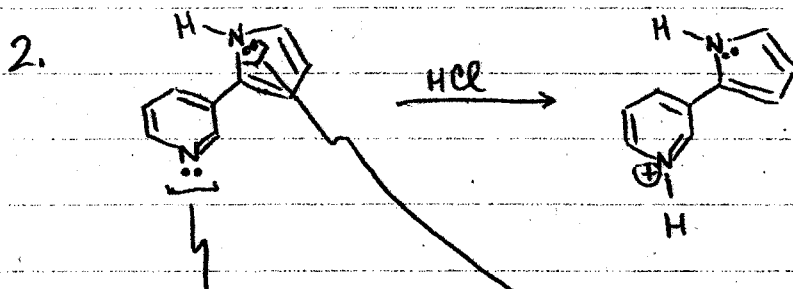
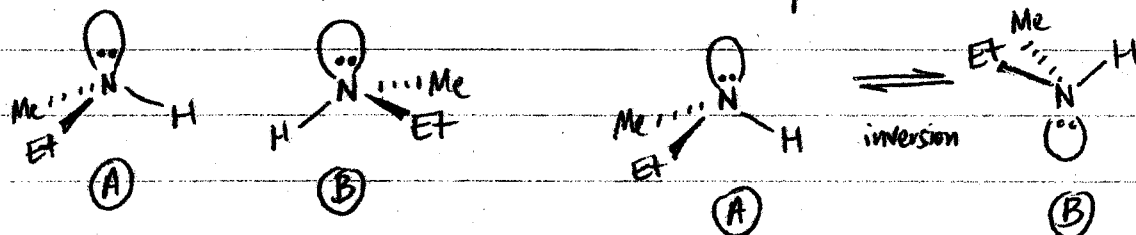


PROBLEM SET 14 SOLUTIONS

CHEM 3231

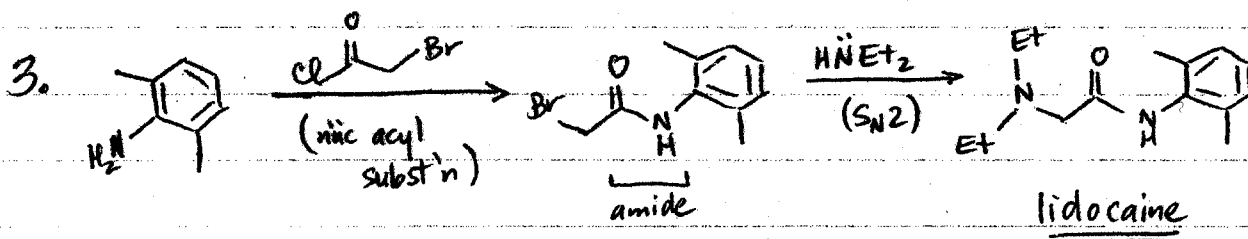
1. Pyramidal amines undergo rapid inversion even at low temperatures; thus the two structures interconvert rapidly so that resolution of the enantiomers is impossible.

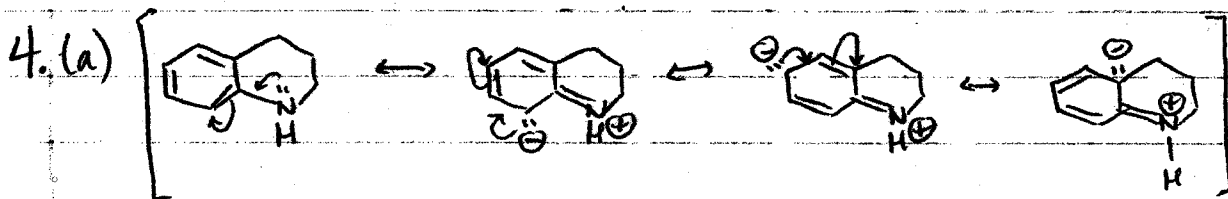


This e^- pair is not part of the aromatic system of this pyridine ring \therefore available for bonding.

