Carboxylic acids and their Derivatives

Carbonyl containing compounds

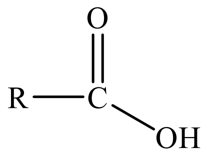
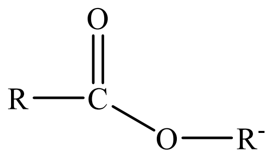
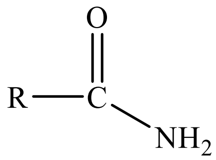
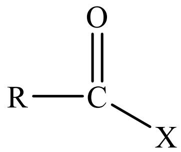
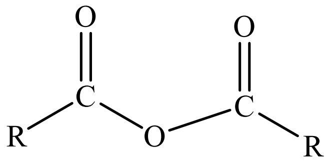
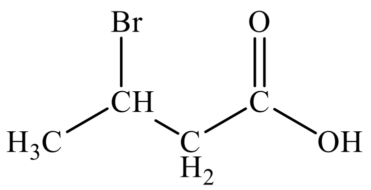
Formula	**Family**	
	Carboxylic acid	
	Ester	
	Amide	
	Acid halide	X= Cl , Br
	Acid anhydride	

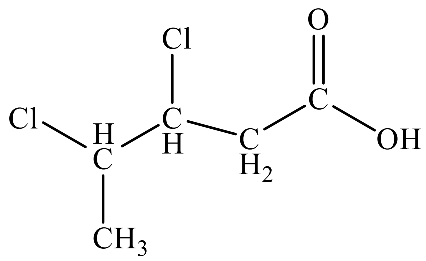
Table (1) :Aliphatic Carboxylic acids

Carbon atom	**Formula**	**Common name**	**Iupac name**
1	HCOOH	Formic acid	methanoic acid
2	CH_3COOH	Acetic acid	ethanoic acid
3	CH_3CH_2COOH	Propionic acid	propanoic acid
4	$CH_3CH_2CH_2COOH$	Butyric acid	butanoic acid
5	$CH_3CH_2CH_2CH_2COOH$	Valeric acid	pentanoic acid
6	$CH_3CH_2CH_2CH_2CH_2COOH$	Caproic acid	hexanoic acid

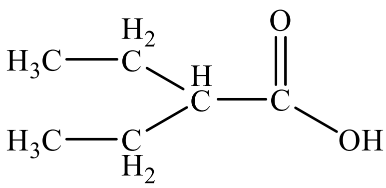
Examples :-



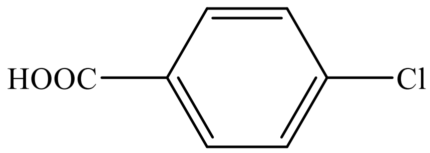
3-bromobutanoic acid



3,4-dichloropentanoic acid



2-ethylbutanoic acid



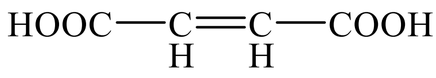
4-chlorobenzoic acid

Di acids

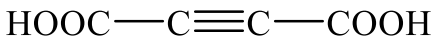
Table (2) :- Aliphatic Di carboxylic acids

Formula	**Common name**	**Iupac name**
$HOOC-COOH$	oxalic acid	ethanedioic acid
$HOOC-\overset{H_2}{C}-COOH$	malonic acid	propanedioic acid
$HOOC-(CH_2)_2-COOH$	succinic acid	butanedioic acid
$HOOC-(CH_2)_3-COOH$	glutaric acid	pentanedioic acid
$HOOC-(CH_2)_4-COOH$	adipic acid	hexanedioic acid
$HOOC-(CH_2)_5-COOH$	pimelic acid	heptanedioic acid

Aliphatic di carboxylic acid are given the suffix –dioic acid in the Iupac system. For example:-



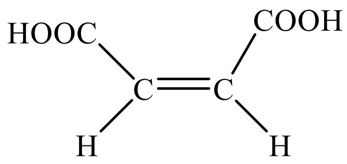
2-butenedioic acid



2-butynedioic acid

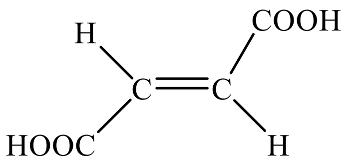
Many di carboxylic acids occur in nature and go by their common names, which are based on their source; table (2) lists some common aliphatic di acids. The most important commercial compound in these groups is adipic acid, used manufacture nylon.

The two-butenedioic acids played a historic role in the discovery of cis-trans isomerism and are usually known by their common names maleic and fumaric acid.



maleic acid

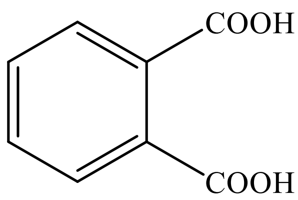
Cis - 2-butenedioic acid



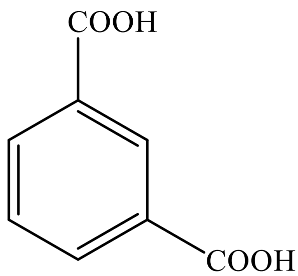
fumaric acid

Trans -2- butenedioic acid

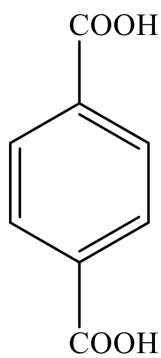
The three benzene di carboxylic acids are generally known by their common names



phthalic acid



isophthalic acid



terephthalic acid

Physical Properties of carboxylic acids

1- Hydrogen bonding

2- Solubility in water (lower acids)

3- Acidity

Note :- first and second properties in table (3) , third properties in table (4).

Table (3) :- physical properties of some carboxylic acids

Name	**b.p C°**	**m.p C°**	**Solubility g / 100 g H_2O at 25 C°**
formic acid	100.5	8	∞
acetic acid	118	16.6	∞
propanoic acid	141	-22	∞
butanoic acid	164	-8	∞
pentanoic acid	187	-34	3.7
hexanoic acid	205	-1.5	1.0

Acidity of Carboxylic Acids

Aqueous solutions of carboxylic acids are much weaker acids than inorganic acids, such as HCl, but are much stronger acids than most other types of hydrocarbons (alcohols, ketones, alkynes, etc.). Carboxylic acids typically have pKa values of 4 to 5. Inorganic acids have negative pKa values. Alcohols have pKa values of about 15 to 16. Carboxylic acids and alcohols can both act as Brønsted–Lowry acids and ionize to give a proton (H+) and an anionic conjugate base. Each base has a negative charge on an oxygen atom. The carboxylate anion is more stable (is a weaker base) than an alkoxide anion. One reason for this stability is that the electrons in the carboxylate anion can be delocalized over both oxygen atoms. Delocalization increases stability. As the stability of an anion increases, the acid dissociation equilibrium shifts to produce more of the anion, concurrently increasing the hydrogen ion concentration (acidity). Acid dissociation equations and Lewis resonance structures of the two anions (carboxylate and alkoxide) are shown in **Fig 1.**

