Identificatiion of Organic Compounds

4th Stage Students

By

Prof. Dr. Farouq E. Hawaiz
Asst. Proff. Dr. Mohammed K. Samad
Lec. Marlin Y. Aziz
Lec. Mzgin M. Ayoob

Contents

SAFETY AND TECHNIQUE RULES

Safety in the laboratory is extremely important. It is expected that you know laboratory safety rules. It is important that if you feel uncomfortable with your knowledge of these rule that you take the time to learn them. There is NO excuse for not following safety rules.

1. Be attentive to instructions and follow them carefully.

2. If you ever have any questions about the procedure, apparatus, or chemicals it is important that you ask the Instructor or Instructional assistant.

3. Do not perform any unauthorized experiments. Anyone found doing so faces permanent expulsion from class.

4. Do not handle chemicals or materials not assigned to you or not called for in the experiment.

5. Learn the location and proper use of the fire extinguisher,

6. Coats, books, etc., should be kept in the good place. Many of the chemicals used in the lab can ruin or stain paper and clothing.

7. Never taste chemicals, nor pipet by mouth. Always use pipet bulbs or wheels.

8. Smell chemicals by fanning a little vapor towards you.

9. Experiments in which dangerous or obnoxious fumes are produced must be done in the fume hood. Be sure to stop these reactions as soon as possible.

10. No eating, drinking or smoking in the lab.

11. Never point test tubes at yourself or others.

12. In the event of any injury, spill or glass breakage, inform the Instructor immediately.

13. Goggles must be worn at all times when in the lab.

14. Chemicals may not be taken out of the lab.

15. Avoid unnecessary contact with ALL chemicals.

16. Do not leave lit burners unattended

17. Every time you use a chemical read its label carefully. If any discrepancies inform the instructor immediately.

18. All containers which contain a chemical or in which a reaction occurs must be labeled.

19. When labeling a storage container include name and/or formula of chemical, any appropriate warnings, concentration, date and your name.

20. NEVER place anything inside a reagent bottle, no spatulas, droppers, nor pipets. If the reagent is a clumpy solid inform the IA. Proper technique is to "roll"

21. Containers from side to side to remove solids and to pour liquids into smaller containers (such as a beaker) first.

22. NEVER return unused chemical (liquids or solids) back to the original container -
offer excess to another student or dispose of it appropriately.
23. Be conservative of reagents; place only the amount you need into a labeled container (such as a beaker). Do not take the reagent bottles to your work area - leave them where everyone can find them.
24. Use tap water to wash glassware - you should rinse with D.W- please be conservative.
25. To dilute acids and bases, add the Acid (or Base) to the Water.
26. Dispose of liquids and solids appropriately, read the board, or your experimental
procedure for special instructions, otherwise dispose of liquids and soluble solids down the sink with lots of water, insoluble Is materials (such as paper towels) should be put in the waste basket. KEEP THE SINKS CLEAN
27. It is very important to keep the lab clean. Before you leave each time be sure to:
a) Return equipment to its proper place
b) Clean up your workspace with the sponge
c) Put away your lab ware
There is NO reason for a messy lab. Everything you need to keep your lab neat and clean is available. Dirty counters, paper left in the sink or troughs, lab ware left out, messes left under the fume hood, chemical spills left on the balance, are BAD technique and as such will not be tolerated.
28. You may not be in the laboratory at any time other than your scheduled laboratory period unless you have the permission of the instructor in charge as well as your course instructor. Do not visit friends during their lab time and do not invite your friends or family to visit you**.**

Solubility of Organic Compounds

Important information about organic compounds and their functional groups can already be obtained by means of simple solubility tests. In Experiment you will acquire a technique that allows you to quickly characterize unknown compounds and to classify them on the basis of their polarity and acid/base properties, respectively. You will become acquainted with a "solubility theory", which you need as a basis to understand and apply the most common working-up procedure.

Generally, most organic compounds are (very) readily soluble in diethyl ether (Et2O, frequently called just ether) and only sparingly soluble in water. Exceptions from this rule are functionalized compounds with only a few carbon atoms (1 to about 5 C atoms, depending on the functional group), poly functionalized compounds, and organic salts. Some of them are very poorly soluble in organic solvents but, as a rule, readily soluble in water instead.

Solubility Groups, Solubility Tree

On the basis of their solubilities, organic compounds can be classified as follows:

Group I: soluble in water and ether.

Monofunctionalized, polar substances with neutral charge and up to about 5 C atoms. This group includes acidic, basic, and neutral compounds in sub-groups.

Group II: soluble in water; not or only sparingly soluble in ether.

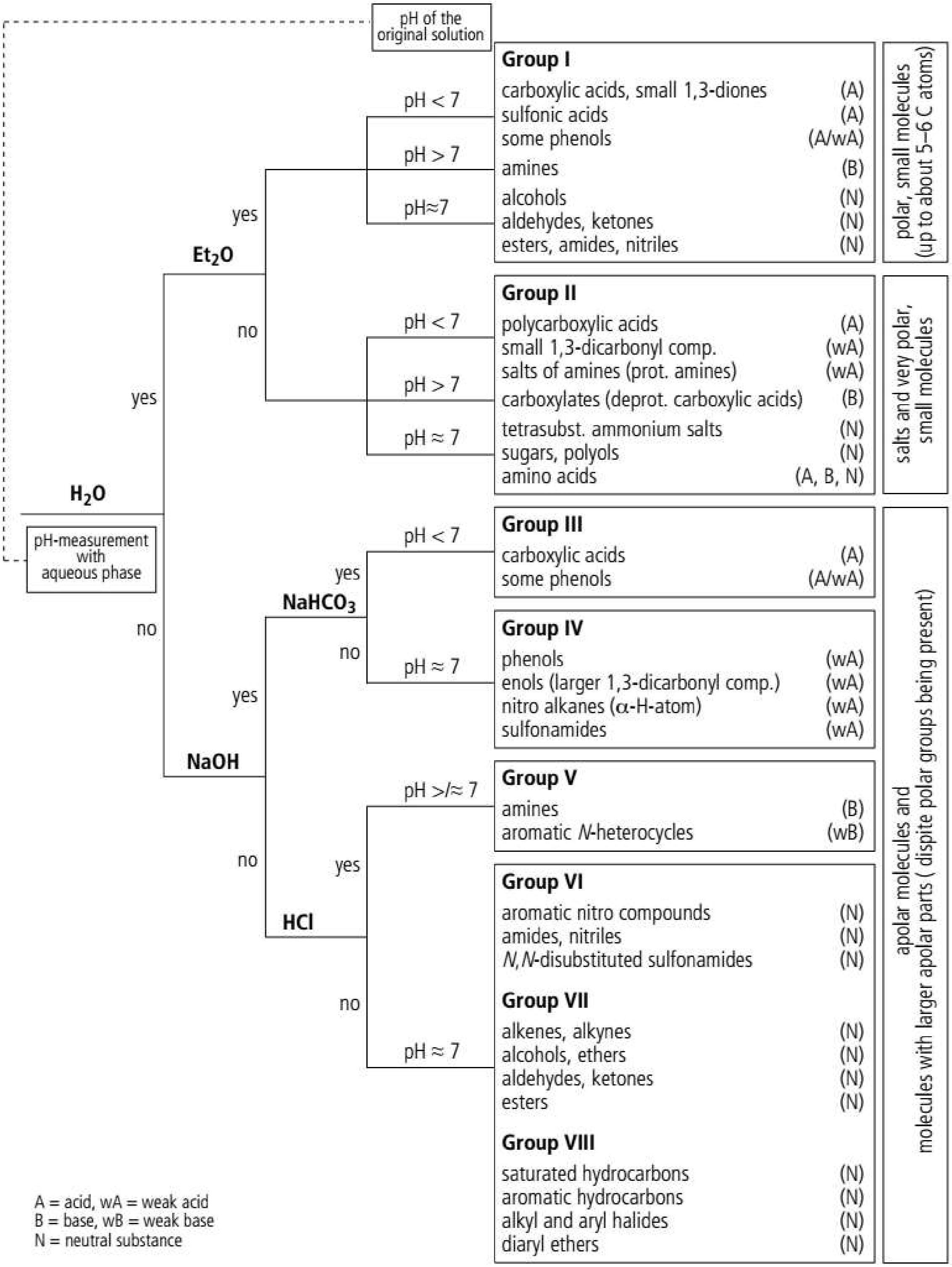
Very polar substances with neutral charge containing several functional groups or organic salts. This group includes acidic, basic, and neutral compounds in sub-groups.

Group III: soluble in ether; not or only sparingly soluble in water and acid; readily soluble in weak or strong base.Relatively strong organic acids ($pKa \leq$ ca. 7–8) with sufficiently large apolar structural parts: carboxylic acids with larger hydrocarbon residues and substituted electron-deficient phenols.

Group IV: soluble in ether; not or only sparingly soluble in water, acid, and weak base; readily soluble in strong base. Weak organic acids (approx. $8 \leq pKa \leq$ ca. 14) with sufficiently large apolar structural parts: substituted electron-rich phenols, enols (dicarbonyl compounds), primary and secondary nitroalkanes, and N-mono/N-unsubstituted sulfonamides.

Group V: soluble in ether; not or only sparingly soluble in water and base; readily soluble in diluted acid. Organic bases ($pKb \leq$ approx. 15, mostly N-containing compounds) with sufficiently large apolar structural parts: amines, aryl amines, and aromatic heterocycles.

Group VI-VIII: soluble in ether; not or only sparingly soluble in aqueous systems. Neutral substances: little polar compounds that can be further classified due to their N/Scontent and their ability to be protonated by conc. H_2SO_4 (see below).


pH of the original solution
H2O
pH-measurement with aqueous phase
yes
Et2O
yes
pH < 7
pH > 7
pH≈7
Group I
carboxylic acids, small 1,3-diones (A)
sulfonic acids (A)
some phenols (A/wA)
amines (B)
alcohols (N)
aldehydes, ketones (N)
esters, amides, nitriles (N)
polar, small molecules (up to about 5–6 C atoms)
no
pH < 7
pH > 7
pH ≈ 7
Group II
polycarboxylic acids (A)
small 1,3-dicarbonyl comp. (wA)
salts of amines (prot. amines) (wA)
carboxylates (deprot. carboxylic acids) (B)
tetrasubst. ammonium salts (N)
sugars, polyols (N)
amino acids (A, B, N)
salts and very polar, small molecules
no
NaOH
yes
NaHCO3
yes
pH < 7
Group III
carboxylic acids (A)
some phenols (A/wA)
no
pH ≈ 7
Group IV
phenols (wA)
enols (larger 1,3-dicarbonyl comp.) (wA)
nitro alkanes (α-H-atom) (wA)
sulfonamides (wA)
no
HCl
yes
pH >/≈ 7
Group V
amines (B)
aromatic N-heterocycles (wB)
no
pH ≈ 7
Group VI
aromatic nitro compounds (N)
amides, nitriles (N)
N,N-disubstituted sulfonamides (N)
Group VII
alkenes, alkynes (N)
alcohols, ethers (N)
aldehydes, ketones (N)
esters (N)
Group VIII
saturated hydrocarbons (N)
aromatic hydrocarbons (N)
alkyl and aryl halides (N)
diaryl ethers (N)
apolar molecules and molecules with larger apolar parts (dispite polar groups being present)
A = acid, wA = weak acid
B = base, wB = weak base
N = neutral substance

Classification of the Neutral Substances

The neutral substances can be sub classified into compounds of the groups VI–VIII. For this, not only the solubility arguments are taken into account. At first, the samples are analyzed qualitatively for their content of N and S (group VI), and the N/S-free compounds are further classified into the groups VII (receptive towards protonation by conc. H_2SO_4) and VIII (inert):

Group VI: not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains N and/or S. Neutral substances with N- and/or S-containing groups and sufficiently large apolar residues.

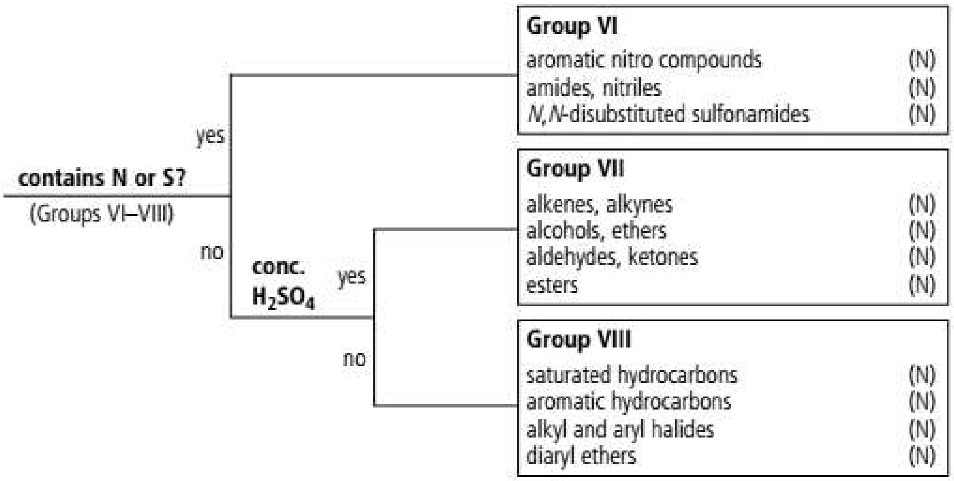
Group VII: not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains neither N nor S; soluble in conc. H_2SO_4.

Neutral substances containing O, double and/or triple bonds that can be protonated by conc.H_2SO_4 (mostly with decomposition!).

Group VIII: not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains neither N nor S; insoluble in conc. H_2SO_4.

Neutral compounds that are inert even towards strong acid.

The "solubility tree" is supplemented, thus, as follows:



To analyze the sample for nitrogen and sulfur (and halogens), the compound is fused with sodium. N-containing compounds produce CN– in the sodium fusion, S-containing compounds produce S2– (and SCN–, provided that N is contained as well), and halogen-containing substances produce the corresponding halides.

Preliminary Evaluation

On the basis of the information collected in your table, classify each of your samples as belonging to the groups I, II, III, IV, V, or VI–VIII. Confirm your results with your teaching assistant before proceeding.

Sodium Fusion and Detection of Nitrogen, Sulfur, and Halogen

To assign the compounds that were found to belong to the groups VI–VIII (only these!) to group VI or to the groups VII/VIII, they are analyzed for their content of N and/or S (group VI). For this purpose, sodium fusion and subsequent anion analysis is performed .

Sodium Fusion

Into a combustion tube, add some liquid sample (to a heighth of about 5 mm, by dipping the pipette completely to the bottom of the tube and avoiding spills on the tube wall) or some solid sample (20–30 mg). Hold the tube with the crucible tongs slightly inclined and introduce a freshly cut piece of Na (about 4×1×1 mm) by means of tweezers so that it lies about 5 mm above the substance. Then heat the Na in the tube, which is still kept inclined, with the small sharp flame of your Bunsen burner to melting avoid heating your sample too strongly. Allow the liquid metal to flow into the sample where it reacts (often violently). Heat the Na and the substance until the glass tube becomes red by heat and the sample got charred. Drop the still hot tube into a test tube with about 8 ml of deionized H_2O, where the combustion tube should break into pieces. Shake shortly to dissolve the Na salts, filter off the solution (= sodium fusion solution); if appropriate, rinse the test tube with 2–3 ml of H_2O and supplement the sodium fusion solution with it.

Attention: There might be some Na left in the combustion tube that will violently react with the water. Therefore, perform this experiment with the appropriate care in the fume hood, with the sash pulled down. Never keep any organic solvent in the immediate proximity of your experiment!
Complete the procedure of heating the fusion tube and crushing it by dipping it into a test tube containing H_2O in any case, even if the sodium fusion fails. It is imperative to destroy any remaining, highly reactive elemental sodium under controlled conditions to avoid accidents.

Organic compounds that contain N form upon sodium fusion CN– (particularly amides, imides, imines — to a lesser extent alkyl amines and their ammonium salts). Organic compound with S^-content form S^{2-} and those with halogen-content Hal–. The several ions can be detected by specific test reactions:

Detection of Nitrogen (Lassaigne Test for CN^-)

Add a small amount of $FeSO_4 \cdot 7\ H_2O$ (tip of the spatula; about 20 mg) to 1 ml of the sodium fusion solution and heat the mixture. The iron(II) salt dissolves, the color of the solution turns yellow to dark green, and iron hydroxides precipitate. Acidify the mixture with a few drops of 2 M H_2SO_4. In the presence of CN^-, Prussian blue, a deeply blue complex salt of the formula $Fe(III)[Fe(III)Fe(II)(CN)_6]_3$, forms, which you can easily observe when you give some drops of the thoroughly shaken solution onto a filter paper.

Detection of Sulfur

Add a few drops of 1 M aq. sodium nitroprusside solution ($Na_2[Fe(CN)_5NO]$) to 0.5 ml of the sodium fusion solution. A purple-violet color indicates the presence of S2$^-$.

The NO^+ of the prusside reacts with S2– to NOS– (sulfur analog of NO2 $^-$) and the purple colored complex anion [Fe(CN)5NOS]4– is formed.

Detection of Chloride (and other Halides)

To decide to which of the three groups VI–VIII your sample belongs, the knowledge of its halogen-content is not necessary. However, having the sodium fusion solution at hand, the additional information can be used for further characterization of the product. For halogen detection:
Acidify 0.5 ml of the sodium fusion solution with 2 M HNO_3, and, in case you have detected N or S, boil the solution in the fume hood to expel HCN (prussic acid!) and/or H_2S. Then add several drops of 0.5 M $AgNO_3$. The formation of a colorless precipitate indicates the presence of a halogenide   in our case this would be Cl^-

Distinction of Groups VII and VIII

To assign the compounds of the groups VII and VIII, their solubility in conc. H_2SO_4 is investigated. Thus, place 5 drops of the liquid substance (or the amount that fits on the tip of a spatula; about 20–50 mg) of the pulverized solid substance into a small test tube and add then dropwise the acid to your sample. Shake carefully and observe dissolution (→ group VII).It is important to know that apart from protonation also other reactionsvmight occur under the strongly acidic conditions (most often subsequent reactions with the protonated species). These reactions are often irreversible. Significant changes of color indicate reactions and, therefore, the presence of functional groups. The respective sample is then also assigned to group VII.

