

Experiment 16

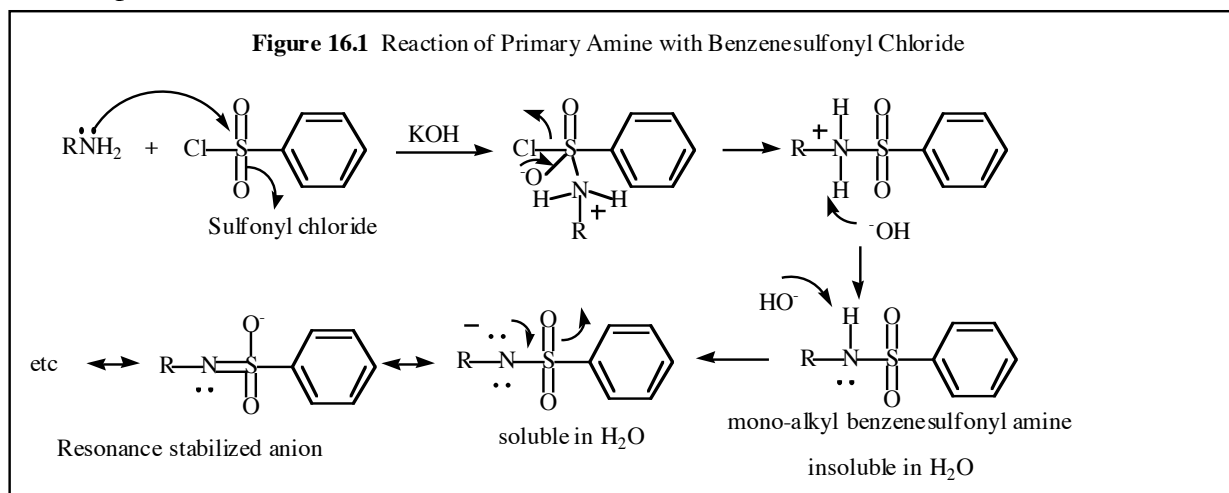
Qualitative Analysis of Amines and Amine Unknown

In this experiment we will use the Hinsberg Test and the Nitrous Acid Test in order to discriminate between primary, secondary and tertiary amines. We will first practice the test using known amines and then we will classify an unknown amine into one of the three categories. We will also use IR spectroscopy to help us in our determination.

Hinsberg Test

Primary, secondary and tertiary amines all have a lone pair that affects their reactivity. As we would expect, amines are basic and nucleophilic. The availability of the lone pair of electrons for attacking an electrophile (reaction as a nucleophile) or attacking a proton (reaction as a base) is strongly influenced by the substituents attached to the nitrogen atom. Alkyl groups are electron donating and increase basicity. Sulfonyl groups, like acyl and aryl groups, withdraw electrons and decrease the strength of the base. We will see that we take advantage of these facts in the Hinsberg test to discriminate between 1°, 2° and 3° amines.

The Hinsberg Test with a primary amine is shown in Figure 16.1. The amine is first reacted with benzenesulfonyl chloride in the presence of KOH. There is an addition-elimination reaction on the highly electrophilic sulfonyl chloride derivative. After step-wise loss of the chlorine and one proton from the amine, we get a mono-alkyl benzenesulfonyl amine that is insoluble in water. But this species does not remain in solution. The benzenesulfonyl group is a very strong electron withdrawing group. Therefore, the remaining hydrogen on the nitrogen is acidic and is lost to a hydroxide ion in the strongly basic conditions to give the final anionic species that is soluble in water. Note the resonance stabilization of this anion.



With secondary amines (Figure 16.2), the initial steps are the same to give a dialkyl benzenesulfonyl amine. This species is insoluble in water and does not have a hydrogen on its nitrogen. It cannot therefore ionize to give a soluble species. The product therefore is not soluble in water and furthermore it will not be soluble in an acidic solution since the lone pair on the amine is not basic due to the strongly electron withdrawing nature of the sulfonyl group.