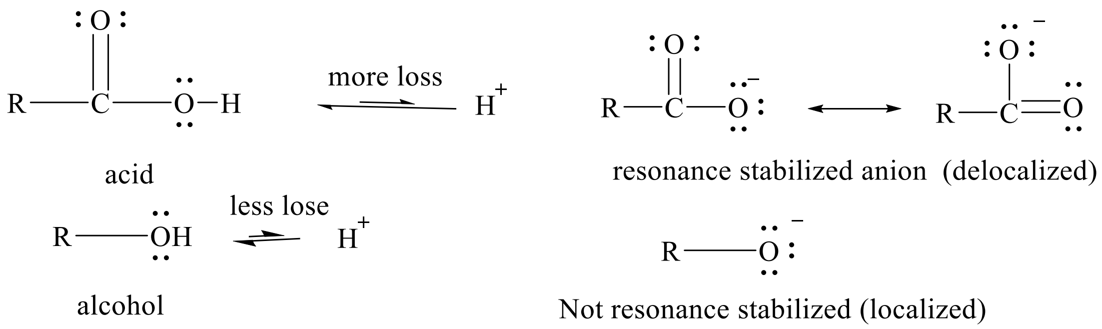
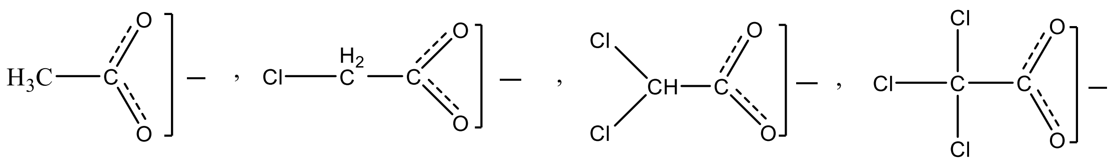


Table (4) :- The Ionization Constants of Some acids

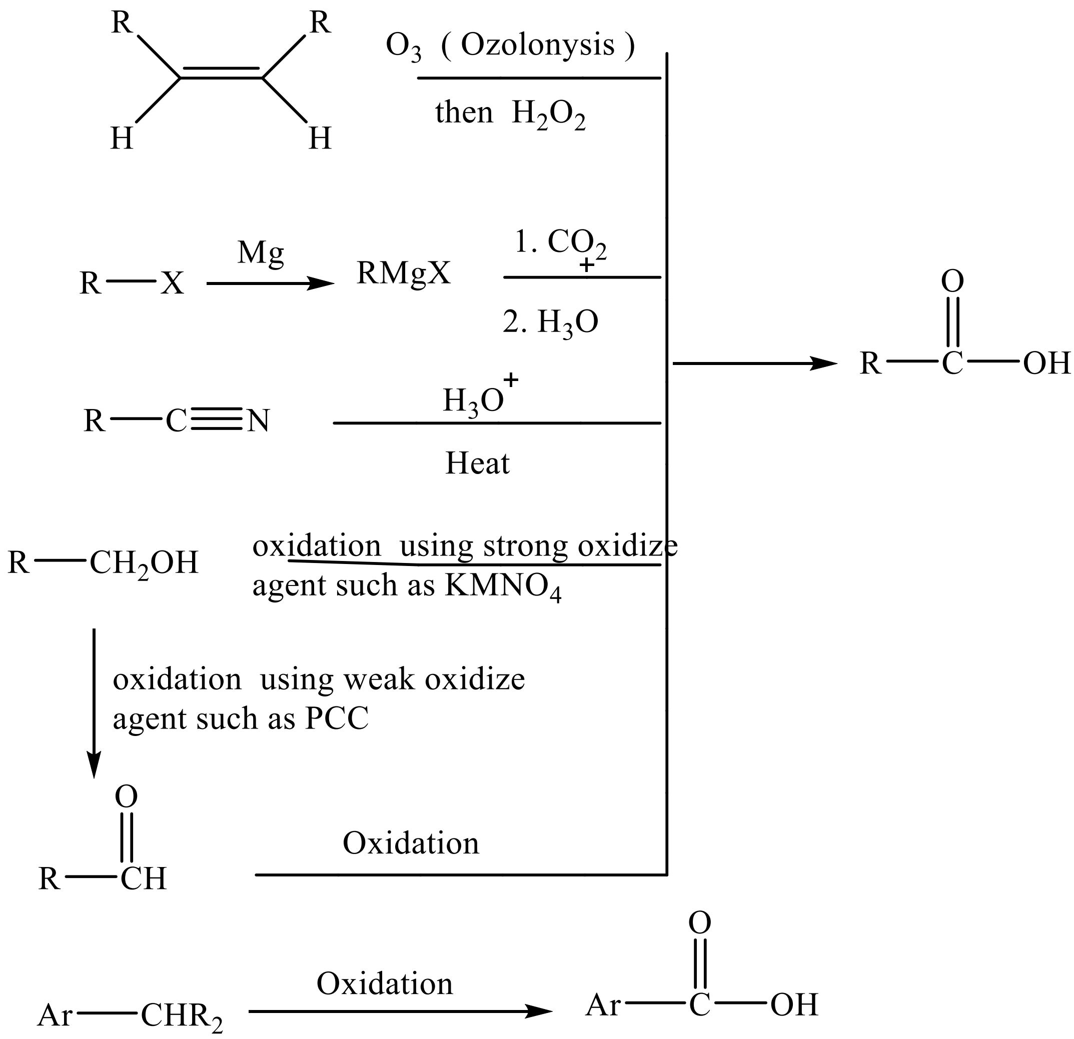
Name	**Formula**	**Ka**	**pka**
formic acid	$HCOOH$	17.7×10^{-5}	3.68
acetic acid	CH_3COOH	1.75×10^{-5}	4.74
propionic acid	CH_3CH_2COOH	1.4×10^{-5}	4.85
butyric acid	$CH_3CH_2CH_2COOH$	1.6×10^{-5}	4.80
chloro acetic acid	$ClCH_2COOH$	136×10^{-5}	2.82
dichloro acetic acid	$Cl_2CHCOOH$	5530×10^{-5}	1.30
trichloro acetic acid	Cl_3CCOOH	23200×10^{-5}	0.7