Attention: conc. H_2SO_4 is aggressive and highly corrosive. Avoid contact with skin. In case of spilling, dilute immediately with cold water.

Ignition Test

Procedure

Place a 1mg sample of the substance in a porcelain crucible lid (or any piece of porcelain) and bring the sample to the edge of a flame to determine flammability. Heat the sample gently over a low flame, behind a safety shield. Heat the sample until ignitionhas occurred.

Note (1) the flammability and nature of the flame (is the compound explosive?); (2) whether the compound is a solid, whether it melts, and the manner of its melting; (3) the odor of the gases or vapors evolved (caution!); and (4) the residue left after ignition.

Discussion

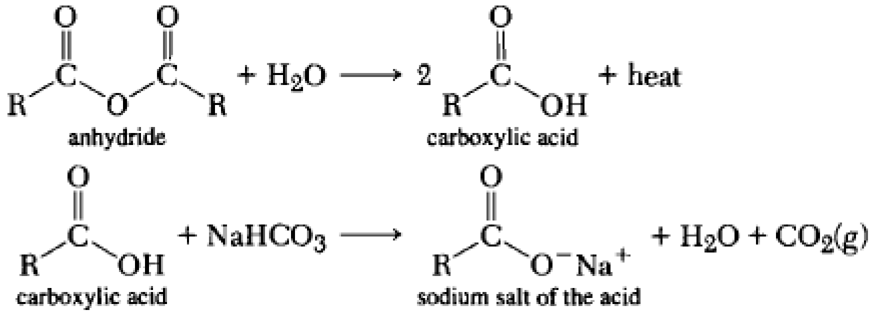
Many liquids burn with a characteristic flame that assists in determining the nature of the compound. Thus, an aromatic hydrocarbon (which has a relatively high carbon content) burns with a yellow, sooty flame. Aliphatic hydrocarbons burn with flames that are yellow but much less sooty. As the oxygen content of the compound increases, the flame becomes more and more clear (blue). If the substance is flammable, the usual precautions must be taken in subsequent manipulation of the compound. This test also shows whether the melting point of a solid should be taken and indicates whether the solid is explosive.

If an inorganic residue l is left after ignition, it should be examined for metallic elements. A few simple tests will often determine the nature of the metal present.2 If the flame test indicates sodium, a sample of the compound should be ignited on a platinum foil instead of a porcelain crucible cover. (Why?)

CHEMICAL TESTS FOR FUNCTIONAL GROUPS

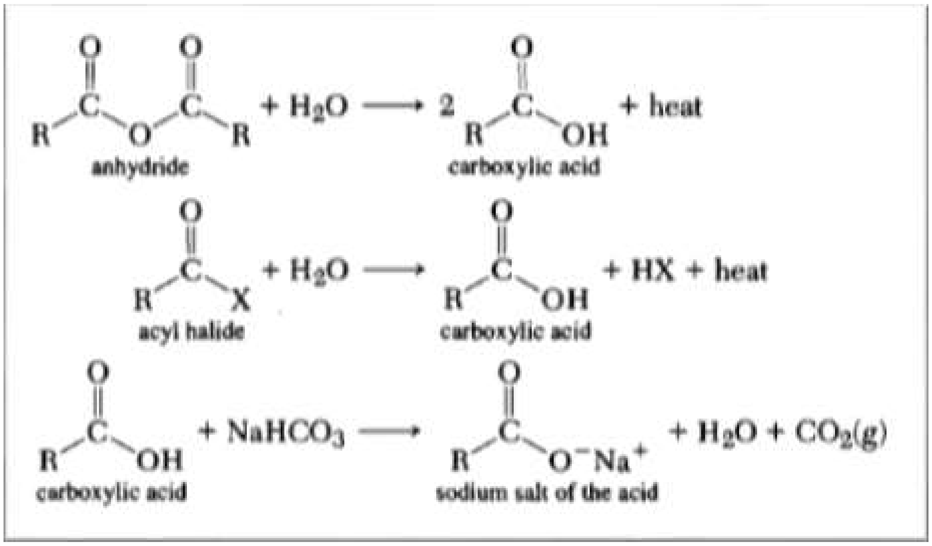
ACID ANHYDRIDES

The presence of acid anhydrides in an unknown sample can be demonstrated by several tests. Many acid anhydrides are rapidly converted by water to the corresponding carboxylic acids (Experiment 1). Large aliphatic anhydrides and aromatic anhydrides are not readily hydrolyzed with water. The presence of the carboxylic acid is detected by the addition of sodium bicarbonate, which results in the evolution of carbon dioxide gas, the sodium salt of the acid, and water.



Experiment (1) Hydrolysis of Acid Anhydrides and Acyl Halides

The anhydride and acid chloride tests are closely related below.



Procedure:

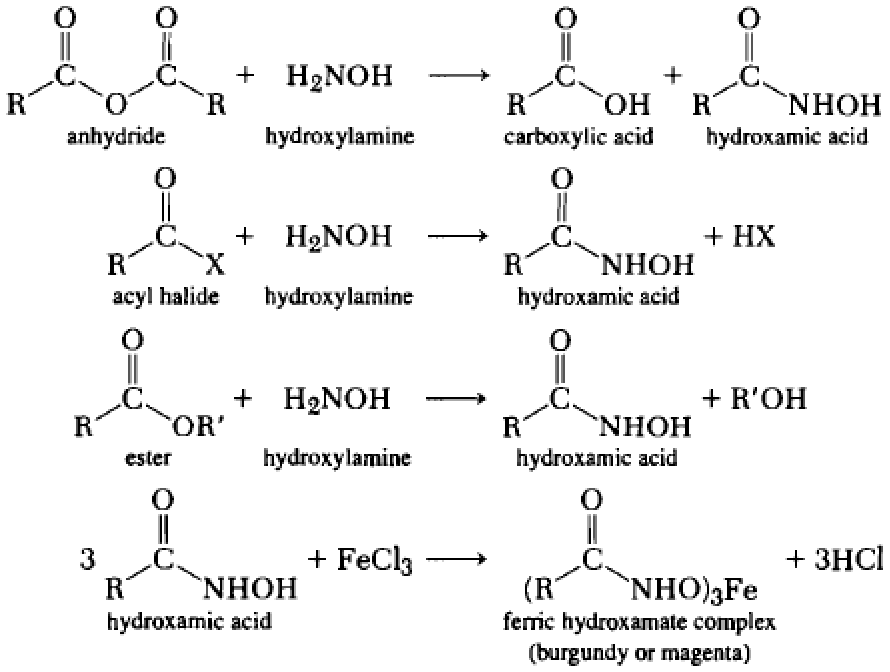
Cautiously add a few drops or a few crystals of the unknown compound to 1 mL of water and touch the test tube to see if heat is evolved. If the test tube is warm, then the test is positive for an acid anhydride or an acyl halide, since water will react with these compounds to form the carboxylic acid with the evolution of heat. Add 1mL of methanol to dissolve the sample. Pour the solution into 1 mL of a saturated solution of sodium bicarbonate. Evolution of carbon dioxide gas is a positive test for the presence of the product carboxylic acid.

Experiment (2) Hydroxamic Acid Test

(a) Preliminary Test

Dissolve a drop or a few crystals of the compound to be tested in 1 mL of 95% ethanol and add 1 mL of 1 M hydrochloric acid. Note the color produced when one drop of 5% ferric chloride solution is added to the solution. If a definite orange, red, blue, or violet color is produced, the following test for the acyl group is not applicable and should be omitted. Too much hydrochloric acid prevents the development ofcolored complexes of many phenols and all enols.

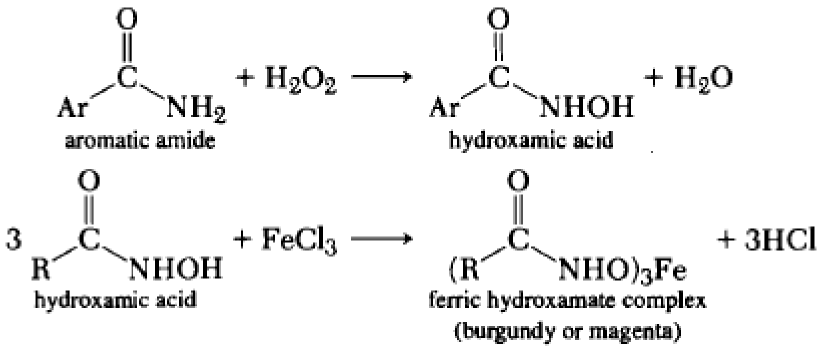
(b) Hydroxamic Acid Fonnation from Anhydrides, Acyl Halides, and Esters



Procedure:

Heat to boiling a mixture of one drop or about 40 mg of the compound, 1 mL of 0.5 M hydroxylamine hydrochloride in 95% ethanol, and 0.2 mL of 6 M sodium hydroxide. After the solution has cooled slightly, cautiously add 2 mL of 1 M hydrochloric acid. Anhydrides, acyl halides, and esters react with hydroxylamine to form the hydroxamic acid, as indicated in the above equations. If the solution is cloudy, add 2 mL of 95% ethanol. Observe the color produced when one drop of 5% ferric chloride solution is added. If the color caused by the drop of ferric chloride solution does not persist, continue to add the ferric chloride solution drop wise until the observed color permeates the entire test solution. Compare the color with that produced in (a). A positive test will be a distinct burgundy or magenta color of the ferric hydroxamate complex, which is formed upon the reaction of the hydroxamic acid with the ferric chloride. Compare the color of this solution with the yellow observed when the original compound is tested with ferric chloride in the presence of acid.

(c) Hydroxamic Acid Formation from Aromatic Primary Amides:

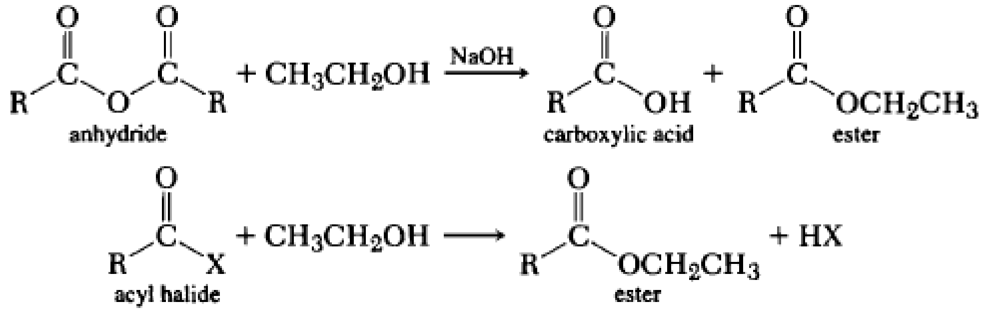


Procedure:

This procedure tests for the presence of an aromatic primary amide, which would give a negative result when analyzed with experiment (c). Place 50 mg of the unknown in 5 mL of water. Add 0.5 mL of 3% hydrogen peroxide and two drops of 5% ferric chloride solution. Heat the solution to boiling. The hydrogen peroxide reacts with the aromatic amide to form the hydroxamic acid, which then reacts with the ferric chloride to form ferric hydroxamate complex. The characteristic magenta color should develop if the compound is an aromatic primary amide.

Experiment (3) Ester Formation

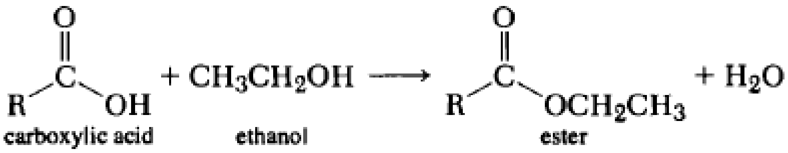
(a) The Schotten-Baumann Reaction



Procedure:

Place 0.5 mL of ethanol, 1mL of water, and 2mL or 0.20g of the unknown compound in a small flask. To this solution add in portions, with vigorous shaking, 2 mL of 20% sodium hydroxide solution. Stopper the flask and shake the mixture for several minutes and then test the solution with litmus paper to make sure that it is still alkaline. The anhydrides and acyl halides will undergo a reaction with alcohols under basic conditions to form esters. Esters are both insoluble in water and less dense than water and thus will form a layer on top of the water.

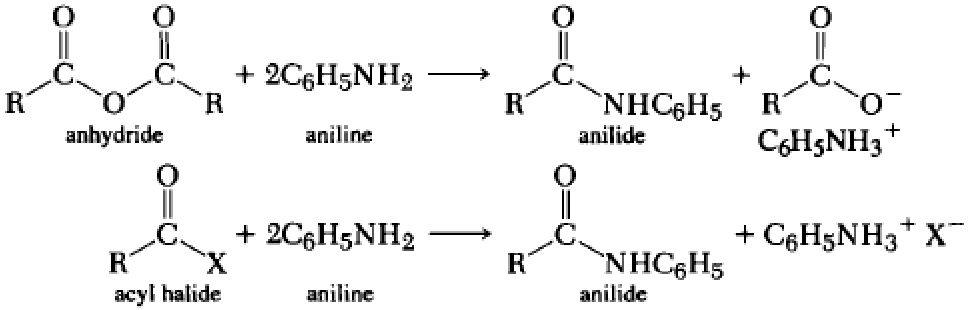
(b) Esterification of a Carboxylic Acid



Procedure:

Warm a mixture of 0.20 g of the compound, 0.40 mL of absolute ethanol, and 0.20 mL of concentrated sulfuric acid over a steam bath or hot-water bath for 2 min. Pour the mixture slowly into an evaporating dish containing 2 mL of saturated sodium bicarbonate solution. A second layer should be formed. Carefully smell the mixture. The presence of a sweet, fruity smell in the product, where no such smell existed in the original unknown, indicates that the original compound was a carboxylic acid and the acid was esterified. Large-molecular-weight carboxylic acids produce esters that are odorless.

Experiment (4) Anilide Formation from Acid Anhydrides and Acyl Halides



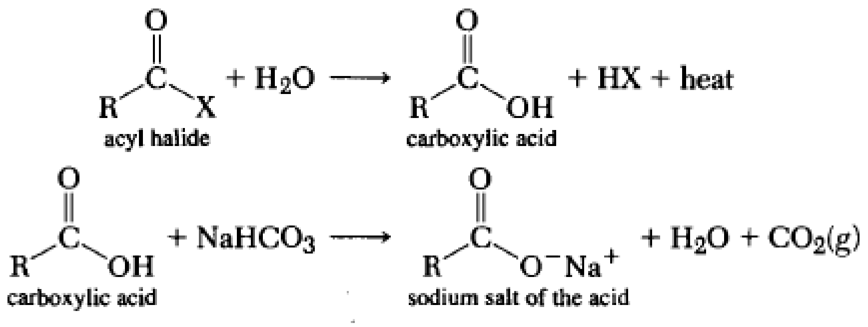
Procedure:

(a) Add a few drops or a few crystals of the unknown sample to 0.5 mL of aniline. Pour the mixture into 5 mL of water. A positive test is the precipitation of the solid anilide.

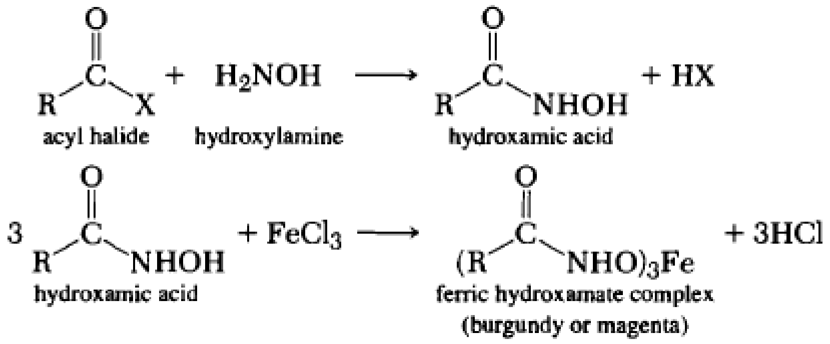
(b) In a small flask, place 0.2 mL of aniline, 1 mL of water, and 0.2 mL or 0.2 g of the unknown. Add in portions, with vigorous shaking, 10 mL of 20% sodium hydroxide solution. Shake the mixture in a stoppered flask for several minutes, and then test the solution with litmus paper to make sure that it is still alkaline. A positive test is the formation of a precipitate.

ACYL HALIDES:

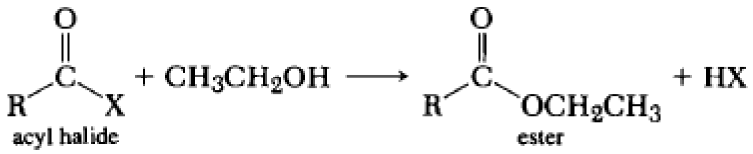
The same experiments that are used to the detect the presence of acid anhydrides can be used for acyl halides. Theory predicts that the acyl halides are more reactive. Acid halides can be hydrolyzed to carboxylic acids (Experiment 1). Addition of sodium bicarbonate to the solution produces the observable evolution of carbon dioxide gas, the sodium salt of the acid, and water.



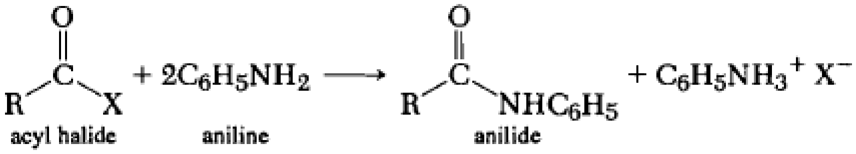
The hydroxamic acid test also will give a positive result for acid halides (Experiment 2b). The acyl halide undergoes reaction with the hydroxylamine to form a hydroxamic acid, which is then treated with ferric chloride to form the magenta-colored ferric hydroxamate complex



Acid halides undergo reaction with alcohols to form esters (Experiment 3a). The esters form an upper layer with the basic aqueous layer.

