

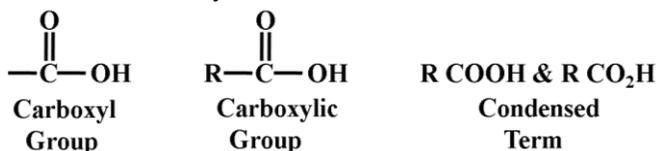
Chapter 7

Carboxylic Acid

Day – 1

Introduction

The combination of carbonyl group & hydroxyl group given carboxyl group. Then compounds are distinctly acid so called carboxylic acid.



Classification

- (i):- Aliphatic acid – have an alkyl group bonded to the carboxyl group.
- (ii):- Aromatic acid: have aryl group with carboxyl group
- (iii):- Fatty acid – are acid derived from hydrolysis of fats & oils.

CH₃COOH
 Ethanoic acid
 (Aliphatic acid)

-COOH
 Benzoic acid
 (Aromatic acid)

CH₃(CH₂)₁₆COOH
 Stearic acid
 (Fatty acid)

Nomenclature

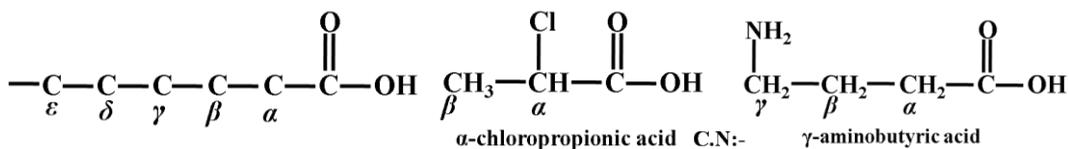
Common Name were derived from where these acids were obtained from ex. Formic acid (HCOOH) is obtained from ants (formic in latin means ants). Acetic acid CH₃COOH derived from Vinegar (acetum means sour in latin). Butyric acid form oxidation of butyraldehyde which is found in butter (butyrum in Latin).

The names and physical properties of some carboxylic acids are shown in Table

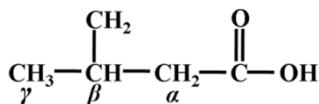
IUPAC Name	Common Name	Formula	mp (°C)	bp (°C)	Solubility (g/100g H ₂ O)
Methanoic ^a	formic	HCOOH	8	101	∞ (miscible)
ethanoic ^a	acetic	CH ₃ COOH	17	118	∞
propanoic	propionic	CH ₃ CH ₂ COOH	-21	141	∞
2-propenoic ^a	acrylic	H ₂ C = CH – COOH	14	141	∞
Butanoic	butyric	CH ₃ (CH ₂) ₂ COOH	-6	163	∞
2-methylpropanoic	isobutyric	(CH ₃) ₂ CHCOOH	-46	155	23
trans-2-butenic ^a	crotonic	CH ₃ – CH = CH –	71	185	8.6

pentanoic	valeric	COOH	- 34	186	3.7
3-methylbutanoic	isovaleric	CH ₃ (CH ₂) ₃	- 29	177	5
2, 2-dimethylpropanoic	pivalic	(CH ₃) ₃ CCH ₂ COOH	35	164	2.5
hexanoic	caproic	(CH ₃) ₃ C - COOH	- 4	206	1.0
octanoic	caprylic	CH ₃ (CH ₂) ₄ COOH	16	240	0.7
decanoic	capric	CH ₃ (CH ₂) ₆ COOH	31	269	0.2
dodecanoic	lauric	CH ₃ (CH ₂) ₈ COOH	44		i
tetradecanoic	myristic	CH ₃ (CH ₂) ₁₀ COOH	54		i
hexadecanoic	palmitic	CH ₃ (CH ₂) ₁₂ COOH	63		i
octadecanoic	stearic	CH ₃ (CH ₂) ₁₄ COOH	72		i
cis-9-octadecenoic ^a	oleic	CH ₃ (CH ₂) ₁₆ COOH	16		i
cis, cis-9, 12-octadecadienoic ^a	linoleic	CH ₃ (CH ₂) ₇ CH = CH(CH ₂) ₇ COOH	= - 5		i
		CH ₃ (CH ₂) ₄ CH = CH(CH ₂) ₇ COOH	= 31	233	0.2
	benzoic	CHCH ₂ CH =	= 122	249	0.3
cyclohexanecarboxylic	<i>o</i> -toluic	CH(CH ₂) ₇ COOH	106	259	0.1
benzoic	<i>m</i> -toluic	<i>c</i> -C ₆ H ₁₁ COOH	112	263	0.1
2-methylbenzoic	<i>p</i> -toluic	C ₆ H ₅ - COOH	180	275	0.03
3-methylbenzoic		<i>o</i> -CH ₃ C ₆ H ₄ COOH			
4-methylbenzoic		<i>m</i> -CH ₃ C ₆ H ₄ COOH			
		<i>p</i> -CH ₃ C ₆ H ₄ COOH			

