Page No.
Date

Aldehyde, ketones & carboxylic acid

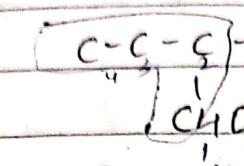
Carbonyl → carbon + Oxygen
>C=O

* Nomenclature.

• Aldehyde. $-\overset{O}{\overset{\|}{C}}-H$ -al [If 'C' of -CHO is included in chain]

- carbaldehyde [If 'C' of -CHO is not included in ch

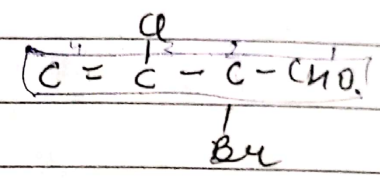
eg: CH_3CH_2CHO
Propan-1-al



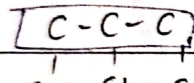
2-methyl butanal

$OHC-C-C-CHO$
1 2 3 4

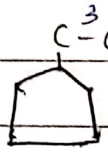
Butane-1,4-dial



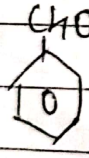
2-Bromo-3-chloro but-3



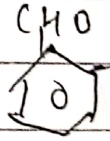
Propan-1,2,3-tricarbaldehyde



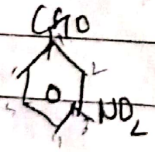
3-cyclopentyl propan-1-



Benzaldehyde / Benzene carbaldehyde.



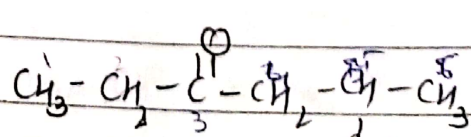
2-hydroxy benzaldeh



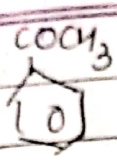
3-nitrobenzaldehyde.

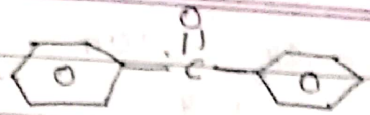
• Ketone. $-\overset{O}{\overset{\|}{C}}-$ -one

eg: $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
Propan-2-one



~~4-bromopent~~ 5-Bromo hex-en-3-


Acetophenone


Benzophenone

* Structure of the carbonyl group.

$>C=O$ • Polar • sp^2 hybridisation • trigonal planar
• 120° Bond angle

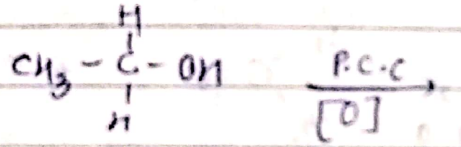
* Preparation of Aldehydes & Ketones

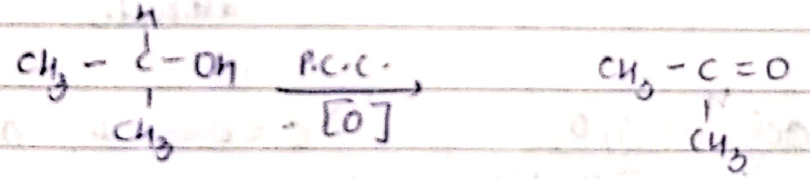
1) By oxidation of alcohol

→ Mild oxidising agent → P.C.C [Pyridinium chloro chromate]

1° alcohol → Aldehyde

2° alcohol → ketone



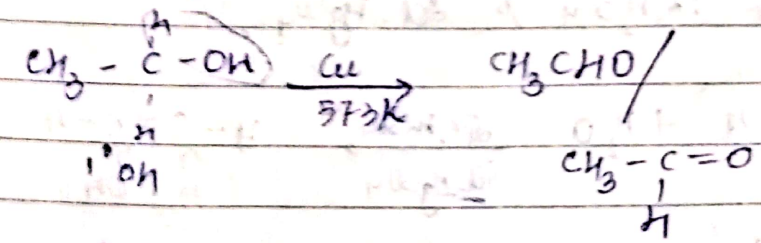


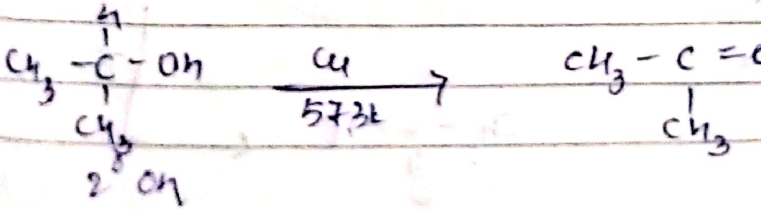
• 3° alcohol [O] can't happen.

