Course Chem 345 Lecturer Gellman

Day 4-18-16, 2 Date Monday

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Chap. 23 Problems — 5-8, 12-26, 29, 30, 35, 36, 42 (not c), 44, 46 (not j), 47, 50, 52, 55, 56 (not f), 57-59, 63-66, 68, 70-73, 75-78, 80.

#77 - Richard Willstätter (Nobel Prize 1915) See article under "in the news" on Website.

Recall: Acid base properties of amines...

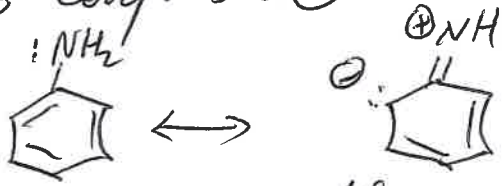
Effects of e⁻ delocalization:

pKa ~5

vs.

pKa ~10

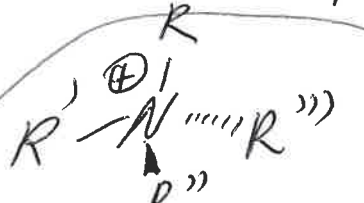
Rationale: Loss of resonance in conj. acid, relative to conj. base —



↔ ↔ etc. Lost on protonation.

Substituent effects on anilinium pKa values... see txt.

4° ammonium ions —



See text → Can be chiral → phase transfer catalysis

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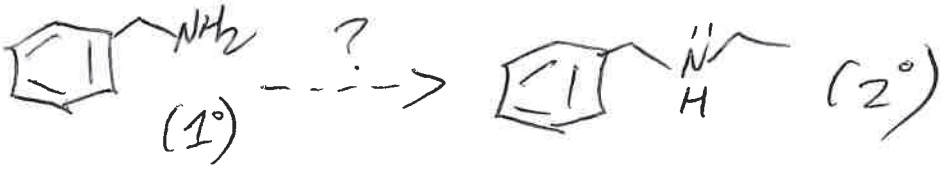
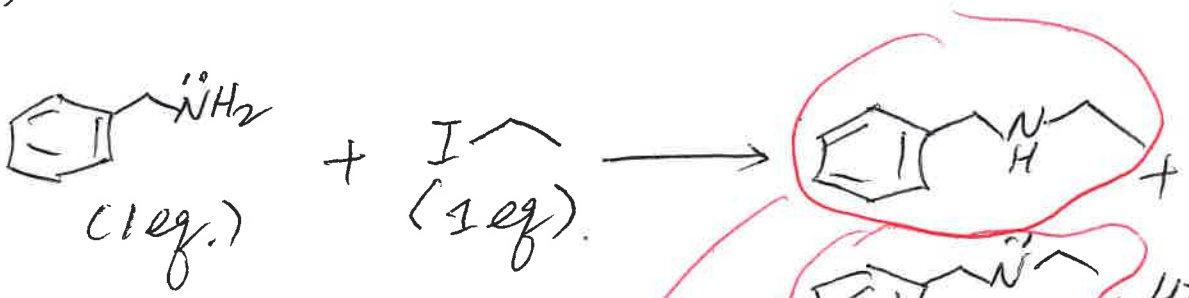
Nucleophilic reactivity of amines

1) SN2 rxns, w/ alkylhalides, tosylates, etc.

However, it can be difficult to control this reactivity, unless one seeks ~~the~~ a 4° ammonium ion.

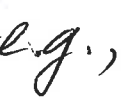


Observe:

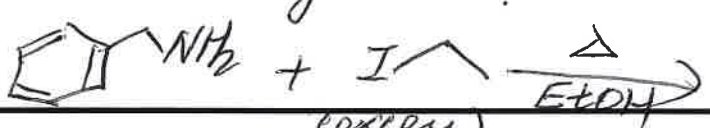


Good nucleophiles too.

(+  ↔ unreacted S.M.)

Note: Similar problems w/ other electrophiles, e.g.,  ,  , 

SN2 approach is useful for "quaternization of a amine", esp. "exhaustive methylation".

