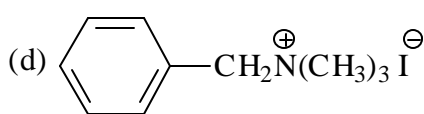
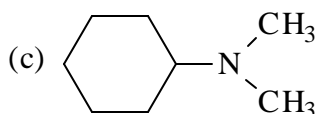
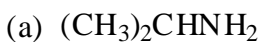


Chapter 12

1. Classify each of the following compounds as either a primary, secondary, or tertiary amine, or as a quaternary ammonium salt.

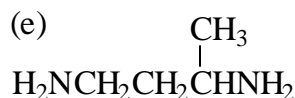
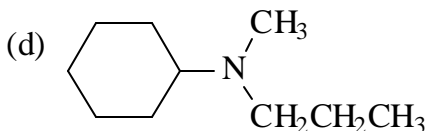
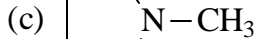
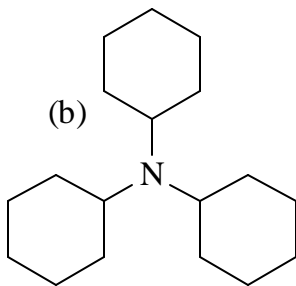


(a) primary: the nitrogen is joined to one carbon, (b) secondary: the nitrogen is joined to two carbons, (c) tertiary: the nitrogen is joined to three carbons, (d) quaternary ammonium salt: the nitrogen is joined to four carbons and bears a positive charge.

3. Name the following compounds by IUPAC rules.



(b)

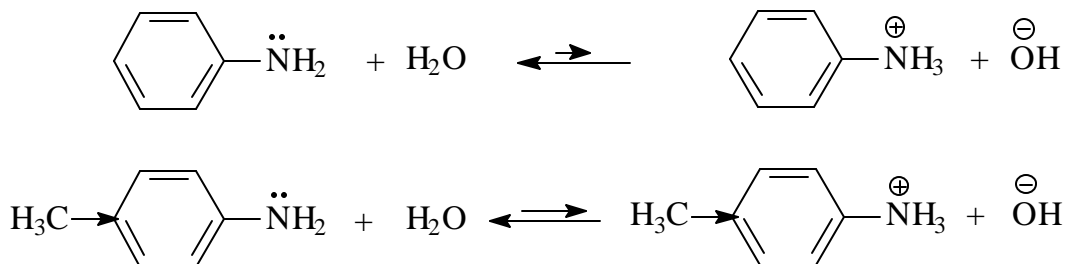


(a) 1-(*N*-methylamino)ethane or *N*-methylethylamine, (b) tricyclohexylamine, (c) *N*-methylpyrrole, (d) (*N*-methyl-*N*-propylamino)cyclohexane or *N*-methyl-*N*-propylcyclohexylamine, (e) 1,3-diaminobutane or 1,3-butanediamine

It must be admitted that, with three competing but similar nomenclature systems in existence, naming amines can be a confusing undertaking.

5. Which would you expect to be a stronger base, aniline or *p*-methylaniline? Explain.

Let's compare these two compounds by having them function as bases in a reaction where water is the acid.

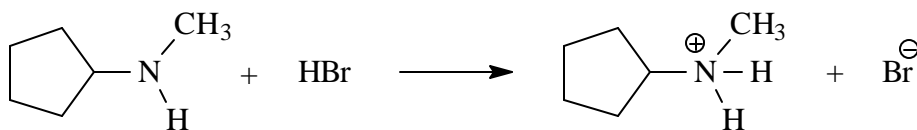


The electron donating methyl group may destabilize this molecule (compared to the one above) by increasing the electron density in the aromatic ring. This effect, if present, would be small since there are no formal charges.

The electron donating methyl group will stabilize this molecule (compared to the one above) by increasing the electron density at the positively charged nitrogen. This effect would be substantial owing to the positive charge on the nitrogen.

The bottom line here is that the *p*-methylaniline is more basic than the aniline because the methyl group stabilizes the *p*-methylanilium cation.