In common names, the positions of substituents are named using Greek letters. Notice that the lettering begins with the carbon atom adjacent to the carboxyl carbon, the α carbon. With common names, the prefix *iso*-is something used for acids ending in the $-\text{CH}(\text{CH}_3)_2$ grouping.

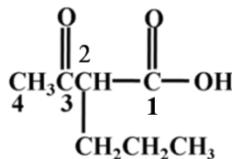


α -chloropropionic acid C.N:- γ -aminobutyric acid
 IUPAC :- 4-amino butanoic acid



isovaleric acid
 (β -methylbutyric acid)

IUPAC :- 3-methyl butanic acid

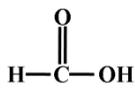
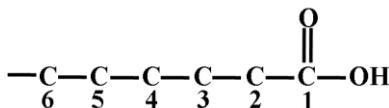


IUPAC :- 3-oxo-2-propylbutanoic acid

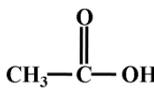
Common Name :- α -acetylvaleric acid

IUPAC Names

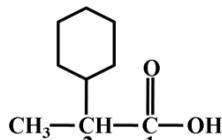
The IUPAC nomenclature for carboxylic acids uses the name of the alkane that corresponds to the longest continuous chain of carbon atoms. The final *-e* in the alkane name is replaced by the suffix *-oic acid*. The chain is numbered, starting with the carboxyl carbon atom, to give positions of substituents along the chain. In naming, the carboxyl group takes priority over any of the functional groups discussed previously.



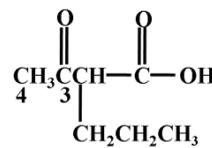
IUPAC name: methanoic acid
Common name: formic acid



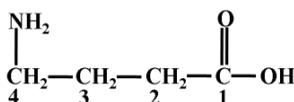
ethanoic acid
acetic acid



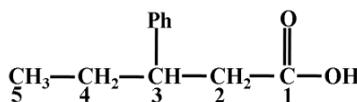
2-cyclohexylpropanoic acid
 α -cyclohexylpropionic acid



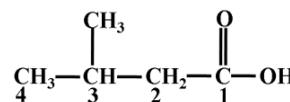
3-oxo-2-propylbutanoic acid
 α -acetylvaleric acid



IUPAC name: 4-aminobutanoic acid
Common name: γ -aminobutyric acid

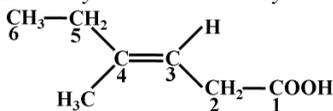


3-phenylpentanoic acid
 β -phenylvaleric acid

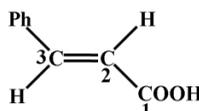


3-methylbutanoic acid
isovaleric acid

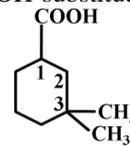
Unsaturated acids are named using the name of the corresponding alkene, with the final *-e* replaced by *-oic acid*. The carbon chain is numbered starting with the carboxyl carbon, and a number gives the location of the double bond. The stereochemical terms *cis* and *trans* (and *Z* and *E*) are used as they are with other alkenes. Cycloalkanes with $-\text{COOH}$ substituents are generally named as *cycloalkanecarboxylic acids*.



