Carbonyl Compounds

Carbonyl Compounds are the organic compounds containing carbon-oxygen double bond (>C=0). >C=O is the most important functional group of organic chemistry.
Carbonyl compounds in which carbonyl group is bonded to a carbon and hydrogen are known as aldehydes.

Carbonyl compounds in which carbonyl group is bonded to carbon atoms are known as ketons.

The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides)

Carbonyl compounds where carbon is attached to nitrogen are called amides.

Carbonyl compounds where carbon is attached to haligen are called acyl halides.

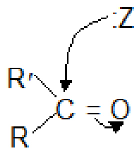
In short, carbonyl compounds can be divided into two major groups

- **Aldehydes & Ketones**
- **Carboxylic Acid & Its derivatives**
- Structure of Carbonyl Group

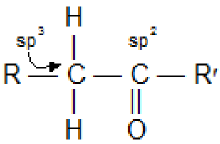
Carbonyl carbon is joined to three other atoms by s bonds; since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining p-orbitals of carbon overlaps a p-orbital of oxygen to form a p bond; carbon and oxygen are thus joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon lies in a plane.

The electrons of a carbonyl double bond hold together atoms of quite different electronegativity and hence the electrons are not equally shared; in particular the polar p-cloud is pulled strongly towards the more electronegative atom, oxygen.

The carbonyl group, C = O, governs the chemistry of aldehydes and ketones. It does this in two ways: a) By providing a site for nucleophilic addition, and



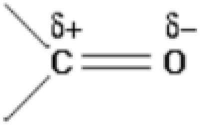
b) By increasing the acidity of hydrogen atoms attached to the alpha carbon.



Physical properties of carbonyl compounds

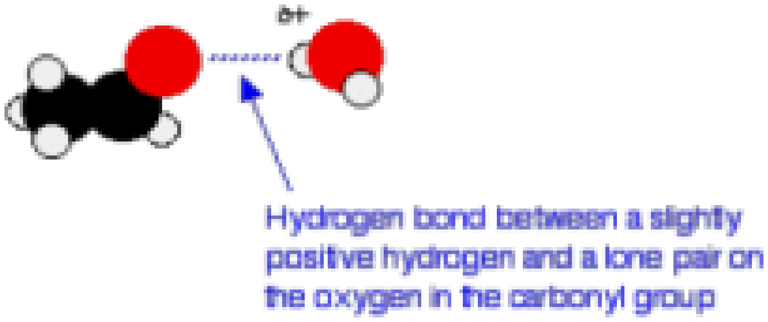
1. The boiling point of carbonyl compounds is higher than the alkanes with similar molecular weight.

2. The boiling point increases with increasing number of carbon atom. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to overcome these forces.



3. Besides temporary dipoles, permanent dipole-dipole forces are also present due to carbonyl compounds being polar
4. Methanal and ethanal are gases at room temperature, while others are liquids

Carbonyl compounds are soluble in This is because they are able to form hydrogen bond with water molecules.



The solubility decreases with increasing number of carbon atoms. This is because the long hydrocarbon chain disrupts the hydrogen bonding.

Preparation of Aldehyde and Ketone

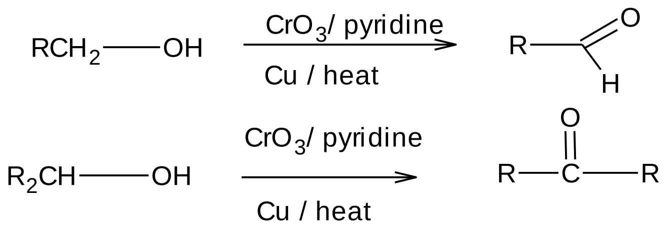
Aldehydes, synthesis:

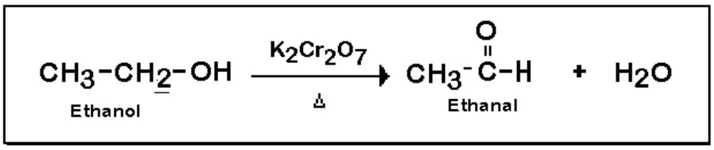
- Oxidation of 1° alcohols
- Oxidation of methylaromatics
- Reduction of acid chlorides

Ketones, synthesis:

- Oxidation of 2° alcohols
- Friedel-Crafts acylation
- Coupling of R_2CuLi with acid chloride

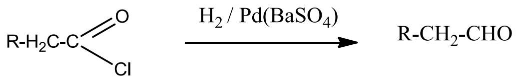
1- Oxidation of alcohols

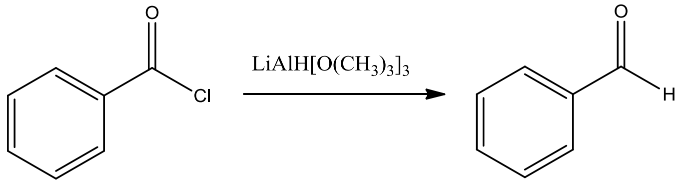




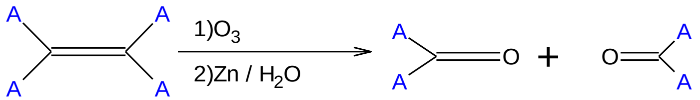
$$CH_3-CH_2-OH \xrightarrow[\Delta]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$$

