04 Aldehydes, Ketones and Carboxylic Acids

Aldehydes and Ketones :

Organic Compounds having $>C=O$ group are called carbonyl compounds and $>C=O$ group is known as carbonyl group. It's general formula is $C_nH_{2n}O$ (n = 1, 2, 3.....) Carbonyl compounds are grouped into two categories.

(a) Aldehydes: Aldehyde group is $-\overset{\overset{O}{\|}}{C}-H$ (also known as formyl group). It is a monovalent group

Carbon atom of $-\overset{\overset{O}{\|}}{C}-H$ group is of 1° nature i.e. $R-\overset{1^\circ}{\underset{H}{\underset{|}{C}}}=O$

(b) Ketones: The carbonyl group $(>C=O)$ is a Ketonic group when its both the valency's are satisfied by alkyl group. It is a bivalent group.

Carbon atom of $>C=O$ group is of 2° nature i.e. $\overset{2^\circ}{\underset{R}{\overset{R}{>}}}C=O$

Ketones are further classified as

(i) Simple or symmetrical ketones: Having two similar alkyl groups. $\overset{R}{\underset{R}{>}}C=O$

(ii) Mixed or unsymmetrical ketones: Having two different alkyl groups. $\overset{R}{\underset{R'}{>}}C=O$

Ex. (Ketones):

Symmetrical	Unsymmetrical
$\overset{CH_3}{\underset{CH_3}{>}}C=O$	$\overset{CH_3}{\underset{CH_3}{>}}C=O$
(Acetone or Dimethyl ketone)	(Ethyl methyl ketone)
Propanone	Butanone

Structure: In $>C=O$ compounds C-atom is sp^2 hybridised which forms three σ bonds and one π bond. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in $>C=O$ group.

$\underset{C}{\overset{C}{\overset{sp^2}{>}}}C\overset{\sigma}{=}O$ The C—C—O / H—C—O bond angle is 120°

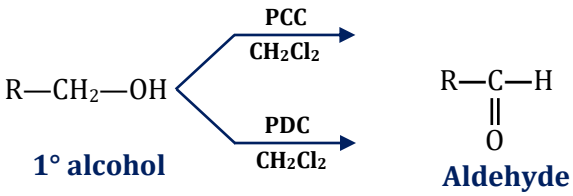
Due to electronegativity difference in C and O atoms, the $>C=O$ group is polar.

$(\overset{\delta+}{>}C=\overset{\delta-}{O})$ Hence aldehydes and Ketones possess considerable dipole moment.

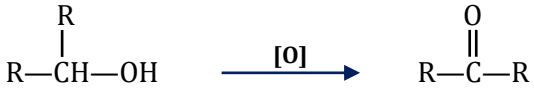
General Methods of Preparation :

1. From Alcohol :

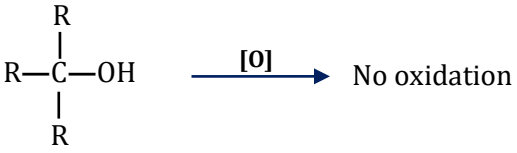
(a) Oxidation of alcohols by PCC or PDC



1° alcohol — Aldehyde



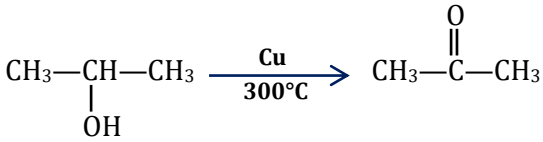
2° alcohol — Ketones



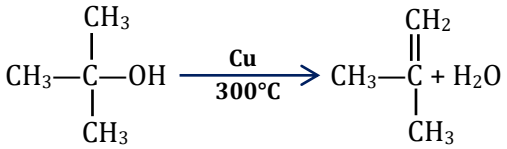
3°alcohol

(b) Dehydrogenation of alcohols by Cu

(Acetaldehyde)



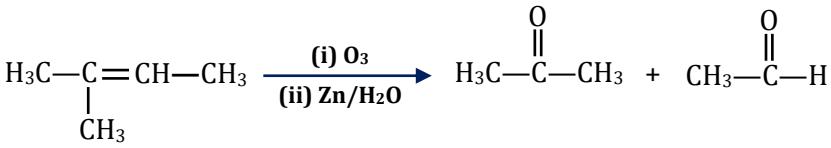
(Acetone)



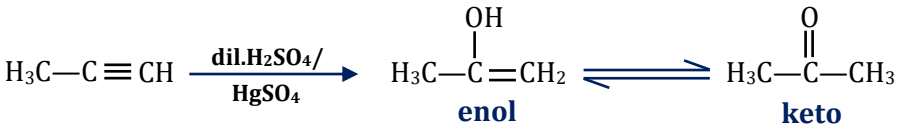
(Isobutylene)

2. From Hydrocarbons :

(a) By ozonolysis of alkenes



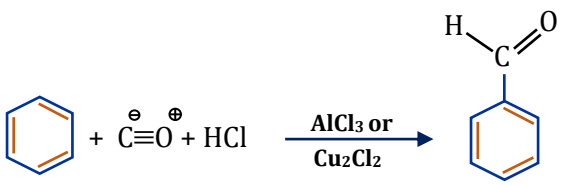
(b) By hydration of alkynes (Kucherov Reaction)



enol — keto

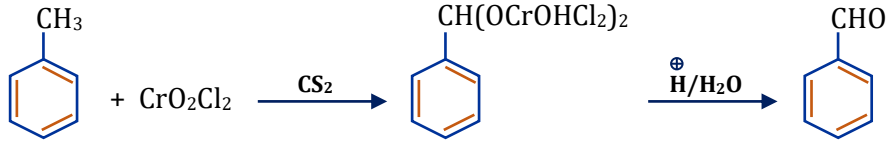
3. From Aromatic Hydrocarbons :

(a) Gatterman koch reaction



(b) Etard reaction

Benzaldehyde is formed by oxidation of methyl benzene in presence of CrO_2Cl_2



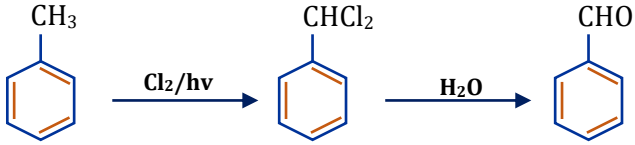
Toluene **Chromyl chloride** **(Chromium complex)**

(c) Oxidation using CrO_3 (Chromic oxide)

(Acetic anhydride) **(Benzylidene diacetate)**

(d) By side chain chlorination followed by hydrolysis

Side chain chlorination of toluene gives benzal chloride which on hydrolysis gives benzaldehyde.



