

Course 345

Day Wed

Notes Taken By Adams

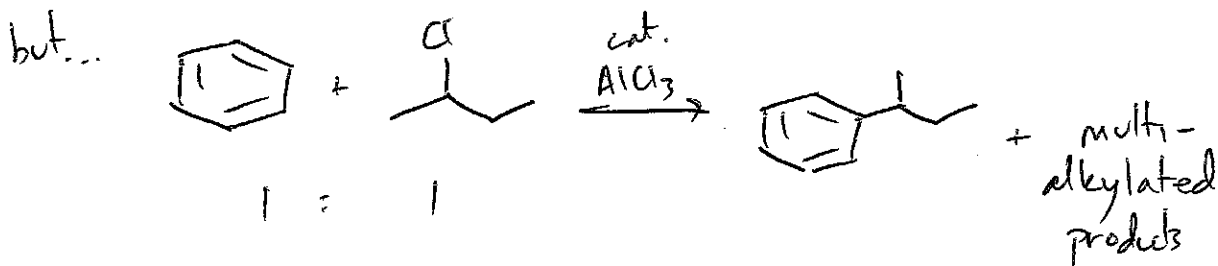
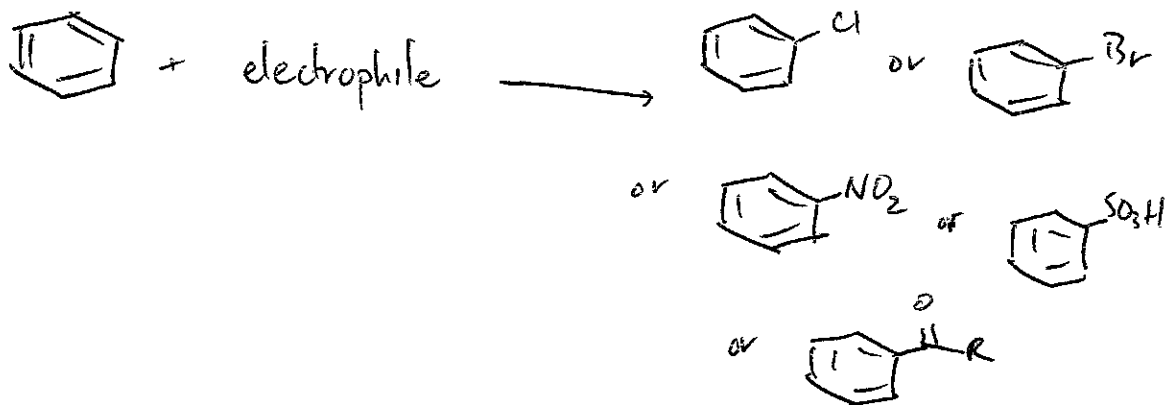
Instructor Gellman

Date 2/12/2014

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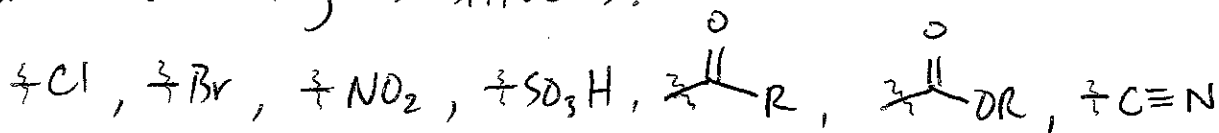
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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

Recall: mechanistic rationale for distinction among EAS reagents - single vs multiple additions



• Crucial distinction between 2 classes of aromatic ring substituents: activating vs deactivating (relative to H)

• Common deactivating substituents:



- these groups make it harder for EAS to occur

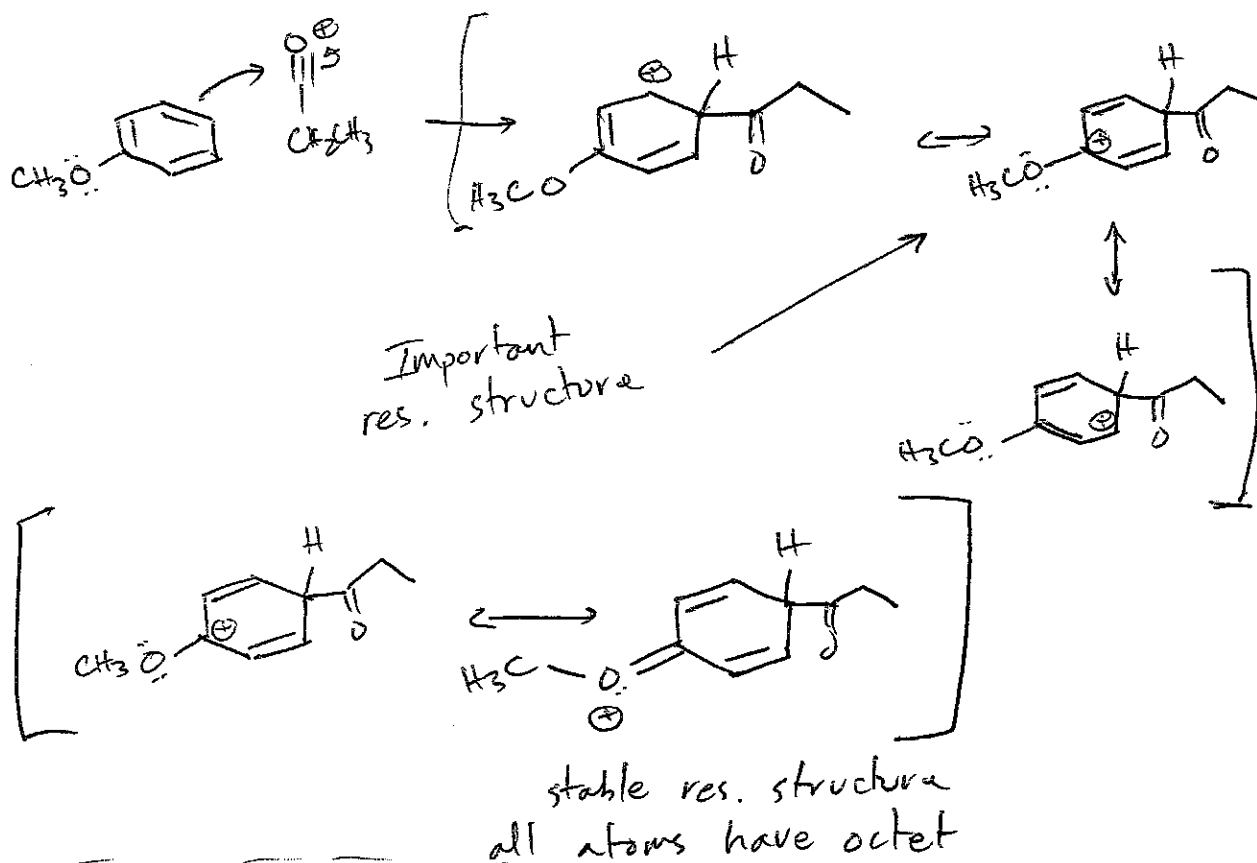
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• Common activating substituents:

-alkyl, -OH, -OR, -NR₂

• Why are O/N examples activating?

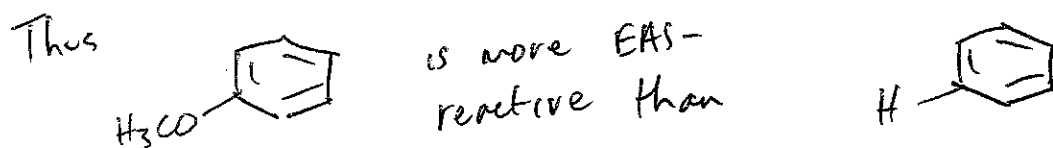
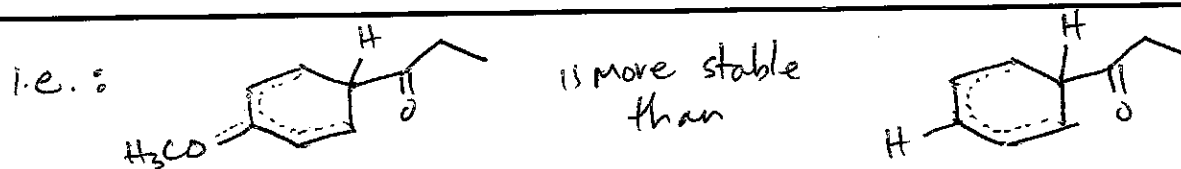
- consider EAS intermediate:



• The additional delocalization indicated by the "extra" res. structure indicates greater stability of this cationic intermediate. (relative to H, vs. -OCH₃)

