Course Chem 345	Instructor Gellman
Day Monday	Date 21 April 2014
Notes Taken By Kaz Skubi	Total # of Pages 4

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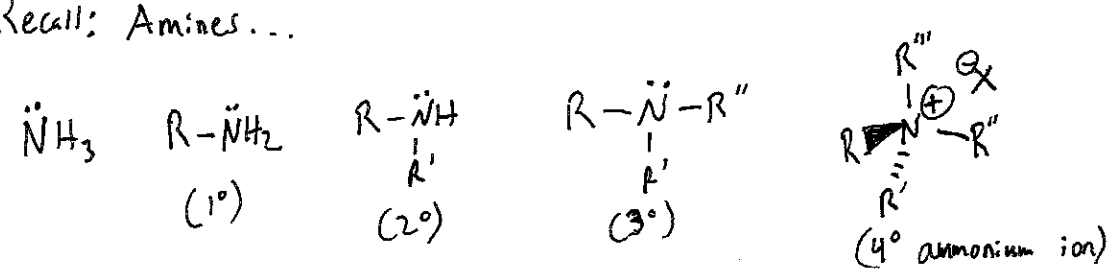
PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

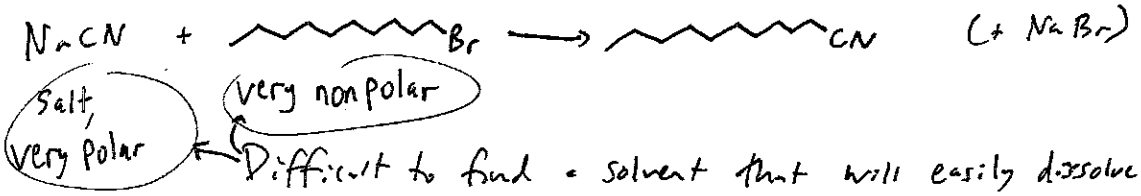
Recall: Amines...



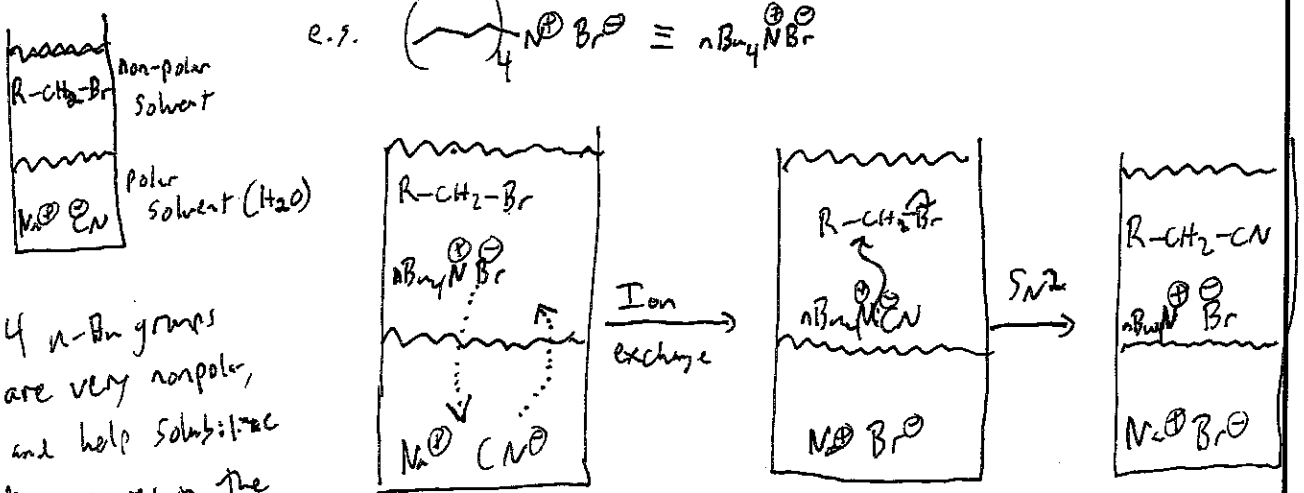
Utility of 4° ammonium ions

→ Phase-Transfer catalysis

Consider: Desired reaction (S_N2) between two molecules of different polarity:



Instead, use 2 solvents and a phase-transfer catalyst (e.g. 4° ammonium ion)



4 n-Bu groups are very nonpolar, and help solubilize this species in the non-polar layer

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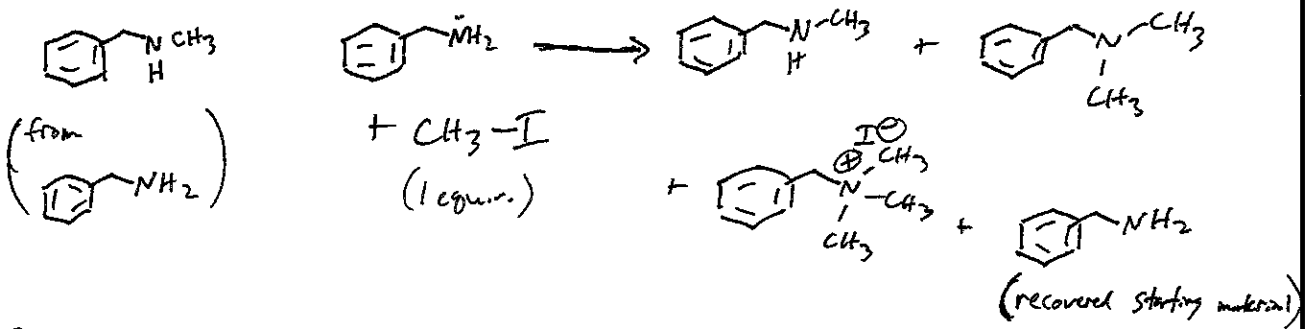
Nucleophilic Reactivity of Amines

1) S_N2 reactivity w/ alkyl halides

→ NH_3, 1°, 2°, and 3° amines are all good nucleophiles. That creates a problem → we often have difficulty controlling the reactivity of NH_3, 1°, or 2° amines with alkyl halides.

Target: Observed:

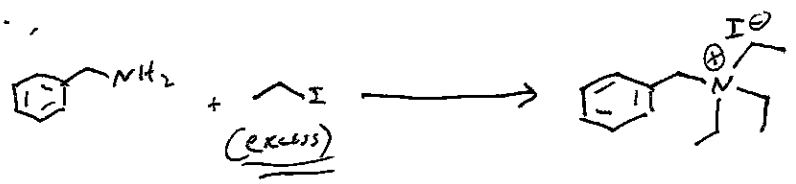


The problem is that our products (except 4° ammonium ion) are also nucleophiles, so they can react with the CH_3–I as well.

Mixture of products

∴ Alkylation (S_N2) is synthetically useful only for 4° ammonium ions.