6. Predict the product of the following reaction.



This is a typical acid-base reaction for an amine, where the amine functions as base and thereby accepts a proton from an acid.

7. Which compound in each of the following pairs is more basic?

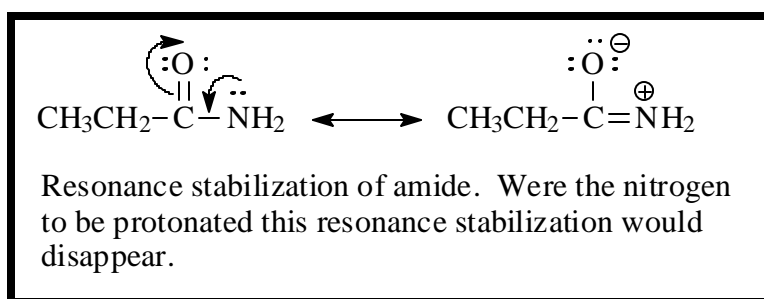


The more basic compound is boxed in each case.

(a) Amides are not basic at the nitrogen because, if the nitrogen were to become protonated, the resonance stabilization of the amide structure would be sacrificed.

Another way of looking at this is that the unshared pair of electrons on the nitrogen in amides is not really on the nitrogen, exclusively, but is shared

between the oxygen and nitrogen and is, therefore, less available for donation (bases are electron-pair donors).



(b) Hydroxide ion is a strong base. Perhaps that's all that needs to be said, but we might note that in picking up a proton the negatively charged hydroxide is joining to a positively charged proton; in the case of the amine a neutral molecule is picking up a proton with the result that a positive charge resides on the nitrogen.

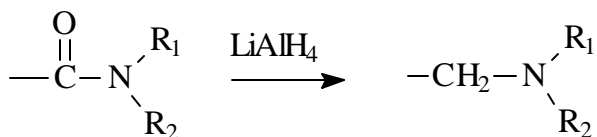
(c) In dimethylamine the unshared pair of electrons is pretty much localized on the nitrogen (and more available) while in *N*-methylaniline it is somewhat delocalized into the aromatic ring.

(d) Each of these compounds can be protonated, in the first case on the oxygen and in the second on the nitrogen. This leads to a positively charged oxygen and a positively charged nitrogen; since oxygen is more electronegative, this situation is a higher energy one for the oxygen.

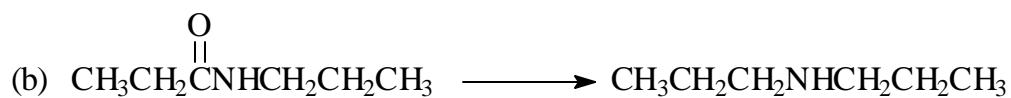
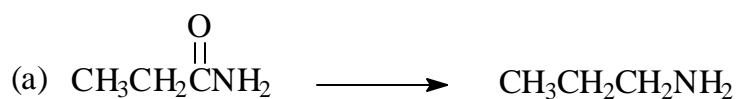
9. Propose structures for amides that might be precursors of the following amines.

(a) propylamine, (b) dipropylamine, (c) benzylamine

If we are going to reduce an amide to get an amine, we should be aware of the following:

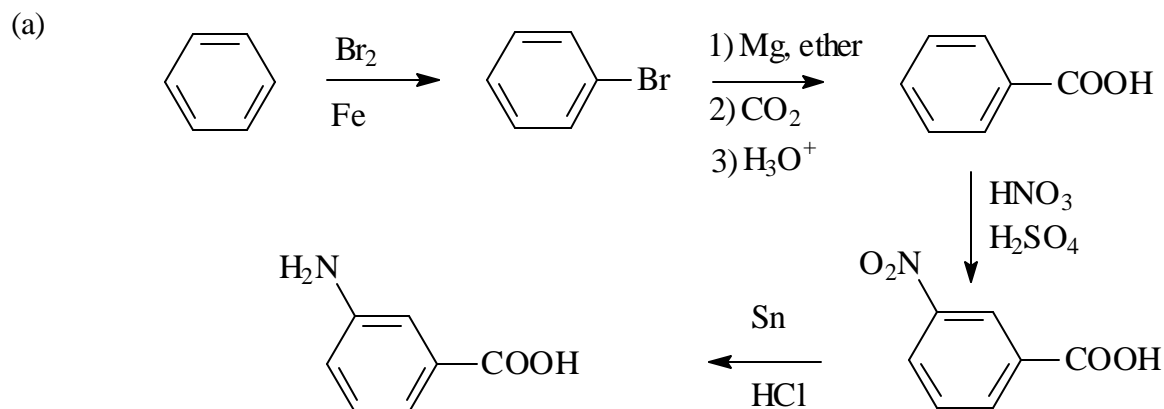


R_1, R_2 may be R or H



11. How could you synthesize the following amines from benzene? More than one step is required in each case.

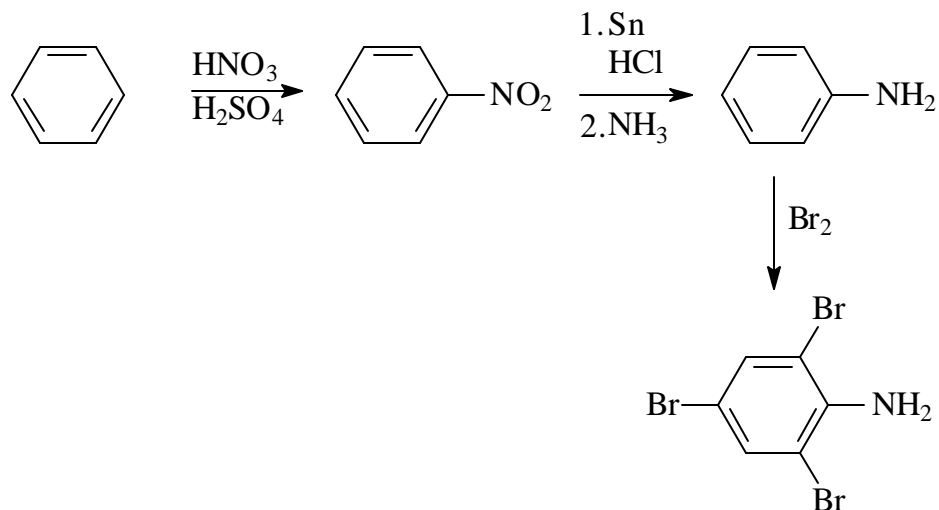
(a) m-aminobenzoic acid, (b) 2,4,6-tribromoaniline



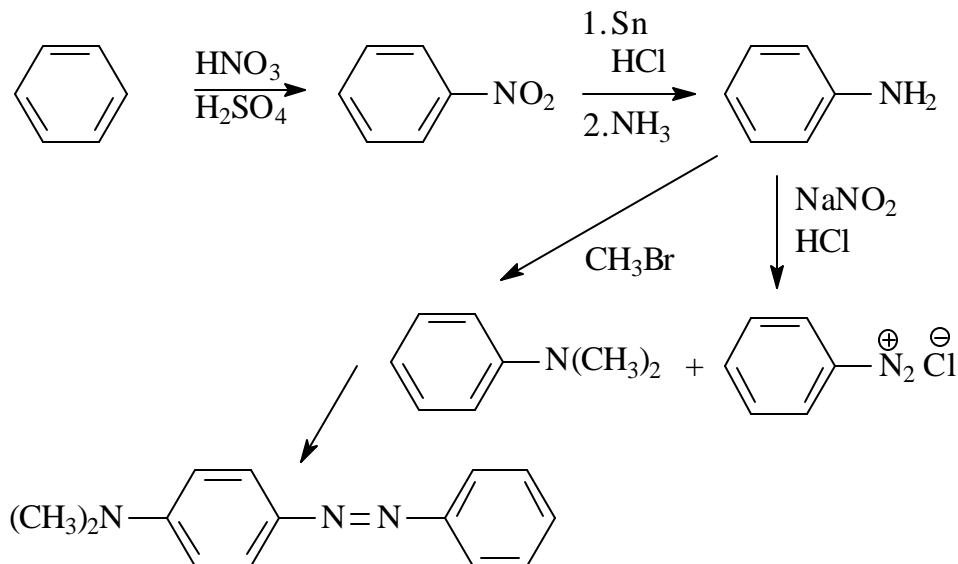
The benzoic acid could also be made by Friedel-Crafts alkylation of benzene, followed by oxidation of the alkyl side chain with KMnO_4 .

