

Course Chem 345

Instructor Gellman

Day Monday

Date 10 Feb 2014

Notes Taken By Kaz Skubi

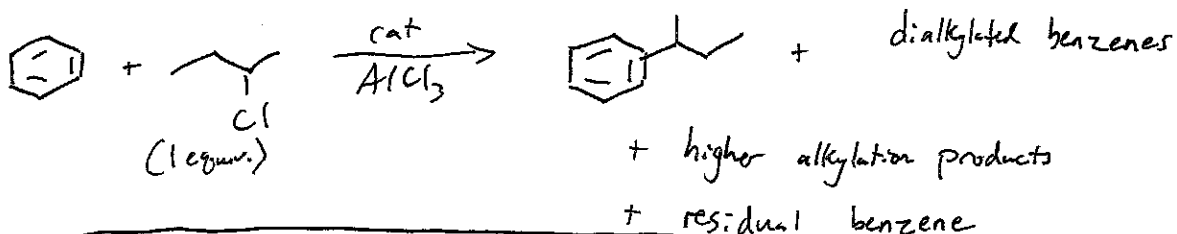
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Recall: Electrophilic Aromatic Substitution (EAS)

Several Variations (introduce different substituents)

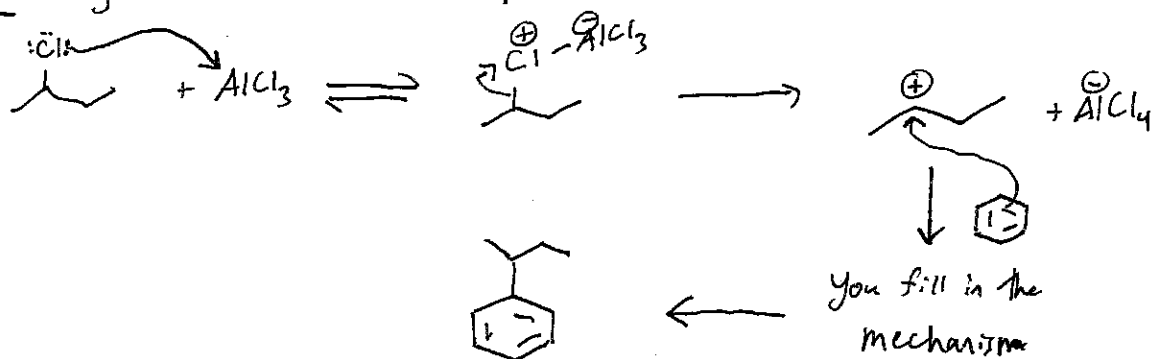
Contrast: FC Alkylation vs. others



Insight on mechanism from this contrast...

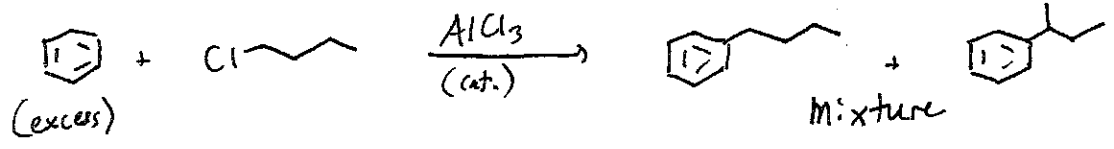
Practical Considerations: FC alkylation is often not useful synthetically. However, for benzene itself, FC alkylation can be useful if we use a large excess of benzene (relative to alkyl halide).
 → see text

Mechanism - generation of electrophile:



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Note: Carbocation rearrangements are possible. Ex:



See text; remind yourself about Carbocation rearrangements from Chem 343.

Once again, why is it impossible to stop the FC alkylation after first cycle, while other EAS reactions are easily stopped at that point?

Answer depends on a classification of aromatic ring substituents:

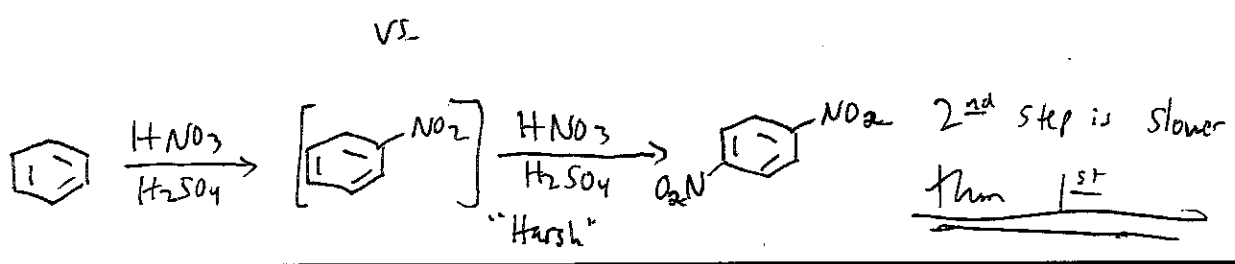
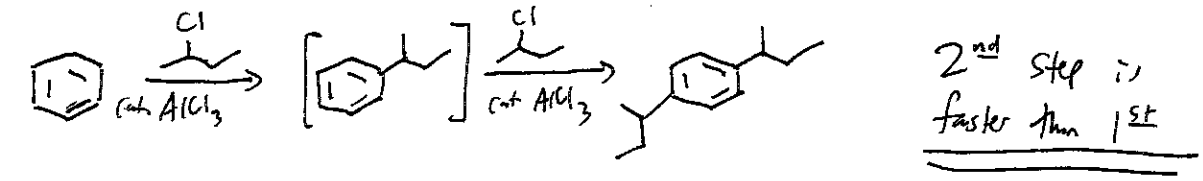
Activating vs. Deactivating (relative to benzene/H substituent)

Activating: Ring is more prone to EAS (relative to H at that position)

Deactivating: Ring is less prone " " " " " " " " " "

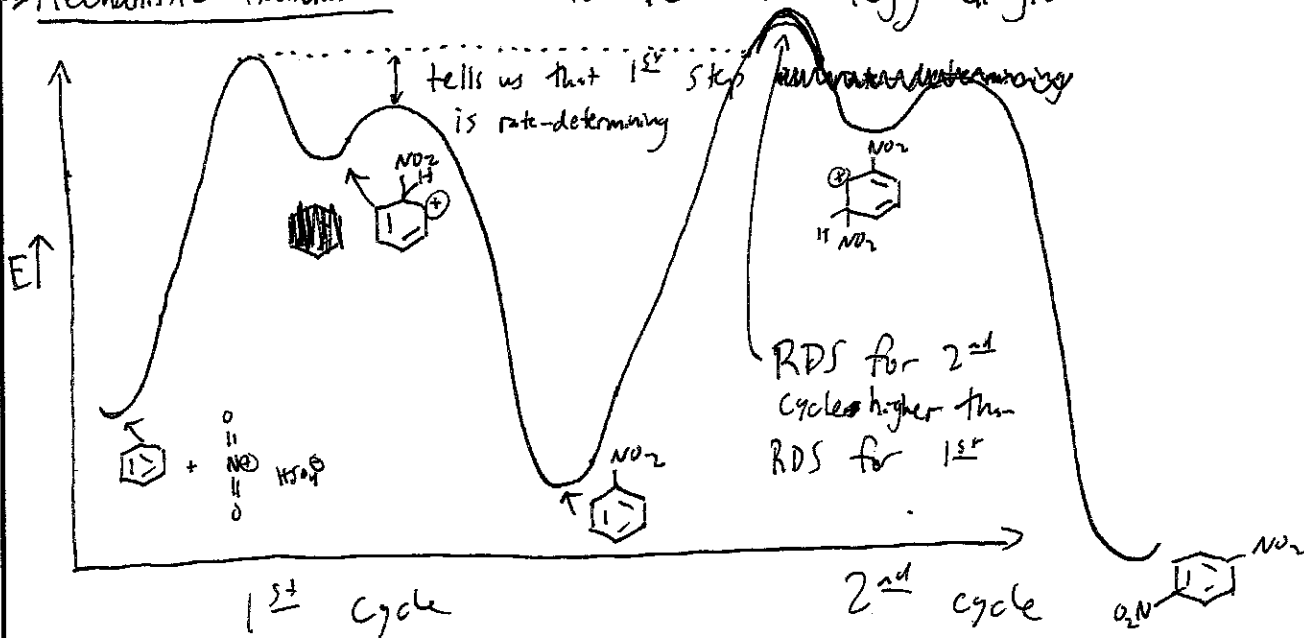
Bottom Line — Alkyl groups are activating, while ~~other~~ other substituents introduced via EAS are deactivating.

