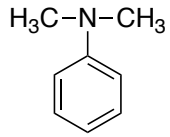
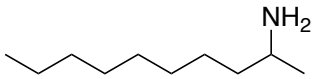
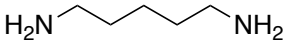
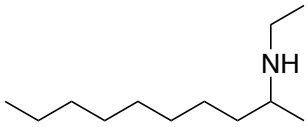
Chapter 20 Worksheet – Amines Name:
Self-paced to be used with the textbook

Study Partners

Categories of amines sound the same as for alcohols or alkyl halide, but they are done differently. See the below for the categories.

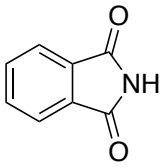
1° amine 2° amine 3° amine 4° ammonium ion (pronounced: quaternary)

Read about the nomenclature of amines and then name each of these amines and give the category

❑ 1° ❑ 2° ❑ 3° ❑ 4°		Name:
❑ 1° ❑ 2° ❑ 3° ❑ 4°		Name:
❑ 1° ❑ 2° ❑ 3° ❑ 4°		Name:
❑ 1° ❑ 2° ❑ 3° ❑ 4°		Name:

Each type of amine can be synthesized in different ways.

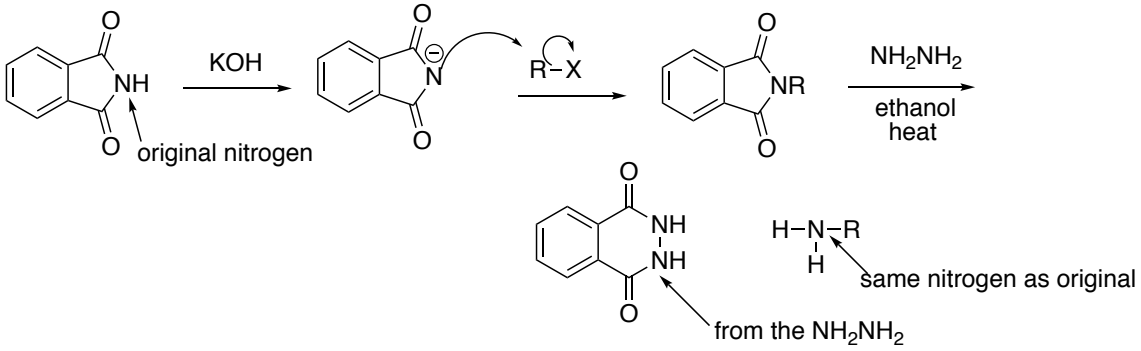
First, 1° aliphatic (meaning non-aromatic) amines are often prepared using a named reaction, called the Gaberiel synthesis, which always begins with this molecule:



phthalimide

Phthalimide has a very acidic nitrogen; about as acidic as a carboxylic acid. Why is it so acidic?

The method goes this way for the ”Gabriel” (phthalimide synthesis):

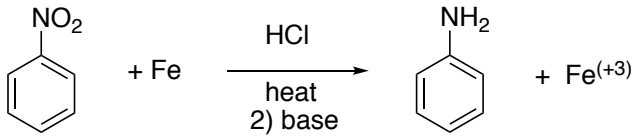


There is a well-known name for the second step of the mechanism. What is it? _____

Outline the Gabriel synthesis for 1- hexanamine.

Aniline cannot be made this way. So the other way to do that is to start with a nitro group and reduce iwith iron or tin in HCl with heat.

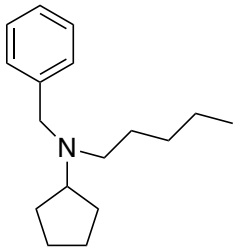
Write the balanced half-reactions for this transformation:



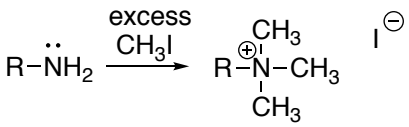
Half reaction: Oxidation of iron
Half reaction: Reduction of nitro
Balanced reaction

Read in the book (section 20.4C) about “reductive amination”which is a common way to make 2° amines. Then outline the synthesis of N-cyclopentyl-2-pentamine (also called N-pentylcyclopentanamine), using appropriate amine and ketone starting materials. Use “Raney Ni” as the reducing agent.