IUPAC name: (*E*)-4-methyl-3-hexenoic acid
Common name: (*E*)-4-methylhex-3-enoic acid

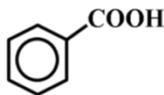


trans-3-phenyl-2-propenoic acid
(*E*)-3-phenylprop-2-enoic acid
(*cinnamic acid*)

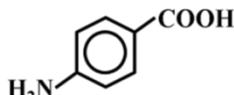


3,3-dimethylcyclohexanecarboxylic acid

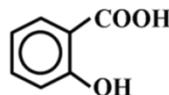
Aromatic acids of the form $\text{Ar}-\text{COOH}$ are named as derivatives of benzoic acid, $\text{Ph}-\text{COOH}$. As with other aromatic compounds, the prefixes *ortho*-, *meta*-, and *para*- may be used to give the positions of additional substituents. Numbers are used if there are more than two substituents on the aromatic ring. Many aromatic acids have historical names that are unrelated to their structures.



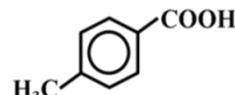
benzoic acid



p-aminobenzoic acid



o-hydroxybenzoic acid
(*salicylic acid*)

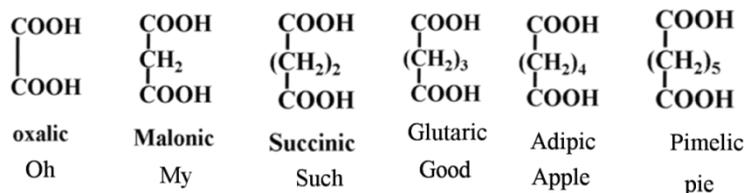


4-methylbenzoic acid
(*p*-toluic acid)

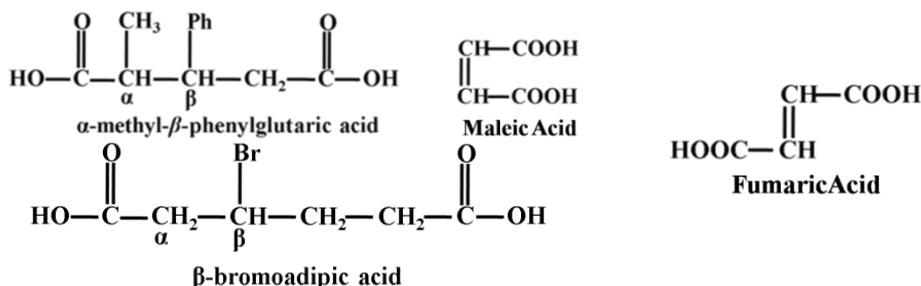
Nomenclature of Dicarboxylic Acids

Common Names of Dicarboxylic Acids A dicarboxylic acid (also called a diacid) is a compound with two carboxyl groups. The common names of simple dicarboxylic acids are used more frequently than their systematic names.

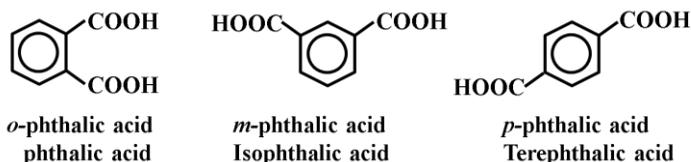
IUPAC Name	Common Name	Formula	mp (°C)	Solubility (g/100 g H ₂ O)
ethanedioic	Oxalic	HOOC – COOH	189	14
propanedioic	malonic	HOOCCH ₂ COOH	136	74
butanedioic	succinic	HOOC(CH ₂) ₂ COOH	185	8
pentanedioic	glutaric	HOOC(CH ₂) ₃ COOH	98	64
hexanedioic	adipic	HOOC(CH ₂) ₄ COOH	151	2
heptanedioic	pimelic	HOOC(CH ₂) ₅ COOH	106	5
<i>cis</i> -2-butenedioic	maleic	<i>cis</i> -HOOCCH = CHCOOH	130.5	79
<i>trans</i> -2-butenedioic	fumaric	<i>trans</i> -HOOCCH = CHCOOH	302	0.7
benzene-1,3-dicarboxylic	phthalic	1,2-C ₆ H ₄ (COOH) ₂	231	0.7
benzene-1,3-dicarboxylic	isophthalic	1,3-C ₆ H ₄ (COOH) ₂	348	
benzene-1,4-dicarboxylic	terephthalic	1,4-C ₆ H ₄ (COOH) ₂	300	0.002
			subl.	