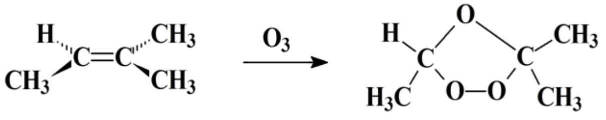
Reduction of acid chloride



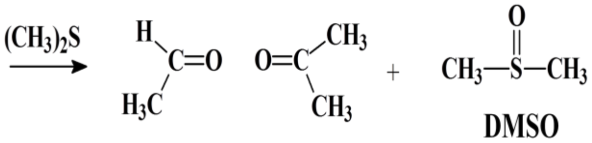


Ozonolysis of alkenes



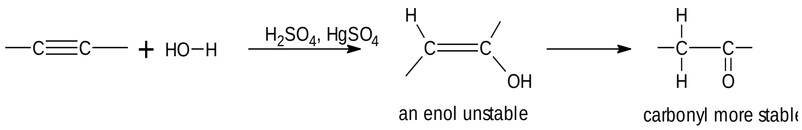


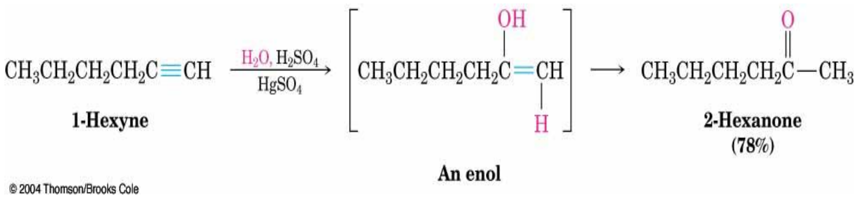
Ozonide



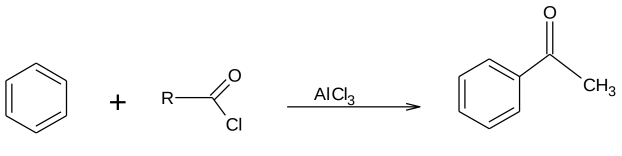
DMSO

Hydration of alkynes

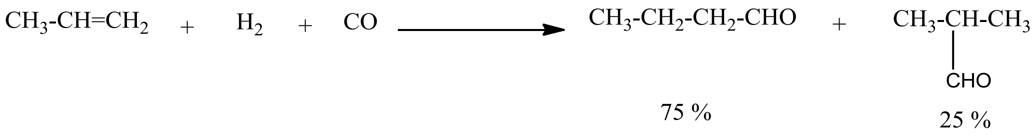




Friedel Crafts acylation

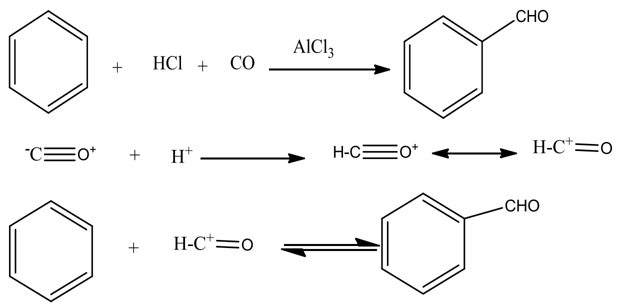


Oxo reaction - Hydroformylation reaction

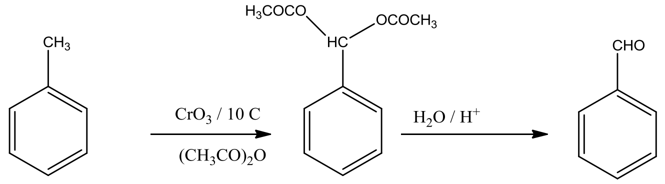


$$CH_3\text{-}CH{=}CH_2 + H_2 + CO \longrightarrow \underset{75\ \%}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO} + \underset{25\ \%}{\underset{CHO}{CH_3\text{-}\overset{|}{C}H\text{-}CH_3}}$$

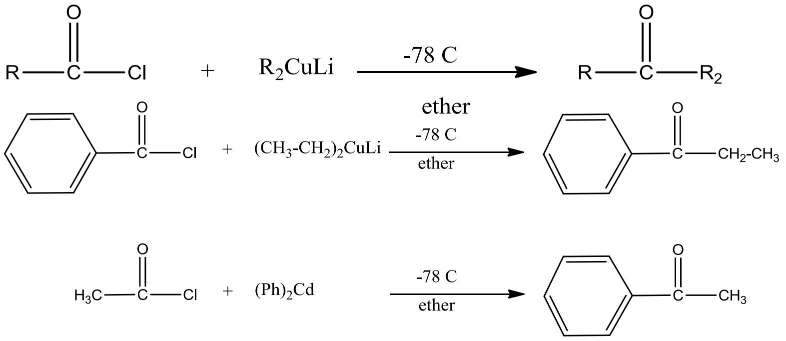
Gattermann-Koch reaction



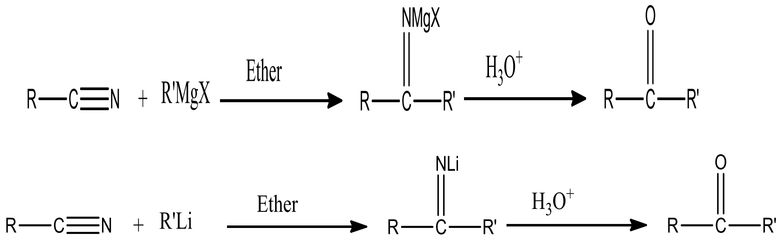
Oxidation of an Alkyl Side of aromatic ring



