Reactions

1) Reaction with metals

Carbonylic acids react with active metals like Na, K, Ca etc to form their respective salts liberating H_2 gas

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$$

② Reaction with Carbonates and bicarbonates

Carbonylic acids decompose Carbonates and bicarbonates producing CO_2 gas

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + H_2O + CO_2$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2$$

This reaction is used to detect the presence of a Carbonyl group in an organic compound.

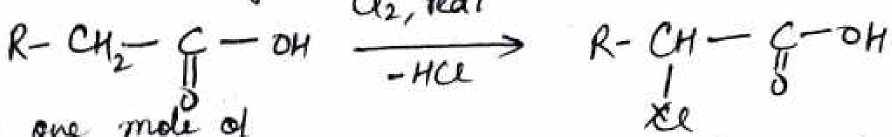
③ Reaction with alkalies:

Carbonylic acids neutralizes alkalies forming salts

$$CH_3COOH + NaOH \longrightarrow \underset{\text{Sodium Acetate}}{CH_3COONa} + H_2O$$

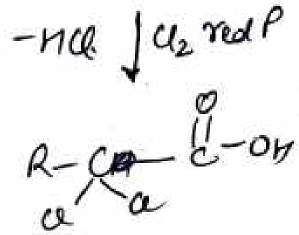
$$CH_3COOH + NH_4OH \longrightarrow \underset{\text{Ammonium Acetate}}{CH_3COONH_4}$$

HVZ → Carboxylic acids reacts with Chlorine & Br in presence of small quantities of red phosphorus to give exclusively α-chloro or α-bromo acids – This reaction is called Hell Volhard Zelinsky reaction.



$$R-CH_2-\underset{\overset{\|}{O}}{C}-OH \xrightarrow[-HCl]{Cl_2,\ red\ P} R-\underset{Cl}{\underset{|}{C}H}-\underset{\overset{\|}{O}}{C}-OH$$

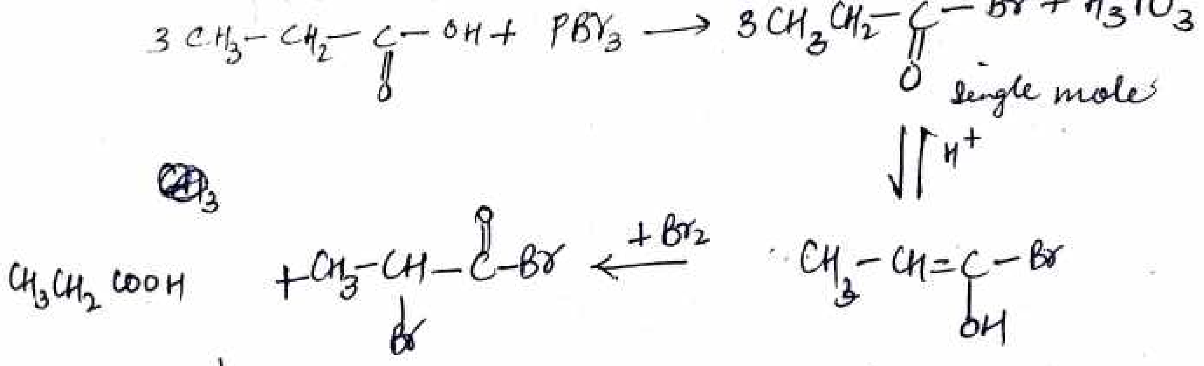
- If more than one mole of Chlorine & Bromine is used the second & third α-hydrogen atoms can be successively replaced



$$\Big\downarrow{\scriptstyle Cl_2\ red\ P}\ {\scriptstyle -HCl}$$
$$R-\overset{}{C}Cl_2-\overset{\overset{O}{\|}}{C}-OH$$

* Bromination exclusively occurs at α-position & the reaction stops after all the α-hydrogens have been replaced by the bromine atoms. In Contrast, Chlorination first occurs at the α-position & when all the α-hydrogens have been ~~replaced~~ displaced it occurs further along the chain.

