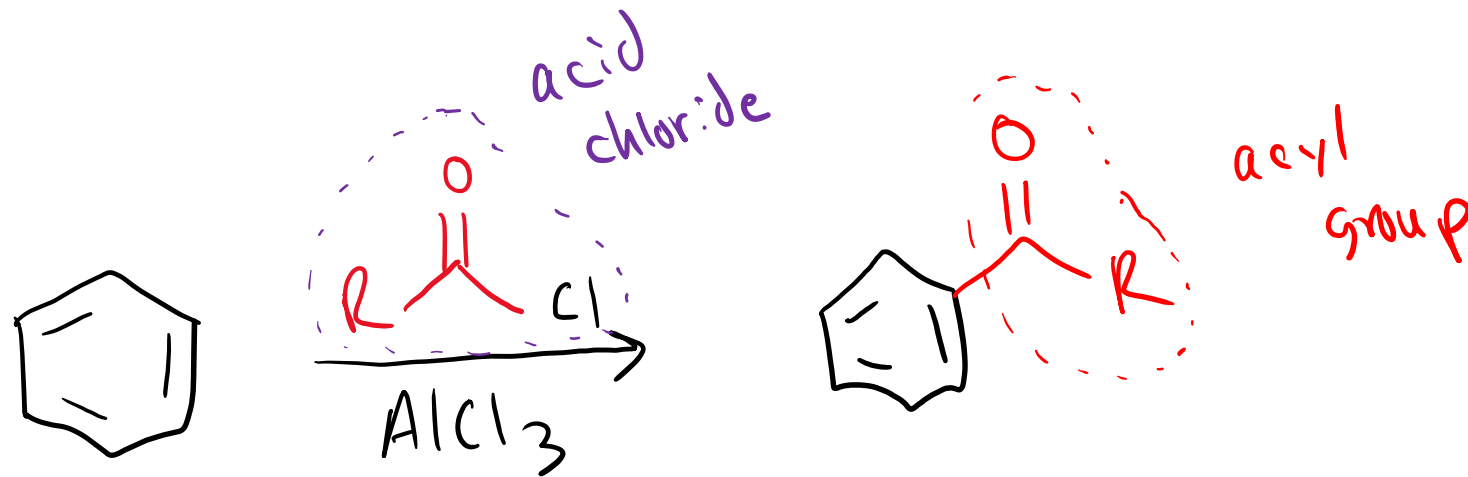
② Can't stop at just one alkylation!

more reactive than benzene!

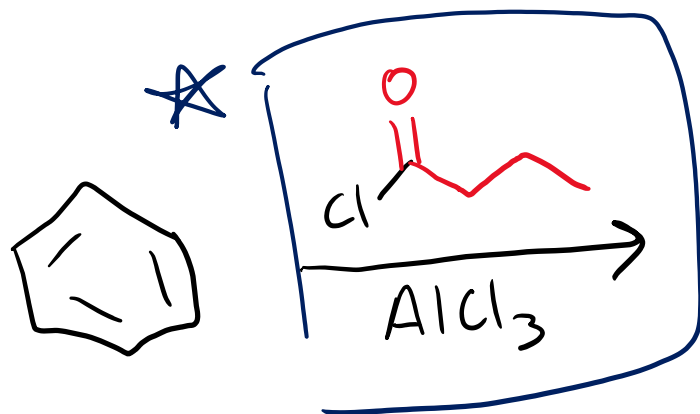
Friedel-Crafts Acylation

(still EAS)