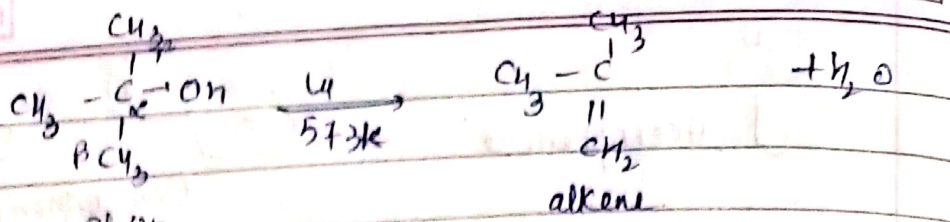
2) By dehydrogenation of alcohols

→ Dehydrogenating agent = Cu at 573k

1° alcohol → CHO
2° alcohol → C=O
3° alcohol $\xrightarrow{\text{dehydration}}$ alkene



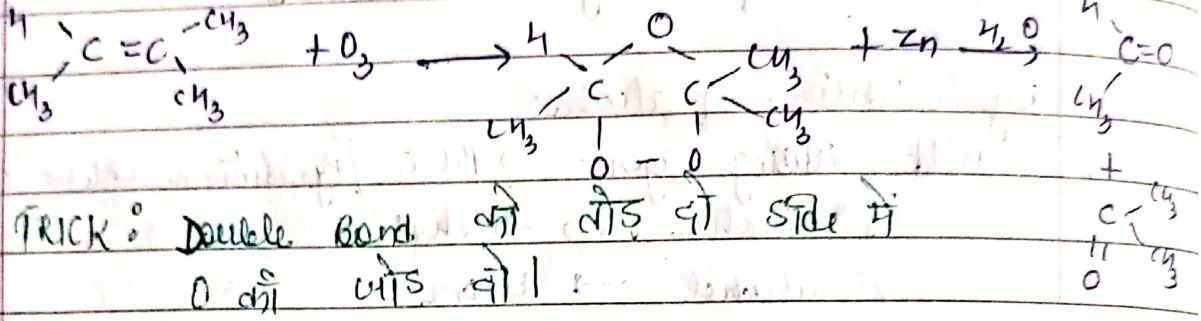




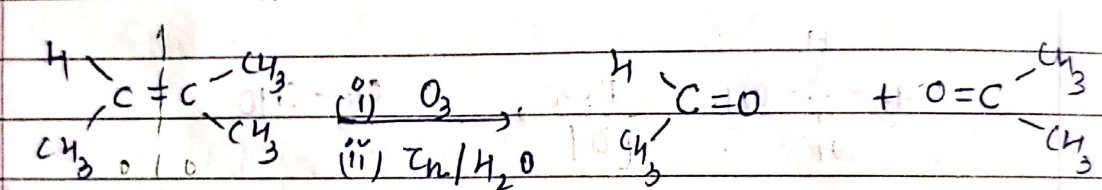
- In case of 3° alcohol dehydration took place % alkene is formed.

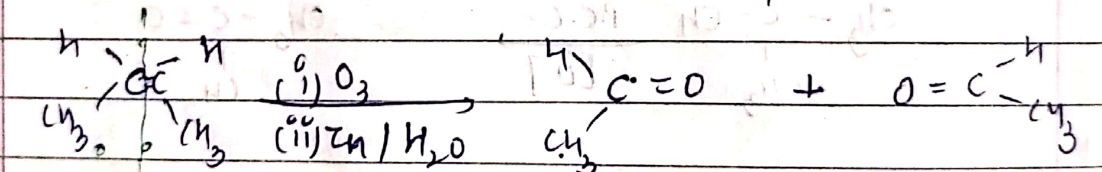
3) From hydrocarbons

i) By ozonolysis of alkenes:



TRICK: Double Bond को तोड़ दो side में O को जोड़ दो।

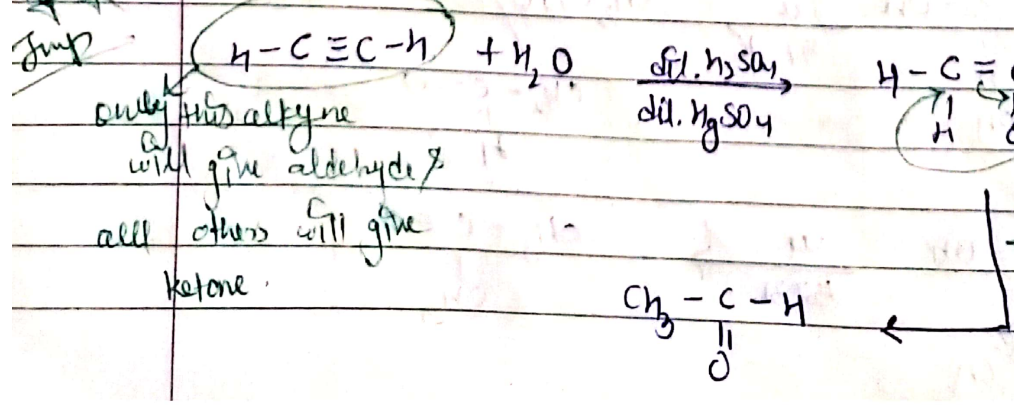




ii) By hydration of alkynes.