Tertiary amines catalyze the decomposition of benzenesulfonyl chloride (Figure 16.3), but do not form stable compounds with it and remain unchanged. If the amine is soluble in water, it will remain soluble; if not, it will form an organic layer on top of the water. This layer, however, will dissolve in 5% hydrochloric acid.

Figure 16.2 Reaction of Secondary Amines with Benzenesulfonyl chloride

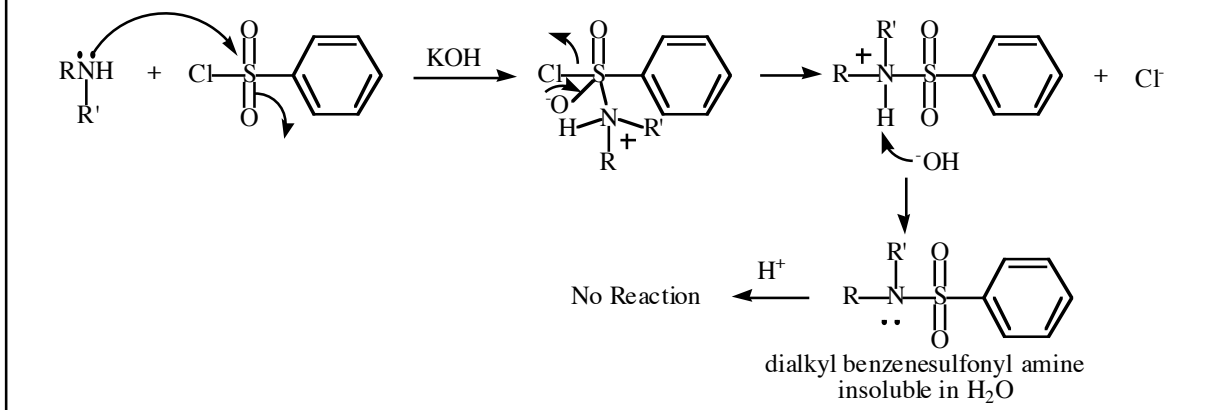
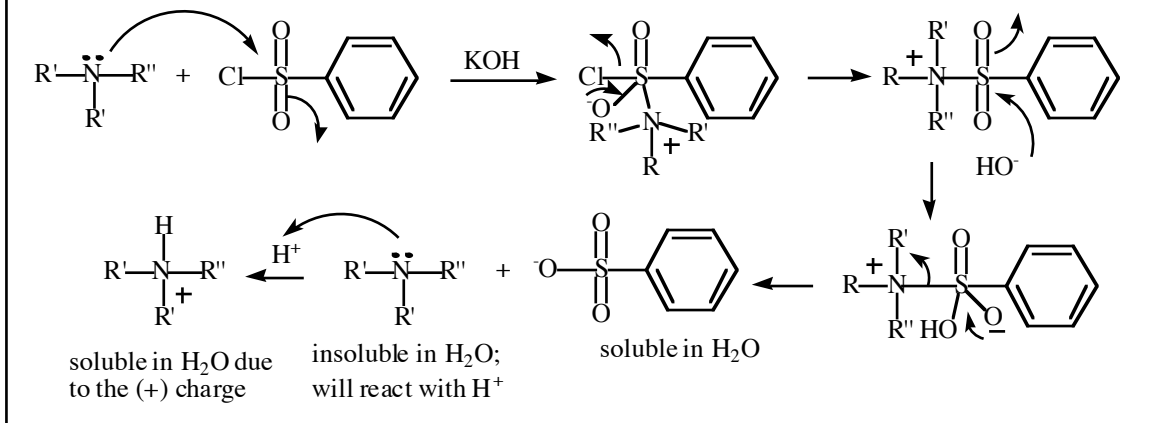


Figure 16.3 Reaction of Tertiary Amines with Benzenesulfonyl Chloride



Procedure:

Test the solubility in water of each amine you will use by adding ten drops of it to 10 mL water in a small test tube, shaking the mixture and checking for any material floating on top.

