

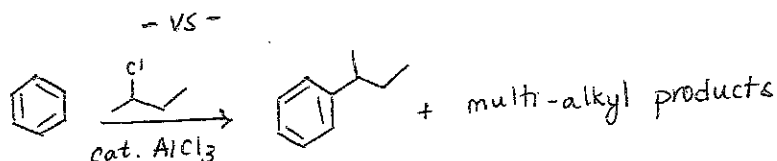
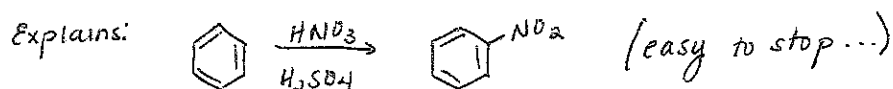
Course Chem 345Lecturer GellmanDay WednesdayDate 2/11/2015Notes Taken By Leslie RankTotal # of Pages 4

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Exam #1 - Next Wed. Chps - 12, 13 + 16 (IR, NMR, EAS)

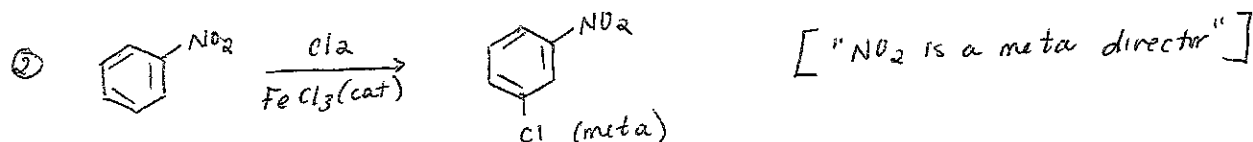
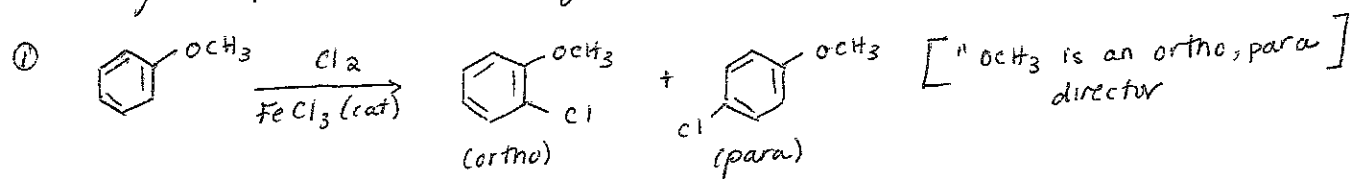
- 2 sites: Chem 1361 and Biochem 1125 (assignments coming)

Recall: Existing ring substituents affect EAS reactivity ("Activating" vs "Deactivating" Substituents)



Existing Substituents affect the location at which new substituents are attached in EAS rxns: "Regioselectivity" $\Rightarrow$ what region of molecule does rxn take place?

- 2 general possibilities, EAS regioselectivity (mono-substituted S.M.)



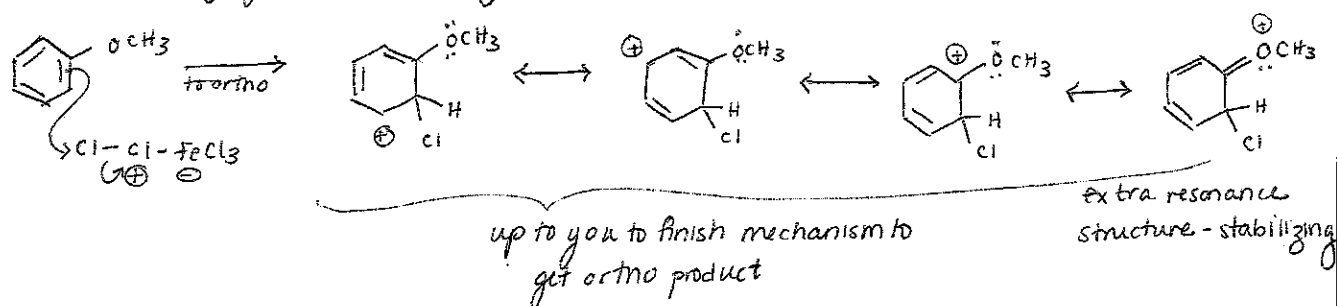
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Correlations between activating/deactivating vs o,p/m-director

