

Today**Next Class**

The affect of substituents on EAS
Activators, deactivators and o,p vs m
Directors
Section 18.12, 18.13

Second Class from Today**Third Class from Today**

Please hand in reworked test 3 at the final on May 5

Reminder: final is on May 5 from 8:00 to 10:00

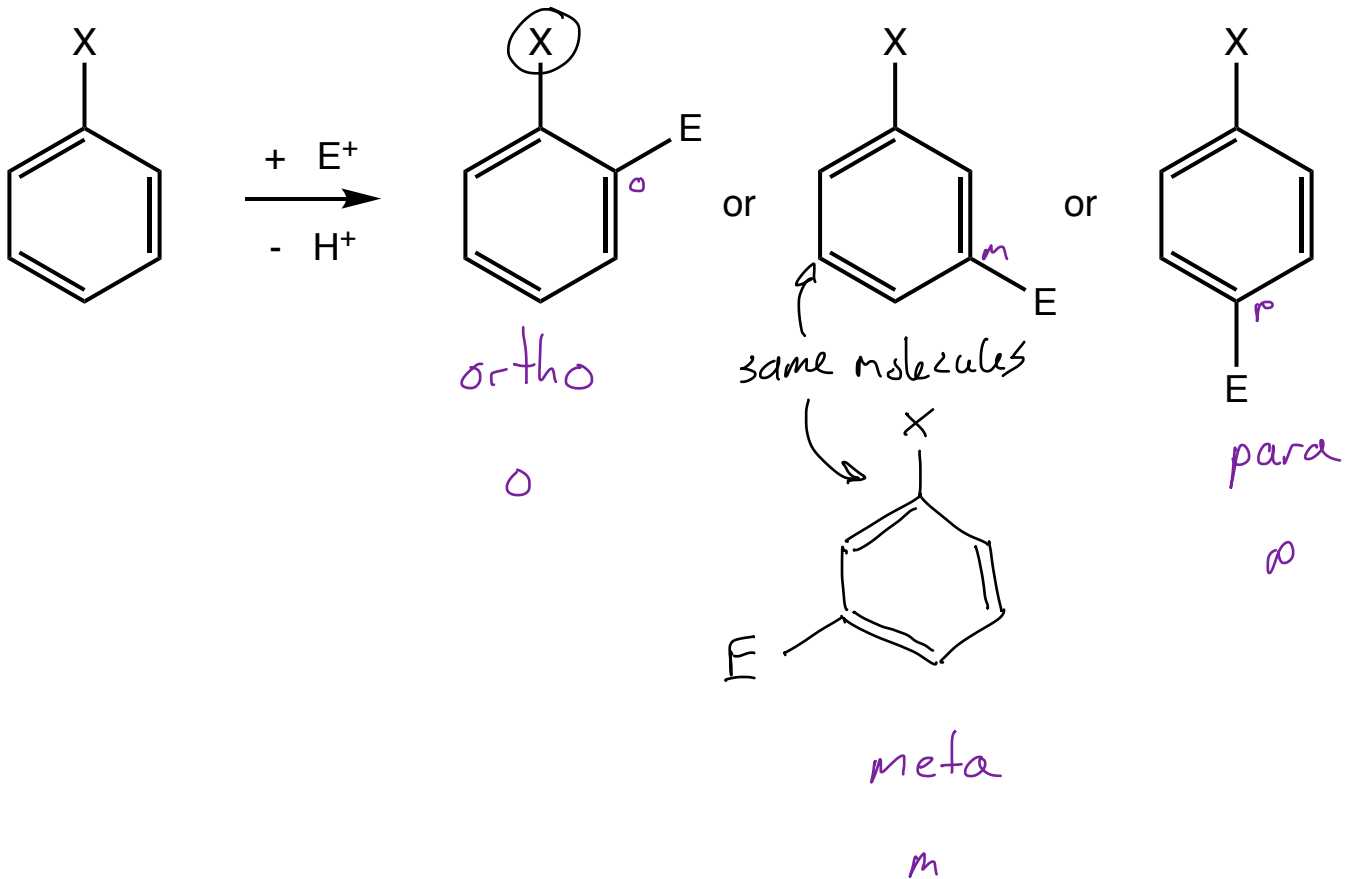
Sorry, reworked test 2s are not graded yet. They can be picked up tomorrow.

7:30 - 9:00 Wilson 134

Ortho, Para, and Meta Directors

relative to X, where is E?