Add 8-10 drops of a primary amine to a large test tube. Add 10 mL 10% KOH . Add 10 drops benzenesulfonyl chloride. Shake vigorously to mix (use a cork). Check for the odor of benzenesulfonyl chloride by waving your hand toward you over the mouth of the tube. (DO NOT TAKE A DEEP BREATH WITH THE TUBE DIRECTLY UNDER YOUR NOSE.). If there is a small layer of material on the bottom of the main layer (and another small layer on the top of the main layer), this is unreacted sulfonyl chloride. Add 1-2 drops more aniline and shake vigorously until the small bottom layer disappears. The amine on the top of the water layer must come into contact with the sulfonyl chloride on the bottom of the water. Be careful to not add too much additional amine as this may form a layer on the top of the aqueous layer if the amine is water insoluble. The trick is to get exactly stoichiometric amounts of the sulfonyl chloride and the amine. At this point you should see only one layer. If there still seems to be benzenesulfonyl chloride, you may need to warm the test tube in a water bath for 10 min at 80-90 °C. Usually, however, this is not necessary.

If you see only one layer with the benzenesulfonyl chloride, then it means you have a primary amine. Confirm this by adding concentrated HCl until the pH is less than 4 (blue to Congo Red). At this point you should see a precipitate.

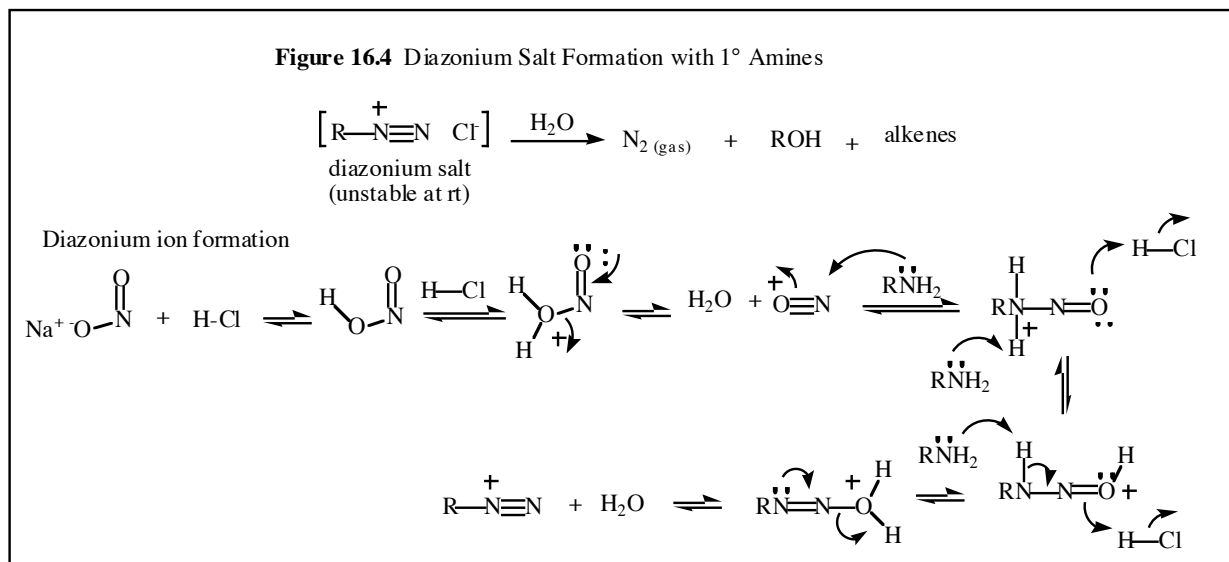
Repeat the benzene sulfonyl chloride treatment using a secondary amine and a tertiary amine. With the secondary amine you should see two layers. Draw off the lower aqueous layer with a separatory funnel and see if the organic layer is soluble in 5% HCl. If it is not, you have a secondary amine. With tertiary amines, solubility will depend on the amine. Those that are water-soluble will remain water-soluble during all of the above procedures. Those that are not water-soluble will remain so and float on top during the Hinsberg test. This top layer, however, will be soluble in 5% HCl and this distinguishes tertiary from secondary amines.

