

Do Not Use Pencil

Do Not Staple, Please!

Course Chem 345

Lecturer Gellman

Day Monday

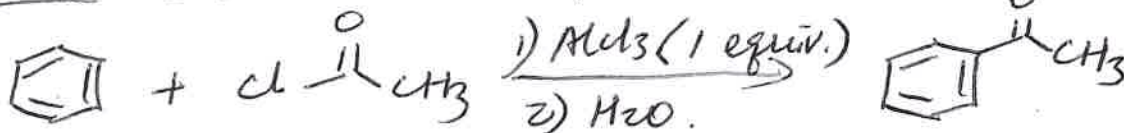
Date 2-8-16

Notes Taken by Justin

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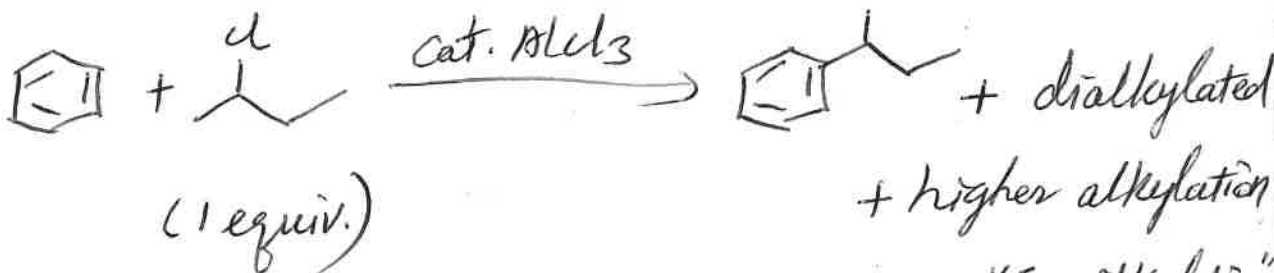
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Recall: EAS rxns, multiple versions.



"FC alkylation"

vs.



"FC Alkylation"

Why multiple rxns in last case??

Origin of this difference is found in the effect of a pre-existing substituent on the EAS-reactivity of an aromatic ring.

2 possibilities —

① "Activating" substituent: ring is more reactive than if the substituent replaced by H.

② "Deactivating" — ring is less EAS-reactive than w/ H @ that position.

Discuss mech origins via examples:



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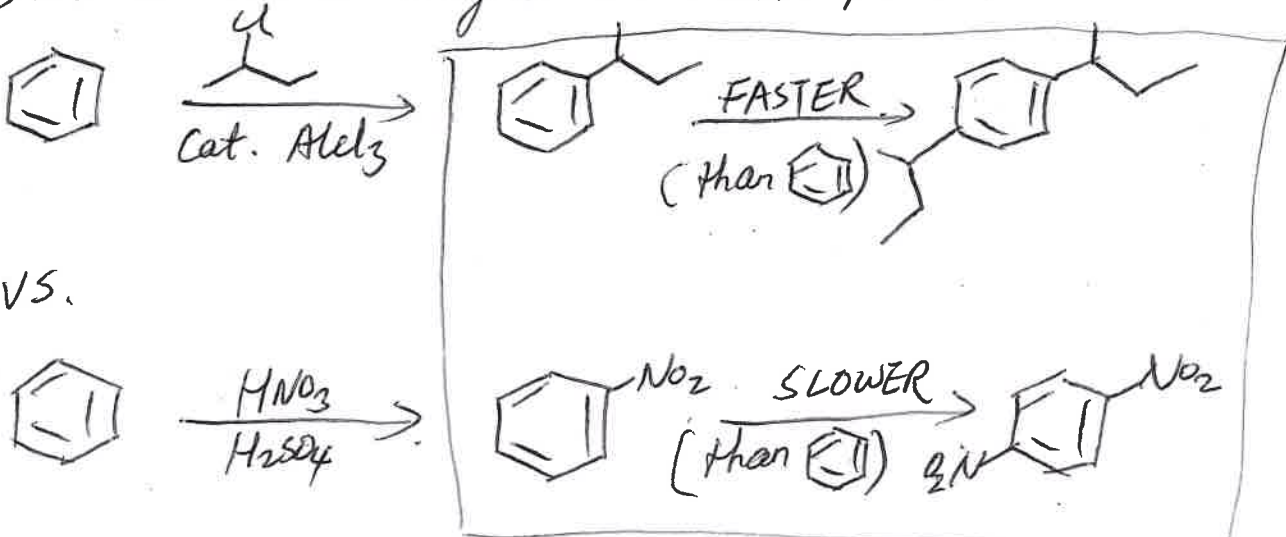
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1) Discuss mech. origins via examples:

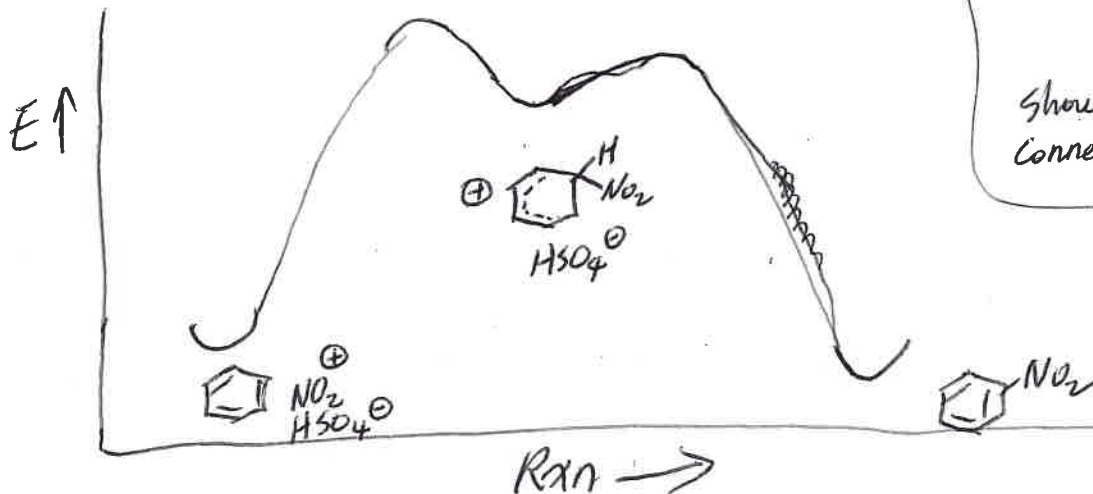


vs.

origin of this difference

Why is an alkyl group "activating" (i.e., 2nd addition faster than first) while a nitro group is "deactivating" (i.e., 2nd addition slower than first?)

Consider nitration:



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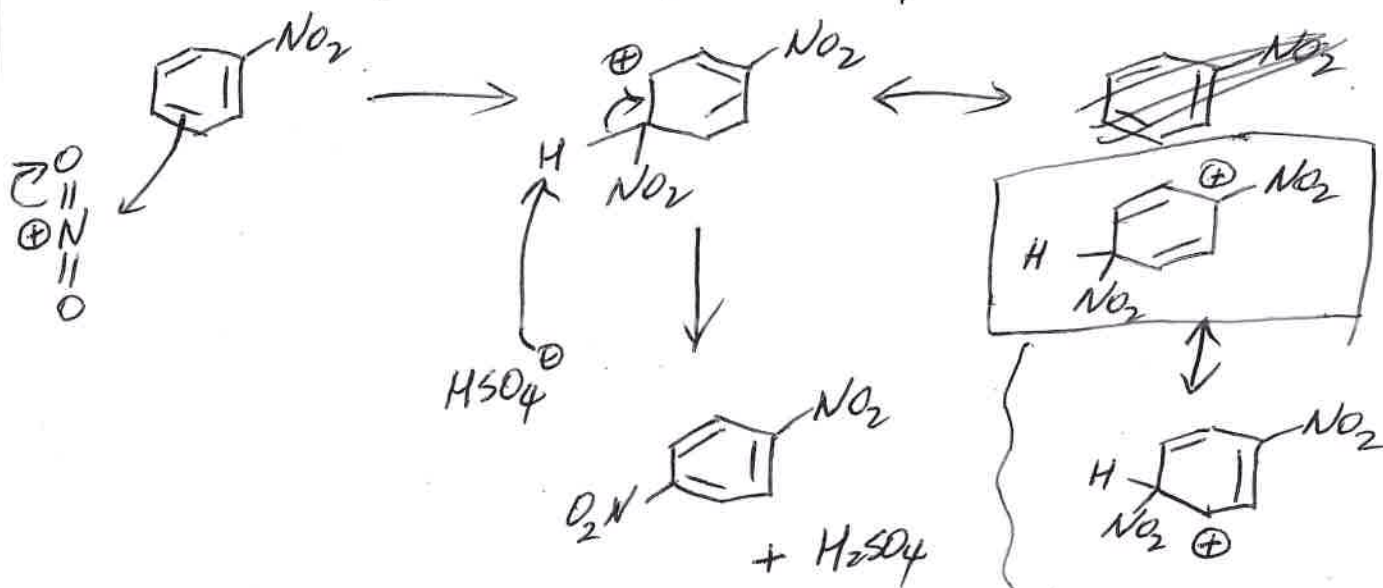
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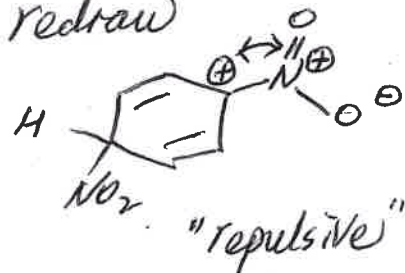
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Mech for (hypothetical) 2nd step:

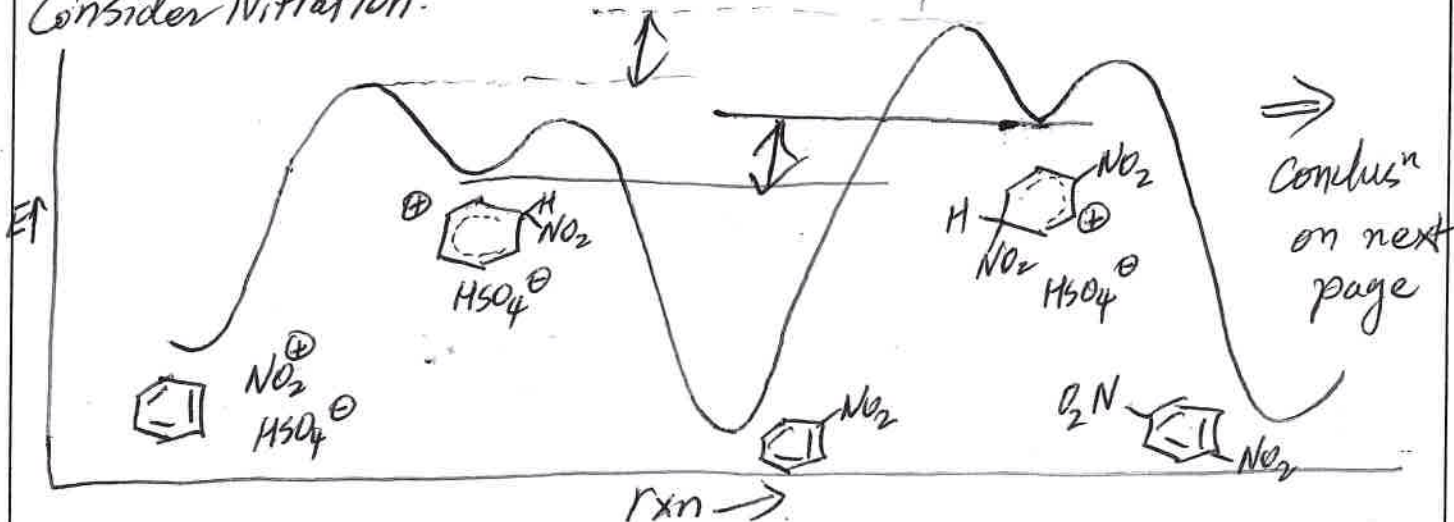


- Nitro group unfavorable for adjacent \oplus

redraw



Consider Nitration:



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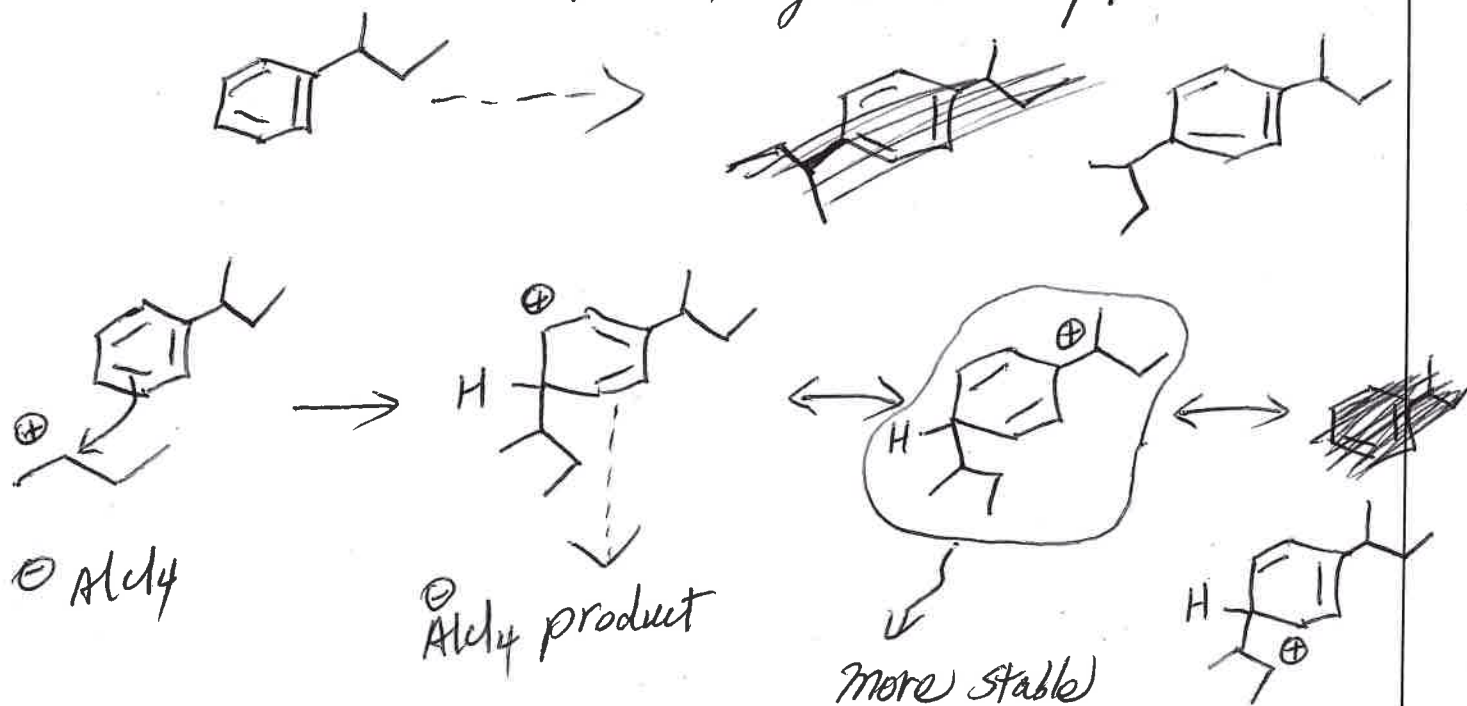
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Rate-determining TS for 2nd addition higher in energy than RDS for 1st addn. ∴ 2nd addn is

~~∴~~ Because 2nd nitration is slower than 1st, easy to stop EAS after one nitro group added. [nitro destabilizing to adjacent \oplus , rel. to H \Rightarrow nitro is deactivating.]