Section 18.13



O and p Directors

three possible intermediates exist

this empty p orbital is adjacent to a π bond... so... resonance contributors

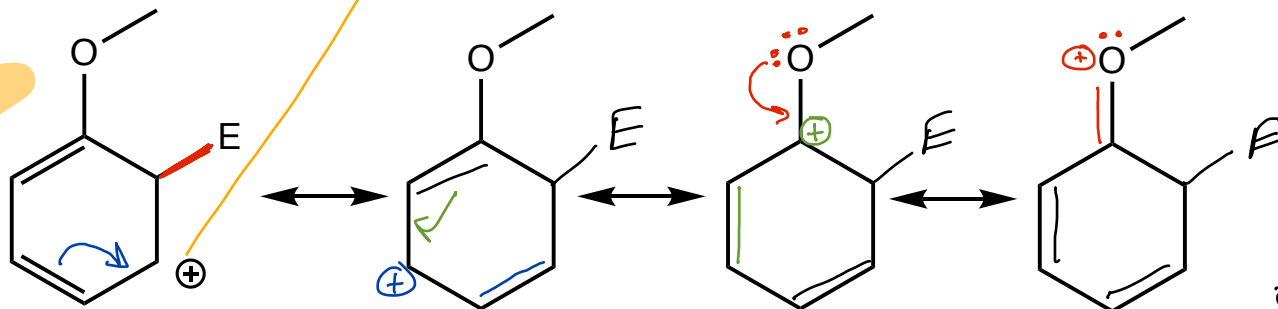
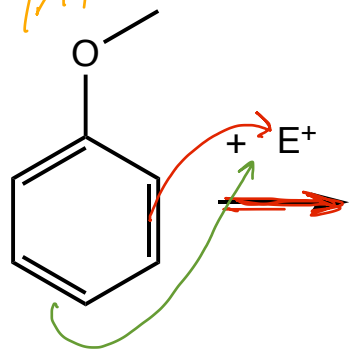
Section 18.13

when E adds to ortho position \oplus charge can be stabilized on 3 C's + qm O

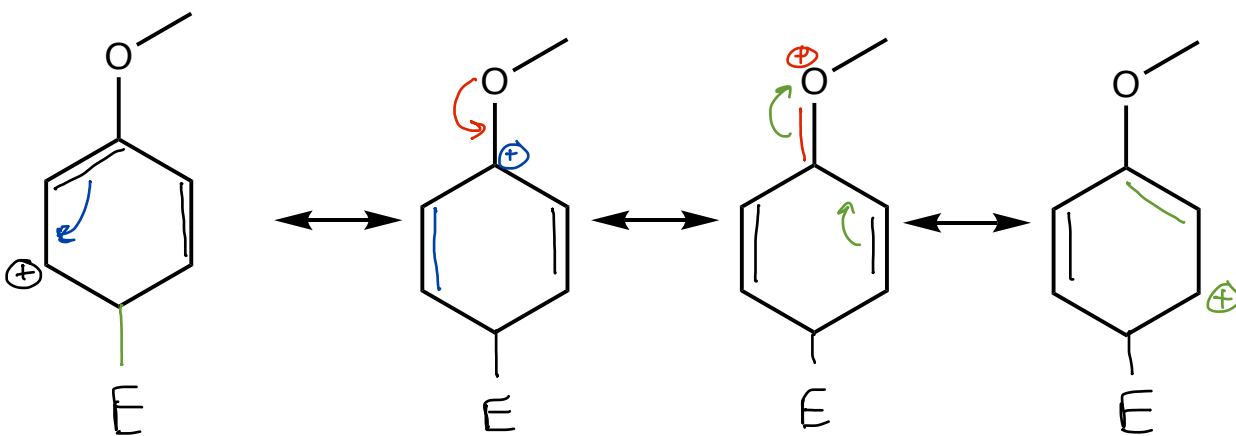
The intermediate is not stabilized by the OMe group. Higher energy intermediate

