

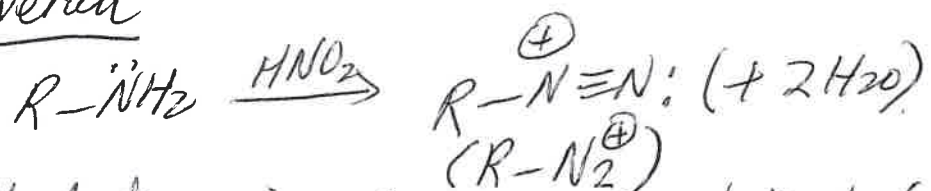
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Office hour & review today.
 Office hour next Monday after class
 Review next Tues 5:00 pm B371
 Exam #3 next Wed (27 Apr) chaps. 20-23
 (same locations)

Recall: Rxns of amines...

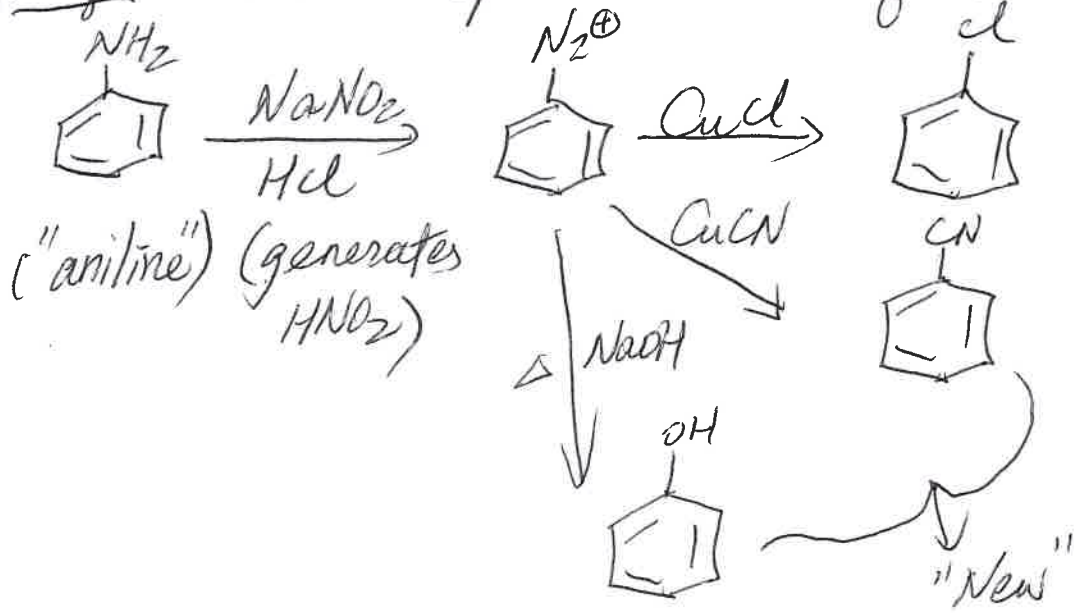
3) Formation of diazonium ions (electrophilic)