In this synthesis we have used the carboxyl group as the meta-directing group. It might appear that, as an alternative, one could nitrate first and then brominate, having the nitro group direct the incoming bromine to the meta position. That would work. But, converting the *m*-bromonitrobenzene to *m*-nitrobenzoic acid would not work since a nitro group cannot be present when a Grignard reagent is formed.

(b)



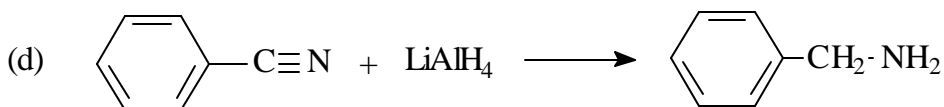
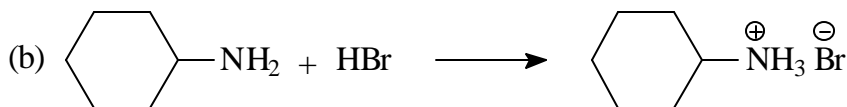
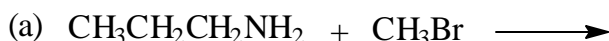
15. Propose a synthesis of *p*-(dimethylamino)azobenzene from benzene.



23. How can you explain the fact that trimethylamine (bp 3°C) has a lower boiling point than dimethylamine (bp 7°C)?

Since trimethylamine does not have a hydrogen attached to a nitrogen, it is not an associated liquid. Dimethylamine has one hydrogen attached to the nitrogen, so it is an associated liquid. So, even though the trimethylamine is more massive the dimethylamine has the higher boiling point owing to hydrogen bonding.

27. Show the products of the following reactions.

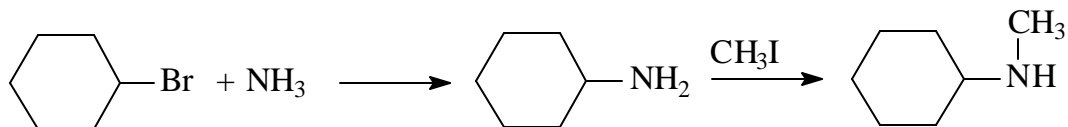
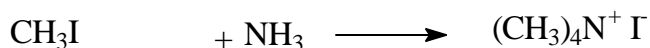
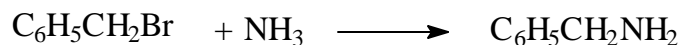
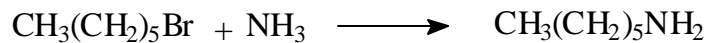


(a) It is very difficult to control the reaction between ammonia (or an amine) and an alkyl halide to give only one class of amine as product. The exception to this is that if you want the quaternary ammonium salt using an excess of the alkyl halide will give you mostly that product.