when E adds to para position \oplus charge can be stabilized on 3 C's + qm O

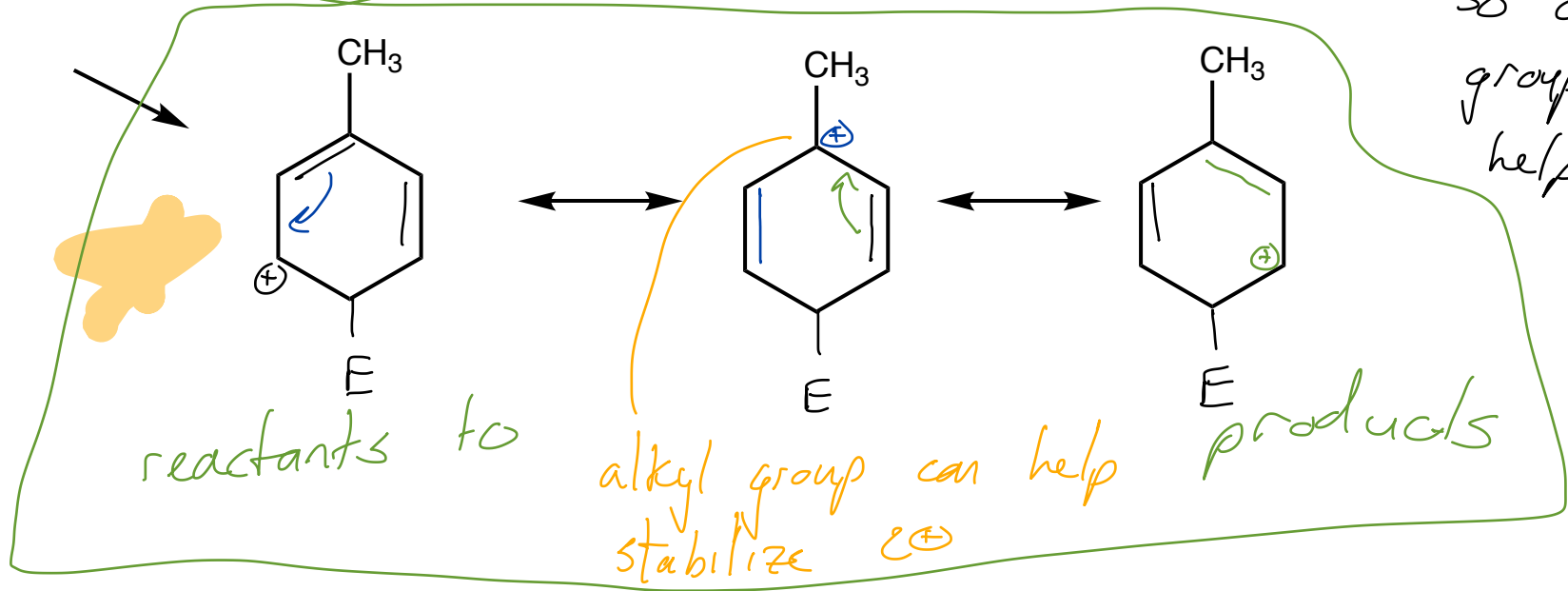
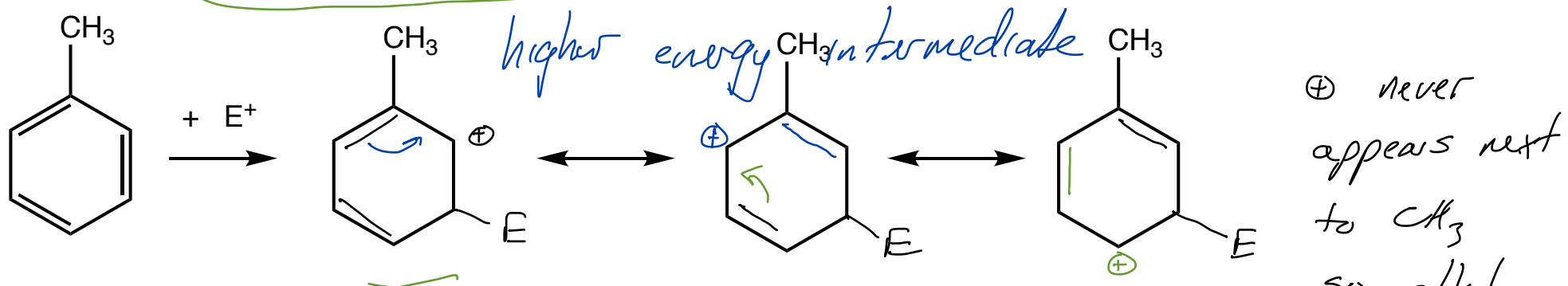
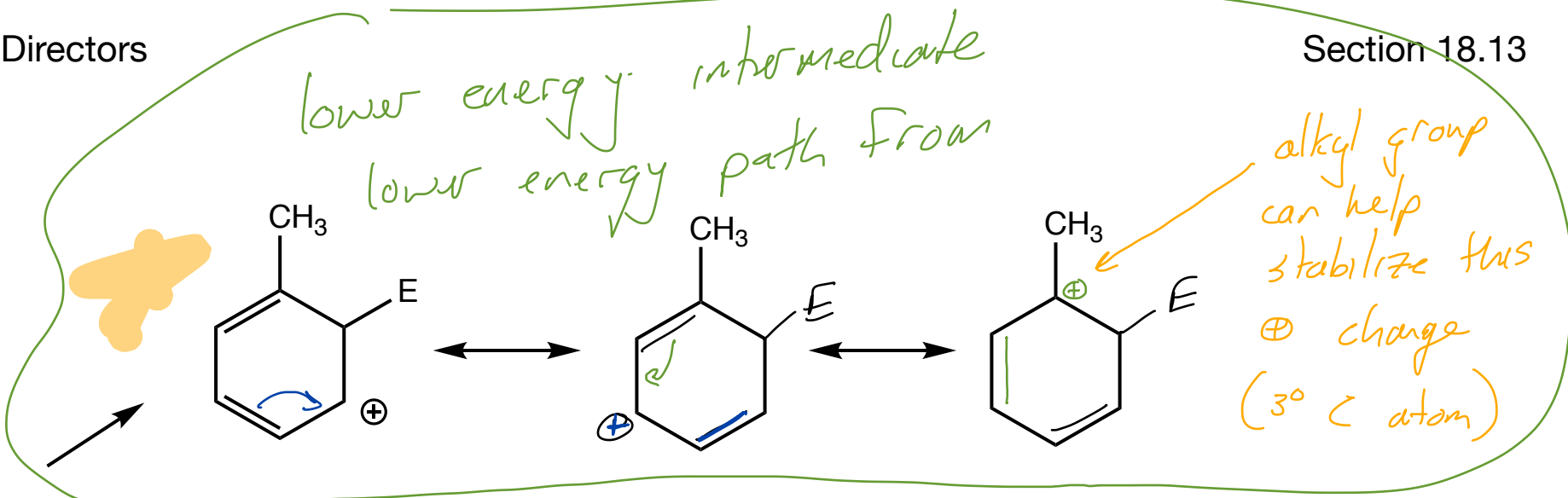
preferred paths because intermediate