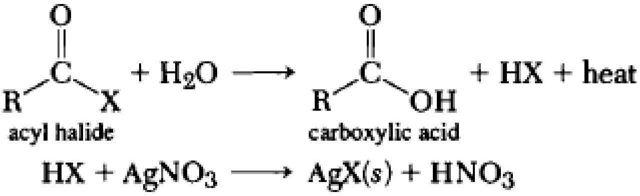


Aniline undergoes reaction with acid halides to form anilides, which precipitate from the solution (Experiment 4).



$$RCOX + 2C_6H_5NH_2 \longrightarrow RCONHC_6H_5 + C_6H_5NH_3^+\,X^-$$

To distinguish between the acid anhydride and the acyl halide, the silver nitrate test for halides is used. The acyl halide is hydrolyzed to form the carboxylic acid and hydrogen halide. The hydrogen halide undergoes reaction with silver nitrate to give an immediate precipitation of silver halide.



$$RCOX + H_2O \longrightarrow RCOOH + HX + \text{heat}$$

$$HX + AgNO_3 \longrightarrow AgX(s) + HNO_3$$

ALCOHOLS

Several methods are available for the analysis of the hydroxyl group, the functional group present in alcohols. Sodium metal undergoes reaction with hydroxyl groups of many alcohols to liberate hydrogen gas and form the salt of the alcohol (Experiment 5). The rate is highly variable and depends upon the alcohol structure.

Experiment (5) Sodium Detection of Active Hydrogen

$$\underset{\text{alcohol}}{2ROH} + 2Na \longrightarrow 2RO^-Na^+ + H_2(g)$$

Procedure:

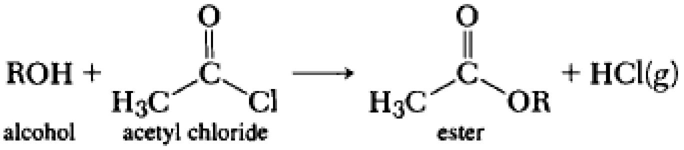
To 0.25 mL or 0.25 g of the sample, add small thin slices of freshly cut sodium until no more will dissolve. Evolution of hydrogen gas indicates the presence of an acidic hydrogen, such as a hydroxyl group in an alcohol, a hydrogen attached to the nitrogen in a primary or secondary amine, or a hydrogen in a terminal alkyne. Cool the solution, and observe. Add an equal volume of ether. Another positive test is the formation of the solid salt. Prior to testing, dry liquid samples with calcium sulfate. Any residual water will undergo reaction with the sodium. This test may be applied to solid compounds or very viscous liquids by dissolving them in an inert solvent such as anhydrous ligroin or toluene.

The order of reactivity of alcohols with sodium is known to decrease with increasing size of the alkyl portion of the molecule.
Structural effects upon acidity are complex. It is well known that liquid samples of alcohols follow this order of reactivity:

$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

Experiment (6) Detection of Active Hydrogen with Acetyl Chloride

Another method of detecting such active hydrogen is by adding acetyl chloride to the alcohol to form the ester, which is less dense than the aqueous layer.

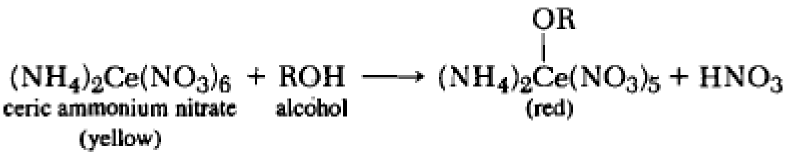


Procedure:

Perform this test in the hood. Add drop by drop 0.2 mL of acetyl chloride to 0.2 mL or 0.2 g of the unknown. Evolution of heat and hydrogen chloride gas is a positive test. To destroy any unreacted acetyl chloride, allow the mixture to stand for a minute or two and the pour it cautiously into 1 mL of water. Alcohols and phenols react with acetyl chloride to form esters, which is indicated by the formation of a top layer in the flask. Primary and secondary amines react with acetyl chloride to form amides, which precipitate from the solution.

Experiment (7) Ceric Ammonium Nitrate

Another method of testing for the presence of the alcoholic hydrogen involves ceric ammonium nitrate. The yellow ceric ammonium nitrate forms a red organometallic compound with alcohols. Positive results are obtained from alcohols of 10 or fewer carbons.



$$\underset{\substack{\text{ceric ammonium nitrate}\\ \text{(yellow)}}}{(NH_4)_2Ce(NO_3)_6} + \underset{\text{alcohol}}{ROH} \longrightarrow \underset{\text{(red)}}{(NH_4)_2\overset{\overset{\displaystyle OR}{|}}{Ce}(NO_3)_5} + HNO_3$$

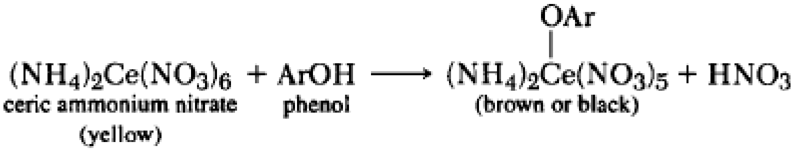
(a) For Water-Soluble Compounds: Add four to five drops of a liquid unknown or 0.1-0.2 g of a solid to 1 mL of the ceric ammonium nitrate reagent. Mix thoroughly and note whether the yellow color of the reagent changes to red. Alcohols react with the reagent to form a red alkoxy cerium (IV) compound. If a red color develops, watch the solution carefully and note the time for the mixture to become colorless. Info change is noted in 15 min, stopper the test tube and allow to stand several hours or overnight. Also note whether bubbles of carbon dioxide are liberated.

(b) For Water-Insoluble Compounds: Add 2 mL of dioxane to 1 mL of the ceric ammonium nitrate reagent. If a red color develops or if the solution becomes colorless, purify the dioxane. If the mixture remains yellow or is only a light orange-yellow, it may be used to test water-insoluble compounds. Divide the 6 mL of the solution in half, reserving 3 mL for observation as a control. To the other 3 mL of the dioxane containing reagent, add four to five drops of a liquid unknown or 0.1-0.2 g of a solid. Mix thoroughly and make the same observations as in (a).

Cerie Ammonium Nitrate Reagent

Add 1.3 mL of concentrated nitric acid to 40 mL of distilled water and then dissolve 10.96g of yellow ceric ammonium nitrate in the dilute nitric acid solution. After the solid has dissolved, dilute to 50 mL. The test is carried out at room temperature (20-25°C). Hot solutions (50-100°C) of Ce(IV) oxidize many types of organic compounds. This reagent is usable for about a month.

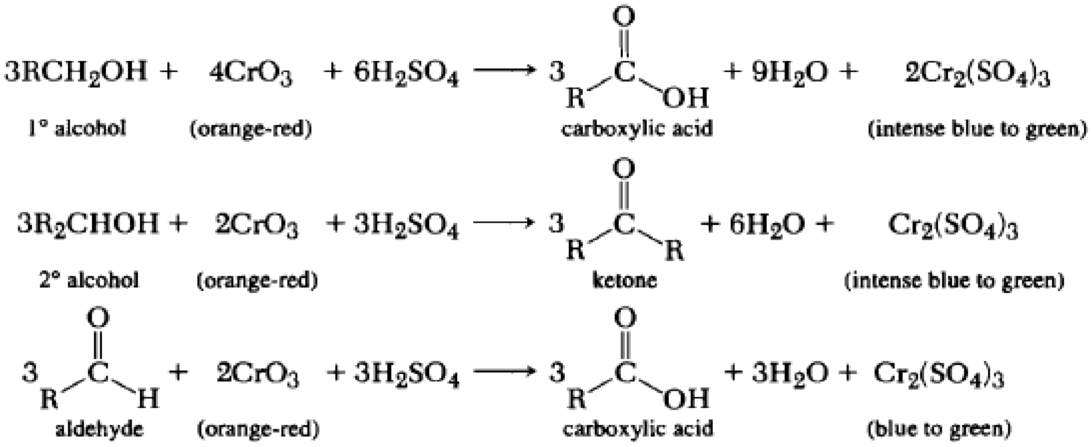
Discussion The ceric ammonium nitrate reagent forms red complexes with primary, secondary, and tertiary alcohols of up to 10 carbons. Also, all types of glycols, polyols, carbohydrates, hydroxy acids, hydroxy aldehydes, and hydroxy ketones give red solutions. Phenols give a brown color or precipitate.



$$\underset{\text{ceric ammonium nitrate (yellow)}}{(NH_4)_2Ce(NO_3)_6} + \underset{\text{phenol}}{ArOH} \longrightarrow \underset{\text{(brown or black)}}{(NH_4)_2\overset{\overset{OAr}{|}}{Ce}(NO_3)_5} + HNO_3$$

The red cerium (IV) compound has been shown to be the intermediate for the oxidation of alcohols by Ce(IV) solutions. Hence, *a second phase* of this test involves the disappearance of the red color due to oxidation of the coordinated alcohol and reduction of the colored Ce(IV) complex to the colorless Ce(III) complex. Thus a positive test includes successively the formation, and then the disappearance of the red color, assuming the oxidation step occurs within a reasonable time.

Experiment (8) Chromic Anhydride (Chromium Trioxide, Jones Oxidation)



Procedure:

To 1 mL of acetone in a small test tube, add one drop of the liquid or about 10 mg of a solid compound. Then add one drop of the ***Jones reagent*** and note the result within 2 sec. Run a control test on the acetone and compare the result. A positive test for primary or secondary alcohols consists in the production of an opaque suspension with a green to blue color. Tertiary alcohols give no visible reaction within 2 sec, the solution remaining orange in color. *Disregard* any changes after 2 sec.

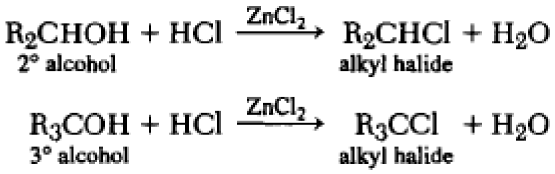
Jones Reagent:

Pour a suspension of 25 g of chromic anhydride (CrO_3) in 25 mL of concentrated sulfuric acid, slowly with stirring into 75 mL of water. Cool the deep orange-red solution to room temperature before use.

Use a good grade of acetone. Some samples of acetone may become cloudy in appearance in 20 sec, but this does not interfere, providing the test solution becomes yellow. If the acetone gives a positive test, purify the acetone by adding a small amount of potassium permanganate and distill the mixture.

Discussion: This test is a rapid method for distinguishing primary and secondary alcohols from tertiary alcohols. Positive tests are given by primary and secondary alcohols without restriction as to molecular weight. Even cholesterol ($C_{27}H_{46}O$) gives a positive test. Aldehydes give a positive test but would be detected by other classification experiments. Aldehydes produce the green color in 5-15 sec, with aliphatic aldehydes reacting more quickly than aromatic aldehydes. Ketones do not react. Olefins, acetylenes, amines, ethers, and ketones give negative tests within 2 sec provided that they are not contaminated with small amounts of alcohols. Enols may give a positive test, and phenols produce a dark-colored solution entirely unlike the characteristic green-blue color of a positive test.

Experiment (9) Hydrochloric Acid/Zinc Chloride (Lucas Test)



$$\underset{2^\circ\text{ alcohol}}{R_2CHOH} + HCl \xrightarrow{ZnCl_2} \underset{\text{alkyl halide}}{R_2CHCl} + H_2O$$

$$\underset{3^\circ\text{ alcohol}}{R_3COH} + HCl \xrightarrow{ZnCl_2} \underset{\text{alkyl halide}}{R_3CCl} + H_2O$$

(a) To 0.2 mL or 0.2 g of the sample in a test tube add 2 mL of the Lucas reagent at *26-27°C*. Stopper the tube and shake; then allow the mixture to stand. Note the time required for the formation of the alkyl chloride, which appears as an insoluble layer or emulsion.

Lucas Reagent

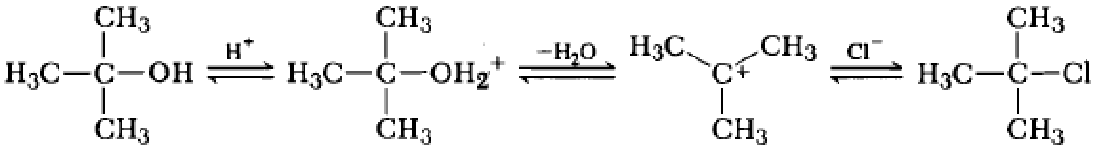
Dissolve 13.6 g (0.1 mole) of anhydrous zinc chloride in 10.5 g (0.1 mole) of concentrated hydrochloric acid, with cooling.

(b) To 0.2 mL or 0.2 g of the alcohol in a test tube add 1.2 mL of concentrated hydrochloric acid. Shake the mixture, and allow it to stand. Observe carefully during the first 2 min.

Controls:

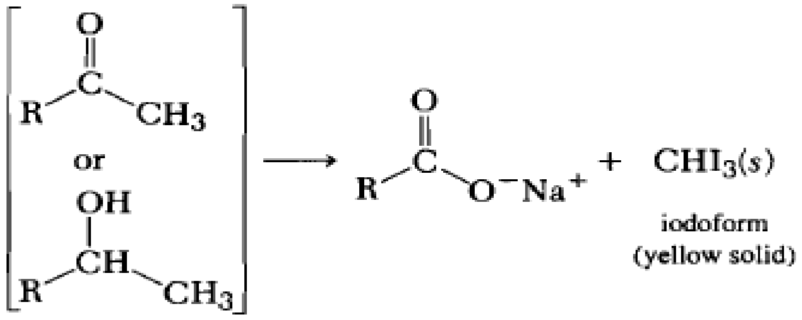
Note the time required for both (a) and (b) to take place with different alcohols.

Discussion: The mechanism of the Lucas test is an S_N1-type process as follows:

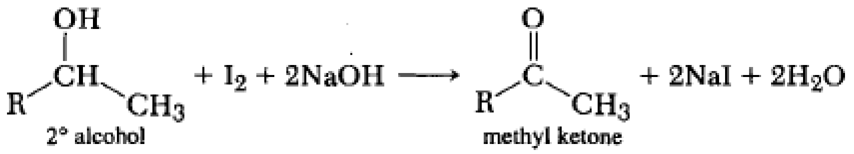


Experiment (10) Iodoform Test

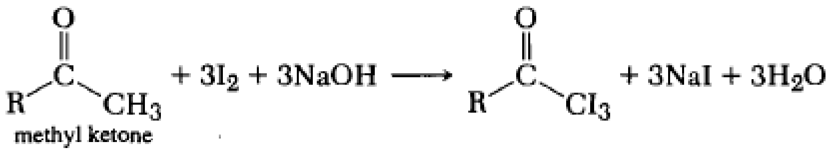
The iodoform is a test for methyl ketones and secondary alcohols that have a methyl group adjacent to the carbon bearing the hydroxyl group.



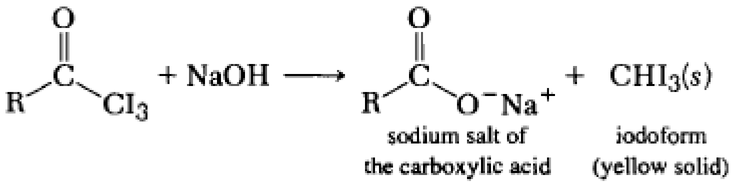
The alcohols are oxidized to the methyl ketones by the "iodine bleach."



Iodination occurs preferentially and completely on the methyl groups.



Cleavage produces the carboxylate salt and iodoform.

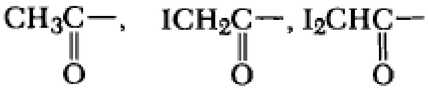


Procedure:

Place four drops of the liquid or 0.1 g of the solid to be tested in a test tube. Add 5 mL of dioxane and shake until all the sample has gone into solution. Add 1 mL of 10% sodium hydroxide solution, and then slowly add the iodine-potassium iodide solution, with shaking, until a slight excess yields a definite dark color of iodine. If less than 2 mL of the iodine solution is decolorized, place the test tube in a water bath at a temperature of 60°C. If the slight excess of iodine already present is decolorized, continue the addition of the iodine solution (keep the iodine solution at 60°C). with shaking, until a slight excess of iodine solution again yields a definite dark color. Continue the addition of iodine until the dark color is not discharged by 2 min of heating at 60°C. Remove the excess of iodine by the addition of a few drops of 10% sodium hydroxide solution, with shaking. Now fill the test tube with water and allow standing for 15 min. A positive test is indicated by the formation of a foul-smelling yellow precipitate (iodoform). Collect the precipitate by filtration and dry.

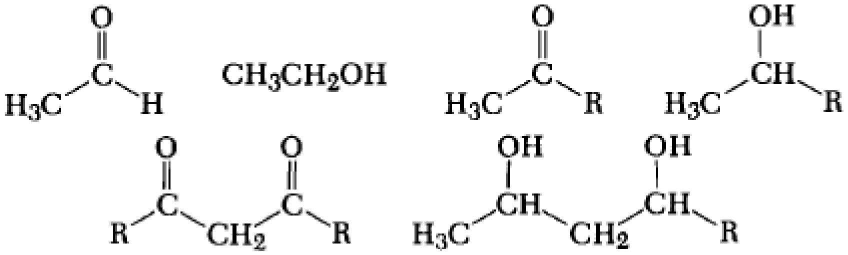
Discussion:

This test positive for compounds that contain the grouping



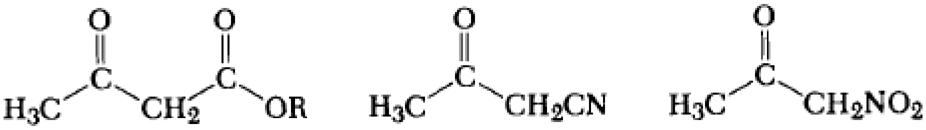
$CH_3\underset{\underset{O}{\|}}{C}—,\quad ICH_2\underset{\underset{O}{\|}}{C}—,\ I_2CH\underset{\underset{O}{\|}}{C}—$

Following are the principal types of compounds that give a positive test:



R = any alkyl or aryl radical except an *ortho*-disubstituted aryl radical

R, however, if large, will sterically inhibit this reaction. The test is negative for compounds of the following, types:

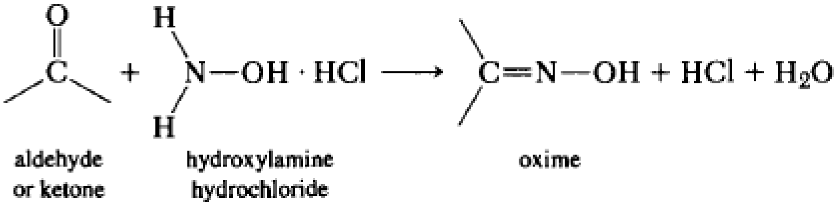


etc.