→ Addition of H_2O acc. to Mark. Rule.

→ Reagent: dil. H_2SO_4 & dil. $HgSO_4$



eg: $CH_3-C\equiv CH + H_2O \xrightarrow[dil.\ H_2SO_4]{dil.\ H_2SO_4} CH_3-\underset{OH}{C}=CH_2$

$CH_3-\underset{O}{\overset{\|}{C}}-CH_3 \leftarrow$ Tautomerism

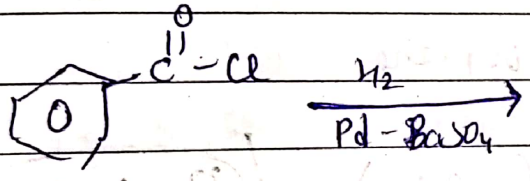
Preparation of Aldehydes.

1) From acyl chloride [acid chloride] [Rosenmund Rxn]

Acid chloride + $H_2 \xrightarrow{Pd-BaSO_4}$ Aldehyde

$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd-BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCl$

$C_2H_5-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd-BaSO_4]{H_2} C_2H_5-\overset{O}{\overset{\|}{C}}-H$



2) From nitriles & esters.

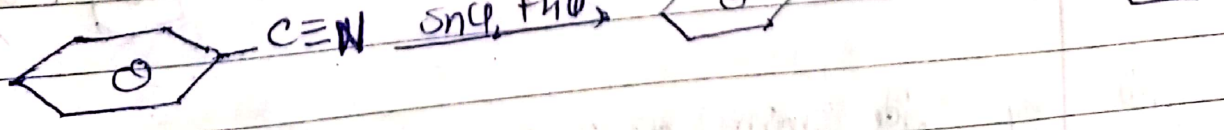
- Stephan's Reaction

$R-C\equiv N + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$

OR

$R-C\equiv N \xrightarrow[(ii)\ H_3O^+]{(i)\ SnCl_2+HCl} R-CHO$

eg: $C_2H_5-C\equiv N \xrightarrow{SnCl_2+HCl} C_2H_5-CH=NH \xrightarrow{H_3O^+} C_2H_5-CHO$



DIBAL - H

$$R-C\equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} R-CHO$$

eg: $CH_3-CH=CH_2-C\equiv N \xrightarrow[H_2O]{DIBAL-H} CH_3-CH=CH_2-CHO$

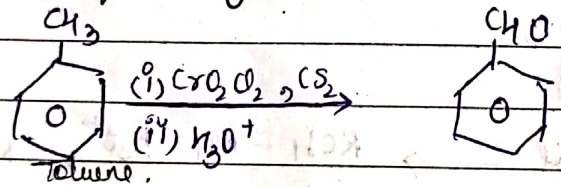
$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[H_2O]{DIBAL-H} R-\overset{O}{\overset{\|}{C}}-H$$

eg: $C_2H_5-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow[H_2O]{DIBAL-H} C_2H_5-\overset{O}{\overset{\|}{C}}-H$

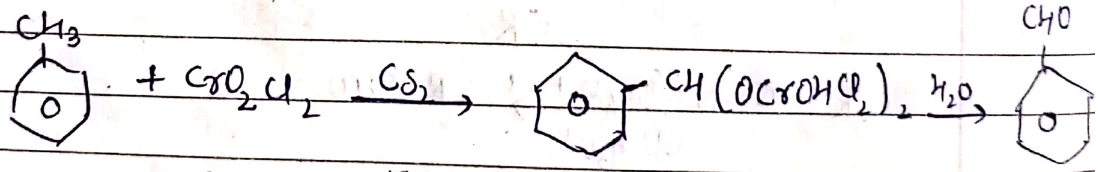
i) From hydrocarbons.

(i) By oxidation of methylbenzene.

