Do Not Use Pencil *Do Not Staple, Please!*

Course Chem 345 Lecturer Gellman

Day Wednesday Date 2-10-16

Notes Taken by Lu Liu Page 1 of 5 (Total Pages)

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Review Session

TODAY (as usual) . B371, 5 PM

Next Week: Monday B371, 5PM

Exam #1 next Wed, chaps 12, 13, 16 (locations: TBA)

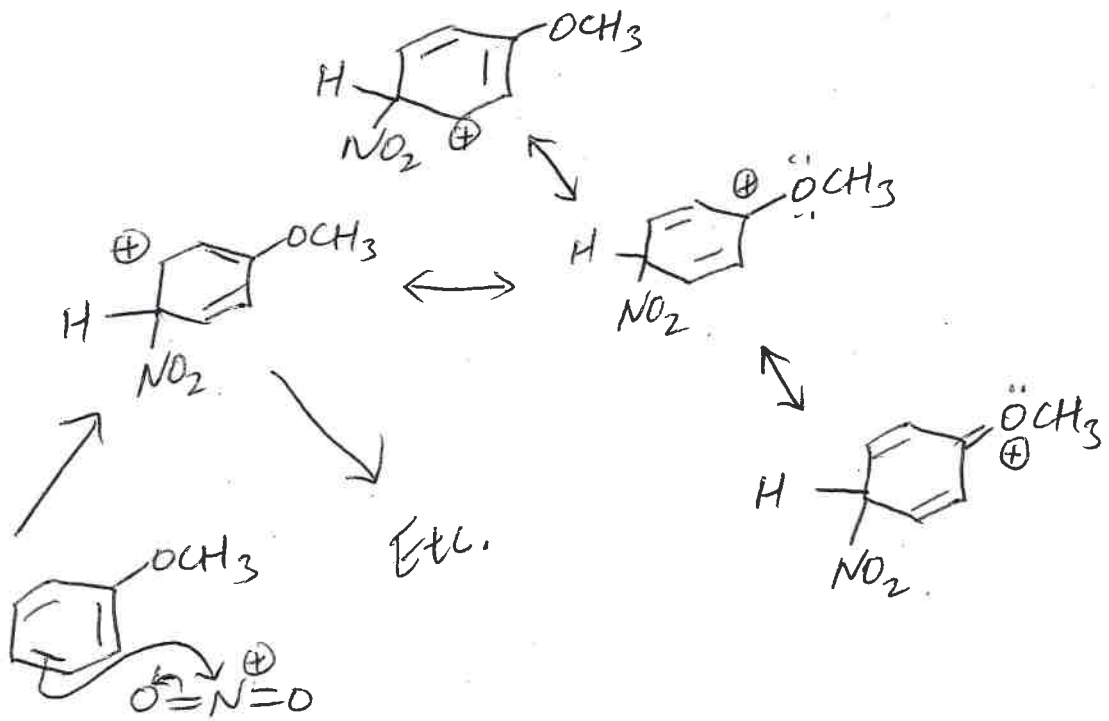
Recall — EAS: effects of pre-existing substituents on aromatic ring reactivity...

Deactivating (rel. to H) Substituents — decrease EAS reactivity

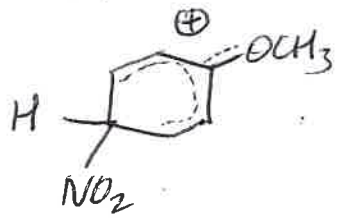
vs.

Activating substituents...

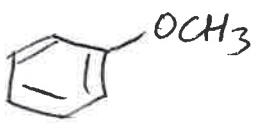
Examples of activating: $-OCH_3$



Thus,



more stable than

$\Rightarrow$  more reactive than 

$\therefore$ $\{\ddot{O}CH_3$ is "activating"

Recall: $\{\ddot{I}:$ & $\{\ddot{B}r:$ are deactivating; different balance of π vs. σ effects relative to O or N. (see text)