4. From Cyanides :

(a) Stephen's reduction

Nitriles are reduced to corresponding imine with $SnCl_2$ in the presence of HCl, which on hydrolysis gives corresponding aldehyde.

$$R—C\equiv N + SnCl_2 + HCl \longrightarrow R—CH=NH \xrightarrow{H_3O^+} R—CH=O$$

DIBAL–H → Diisobutyl aluminum hydride [AlH(i-Bu)$_2$]: is also used to obtain aldehyde from cyanide/ester

$$R—C\equiv N \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} R—CH=O$$

(b) Reaction with Grignard reagent

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.

$$CH_3—CH_2—C\equiv N + C_6H_5MgBr \xrightarrow{ether} CH_3CH_2—C(=NMgBr)(C_6H_5) \xrightarrow{H_3O^+}$$

$$CH_3—CH_2—C(=NH)(C_6H_5) \xrightarrow{H_3O^+} C_2H_5—C(=O)(C_6H_5) + NH_3$$

(1-Phenylpropanone)

5. From Acid Chloride :

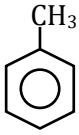
$$2RMgX + CdCl_2 \rightarrow R_2Cd + 2MgXCl$$

$$2R'—\underset{\underset{O}{\|}}{C}—Cl + R_2Cd \rightarrow 2R'—\underset{\underset{O}{\|}}{C}—R + CdCl_2$$

ketone

BEGINNER'S BOX-1

1. Which reaction gives Benzaldehyde

(1)  $+ CrO_3 + (CH_3-CO)_2O \longrightarrow$

(2)  $+ CO + H-Cl \xrightarrow{AlCl_3}$

(3) $Ph-CN \xrightarrow[HCl]{SnCl_2} A \xrightarrow{H_3\overset{+}{O}}$

(4) All of them

CAA155

2. Which reagent below cannot reduce an acid chloride to an aldehyde?

(1) $H_2/Pd\text{-}BaSO_4$ (2) NaH (3) $LiAlH_4$ (4) DIBAL-H

CAA156

3. Compound which gives only acetone on ozonolysis

(1) $CH_3-CH=CH-CH_3$ (2) $(CH_3)_2C=C(CH_3)_2$ (3) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$ (4) $CH_3CH=CH_2$

CAA157

4. Catalyst $SnCl_2/HCl$ is used in

(1) Stephen's reduction (2) Cannizzaro reaction

(3) Clemmensen reduction (4) Rosenmund's reduction

CAA158

5. Hydrogenation of benzoyl chloride in the presence of Pd gives

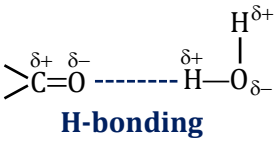
(1) Benzyl alcohol (2) Benzaldehyde (3) Benzoic acid (4) Phenol

CAA159

Physical Properties :

State: Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} onwards solid.

Solubility: C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are highly soluble in water due to polarity of $>\overset{\delta+}{C}=\overset{\delta-}{O}$ bond and can form H–bond with water molecule. C_5 onwards are insoluble in water.



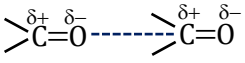
H-bonding

$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

Boiling point: Boiling point $\propto$ Molecular weight

Boiling point order is - **Alcohol > Ketone > Aldehydes > Alkane** (of comparable molecular mass)

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole and Vander Waal force of attraction is present. Alkanes are non-polar.



Density: Density of carbonyl compounds is lower than water.

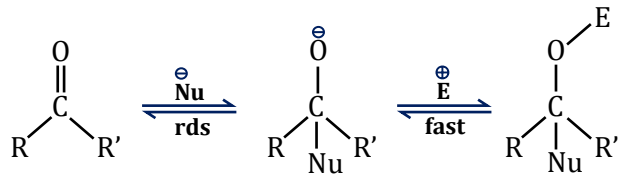
Chemical Properties :

Carbonyl compounds undergo following reactions:

1. Nucleophilic Addition Reactions (NAR) :

NAR is characteristic reaction of aldehydes and ketones

Mechanism



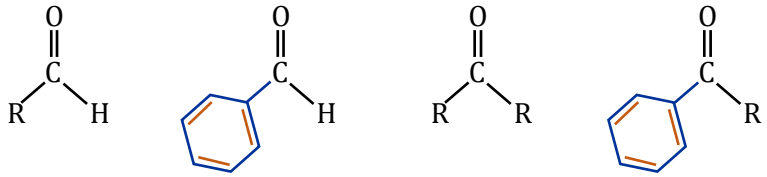
Aldehyde/Ketone

Generally rate towards NAR $\propto$ Electrophilicity of carbonyl group.

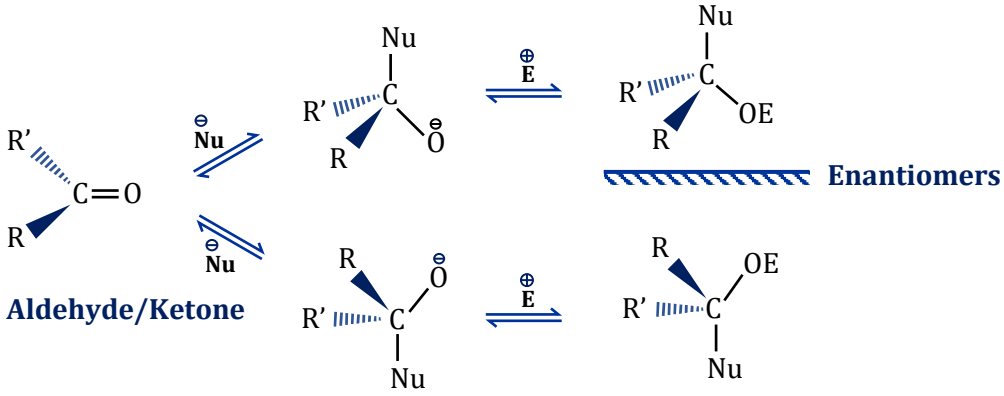
$$\propto \frac{1}{\text{Steric hindrance}}$$

Generally, Rate towards NAR:

Aliphatic aldehyde > Aromatic aldehyde > Aliphatic ketone > Aromatic ketone



Stereochemistry of reaction :



Note: If R ≠ R' then racemic mixture will be formed.

(50% 'd' and 50% 'l')

If R = R' then racemic mixture is not obtained.

(i) Reaction with $HCN/\overset{\ominus}{O}H$

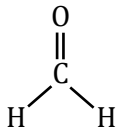
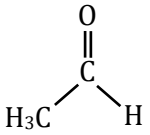
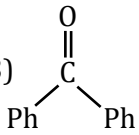
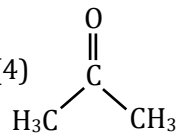
HCN – weak acid

$HCN + \overset{\ominus}{O}H \rightleftharpoons \overset{\ominus}{C}N + H_2O$

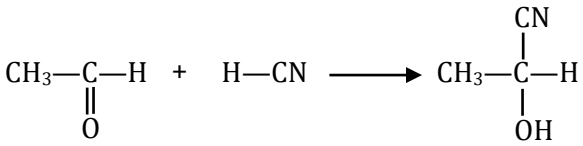
Pure HCN – Rate of reaction is slow so reaction is base catalyzed.