28. How might you prepare the following amines from ammonia and any alkyl halides needed?

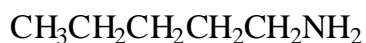
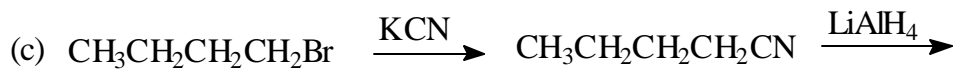
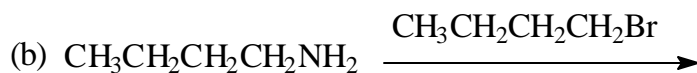
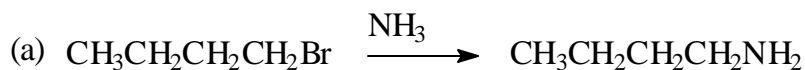
- (a) hexylamine, (b) benzylamine, (c) tetramethylammonium iodide,
(d) *N*-methylcyclohexylamine

It is very difficult to control the reaction between ammonia (or an amine) and an alkyl halide to give only one class of amine as product. The exception to this is that if you want the quaternary ammonium salt using an excess of the alkyl halide will give you mostly that product. On the other hand it is easy to write them down, so that is what we shall do.



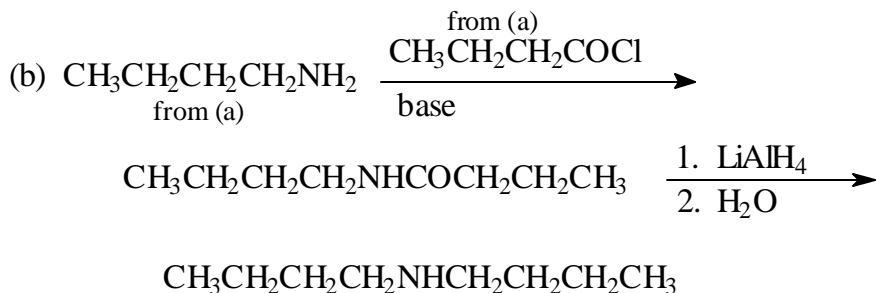
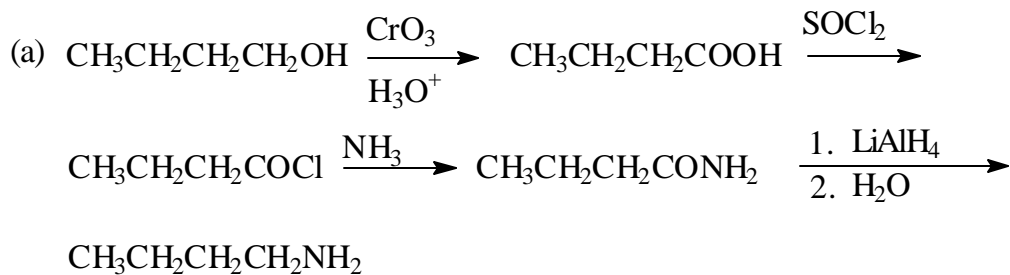
29. How might you prepare the following amines from 1-bromobutane?

(a) butylamine, (b) dibutylamine, (c) pentylamine



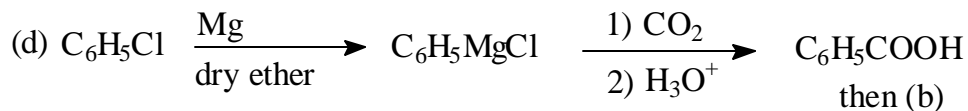
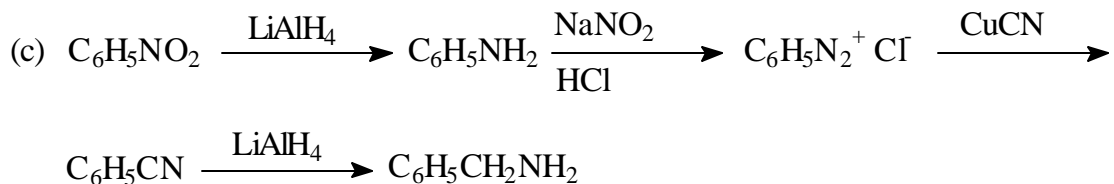
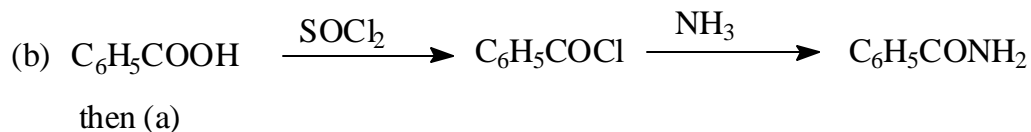
30. How might you prepare each of the amines in question #29 from 1-butanol?