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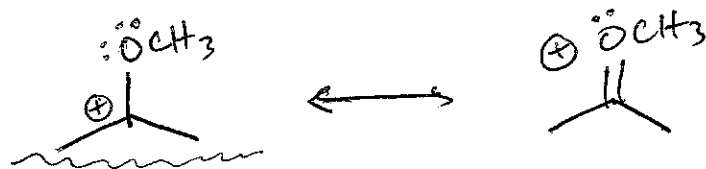
(Recall Hammond postulate from 343)

Note: Competing considerations: $-\text{OCH}_3$ could be considered e^- withdrawing due to its high electronegativity

$-\text{OCH}_3$ is e^- -withdrawing via σ bond (inductive effects)

but

$-\text{OCH}_3$ is e^- -donating via π -type interactions



The π factor is dominant overall \rightarrow so $-\text{OCH}_3$ is activating overall

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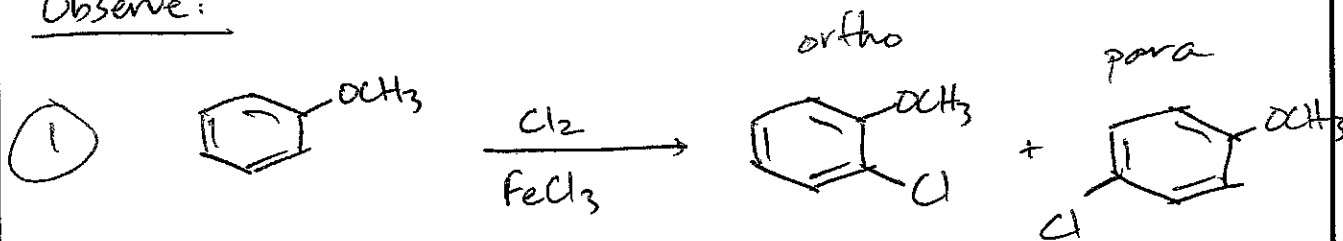
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• See text \rightarrow for halogens, inductive e^- -withdrawing aspect wins out \rightarrow \equiv deactivating group

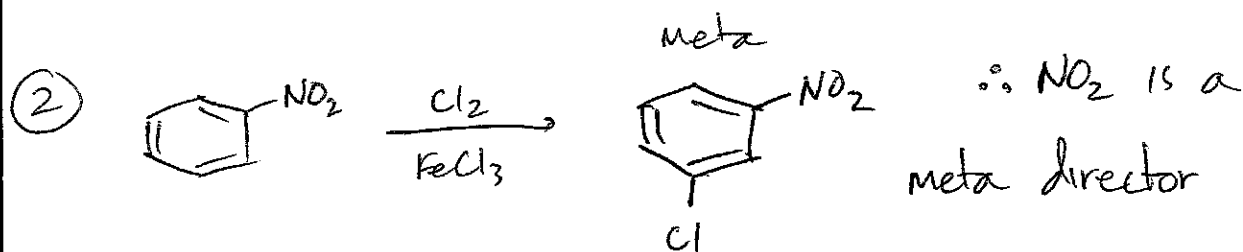
• Second factor in EAS reactions when ring has pre-existing substituents: regioselectivity

i.e., where does the new substituent go, relative to pre-existing group?

Observe:



\therefore OCH_3 is an ortho/para director

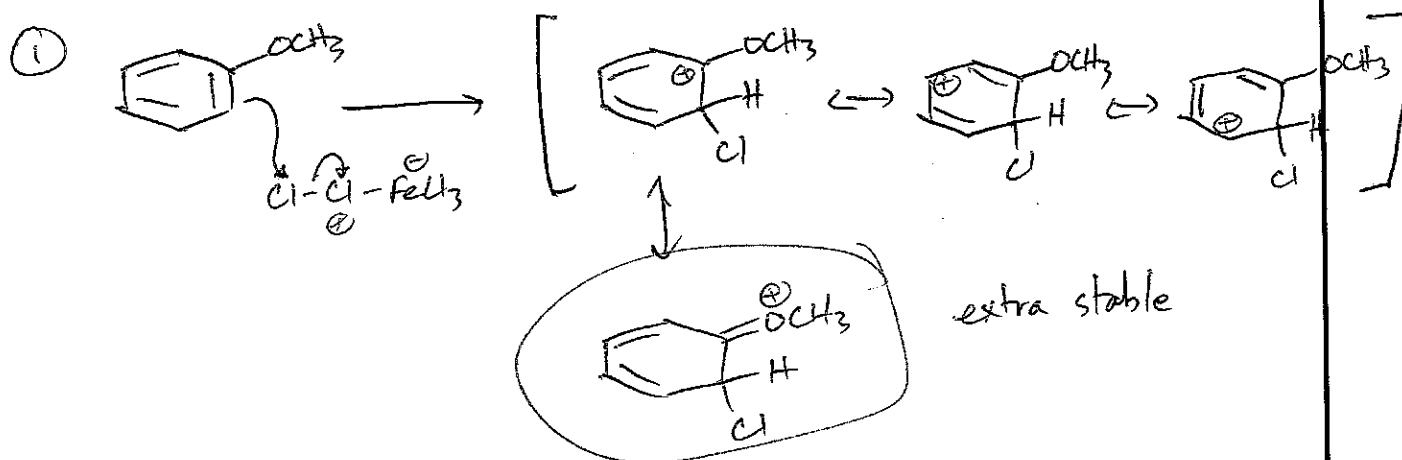


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Relationships

- All meta-directors are deactivating (but not vice versa)
- All ortho/para directors (except halogens) are activating.
- Halogens are deactivating, but ortho/para directors (see text for explanation)

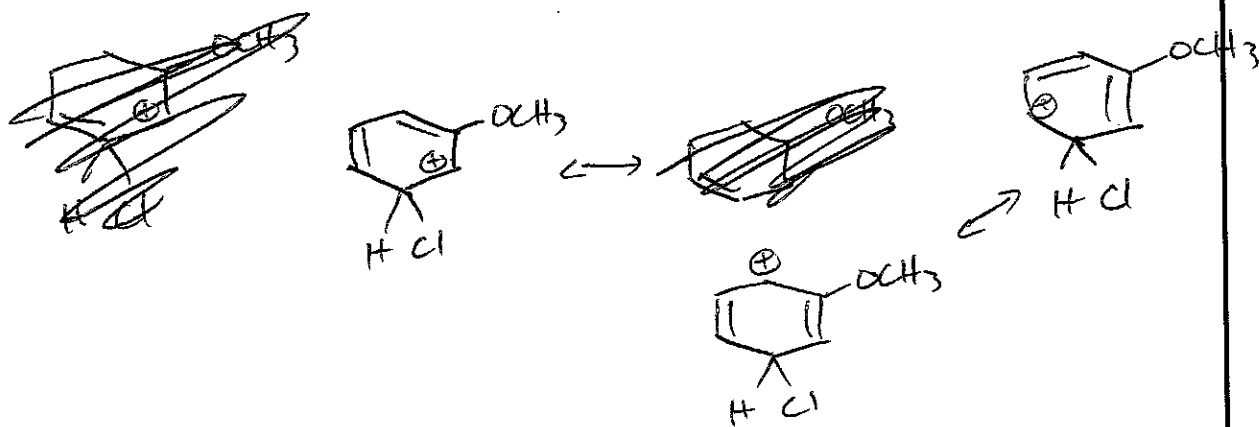
Mechanistic rationale for directing effects:



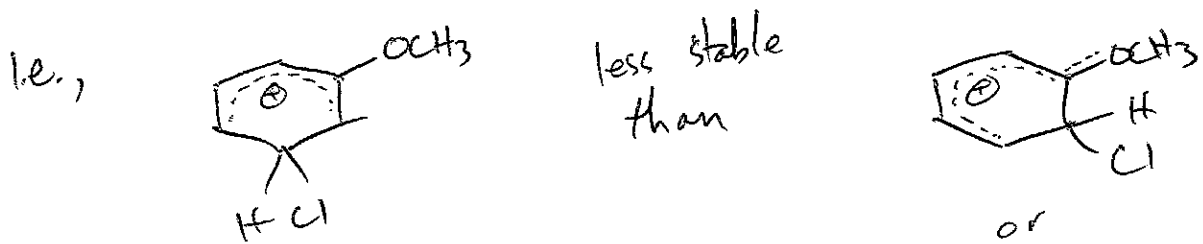
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• Consider hypothetical intermediate required for the meta product



Note: \oplus never adjacent to $-OCH_3$, thus no "extra" res. structure, \therefore less stable.



thus, ortho/para products form