A common mnemonic for these names is “*Oh my, such good apple pie,*” standing for *oxalic, malonic, succinic, glutaric, adipic, and pimelic* acids. The names and physical properties of some dicarboxylic acids are given in Table. Substituted dicarboxylic acids are given common names using Greek letters, as with the simple carboxylic acids. Greek letters are assigned beginning with the carbon atom adjacent to the carboxyl group that is closer to the substituents.

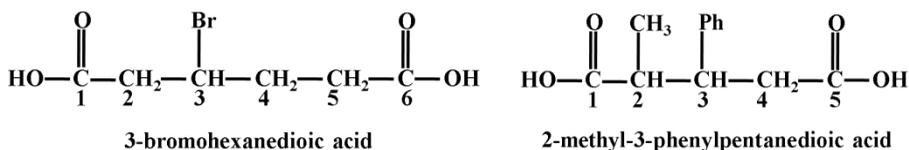


Benzenoid compounds with two carboxyl groups are named **phthalic acids**. Phthalic acid itself is the two ortho isomer. The meta isomer is called isophthalic acid, and the para isomer is called terephthalic acid.

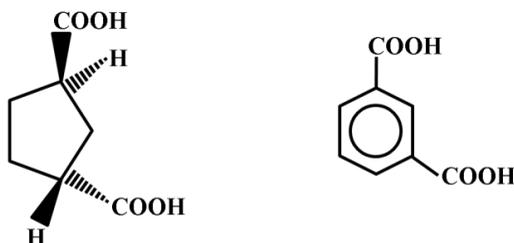


IUPAC Names of Dicarboxylic Acids

Aliphatic dicarboxylic acids are named simply by adding the suffix– *dioic* to the name of the parent alkane. For straight-chain dicarboxylic acids, the parent alkane name is determined by using the longest continuous chain that contains both carboxyl groups. The chain is numbered beginning with the carboxyl carbon atom that is closer to the substituents, and these numbers are used to give the positions of the substituents.



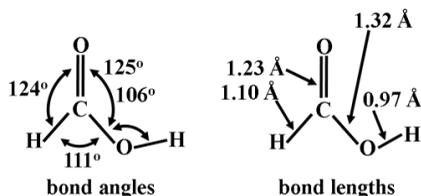
The system for naming cyclic dicarboxylic acids treats the carboxyl groups substituents on the cyclic structure.



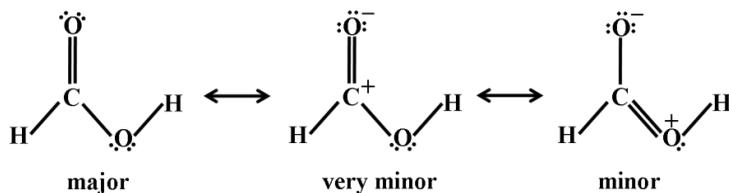
trans-1, 3-cyclopentanedicarboxylic acid 1, 3-benzenedicarboxylic acid

Structure and Physical Properties of Carboxylic Acids

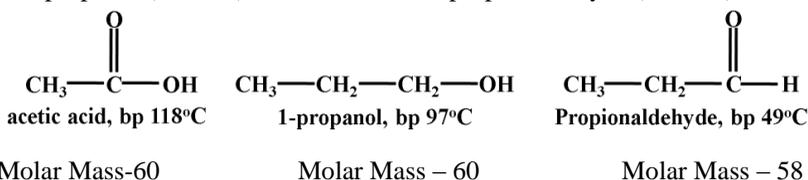
Structure of the Carboxyl Group the structure of the most stable conformation of formic acid is shown below. The entire molecule is approximately planar. The sp^2 hybrid carbonyl carbon atom is planar, with nearly trigonal bond angles. The O — H bond also lies in this plane, eclipsed with the C = O bond.