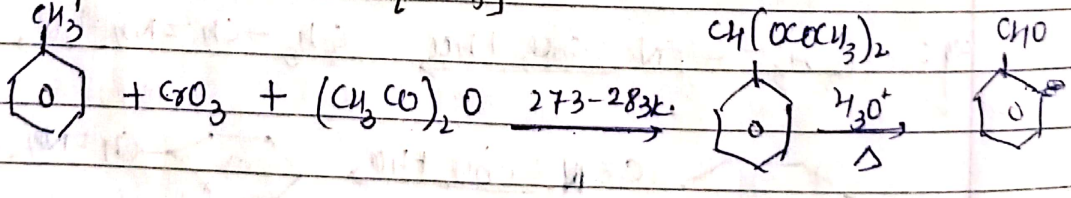
(a) use of chromyl chloride (CrO_2Cl_2) / Etard Rxn



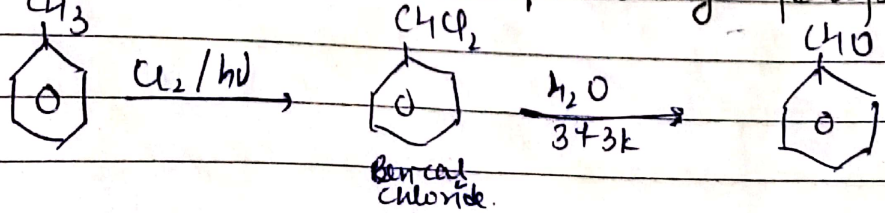
Toluene.



(b) use of chromic oxide [CrO_3]:

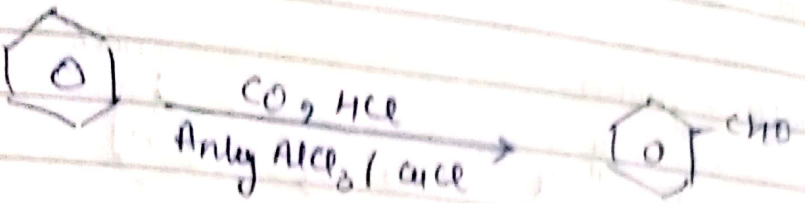


(ii) By side chain chlorination followed by hydrolysis.



Benzal chloride.

iii) Friedel-Crafts reaction



* Preparation of Ketones

1) From acyl chlorides.

$$2R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

(Stable addition)

$$2R'-\overset{O}{\overset{\|}{C}}-Cl + R_2Cd \longrightarrow R'-\overset{O}{\overset{\|}{C}}-R + CdCl_2$$

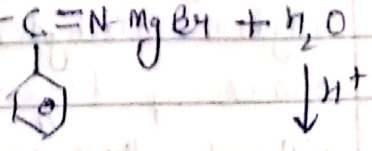
Preparation

$$Eg: 2\left(C_2H_5-\overset{O}{\overset{\|}{C}}-Cl\right) + (CH_3)_2Cd \longrightarrow C_2H_5-\overset{O}{\overset{\|}{C}}-CH_3$$

2) From nitriles.

$$R-C\equiv N + R'-Mg-X \longrightarrow R-\underset{R'}{\underset{|}{C}}=N-MgX + H_2O \xrightarrow{H^+}$$

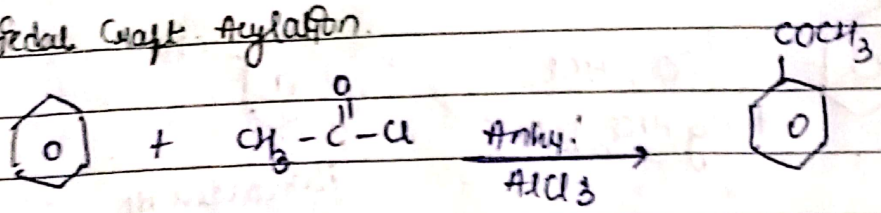
$$R-\underset{R'}{\underset{|}{C}}=O + Mg\begin{matrix}NH_2\\X\end{matrix}$$

Eg: $C_2H_5-C\equiv N$ +  $\longrightarrow$ 

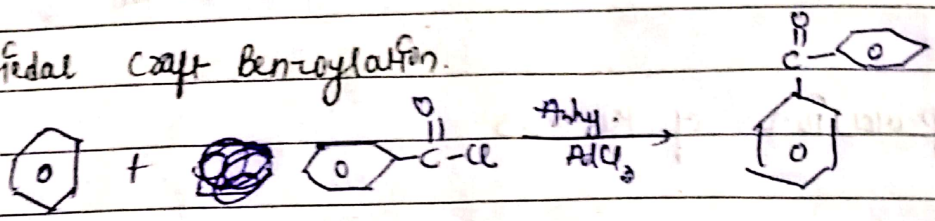
$$C_2H_5-\underset{\text{C}_6\text{H}_5}{\underset{|}{C}}=O$$

3) From benzene or substituted benzenes.

- Friedal Craft Acylation



- Friedal Craft Benzoylation.



* Physical properties.

B.P ∝ MM ∝ 1/Branching.

a) Boiling point

⇒ The B.P of aldehyde & ketones are higher than hydrocarbon & ethers of comparable molecular mass because carbonyl group is a polar group. so these have dipole - dipole attractions.

⇒ They have less B.P than alcohols because of absence of intermolecular hydrogen bonding.