Overall

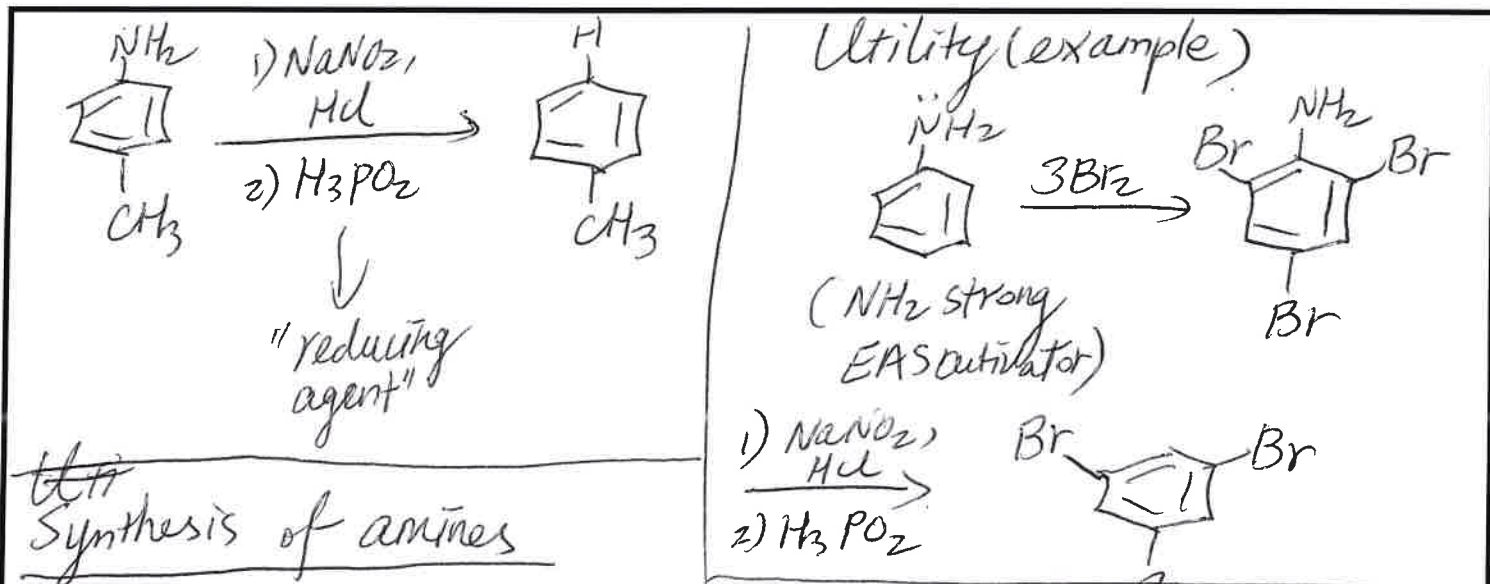


Alkyl diazonium species — see text (S_N1/E1; S_N2)

Aryl diazonium species have unique & useful reactivity



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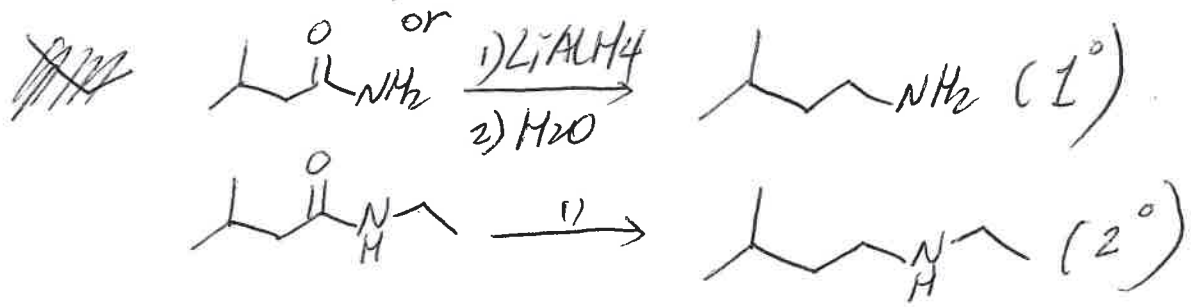
~~Note:~~ One general approach = "amines from simpler amines" — i.e., form N-C bond(s) to amine N.

1) $\text{S}_{\text{N}}2$ — over reaction problem (from from 1° or 2°)
 Hard to avoid going all the way to 4° ammonium.

