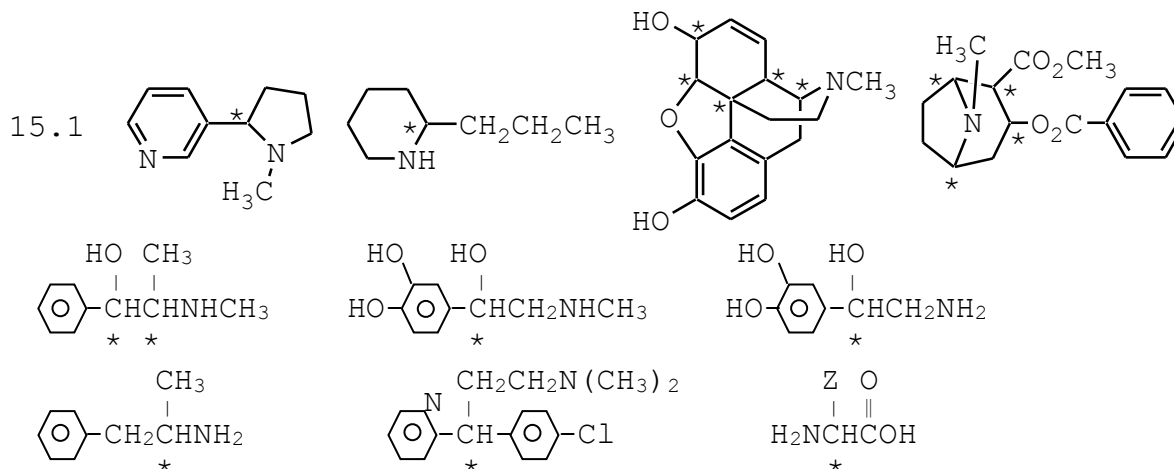
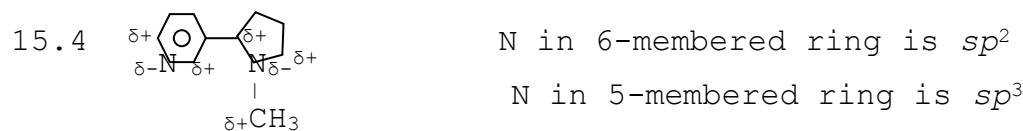
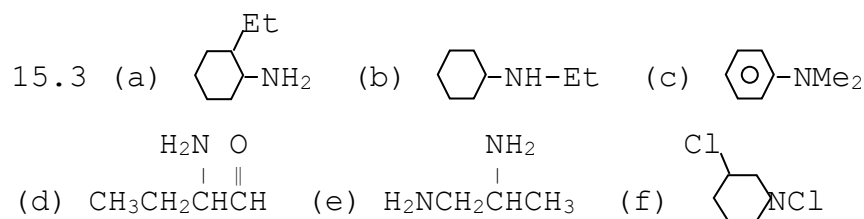


Answers to Puzzles of Chapter 15
Amines

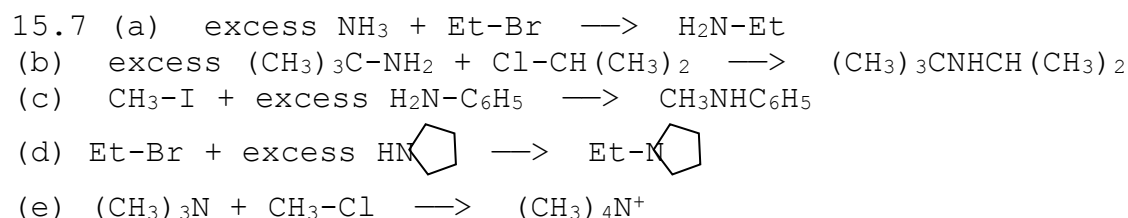


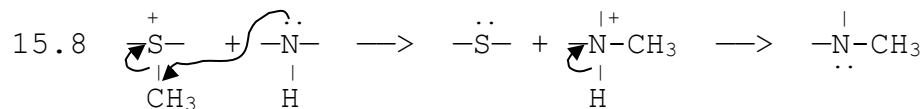
- 15.2 (a) 1°, 2-pentanamine (b) 3°, *N,N*-dimethylethylamine (c) 3°, 3-chloro-*N*-ethylpyrrolidine
(d) 2°, methyl *N*-methyl-3-aminopropanoate (e) 1°, 3-bromoaniline
(f) 2 x 1°, 3-iodo-1,2-propanediamine