Now consider 2nd FC alkylation step:



more stable w/ alkyl next to \oplus rel. to H next to \oplus !

you fill in energy diagram

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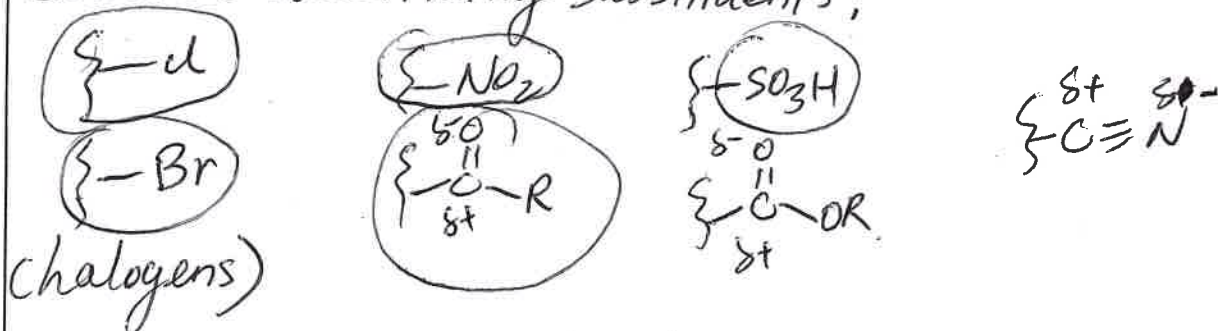
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Because 2nd alkylation occurs more rapidly than 1st, we cannot stop rxn "cleanly" after 1st addition of alkyl group. [Alkyl group = "Activating"]

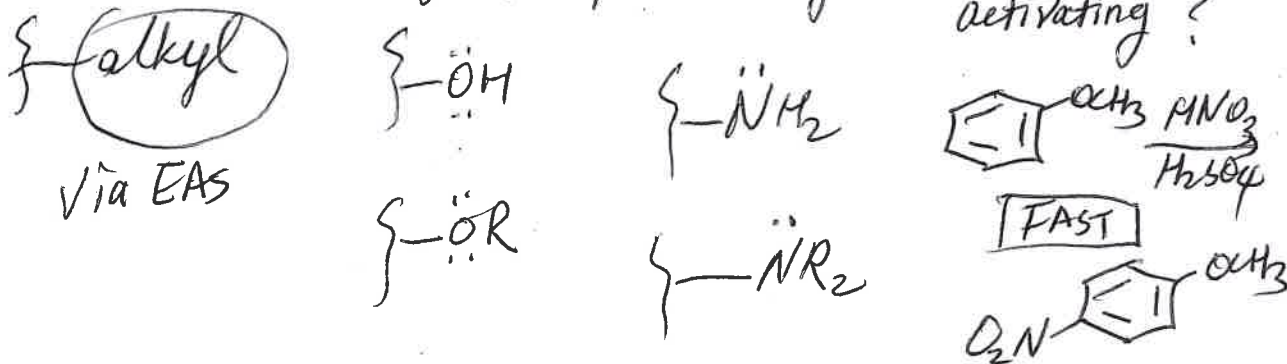
General dichotomy among groups that can be found on aromatic rings — "Activating" vs. "deactivating".

Common deactivating substituents:



"O" = can be introduced EAS.

Common activating groups: why is o/N substituent activating?