e.g.,



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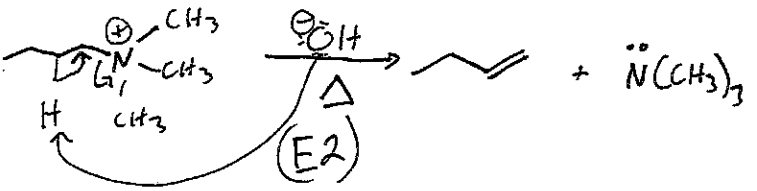
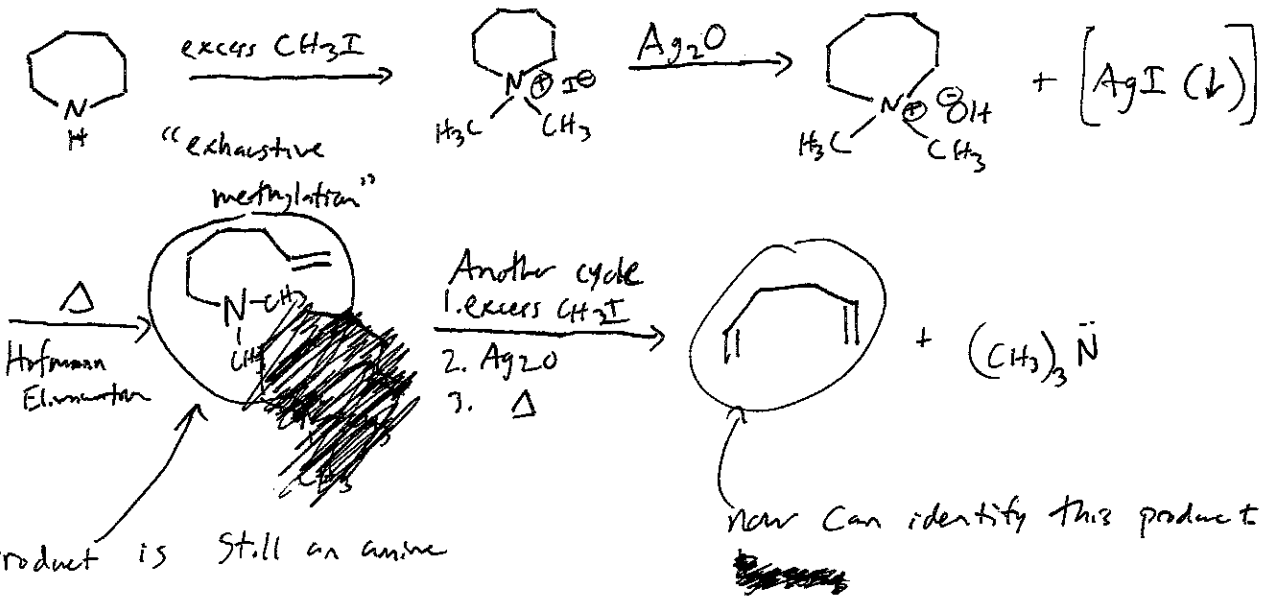
Historical value of 4° ammonium ions → structure elucidation via controlled degredation.

Hoffmann Elimination

4° ammonium hydroxide, ex:



Ex. of application



Note: must be CH_3I, not ~~anything~~ EtI ~~or~~ PrI, etc.

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2) Reductive Amination

- Amine + aldehyde/ketone → imine, then reduce imine to amine.
- Good for 2° amine → 3° amine or 1° amine → 2° amine

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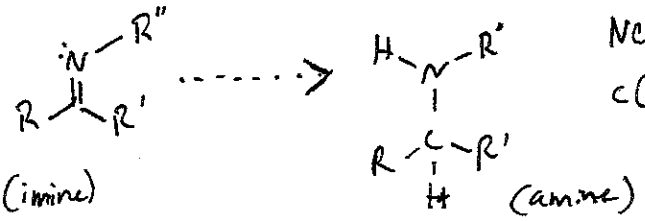
Recall: Imine

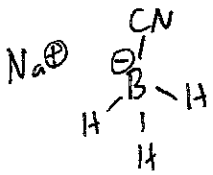


(imine) (amine)

Net reduction

C(+2) → C(+1)

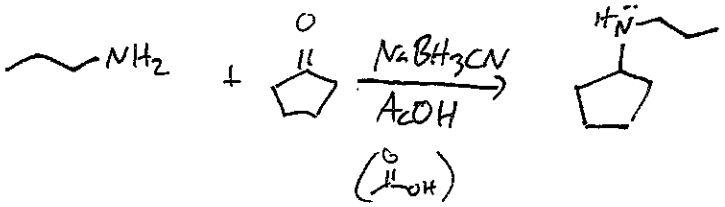
we use $NaBH_3CN$ (Sodium cyanoborohydride)



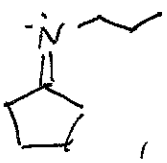
Not $NaBH_4$ or $LiAlH_4$ .... why?

Everything occurs in one reaction vessel ("one-pot reaction")

Ex:



Intermediate:



reduced by $NaBH_3CN$.

$LiAlH_4$ is too reactive. Will deprotonate AcOH (and catch on fire)

$NaBH_4$ will reduce the ketone before the imine can form.