Illustration 1

Which of the following will react with HCN to form racemic mixture ?

(1) 
(2) 
(3) 
(4) 

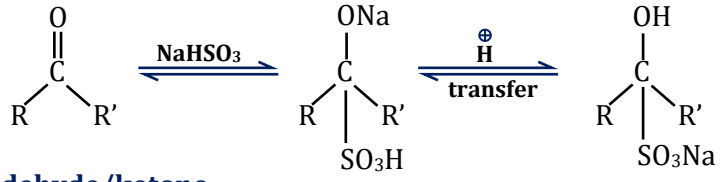
Solution:



Product has chiral carbon

In remaining no chiral carbon in product.

(ii) Reaction with $NaHSO_3$ (sodium hydrogensulpite/sodium bisulphite)



Aldehyde/ketone

Bisulphite addition compound

(White crystalline product)

(Water soluble)

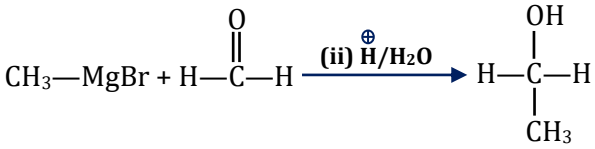
Note: Reaction is sterically sensitive and given by all aldehydes, aliphatic methyl ketones

(methyl ketone) **(aliphatic methyl ketone)**

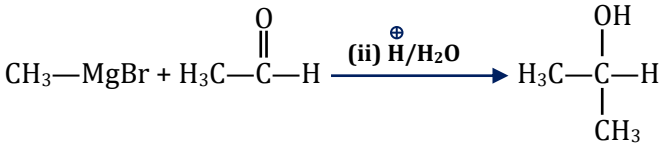
Note: The bisulphite addition compound can be converted back to the original carbonyl compound by treating it with dilute acid or base.

Hence this reaction is useful for separation and purification of aldehydes (and some ketones)

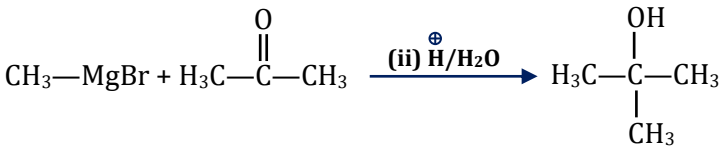
(iii) Reaction with Grignard reagent (RMgX)



1° alcohol

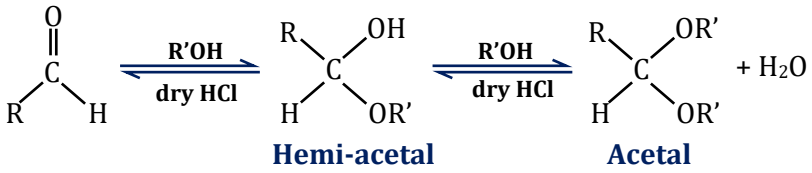


2° alcohol

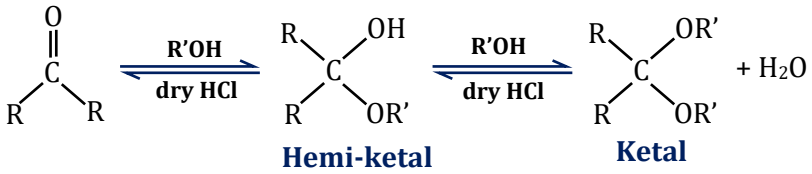


3° alcohol

(iv) Reaction with ROH (Alcohol) (addition then elimination)



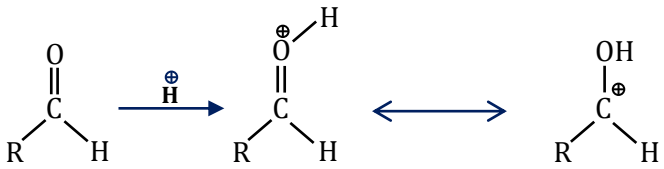
Hemi-acetal **Acetal**



Hemi-ketal **Ketal**

Note:

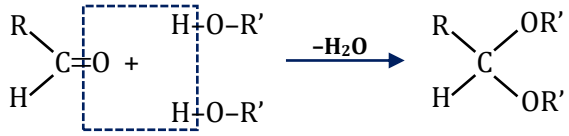
1. To move equilibrium in forward direction excess ROH is used and H_2O is removed.
2. Aq. HCl not used as it will shift equilibrium in backward direction.
3. HCl used to make 'C' of carbonyl group more electrophilic.



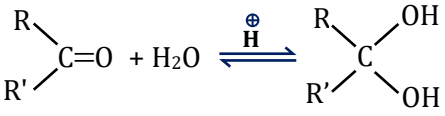
more electrophilic

4. Acetals and ketals are hydrolysed with aq. mineral acid to yield corresponding aldehydes and ketones.

Directly

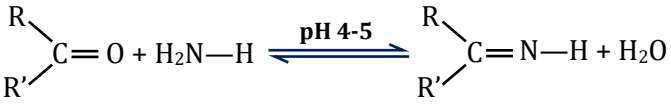


(v) Reaction with H_2O

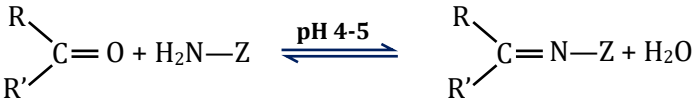


Aldehdye/Keto **Unstable hydrate (generally)**

(vi) Reaction with NH_3 and It's Derivatives (addition then elimination)



Aldehyde/Ketone

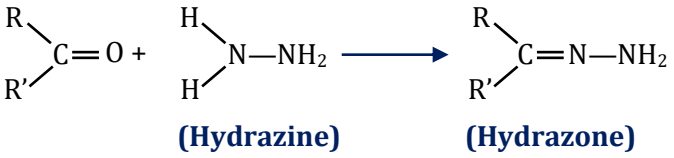


Aldehyde/Ketone **NH_2–Z – Ammonia derivatives**

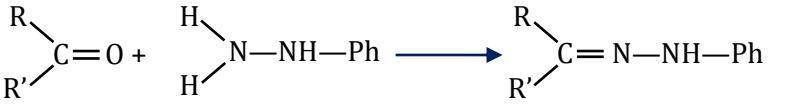
Ex : NH_2OH (hydroxyl amine)
NH_2NH_2 (hydrazine)

Note:

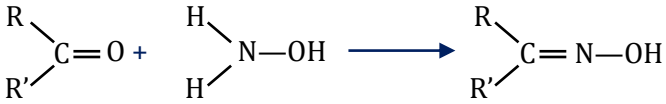
1. Mild acidic medium used – To make 'C' of carbonyl group more electrophilic.
2. It is an addition elimination reaction.