$2P + 3Br_2 \longrightarrow 2PBr_3$ (in situ)

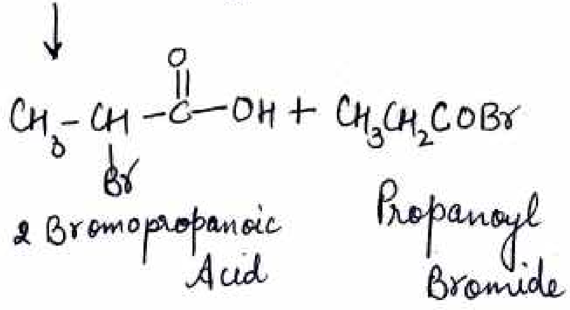


$$3\,CH_3-CH_2-\underset{\overset{\|}{O}}{C}-OH + PBr_3 \longrightarrow 3\,CH_3CH_2-\underset{\overset{\|}{O}}{C}-Br + H_3PO_3$$

single mole

$$\big\downarrow\!\uparrow H^+$$

$$CH_3CH_2COOH \quad + CH_3-\underset{Br}{\underset{|}{C}H}-\overset{\overset{O}{\|}}{C}-Br \xleftarrow{+Br_2} CH_3-CH=\underset{OH}{\underset{|}{C}}-Br$$



$$\downarrow$$

$$CH_3-\underset{Br}{\underset{|}{C}H}-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2COBr$$

2 Bromopropanoic Acid

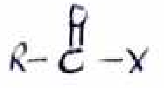
Propanoyl Bromide

(Exchange reaction b/w two results in the formation of 2-bromopropanoic acid & propanoyl bromide

The acid bromide undergoes above step again & continues the reaction.

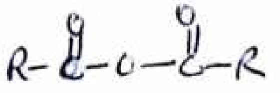
Carboxylic Acid Derivatives

Compounds such as acyl halides, acid anhydrides, esters and amines which are obtained by replacement of OH part the COOH group of a Carboxylic acid by a halogen atom, -OR, OCOR & NH_2 respectively collectively Called functional derivatives of Carboxylic acids.



$R-\overset{O}{\overset{\|}{C}}-X$

Acid halide

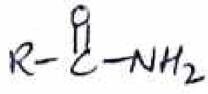


$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$

Acid Anhydride

$R-\overset{O}{\overset{\|}{C}}-OR$

Ester



$R-\overset{O}{\overset{\|}{C}}-NH_2$

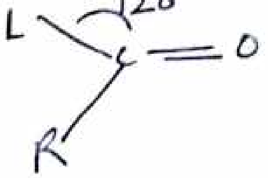
Acid Amide

Since all these derivatives contain the same acyl group ($R-\underset{|}{C}=O$) in their respective molecules they are also known as acyl compounds

$R-\overset{O}{\overset{\|}{C}}-L$

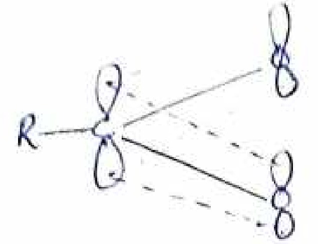
$L = OH,\ OCOR',\ OR',\ NH_2$

(R & R' may be same or different alkyl groups)



C - sp^2 hybridised

The L group (Cl in acyl Chlorides: O in anhydrides and esters; N in amides) directly linked to the Carbonyl Carbon has atleast one lone pair of electrons in a p-orbital. This p-orbital on group L may also overlap with p-orbitals on C and O-atoms of $C=O$ group to provide additional bonding



Orbital structure of R-CO-L showing π-bonding between Carbonyl Carbon, oxygen and the atom of group L directly linked to Carbonyl Carbon.


I II

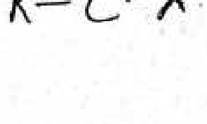
The extent of contribution of structure (II) towards resonance hybrid, however depends upon the electron donating - ability of group L.

Greater the contribution of structure (II), lesser is the electrophilicity of the Carbonyl Carbon and hence less reactive is the acid derivative towards nucleophilic acyl substitution reactions.

ACYL HALIDES

Derivative of Carboxylic acids in which -OH gp has been replaced by a halogen atom X. They are named as acid chlorides., bromides, iodides

X = Cl, Br, I


$R-\overset{O}{\overset{\|}{C}}-X$

Preparations

① From Carboxylic Acids :- Acid chlorides are easily prepared from the corresponding Carboxylic acids by their reaction with PCl_5, PCl_3 or $SOCl_2$.

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2\uparrow + HCl$$

② From Carboxylic acid salts:-

Acid Chlorides can also be prepared by distilling Sodium or calcium Salts of Carboxylic acids with PCl_3, SO_2Cl_2 or $POCl_3$

$$3CH_3COONa + PCl_3 \xrightarrow{Distil} 3\,CH_3COONa + Na_3PO_3$$

$$(CH_3CH_2COO)_2Ca + SO_2Cl_2 \xrightarrow{Distil} 2\,CH_3CH_2COCl + CaSO_4$$

$$2\,C_6H_5COONa + POCl_3 \xrightarrow{Distil} 2\,C_6H_5COCl + NaCl + NaPO_3$$

Physical Properties

1) Physical state, Smell etc

The lower acid chlorides are Colourless low boiling liquids while higher members are colourless, low melting Solids with pungent and irritating odours. They fume in air due to the formation of hydrochloric acid by hydrolysis.