From acid chloride and lithium dialkyl cuperate or R_2Cd



From nitrile and Grignard reagent or alkyl lithium

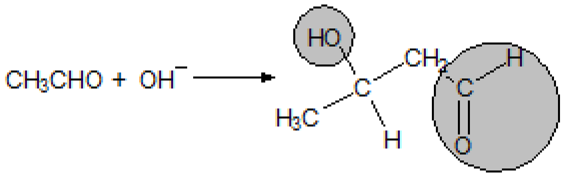


Aldehydes and ketones are moderately reactive as electrophiles (electron acceptors) among the carboxylic acid derivatives.

acid chloride
acid anhydride
aldehyde
ketone
ester
carboxylic acid
amide
nitrile
carboxylate

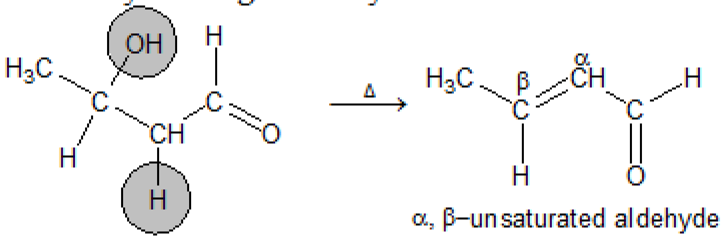
least reactive

Reactions of Aldehydes and Ketones:
a) Aldol condensation
Aldehydes and ketones having alpha hydrogen atom:



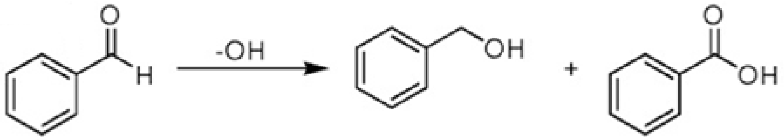
(Since it contains two functional groups aldehydes and alcohol)

Aldol easily undergoes dehydration

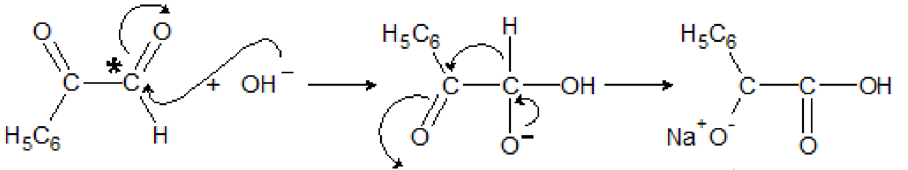


α, β–unsaturated aldehyde

b) Cannizzaro reaction:
Aldehydes and ketones having no alpha hydrogen atom:



When two carbonyl groups are present within a molecule, think of intramolecular reaction. OH- will attack more positively charged carbon. In this case, it is right >c=0 group.



Sodium salt of Mandelic acid

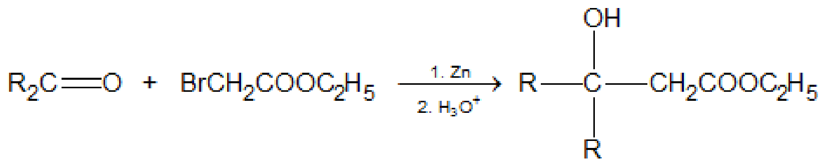
c) Formation of Keto Esters

Esters having a-hydrogen on treatment with a strong base e.g. C_2H_5ONa. Undergo self condensation to produce b-keto esters. This reaction is Claisen Condensation.

$$2CH_3COOC_2H_5 \xrightarrow[2.\ H^+]{1.\ C_2H_5ONa} CH_3COCH_2COOC_2H_5$$

d) Reformatsky Reaction

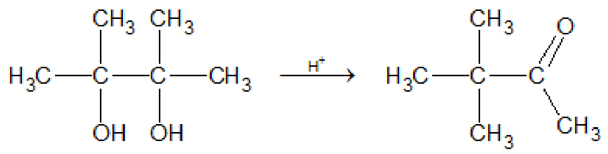
This is the reaction of a-haloester, usually an a-bromoester with an aldehyde or ketone in the presence of Zinc metal to produce b-hydroxyester.



$$R_2C{=}O + BrCH_2COOC_2H_5 \xrightarrow[2.\ H_3O^+]{1.\ Zn} R\text{—}\overset{OH}{\underset{R}{C}}\text{—}CH_2COOC_2H_5$$

e) Pinacol-pinacolone Rearrangement

The acid catalysed rearrangement of 1,2 diols (Vicinal diols) to aldehydes or ketones with the elimination of water is known as pinacol pinacolone rearrangement.