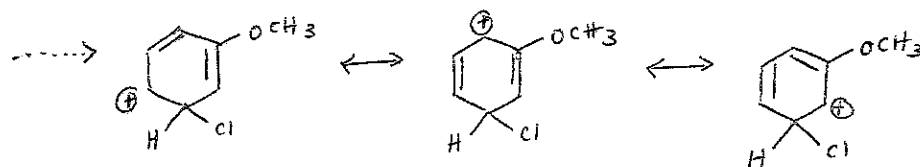
- all m-directors are deactivating (not vice versa)
- all o,p-directors are activating, except halogens
- Halogens have a distinctive profile - see text

Mechanistic rationale for directing effects

1. e^- -donating groups (activating)



- observe - comparable situation (extra-resonance structure for para pathway)
- CONTRAST: Intermediate for the (hypothetical) meta pathway



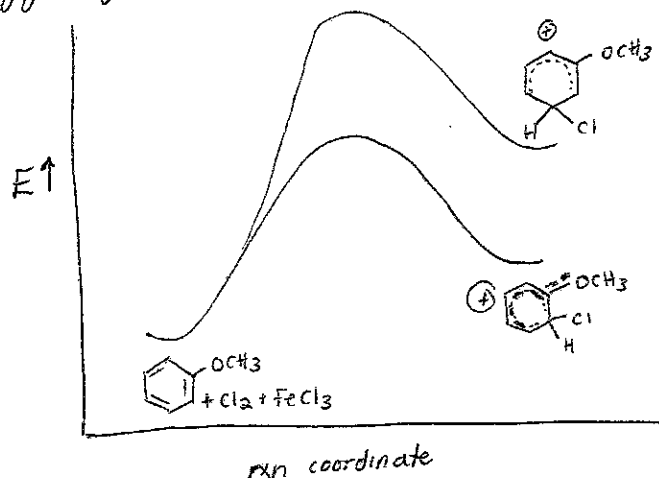
No chance for OCH_3 to form 'extra' res. structure

* Thus, intermediate on meta pathway is of higher energy than intermediates on ortho or para pathways

$\Rightarrow$ see next page for free energy diagram

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Free Energy Diagram



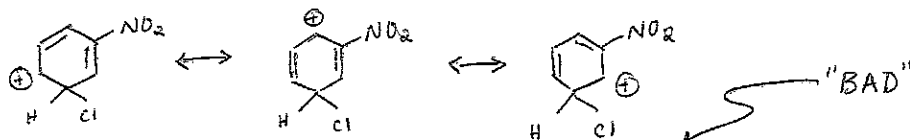
* Thus, expect ortho (or para) product to form faster (in preference to) meta product

Mechanistic rationale for directing effects continued...

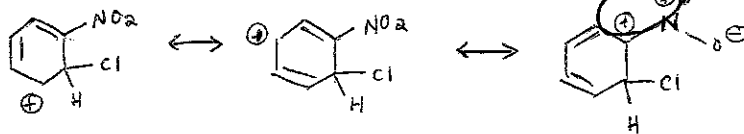
2. e^- - withdrawing groups (deactivating): $-NO_2$

Compare cationic intermediates

For meta: $\cdots \rightarrow$



For ortho: $\cdots \rightarrow$

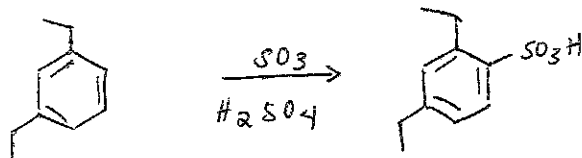


You do para!

* Thus, intermediate for ortho (or para) is less favorable than for meta product and meta product preferentially (You fill in partial energy diagram)

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1. Substituent directing effects are consistent



[Ethy] = o,p]