Resonance and Inductive effect

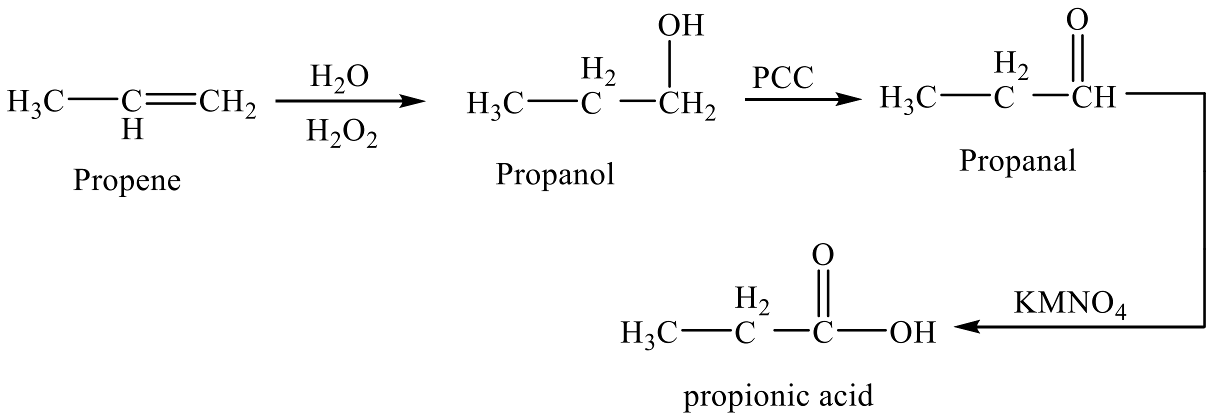


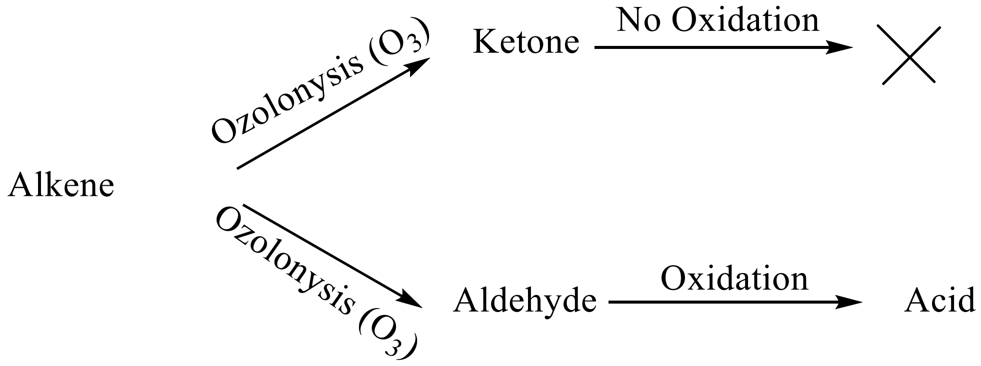
The acidity of trichloro acetic acid is stronger than the dichloro acetic acid and chloro acetic acid.

Preparation of Carboxylic acid

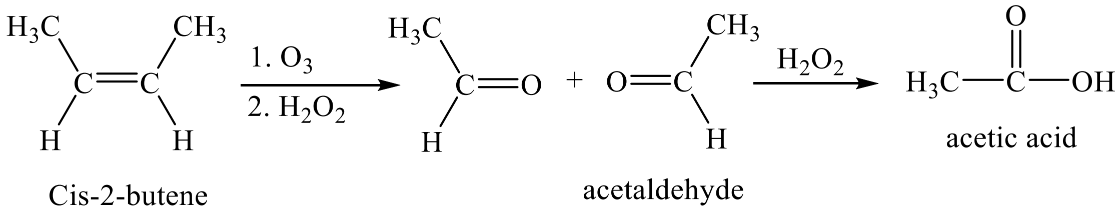


Example :-

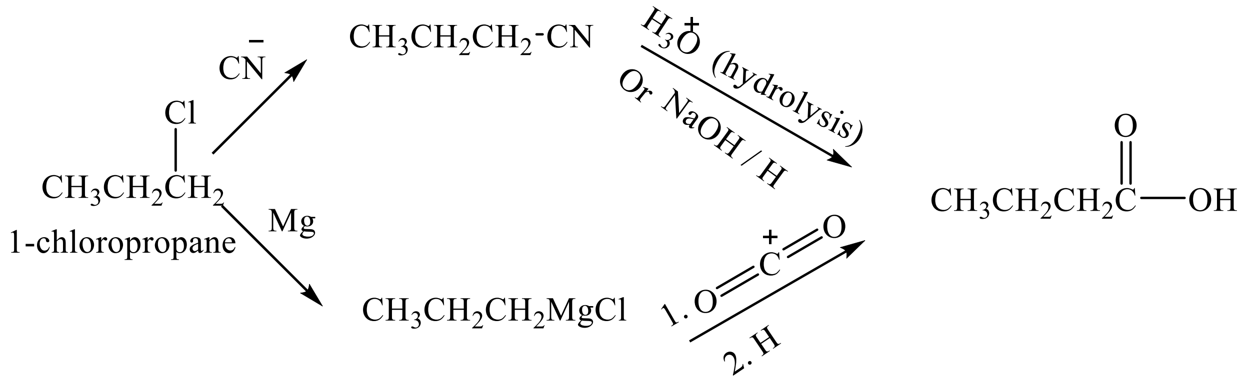




Example :-



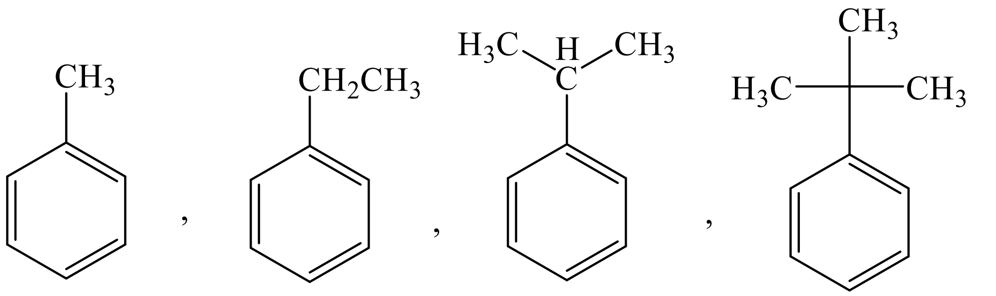
Example :-



Preparation of Benzoic acid from benzene from two methods

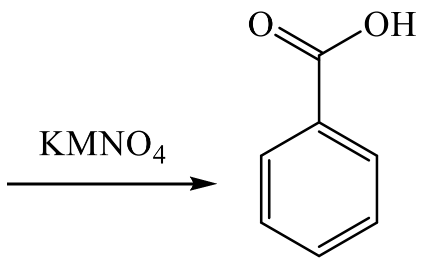
1. Oxidation of aliphatic chain using potassium permanganate ($KMNO_4$)

2. Using Grignard reagent.



toluene 1, ethylbenzene 2, cumene 3, *tert*-butylbenzene 4

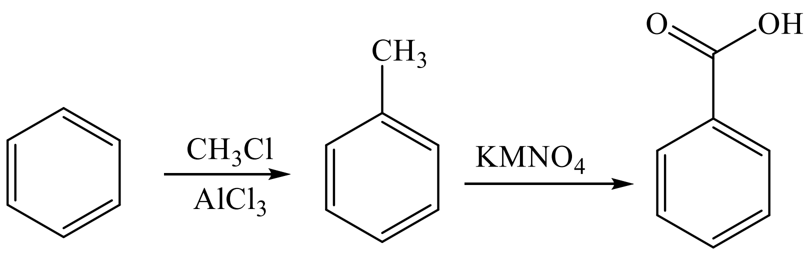
Comp 1 and Comp 2 and Comp 3



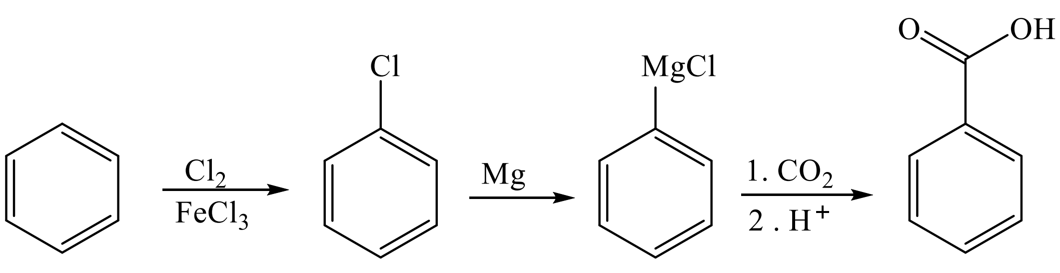
benzoic acid

Comp 4 $\xrightarrow{KMNO_4}$ NO Reaction

1.

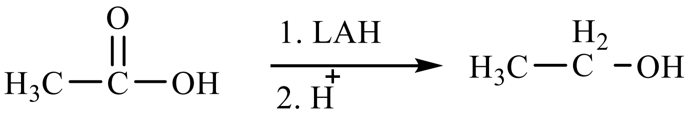


2.