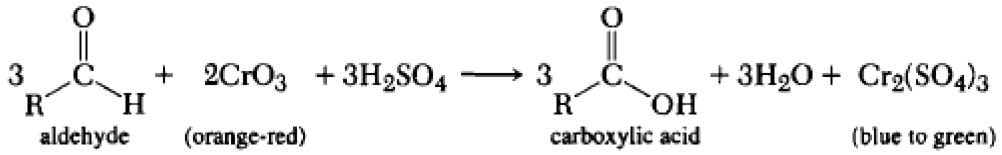
(Note) In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.

ALDEHYDES

In the reaction of hydroxylamine hydrochloride with aldehydes the formation of the oximes results in the liberation of hydrogen chloride, which can be detected by the change in color from orange to red of a pH indicator.

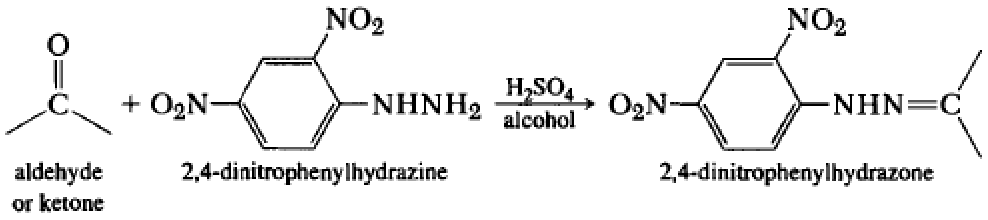


A simple chemical test for aldehydes involves the use of CrO_3 in Jones oxidation (Experiment 8). As the aldehyde *is* oxidized to the carboxylic acid, the chromium *is* oxidized from a +3 oxidation state, which is an orange-red color, to a +6 oxidation state, which is a deep-blue-green color.



The reaction of aldehydes and ketones with 2,4-dinitrophenylhydrazine (Experiment 11) to form the 2,4-dinitrophenylhydrazone probably represents the most studied and most successful of all qualitative tests and derivatizing procedures. In addition, the general details of the reaction serve as a model for a number of other chemical reactions (semicarbazone, oxime, and other arylhydrazone preparations). The 2,4dinitrophenylhydrazone precipitates from the solution.

Experiment (11) 2,4-Dinitrophenylhydrazine



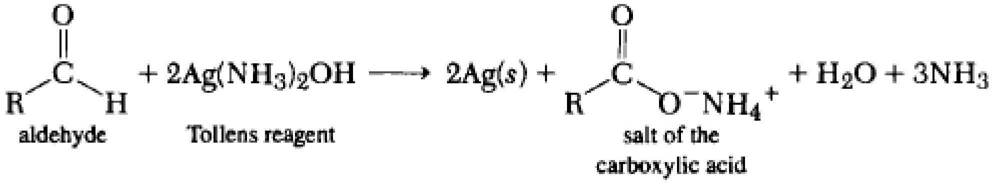
Add a solution of one or two drops or about 50 mg of the compound to be tested in 2 mL of 95% ethanol to 3 mL of 2,4-dinitrophenylhydrazine reagent. Shake vigorously and, if no precipitate forms immediately, allow the solution to stand for 15 min. If needed, the precipitate can be recrystallized from ethanol.

2,4-Dinitrophenylhydrazine Reagent: Dissolve 3 g of 2,4-dinitrophenylhydrazine in 15 mL of concentrated sulfuric acid. Add the solution, with stirring, to 20 mL of water and 70 mL of 95% ethanol. Mix thoroughly and filter.

Discussion: Most aldehydes and ketones yield dinitrophenylhydrazones that are insoluble solids. The precipitate may be oily at first and become crystalline on standing. The color of a 2,4-dinitrophenylhydrazone may give an indication as to the structure of the aldehyde or ketone from which it is derived. The dinitrophenylhydrazones of aldehydes and ketones in which the carbonyl group is not conjugated with another functional group are yellow. Conjugation with a carbon-carbon double bond or with a benzene ring shifts the absorption maximum toward the visible and is easily detected by an examination of the ultraviolet spectrum. However, this shift is also responSible for a change in color from yellow to orange-red. In general, a yellow dinitrophenylhydrazone may be assumed to be unconjugated.

Experiment (12) Tollens Test

Aldehydes produce a silver *mirror* when mixed with Tollens reagent. As the aldehyde is oxidized to an acid, the silver is reduced from a + 1 oxidation state to elemental silver and is deposited as a silver mirror or colloidal silver inside the reaction flask.



$$RCHO + 2Ag(NH_3)_2OH \longrightarrow 2Ag(s) + RCOO^-NH_4^+ + H_2O + 3NH_3$$

Procedure:

Add one drop or a few crystals of the sample to the freshly prepared Tollens reagent. A positive test is the formation of silver metal or colloidal silver. If no reaction takes place in the cold, the solution should be warmed slightly on a steam bath or in a hotwater bath. However, excessive heating will cause the appearance of a false positive test by decomposition of the reagent.

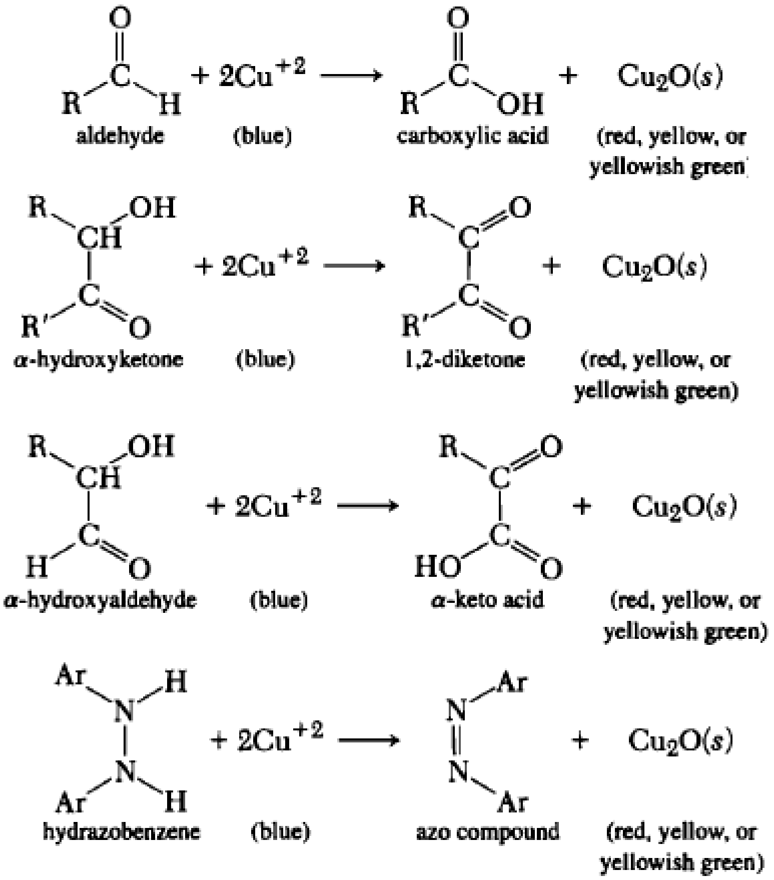
Tollens Reagent: Clean a test tube with 10% sodium hydroxide. Add 2 mL of a 5% silver nitrate solution and a drop of 10% sodium hydroxide. Add 2% ammonia solution, drop by drop, with constant shaking, until the precipitate of silver oxide just dissolves. In order to obtain a sensitive reagent, it is necessary to avoid a large excess of ammonia.

This reagent should be prepared just before use and should not be stored, because the solution decomposes on standing and deposits a highly explosive precipitate.

Cleaning Up: Pour the solution into a beaker. Add a few drops of 5% nitric acid to dissolve the silver mirror or colloidal silver. Combine all solutions. Make the solution acidic with 5% nitric acid, then neutralize with sodium carbonate. Add 5 mL of saturated sodium chloride solution to precipitate the silver as silver chloride. Isolate the silver chloride by filtration.

Experiment (13) Benedict's Solution

(Compounds Containing No Sulfur)



Procedure:

To a solution or suspension of 0.2 g of the compound in 5 mL of water, add 5 mL of Benedict's solution. Benedict's solution oxidizes a variety of compounds, with the corresponding reduction of Cu+2 to Cu+ 1. The precipitation of the copper (I) oxide as a red, yellow, or yellowish-green solid is a positive test. If no precipitate is formed, heat the mixture to bOiling and cool. Note whether any solid is formed. To a solution of 0.2 g of sucrose in 5 mL of water, add two drops of concentrated hydrochlOriC acid and boil the solution for a minute. Cool the solution, neutralize the acid with dilute sodium hydroxide solution, and try the action of Benedict's solution. Explain the result.

Benedict's Solution

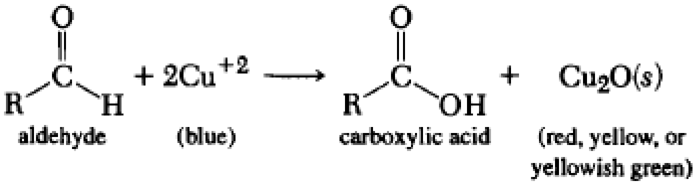
Heat a solution of 17.3 g of sodium citrate and 10.0 g of anhydrous sodium carbonate in 80.0 mL of water until the salts are dissolved. Add additional water to bring the volume up to 85.0 mL. Slowly pour a solution of 1.73 g of hydrated copper sulfate in 10.0 mL of water, with stirring, into the solution of the citrate and carbonate. Add additional water to bring the volume of the solution up to 100 mL.

Discussion

Benedict's solution, which contains the copper bound in the complex anion, functions as a selective oxidizing agent. It was introduced as a reagent for reducing sugars to replace Fehling's solution, which is very strongly alkaline. Benedict's reagent will detect 0.01 % of glucose in water. The color of the precipitate may be red, yellow, or yellowish green, depending on the nature and amount of the redUCing agent present. Benedict's reagent is reduced by a-hydroxy aldehydes, a-hydroxy ketones, and a-keto aldehydes. It does not oxidize simple aromatic aldehydes. Molecules containing only the alcohol functional group or only the keto group are not oxidized by Benedict's solution.

Hydrazine derivatives, as exemplified by phenylhydrazine and hydrazobenzene, are oxidized by this reagent. Other easily oxidizable systems, such as phenylhydroxylamine, aminophenol, and related photographic developers, also reduce Benedict's solution.

Experiment (14) Fehling's Solution



Procedure:

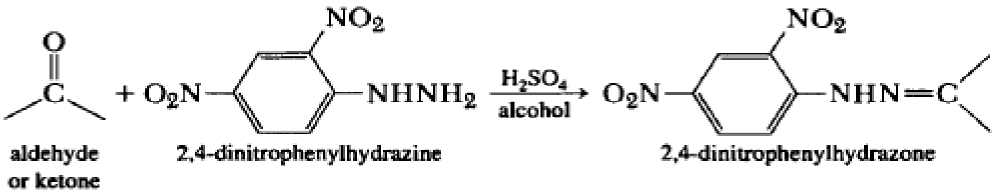
To a solution of 0.2 g of the compound in 5 mL of water, add 5 mL of Fehling's solution and heat the mixture to boiling. Cool the solution. Fehling's solution oxidizes many compounds, and copper in the reagent is reduced from Cu^{+2} to $Cu^{+\ 1}$. The precipitation of the copper (I) oxide as a red, yellow, or yellowish-green solid is a positive test.

Fehling's Solution:

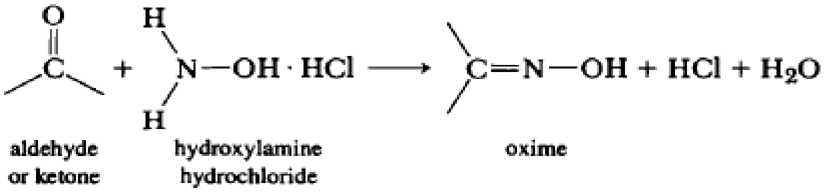
Mix 2.5 mL of the following two solutions immediately before use. *Fehling's solution* #1: Dissolve 8.65 g of hydrated copper sulfate crystals in 100 mL of water and dilute the solution to 125 mL. *Fehling's solution* #2: Dissolve 43.2 g of sodium potassium tartrate and 17.5 g of sodium hydroxide in 50 mL of water and dilute the solution to 125 mL.

KETONES

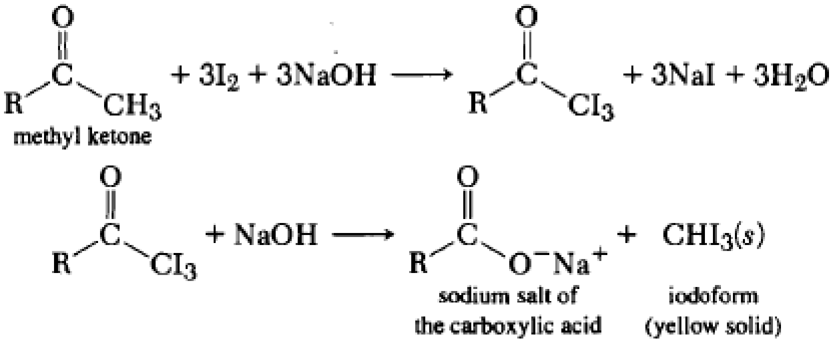
Many of the same reactions that are described in the classification of aldehydes can also be used to classify ketones. The addition of 2,4dinitrophenylhydrazine to ketones to precipitate the 2,4-dinitrophenylhydrazones (Experiment 11) is probably the most useful of these reactions.



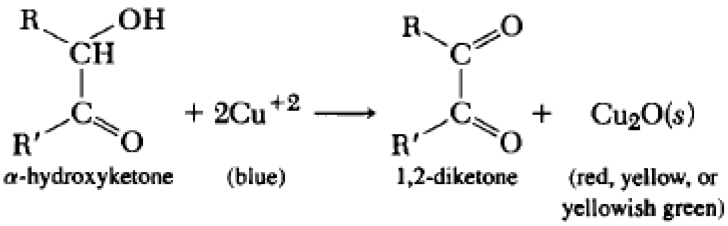
The reaction of hydroxylamine hydrochloride with ketones produces oximes and results in the liberation of hydrogen chloride, which can be detected by an indicator.



The iodoform test (Experiment 10) will give positive results with methyl ketones. A positive test is indicated by the precipitation of iodoform, a foul-smelling yellow solid.

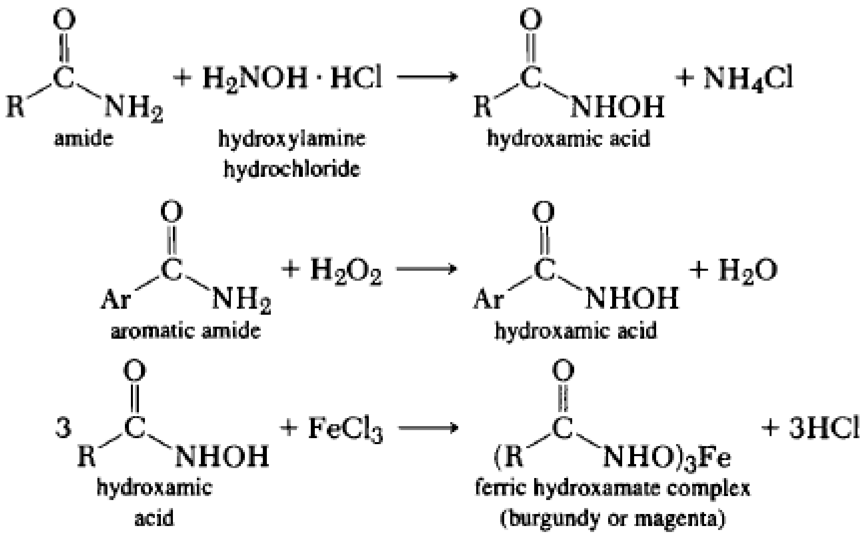


Benedict's solution (Experiment 13) and Fehling's solution (Experiment 14) will undergo reaction with reducing sugars such as a-hydroxy ketones. The solution is initially a blue color from Cu+2 complex, but as the reaction proceeds, copper(I) oxide precipitates as a red, yellow, or yellowish-green solid.



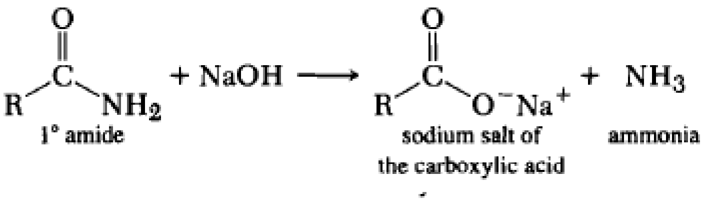
AMIDES

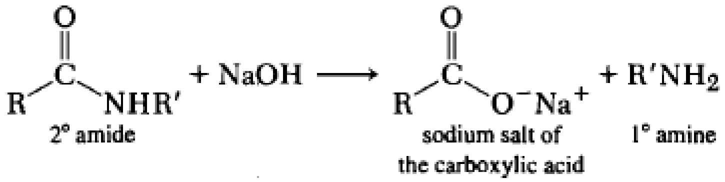
Aliphatic amides react with hydroxylamine hydrochloride to form hydroxamic acid (Experiment 2b). Similarly, aromatic primary amides react with hydrogen peroxide to produce hydroxamic acid (Experiment 2c). The hydroxamic acid then reacts with ferric chloride to form the ferric hydroxamate, which has a characteristic magenta color.