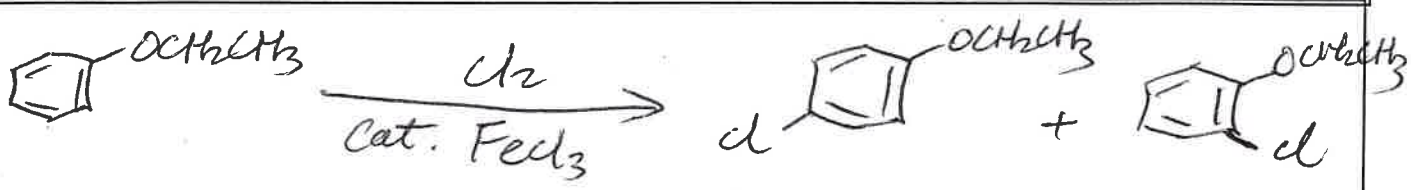
Note: "conflict" – O is e^- donating in a π-sense, but e^- withdrawing in a σ-sense (electronegative)

In addition to EAS reactivity, ~~pre~~ the location of new substituents introduced via EAS is influenced by pre-existing substituents.

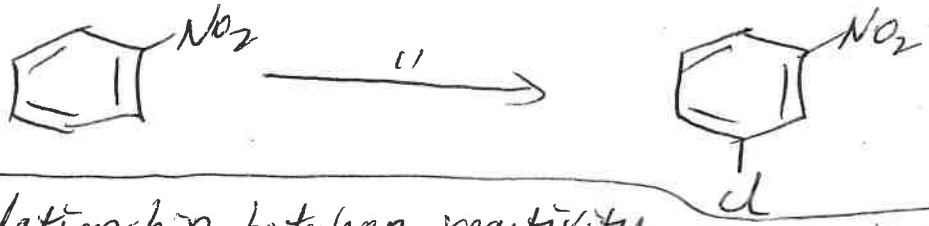
"Directing Effects"

2. possibilities — (i) ortho, para-directors
(ii) meta-directors.

Examples



vs.



Relationship between reactivity & regioselectivity preferences—

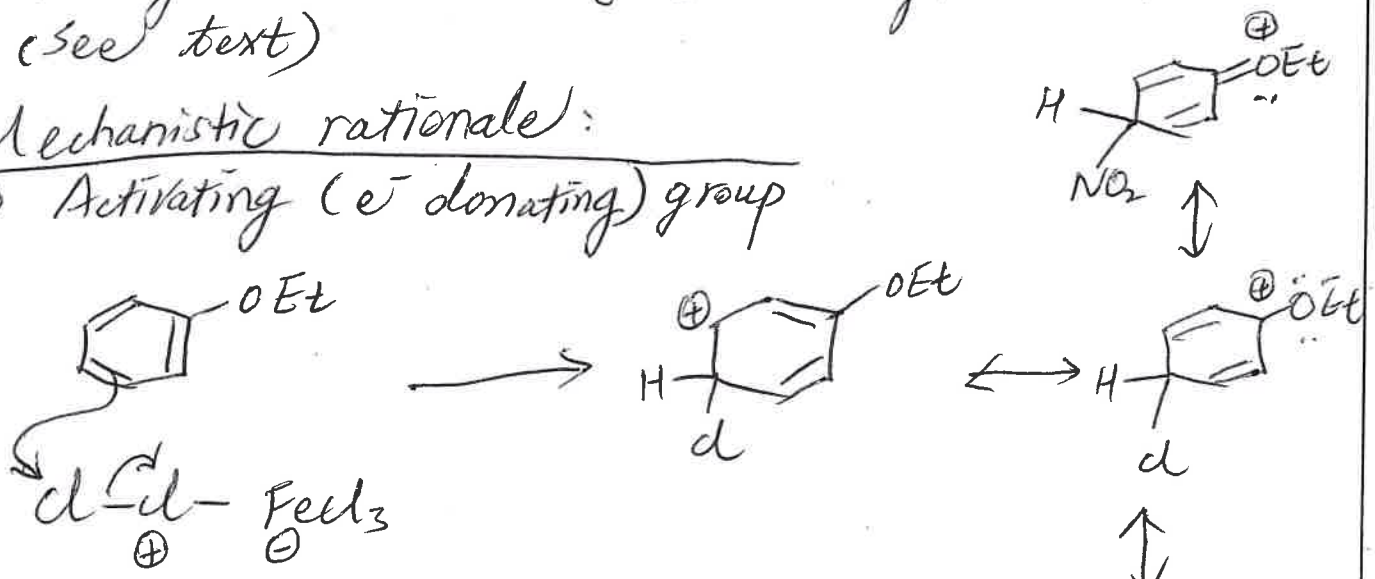
① All meta-directors are deactivating (not vice versa)