This e^- pair is part of the pyrrole aromatic system \therefore not ^{as} available for bonding, because doing so would destroy aromaticity.

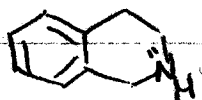
This problem is a good review on aromaticity and counting π e's!





base (amine) stabilized by resonance - delocalization of N lone e^- pair into aromatic ring \therefore less reactive lone e^- pair so WEAKER base

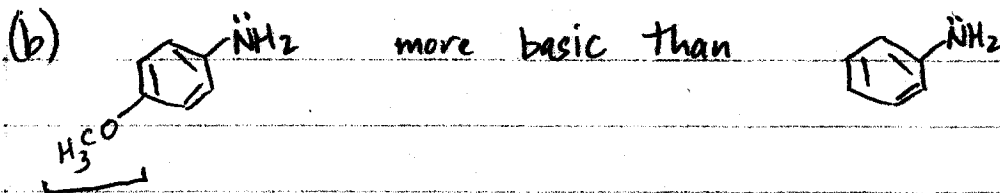
(vs)




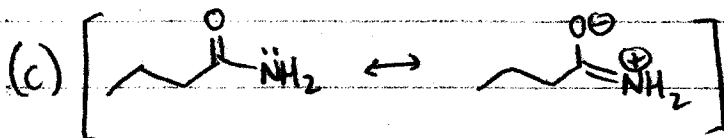
cannot delocalize N lone e^- pair into aromatic ring; too far away

\therefore more reactive lone e^- pair, so

STRONGER base



$-OCH_3$ is edg, so the electron donation increases e^- density at $-NH_2$, which makes  more reactive (more basic)



N lone e^- pair of an amide is tied up in resonance

\therefore less available for donation (more stabilized) so WEAKER base

(vs)



- N lone pair of e^- s more reactive so

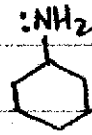
STRONGER base

#4 (cont)

(d)

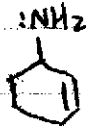


VS



WEAKER base

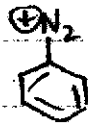
STRONGER base



double bond is electron-withdrawing (to a certain extent) so that NH_2 are less reactive

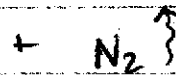
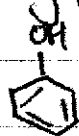
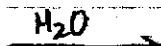
⊗ This is not a good problem in that the reasoning is kind of shady. Do not worry if you are confused by this problem — it was a poor choice on my part. Sorry !!

5. Recall that aniline can be converted to diazobenzene by reaction with nitrous acid (HONO):



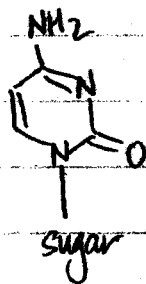
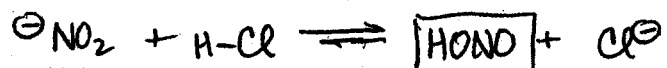
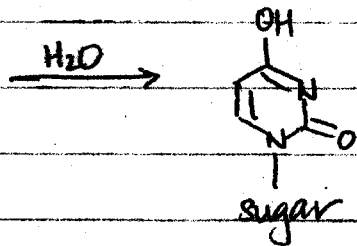
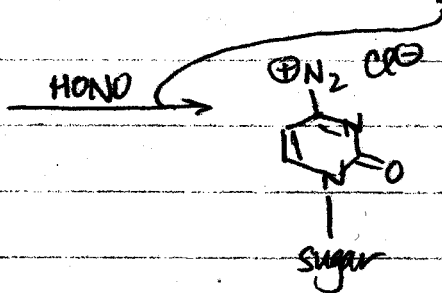
This is diazotization.

Reaction of diazo salts with nucleophiles is a facile process since N_2 is an EXCELLENT leaving group:



Use these concepts for solving this problem (see over):

#5 (cont)

cytidine residueuridine residue