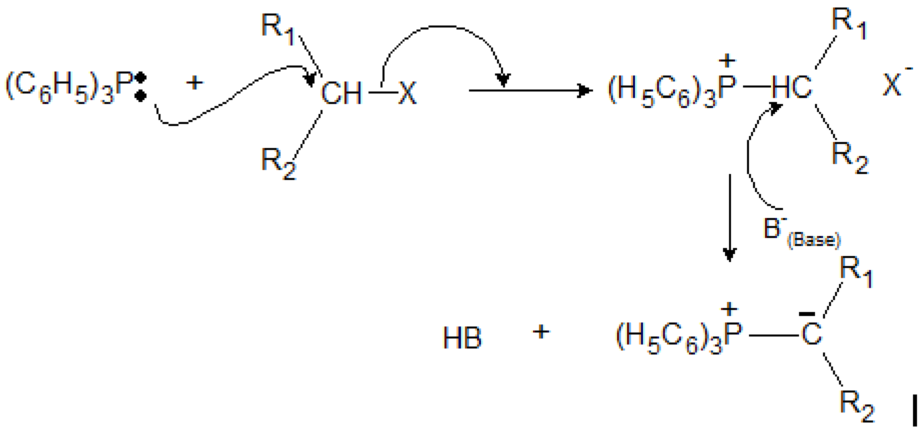
pinacol

Pinacolone
(Methyl t-butylketone)

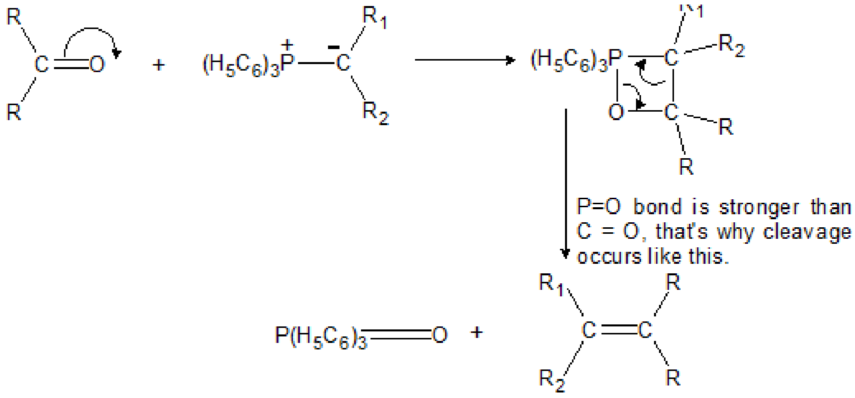
a) Wittig-Ylide Reaction

Aldehydes and Ketones react with phosphorus Ylides to yield alkenes and triphenyl phosphine oxide. An Ylide is a neutral molecule having a negative carbon adjacent to a positive hetero atom. Phosphorus ylides are also called phosphoranes.

Preparation of Ylides

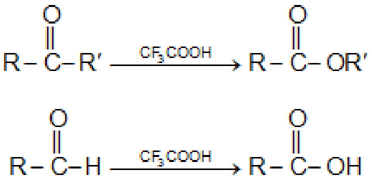


Reaction of Ylide with >C=O



P=O bond is stronger than C = O, that's why cleavage occurs like this.

d) Baeyer-Villiger Oxidation

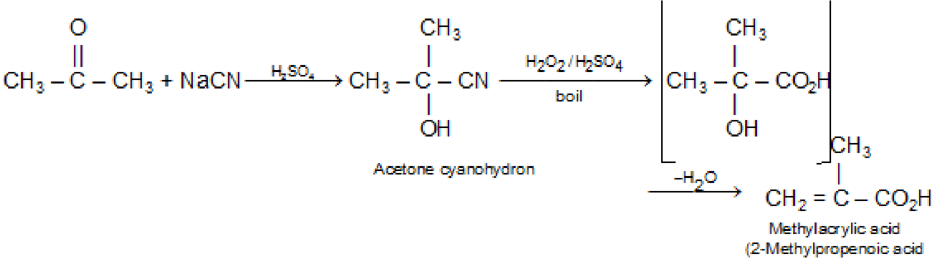


$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{CF_3COOH} R-\overset{\overset{O}{\|}}{C}-OR'$$

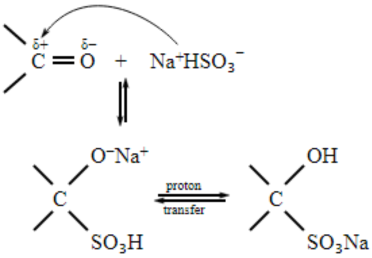
$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{CF_3COOH} R-\overset{\overset{O}{\|}}{C}-OH$$

Above things happens in BVO (Bayer Villiger oxidation). Reagents are either per acetic acid or perbenzoic acid or pertrifluoroacetic acid or permonosulphuric acid.