Ex: 

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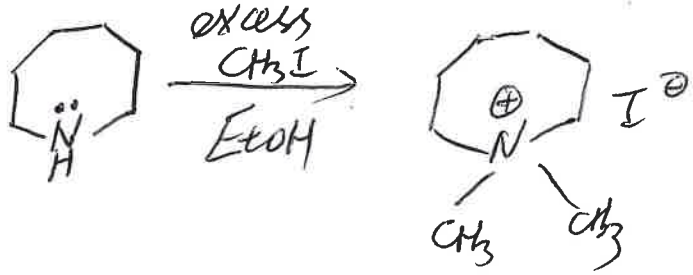
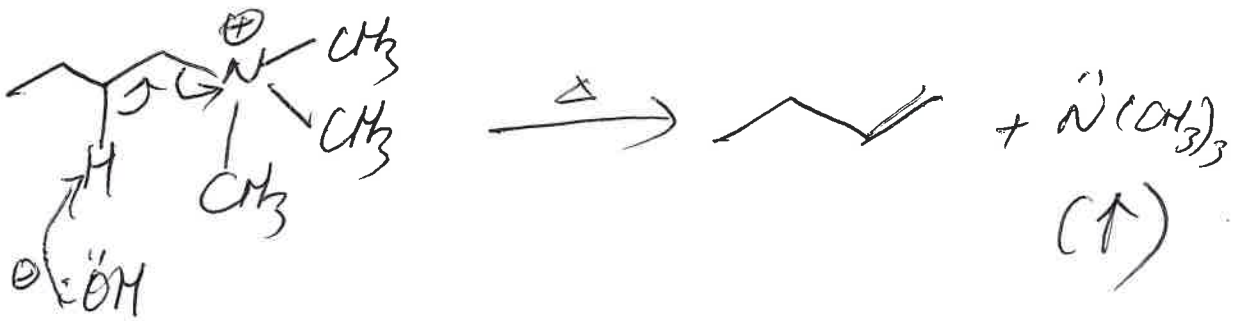
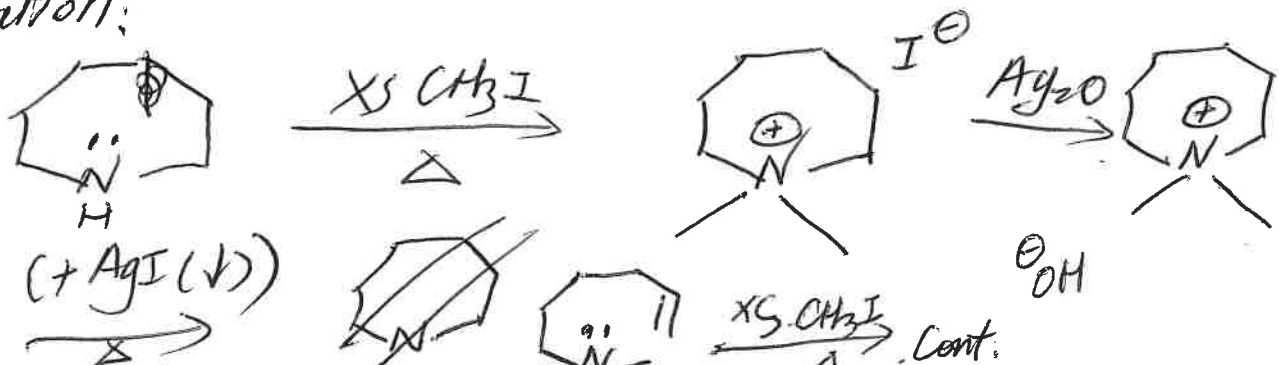


Control degradation via elimination rxn(s) of a ~~ammonium~~ ions, generated via "exhaustive ~~Ex~~ methylation"!

Elimination = E2



Structure elucidation of amin compounds via controlled degradation:



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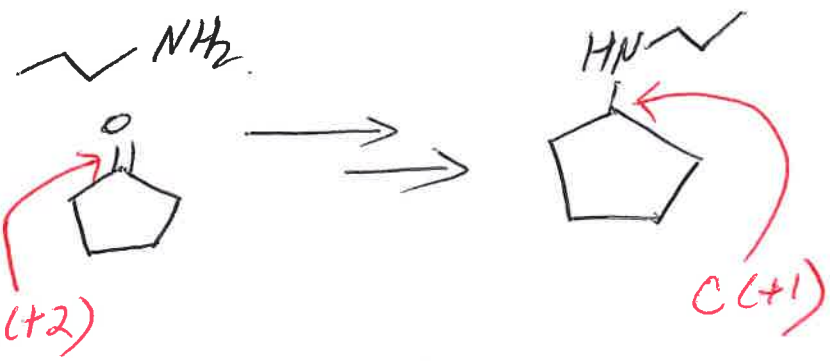
How form C-N bonds to amine nitrogens w/ greater control than provided by SN2 rxns?

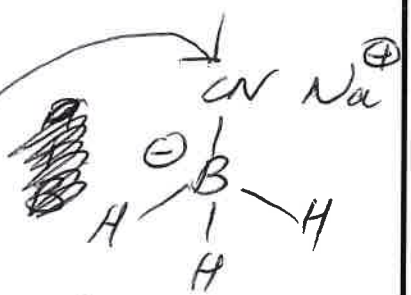
→ Reductive amination

General: amine + aldehyde / ketone to form an imine, then reduce imine to amine.