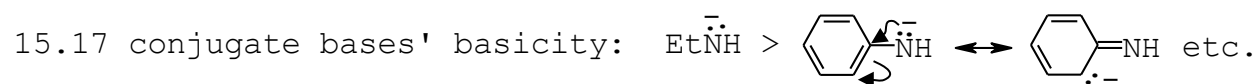
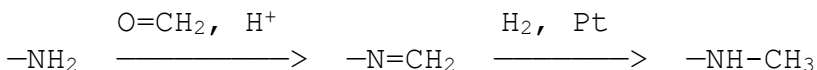
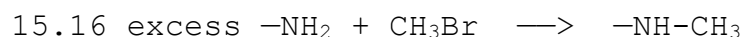
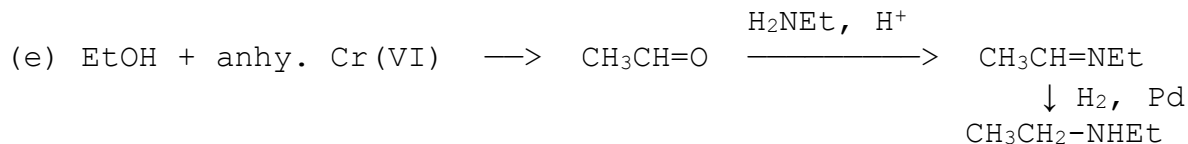
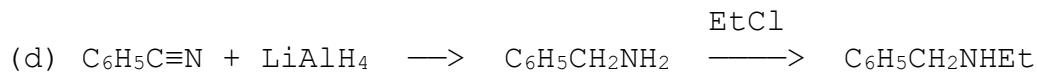
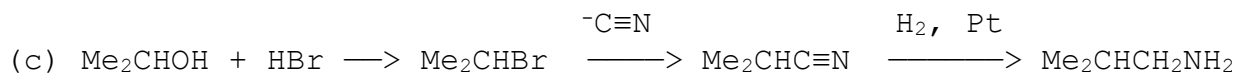
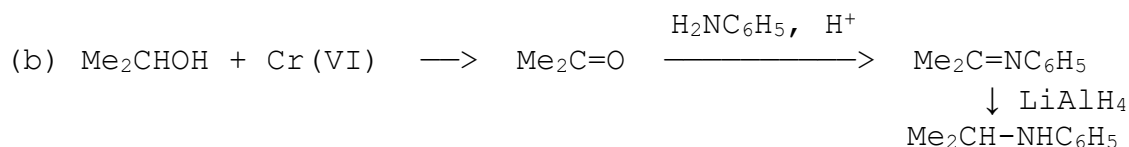
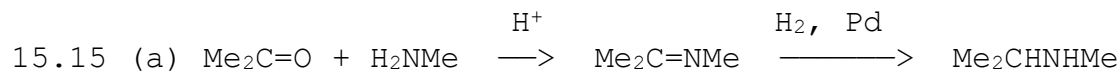
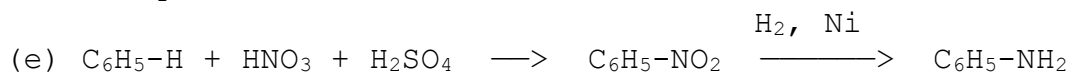
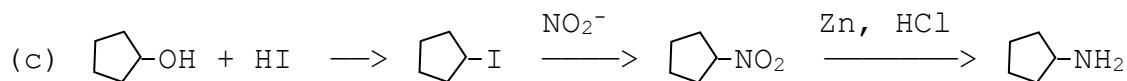
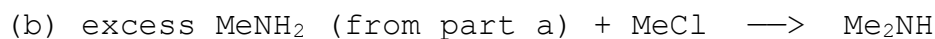
- 15.5 (a) in bp: $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 > \text{Pr}_2\text{NH} > \text{Et}_3\text{N} > \text{Me}_3\text{N}$
 Me_3N is smaller with smaller dispersion forces than Et_3N . Et_3N has no H "bonds", while $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ has more opportunities for H "bonds" than Pr_2NH .
(b) in H_2O solubility: $\text{Me}_3\text{N} > \text{Et}_3\text{N}$
because Me_3N is more polar (fewer C's/polar N group) than Et_3N
(c) in H_2O solubility: $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 > \text{Pr}_2\text{NH}$
because $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ has fewer C's/polar N group.