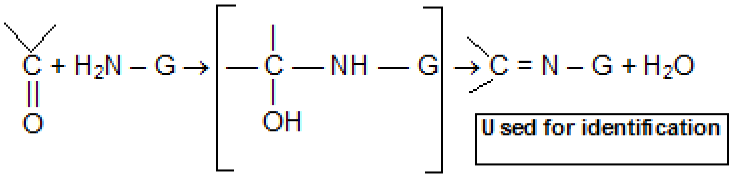
e) Addition of cyanide

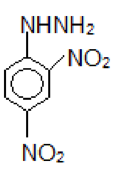
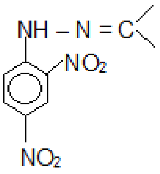


f) Addition of bisulfite:

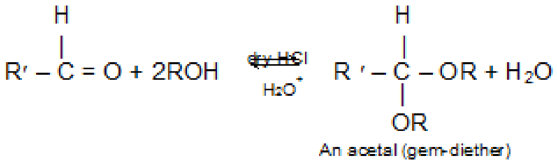


g) Addition of derivative of ammonia



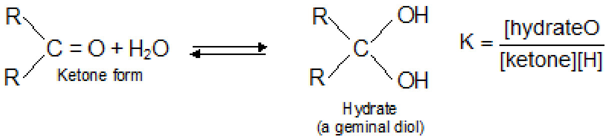
	$H_2N - G$	**Product**	
H_2NOH	Hydroxylamine	$> C = N - OH$	Oxime
$H_2N - NH_2$	Hydrazine	$> C = N - NH_2$	Hydrazone
$H_2N - NH - C_6H_5$	Phenylhydrazine	$> C = N - NHC_6H_5$	Phenylhydrazone
$H_2N - NH - CO - NH_2$	Semicarbazide	$> C = N - NHCONH_2$	Semicarbazone
	2, 4-Dinitrophenyl hydrazine		2, 4-dinitrophenylhydrazone (bright orange or yellow precipitate used for identifying aldehydes and ketones

h) Addition of Alcohols; Acetal Formation

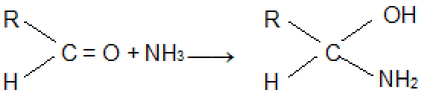


In H_3O^+, RCHO is regenerated because acetals undergo acid catalyzed cleavage much more easily than do ethers. Since acetals are stable in neutral or basic media, they are used to protect the – CH = O group.

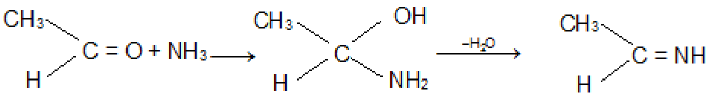
i) Addition of Water



j) Addition of Ammonia:



Aldehyde ammonia

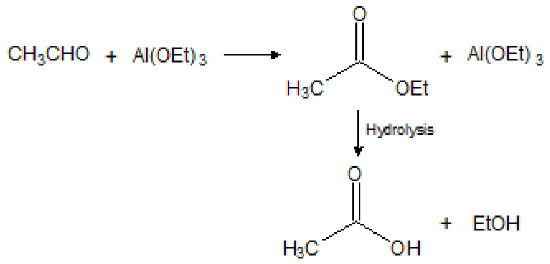


Aldehyde ammonia (unstable)

Aldimine (very reactive)

k) Tischenko reaction:

All aldehydes can be made to undergo the Cannizzaro reaction by treatment with aluminium ethoxide. Under these conditions the acids and alcohols are combined as the ester, and the reaction is then known as the Tischenko reaction; eg, acetaldehyde gives ethyl acetate, and propionaldehyde gives propyl propionate.



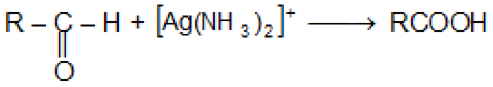
Oxidation of Aldehydes and Ketones

a)

$$R\,CH=O/\,Ar\,CH=O \xrightarrow{KMnO_4\ \text{or}\ K_2Cr_2O_7/H^+} R-CO_2H/\,ArCO_2H$$

b) Tollen's Reagent

A specific oxidant for RCHO is $[Ag(NH_3)_2]^+$

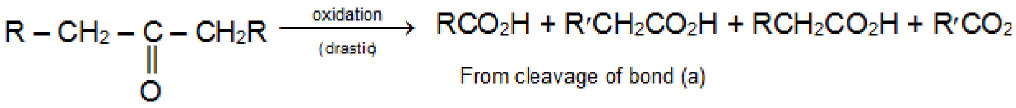


$$R-\underset{\underset{O}{\|}}{C}-H + [Ag(NH_3)_2]^+ \longrightarrow RCOOH$$

Tollen's test chiefly used for the detection of aldehydes.

Tollen's reagent doesnot attack carbon-carbon double bonds.

c) Strong Oxidants: Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C – C bonds on either sides of the carbonyl group.