Use the methods of section 20.4D to convert the amine in the last example into:



One more thing. To make 4° salt, we almost always begin with a 1° amine and then treat it with a so-called quaternizing agent – which is really just a very good S_N2 substrate, CH_3I.

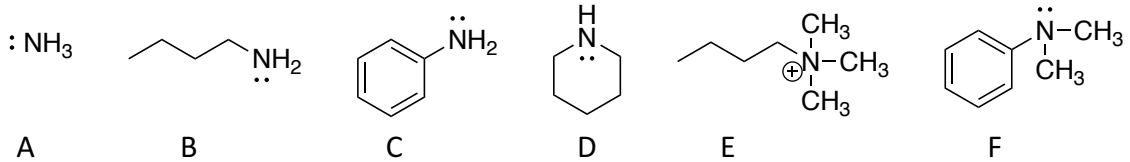


Amines are bases and, thus, nucleophiles (like above) chemically. They share the lone pair of electrons on the nitrogen to accept protons or to attach to positive atoms in a substitution.

They are usually less basic than hydroxide and more basic than carboxlate ions. They become a little more basic when more electron-releasing R groups are on the nitrogen. They become much less basic when attached to an aromatic ring. Why? Be specific and use good organic vocabulary.

I call hydroxide the weakest strong base and ammonia the strongest weak base. Aren't I clever?

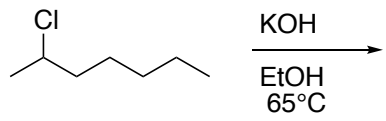
Organize these from *least* basic to *most* basic.



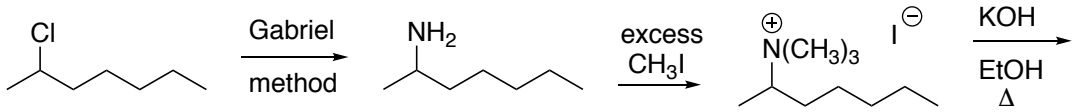
A B C D E F

Least basic : ___ ___ ___ ___ ___ ___ : Most basic

So now reactions. Remember Zaitsev, elimination? What is the major product in the reaction below?

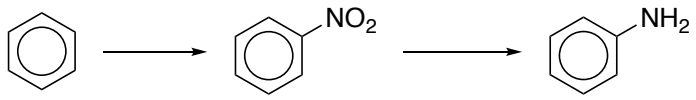


But, interestingly, if we convert that alkyl halide into a 4° salt, the reaction goes the opposite way, often referred to as Hofmann elimination. So with this news, predict the major product of this reaction (for more background read 20.12A):

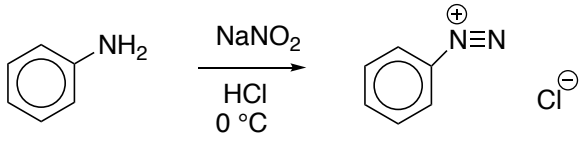


The next reaction is only for 1° aromatic amines, aka anilines. Any molecule with an aniline group can do this.

First, let's remember how anilines are prepared. Fill in the missing reagents.

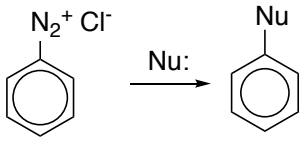


Now we will introduce a new reagent, Nitrous acid, HONO. It is very unstable so you have to prepare it as needed by mixing $NaNO_2$ with a strong acid like HCl, this is done near 0 °C to prevent it from decomposing. HONO converts anilines into an "arendiazonium salt"as below (see section 20.6):



What type of chemical transformation is this reaction?

The N_2^+ group on the ring is a powerfully good leaving group. So any sort of nucleophile can replace it. (see section 20.7)



What would be the product with the following reagents?

H_2O	
CuCl	
CuBr	
KI	
CuCN	
HBF_4	
H_3PO_2 (hint: this is a reducing agent	

This can be used to make molecules that would be difficult to make in other ways. For example, m–bromochlorobenzene. Why would this be difficult to make this from benzene using our chapter 15 methods? Be specific.

Show how m–bromochlorobenzene can be made from benzene using this new method. Then do problems 20.11abcd in the book.

Read the solved problem 20.6 on page 916 then explain why it is sometimes useful to convert the NH_2 to an H using H_3PO_2.

Well done. Now start seriously prepping for the final!