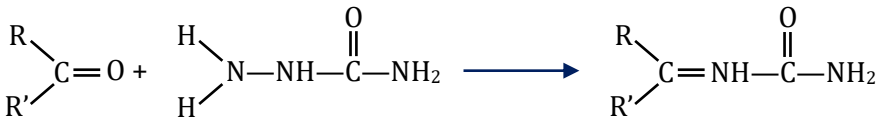
(Hydrazine) (Hydrazone)



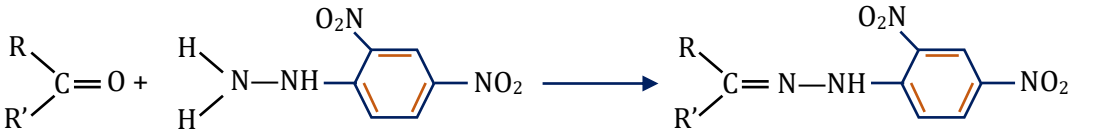
(Phenyl hydrazine) (Phenyl hydrazone)



(Hydroxyl amine) (Oxime)



(Semi-carbazide) (Semi-carbazone)



(2,4 Dinitrophenyl hydrazine) (2,4 Dinitrophenyl hydrazone)

(2,4-DNP or Brady's reagent)

2,4-DNP Test : Aldehydes and ketone react with 2,4-DNP to give red, orange or yellow ppt.

BEGINNER'S BOX-2

1. Which gives stable hydrate?

(1) $CH_3-\underset{\underset{O}{\|}}{C}-H$ (2) Ph—CHO (3) CCl_3—CHO (4) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

CAA160

2. $Ph-CHO + Ph-NH_2 \xrightarrow{\oplus H}$

(1) Ph—CH_2—Ph (2) Ph—CH_2—NH_2 (3) Ph—CH=N—Ph (4) Ph—CH_2—NH—Ph

CAA161

3. Which is the best nucleophile ?

$\overset{1}{NH_2}-\underset{\underset{O}{\|}}{C}-\overset{2}{NH}-\overset{3}{NH_2}$

(1) 1 (2) 2 (3) 3 (4) All are same

CAA162

4. Which gives DNP test?

(1) Ph—CO—CH_3 (2) Ph—CHO (3) CH_3—$COCH_2$—CH_3 (4) All of these

CAA163

5. Which gives two oxime when reacted with NH_2—OH?

(1) H—CHO (2) Ph—COPh (3) CH_3—$COCH_3$ (4) Ph—$COCH_3$

CAA164

2. Reduction of Aldehyde/Ketone:

The nature of product depends upon the reducing agent used.

(i) $\boxed{>C=O \longrightarrow >CH_2}$

(A) Clemmensen reduction

Reagent : Zn-Hg/Conc. HCl

Function : Aldehyde/Ketone to Alkane

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{\text{Zn–Hg/Conc. HCl}} CH_3-CH_2-CH_3$$

In this reaction $-\overset{\overset{O}{\|}}{C}-$ is converted into $-CH_2-$ (Methylene).

(B) Wolff-Kishner reduction

Reagent : $NH_2NH_2/\overset{\ominus}{O}H$

$$+ \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

Function : Aldehyde/Ketone to Alkane

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{NH_2NH_2/\overset{\ominus}{O}H} CH_3-CH_2-CH_3 + N_2$$

In this reaction $-\overset{\overset{O}{\|}}{C}-$ is converted into $-CH_2-$ (Methylene).

(ii) $\boxed{>C=O \longrightarrow >CHOH}$ Reducing agents are

- Metal + H_2
- $LiAlH_4$
- $NaBH_4$
- Na + C_2H_5OH

3. Oxidation of Aldehyde/Ketone:

Aldehydes are easily oxidised to carboxylic acids on treatment with strong oxidising agents like $KMnO_4$, $K_2Cr_2O_7$.

Ketones are oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures.

$$R-CHO \xrightarrow{[O]} R-COOH$$

$$R-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-R' \xrightarrow{[O]} \underset{\text{(By cleavage of } C_1-C_2 \text{ bond)}}{R-COOH + R'-CH_2COOH} \quad + \quad \underset{\text{(By cleavage of } C_2-C_3 \text{ bond)}}{R-CH_2COOH + R'-COOH}$$

Oxidation of only aldehyde

Reducing character: Aldehydes are easily oxidised so they are strong reducing agents.

(i) Tollens' reagent: It oxidises aldehydes. Tollens' reagent is ammoniacal silver nitrate solution

$(AgNO_3 + NH_4OH) \longrightarrow [Ag(NH_3)_2]OH$

$RCHO + [Ag(NH_3)_2]OH \longrightarrow \underset{\text{Silver mirror}}{RCO\overset{\ominus}{O} + Ag} + H_2O$

(ii) Fehling's solution: It is a mixture of aqueous $CuSO_4$, NaOH and sodium potassium tartarate.

Fehling solution A– aq. solution of $CuSO_4$

Fehling solution B– Roschelle salt (Sodium potassium tartarate + NaOH)

Fehling solution A + Fehling solution B (Dark blue colour of cupric tartarate)

$$RCHO + Cu^{+2} + OH^- \longrightarrow RCO\overset{\ominus}{O} + Cu_2O$$

(Cuprous oxide–Red ppt.)

$$Cu^{2+} \longrightarrow Cu^{+}$$

(Cupric - Blue) **(Cuprous - Red ppt.)**

(iii) Benedict's solution: It is a mixture of $CuSO_4$ + sodium citrate + NaOH. It provides Cu^{+2}. It is reduced by aldehyde to give red ppt of cuprous oxide.

$$RCHO + Cu^{2+} + OH^- \longrightarrow RCO\overset{\ominus}{O} + Cu_2O$$

(Cuprous oxide–Red ppt.)

(iv) Schiff's reagent: Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff's dye.

Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent aldehyde reacts with this reagent to restore the pink colour.

Note:

1. All above four methods are used to distinguished aldehydes and ketones.
2. Aromatic aldehyde does not give F.S. and B.S. test.

4. Oxidation of Methyl Ketone (Haloform Reaction) :

When methyl ketones react with halogen in the presence of base oxidation of methyl ketones takes place.