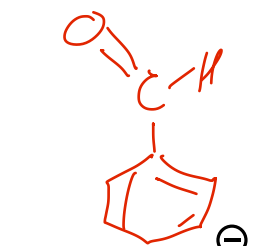
is lower in energy



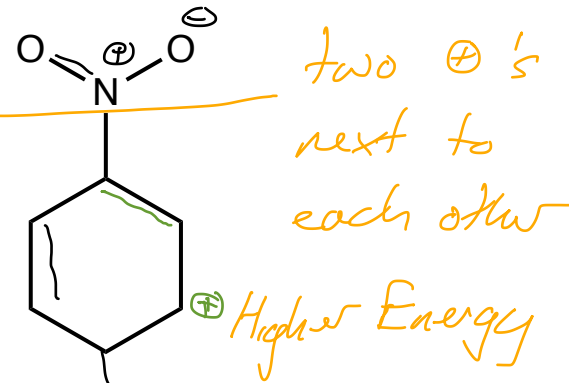
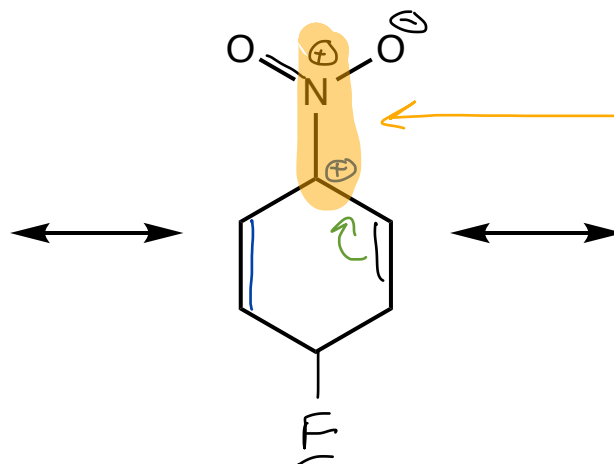
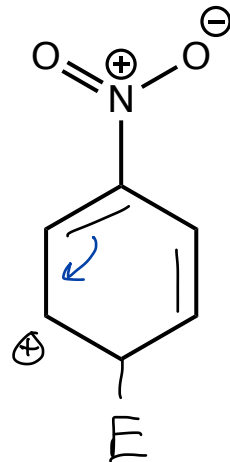
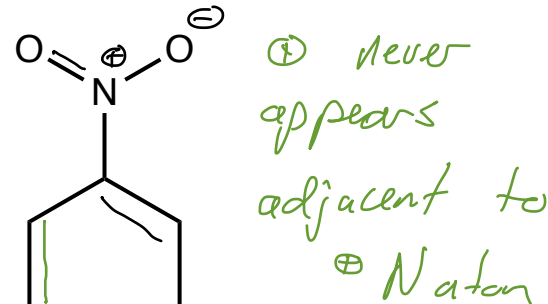
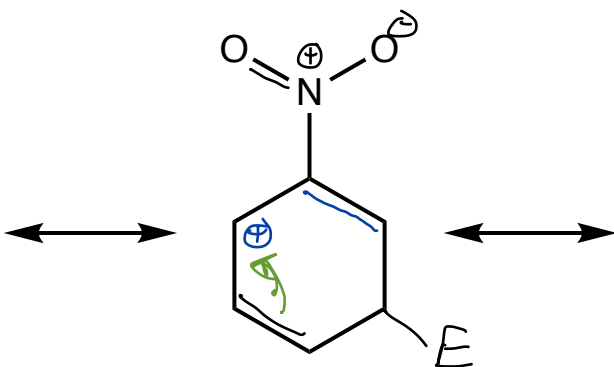
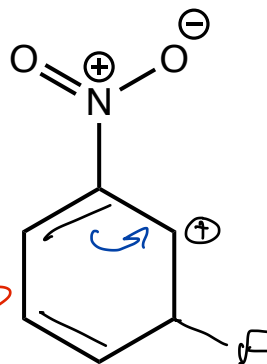
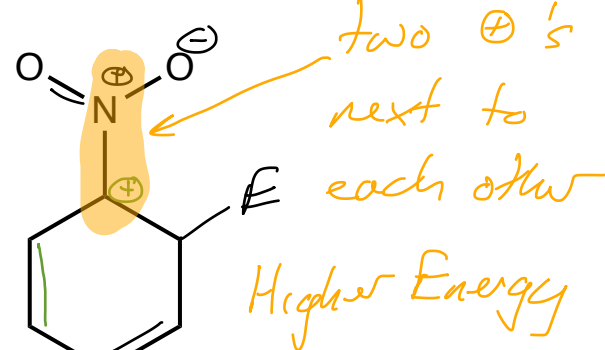
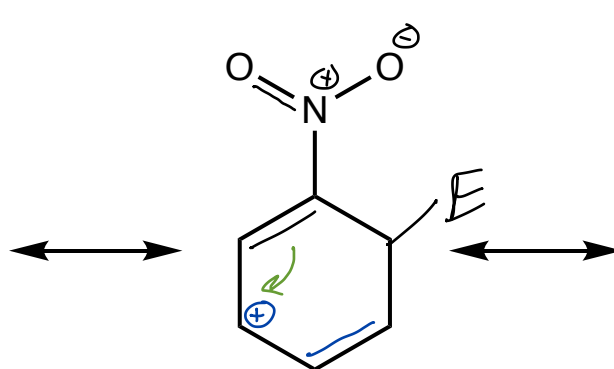
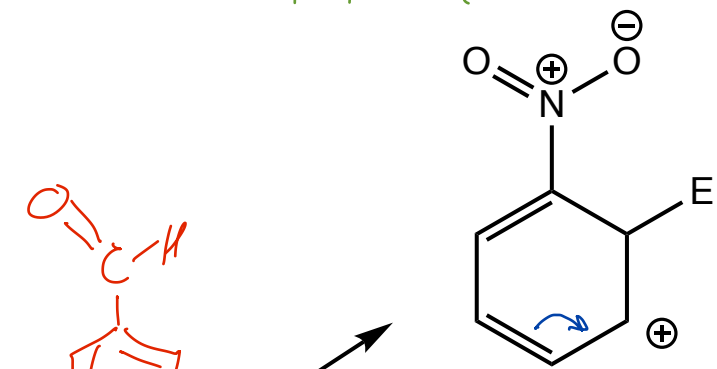
which is/are better?