⇒ Among aldehyde & ketones, ketones have higher B.P than aldehydes because ketones are polar, have higher dipole moment & more strongen dipole - dipole attractions than aldehydes.

- Hydrocarbon < Haloalkane < ether < Aldehyde < Ketone < Amine < Alcohol < C...

b) Solubility.

⇒ Aldehydes & ketones upto 4-carbons are soluble in water because of formation of hydrogen bonding of carbonyl group with the hydrogen of water molecules.

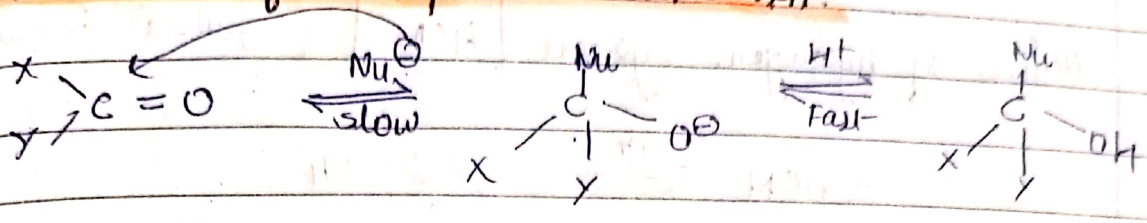
⇒ Higher aldehydes & ketones are insoluble in water because of larger hydrophobic alkyl group.

⇒ Although these are soluble in organic solvents like benzene, ether, $CHCl_3$ etc.

* Chemical Properties.

(1) Nucleophilic addition rxn.

(i) Mechanism of nucleophilic addition rxn.



sp^2 hybridised planner molecule | Tetrahedral molecule | sp^3 hybridised Addition Product

⇒ sp^2 hybridised carbon atom changes to sp^3 hybridised carbon atom.

(ii) Reactivity.

⇒ Aldehydes are more reactive than ketones because -

• In case of ketone, due to presence of more +I group [electron donating group], the electrophilicity of carbonyl carbon atom decreases & hence, ketone is less reactive towards nucleophilic addition rxn.

need of electron.

eg: $\underset{H}{\overset{H}{}}\!>\!C=O > \underset{H}{\overset{CH_3}{}}\!>\!C=O > \underset{CH_3}{\overset{CH_3}{}}\!>\!C=O$

→ steric

• Steric Factor:

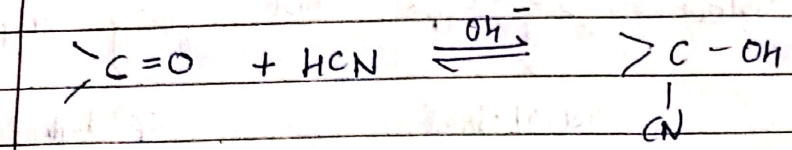
⇒ Larger alkyl group in ketones cause more steric hindrance, so nucleophile cannot approach easily the carbonyl carbon.

⇒ Among aliphatic & aromatic aldehyde, the aliphatic aldehyde are more reactive

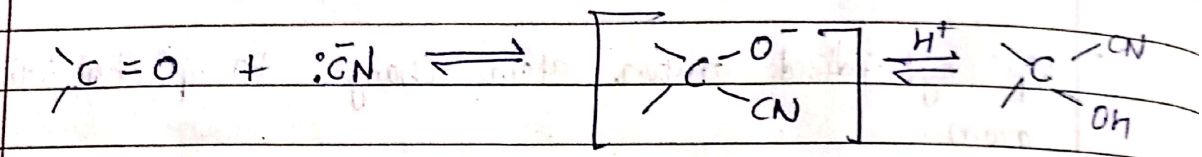
⇒ Among aromatic aldehyde & ketones, aldehydes are more reactive.

(iii) some important eg. of nucleophilic addition & nucleophilic addition - elimination rxns.

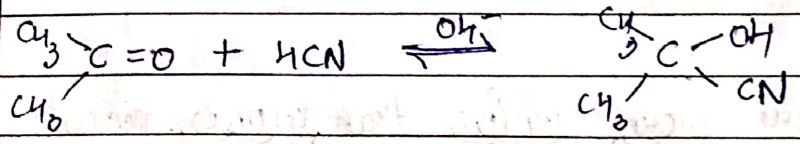
a) Addition of hydrogen cyanide [HCN] (Cyanohydrins are useful synthetic intermediates)