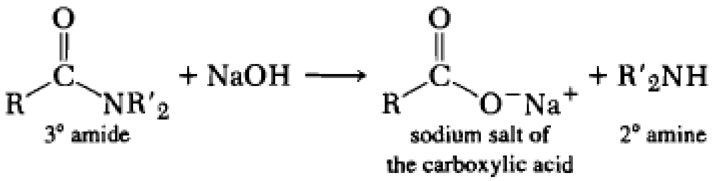


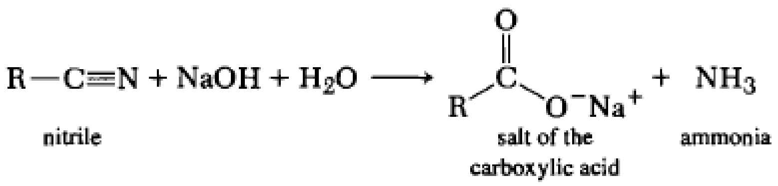
Experiment (15) Sodium Hydroxide Hydrolysis of Amides and Nitriles

Amides can be hydrolyzed to yield the salt of the carboxylic acid and ammonia or amine .The presence of ammonia or a low-molecular-weight amine is detected with litmus paper.







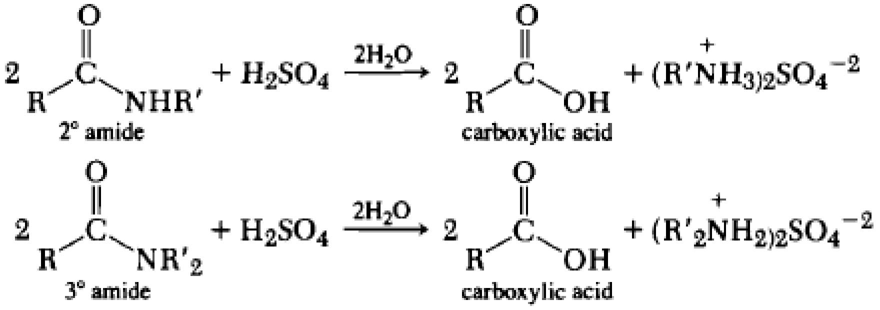


Procedure:

Add 0.2 g of the unknown in a test tube with 5 mL of 10% sodium hydroxide solution. Shake the mixture and note whether or not ammonia is evolved. Heat the solution to boiling and note the odor. Test the action of the vapor on either pink moist litmus paper or filter paper moistened with a copper sulfate solution. If ammonia or amine is being evolved, the litmus paper turns blue. Ammonia, which is evolved only from primary amines, will tum the copper sulfate solution on the filter paper blue. Nitriles and ammonium salts will also give a positive test with the copper sulfate.

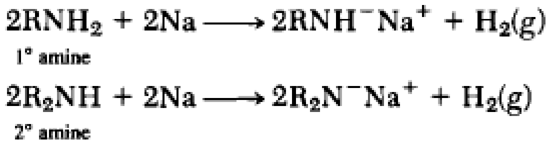
Discussion:

The ammonia or amine that is the product of this alkaline hydrolysis may be characterized by the Hinsberg test (Experiment 16). Many substituted amides are hydrolyzed more easily by heating under reflux with 20% sulfuric acid.



AMINES AND AMINE SALTS

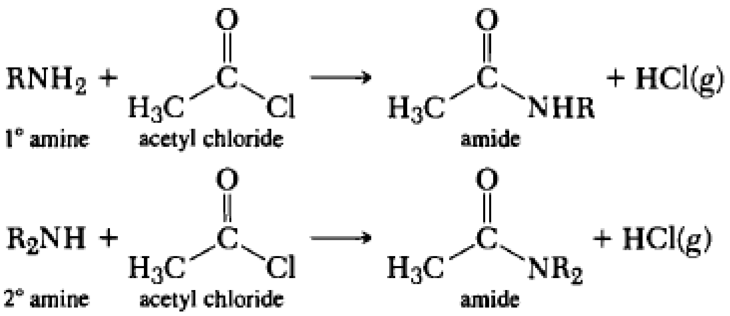
The active hydrogen on primary and secondary amines undergoes reaction with sodium to form the salt and to liberate hydrogen gas (Experiment 5). A tertiary amine does not undergo reaction, since it does not have an active hydrogen.



$$\underset{\text{1° amine}}{2RNH_2} + 2Na \longrightarrow 2RNH^-Na^+ + H_2(g)$$

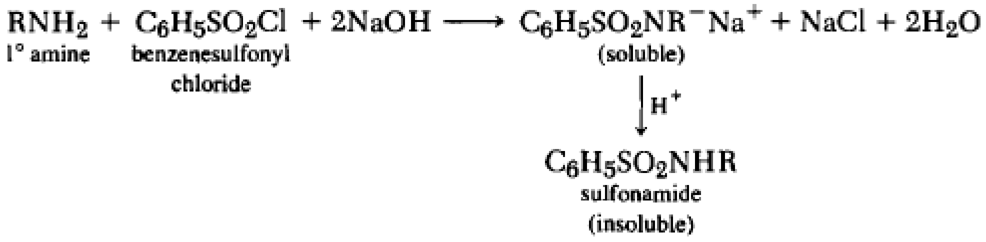
$$\underset{\text{2° amine}}{2R_2NH} + 2Na \longrightarrow 2R_2N^-Na^+ + H_2(g)$$

Primary and secondary amines react with acetyl chloride to produce amides, which often precipitate from the solution (Experiment 6). This reaction is usually accompanied by the evolution of heat. Tertiary amines do not react with acetyl chloride due to the lack of a hydrogen on the nitrogen.



Experiment (16) Benzenesulfonyl Chloride (Hinsberg's Method for Characterizing Primary, Secondary, and Tertiary Amines)

The Hinsberg test can be used to distinguish among primary, secondary, and tertiary amines. Benzenesulfonyl chloride undergoes reaction with primary amines in basic solution to form the sodium salts of the sulfonamide, which are soluble in the reaction mixture. Acidification of the reaction mixture results in the precipitation of the sulfonamides

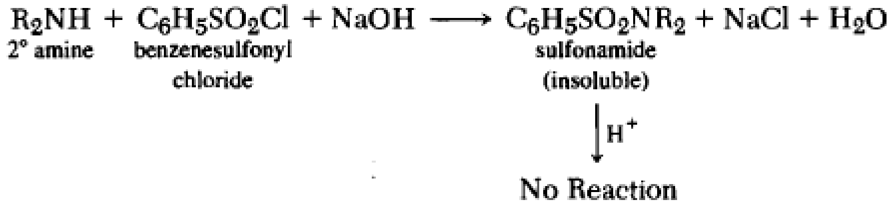


$$\underset{1^\circ\text{ amine}}{RNH_2} + \underset{\text{benzenesulfonyl chloride}}{C_6H_5SO_2Cl} + 2NaOH \longrightarrow \underset{\text{(soluble)}}{C_6H_5SO_2NR^-Na^+} + NaCl + 2H_2O$$

$$\Big\downarrow H^+$$

$$\underset{\substack{\text{sulfonamide}\\\text{(insoluble)}}}{C_6H_5SO_2NHR}$$

Secondary amines, when treated with benzenesulfonyl chloride, yield the sulfonamides, which precipitate from the solution. Acidification of the solution does not dissolve the sulfonamide.

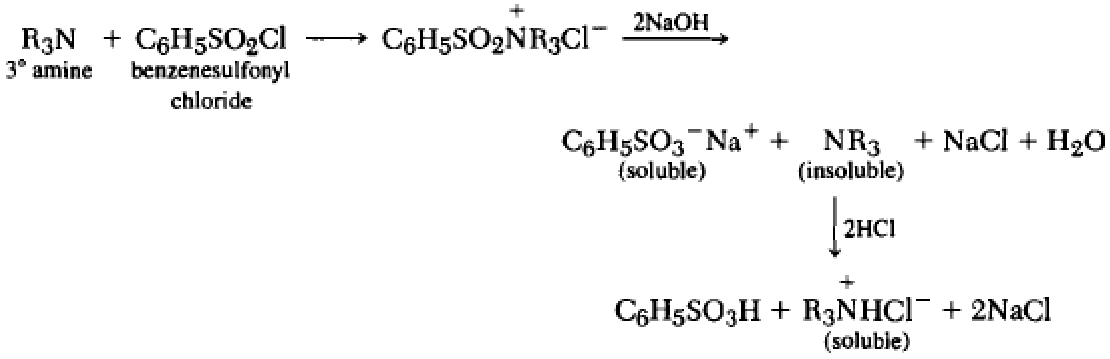


$$\underset{2^\circ\text{ amine}}{R_2NH} + \underset{\text{benzenesulfonyl chloride}}{C_6H_5SO_2Cl} + NaOH \longrightarrow \underset{\substack{\text{sulfonamide}\\\text{(insoluble)}}}{C_6H_5SO_2NR_2} + NaCl + H_2O$$

$$\Big\downarrow H^+$$

$$\text{No Reaction}$$

Tertiary amines undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonates and insoluble tertiary amines in basic solution. Acidification of the reaction mixture results in the formation of sulfonic acids and soluble amine salts.



$$\underset{3^\circ\text{ amine}}{R_3N} + \underset{\text{benzenesulfonyl chloride}}{C_6H_5SO_2Cl} \longrightarrow C_6H_5SO_2\overset{+}{N}R_3Cl^- \xrightarrow{2NaOH}$$

$$\underset{\text{(soluble)}}{C_6H_5SO_3^-Na^+} + \underset{\text{(insoluble)}}{NR_3} + NaCl + H_2O$$

$$\Big\downarrow 2HCl$$

$$C_6H_5SO_3H + \underset{\text{(soluble)}}{R_3\overset{+}{N}HCl^-} + 2NaCl$$

Procedure:

To 0.3 mL or 300 mg of the unknown sample in a test tube, add 5 mL of 10% sodium hydroxide solution and 0.4 mL of benzenesulfonyl chloride. Stopper the test tube, and shake the mixture very vigorously. Test the solution to make sure that it is alkaline. After all the benzenesulfonyl chloride has reacted, cool the solution and separate the residue, if present, from the solution. Test the residue for solubility in 10% hydrochloric acid. If no residue remains, then treat the solution with 10% hydrochloric acid and observe whether a precipitate forms.

If all of the original compound dissolves in the base, no residue remains, and acidification produces a precipitate, the original unknown is a primary amine. *Primary amines react with benzenesulfonyl chloride in basic solution to form the sodium salt of the sulfonamide, which is normally soluble in basic solution, but the sulfonamide precipitates upon acidification.*

If a residue is formed and it is insoluble in acid, the original unknown is a secondary amine. *Secondary amines undergo reaction with benzenesulfonyl chloride to precipitate the sulfonamide, and acidification does not result in any change.*

If a residue is present that is soluble in acid, it indicates that the residue is the unreacted tertiary amine. *Tertiary amines undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonates and water-insoluble tertiary amines in basic solution. Acidification of the reaction mixture results in the formation of sulfonic acids and water-soluble amine salts.* Any solid that is formed should be isolated and purified, and its melting point should be compared against the original amine. If the amount of the solid is in sufficient quantity, it may be saved and used as a derivative for that unknown.

Experiment (17) Nitrous Acid

The reaction of amines with nitrous acid (Experiment 20, p. 294) classifies the amine not only as primary, secondary, or tertiary, but also as aliphatic or aromatic. Primary aromatic and aliphatic amines react with nitrous acid to form an intermediate diazonium salt. The aliphatic diazonium salts decompose spontaneously by rapid loss of nitrogen, particularly when the original amino group is attached to a secondary or tertiary carbon. Most aromatic diazonium salts are stable at O°C but lose nitrogen slowly on warming to room temperature.

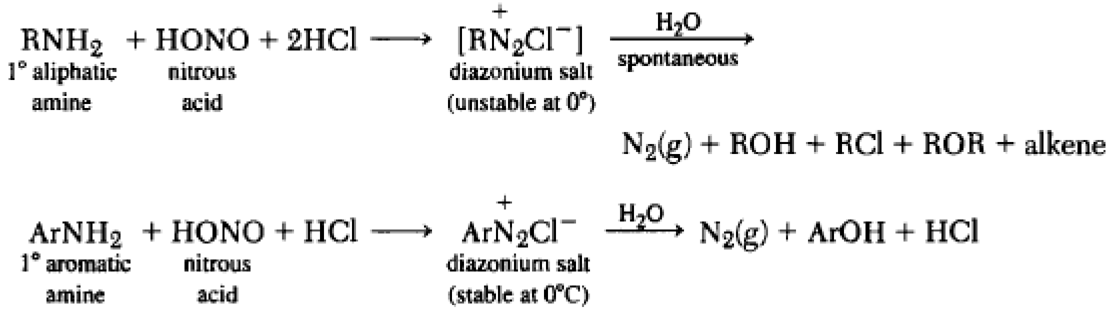
(a) Diazotization

Procedure:

Dissolve 0.5 mL or 0.5 g of the sample in 1.5 mL of concentrated hydrochloric acid diluted with 2.5 mL of water, and cool the solution to 0°C in a beaker of ice. Dissolve 0.5 g of sodium nitrite in 2.5 mL of water, and add the solution dropwise, with shaking, to the cold solution of the amine hydrochloride. Continue the addition until the mixture gives a positive test for nitrous acid. Perform the test by placing a drop of the solution on starch-iodide paper; a blue color indicates the presence of nitrous acid. If the test is positive, move 2 mL of the solution to another test tube, warm gently, and examine for evolution of gas.

The observation of rapid bubbling or foaming as the aqueous sodium nitrite solution is added at 0°C indicates the presence of a primary aliphatic amine.

The evolution of gas upon warming indicates that the amine is a primary aromatic amine, and the solution should be subjected to the coupling reaction (b). If a pale yellow oil or low-melting solid, which is the N-nitrosoamine, is formed with no evolution of gas, the original amine is a secondary amine. The oil or solid is isolated and treated under conditions of the Liebermann nitroso reaction (c) to provide confirmation of the presence of the N-nitrosoamine.



$$\underset{\substack{\text{1° aliphatic}\\ \text{amine}}}{RNH_2} + \underset{\substack{\text{nitrous}\\ \text{acid}}}{HONO} + 2HCl \longrightarrow \underset{\substack{\text{diazonium salt}\\ \text{(unstable at 0°)}}}{[R\overset{+}{N}_2Cl^-]} \xrightarrow[\text{spontaneous}]{H_2O} N_2(g) + ROH + RCl + ROR + \text{alkene}$$

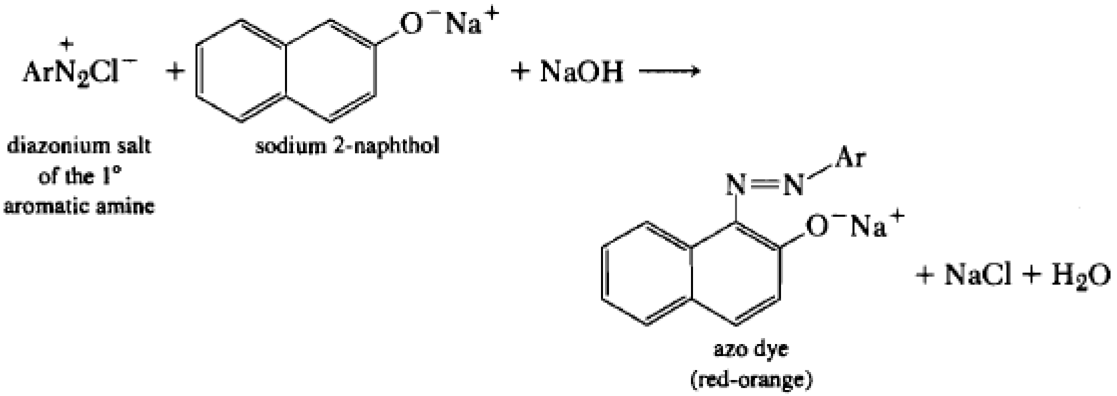
$$\underset{\substack{\text{1° aromatic}\\ \text{amine}}}{ArNH_2} + \underset{\substack{\text{nitrous}\\ \text{acid}}}{HONO} + HCl \longrightarrow \underset{\substack{\text{diazonium salt}\\ \text{(stable at 0°C)}}}{Ar\overset{+}{N}_2Cl^-} \xrightarrow{H_2O} N_2(g) + ArOH + HCl$$

(b) Coupling

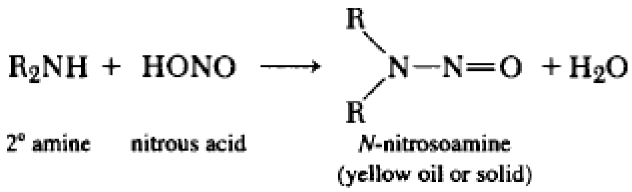
The diazonium salt of the primary aromatic amine reacts with sodium 2-naphthol to produce a red-orange azo dye.

Procedure:

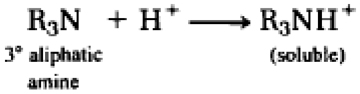
Add 2 mL of the cold diazonium solution to a solution of 0.1 g of 2-naphthol in 2 mL of 10% sodium hydroxide solution and 5 mL of water. The formation of the orange-red dye, with the evolution of gas only upon warming as noted in (a), indicates the original compound is a primary aromatic amine.



Secondary amines undergo a reaction with nitrous acid to form N-nitrosoamines, which are usually yellow solids



Tertiary aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.



$$R_3N + H^+ \longrightarrow R_3NH^+$$

Tertiary aromatic amines react with nitrous acid to form the orange-colored hydrochlOride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.

CARBOXYLIC ACIDS

Carboxylic acids are primarily identified by spectroscopy and solubility tests. However, a few classification tests can be used to confirm the presence of the carboxylic group. Carboxylic acids react with a sodium bicarbonate solution to form the carboxylate anion and carbon dioxide gas.