- 15.6 (a) With 18 C's/N group, it resembles fat in having only slight polarity.
(b) By protonating the N, the acid makes it ionic, more polar, & more soluble in aqueous blood.



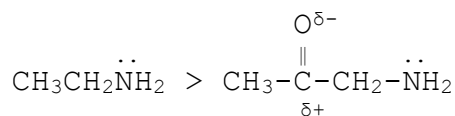


15.13 The 3° elie makes this an S_N1 reaction. Therefore the nitrite ion reacts with a hard C⁺. So the harder O nuc atom on nitrite (more δ- than on N) bonds to the hard C.



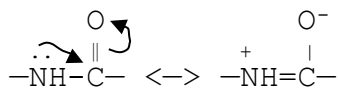
because resonance stabilizes the base e's of the 2nd base. So in acidity: EtNH₂ < C₆H₅NH₂

15.18 (a) in basicity:



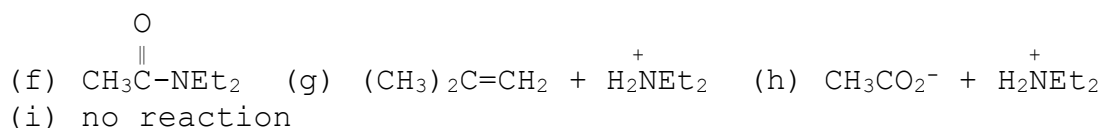
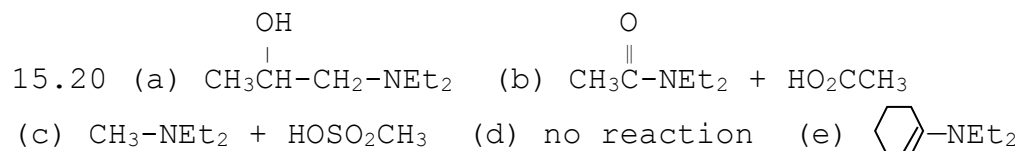
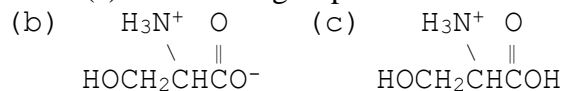
because the EN O puts a δ+ on the C, which attracts & stabilizes the base e's inductively.

(b) in basicity: amine N > amide N because resonance stabilizes the base e's on the amide base:



(c) in basicity: pyrrolidine N > pyridine N
because pyridine's sp^2 N has only 2 e^- pairs repelling & destabilizing its base e's, while pyrrolidine's sp^3 N has 3 e^- pairs repelling & destabilizing its base e's.