$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3X_2 + 4NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus\oplus}{O}Na + CHX_3$$

(Haloform)

Salt of carboxylic acid

$CHCl_3$ – Chloroform (liquid)

$CHBr_3$ – Bromoform (liquid)

CHI_3 – Iodoform (yellow solid)

Ketones → Methyl ketones undergo haloform reaction

$$R-\overset{\overset{O}{\|}}{C}-CH_3$$

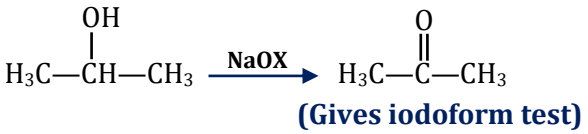
Aldehydes → Only acetaldehyde can undergo haloform reaction

$$H_3C-\overset{\overset{O}{\|}}{C}-H$$

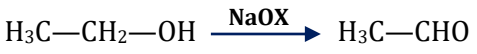
Alcohols → Alcohols of the following type also undergo haloform reaction

$$-\overset{\overset{OH}{|}}{CH}-\overset{\alpha}{C}H_3$$

$NaOH + X_2$ is also a mild oxidizing agent



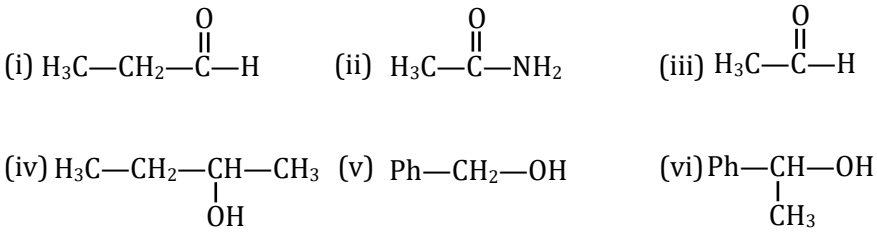
(Gives iodoform test)



(Gives iodoform test)

Illustration 2

Which of the following compounds will give positive iodoform test?

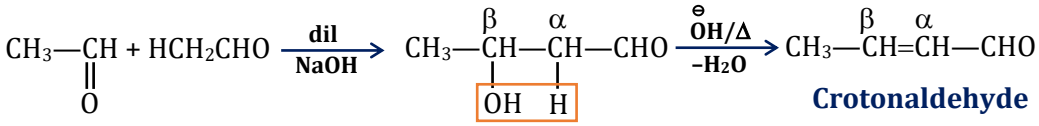


Solution:

Ans. (iii), (iv), (vi)

5. Aldol Condensation :

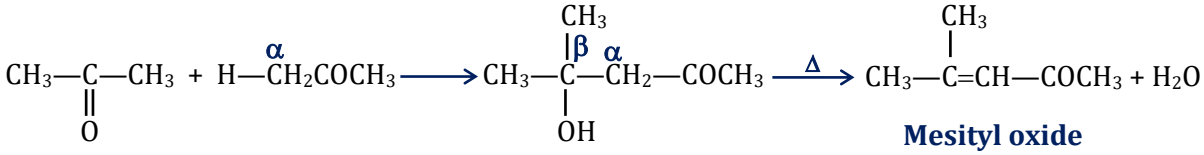
Carbonyl compounds which contain α-H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α, β-unsaturated carbonyl compound.



Crotonaldehyde

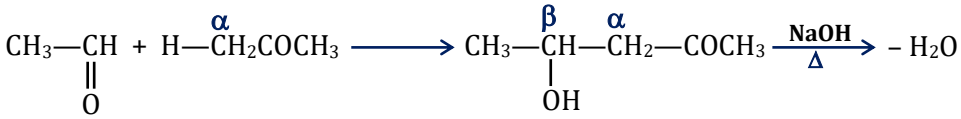
Identical carbonyl compounds ⟶ Simple or self aldol condensation.
Different carbonyl compounds ⟶ Mixed or crossed aldol condensation.

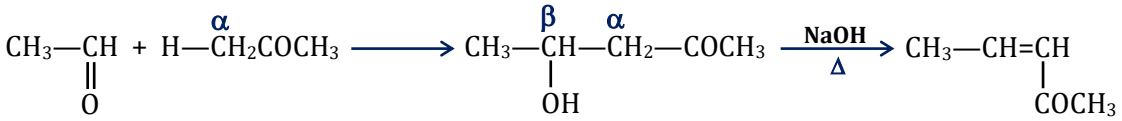
Simple or self condensation



Mesityl oxide

Mixed or crossed aldol condensation





6. Cannizzaro Reaction :

Those aldehydes which do not contain α - H atom give this reaction, with conc. NaOH or KOH: Products are Salt of carboxylic acid and alcohol

In this reaction one molecule of aldehyde is oxidised to acid, while other is reduced to alcohol, such type of reactions are called redox reaction.

$HCHO + HCHO \xrightarrow[NaOH,\Delta]{Conc.} HCOONa + CH_3OH$

When molecules are same ⟶ Simple cannizzaro reaction
Two different molecules ⟶ Mixed cannizzaro reaction

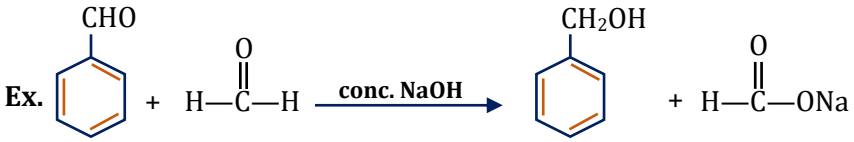
Note:

1. In mixed or crossed cannizzaro reaction more reactive aldehyde is oxidised and less reactive aldelyde is reduced.

$HCHO + C_6H_5CHO \xrightarrow[\Delta]{NaOH} HCOONa + C_6H_5CH_2OH$

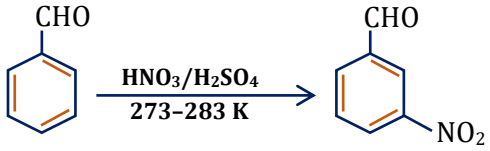
Oxidized (Sodium formate) **Reduced (Benzyl alcohol)**

2. Ketone does not give Cannizzaro due to poor leaving tendency.



7. Electrophilic Substitution Reaction :

Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



Benzaldehyde **m-Nitrobezaldehyde**

BEGINNER'S BOX-3

1. The compounds capable in reaction with Tollen's reagent is (are) :

(1) Formaldehyde (2) Formic acid (3) Acetaldehyde (4) All the above

CAA165

2. Acetaldehyde reacts with NaOH to form :-

(1) $CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{H}{\underset{|}{C}}=O$

(2) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{H}{\underset{|}{C}}=O$

(3) $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{O}{\underset{||}{C}}-CH_3$

(4) $\underset{OH}{\underset{|}{CH_2-CH_2-CH_2}}-\underset{H}{\underset{|}{C}}=O$

CAA166

3. Fehling's solution is a :-

(1) Solution of magenta dye bleached by SO_2

(2) Ammonical solution of $AgNO_3$

(3) Mixture of a solution of $CuSO_4$ and a solution of caustic soda and sodium potassium tartarate

(4) Alcoholic solution of 2,4-dinitrophenylhydrazine

CAA167

4. The compound that will not give iodoform on treatment with alkali and iodine is:
(1) Acetone (2) Ethanol (3) Diethyl ketone (4) Isopropyl alcohol

CAA168

5. Which of the following will not give the iodoform test?
(1) Acetophenone (2) Ethanal (3) Benzophenone (4) Ethanol

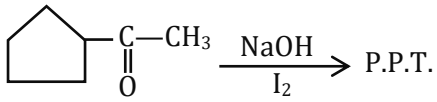
CAA169

6. Which of the following give yellow precipitate with $NaOH+I_2$?
(1) Acetone (2) $CH_3-\overset{\overset{O}{\|}}{C}-Cl$ (3) Benzaldehyde (4) $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$

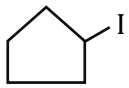
CAA170

7. How will you convert butan-2-one to propanoic acid?
(1) Tollens reagent (2) Felling's solution (3) $NaOH/I_2/\Delta$ and H^+ (4) NaOH/NaI/H^+

CAA171

8. 