no intermediate is stabilized by the nitro group
but the nitro group destabilizes the o, + p
intermediate

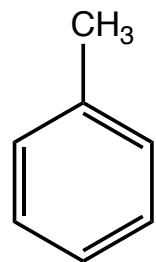
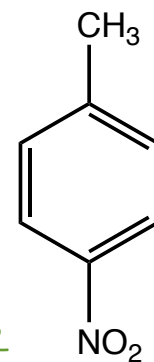
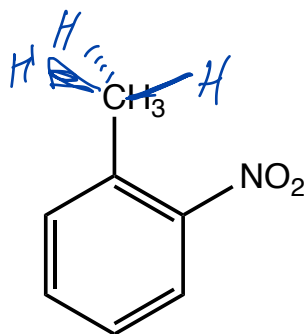


meta is
more favorable
because it is
less bad



o:p Ratios

Why more
ortho
substitution?

+ HNO₃
 $\xrightarrow{\text{H}_2\text{SO}_4}$


61% 39%

ortho position has a 2:1 statistical advantage

steric bulk

is increasing

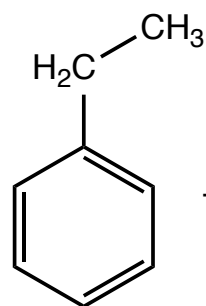
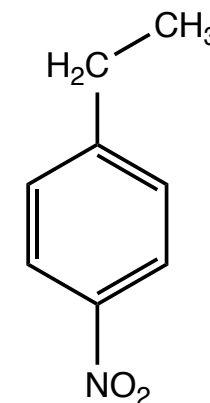
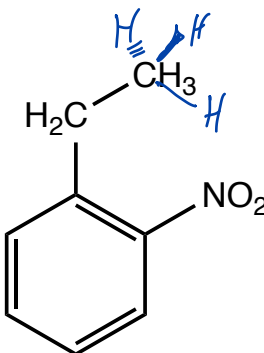
and as the

substituent

gets larger +

blocks access

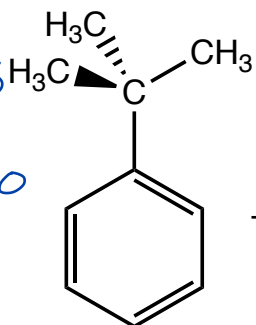
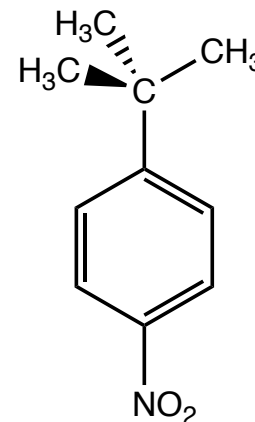
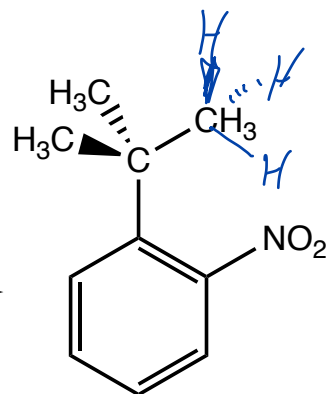
to the ortho
position....

+ HNO₃
 $\xrightarrow{\text{H}_2\text{SO}_4}$


50% 50%

to the ortho
position....