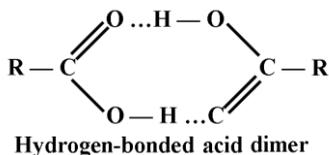
It seems surprising that an eclipsed conformation is most stable. It appears that one of the unshared electron pairs on the hydroxyl oxygen atom is delocalized into the electrophilic system of the carbonyl group. We can draw the following resonance form to represent this delocalization:



Boiling Points carboxylic acids boil at considerably higher temperatures than do alcohols, ketones, or aldehydes of similar molecular weights. For example, acetic acid (MW 60) boils at 118°C, 1-propanol (MW 60) boils at 97°C, and propionaldehyde (MW 58) boils at 49°C.



The high boiling points of carboxylic acids result from formation of a stable, hydrogen-bonded dimer. This dimer contains an eight-membered ring joined by two hydrogen bonds, effectively doubling the molecular weight of the molecules leaving the liquid phase.

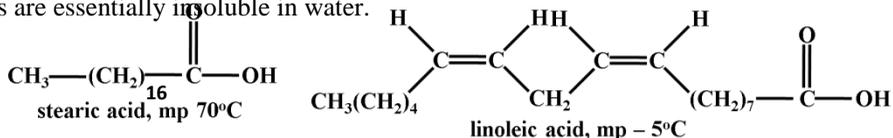


Melting Points The melting points of some common carboxylic acids are given in Table. Acids containing more than eight carbon atoms are generally solids, unless they contain double bonds. The presence of double bonds (especially *cis* double bonds) in a long chain impedes formation of a stable crystal lattice, resulting in a lower melting point. For example, both Stearic acid (octadecanoic acid) and linoleic acid (*cis,cis*-9, 12-octadecadienoic) have 18 carbon atoms, but Stearic acid melts at 70°C and linoleic acid melts at – 5°C.

The melting point of dicarboxylic acids are relatively high. With two carboxyl groups per molecule, the forces of hydrogen bonding are particularly strong in diacids; a high temperature is required to break the lattice of hydrogen bonds in the crystal and melt the diacid.

Solubilities Carboxylic acids form hydrogen bonds with water, and the lower-molecular-weight carboxylic acids (up through four carbon atoms) are miscible with water. As the length of the

hydrocarbon chain increases, water solubility decreases until acids with more than 10 carbon atoms are essentially insoluble in water.

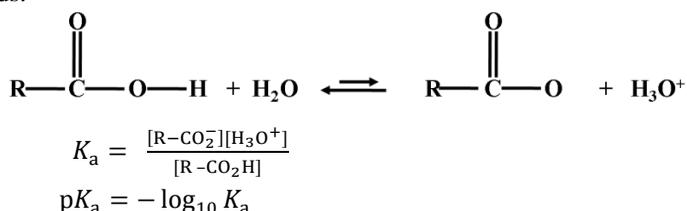


Carboxylic acids are very soluble in alcohols because acids form hydrogen bonds with alcohols. Also, alcohols are not as polar as water, so the longer-chain acids are more soluble in alcohols than they are in water. Most carboxylic acids are quite soluble in relatively nonpolar solvents such as chloroform because the acid continues to exist in its dimeric form in the nonpolar solvent. Thus, the hydrogen bonds of the cyclic dimer are not disrupted when the acid dissolves in a nonpolar solvent.

Acidity of Carboxylic Acids

Measurement of Acidity

A carboxylic acid may dissociate in water to give a proton and a carboxylate ion. The equilibrium constant K_a for this reaction is called the *acid-dissociation* constant. The pK_a of an acid is the negative logarithm of K_a , and we commonly use pK_a as an indication of the relative acidities of different acids.

