

Course 345

Instructor Gellman

Day Wed

Date 4/23/2014

Notes Taken By Adams

Total # of Pages

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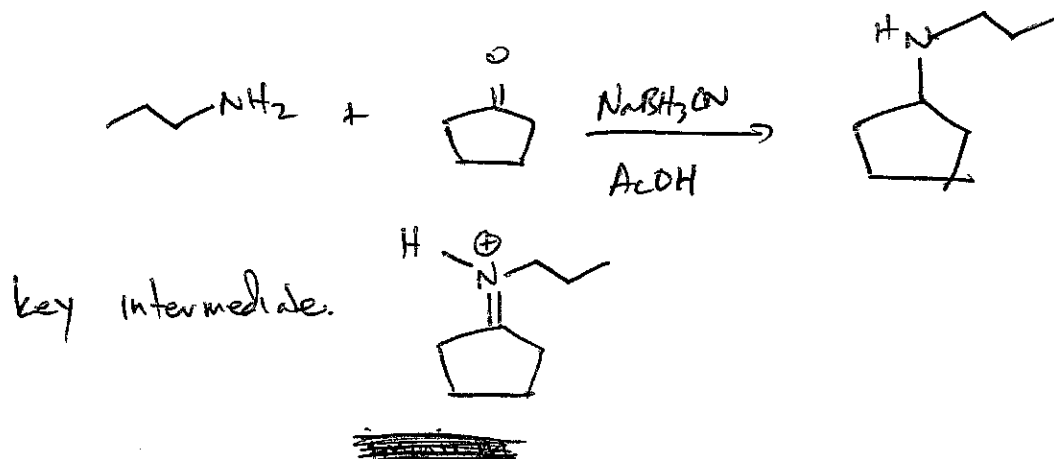
Exam 3: Wed 30 Apr (covers through Ch 23)
↑ amines

Extra office hours: Thurs 5 pm
Next Mon after class

Review: Tues, 5 pm, B371

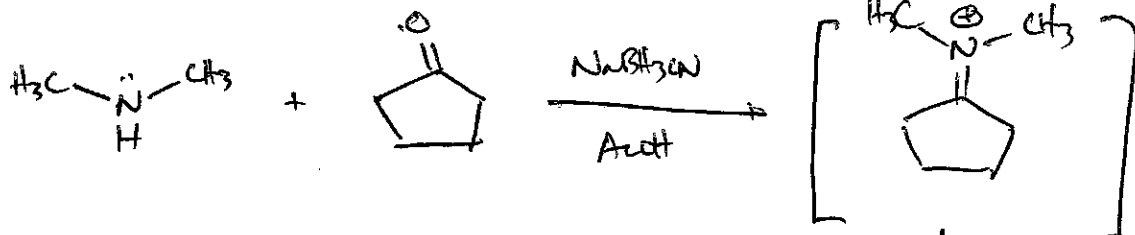
Recall: Nucleophilic reactivity of amines

- 1) S_N2 rxns/alkylation (control problems)
- 2) reductive alkylation, e.g. ↓

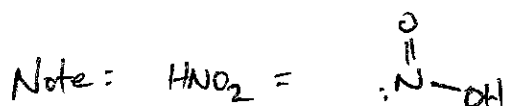
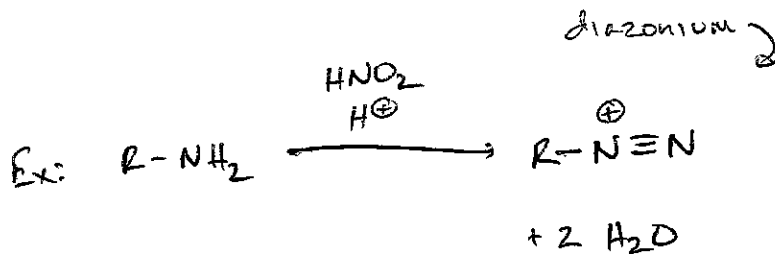


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• Start w/ 2° amine, produce tertiary amine.