Ex:



Key reagent — $NaBH_3CN$ ≡



allows a "one-pot" rxn.

e⁻-withdrawing ∴ diminished reactivity relative to $NaBH_4$

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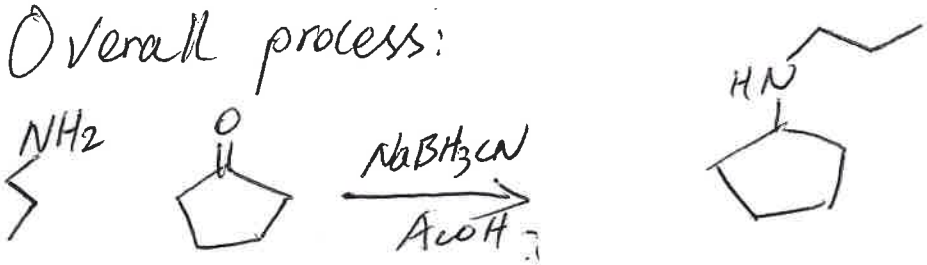
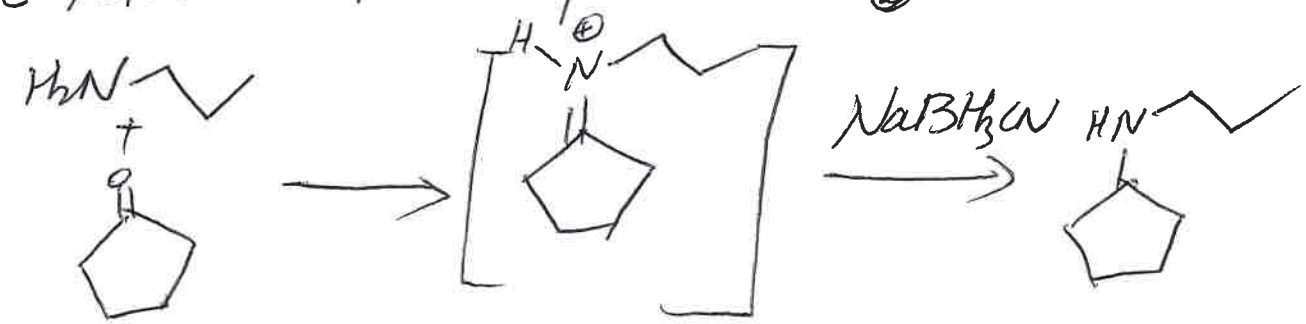
Overall process:



(imine)

Imine intermediate is protonated.

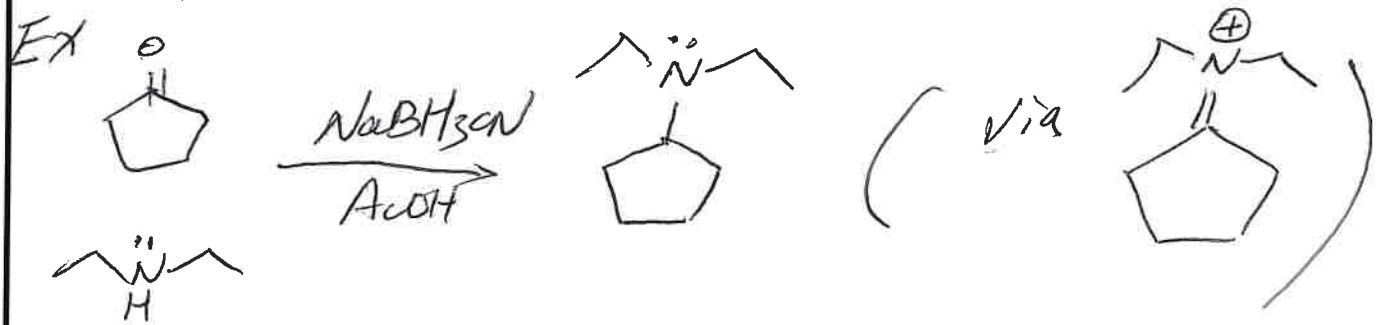


("iminium")

Note: 1° amine → 2° amine ~~also possi~~

Also possible: 2° amine → 3° amine

Ex



Another pattern of amine reactivity — Conversion of $-NH_2$ group to a leaving group $-\overset{\oplus}{N}\equiv N:$ ("diazonium"

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Overall:

See text for rxns of alkyl diazonium ions
→ form carbocations.

Very useful – aromatic diazonium ions...