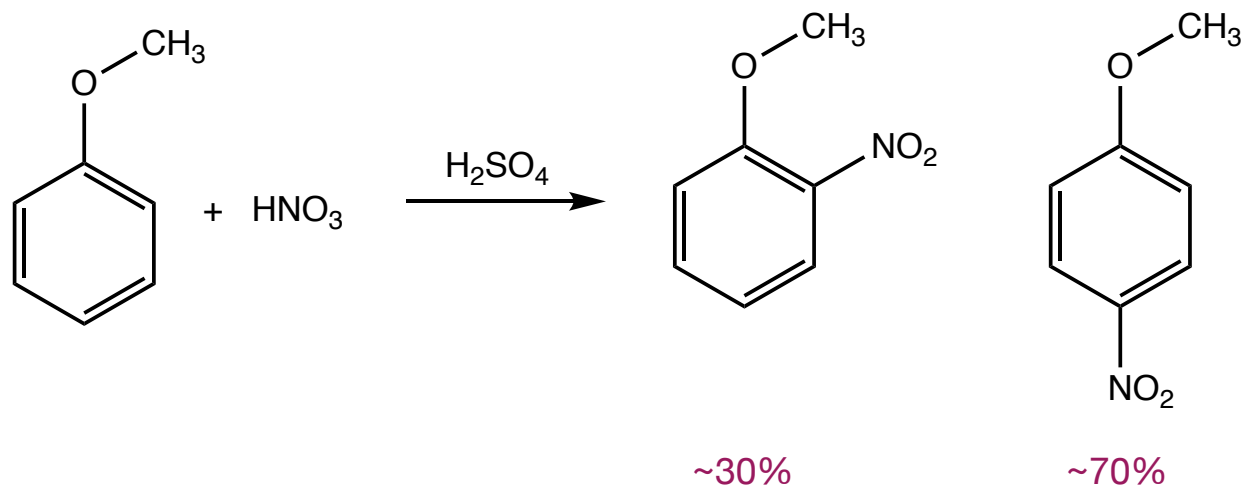
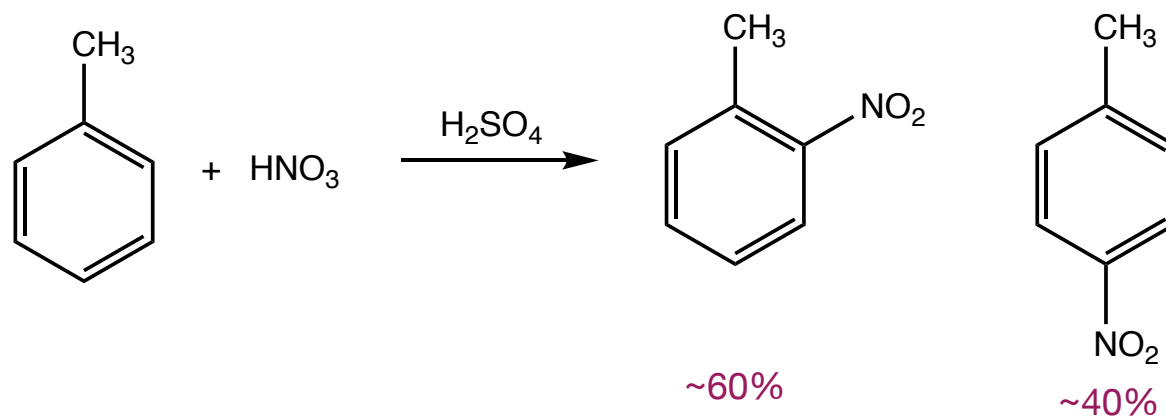
para becomes favored

+ HNO₃
 $\xrightarrow{\text{H}_2\text{SO}_4}$


18% 82%

o:*p* Ratios (Summary)