OR

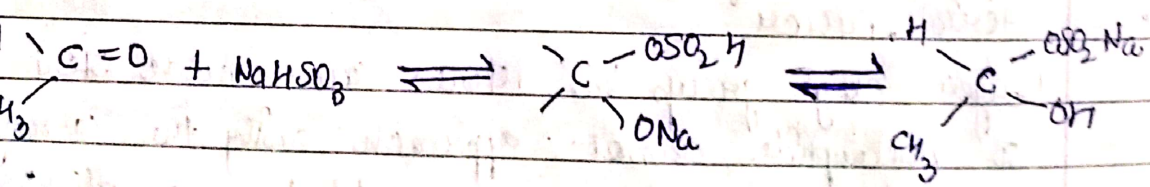


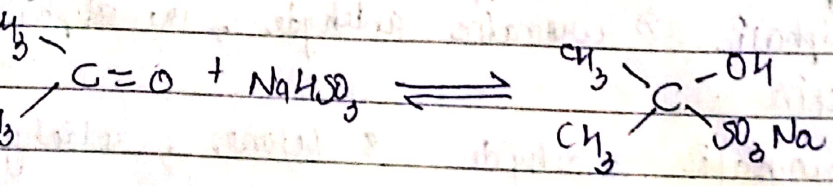
cyanohydrin



b) Addition of sodium hydrogensulphite [$NaHSO_3$]

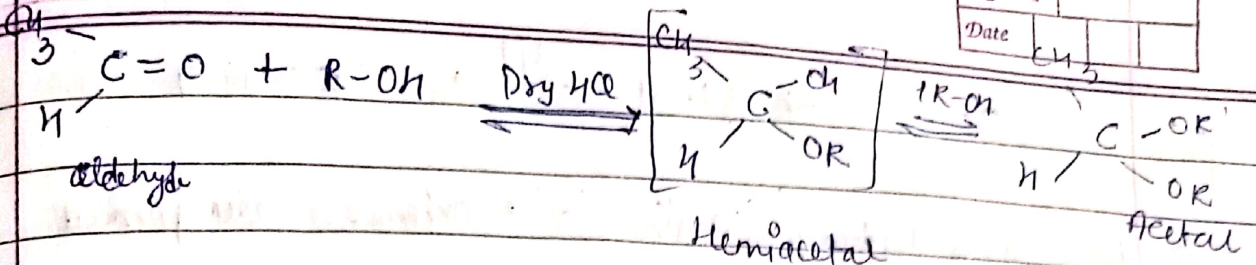
- when aldehyde or ketone is treated with sodium bisulphite, then fine white crystals are formed. So, this rxn is used as a test for carbonyl group.
- Diethyl ketone, acetophenone & benzophenone do not give this rxn due to more steric hindrance.



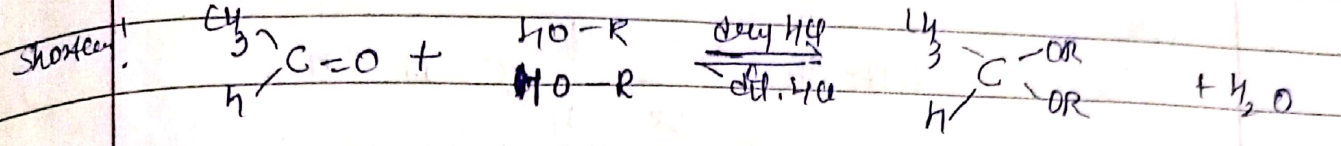


(c) Addition of Alcohol

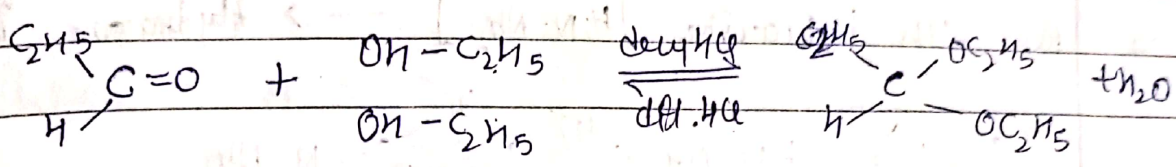
- This rxn takes place in two steps. In first step, one molecule of alcohol add up & a hemi acetal is formed. Then one more molecule add up to hemi acetal & give acetal.



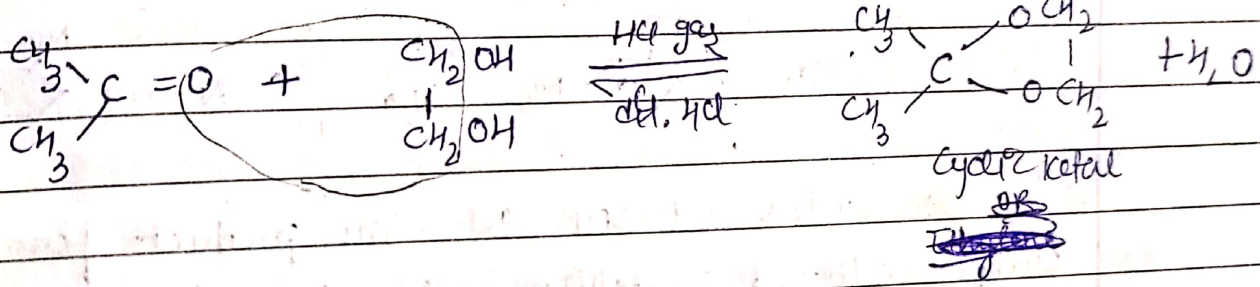
Shortcut:



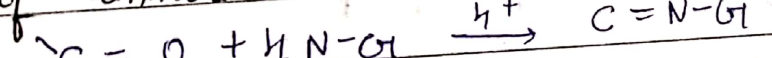
eg:



⇒ ketones react with dihydric alcohol to form ketone.



(d) Addition of ammonia & its derivatives.



	Name	Product str.	Product Name
NH_2-G		$>C=N-G$	
NH_2-OH	Hydroxylamine	$>C=N-OH$	oxime
NH_2-NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
$NH_2-NH-C_6H_5$	Phenyl hydrazine	$>C=N-NH-C_6H_5$	Phenyl hydrazone
$NH_2-NH-C_6H_3(NO_2)_2$	2,4-Dinitro Phenyl hydrazine	$>C=N-NH-C_6H_3(NO_2)_2$	2,4-Dinitro phenyl hydrazone
$NH_2CONHNH_2$	Semicarbazide	$>C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$	Semicarbazone

eg: $>C=O + H_2N-H \xrightarrow{H^+} >C=N-H$

3. ⇒ Rxn with hydroxyl amine → oximes are formed.

$$CH_3-\underset{H}{C}=O + H_2N-OH \xrightarrow[-H_2O]{H^+} CH_3-\underset{H}{C}=N-OH$$

⇒ Rxn with hydrazine $[H_2N-NH_2]$ → Hydrazone is formed

$$CH_3-\underset{H}{C}=O + H_2N-NH_2 \xrightarrow{H^+} CH_3-\underset{H}{C}=N-NH_2$$

4. Rxn with 2,4-dinitrophenyl hydrazine → 2,4-dinitro phenyl hydrazone

$$CH_3-\underset{H}{C}=O + H_2N-NH-C_6H_3(NO_2)_2 \xrightarrow[-H_2O]{H^+} CH_3-\underset{H}{C}=N-NH-C_6H_3(NO_2)_2$$

It is also called 2,4-DNP Test. The product formed is orange coloured crystalline solid. This test is used to identify the carbonyl group.

② Reduction Rxn

(i) Reduction to hydrocarbons: A.K (Aldehyd, keetone..) convert into hydrocarbon

(a) Clemmensen reduction.

$$H-\underset{CH_3}{C}=O \xrightarrow[HCl]{Zn-Hg} CH_3-CH_3 + H_2O$$

$$CH_3-\underset{CH_3}{C}=O \xrightarrow[HCl]{Zn-Hg} CH_3CH_2CH_3 + H_2O$$

(b) Wolff-Kishner Reduction.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[-H_2O]{NH_2NH_2} CH_3-CH_2-CH_3$$

ethylene glycol / KOH

(6) Oxidation Rxn.

(a) oxidation of aldehydes

$$R-CHO \xrightarrow[[O]]{K_2Cr_2O_7/H_2SO_4} R-COOH$$

eg: $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[[O]]{K_2Cr_2O_7/H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH$

(b) oxidation of ketones

$$\text{ketone} \xrightarrow[[O]]{K_2Cr_2O_7/H_2SO_4} \text{No Product}$$

- Ketone in presence of conc. HNO_3 [drastic condition] oxidise

$$\text{ketone} \xrightarrow[\Delta]{\text{conc. } HNO_3} \text{Two carboxylic acid}$$

- In case of unsymmetrical ketones such as butan-2-one or pentan-2-one etc, the point of cleavage is such that keto group stays with smaller alkyl group preferentially [Popoff's Rule]

eg: $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[[O]]{\text{conc. } HNO_3} CH_3COOH + CH_3COOH$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3 \xrightarrow[[O]]{\text{conc. } HNO_3} CH_3-COOH + CH_3CH_2COOH$$

Imp Distinguish b/w Aldehyde & ketones. [mild oxidising agent are used]

⇒ Tollen's Reagent Test: Tollens reagent is ammonical silver nitrate solution.