Repeat the Hinsberg test with your unknown.

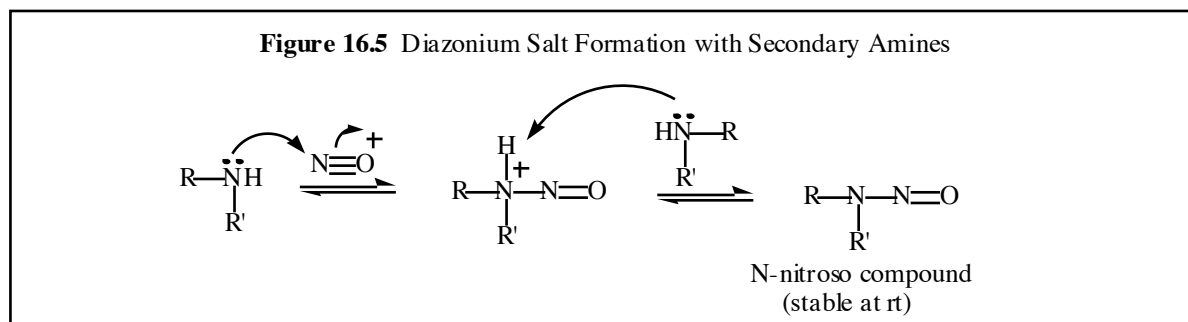
Nitrous Acid Test:

Confirm the results of your Hinsberg Test using the nitrous acid test. Practice the test first using a known primary, a secondary and a tertiary amine before trying it with your unknown.

Treatment of the primary aliphatic amine (Figure 16.4) with sodium nitrite in the presence of hydrochloric acid generates the very reactive and electron deficient nitrosyl ion which reacts rapidly with the nucleophilic amine to give an adduct which then loses water to give the diazonium salt. This is unstable and immediately loses N₂ gas, which bubbles out of the solution.

