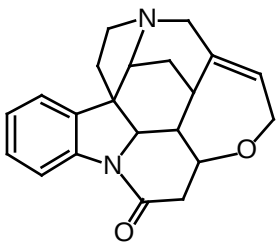
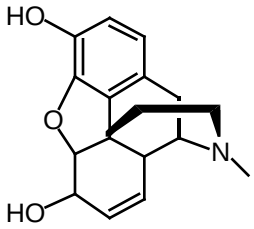
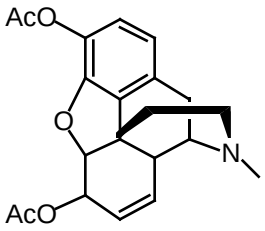
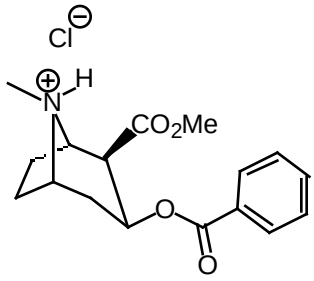
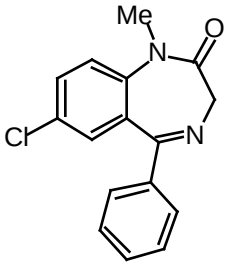
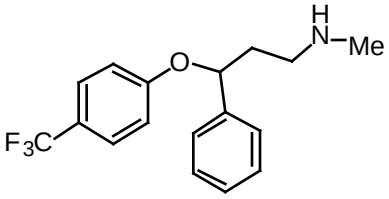
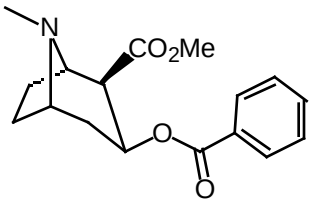
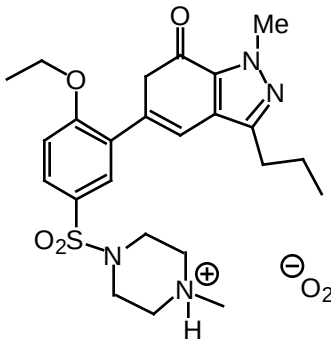
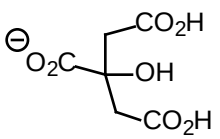
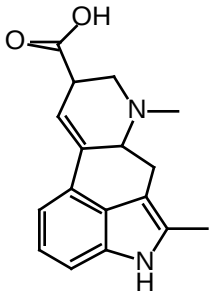
**Chemistry 304B Spring 1999** **Lecture 26 (no lecture 25)**

**Exam: Average 44** **Grade breakdown:** **A: 57-99**
**B: 37-56**
**C: 18-36**
**D: <18**

**Chapter 21 material: amines and related nitrogen compounds.**
**See the Web for problem and reading assignments**

Naturally occurring nitrogen compounds are among the most interesting for biological activity: Alkaloids, etc.

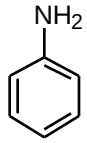











**Basic structure of amines:**

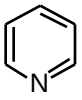



**Nomenclature: p 1077**

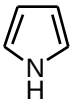
Basic structural types:



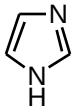

aniline



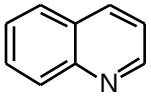

pyridine



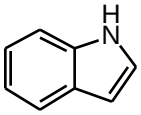

pyrrole



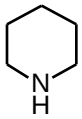

imidizole



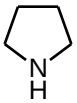

quinoline



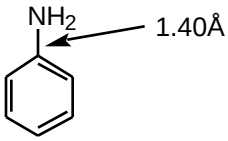

indole

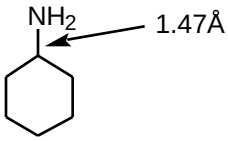


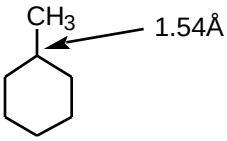

piperidine



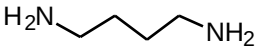

pyrrolidine



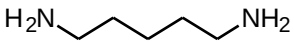




**Odor:**



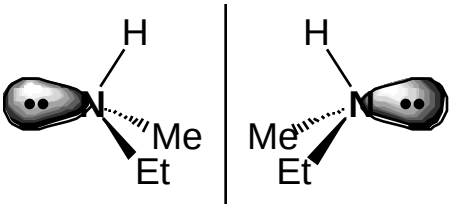

putrescine




cadaverine

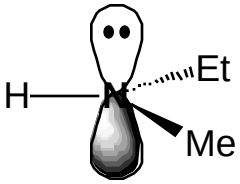
effect of lemons:

**3D Structure:**

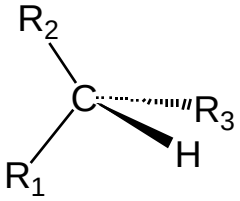


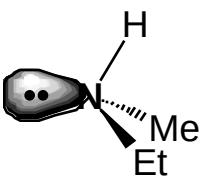

enantiomers

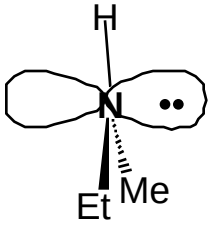
OR

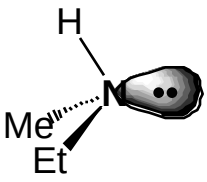



achiral

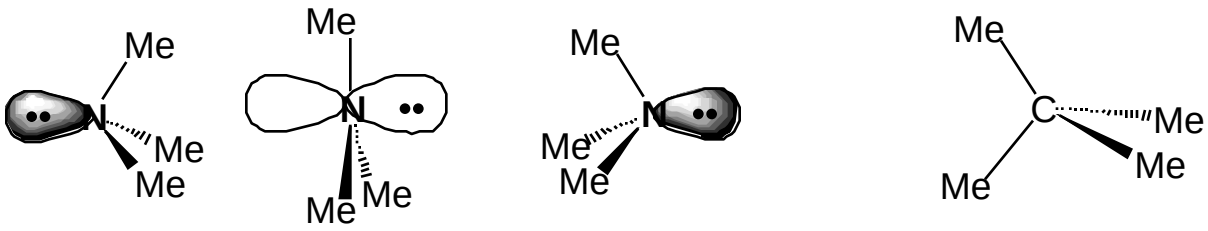


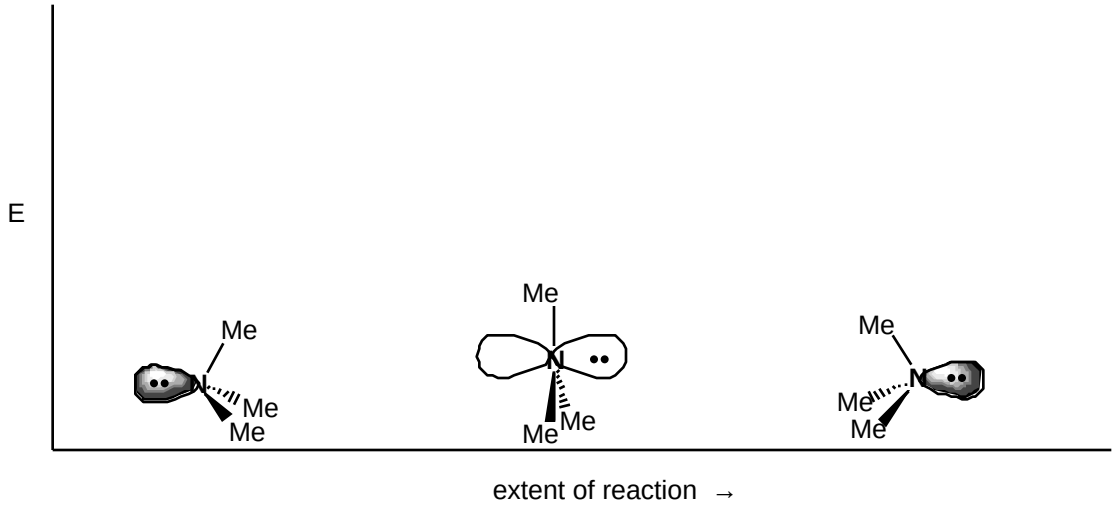
**Calculate the trimethyl system**




**Heat of formation:**

**Flattening of pyramid?**

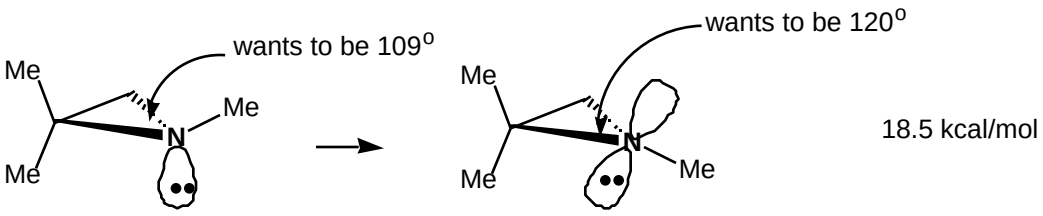
Cannot isolate one enantiomer, in general. Not planar, but rapidly inverting via a planar transition state.




How influence the barrier?

Increase the barrier: Destabilize lone pair in $sp^2$ hybridization

Bond angle: wants to expand to 120° in the planar form.