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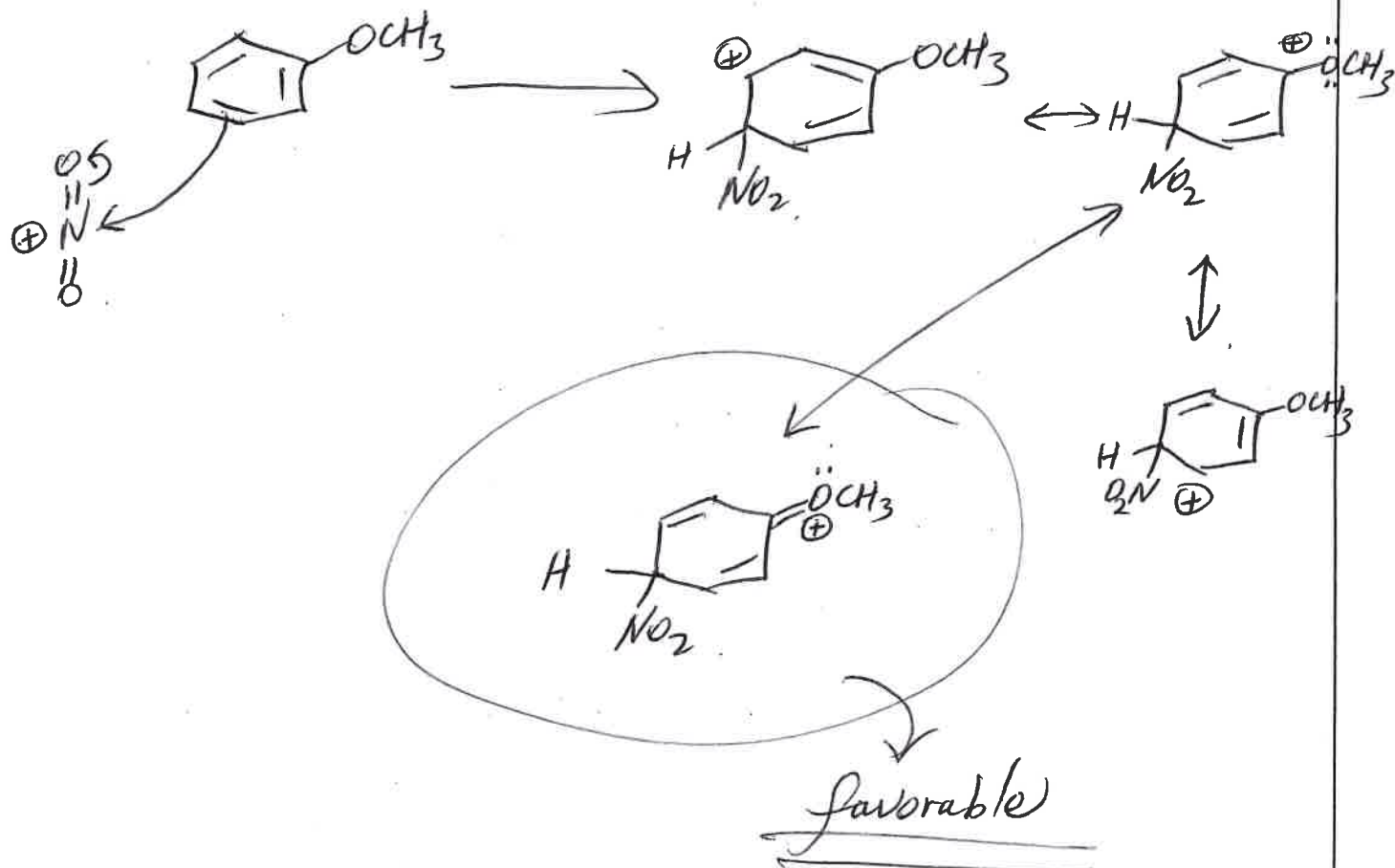
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Because of "extra" res. structure, ring w/ OCH_3 more EAS-reactive than a ring w/ H @ that position.