Section 18:14

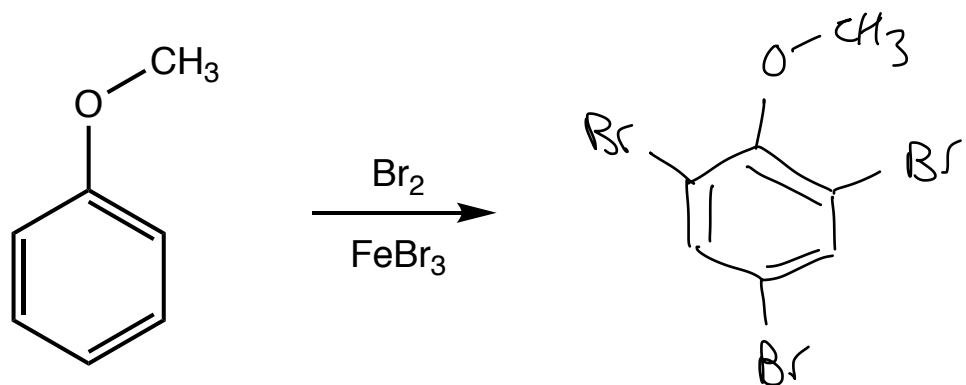


The *para* position has steric and electronic advantages

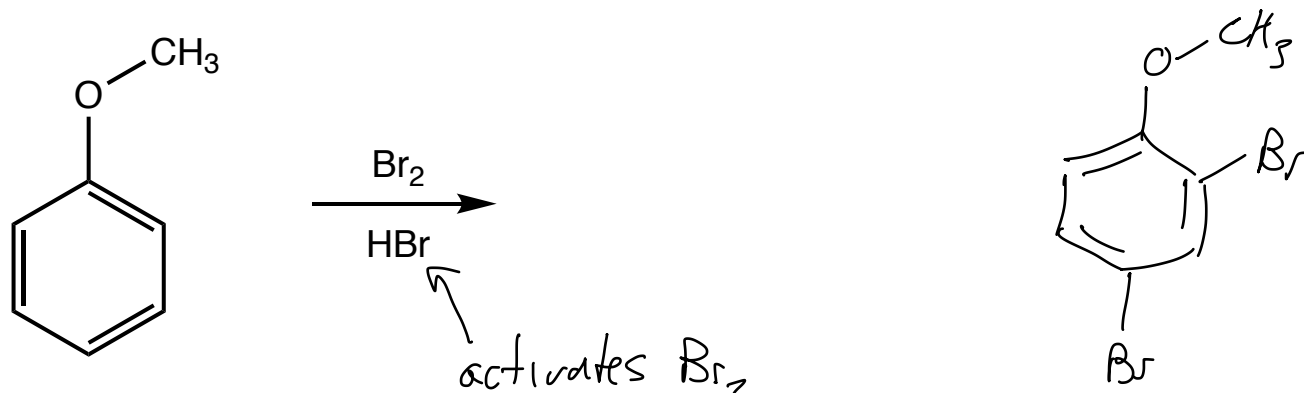
The *ortho* position has a statistical advantage

Mixtures of *o* and *p* isomers typically result

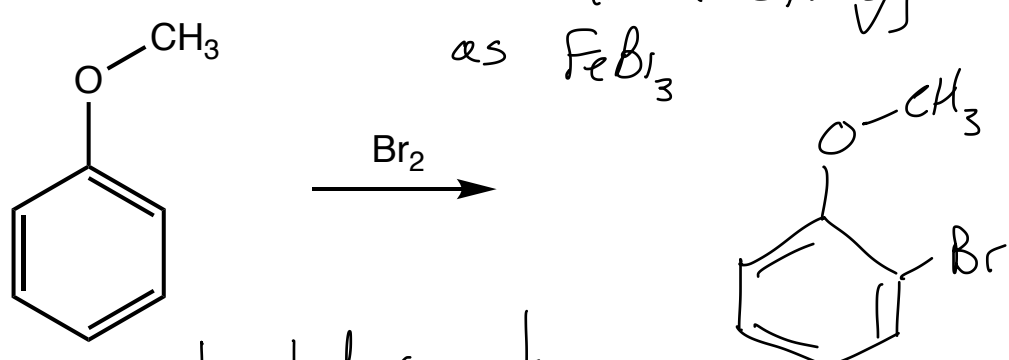
As the substituent gets larger, the *para* position become the more preferable position.



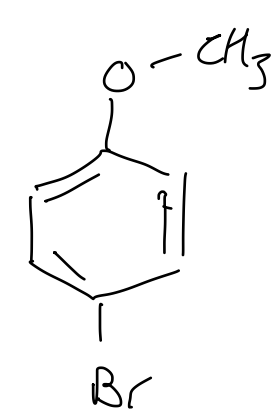
activation encourages multiple EAS reactions

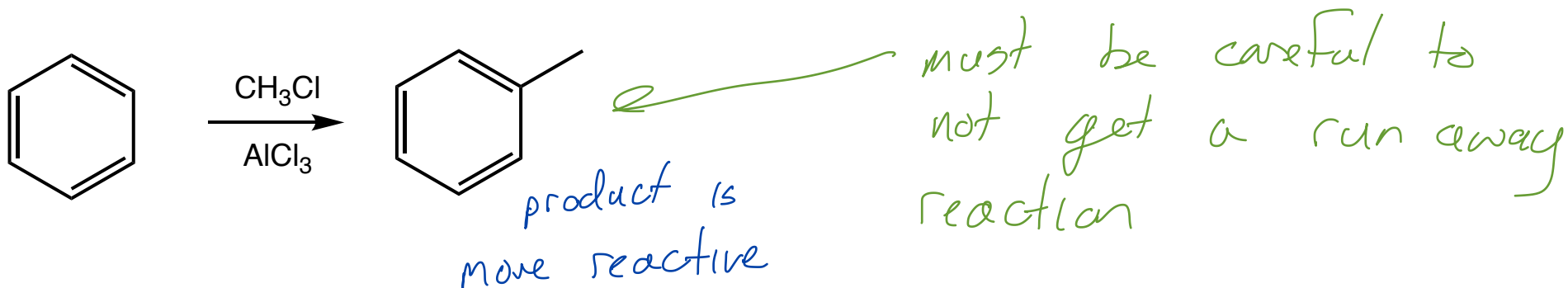


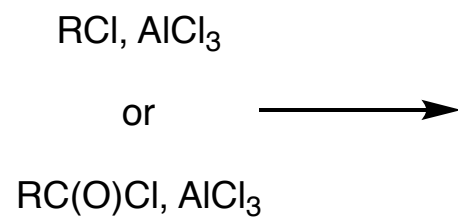
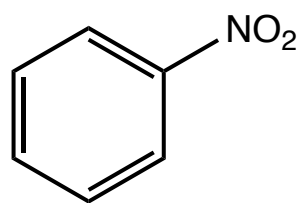
activates Br_2 but not as strongly as FeBr_3



