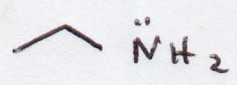


5/7/12

quaternary ammonium salt

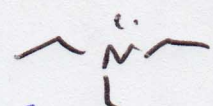
# Amines



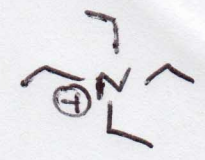
primary (1°)



secondary (2°)



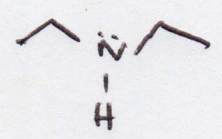
tertiary (3°)



The designation of 1°, 2°, or 3° for amines depends on the number of alkyl groups on the nitrogen itself, and not on the type of carbon adjacent to the N.

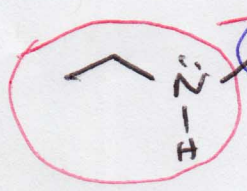
Common nomenclature

- List the alkyl groups attached to N.



diethylamine

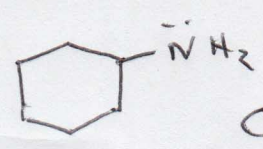
Systematic IUPAC nomenclature longest



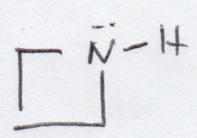
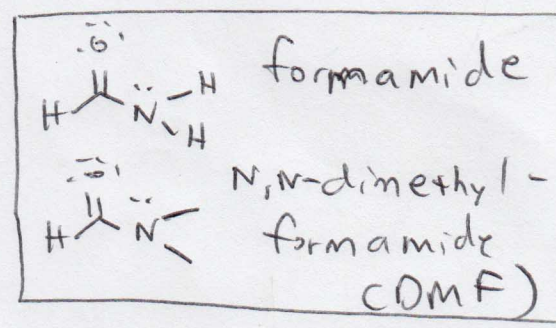
parent chain - chain w/ the most important functional group  
substituent to nitrogen

N-ethyl ethylamine

Cyclic amines



N not in ring  
cyclohexanamine



N in ring

Heterocycle - a cyclic molecule in which an atom other than carbon is part of the ring.

replacement "aza" = replace C w/ N

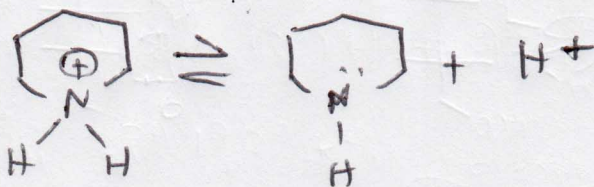
azacyclobutane



# Acid/base properties



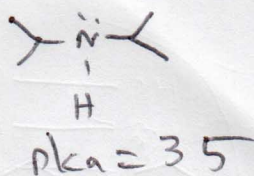
$pK_a$  of conj. = 11.27



Amines are weak bases with

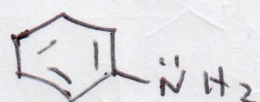
base strengths ( $pK_b$ ) that are comparable to the average acid strength ( $pK_a$ ) of a carboxylic acid: 4-6

→ Average  $pK_a$  of conjugate 9-11



$NH_4^+$   $pK_a = 9.25$

$NH_3$   $pK_b = 4.75$



conj.  $pK_a = 4.58$

aniline

Question: Which is a stronger base: piperidine or aniline?

Follow-up: Which is the stronger acid conjugate?

piperidinium ion

$pK_a = 11.27$

or

anilinium ion?

$pK_a = 4.58$

← lower  $pK_a$   
≡  
Stronger acid

Since the anilinium ion is the stronger acid, its conjugate

(~~conj~~ aniline) is the weaker base.

Why? The lone pair on N is heavily conjugated with the neighboring aromatic ring, so it is less able to act as a base.

conj.  $pK_a = -3.8$  → very strong acid

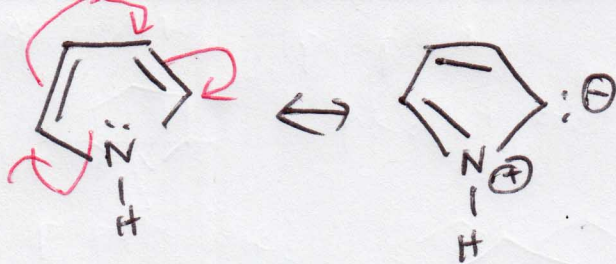
Since the pyrrolinium ion is a very strong acid, pyrrole itself is a weaker base.