**BP:**

| **$CH_3$**$CH_3$ | **$H_2N$**-$CH_3$ | **HO**-$CH_3$ |
|---|---|---|
| -89°C | -6.3°C | 65°C |

H-bonding

$^1$H NMR chemical shifts: effect of amino substituent on adjacent C-H

| **$CH_3$**$CH_3$ | **$H_2N$**-$CH_3$ | **HO**-$CH_3$ |
|---|---|---|
| 0.9 ppm | 2.6 ppm | 3.4 ppm |

NOTE: -$NH_2$ protons are generally in rapid exchange--no coupling observed with adjacent H. Broad lump

Chemical shift of -$NH_2$ depends on conditions: around 3-4 ppm

More acidic N-H: more downfield

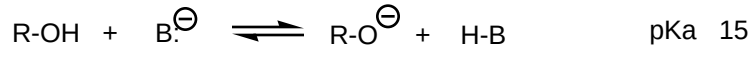

IR: N-H stretch at 3100-3500 [same as O-H stretch]

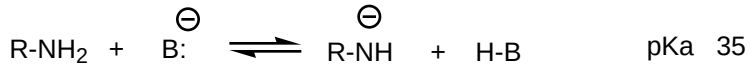
**Basicity:**

| | **$NH_3$** | **Me-$NH_2$** | **$Me_2NH$** | **$Me_3N$** | |
|---|---|---|---|---|---|
| pKa (water) | 9.2 | 10.6 | 10.8 | 9.8 | (of ammonium ion, conj. acid) |
| pKa (gas) | lowest | 2nd lowest | 2nd highest | highest | (weakest acid, strongest base) |

Alkyl groups have two effects: stabilize the ammonium ion by dispersing charge
destabilize the ammonium ion by interfering with solvation

**Acidity:**



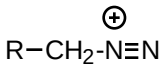



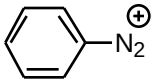
**Lewis Base:**

$R_3N$:

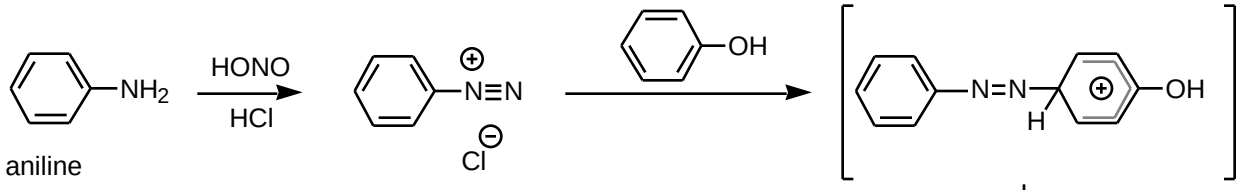
$R_2O$:

Important derivatives of nitrogen: **diazonium ions**

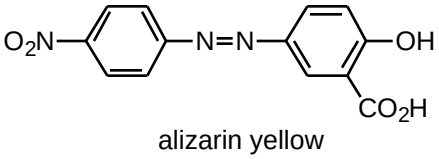




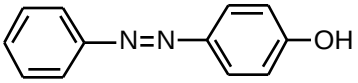
**Aromatic diazonium ions:** (mechanism of formation: Fig 21.49)




Diazo dyes:

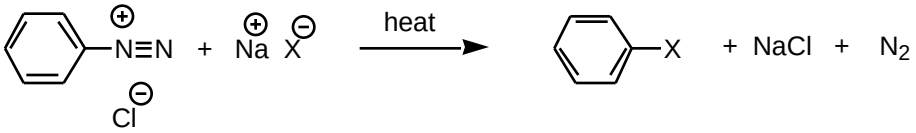



alizarin yellow




diazo compound

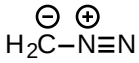
**Substitution:**



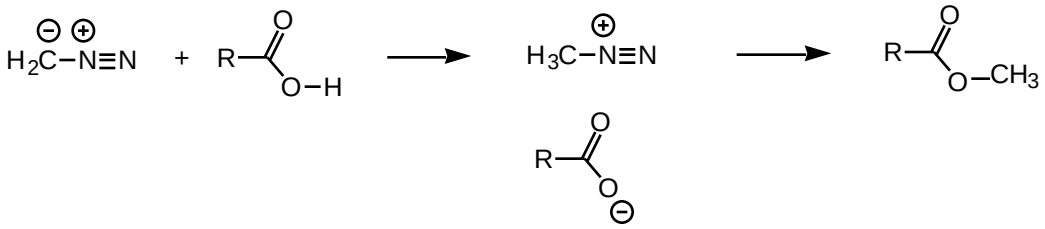

X = OH, I, F, Cl, Br, H

**Diazoalkanes:**

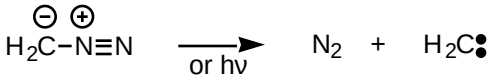
diazomethane



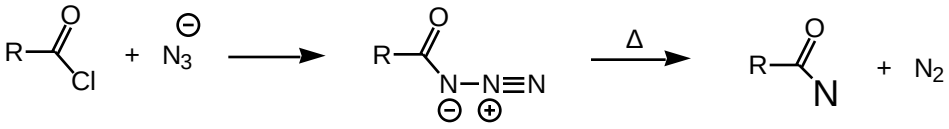
Powerful esterification reagent:



Source of carbenes: Divalent Carbon (Chapter 10, p 436. 303?)



Special cases of divalent nitrogen:



Curtius Rearrangement

Related:

Hoffman Rearrangement