REDUCTION OF CARBOXYLIC ACIDS

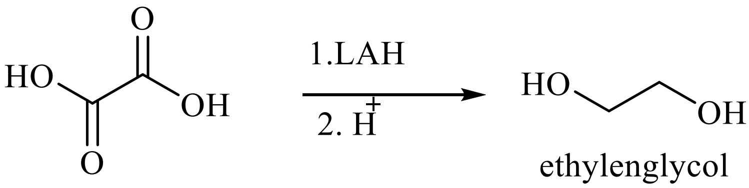
Carboxylic acids are reduced to alcohols by LAH. The initial reduction product is an aldehyde which is subsequently reduced to an alkoxide anion. In a second step, the alkoxide anion is protonated to give the corresponding primary alcohol.



acetic acid — ethanol primary alcohol

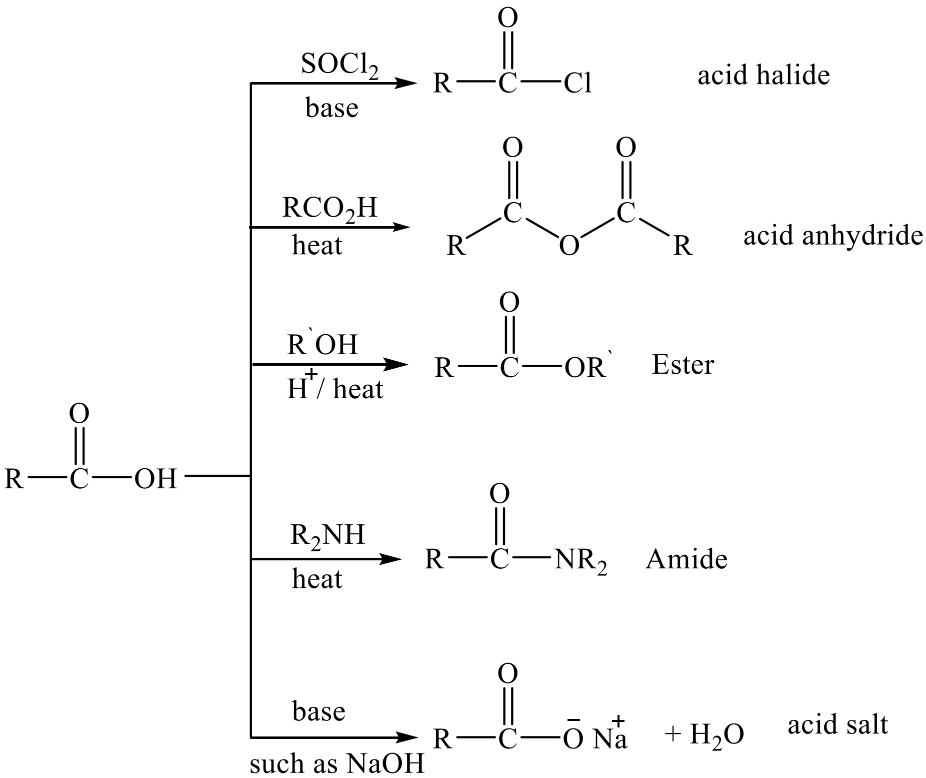
Note :- that both carbonyl groups are reduced.

Reduction of oxalic acid by LAH to give ethylene glycol



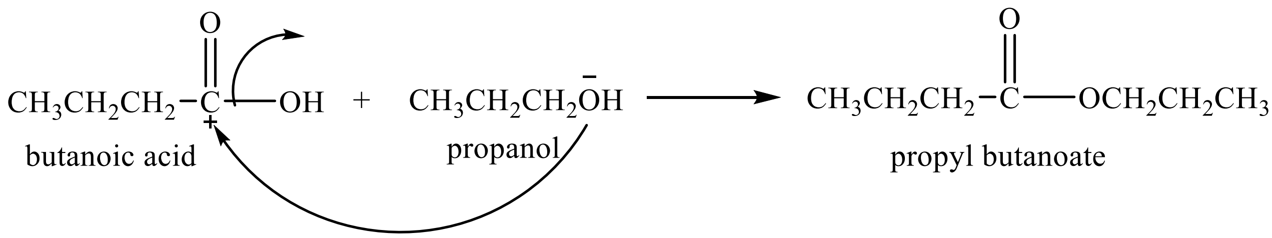
oxalic acid — ethylenglycol

Derivatives of Carboxylic acids



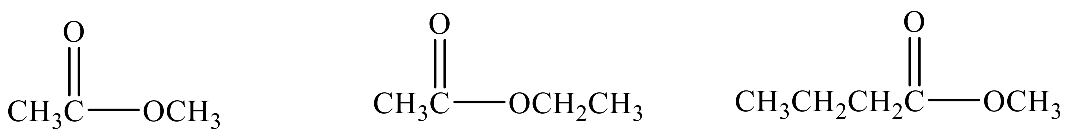
$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$ **neutralization reaction**

substitution reaction



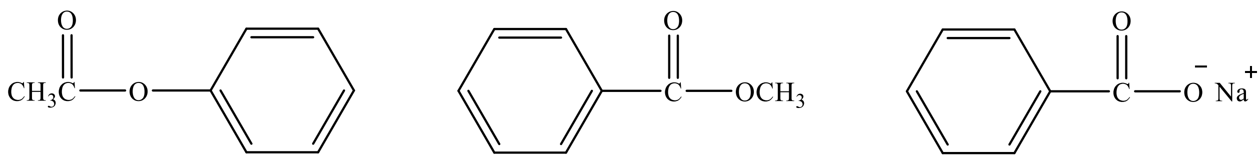
ESTERS

Esters are derived from acids by replacing the OH group by an OR group . They are named in a manner analogous to carboxylic acid salt. The R part of the OR group is named first followed by the name of the acid , with the –ic ending changed to –ate.



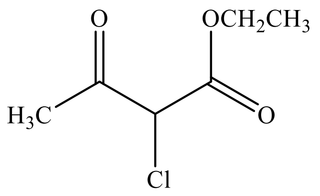
methyl acetate	ethyl acetate	methyl butyrate
(methyl ethanoate)	(ethyl ethanoate)	(methyl butanoate)
b.p 57C°	b.p 77C°	b.p 102C°

Notice: - the different names of the following pair of isomeric esters, where the R and R` groups are interchanged

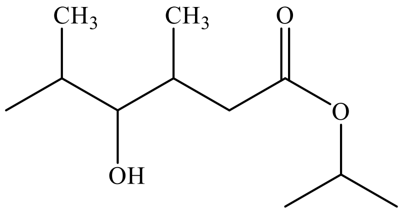


phenyl acetate	methyl benzoate	sodium benzoate
b.p 195.7 C°	b.p 196.8 C°	

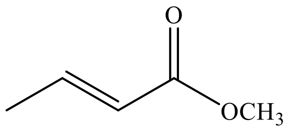
Nomenclature of esters



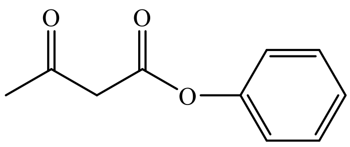
ethyl 2-chloro-3-oxobutanoate



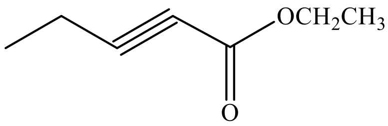
isopropyl 4-hydroxy-3,5-dimethylhexanoate