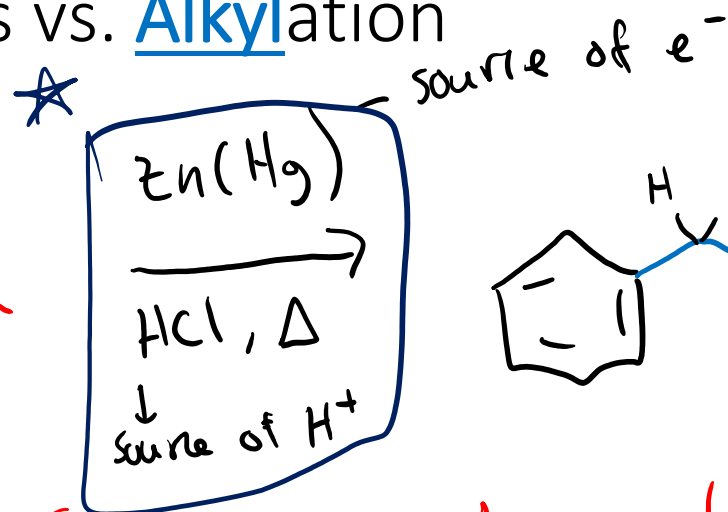
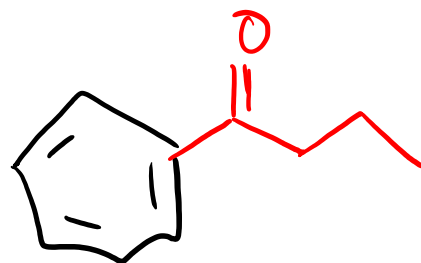
Text: 18.6



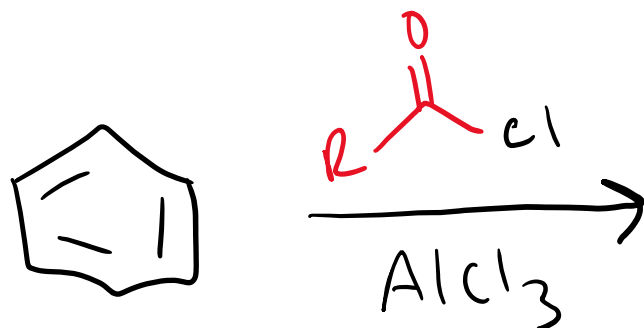
Friedel-Crafts Acylation: Differences vs. Alkylation



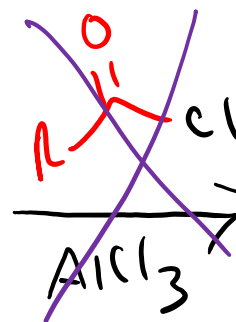
① no e^+ rearrangements!



② can convert acyl group into alkyl group via "Clemmensen Reduction"



less reactive than benzene
"deactivated"

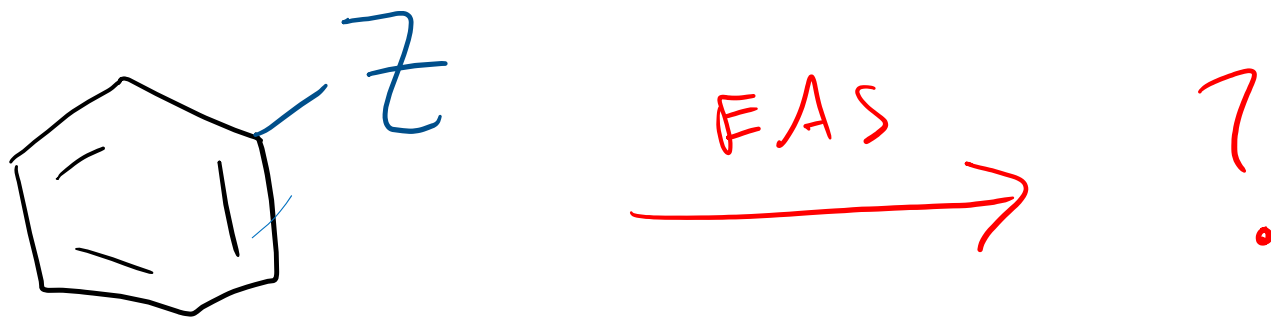


③ always stops after one acyl group

④ doesn't work on a deactivated benzene!