3) formation and reactions of diazonium ion.



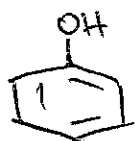
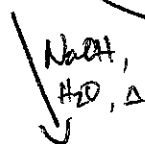
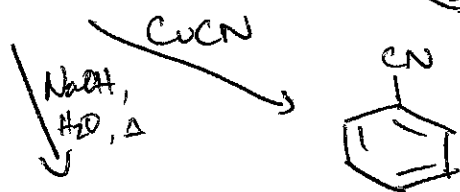
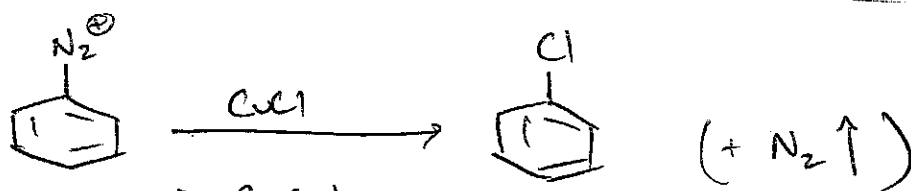
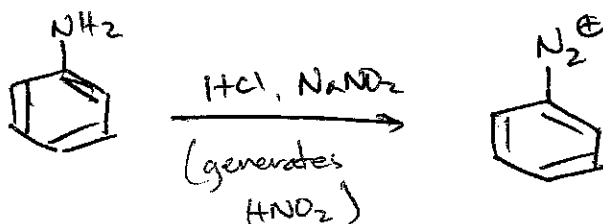
~~mechanism~~ mechanism based on R-NH₂ attacking N in similar fashion to carbonyl

Note: $\text{:N}\equiv\text{N:} = \text{N}_2$ superb ~~leaving~~ leaving group!!

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Aryl diazonium ions: (R = aromatic ring)

Formed from anilines:



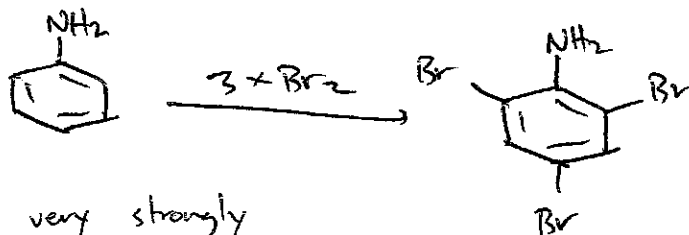
can't synthesize
via E.A.S.

• Can replace N₂⁺ with H

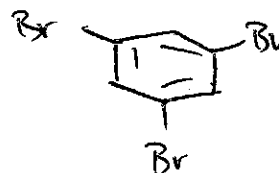
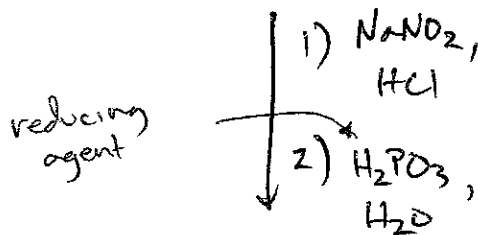
- this can be useful for controlling aromatic
ring substitution partners

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Example of utility:



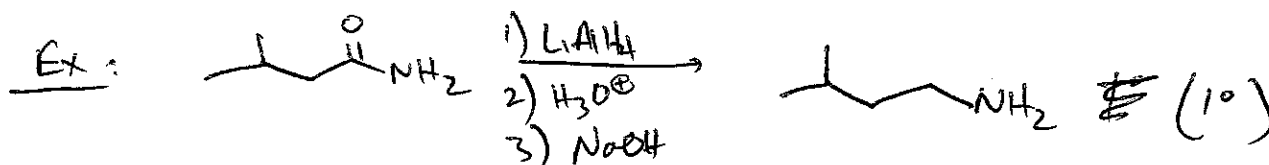
Recall: NH_2 is very strongly activating for EAS