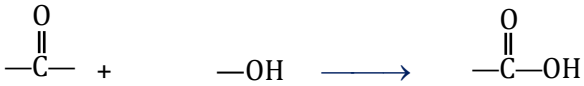
PPT of-

(1) CH_3I (2) CHI_3 (3) 
 (4) CH_2I_2

CAA172

Carboxylic Acid :

Organic compounds having –COOH group are called Carboxylic acids. This functional group is composed of Carbonyl $(-\overset{\overset{O}{\|}}{C}-)$ and hydroxyl (–OH) group.



Carbonyl group **Hydroxyl group** **Carboxylic group**

The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group.

Classification :

Monocarboxylic acid (RCOOH): Having one carboxylic group, also called monobasic acid.
General molecular formula - $C_nH_{2n}O_2$ (n = 1, 2, 3, ...). Higher mono carboxylic acids are called **fatty acids**.
Dicarboxylic acid: Having two carboxylic groups, also called dibasic acid.

Ex. $\begin{matrix}COOH\\|\\COOH\end{matrix}$ **Oxalic acid**

Tricarboxylic acid: Having three carboxylic groups also called tribasic acid.

Ex. $HO-\overset{\overset{CH_2COOH}{|}}{\underset{\underset{CH_2COOH}{|}}{C}}-COOH$ **Citric acid**

Structure: The carbon atom of –COOH group is sp^2 hybridised, this C-atom is in centre and thus bond angle around C–atom is 120°.

General Methods of Preparation :

1. By Oxidation of Alcohols and Carbonyl Compounds :

Oxidation is carried out by acidified $K_2Cr_2O_7$ or $KMnO_4$.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} RCHO \xrightarrow{[O]} RCOOH$$

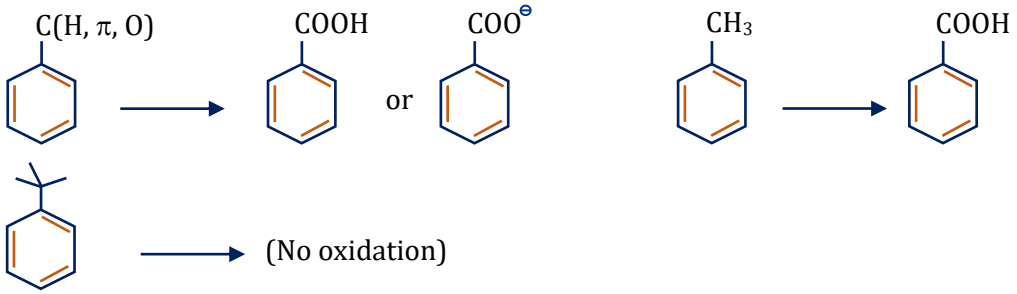
2. From Alkyl Benzenes :

Oxidation using

(a) $KMnO_4/\overset{\oplus}{H}$

(b) $KMnO_4/\overset{\oplus}{O}H/\Delta$

(c) $K_2Cr_2O_7/\overset{\oplus}{H}$



(No hydrogen, no π bond, no oxygen)

3. By Hydrolysis of Alkane Nitriles or Cyanides :

Complete hydrolysis takes place in acidic medium (dil. HCl) or in alkaline medium

$$R-C\equiv N \xrightarrow[\Delta]{H_2O/\overset{\oplus}{H}} R-\underset{OH}{\overset{|}{C}}=NH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{H_2O/\overset{\oplus}{H}} R-\overset{O}{\overset{\|}{C}}-OH + NH_3$$

4. From Grignard's Reagent :

$$RMgX + O=C=O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OMgX \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{matrix}X\\OH\end{matrix}$$

Carbon dioxide

Solid CO_2 (dry ice) is used

5. By Hydrolysis of Acid Derivatives :

$$R-\overset{O}{\overset{\|}{C}}-Z + H-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + HZ$$

Z = —Cl, —OCOR, —OR, —NH_2

Reactivity order of acid derivatives: **RCOCl > $(RCO)_2O$ > RCOOR > $RCONH_2$**

$$RCOCl \xrightarrow[\text{dil.acid}]{HOH} RCOOH + HCl$$

$$(RCO)_2O \xrightarrow[\text{dil.acid}]{HOH} 2RCOOH$$

$$RCOOR' \xrightarrow[\text{dil.acid}]{HOH} RCOOH + R'OH$$

$$R-CONH_2 \xrightarrow[\text{dil.acid}]{HOH} RCOOH + NH_3$$

Physical Properties :

Carboxylic acids from C_1— C_4 are completely soluble in water.

$$\text{Solubility} \propto \frac{1}{\text{molecular weight}}$$

Solubility is due to intermolecular H - bonding with water molecules.

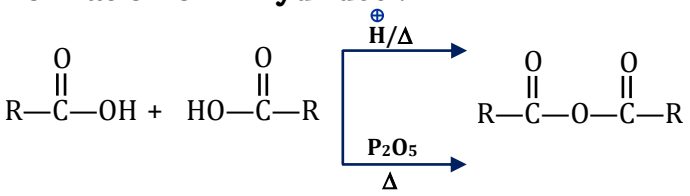
Boiling point: B. P. $\propto$ Molecular weight

B. P. : Carboxylic acids > alcohol

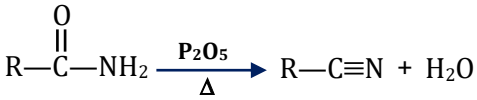
This is because in acids two oxygen atoms take part in H – bonding (while in alcohol only one O – atom takes part).

Reactions of Carboxylic Acids (Chemical Properties) :

1. Formation of Anhydrides :

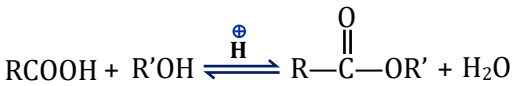


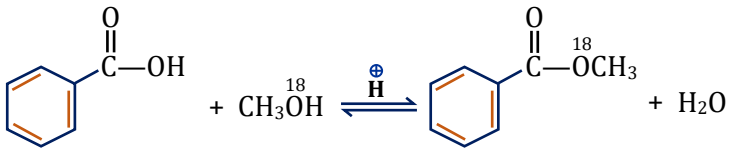
Note:



2. Esterification Reaction :

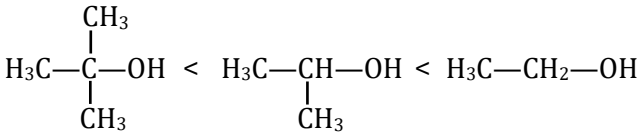
Carboxylic acids react with alcohols or phenols in the presence of an acid (conc.H_2SO_4 or dry HCl) to form esters. This method is called Fischer esterification.