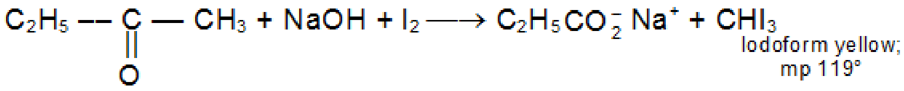
$$R-CH_2-\underset{\underset{O}{\|}}{C}-CH_2R \xrightarrow[\text{(drastic)}]{\text{oxidation}} RCO_2H + R'CH_2CO_2H + RCH_2CO_2H + R'CO_2$$

From cleavage of bond (a)

d) Haloform Reaction

CH_3COR are readily oxidised by NaOI (NaOH + I_2) to iodoform, CHI_3, and RCO_2Na

Example:

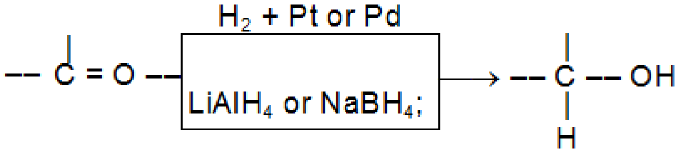


$$C_2H_5-\underset{\underset{O}{\|}}{C}-CH_3 + NaOH + I_2 \longrightarrow C_2H_5CO_2^-\,Na^+ + CHI_3$$

Iodoform yellow;
mp 119°

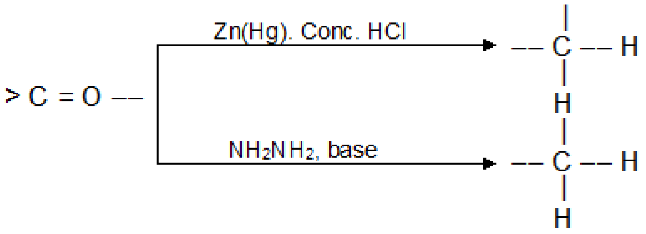
- Reduction:

a) Reduction to alcohols



Aldehydes → 1° alcohols; Ketones → 2°alcohols

b) Reduction to hydrocarbons



Clemmensen reduction for compounds sensitive to base

Wolff-Kishner reduction for compounds sensitive to acids

Carboxylic Acids:

Physical Properties of Carboxylic Acids

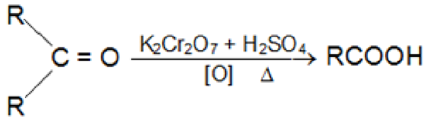
- The first three acids are colourless, pungent smelling liquids.
- First four members are miscible in water due the intermolecular hydrogen bonding whereas higher members are miscible in non – polar solvents like ether.
- Benzene or ethanol but immiscible in water due to the increase in the size of lyophobic alkyl chain.
- The b.p. of carboxylic acids are higher than alcohols because carboxylic acids exist as dimers due to the presence of intermolecular H-bonding
- Increase in the number of Halogen atoms on a-position increases the acidity, eg. $CCl_3COOH > CHCl_2COOH > ClCH_2COOH > CH_3COOH$
- Increase in the distance of Halogen from COOH decreases the acidity e.g $CH_3 - CH_2 - CH(Cl) - COOH > CH_3 - CH(Cl) - CH_2 - COOH > CH_2 - CH_2 - CH_2 - COOH$
- Increase in the electro negativity of halogen increases the acidity. $FCH_2COOH > BrCH_2COOH > ICH_2COOH$

Methods of Preparations of Carboxylic Acids

a. Oxidation of Aldehydes & Ketones

$$R-CH_2OH \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} RCHO \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} RCOOH$$

$$R-CHO \xrightarrow[2.\ H_3O^+]{1.\ Ag_2O \text{ or } Ag(NH_3)_2^+} RCO_2H$$



b. Oxidation of Alkanes:

$$RCH = CHR' \xrightarrow[2.\ Heat,\ H_2O]{1.\ KMnO_4,\ OH^-} RCO_2H + R'CO_2H$$

c. Hydrolysis of Nitriles (Cyanides)

$$R-C \equiv N \xrightarrow[H^+,\ HOH]{Acid\ hydrolysis} R.COOH + NH_3$$

d. Carbonation of Grignard Reagents

$$R-X + Mg \xrightarrow{Diethyl\ ether} RMgX \xrightarrow{CO_2} RCO_2MgX \xrightarrow{H_3O^+} RCO_2H$$

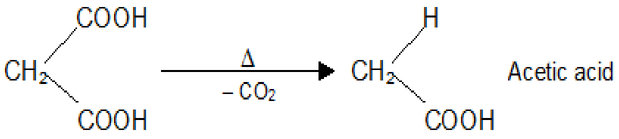
$$\text{or } Ar-Br + Mg \xrightarrow{Diethyl\ ether} ArMgBr \xrightarrow{CO_2} ArCO_2MgBr \xrightarrow{H_3O^+} ArCO_2H$$

e. Koch Reaction:

An olefin is heated with carbon monoxide and steam under pressure at 300-400° in the presence of a catalyst, e.g. phosphoric acid.