Synthesis of amines

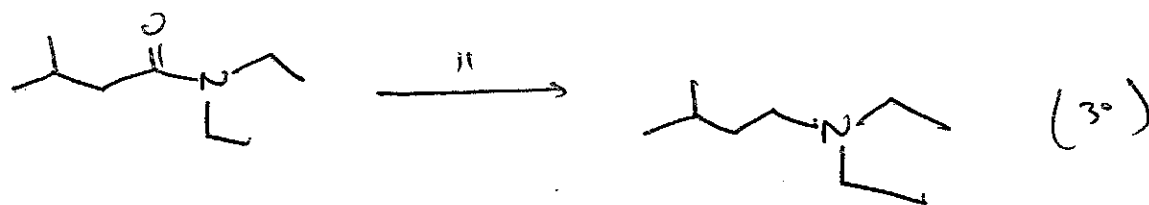
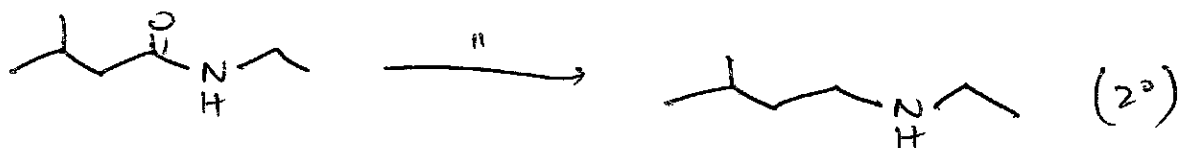
- 1) Reductive amination
- 2) Reduction of amides (Ch 21)

versatile for $1^\circ, 2^\circ, 3^\circ$ amines

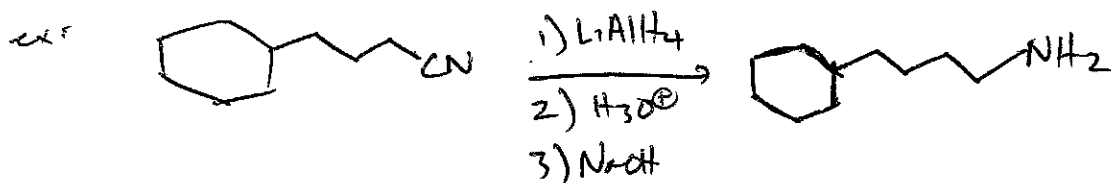


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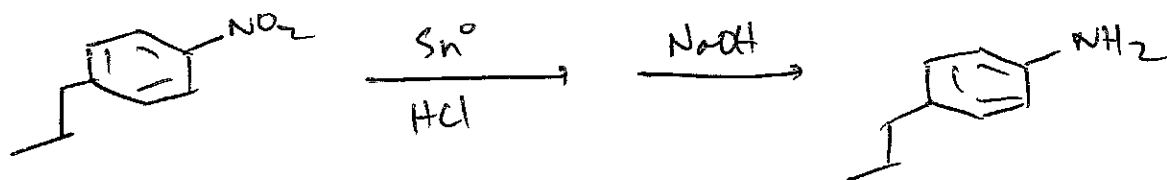
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3) Reduction of nitriles