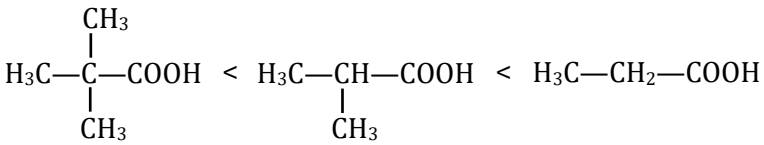
$$\text{Rate of esterification} \propto \frac{1}{\text{Steric hindrance}}$$

Reactivity of alcohols



3°Alcohol **2°Alcohol** **1°Alcohol**

Reactivity of acids



3. Reaction with PCl_3, PCl_5, $SOCl_2$:

$3R—COOH \xrightarrow{PCl_3} 3R—COCl + H_3PO_3$

$R—COOH \xrightarrow{PCl_5} R—COCl + POCl_3 + HCl$

$R—COOH \xrightarrow{SOCl_2} R—COCl + SO_2 + HCl$

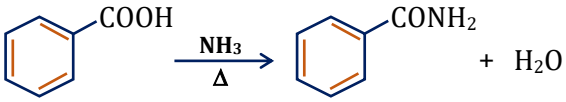
4. Reaction with Ammonia :

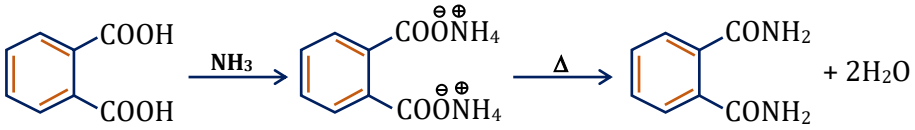
$R—COOH + NH_3 \rightleftharpoons R—C(=O)\overset{\ominus\ \oplus}{O}NH_4 \xrightarrow{\Delta} R—CONH_2 + H_2O$

(Ammonium carboxylate) (Amide)

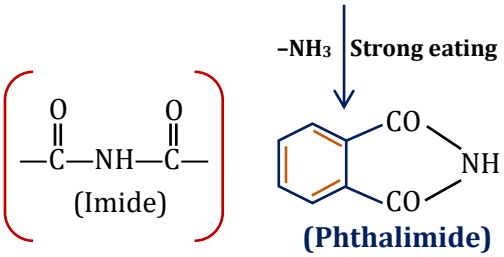
$H_3C—COOH + NH_3 \rightleftharpoons H_3C—C(=O)\overset{\ominus\ \oplus}{O}NH_4 \xrightarrow{\Delta} H_3C—CONH_2 + H_2O$

(Acetic acid) (Ammonium acetate) (Acetamide)





(Phthalic acid) (Ammonium phthalate) (Phthalamide)



(Phthalimide)

5. Reduction :

Carboxylic acids are reduced to primary alcohols by lithium aluminum hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

$R—COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ether or } B_2H_6} R—CH_2OH$

6. Decarboxylation :

Removal of CO_2 from carboxylic acid is known as decarboxylation.

Reagent used: **NaOH + CaO (Soda lime)**

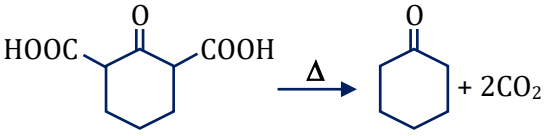
$CH_3COOH \xrightarrow[\Delta]{NaOH/CaO} CH_4 + Na_2CO_3$

β-keto carboxylic acids

β-keto acid can be easily decarboxylated by heating only (no need of sodalime)

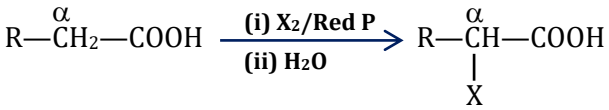
$CH_3—\overset{O}{\overset{\|}{C}}—CH_2—COOH \xrightarrow{\Delta} CH_3—\overset{O}{\overset{\|}{C}}—CH_2—H + CO_2$

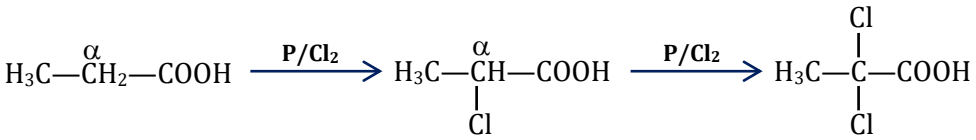
(β-Keto acid) (Acetone)



7. Hell Volhard Zelinsky (HVZ) Reaction :

Carboxylic acids having α hydrogen atom are halogenated at the α position on treatment with chlorine or bromine in the presence of small amount of red phosphorous to give α-halocarboxylic acids.

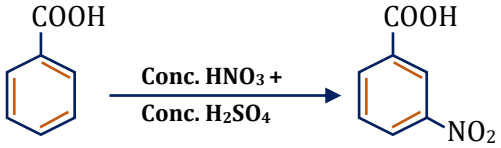




8. Ring Substitution :

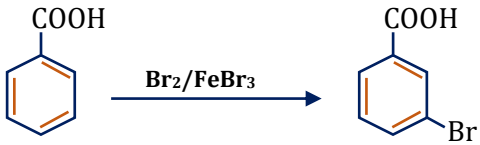
Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo Friedel-Crafts reaction (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).

(i)



m-Nitrobenzoic acid

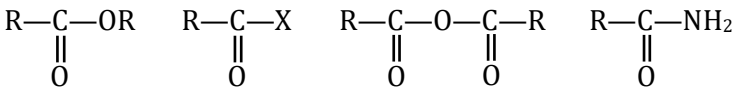
(ii)



m-Bromobenzoic acid

Chemical Reaction of Acid Derivatives $\left(R-\underset{\underset{O}{\|}}{C}-\ddot{Z}\right)$:

$-\ddot{Z}$ may be $\rightarrow$ $-\ddot{O}R$, $-\ddot{X}$, $-\ddot{O}COR$, $-\ddot{N}H_2$



Ester **Acid halide** **Anhydride** **Amide**

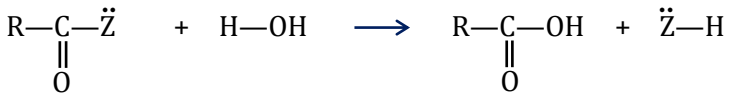
Characteristic reaction of acid derivative is nucleophilic substitution reaction (NSR)

Ex. 

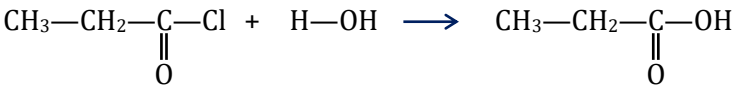
Acid derivative **Product**

Reactivity order: $CH_3COCl > CH_3COOCOCH_3 > CH_3COOC_2H_5 > CH_3CONH_2$

1. Reaction with water (Hydrolysis) :

Ex. 

