

Course 345Instructor GellmanDay WedDate 4/23/2014Notes Taken By AdamsTotal # of Pages 7

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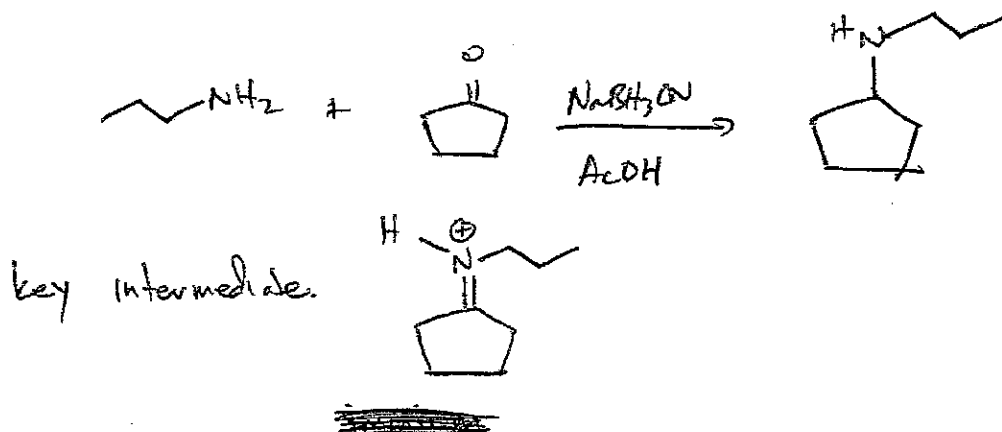
Exam 3: Wed 30 Apr (covers through Ch 23)
↑ amines

Extra office hours: Thurs 5 pm
Next Mon after class

Review: Tues, 5 pm, B371

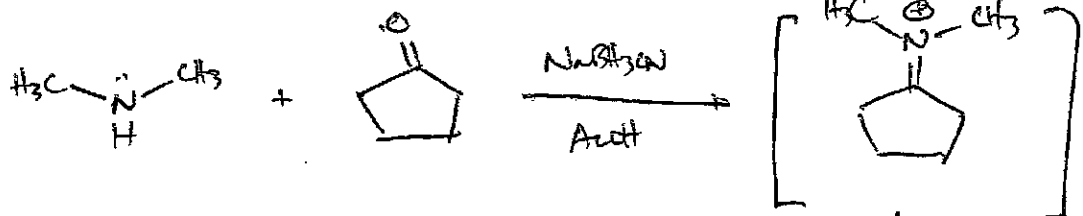
Recall: Nucleophilic reactivity of amines

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

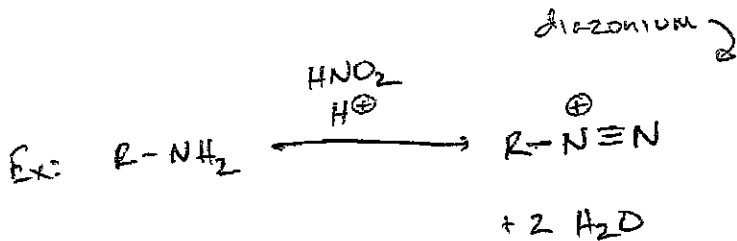


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• Start w/ 2° amine, produce tertiary amine.



3) Formation and reactions of diazonium ion.



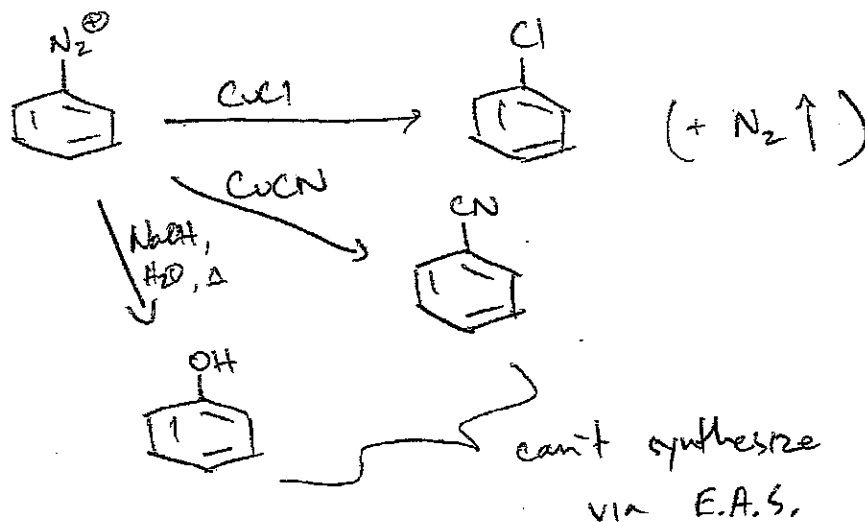
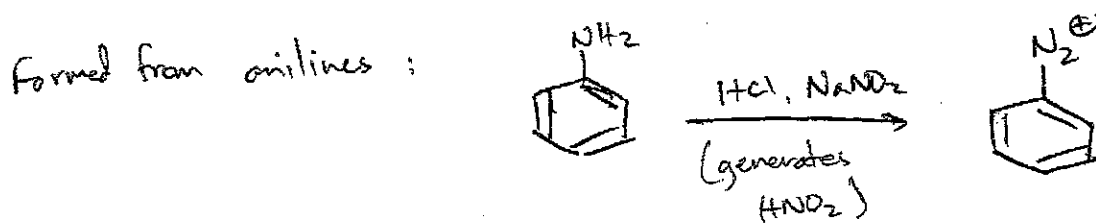
Note: $\text{HNO}_2 = \text{:}\overset{\text{O}}{\parallel}\text{N}-\text{OH}$ ~~mechanism~~ mechanism based on R-NH₂ attacking N in similar fashion to carbonyl