We could convert the 1-butanol to 1-bromobutane using PBr_3 or HBr and then use the reactions in question #29. The following are additional possibilities for (a) and (b).



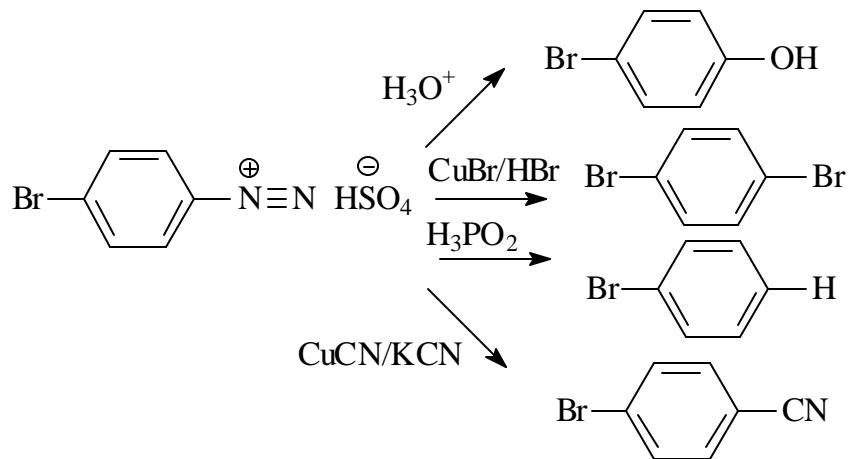
31. How would you prepare benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, from each of the following starting materials?

(a) benzamide, (b) benzoic acid, (c) nitrobenzene, (d) chlorobenzene

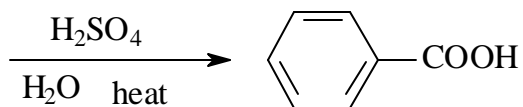
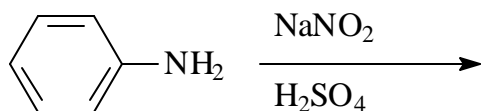


32. Write equations for the reaction of *p*-bromobenzenediazonium bisulfate with the following reagents.

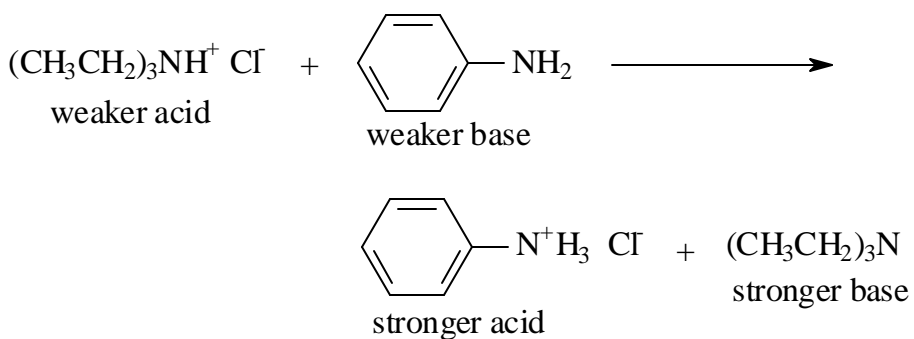
(a) H_3O^+ , (b) HBr , CuBr , (c) H_3PO_2 , (d) KCN , CuCN



33. Show how you might prepare benzoic acid from aniline. A diazotio replacement reaction is needed.



37. Which compound is more basic, triethylamine or aniline? Does the following reaction proceed as written?



Aliphatic amines are ordinarily more basic than aromatic ones. Since the weaker acid/weaker base pair will predominate in an acid-base equilibrium, the reaction would proceed to only a small extent in the direction shown.