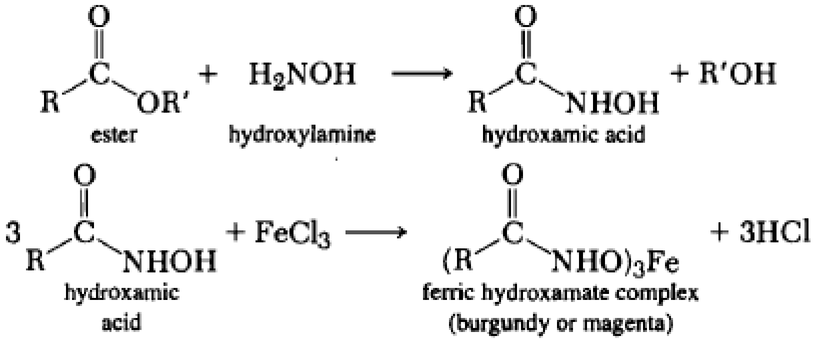
Experiment (18) Sodium Bicarbonate Test

Procedure:

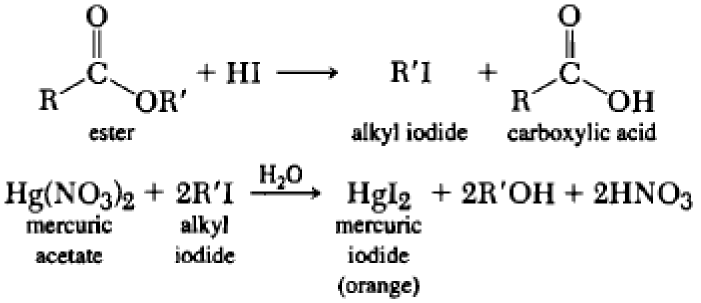
Dissolve a few drops or a few crystals of the unknown sample in 1 mL of methanol and slowly add to 1 mL of a saturated solution of sodium bicarbonate. Evolution of carbon dioxide gas is a positive test for the presence of the carboxylic acid.

ESTERS:

Esters characteristically have a sweet fruity smell. Esters combine with hydroxylamine to yield an alcohol and hydroxamic acid (Experiment 2b). The solution is then treated with ferric chloride to produce the ferric hydroxamate complex, which has a characteristic burgundy or magenta color.

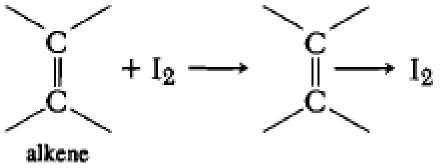


Esters are cleaved by hydroiodic acid to form an alkyl iodide and a carboxylic acid. The alkyl iodide is treated with mercuric nitrate to yield mercuric iodide, which is an orange color.

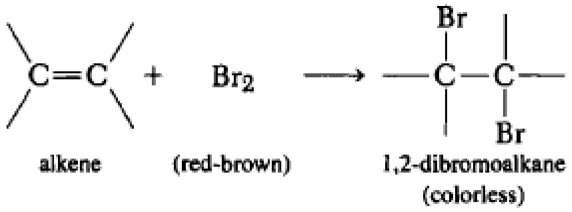


HYDROCARBONS-ALKENES:

The carbon-carbon double bond of alkenes (olefins) can be detected very easily by chemical tests. Alkenes can be detected by the use of iodine. If an alkene is present, a tan solid is formed while retaining the purple solution of the iodine solution.

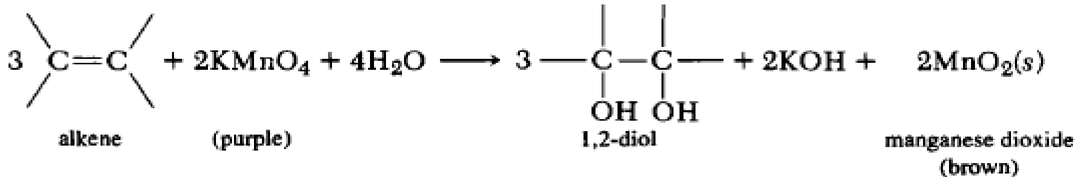


Addition across the double bond occurs in both the bromine test and the potassium permanganate test (Experiment 19). *Since the ionic characters of the bromine and potassium permanganate reactions are very different*, there is some complementary character between the two tests. *For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with potassium permanganate but often slow or negligible reaction with bromine. Bromine adds across the carbon-carbon double bond, with dissipation of the brown-red bromine color.*



Experiment (19) Potassium Permanganate Solution

Alkenes are oxidized to 1,2-diols with potassium permanganate, with reduction of the manganese from +7, which is purple, to +4, which is brown.

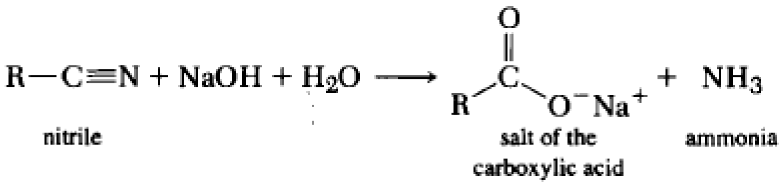


Baeyer Test-Aqueous Solutions: Add 0.1 g or 0.2 mL of the compound to 2 mL of water or ethanol. Add a 2% aqueous potassium permanganate solution drop by drop with shaking until the purple color of the permanganate persists.

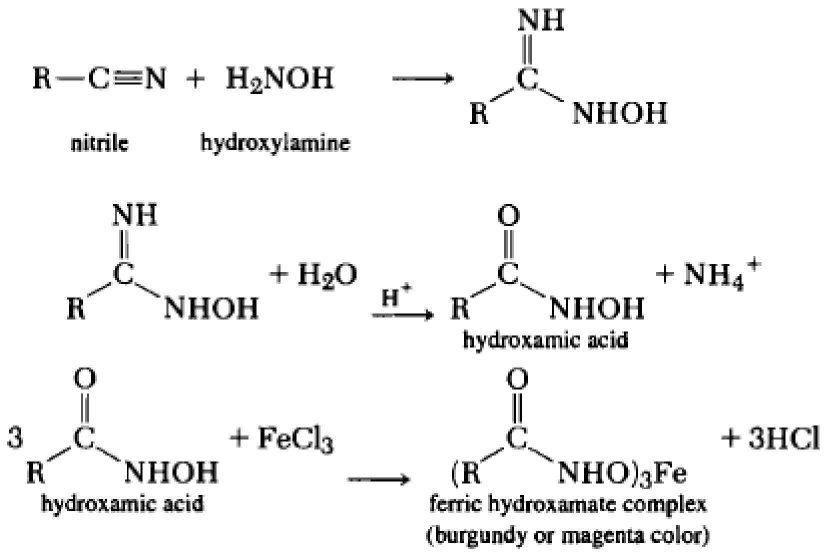
If the permanganate color is not changed in 0.5-1 min, allow the tubes to stand for 5 min with occasional vigorous shaking. Do not be deceived by a slight reaction, which may be due to the presence of impurities.The disappearance of the purple color and the formation of a brown suspension, which is manganese(II) oxide, at the bottom of the test tube is a positive indication for a carbon-carbon double or triple bond.

NITRILES:

Nitriles can be hydrolyzed under basic conditions to yield the salt of the carboxylic acid and ammonia (Experiment 15). The ammonia vapor is detected by litmus paper.



Nitriles along with many other compounds give a positive hydroxamic acid test (Experiment 2c. p. 254). The hydroxamic acid is detected with ferric chloride to form the ferric hydroxamate complex which has a burgundy or magenta color.



NITRO COMPOUNDS:

The presence of a nitro group is detected in several different ways. In the ferrous hydroxide reduction, a positive test is noted by the change in color from green to red-brown or brown due to the oxidation of iron from + 2 to + 3.

$$RNO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow RNH_2 + 6Fe(OH)_3$$

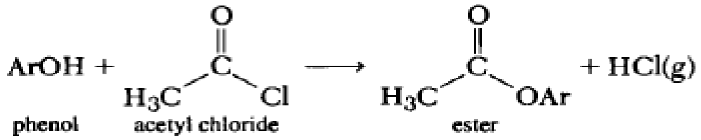
nitroalkane ferrous hydroxide (green) — ferric hydroxide (red-brown to brown)

PHENOLS:

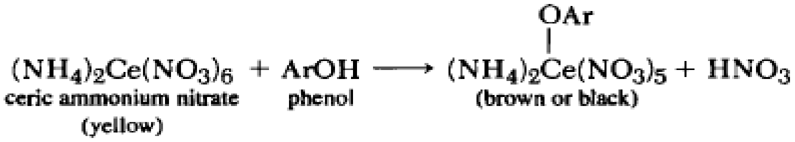
As with alcohols, the acidic hydrogen in a phenol can be detected with sodium (Experiment 5) or acetyl chloride (Experiment 6). Hydrogen gas is evolved with sodium, and an ester layer is formed with acetyl chloride.

$$2ArOH + 2Na \longrightarrow 2ArO^-Na^+ + H_2(g)$$

phenol

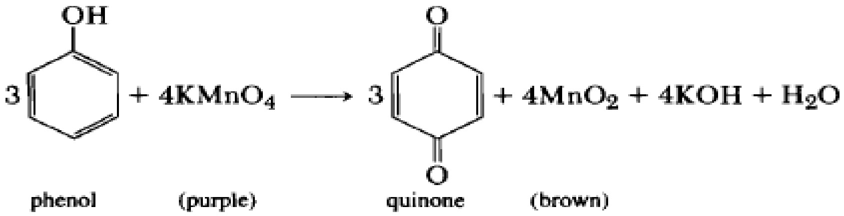


Phenols undergo reaction with the yellow ceric ammonium nitrate (Experiment 7) to produce brown or black products.



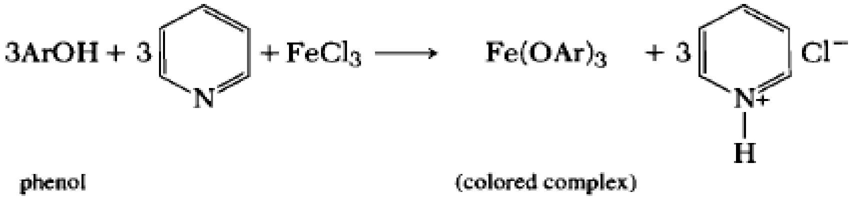
$$(NH_4)_2Ce(NO_3)_6 + ArOH \longrightarrow (NH_4)_2Ce(NO_3)_5(OAr) + HNO_3$$

Phenols reduce potassium permanganate solutions and undergo oxidation to quinones; an excess ofthe reagentyields aseries ofoxidation products, including maleic acid, oxalic acid, and carbon dioxide (Experiment 19). The manganese is reduced from +7, which gives a purple solution, to +4, which is brown.



Experiment (20) Ferric Chloride-Pyridine Reagent

Phenols can be detected by treatment with ferric chloride (Experiment 45, p. 345). The procedure using pyridine solvent has resulted in accurate results in 90% of the phenolic substrates tested; previous procedures using water or alcohol-water solvents had only a 50% success rate. The color of the solution changes immediately to blue, violet, purple, green, or red-brown.



Procedure:

This test must be done in the hood. Add 30 to 50 mg of the solid unknown or four to five drops of the liquid unknown to 2 mL or pure chloroform in a clean, dry test tube. Stir the solution. If the unknown does not seem to dissolve, even partially, add an additional 2-3 mL of chloroform and warm gently. Cool to 25°C and add two drops of 1% solution of anhydrous ferric chloride in chloroform followed by three drops of pyridine. Shake the tube and note the color produced *immediately.* A positive test is shown by production of a blue, violet, purple, green, or red-brown solution. Frequently the colors change in a few minutes.

1% Ferric Chloride in Chlorofom

Add 1 g of the black crystals of *anhydrous* ferric chloride to 100 mL of pure chloroform. Shake the mixture occasionally for about an hour, and allow standing to permit the insoluble material to settle. Decant the pale-yellow solution into a dropper.

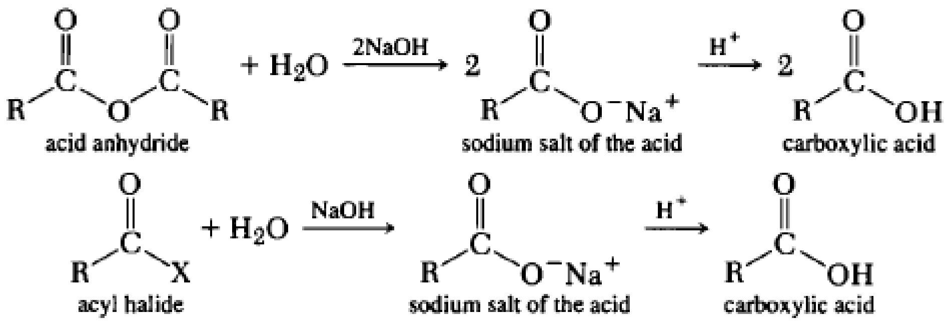
THE PREPARATION OF DERIVATIVES

1- CARBOXYLIC ACIDS

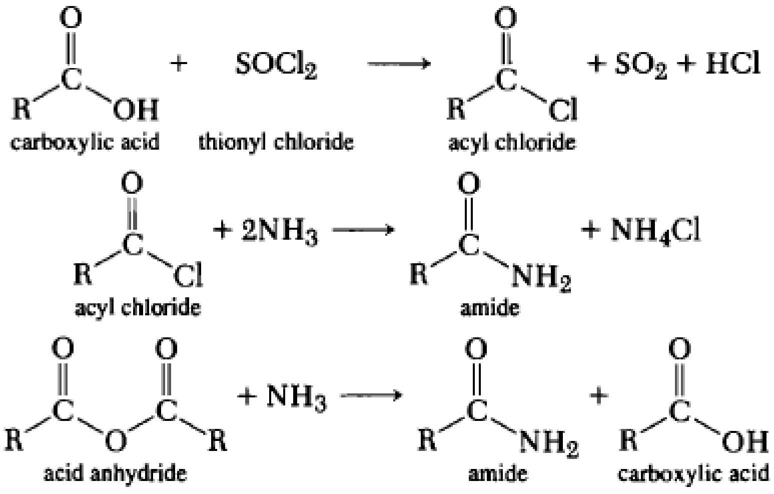
Acid anhydrides, acyl halides, and carboxylic acids can be derivatized by using some of the same procedures.

Acid anhydrides and acyl halides can be hydrolyzed to the carboxylic acids or the sodium salts of the acid

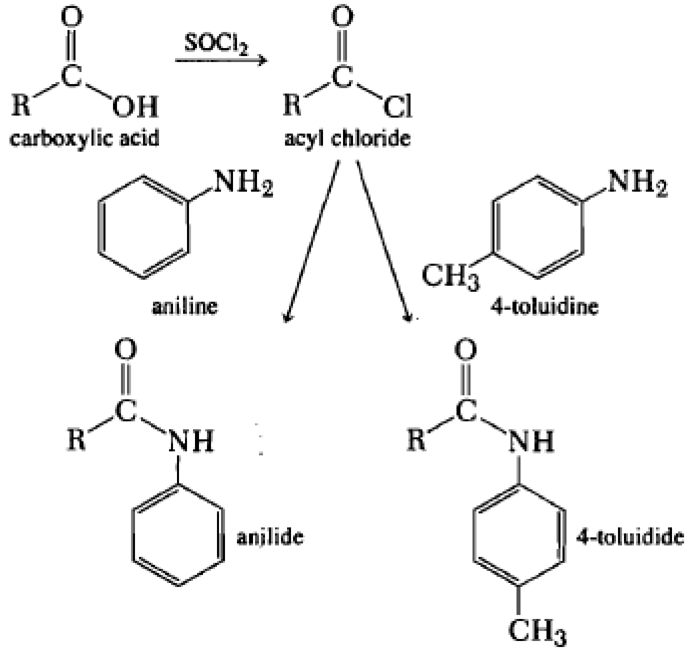
If the acid is a solid, it will frequently serve as a derivative of anhydrides and acyl halides. Otherwise, the mixture of the sodium salt of the acid and sodium chloride obtained from the basic hydrolysis of the acyl halide may be used for preparing other solid derivatives such as amides

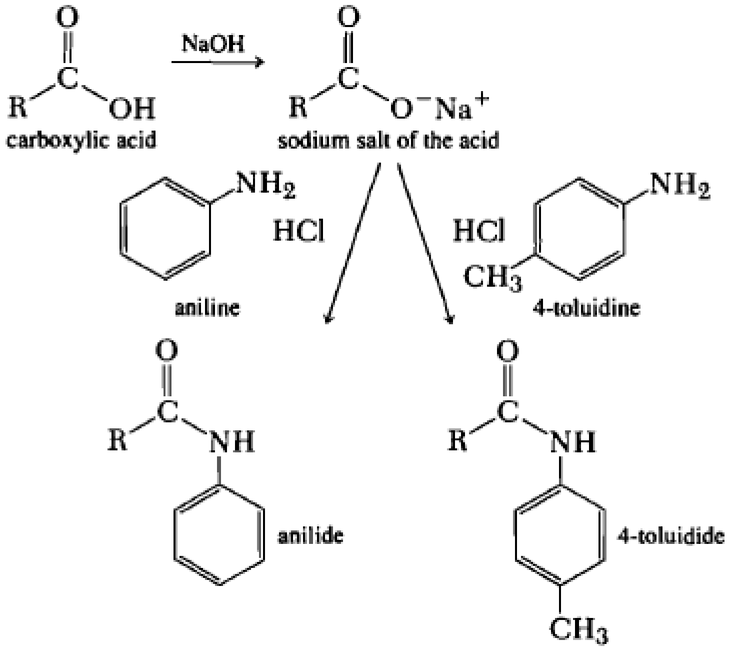


Acids may be converted to amides by reaction with thionyl chloride, followed by treatment of the intermediate acyl chloride with concentrated aqueous ammonia, Acid anhydrides undergo reaction with aqueous ammonia to yield amides and carboxylic acids.