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

Course 345 Instructor Gellman
Day _____ Date _____
Notes Taken By _____ Total # of Pages _____

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Aryl diazonium ions: ($R = \text{aromatic ring}$)

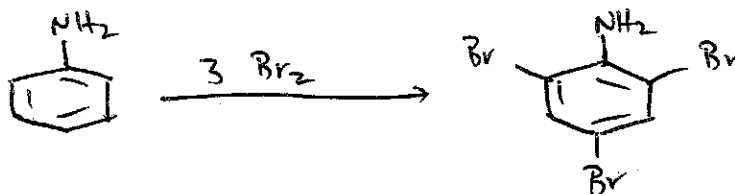


- Can replace N_2^{\oplus} with H

- this can be useful for controlling aromatic ring substitution partners

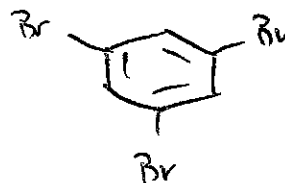
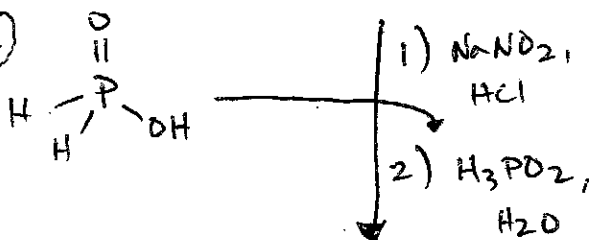
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Example of utility:



Strong
reducing agent!

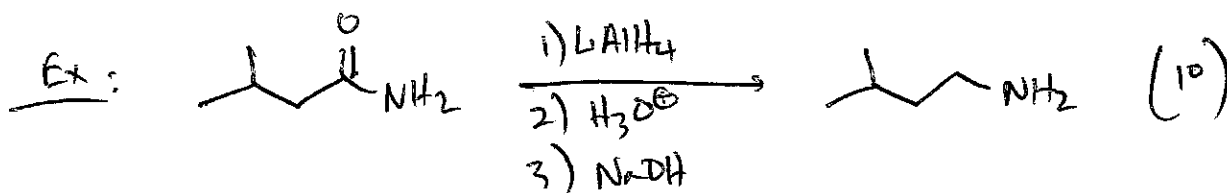
Hypophosphorous
acid



Synthesis of amines

- 1) Reductive amination
- 2) Amide reduction

versatile for 1°, 2°, 3° amines



Course 345

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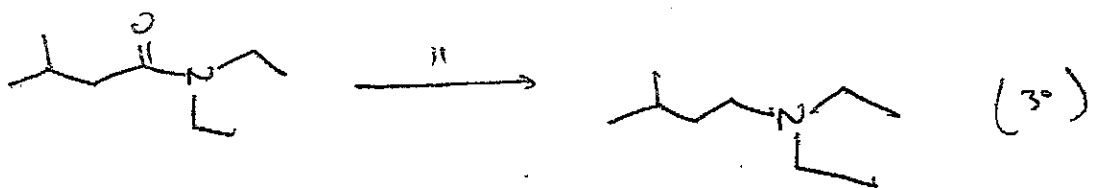
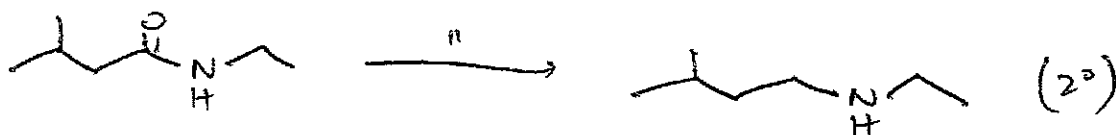
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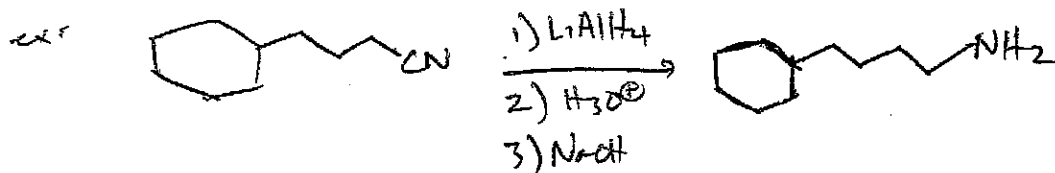
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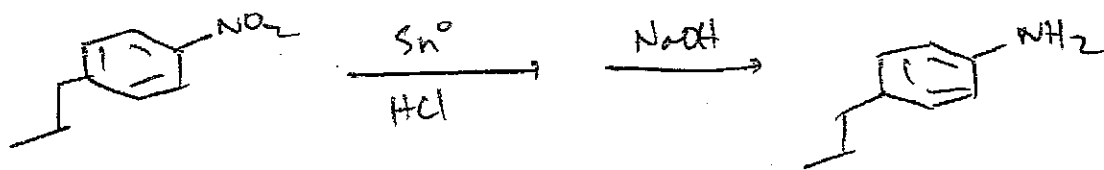
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3) Reduction of nitriles