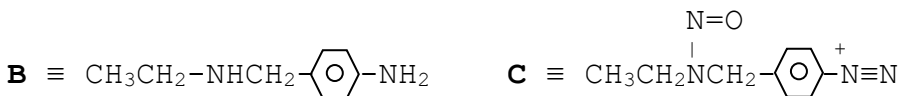
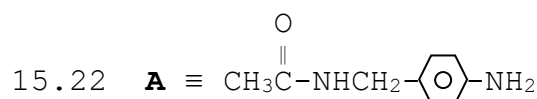
15.19 (a) The amino group is most basic.



15.21 (a) An amide N is less basic & nucleophilic because resonance stabilizes its base e's:



(b) The protected N is less nucleophilic because it is an amide N, not an amine N.



15.23 $\text{C}_3\text{H}_9\text{N} \equiv \text{Me}_3\text{N}$

IR: 3000-2800 cm^{-1} (s): sp^3 C-H

15.24 (a) Doubling [amine] \uparrow δ of H on N, because it \uparrow H "bonding" between amine molecules.

(b) Changing to methanol \uparrow δ of H on N, because it \uparrow H "bonding" between solvent & amine.

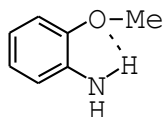
15.25 *N*-ethylaniline

^1H NMR: δ 7.1, 6.6, 6.5: Ar H; δ 3.4 (s, broad): NH; δ 3.1 (q): CH_2 ; δ 1.2 (t): CH_3

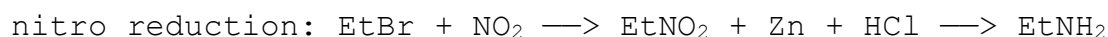
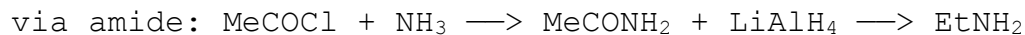
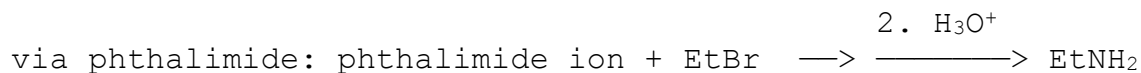
15.26 (a) ethylamine (b) ethanamine (c) ethanediamine (d) 4-amino-2-butanol
 (e) e.g., *N*-methylpropylamine (f) 2,4-dichloropyrrolidine (g) *N*-methylethylamine

15.27 The ammonium ion has no lone pair that freely inverts. Its 4 bonds stay in place.

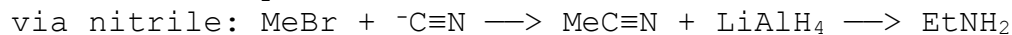
15.28 Unlike 3-methoxyaniline, 2-methoxyaniline has an intramolecular H "bond", which



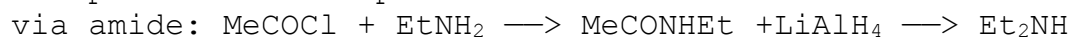
inhibits intermolecular H "bonds":