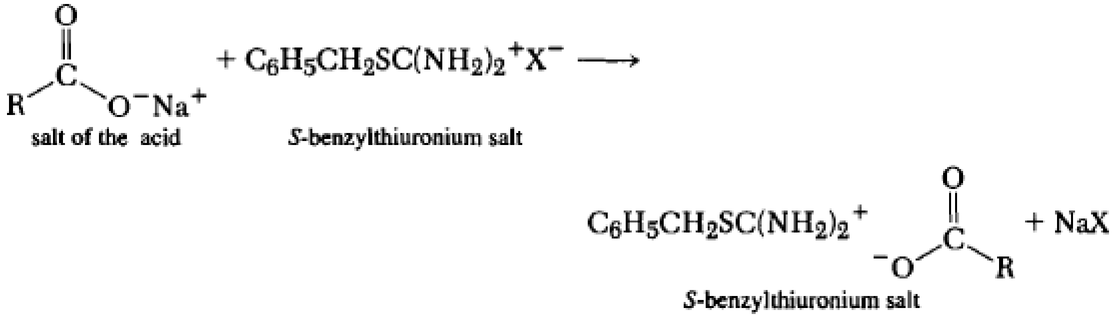


Anilides and 4-toluidides are excellent derivatives because of the ease with which they may be made and purified. They may be prepared from the free acid, the salt of the acid, the acyl halide, or the anhydride.

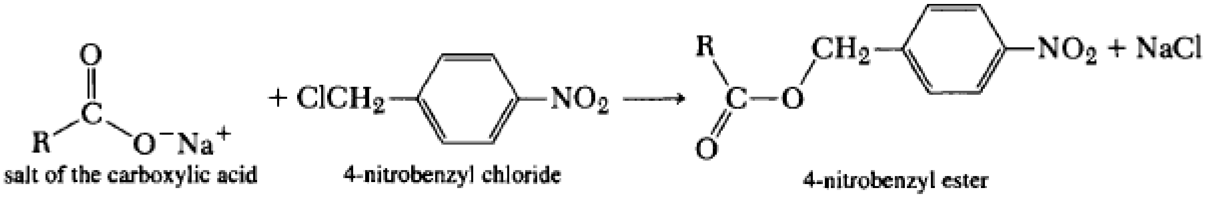


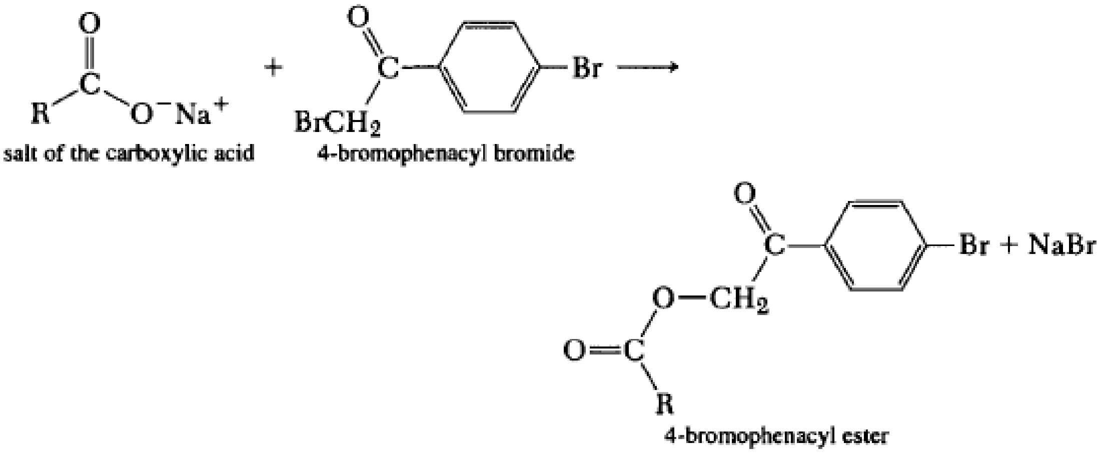


S-Benzylthiuronium halide undergoes reaction with the salt of the carboxylic acid to yield the corresponding S-benzylthiuronium salt



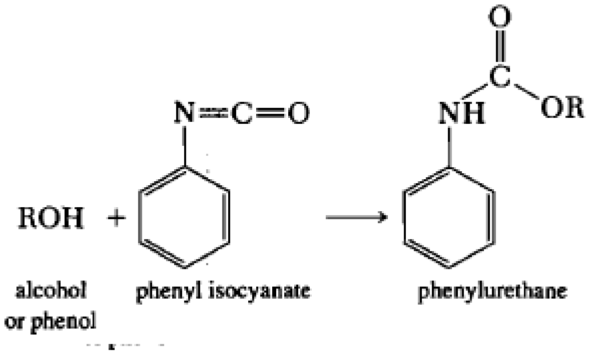
4-nitrobenzyl or the 4-bromophenacyl esters are preferred. These are prepared by treating the salts ofthe acids with either 4-nitrobenzyl chloride or 4-bromophenacyl bromide

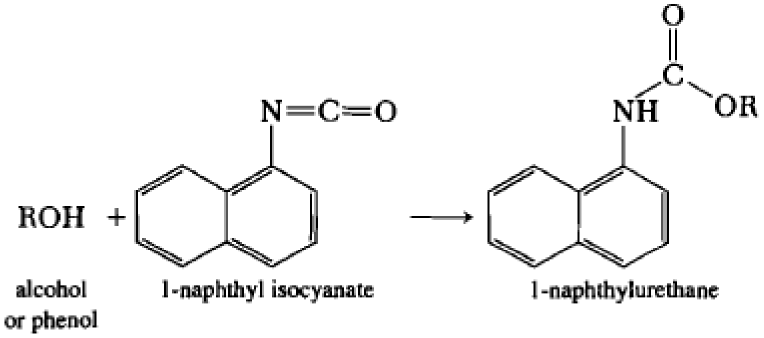




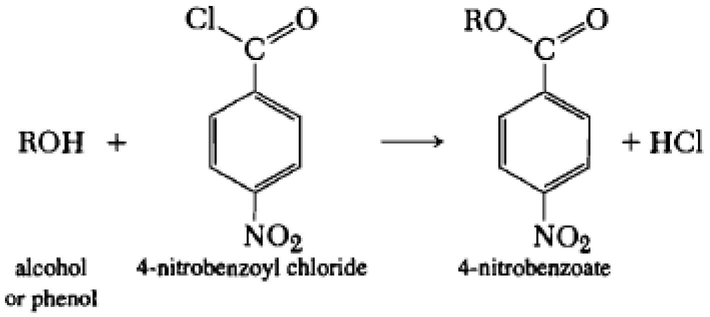
2- ALCOHOLS

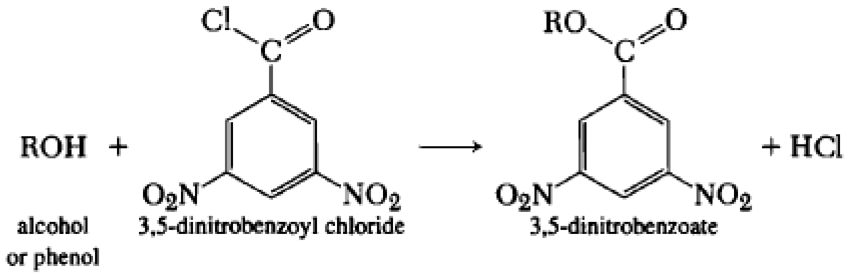
The most general derivatives of primary and secondary alcohols are the phenylurethanes and I-naphthylurethanes. Urethane derivatives are prepared when the alcohol is treated with either phenyl isocyanate or naphthyl isocyanate





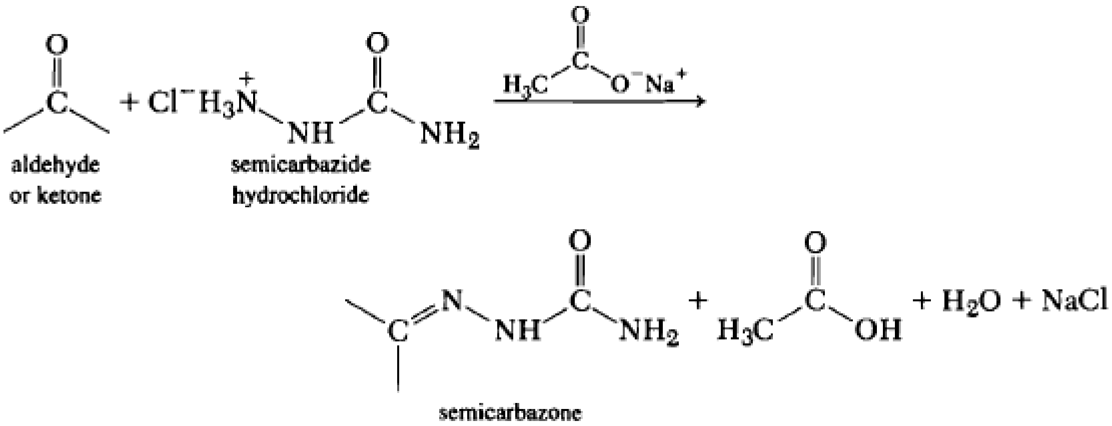
4-Nitrobenzoates or 3,5-dinitrobenzoates are easily prepared from the reaction of the alcohol with the corresponding acyl halide, For water-soluble alcohols that are likely to contain traces of moisture, the 3,5dinitrobenzoates are generally more satisfactory as derivatives than the urethanes.



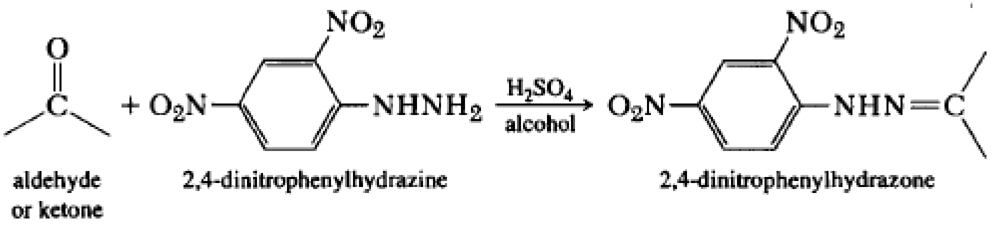


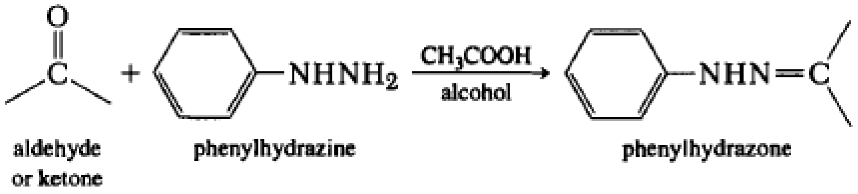
3- ALDEHYDES AND KETONES

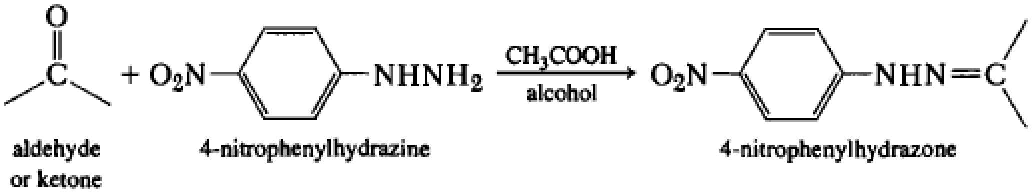
For low-molecular-weight, water-soluble aldehydes and ketones, it is often advantageous to prepare the semicarbazones from the reaction of the aldehyde or ketone with semicarbazide hydrochloride. All semicarbazones are solids and generally can be obtained nearly pure without recrystallization. Sometimes these derivatives form slowly, and care must be taken to allow sufficient time for the reaction to go to completion.



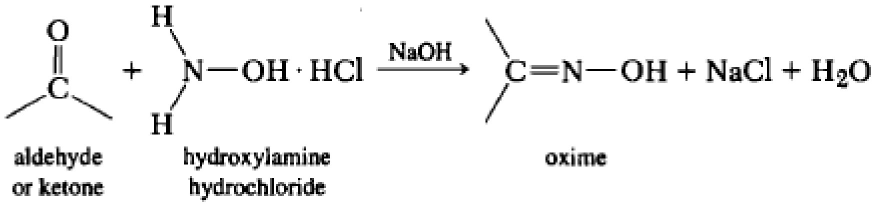
The most useful derivatives of aldehydes are the 2,4-dinitrophenylhydrazones, phenylhydrazones, and 4-nitrophenylhydrazones. of these, the 2,4-dinitrophenylhydrazones are recommended because they are most likely to be solids. Low-molecular-weight ketones may also be derivatized by 2,4-dinitrophenylhydrazones or 4-nitrophenylhydrazones. For high-molecular-weight ketones, phenylhydrazones are suitable. The 2,4-dinitrophenylhydrazone, phenylhydrazone, and 4-nitrophenylhydrazone are prepared from the reaction of the aldehyde or ketone with 2,4-dinitrophenylhydrazine, phenylhydrazine, or 4-nitrophenylhydrazine, respectively.





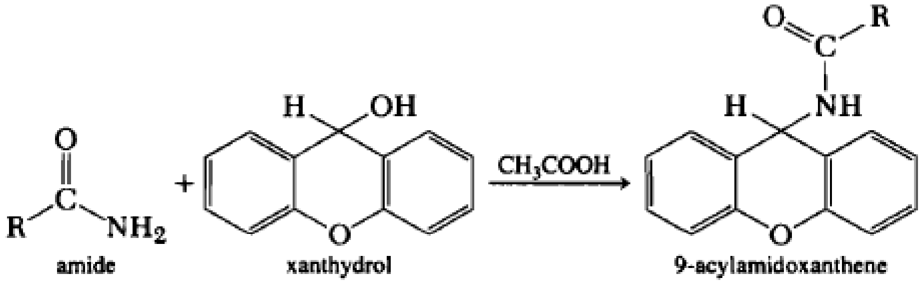


Oximes are prepared from the reaction of the aldehyde or ketone with hydroxylamine hydrochloride. However, these derivatives are likely to melt lower than the corresponding 2,4-dinitrophenylhydrazones and semicarbazones. The reaction between carbonyl compound and hydroxylamine is reversible, and care must be taken to avoid unnecessary contact with strongly acidic solutions; under these conditions the oxime may be hydrolyzed to the original compound.

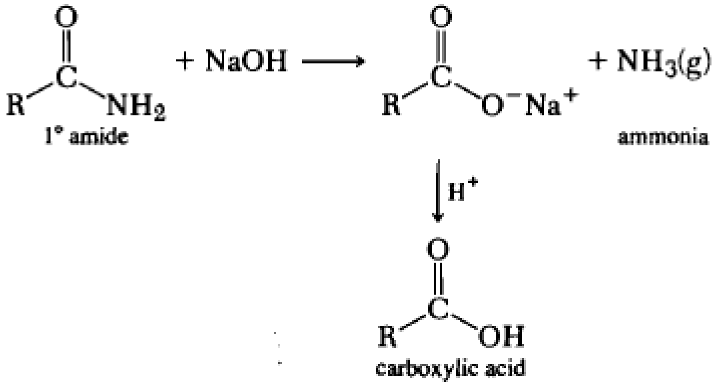


4- AMIDES

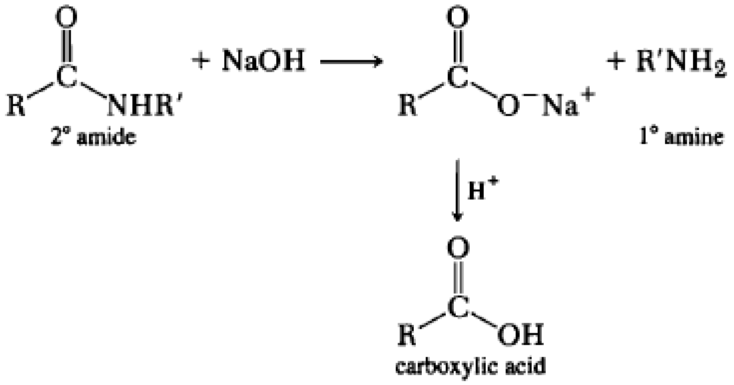
Xanthydrol reacts readily with unsubstituted amides and imides to form 9-acylamidoxanthenes. These are the only derivatives that are prepared directly from the amide.

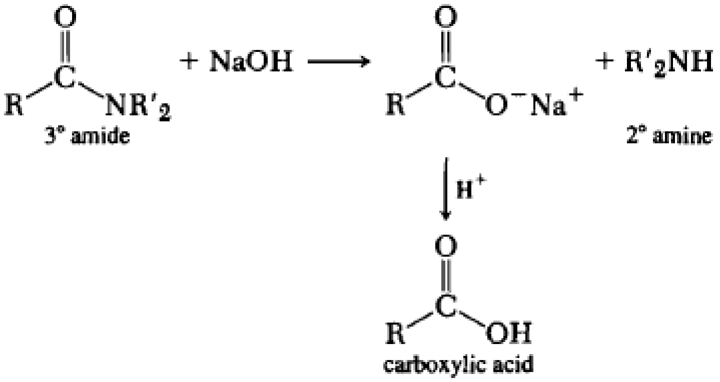


The most general method for chemically characterizing primary amides consists in hydrolyzing them with alkali to the salt of the carboxylic acid and ammonia. Acidification of the salt produces a carboxylic acid. Either the salt or the acid can be characterized.



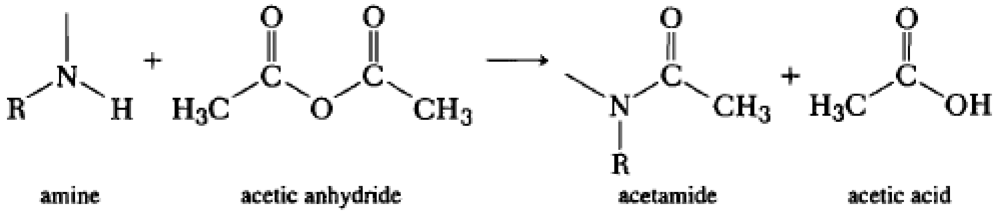
Hydrolysis of substituted amides yields carboxylic acids and primary or secondary amines instead of ammonia. The hydrolysis occurs faster **in acidic** conditions than in basic conditions. **In basic hydrolysis**, the amide is hydrolyzed to the amine and the salt of the carboxylic acid. The carboxylic acid is liberated by acidification.