② All o, p – directors except halogens are activating

③ Halogens are "odd" (deactivating & o, p–directors) (see text)

Mechanistic rationale:

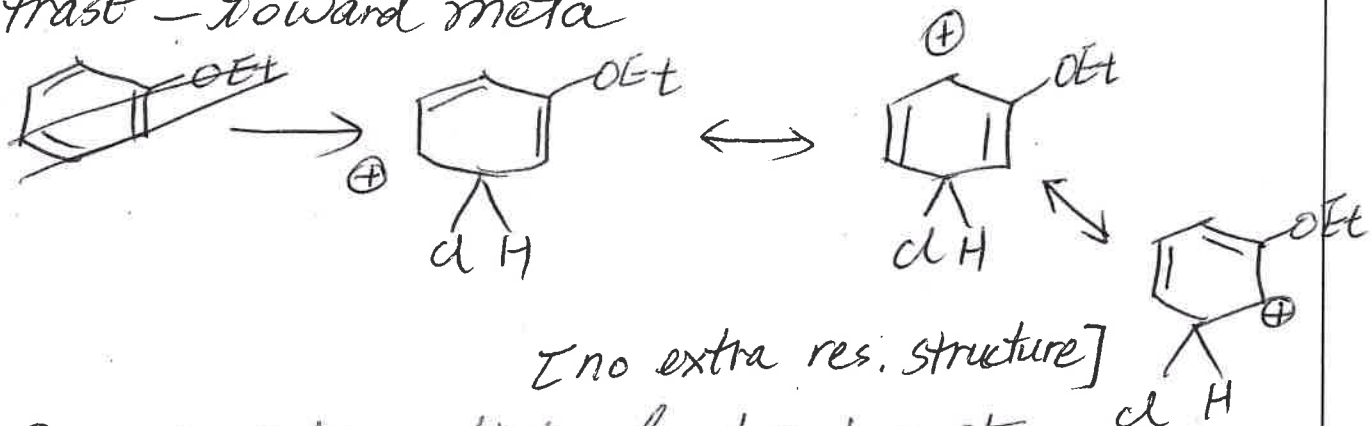
① Activating (e⁻ donating) group



You fill in the ortho Mechanism

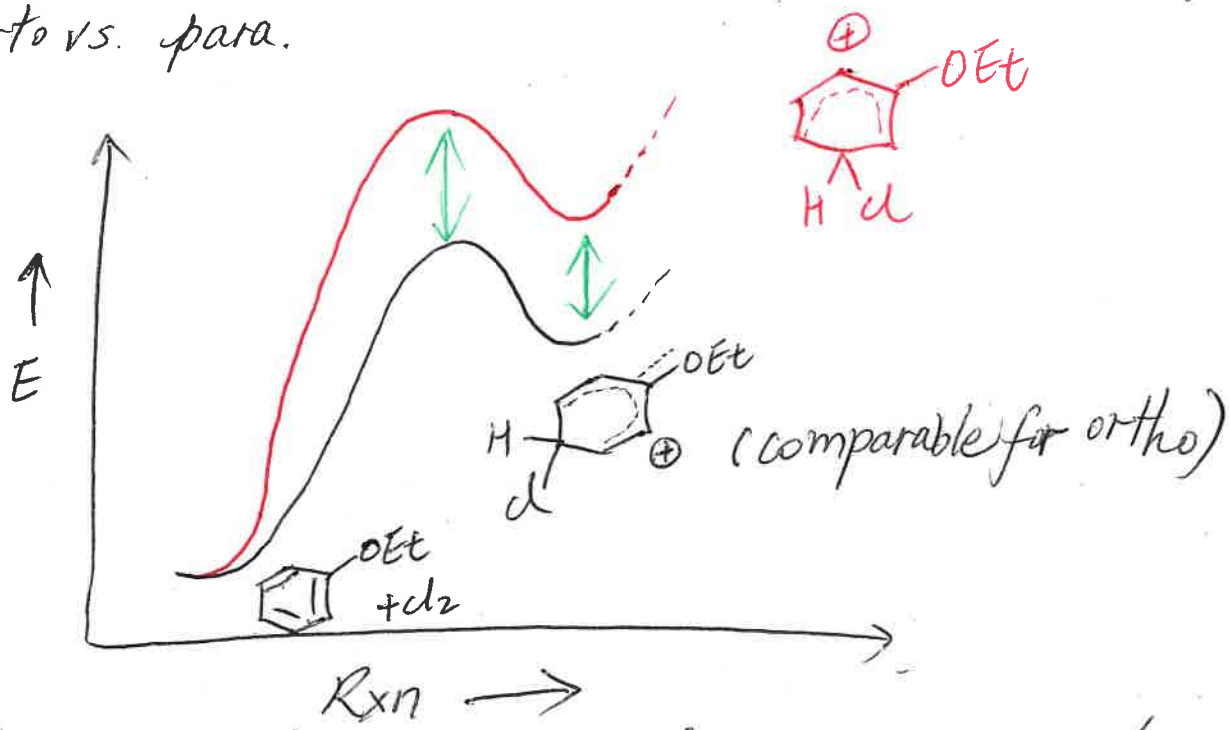
(Again, an "extra" res. structure

Contrast – toward meta



[no extra res. structure]

∴ Cationic intermediate leading to meta is much less stable than intermediates leading to ortho vs. para.