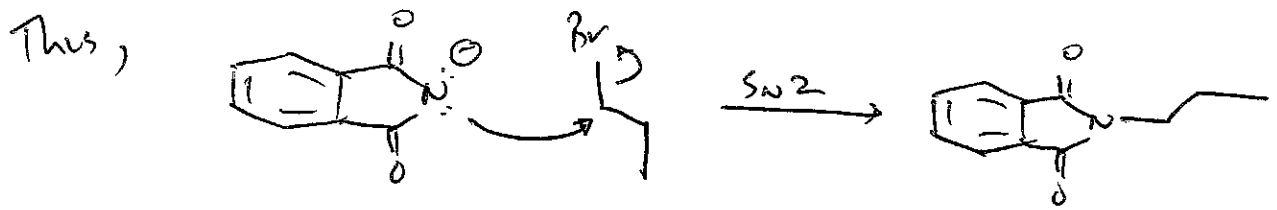
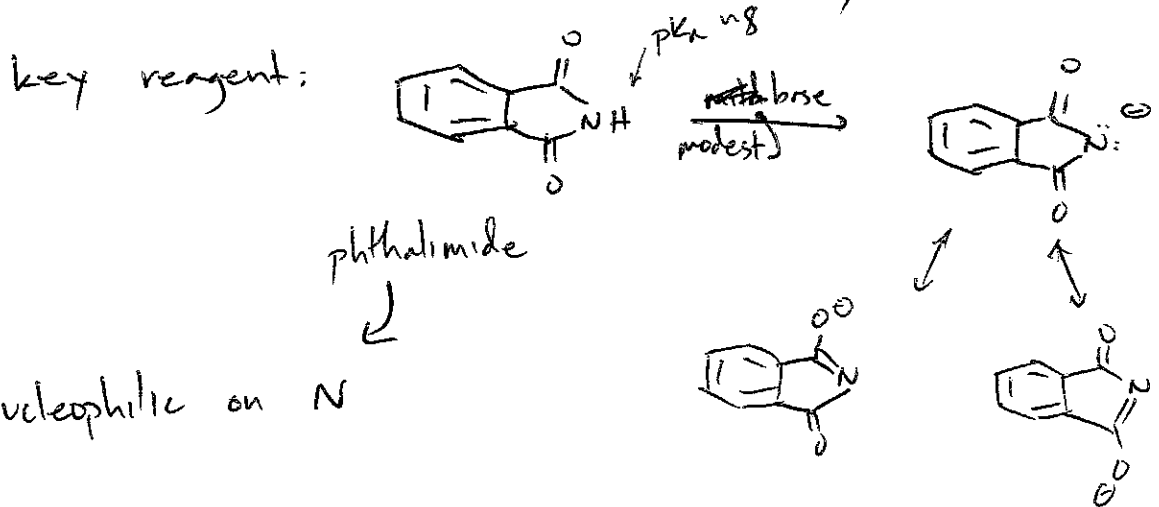


4) Reduction of aryl nitro groups (to make anilines)

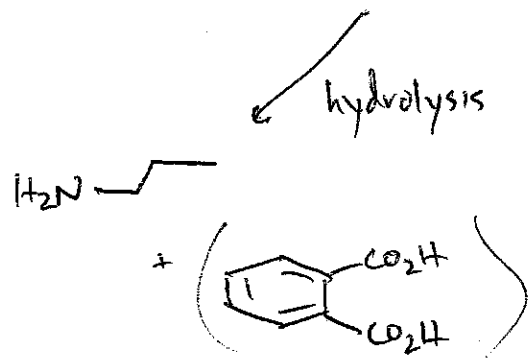


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5) Gabriel synthesis - 1° amines only

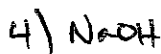
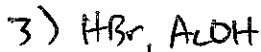
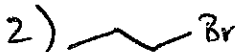
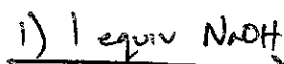
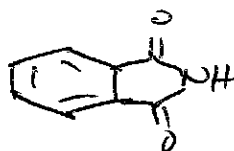


only 1 alkyl group can be added

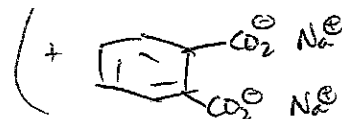


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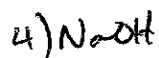
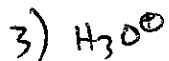
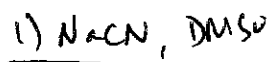
Overall:



(3 C's)



Note: complementarity to "nitrile process"



(4 C's)

Hofmann Rearrangement