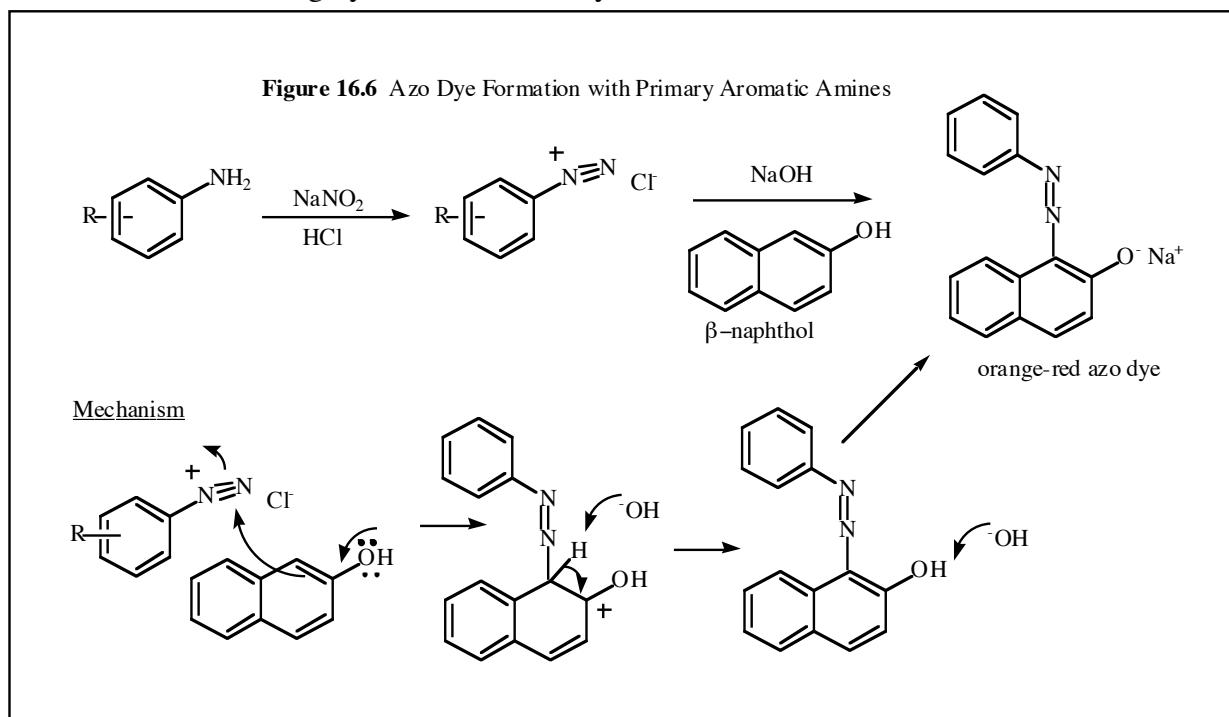


With secondary amines, an N-nitroso compound is formed when the amine attacks the nitroso ion (Figure 16.5). This is relatively stable and separates from the aqueous solution as a yellow or orange liquid. No N₂ gas is evolved.



With tertiary amines there is no reaction. With primary aromatic amines the diazonium salt is stable at low temperature and does not decompose to release N₂ gas. The presence of a primary aromatic amine can be confirmed by treatment with β-naphthol in the presence of sodium hydroxide. The highly electron rich β-

naphthol attacks the electron deficient diazonium salt to form a new carbon-nitrogen bond as shown in Figure 16.6. The adduct is a highly colored red azo dye.



Procedure:

Dissolve 2-3 drops of your liquid amine in 2.0 mL of 2.0 M HCl in a small test tube. Cool to 5-10 °C in an ice bath and add 5 drops of cold 20% aqueous sodium nitrite solution.

The immediate evolution of a colorless gas (nitrogen) indicates a primary, aliphatic amine.

If no gas was evolved but an insoluble yellow or orange liquid separated from the solution, then this is indicative of a secondary aliphatic or aromatic amine.

If no gas was evolved and no yellow liquid separated then this is indicative that no reaction occurred and the amine tested is a tertiary amine.

Another possibility is that the compound is a primary, aromatic amine. These form diazonium salts that are stable at low temperatures. If no nitrogen gas was observed evolving, then add a few drops of the cold reaction mixture to a cold solution of 50 mg beta-naphthol in 2 mL of 2.0 M sodium hydroxide. The formation of an orange/red azo dye indicates a primary aromatic amine.