Thus, rate-determining TS leading to para (or ortho) is lower in energy than rate-determining TS leading to meta. ∴ ortho & para products are preferred.

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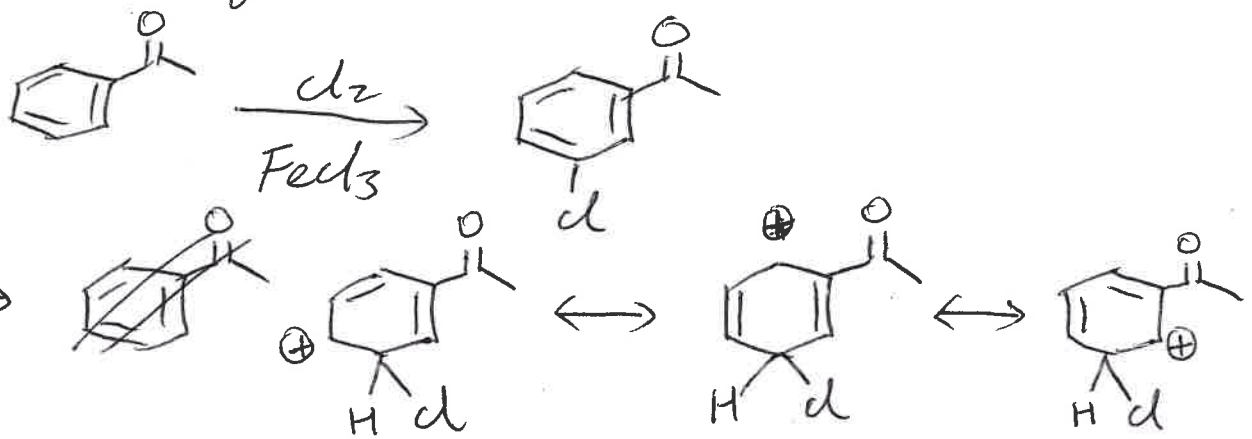
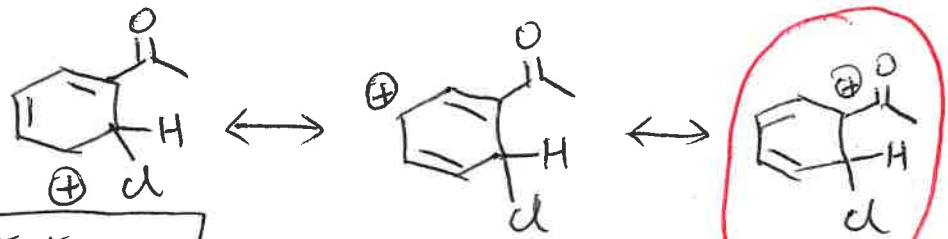
Extend reasoning to meta-directors (e⁻ withdrawing)

Ex:



vs.



you fill in para intermediate

∴ Intermediates leading to ortho or para are higher energy rel. to interm. leading to meta.

∴ meta product favored [Energy diagrams]

⊕ next to δ+ → "Bad".