methyl 2-butenoate



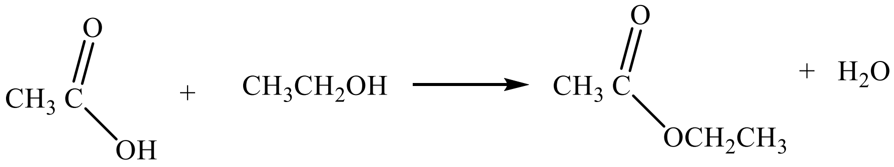
phenyl 3-oxobutanoate



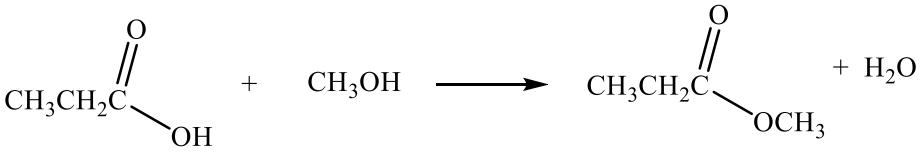
ethyl 2-pentynoate

Reactions of Carboxylic acid

Formation of esters

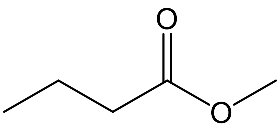


ethyl ethanoate

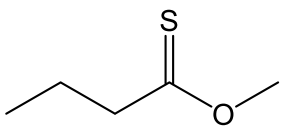


methyl propanoate

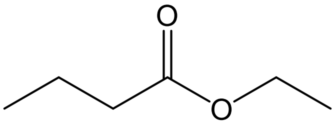
Smelly Stuff



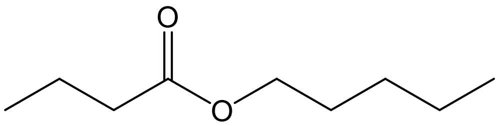
methyl butanoate
Apple



O-methyl butanethioate
Strawberries



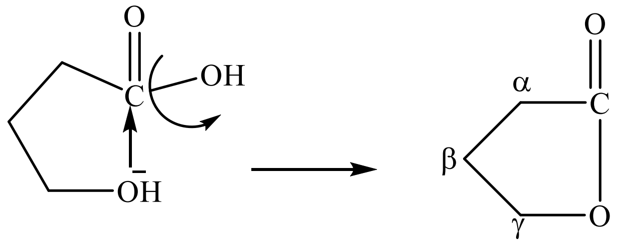
ethyl butanoate
Pineapples



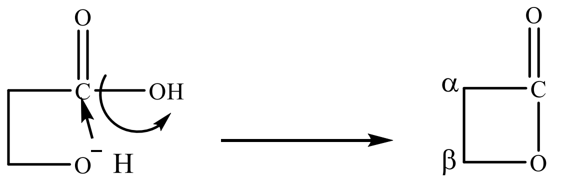
pentyl butanoate

Apricots

Lactones (Cyclic Esters)

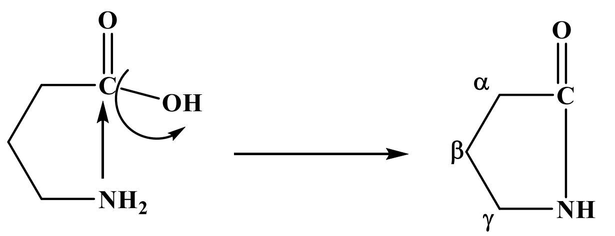


γ- Lactones

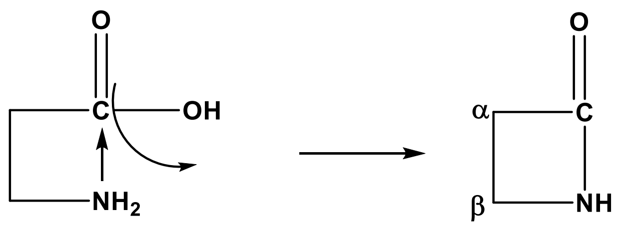


β- Lactone

Lactam is cyclic amide



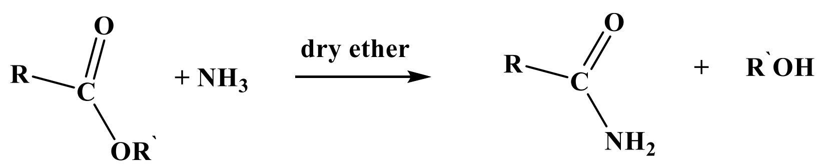
γ - Lactam



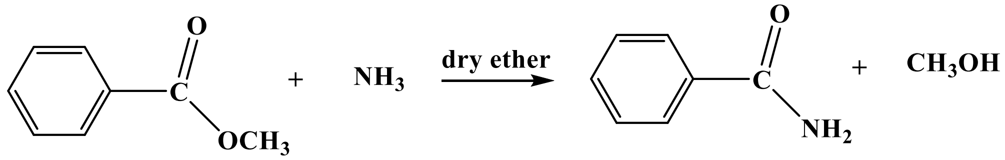
β - Lactam

Ammonolysis of Esters

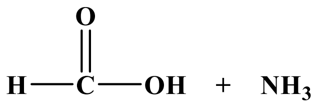
Ammonia converts esters to amides



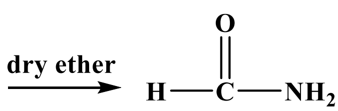
For example



benzamide



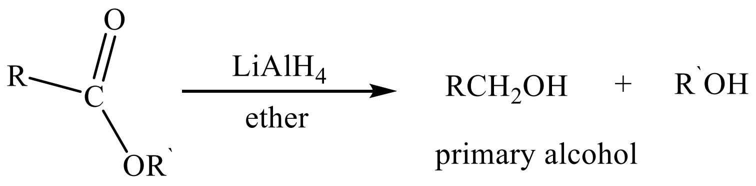
formic acid



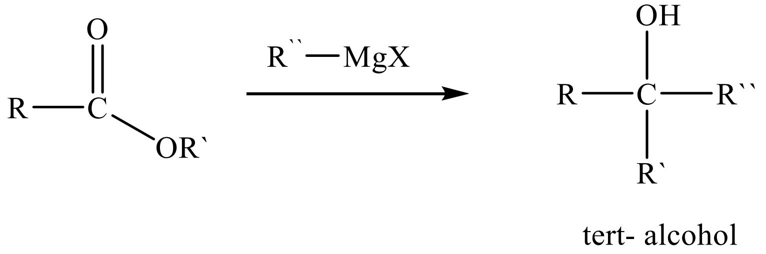
formamide

Reduction of Esters

Esters can be reduced to primary alcohols



Esters reacted with Grignard reagent produced tert- alcohols

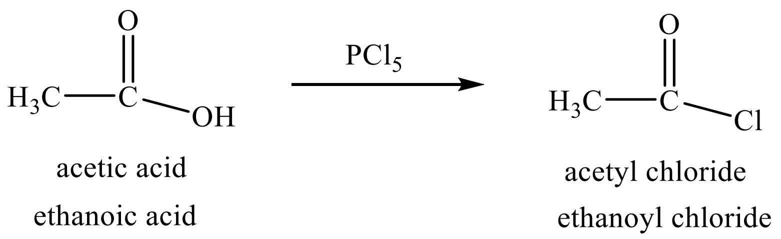


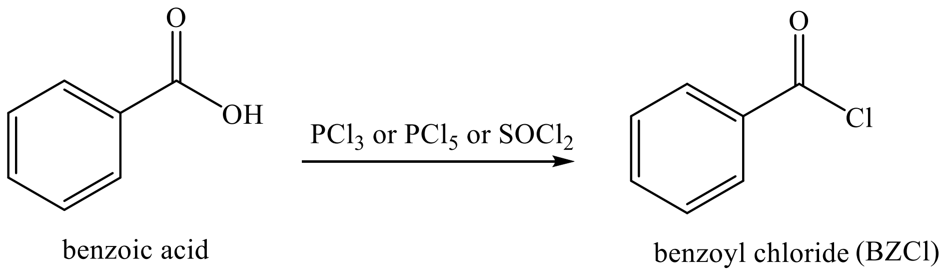
Acid Halides

They are prepared from the reaction of acids with thionyl chloride or phosphorus halides