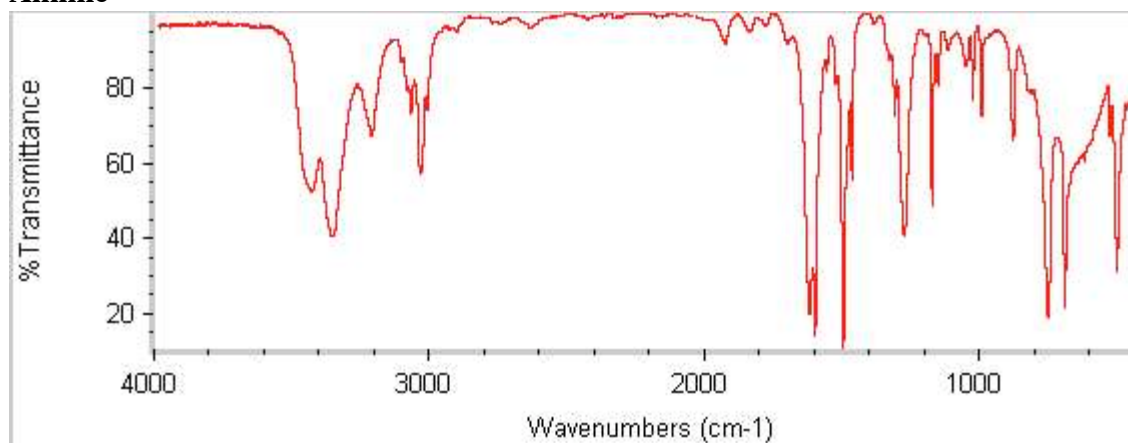
IR Spectroscopy

Infrared spectroscopy is an excellent way to confirm the results of your Hinsberg test and nitrous acid test. When you have finished the Hinsberg test and the nitrous acid test and are reasonably confident that you have the correct answer, take an IR of your unknown amine. With a 1° amine, you should see two N-H stretching bands in the 3300-3500 cm^{-1} region. With a 2° amine you should see only one band in this region and if you have a tertiary amine, there are no N-H stretching bands since you do not have any N-H bonds. You can confirm the exact identity of your unknown amine by matching it with one of the spectra of the amines given in Appendix 16.1.

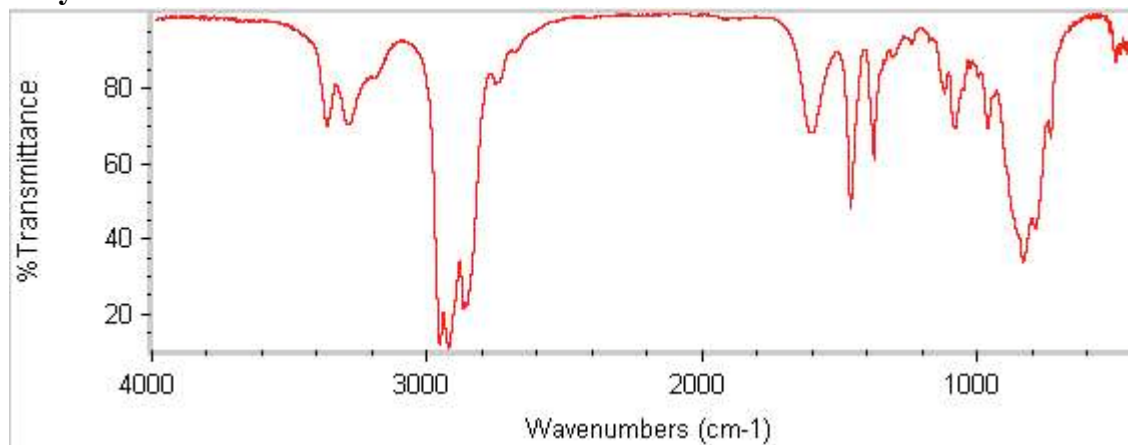
When you are confident of your answer, fill out an Unknown Organic Report Sheet and turn it in.