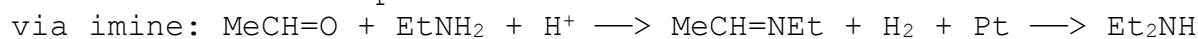
via imine: impossible



via phthalimide: impossible



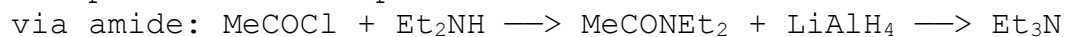
nitro reduction: impossible



via nitrile: impossible



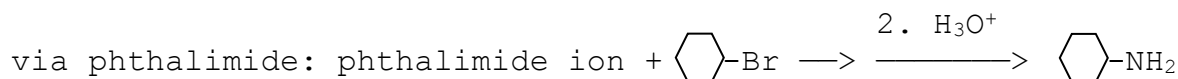
via phthalimide: impossible



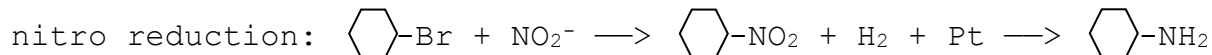
nitro reduction: impossible

via imine: impossible

via nitrile: impossible



via amide: impossible



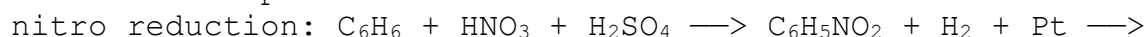
via imine: impossible

via nitrile: impossible



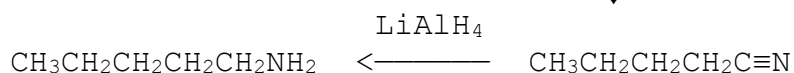
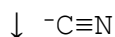
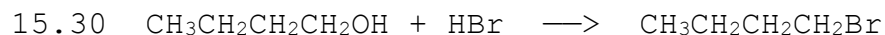
via phthalimide: impossible

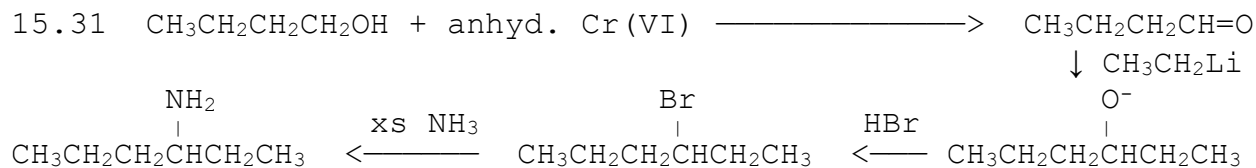
via amide: impossible



via imine: impossible

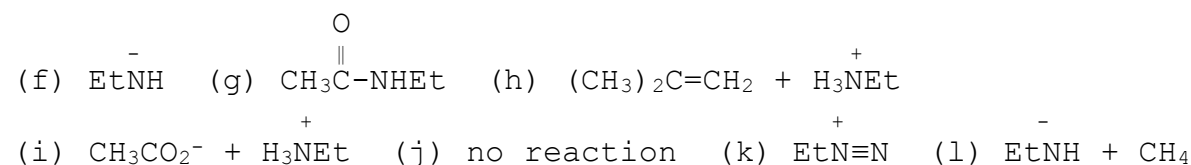
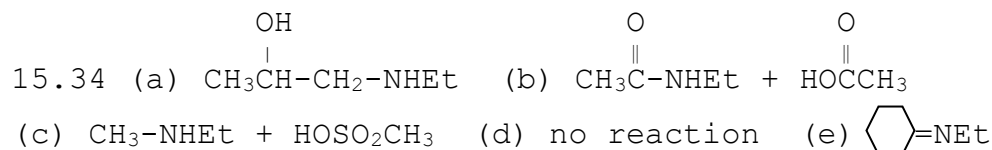
via nitrile: impossible





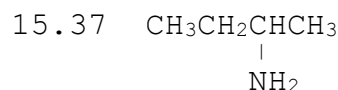
15.32 conjugate bases' basicity: $\text{Et}_2\text{N}-\overset{\ominus}{\text{C}}\text{H}-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3 < \text{H}_3\text{C}-\overset{\ominus}{\text{C}}\text{H}-\text{CH}_3$
 because EN N puts a δ^+ on the C, which stabilizes the base e's. So triethylamine is more acidic.

15.33 (a) $[\text{H}_3\text{O}^+] = 2 \times 10^{-11}$ (b) aniline because the K_a of its conjugate acid $\approx 10^{-5} > [\text{H}_3\text{O}^+]$