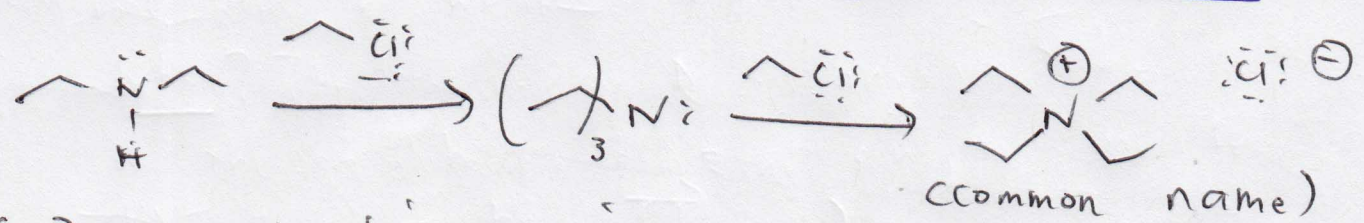
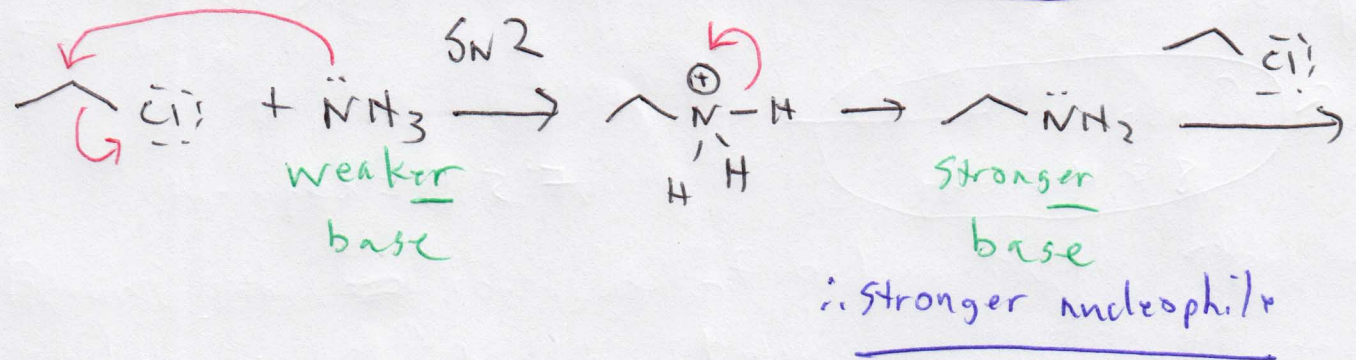
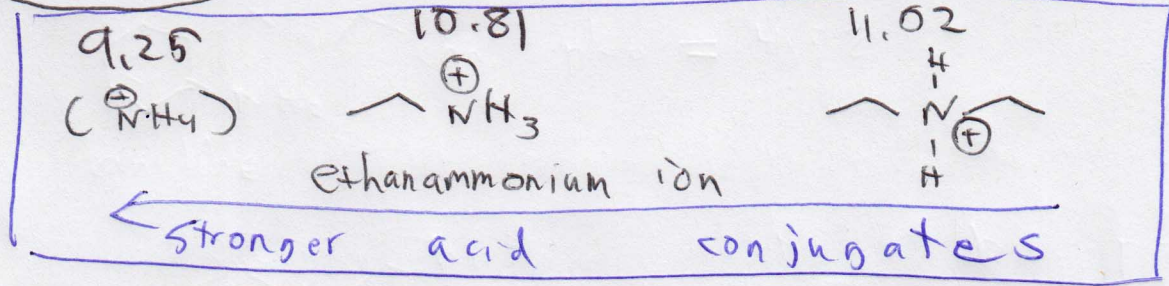
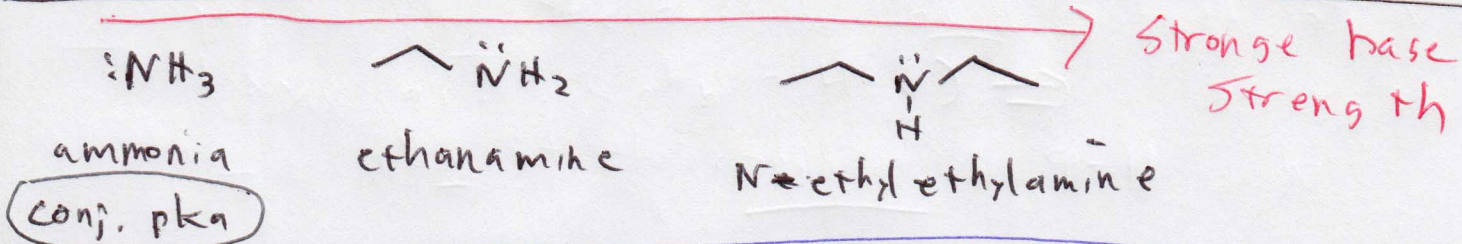
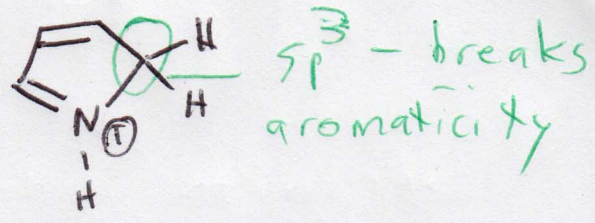
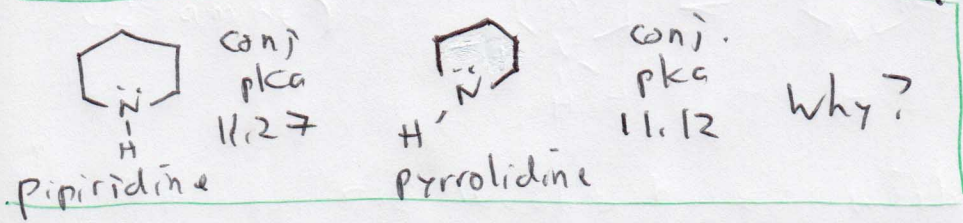
pyrrole

Protonating pyrrole breaks its aromaticity, which is highly unfavorable, which is why the pyrrolinium ion is so acidic.





Directed electrophilic aromatic substitution



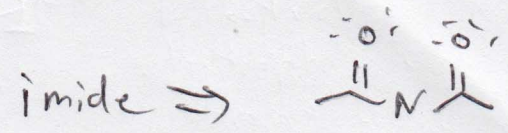
SN2 rxns involving amines are generally problematic since the product is usually more basic than the reactant so it can be difficult to prevent multiple rxns.

Extensive alkylation - add as many alkyl groups as possible.



A10 - Appendix: List of amine synthesis rxns

Gabriel amine synthesis



phthalimide