EAS with Substituted Benzenes

EAS reactions are more interesting when we use derivatives of benzene



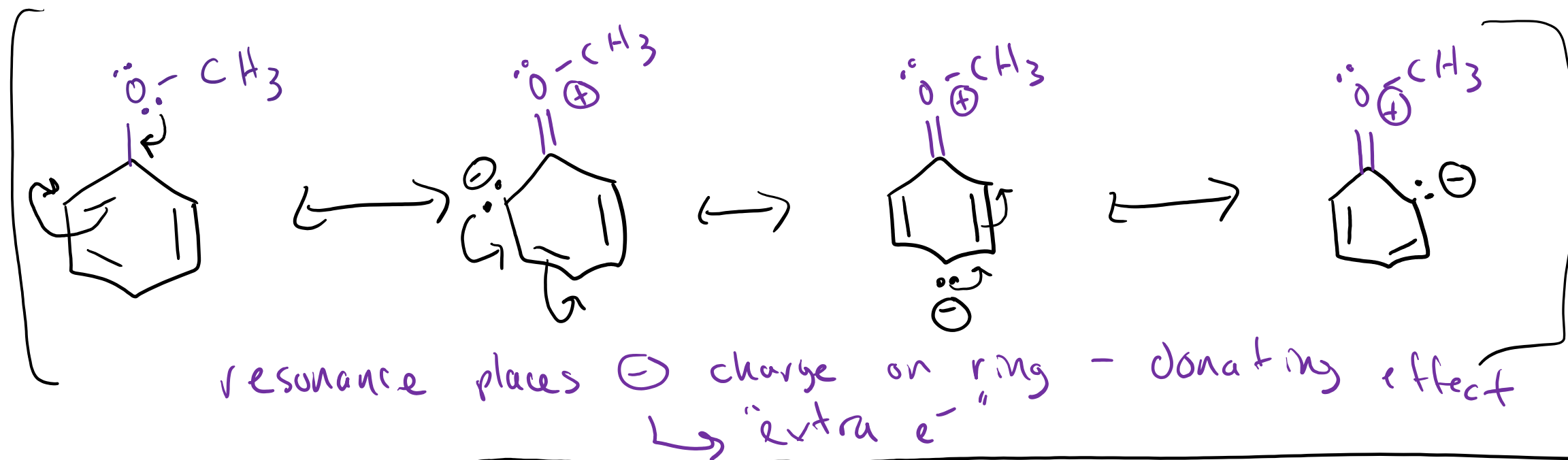
BUT....reactivity changes significantly depending on the substituent!

identity of "Z" group influences: rate of rxn

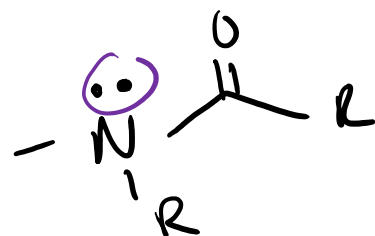
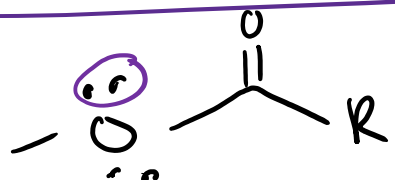
+ position new group
is added to (regioselectivity)

Electron Donating Groups (EDG)

Text: 18.7



Common Electron Donating Groups:



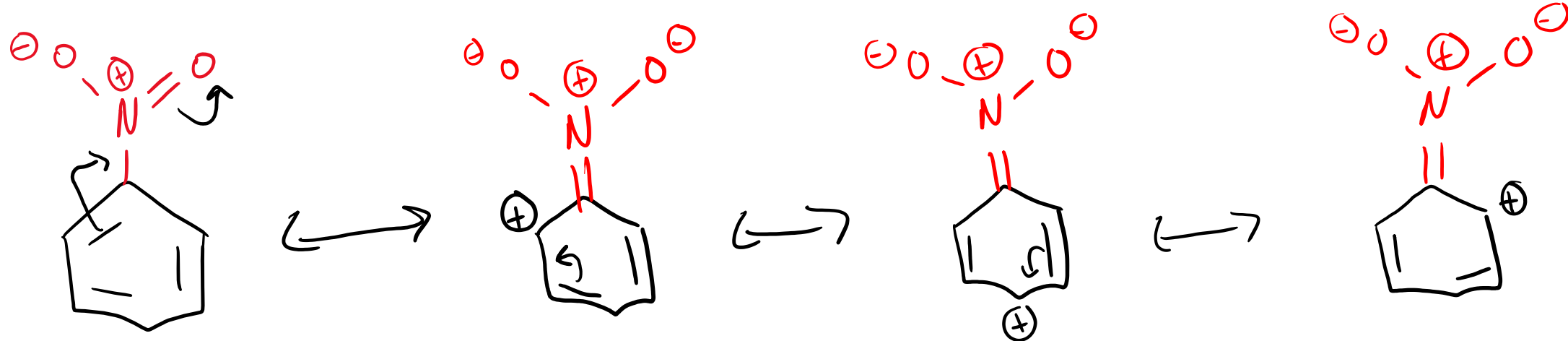
e^- donation
via resonance

-R (alkyl)

donates via induction
only (bond polarity)

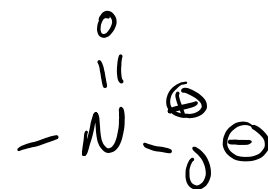
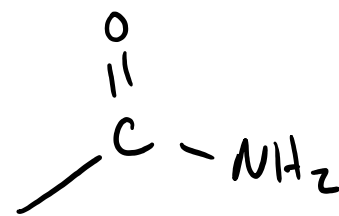
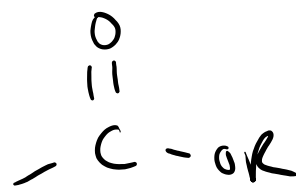
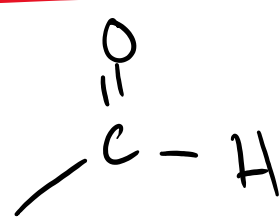
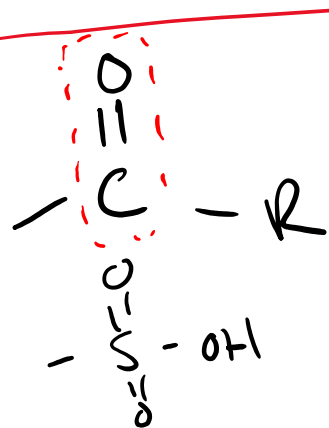
Electron **Withdrawing** Groups (**EWG**)

Text: 18.8



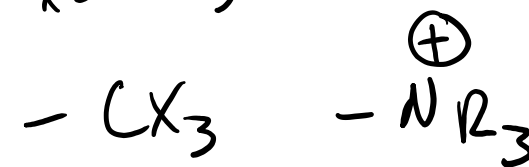
put (+) charge on ring via resonance - e^- withdrawing
 \rightarrow "missing e^- "

Common Electron Withdrawing Groups:



} via resonance
(+ induction)