activated so it can react with Br_2

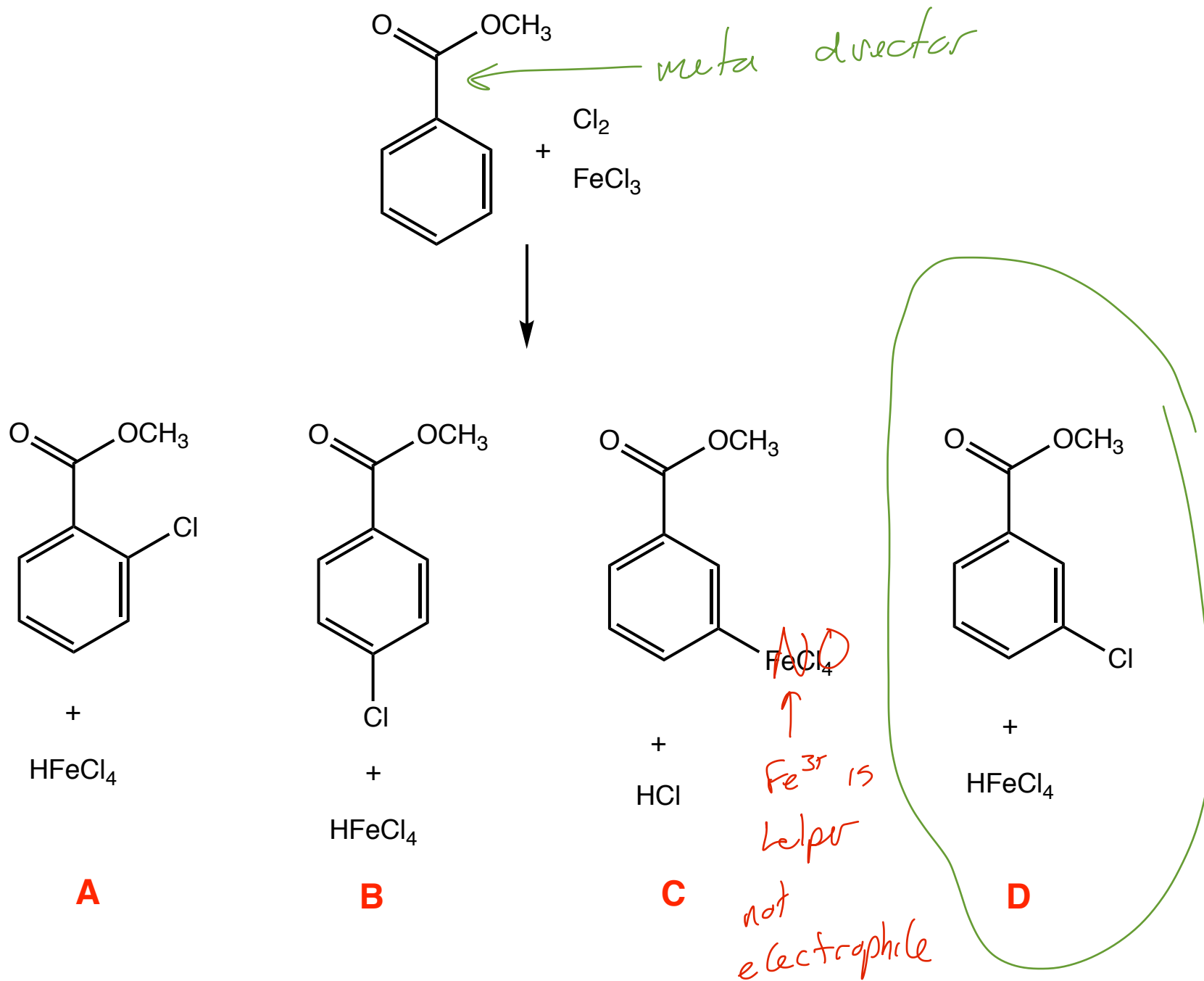




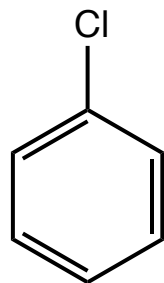


NR

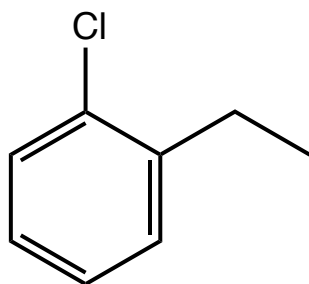
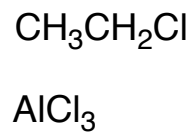
Practice



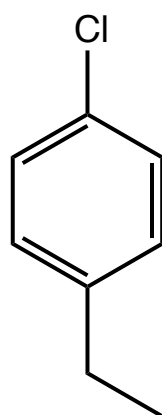
Practice



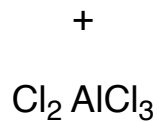
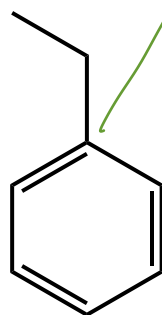
o p director



A

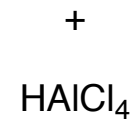
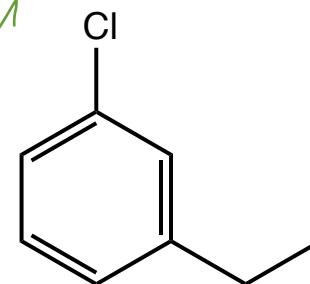


B



C

wrong kind of substitution



D