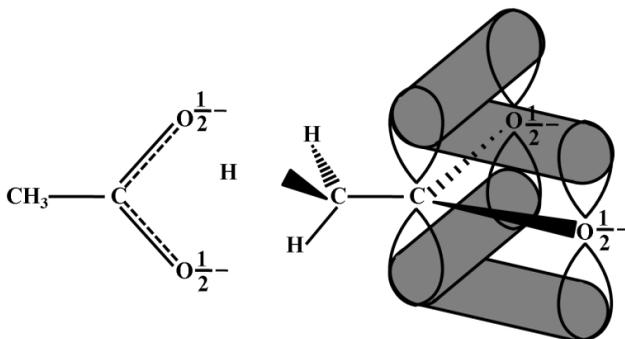
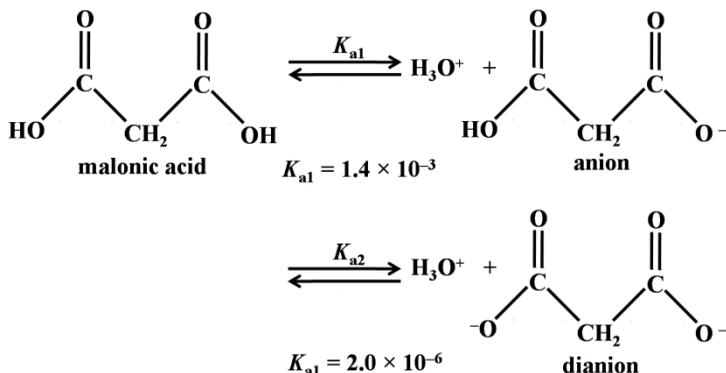


Values of pK_a are about 5 ($K_a = 10^{-5}$) for simple carboxylic acids. For example acetic acid has a pK_a of 4.7 ($K_a = 1.8 \times 10^{-5}$). Although carboxylic acids are not as strong as most mineral acids, they are still much more acidic than other functional groups we have studied. For example, alcohols have pK_a values in the range 16 to 18. Acetic acid ($pK_a = 4.74$) is about 10^{11} times as acidic as the most acidic alcohols! In fact, concentrated acetic acid causes acid burns when it comes into contact with the skin.

Dissociation of either an acid or an alcohol involves breaking an O—H bond, but dissociation of a carboxylic acid gives a carboxylate ion with the just one oxygen in an alkoxide ion. The delocalized charge makes the carboxylate ion more stable than the alkoxide ion; therefore, dissociation of a carboxylic acid to a carboxylate ion is less endothermic than dissociation of an alcohol to an alkoxide ion.

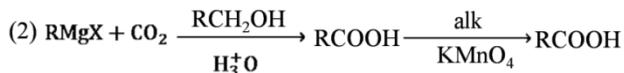
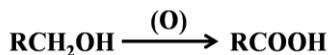
The carboxylate ion can be visualized either as a resonance hybrid (as in Figure) or as a conjugated system of three p orbitals containing four electrons. The carbon atom and the two oxygen atoms are sp^2 hybridized, and each has an unhybridized p orbital. Overlap of these three p orbitals gives a three-center π molecular orbital system. There is half a π bond between the carbon and each oxygen atom, and there is half a negative charge on each oxygen atom.

Table gives pK_a values for dicarboxylic acid in addition to those for simple carboxylic acid. Diacids have two dissociation constants: K_{a1} is for the first dissociation, and K_{a2} is for the second dissociation, to give a dianion. The second carboxyl group is always less acidic than the first ($K_{a2} \ll K_{a1}$) because extra energy is required to create a second negative charge close to another, mutually repulsive, negative charge.



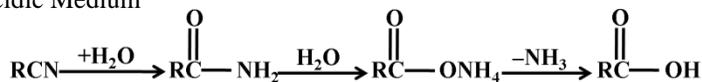
Preparation

(1) Oxidation of Aldehyde, Ketone & Alcohols. Already done in earlier chapters)

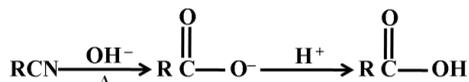


(3) Hydrolysis of CN

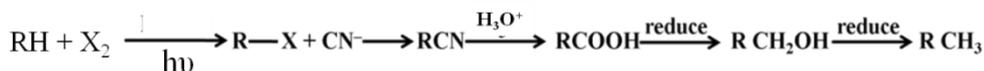
(a) In Acidic Medium



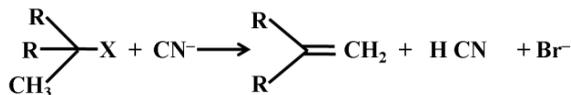
(b) In Alkaline Medium



This is generally used as a step up reaction



But not for 3° Alkyl Halide

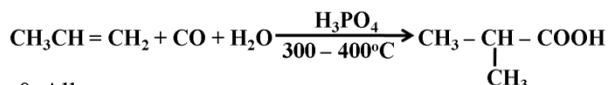


As CN^- strong nucleophile we get Alkene by elimination reaction in place of S_N reaction.