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[steam\ 300\text{–}400^\circ C]{H_3PO_4} CH_3 - CH_2 - COOH$$

f. Heating Gem Dicarboxylic Acids:



Chemical Reactions of Carboxylic Acids

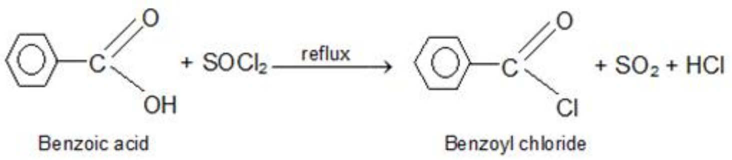
a. Salt formation:

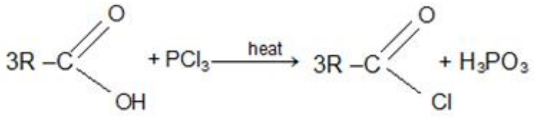
$2CH_3COOH + 2Na \rightarrow 2CH3COO–Na^+ + H_2$

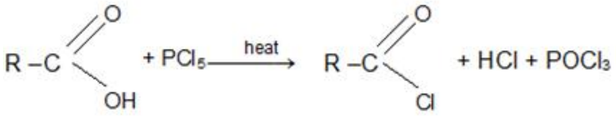
$CH_3COOH + NaOH \rightarrow CH3COO–Na^+ + H_2O$

$CH_3COOH + NaHCO_3 \rightarrow CH3COO–Na^+ + H_2O + CO_2$

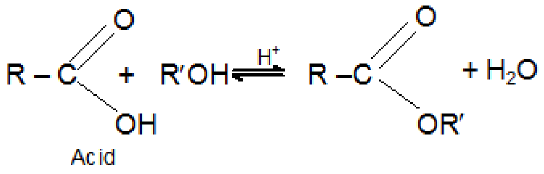
b. Conversion into Acid Chlorides:



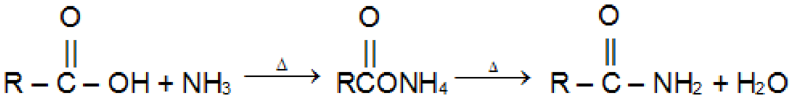




c. Conversion into Esters (Esterification)



d. Conversion into Amides



$$R-\overset{O}{\overset{||}{C}}-OH + NH_3 \xrightarrow{\Delta} R\overset{O}{\overset{||}{C}}ONH_4 \xrightarrow{\Delta} R-\overset{O}{\overset{||}{C}}-NH_2 + H_2O$$

e. Conversion into Anhydrides

$$2CH_3COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CO)_2O + H_2O$$

f. Reduction:

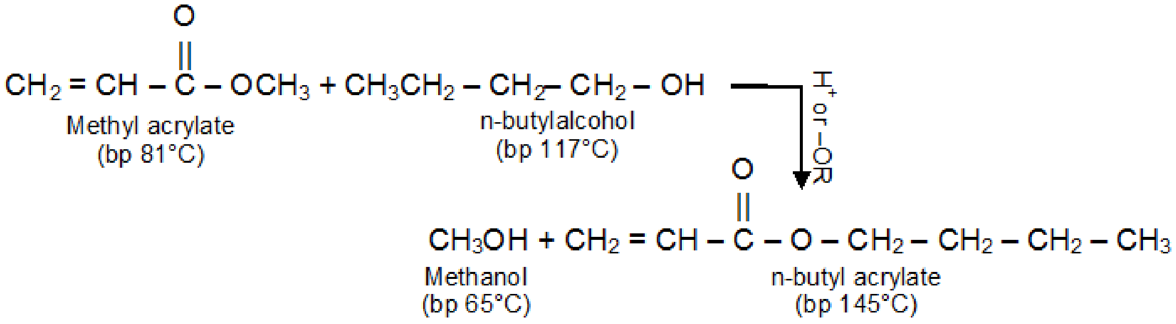
$$4R\text{–}COOH + 3LiAlH_4 \longrightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4\,AlLi \xrightarrow{H_2O} RCH_2OH$$

g. Halogenation:

$$CH_3-COOH \xrightarrow{Cl_2,P} Cl-CH_2-COOH \xrightarrow{Cl_2,P} Cl_2CH-COOH \xrightarrow{Cl_2,\ P} Cl_3CCOOH$$

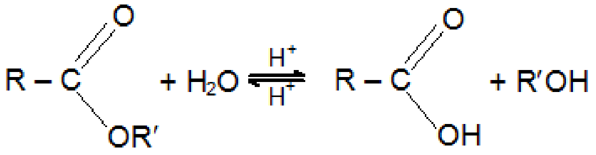
Esters

a) Transesterification :



$$CH_2=CH-\overset{O}{\overset{||}{C}}-OCH_3 + CH_3CH_2-CH_2-CH_2-OH \xrightarrow{H^+ \text{ or } -OR} CH_3OH + CH_2=CH-\overset{O}{\overset{||}{C}}-O-CH_2-CH_2-CH_2-CH_3$$

b) Hydrolysis:



c) Reduction:

$$CH_3-(CH_2)_{10}-COOCH_3 \xrightarrow[150^\circ \text{ High pressure}]{H_2,\ CuO,\ CuCr_2O_4} CH_3(CH_2)_{10}CH_2OH + CH_3OH$$

Methyl laurate Lauryl alcohol

$$CH_3-(CH_2)_{14}-COOC_2H_5 \xrightarrow{LiAlH_4} \xrightarrow{H^+} CH_3-(CH_2)_{14}-CH_2-OH$$