Reactions of carboxylic acids (Formation of derivatives)

1. Acid chlorides

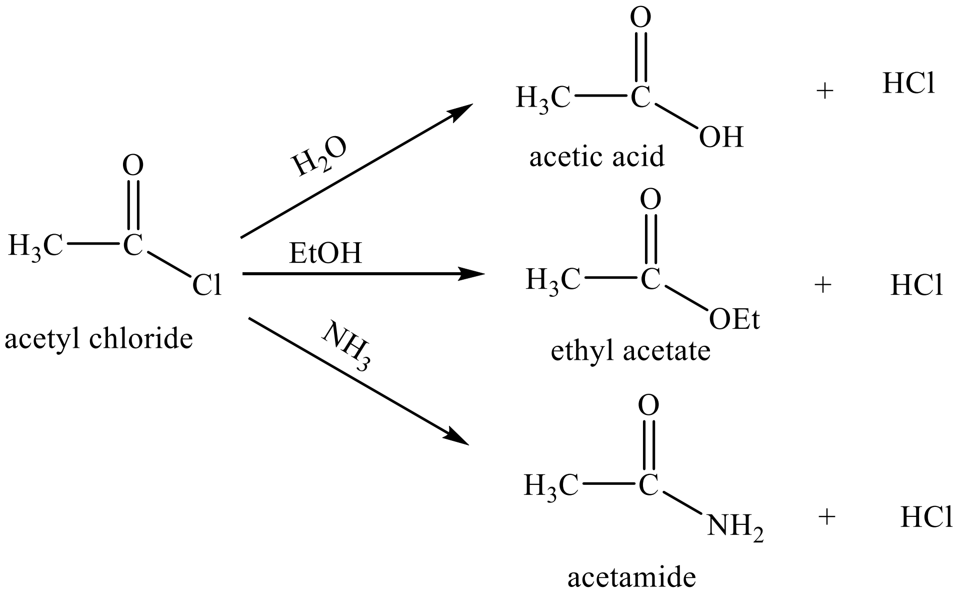




Reactions of acid chlorides

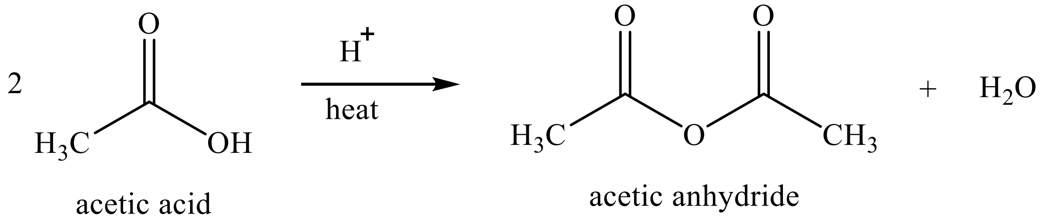
Acid chlorides react rapidly with most nucleophiles such as water , alcohols and ammonia.

Acyl halides have irritating odors . Benzoyl chloride is a lachrymator (tear gas).

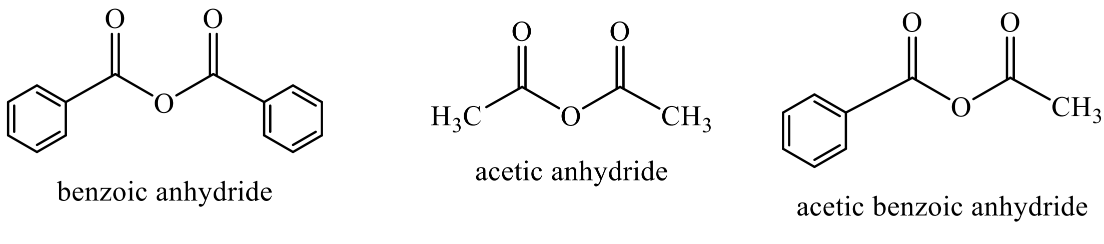


2. Acid anhydrides

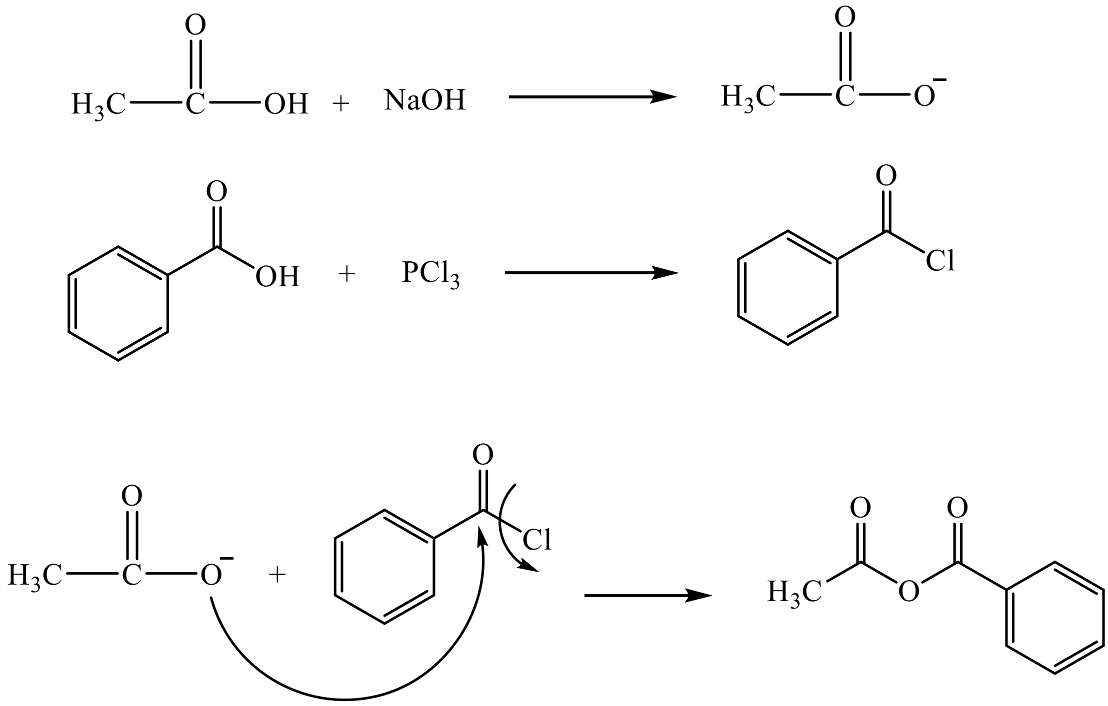
Formed from the combination of two acids and the loss of water.