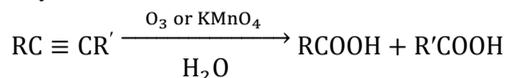
(4) Alkoxide Carboxylation



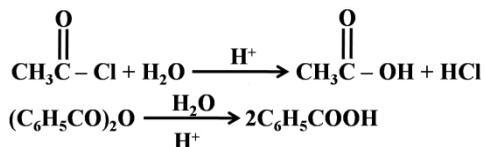
(5) From Alkene. Carboxylation



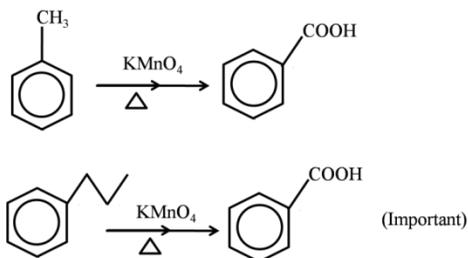
(6) Ozonolysis & Alkynes



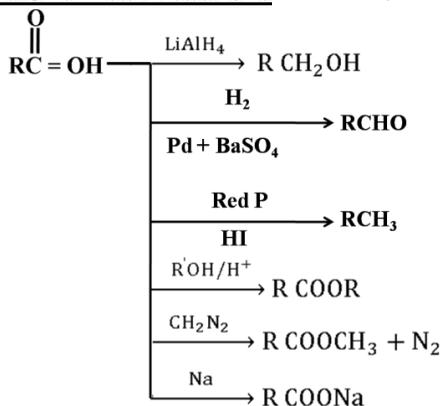
(7) Hydrolysis of Ester, Acid halides & anhydrides.

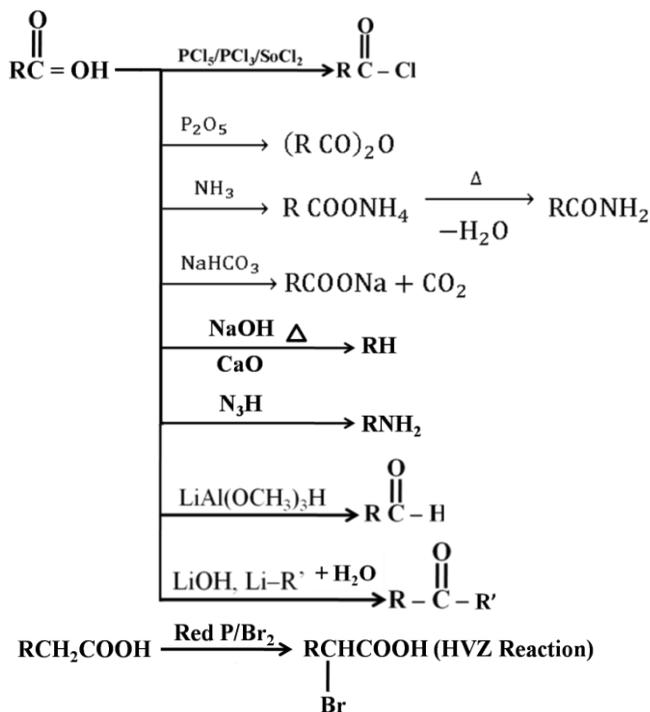


(8) Oxidation of Alkyl Benzene



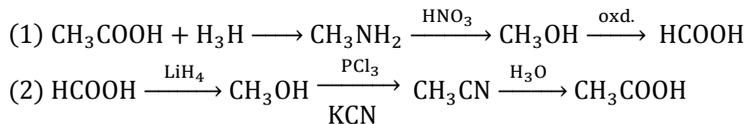
Important Chemical Reactions





Conversion

CH₃COOH to HCOOH & vice versa



Example:-

CH ≡ CH to CH₃COCH₃