Ethyl palmitate 1–Hexadodecanol

Acid Chlorides:

a) Acetylation

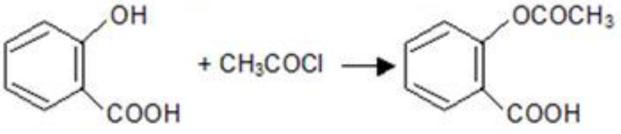
$CH_3COCl + HOH \longrightarrow CH_3COOH + HCl$

$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$

Acetyl chloride Ethyl acetate

$CH_3COCl + H_2NC_6H_5 \longrightarrow C_6H_5NHCOCH_3 + HCl$

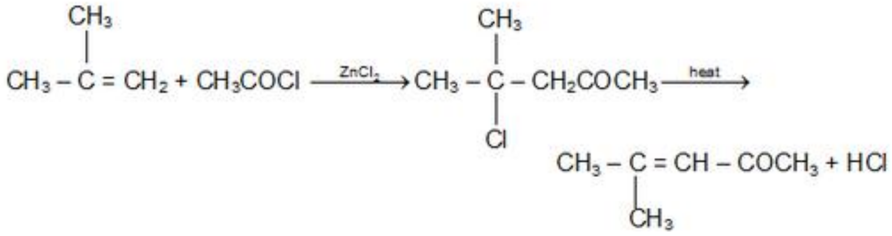
Aniline Acetanilide



Salicylic acid

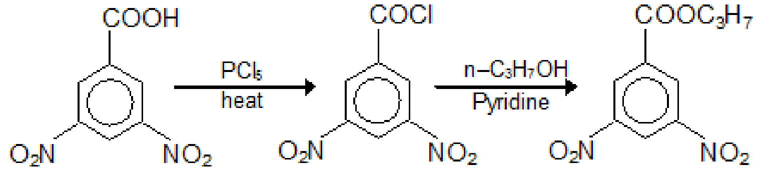
Acetyl Salicylic acid (Aspirin)

b) Reaction with Olefins:



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3COCl \xrightarrow{ZnCl_2} CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2COCH_3 \xrightarrow{heat} CH_3-\underset{CH_3}{C}=CH-COCH_3 + HCl$$

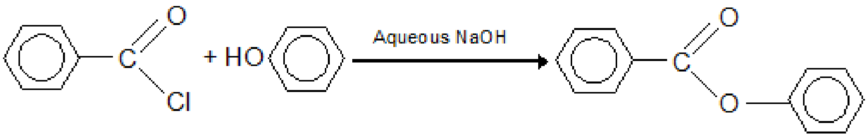
c) Conversion of Acid Chlorides into Acid Derivatives:



3-5, Dinitrobenzoic acid

3-5, Dinitrobenzoyl chloride

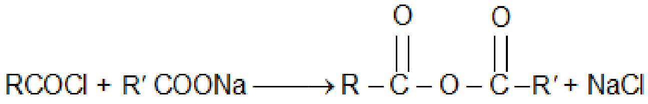
n-propyl 3, 5 – dinitrobenzoate



Benzoyl chloride

Phenol

Phenyl benzoate

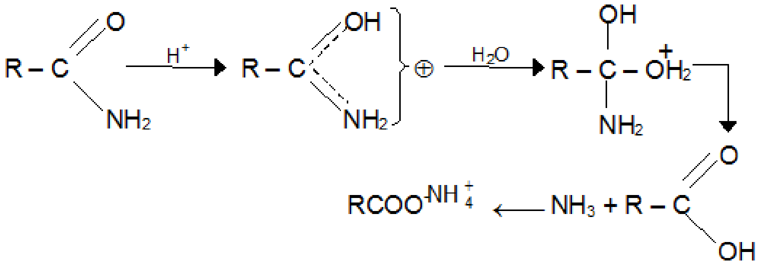


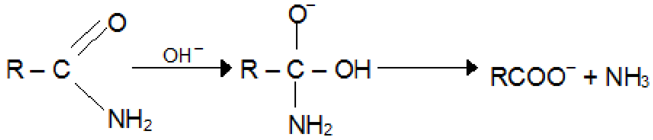
$$RCOCl + R'COONa \longrightarrow R-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-R' + NaCl$$

Acid anhydride

Amides

a. Hydrolysis:



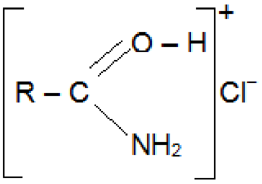


b. Acidic Character of Amides:

$2RCONH_2 + HgO \rightarrow (RCONH)_2Hg + H_2O$

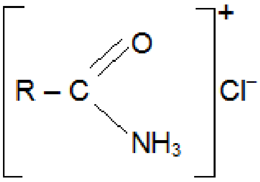
c. Basic Character of Amides:

Amides are very feebly basic and form unstable salts with strong inorganic acids. e.g. $RCONH_2HCl$. The structure of these salts may be I or II



I

or



II

d. Reduction:

$RCONH_2 + 4H \xrightarrow{Na\,/\,C_2H_5OH} R-CH_2-NH_2 + H_2O$

e. Reaction with Phosphorus Pentaoxide:

$R\text{-}CONH2 + P_2O_5 \rightarrow R\text{-}CN$

f. Reaction with Nitrous Acid:

$RCONH_2 + HNO_2 \rightarrow RCO_2H + N_2 + H_2O$