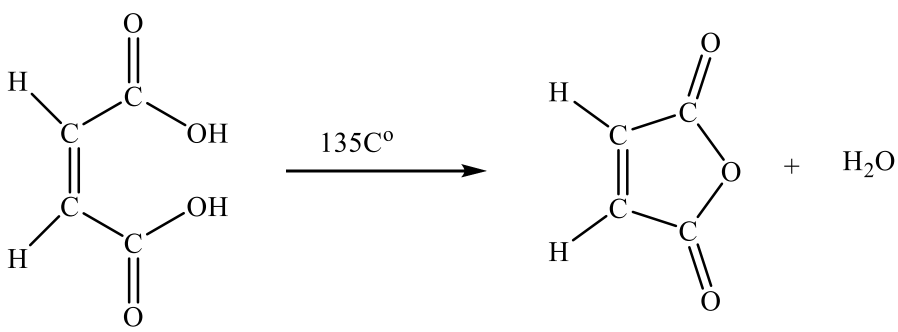
Nomenclature of acid anhydride



Preparation of mixed anhydride

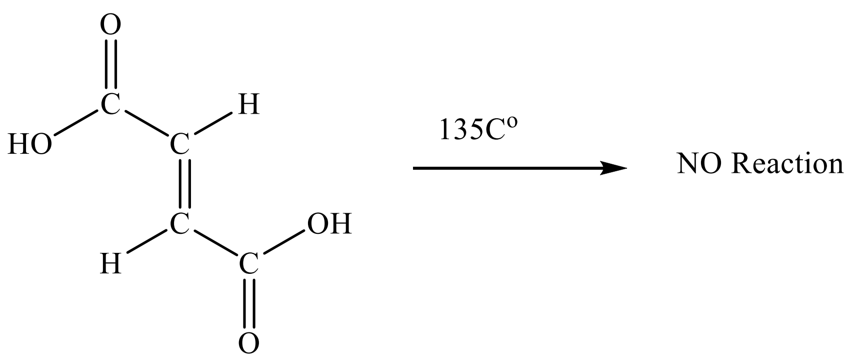


Di Acids

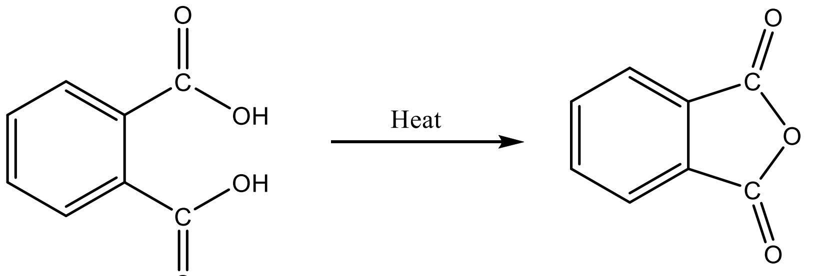


maleic acid

maleic anhydride

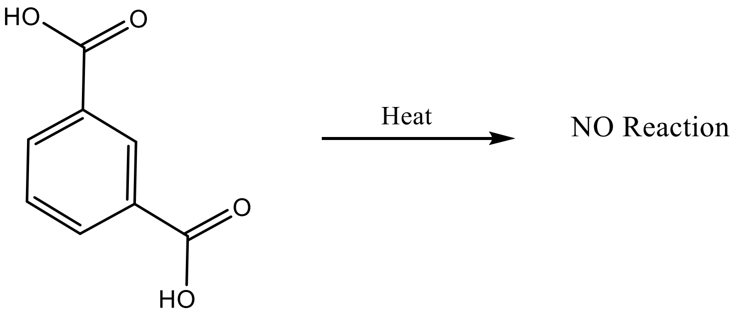


fumaric acid

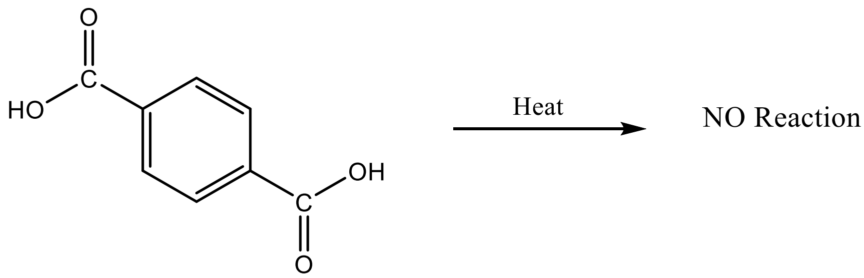


phthalic acid

phthalic anhydride

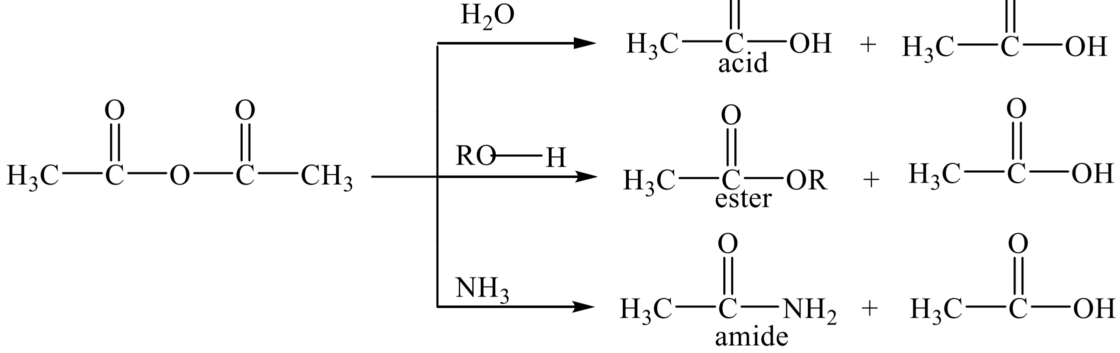


isophthalic acid

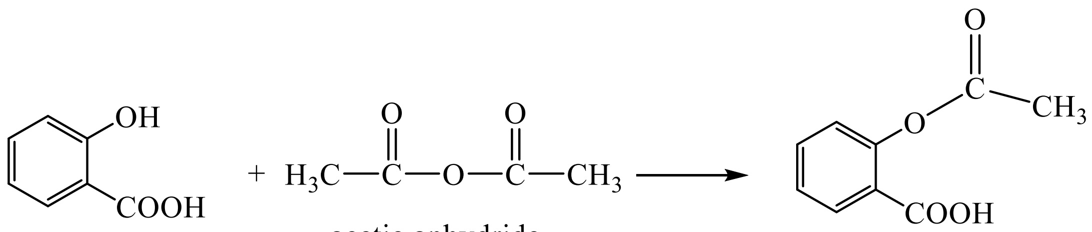


terephthalic acid

Nucleophilic Substitution of anhydride



Example :-



Salicylic acid
2-hydroxybenzoic acid

acetic anhydride

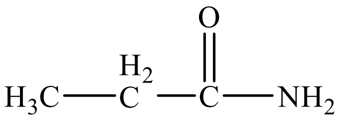
2-acetoxybenzoic acid
acetyl salicylic acid
Aspirin

Amide

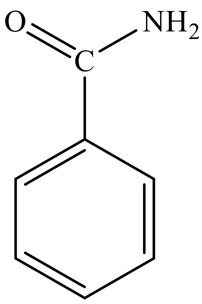
Amide Nomenclature

Similar to carboxylic acid

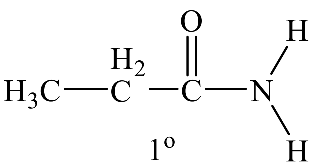
Drop-oic acid ending and replace with amide