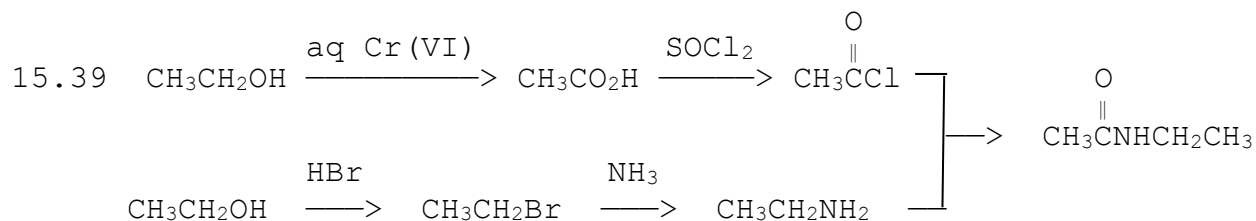
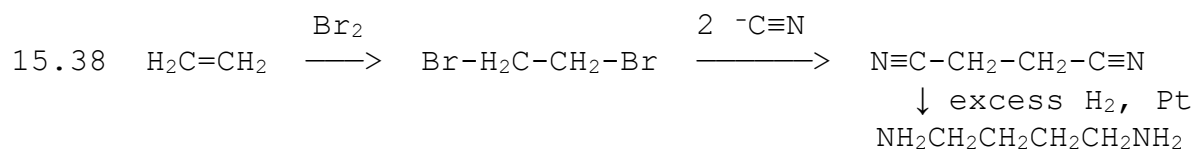


15.35 **A** $\equiv \text{EtBr}$; **B** $\equiv \text{EtNO}_2$; **C** $\equiv \text{EtNH}_2$; **D** $\equiv \text{EtN}=\text{CHCH}_3$; **E** $\equiv \text{Et}_2\text{NH}$; **F** $\equiv \text{Et}_2\text{N}-\text{N}=\text{O}$

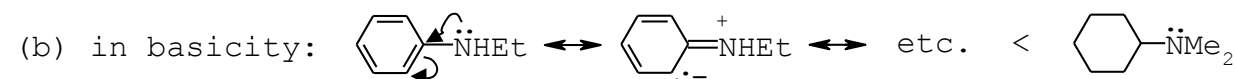
15.36 at lower frequency (& energy) because C-N bond is weaker than $\text{C}\equiv\text{N}$ bond.



IR: 3360, 3280 cm^{-1} (s): NH_2 ; 3000-2850 (s): sp^3 C-H; 1600 (m): NH_2 bend; 870 (s): N-H bend
 ^1NMR : δ 2.8 (m): NCH ; δ 1.3 (m): CCH_2C ; δ 1.1 (s): NH_2 ; δ 1.0 (d): $\text{H}_3\text{C}-\text{C}-\text{N}$;
 δ 0.9 (t): $\text{H}_3\text{C}-\text{C}-\text{C}-\text{N}$

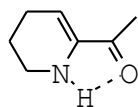


15.40 (a) *N*-ethylaniline has the higher bp because it alone has H "bonds".



because resonance stabilizes the base e's of *N*-ethylaniline.

15.41 Because an intramolecular H “bond”, unavailable to the imine, stabilizes the enamine:



15.42 (a) conjugate bases' basicity: $\text{H}_2\ddot{\text{N}}-\overset{\text{H}_3\text{C}}{\underset{\delta^+}{\text{C}}}-\overset{\text{O}^{\delta-}}{\text{O}} < \text{H}_2\ddot{\text{N}}-\text{CH}_2\text{CH}_3$

because alanine's EN O puts a δ^+ on a C, stabilizing the base e's. So alanine is more acidic.

(b) By itself, the $-$ repels & destabilizes the base e's of alanine's conjugate base, weakening the acidity of alanine itself. Evidently the opposite effect of the δ^+ is stronger.

15.43 Base e's are stabler on the more EN O than on the N.

15.44 (a) All 3 slightly polar components are mostly in the slightly polar CH_2Cl_2 .

(b) Benzoic acid as very polar benzoate ion is in the very polar aqueous base. The other 2 components remain in the CH_2Cl_2 .

(c) *N,N*-dimethylaniline as a very polar ammonium ion is in the aqueous acid. Phenylmethanol remains in the CH_2Cl_2 .

6/05