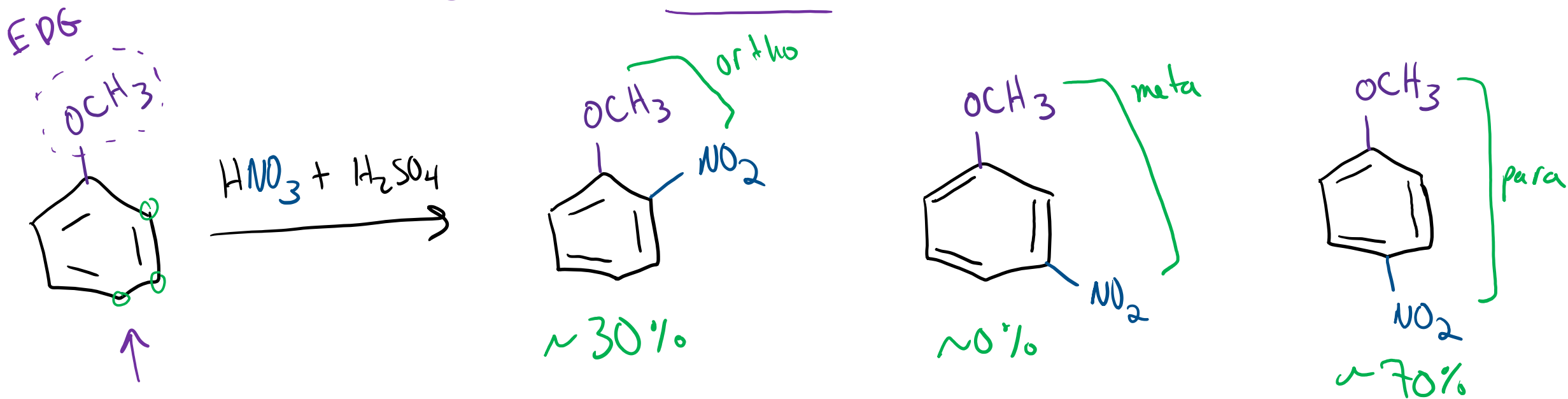
$x = \text{halogen}$



withdrawing via

induction only

Electron **Donating** Groups: "Directing" EAS Regioselectivity



- reacts ~ 400 times faster than regular benzene

EDG are "activating groups"

- EDG direct new group to ortho + para positions!
(NO_2 here)

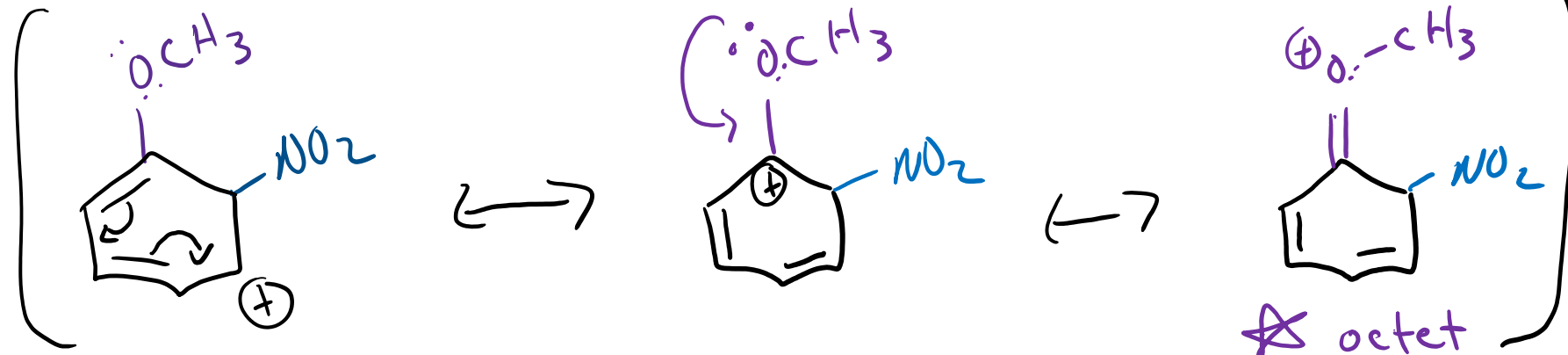
Electron **Donating** Groups: "Directing" EAS Regioselectivity

If
adds

NO_2

ortho

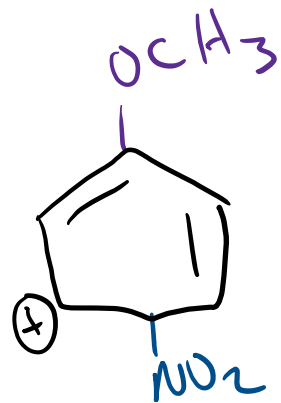
:



If

NO_2

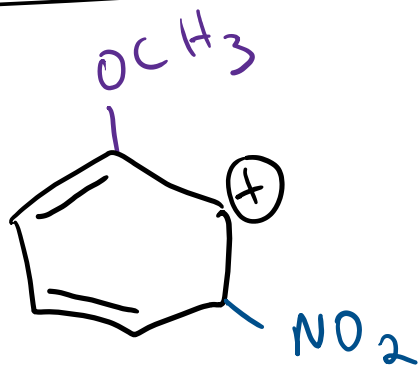
adds para:



If

NO_2

adds ~~meta~~:



can't get \oplus onto oxygen
via resonance!
much less stable intermediate
vs. ortho- or para-