2) Solubility

They are readily Soluble in most of the common organic Solvents Such as ether, benzene, Chloroform etc.

3) Boiling Points

The boiling points of acyl chlorides are lower than those of their parent acids inspite of their greater molecular masses. This is due to the reason that unlike Carboxylic acids, acyl Chlorides do not form intermolecular H-bonds.

Chemical Properties

The chlorine atom in acyl chloride because of its strong electron withdrawing inductive effect (-I) and weak electron resonance effect makes the acyl Carbon Sufficiently electron deficient.

As a result, both aliphatic and aromatic acyl chlorides readily undergo a number of nucleophilic acyl Substitution reactions even with weak nucleophiles Such as water, alcohols

Reactions

① **Hydrolysis** :- Acyl chlorides are readily hydrolyzed by water to form corresponding acids.

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

$$C_6H_5COCl + H_2O \longrightarrow C_6H_5COOH + HCl$$

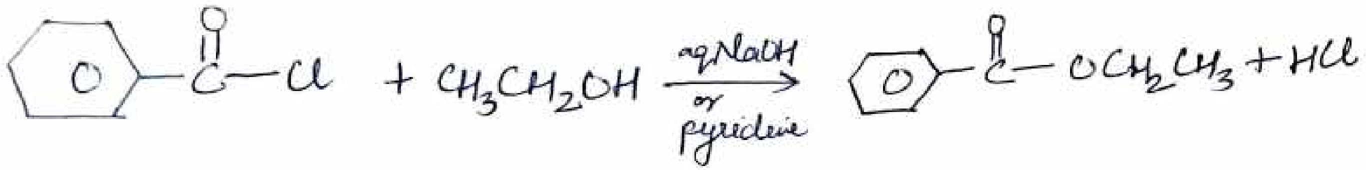
lower aliphatic acid chlorides reacts voilently with water at room temperature, higher aliphatic acid chlorides and aromatic acid chlorides react only slowly.

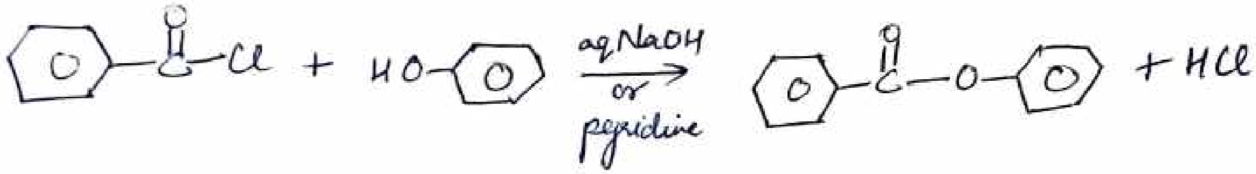
② **Alcoholysis** :- Alcohols and phenols readily react with acid chlorides to form esters.

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

$$CH_3COCl + C_6H_5OH \longrightarrow CH_3COOC_6H_5 + HCl$$

The reaction of an aromatic acyl chloride with alcohol or a phenol is usually carried out in presence of base such as aq. NaOH or pyridine





This reaction is Called Schotten-Baumann reaction.

Ammonolysis :- Acid Chlorides react with NH_3, primary and Secondary amines to form amides. This reaction is Called ammonolysis.

$$RCOCl + 2NH_3 \longrightarrow \underset{\text{Amide}}{RCONH_2} + NH_4Cl$$

$$CH_3COCl + 2NH_3 \longrightarrow CH_3CONH_2 + NH_4Cl$$

$$CH_3COCl + 2C_2H_5NH_2 \longrightarrow CH_3CONHC_2H_5 + C_2H_5\overset{+}{N}H_3Cl^-$$

$$C_6H_5COCl + H_2NC_6H_5 \xrightarrow{NaOH} C_6H_5CONHC_6H_5 + HCl$$

Reaction with Carboxylic acids:-

Acyl Chlorides react with Carboxylic acids in presence of pyridine to form anhydride

$$R-COCl + RCOOH \xrightarrow{pyridine} RCOOCOR + HCl$$

$$CH_3COCl + CH_3COOH \xrightarrow{pyridine} CH_3COOCOCH_3 + HCl$$

This conversion can be carried out by treating an acid chloride with salt of a Carboxylic acid

$$CH_3COCl + CH_3COO^-Na^+ \longrightarrow CH_3COOCOCH_3 + Na^+Cl^-$$