Appendix 16.1 Infrared Spectra of Unknown Amines

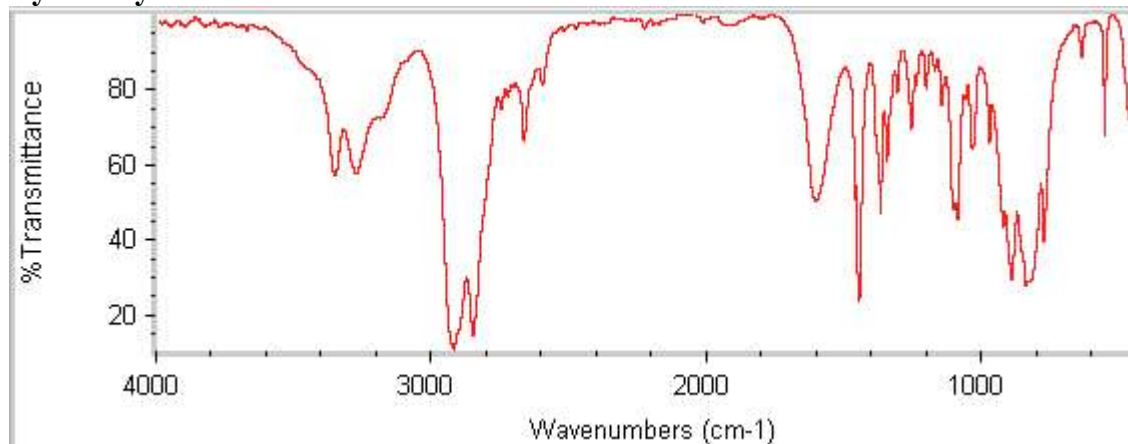
Aniline



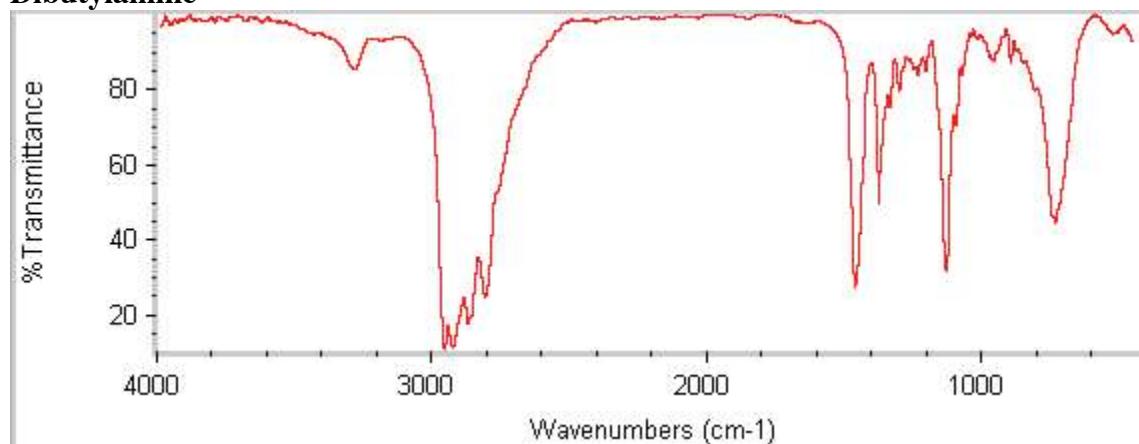
Butylamine



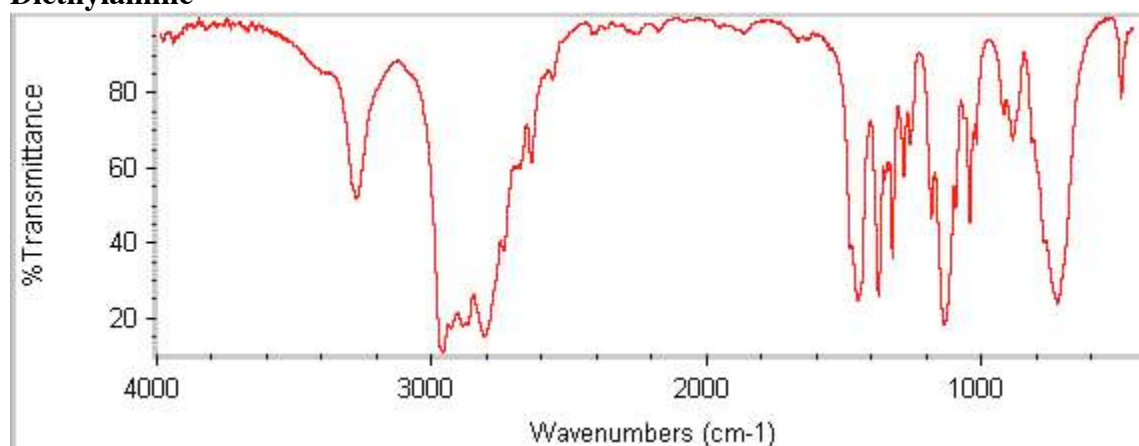