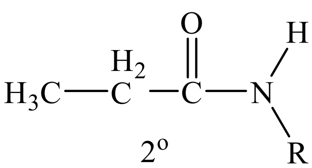
propionamide
propanamid



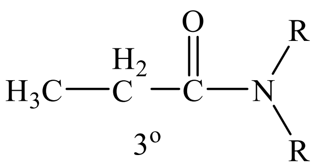
benzamide



1°



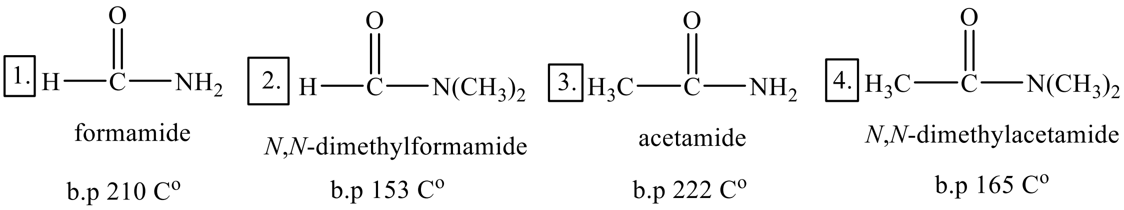
2°



3°

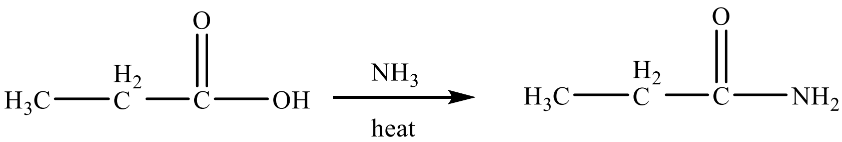
Properties of amide

They have exceptionally high boiling points for their molecular weight , although alkyl substitution on the nitrogen lowers the boiling and melting points by decreasing the hydrogen bonding possibilities , as shown in the following two pairs of compounds :-

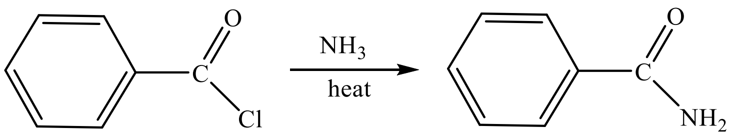


Preparation of amides

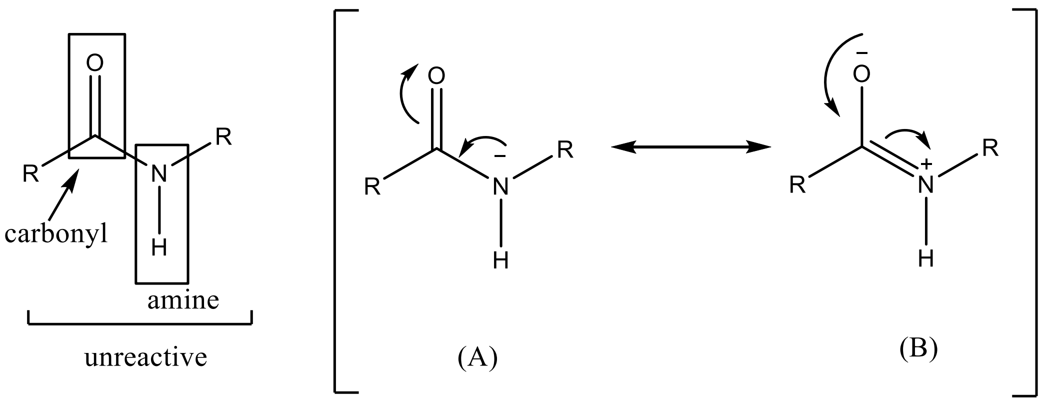
Production from a carboxylic acid



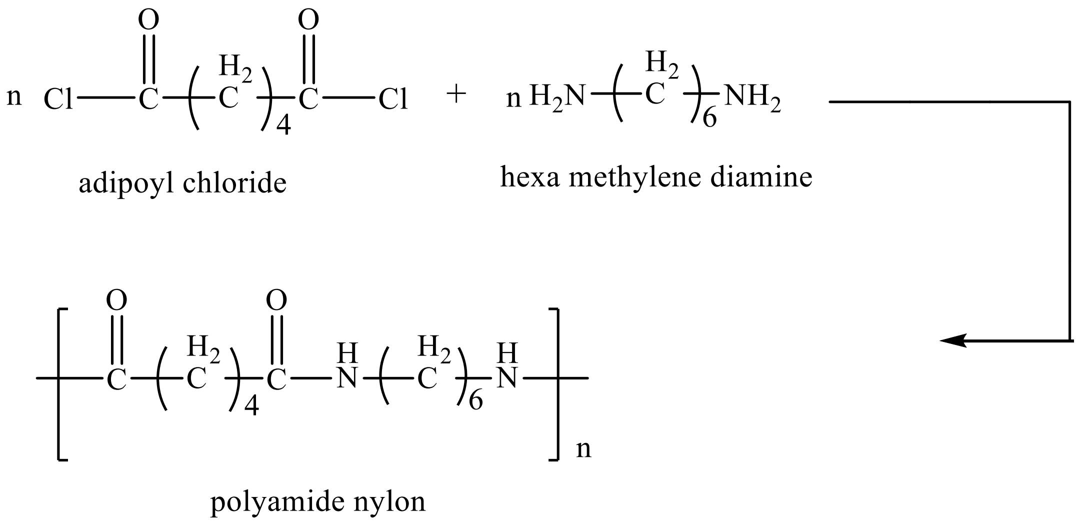
Production from an acid chloride



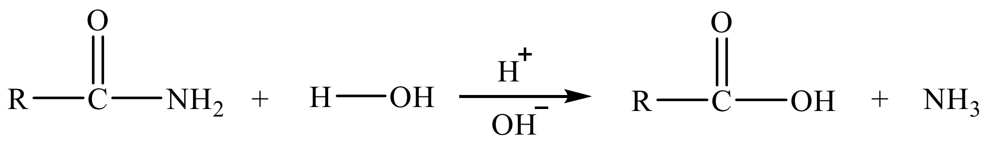
The amide is not reactive and that because the resonance.



If we have a diamine and a diacid chloride, we can produce a polymer using amide bonds, Nylon is an example.

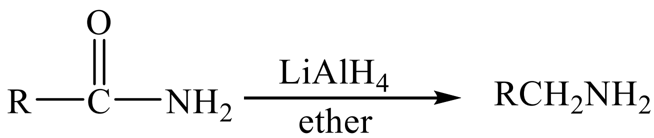


Reactions of amides (Hydrolysis and Reduction)



The reactions are slow and prolonged heating or acid or base catalysts is usually necessary.

Amides can be reduced by lithium aluminum hydride to give amines.

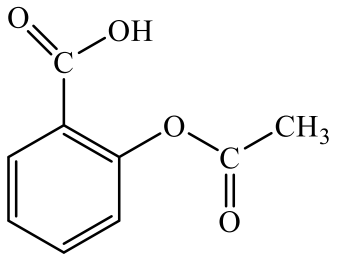


This is an excellent way to make primary amines, whose chemistry is discussed.

Some significant examples

Analgesics – painkillers

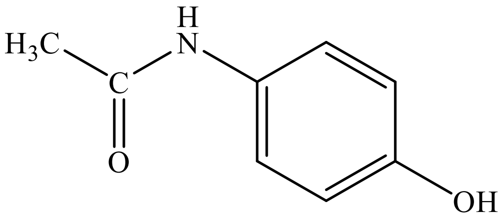
Antipyretics – fever reduces



2-acetoxybenzoic acid

Acetyl salicylic acid

(Aspirin)



Acetaminophen

(Tylenol)