Illustration 1: Double alkylation vs. double nitration (para only)

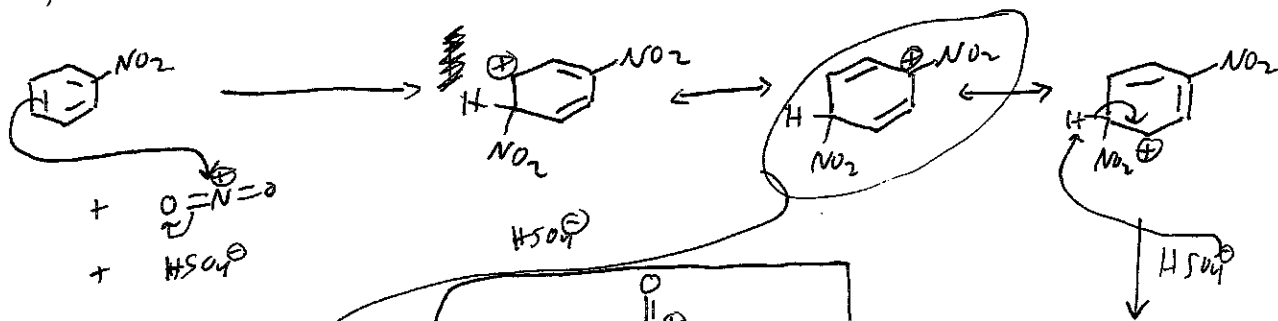


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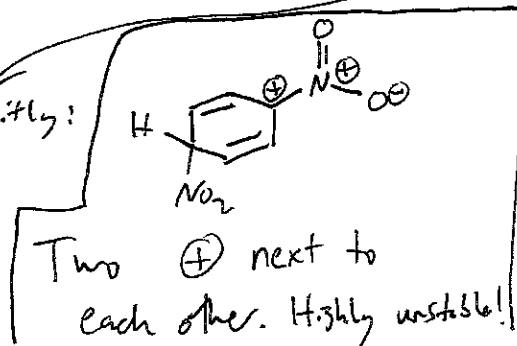
Alkyl substituent is ~~de~~ activating, while nitro substituent is deactivating.
 → Mechanistic Rationale - turn to reaction energy diagram



Why is RDS for 2nd cycle than for 1st?

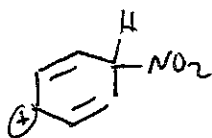


Redraw this explicitly!



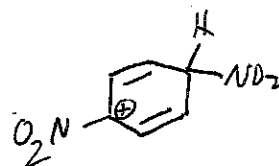
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More explicitly, the comparison is between:



1st cycle
intermediate

vs.



2nd cycle
intermediate (less stable)

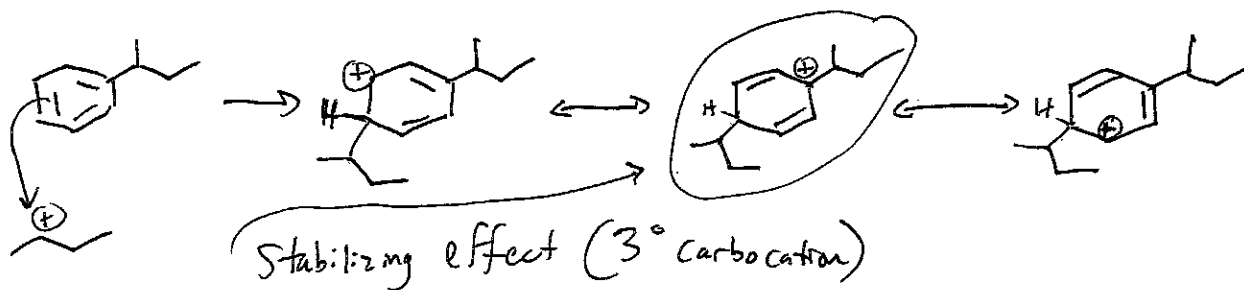
Higher-energy transition state (Hammett Postulate)

The nitro group is "e⁻-withdrawing" and thus its presence makes an aromatic ring less prone to EAS, relative to just an H at that position.

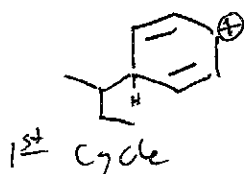
∴ Nitro group is "deactivating"

Comparable arguments allow us to understand that an alkyl substituent stabilizes the EAS intermediate.

Thus, (2nd cycle) ∴

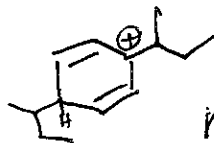


Comparison:



1st cycle

vs.



2nd cycle

more stable

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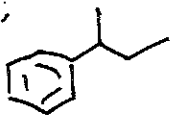
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So,



is more reactive than benzene in an EAS reaction. So as soon as you generate any, it reacts faster than benzene and you get over-alkylation, rather than stopping cleanly at one addition.

Note: All EAS rxns other than FC alkylation place deactivating groups on the ring, so all can be stopped after one ~~addition~~ addition.