Cyclohexylamine



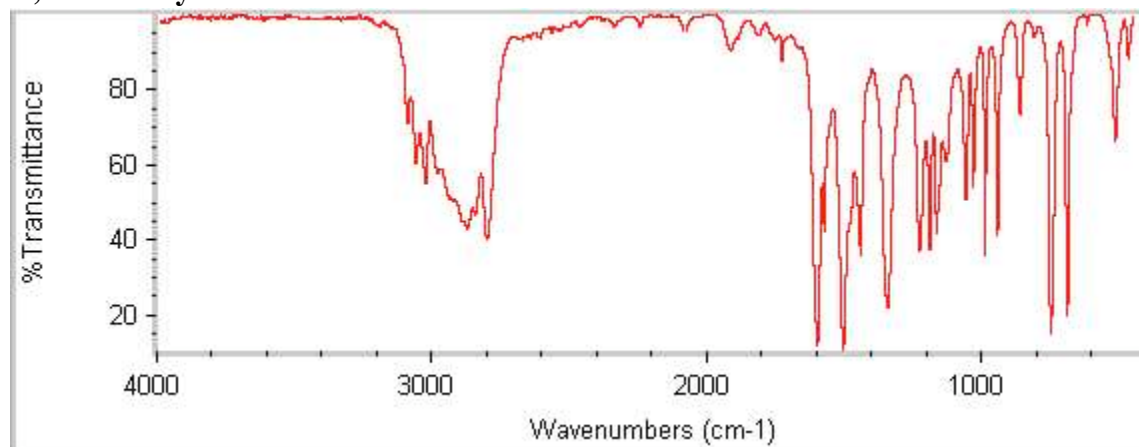
Dibutylamine



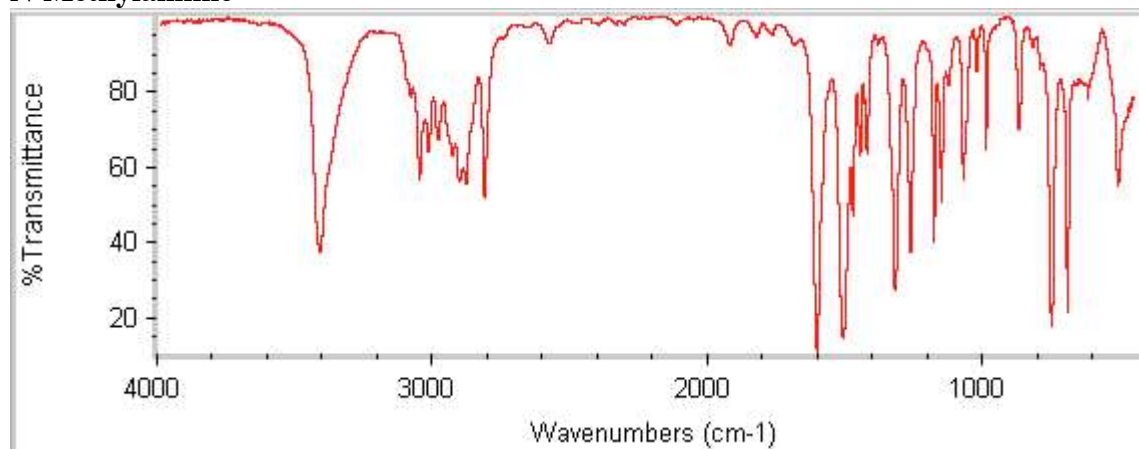
Diethylamine



N,N-Dimethylaniline



N-Methylaniline



Triethylamine