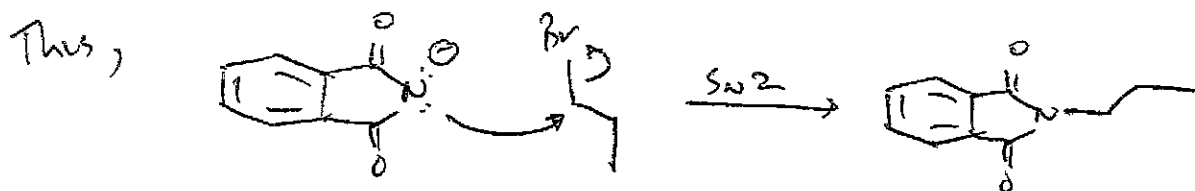
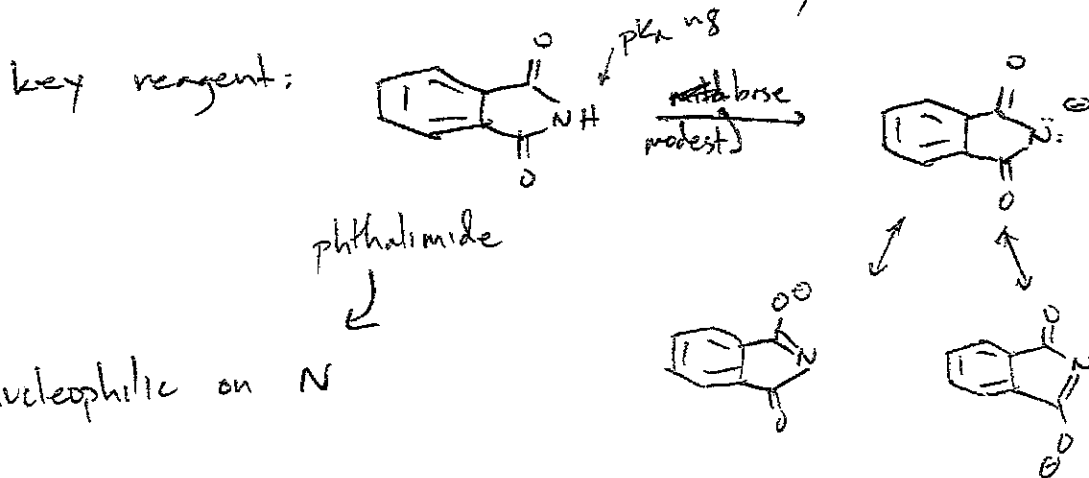


4) Reduction of aryl nitro groups (to make anilines)

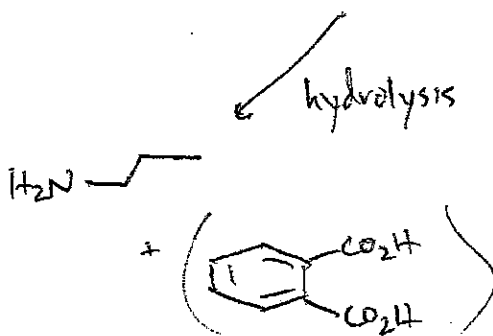


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5) Gabriel synthesis - 1° amines only

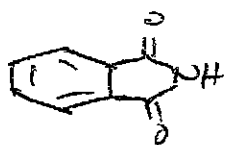


only 1 alkyl group can be added



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Overall:

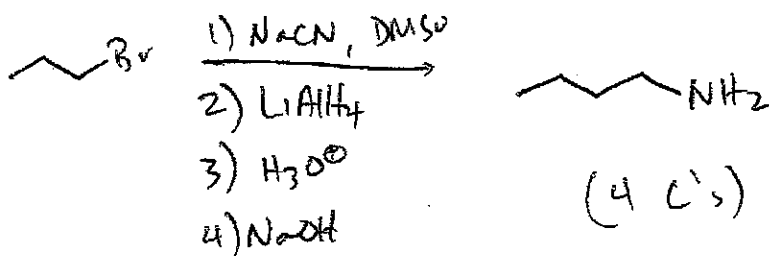


- 1) 1 equiv NaOH
- 2) Br
- 3) HBr, AcOH
- 4) NaOH

(3 C's)



Note: complementarity to "nitrile process"



Hofmann Rearrangement