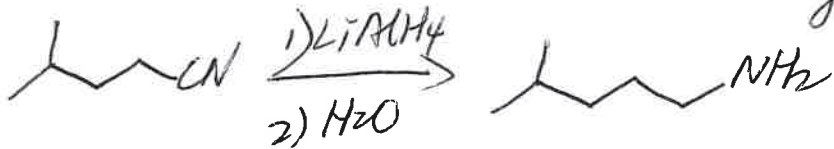
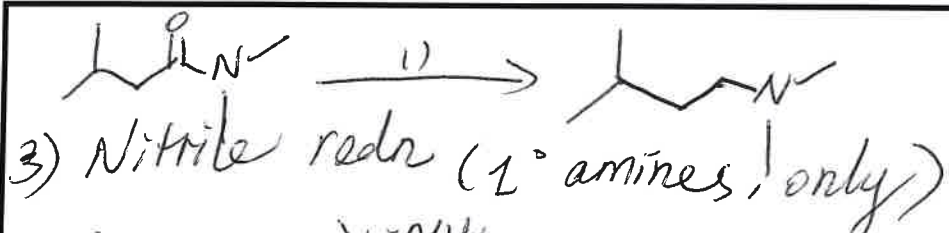
1) Reductive amination — allows selective formation of one C-N bond.

2) Reduction of amides to amine — discussed already.

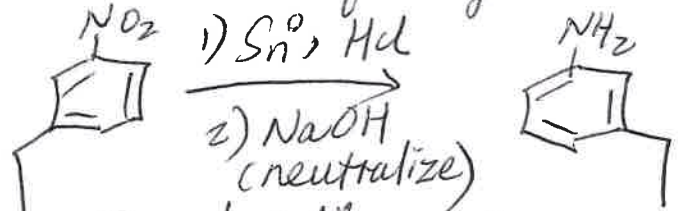
Versatile — 1°, 2°, 3° amines



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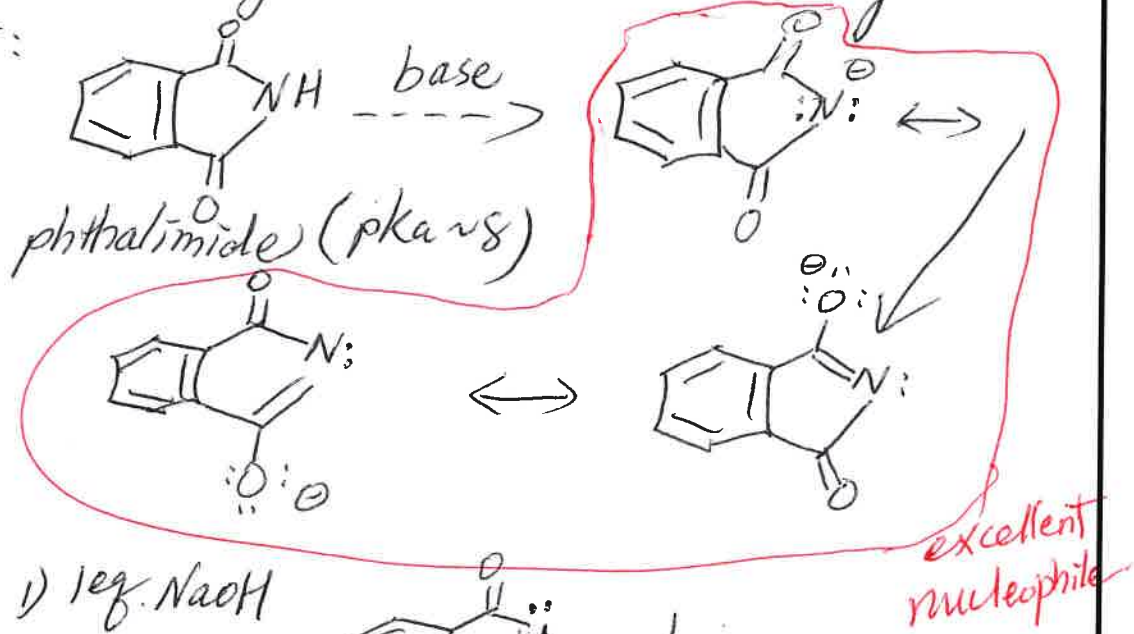