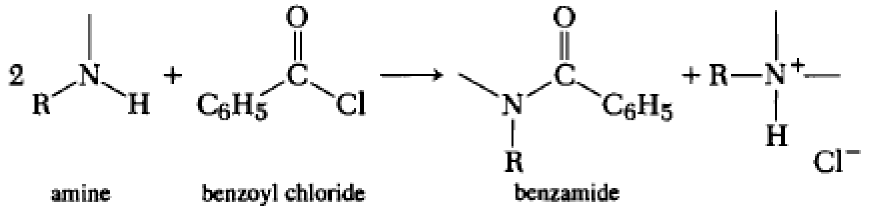




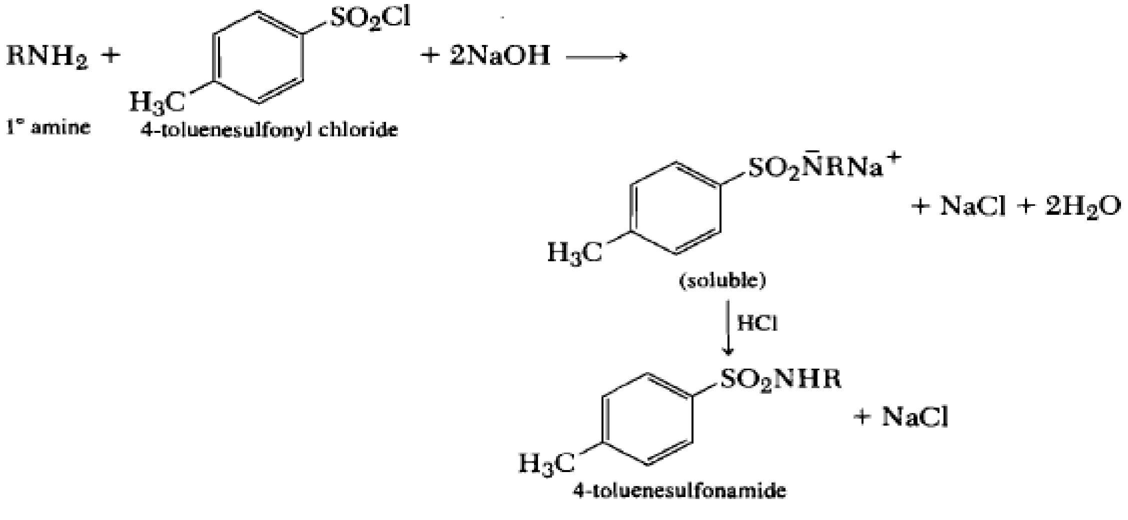
5- AMINES

The most useful derivatives of primary and secondary amines take advantage of their reactive N-H bond. The amides of acetic and benzoic acids. are conveniently prepared by treatment of the amine, respectively, with acetic anhydride or benzoyl chloride. Acetyl and benzoyl derivatives are known for most primary and secondary amines, and for this reason these derivatives are useful.

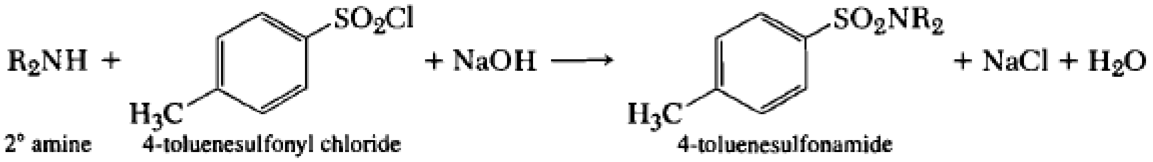




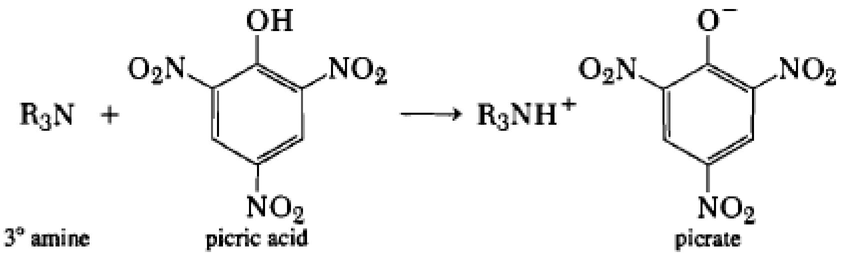
Arylsulfonamides are frequently used as derivatives. The benzenesulfonamides are frequently used, and their preparation is related to the Hinsberg method for classifying amines. The reaction of a primary amine with alkaline 4-toluenesulfonyl chloride produces the soluble salt of the arylsulfonamide. Acidification results in precipitation of the arylsulfonamide.



A secondary amine reacts with 4-toluenesulfonyl chloride to give the arylsulfonamide, which is usually insoluble.

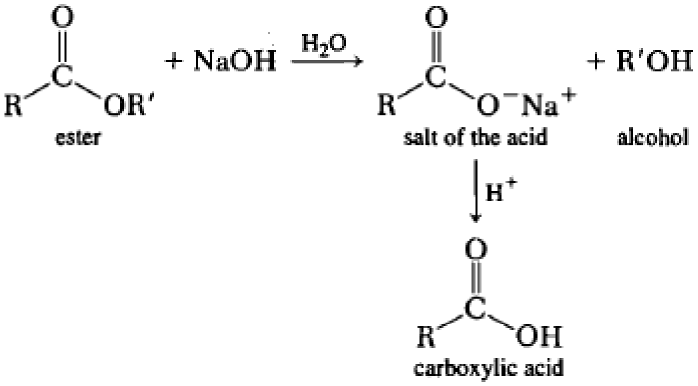


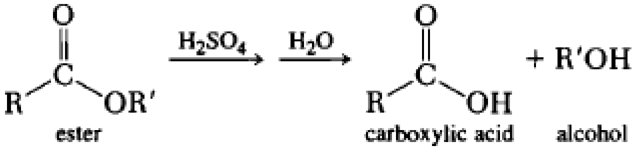
Picric acid undergoes reaction with tertiary amines to yield the picrates.



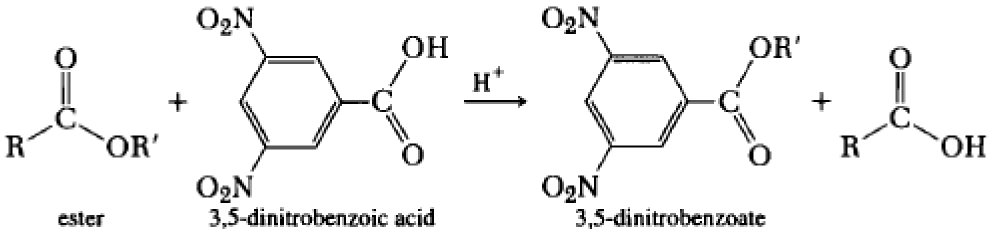
6- ESTERS

The most fundamental reaction of esters is the saponification reaction. Saponification converts an ester to an alcohol and the salt of a carboxylic acid. The carboxylic acid is liberated by acidification of the salt solution. Acid hydrolysis of the ester yields the carboxylic acid and the alcohol. Although the carboxylic acids and the alcohols can each be characterized, experience has shown that direct derivatization of the ester is a more efficient approach.

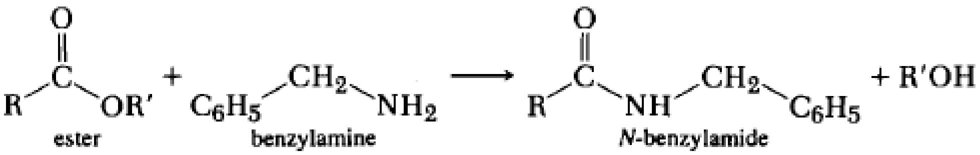




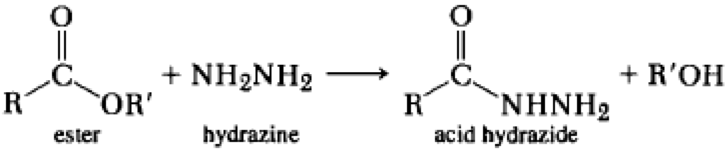
The 3,5-dinitrobenzoates, formed from the alcohol portion of a simple ester, are produced by effecting an interchange reaction between 3,5-dinitrobenzoic acid and the ester in the presence of concentrated sulfuric acid.



The reaction of esters with **benzylamine** in the presence of a little ammonium chloride yields N-benzylamides.

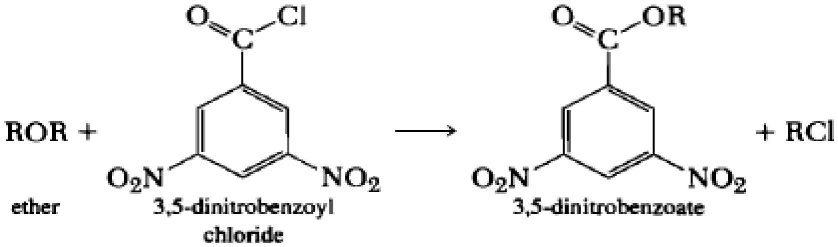


Hydrazine undergoes reaction readily with esters to produce acid hydrazides, which serve as satisfactory derivatives.



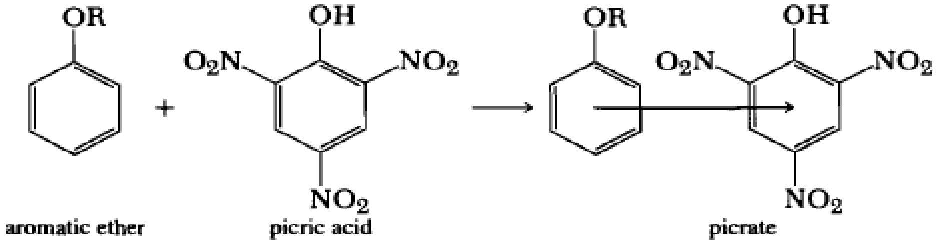
7- ETHERS-ALIPHATIC

Derivatives of symmetrical aliphatic ethers can be prepared by treating the ether with 3,5-dinitrobenzoyl chloride in the presence of zinc chloride. This method cleaves symmetrical ethers and forms the corresponding 3,5-dinitrobenzoate. The melting points of the 3,5-dinitrobenzoates can be found in the derivative tables under alcohols.

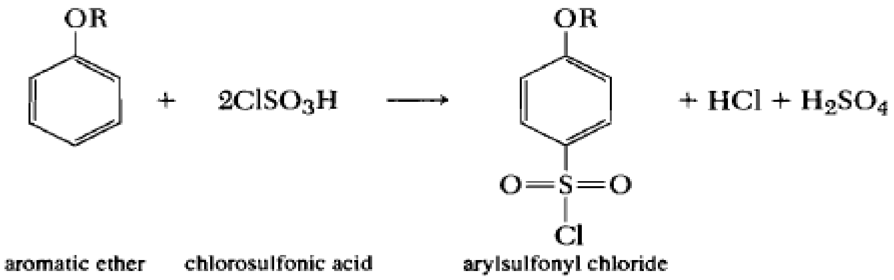


8- ETHERS-AROMATIC

Picrates are used as derivatives of aromatic ethers. The picrates are prepared by the treatment of the aromatic ether with picric acid.

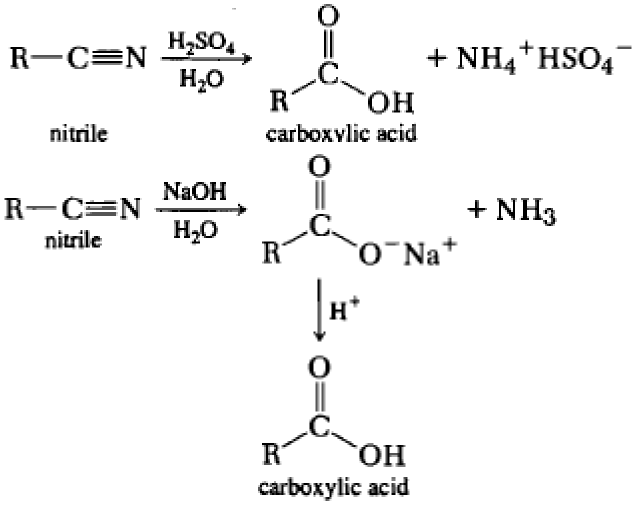


Aromatic ethers undergo reaction with chlorosulfonic acid at 0°C to produce arylsulfonyl chlorides.



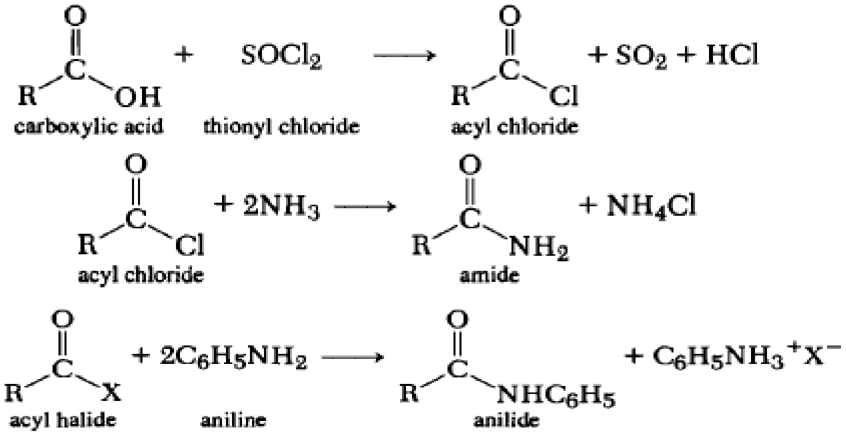
9- NITRILES

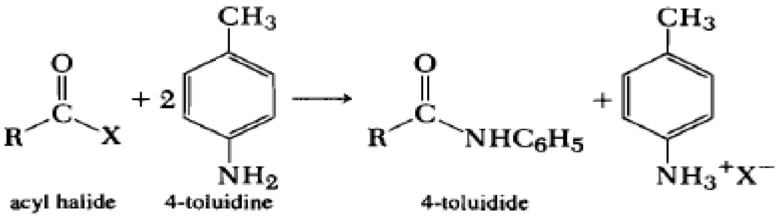
The nitriles may be hydrolyzed to the corresponding carboxylic acid by means of a mineral acid or an aqueous base.



If the resulting acid is a solid, it serves as an excellent derivative

The carboxylic acid can be derivatized by preparing the **acyl chloride**, followed by treatment with **ammonia, aniline, or 4-toluidine** to form the amide, the anilide, or 4-toluidide, respectively





Reduction of Nitriles with sodium and an alcohol forms Primary Amines

$$\underset{\text{nitrile}}{R{-}C{\equiv}N} \xrightarrow[CH_3CH_2OH]{Na} \xrightarrow{HCl} RCH_2NH_3^+Cl^- \xrightarrow{NaOH} \underset{1^\circ\ \text{amine}}{RCH_2NH_2}$$

10- NITRO COMPOUNDS

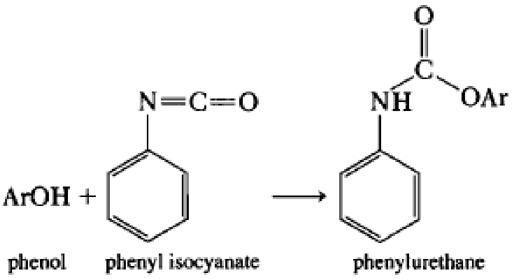
The reduction of nitro compounds in acidic media leads to the formation of primary Amines.

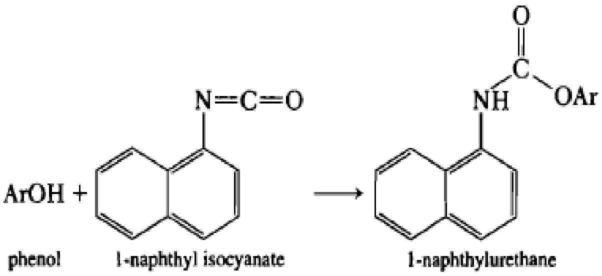
$$\underset{\text{nitro compound}}{RNO_2} \xrightarrow[HCl]{Sn} RNH_3^+Cl^- \xrightarrow{NaOH} \underset{1^\circ\ \text{amine}}{RNH_2}$$

These primary amines can then be converted into suitable derivatives such as acetamides, benzamides, or benzenesulfonamides. The acetamide is prepared by the reaction of the amine with acetic anhydride.

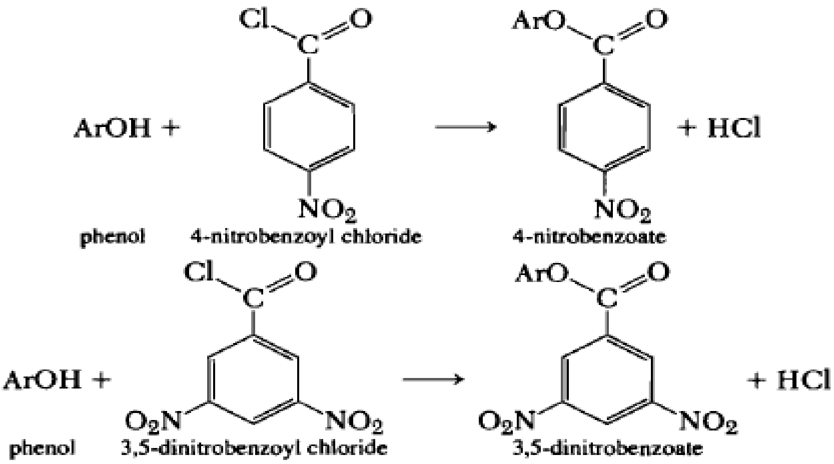
11- PHENOLS

Phenols, like alcohols yield urethanes when treated with isocyanates. Both the phenylurethanes and the I-naphthylurethanes (a-naphthylurethanes) are generally useful derivatives in identifYing phenols.





4-nitrobenzoates , or 3,5dinitrobenzoates are easily prepared from the reaction of the phenol with the corresponding acyl halide.


ArOH +
Cl
C
O
NO2
+ HCl
ArO
phenol
4-nitrobenzoyl chloride
4-nitrobenzoate
ArOH +
Cl
O2N
NO2
ArO
phenol
3,5-dinitrobenzoyl chloride
3,5-dinitrobenzoate