Hydrolysis of acid derivative gives carboxylic acid.

(i) 

Acid halide

(ii) $Ph-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_3 + H-OH \xrightarrow{H^{\oplus}} Ph-CH_2-\underset{\underset{O}{\|}}{C}-OH + CH_3-OH$

(ester)

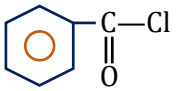
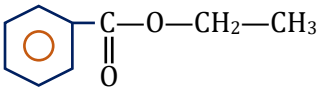
(iii) $CH_3-\underset{\underset{O}{\|}}{C}-NH-CH_3 + H-OH \xrightarrow{H^{\oplus}} CH_3-\underset{\underset{O}{\|}}{C}-OH + CH_3-NH_2 \xrightarrow{H^{\oplus}} CH_3-\overset{\oplus}{N}H_3$

(Amide)

2. Reaction with Alcohol :

$R-\underset{\underset{O}{\|}}{C}-\ddot{Z} + R-\ddot{O}H \longrightarrow R-\underset{\underset{O}{\|}}{C}-OR + \ddot{Z}-H$

(ester)

(i)  $+ CH_3-CH_2-OH \xrightarrow{-HCl}$ 

(ii) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3 + CH_3-OH \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3 + CH_3-CH_2-OH$

Transesterification → formation of ester from another ester

3. Reaction with Ammonia :

$R-\underset{\underset{O}{\|}}{C}-\ddot{Z} + \ddot{N}H_2-H \longrightarrow R-\underset{\underset{O}{\|}}{C}-NH_2 + \ddot{Z}-H$

(amide)

(i) $CH_3-\underset{\underset{O}{\|}}{C}-Cl + NH_2-H \xrightarrow{Base} CH_3-\underset{\underset{O}{\|}}{C}-\ddot{N}H_2$

(ii) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3 + R-NH-H \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-NH-R + CH_3-OH$

Amine **Amide**

(iii) $CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 + NH_2-NH-H \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-NH-NH_2 + CH_3-\underset{\underset{O}{\|}}{C}-OH$

4. Reaction with Grignard Reagent :

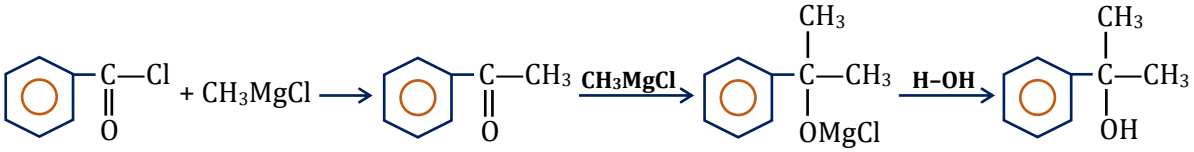
$R-\underset{\underset{O}{\|}}{C}-\ddot{Z} + \overset{\ominus\oplus}{R}MgX \xrightarrow{NSR} R-\underset{\underset{O}{\|}}{C}-R + \ddot{Z}MgX$

ketone

(i) $CH_3-\underset{\underset{O}{\|}}{C}-Cl + EtMgCl \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-Et + MgCl_2$

ketone

If RMgX is used in excess then alcohol is obtained



(ii) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3 + PhMgBr \xrightarrow{NSR} CH_3-\underset{\underset{O}{\|}}{C}-Ph$

ketone

BEGINNER'S BOX-4

1. Alkanoic acids can be prepared by hydrolysis of:-

(1) Trihaloalkanes (2) 1,1,1–trihaloalkanes

(3) Grignard reagents (4) Ketones

CAA173

2. Acids have much higher boiling points than isomeric esters because :-

(1) Acids form dimers by H–Bonding

(2) Acids are volatile in steam

(3) Esters are non–volatile

(4) Acids can ionise to give protons in aqueous solution

CAA174

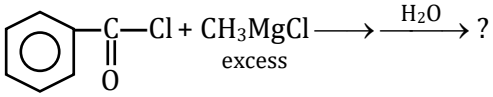
3. Which of the following compounds can form intermolecular H–bonds :-

(1) Ethyl acetate (2) Methyl formate (3) Acetamide (4) Acetic anhydride

CAA175

4. In which reaction 3° Alcohol is obtained ?

(1) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3 + CH_3-CH_2MgBr \longrightarrow \xrightarrow{H_2O} ?$

(2)  $\xrightarrow{H_2O} ?$ (excess CH_3MgCl)

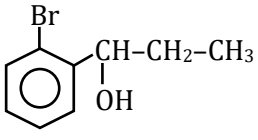
(3) $CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-CH_3 + H_2O \longrightarrow$

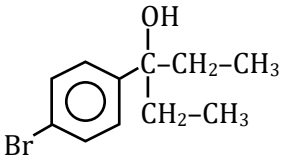
(4) $CH_3-\underset{\underset{O}{\|}}{C}-Cl + (CH_3)_2Cd \longrightarrow$

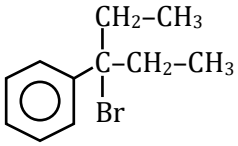
CAA176

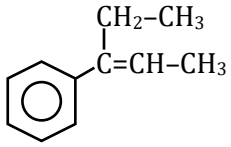
5. What is end product ?

 $\xrightarrow{H_2O} \xrightarrow{H\text{-}Br} ?$

(1) 

(2) 

(3) 

(4) 

CAA177

6. Which ester does not give alcohol after hydrolysis ?

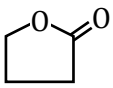
(1) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3$

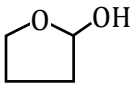
(2) $CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(3) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-Ph$

(4) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH=CH_2$

CAA178

7.  $+ H_2O \xrightarrow{H^{\oplus}} ?$

(1) 

(2) $HO-(CH_2)_4-OH$

(3) $HO-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-H$

(4) $HO-(CH_2)_3-COOH$

CAA179

8. Acids do not give the characteristic reactions of C=O group because of :-

(1) Dimerisation

(2) Resonance

(3) Cyclic structures

(4) Attached alkyl radical

CAA180

BEGINNER'S BOX — ANSWER KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	4	5			
	Ans.	**4**	**3**	**2**	**1**	**1**			
BEGINNER'S BOX-2	**Que.**	1	2	3	4	5			
	Ans.	**3**	**3**	**3**	**4**	**4**			
BEGINNER'S BOX-3	**Que.**	1	2	3	4	5	6	7	8
	Ans.	**4**	**2**	**3**	**3**	**3**	**1**	**3**	**2**
BEGINNER'S BOX-4	**Que.**	1	2	3	4	5	6	7	8
	Ans.	**2**	**1**	**3**	**2**	**3**	**4**	**4**	**2**