4) Reduction of aryl nitro to amino

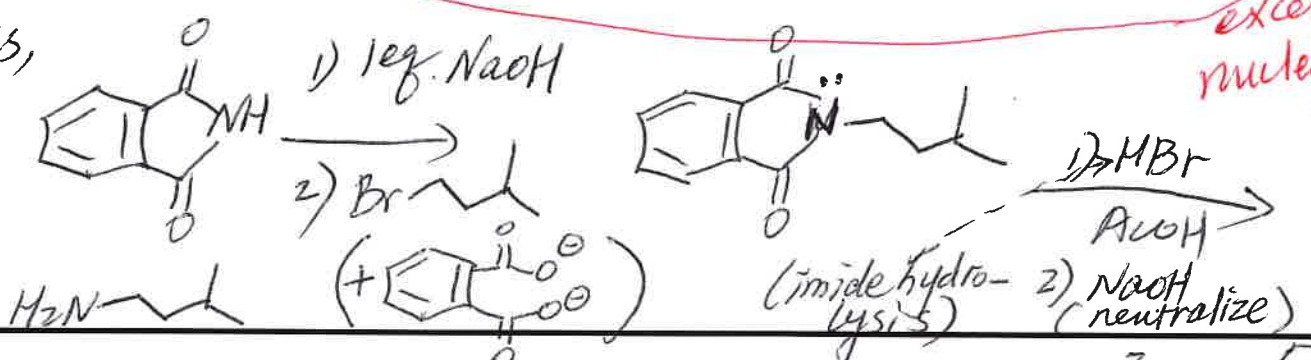


5) Gabriel amine synthesis — 1° amines only.

Key reagent:

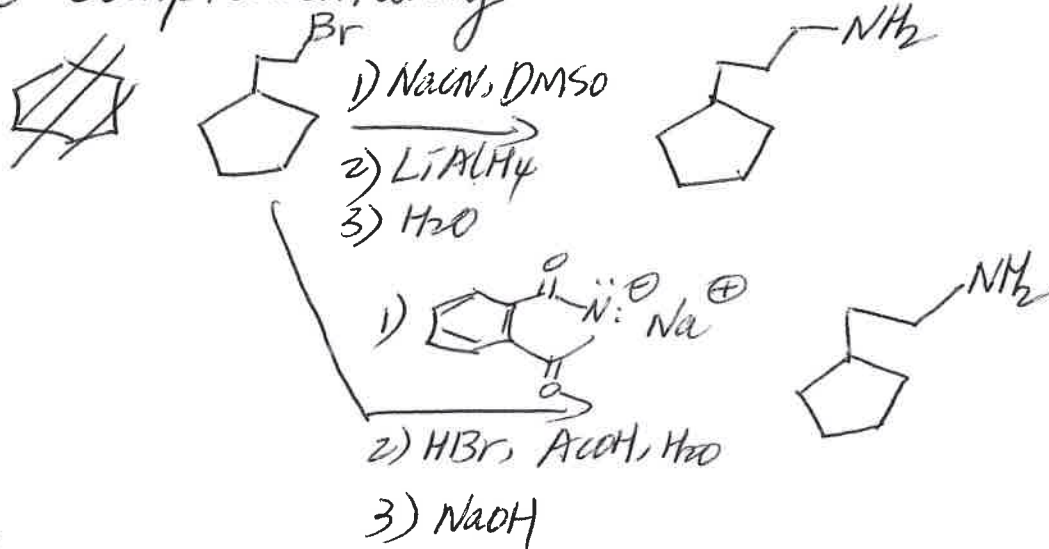


thus,



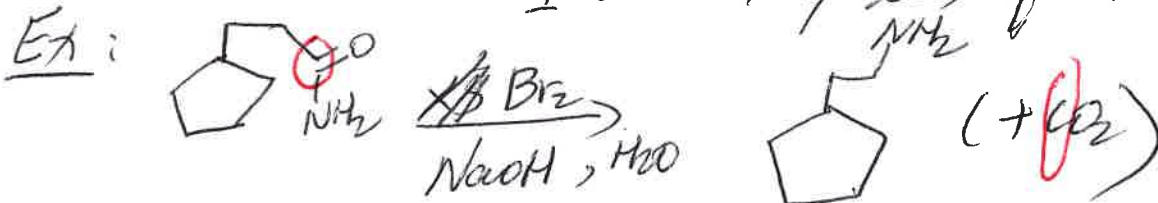
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Note Complementarity:



~~Hoffmann~~ Hofmann rearrangement

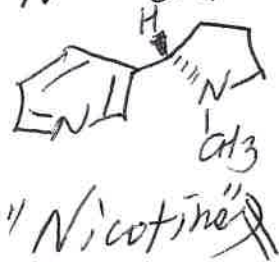
1° amide \rightarrow 1° amine, w/ loss of 1 C.



(Note: Complementarity rel. to redn of 1° amide)

Read Section @ end on "alkaloids"

Amiano N-containing natural ~~nat~~ molecules



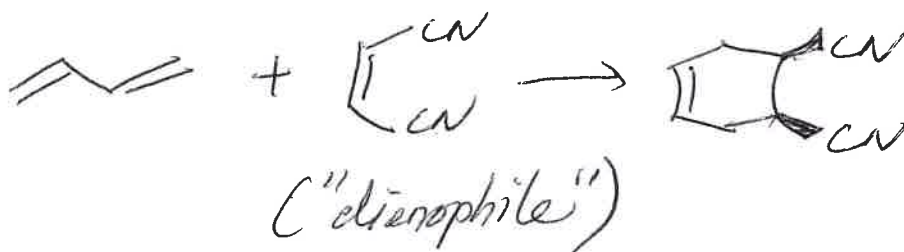
Chap. 27 - pericyclic Reactions

All problems are recommended
 rxns w/ a concerted mechanism, w/ a
 cyclic array of partial bonds @ the Transition
 state.

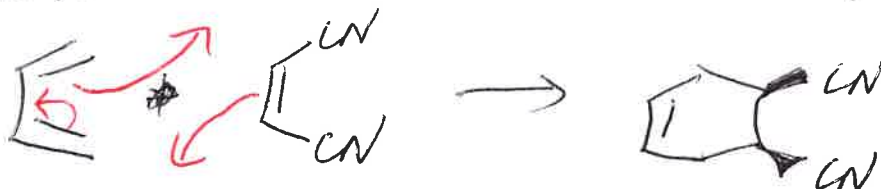
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Ex: Diels - Alder Rxn

Specific example

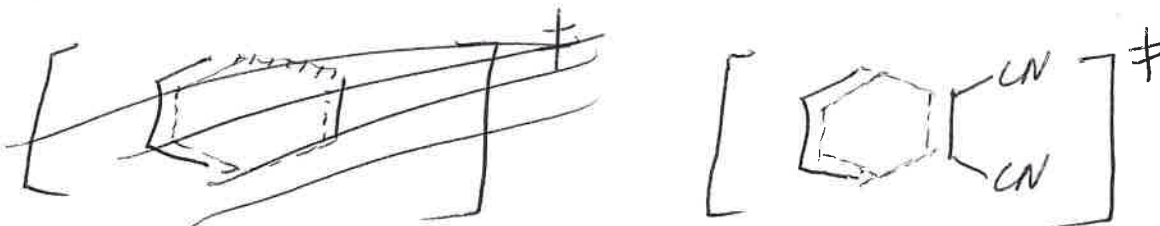


Mech:



(S-Cis)

TS:



Note: Cyclic array of partial bonds

D.A. rxn is one type of “cycloaddition” rxn.