- It is the confirmatory test of aldehyde

$$R-CHO + [Ag(NH_3)_2]^+ + OH^- \longrightarrow RCOO^- + Ag + NH_3$$

eg: $CH_3CHO + [Ag(NH_3)_2]^+ + OH^- \longrightarrow CH_3COO^- + Ag + NH_3$ (silver mirror)

$$\text{Ketone} + [Ag(NH_3)_2]^+ + OH^- \longrightarrow \text{No silver mirror [No Rxn]}$$

⇒ Oxidation by Fehling's solution: → only for aliphatic aldehyde

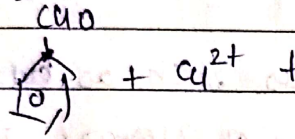
Fehling solution → Fehling A (aq. $CuSO_4$) + Fehling B (Alkaline sodium potassium tartrate i.e (Rochelle salt))

$$R\text{-}CHO + Cu^{2+} + OH^- \longrightarrow RCOO^- + Cu_2O + H_2O$$

(Red Brown ppt)

eg: $CH_3CHO + Cu^{2+} + OH^- \longrightarrow CH_3COO^- + Cu_2O + H_2O$

NOTE: It is a confirmatory test for aliphatic aldehyde. Aromatic aldehyde [benzaldehyde] however don't reduce fehling soln



$$+ Cu^{2+} + OH^- \longrightarrow \text{No Rxn}$$

⇒ Iodoform test: It is a chemical test to confirm the presence of $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}$ group or carbonyl group.

$CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$ → doesn't give iodoform test

$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$ → gives iodoform test.

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + NaOH + I_2 \longrightarrow CHI_3 + R\text{-}COONa + H_2O + NaI$$

$$R\text{-}\overset{O}{\overset{\|}{C}}CH_3 + NaOI \longrightarrow RI_3 + RCOONa$$

Q How will you distinguish b/w ethanal & propanal

- $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$ (ethanal) $+ I_2 + NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + H_2O + NaI$ (CHI_3: yellow ppt)
- $CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$ (propanal) $+ I_2 + NaOH \longrightarrow$ No Rxn.

Q Pentan-2-one & pentan-3-one

$CH_3CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + I_2 + NaOH \xrightarrow{\Delta} I^- + H_2O + CH_3CH_2CH_2COONa + CHI_3$

$CH_3CH_2\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_3 + I_2 + NaOH \longrightarrow$ No Rxn.

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Oxidation of methyl ketones by haloform rxn.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaOX} R-\overset{O}{\overset{\|}{C}}-ONa + CHX_3 \quad [X = Cl, Br, I]$$

(iv) Reaction due to α-hydrogen

Acidity of α-hydrogen of aldehydes & ketones.

- The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong e⁻ withdrawing effect of the carbonyl grp & resonance stabilisation of the conjugate base.

↷ α-hydrogen grp.

(i) Aldol condensation: Aldol is defined as the combination of both the alcohol & carbonyl group in two consecutive carbon atoms.

- The aldehyde or ketone must have one α-hydrogen atom.

Self Aldol condensation

$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[NaOH]{dil.} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

Short cut

$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[NaOH]{dil.,\ \Delta} CH_3-CH=CH-CHO + H_2O$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[NaOH]{dil.,\ \Delta} CH_3-\underset{CH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-H$$

ketone

(ii) Cross Aldol condensation: when 2 different aldehyde both having α-hydrogen atom reacts with dilute NaOH we get 4 Aldol.

[A-A, B-B, A-B, B-A]

A B

$CH_3-\underset{H}{\underset{|}{C}}=O + CH_3-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow[\Delta]{\text{① dil. NaOH}\ \text{②}}$

A+B

$CH_3-\underset{H}{\underset{|}{C}}=O + CH_3-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow[\Delta]{\text{dil. NaOH}} CH_3-\underset{H}{\underset{|}{C}}=CH-\underset{CH_3}{\underset{|}{C}}=O$

$-H_2O$

B+A

$CH_3-\underset{CH_2}{\underset{|}{C}}=O + CH_2-\underset{H}{\underset{|}{C}}=O \xrightarrow[\Delta]{\text{dil. NaOH}} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\underset{H}{\underset{|}{C}}=O$

A+A

$CH_3-\underset{H}{\underset{|}{C}}=O + CH_3-\underset{OH}{\underset{|}{C}}H_2 \xrightarrow[\Delta]{\text{dil. NaOH}} CH_3-\underset{H}{\underset{|}{C}}=CH-\underset{H}{\underset{|}{C}}=O$

B+B

$CH_3-\underset{CH_3}{\underset{|}{C}}=O + CH_3-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow[\Delta]{\text{dil. NaOH}} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\underset{CH_3}{\underset{|}{C}}=O$

(5) Other Rxns.

(i) Cannizzaro rxn: Aldehyde which do not have α-hydrogen atom, undergo self oxidation & reduction in presence of conc. NaOH which is reduced to alcohol & oxidised to acid

$CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-\underset{H}{\underset{|}{C}}=O + CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-\underset{H}{\underset{|}{C}}=O + \text{conc. NaOH} \longrightarrow$

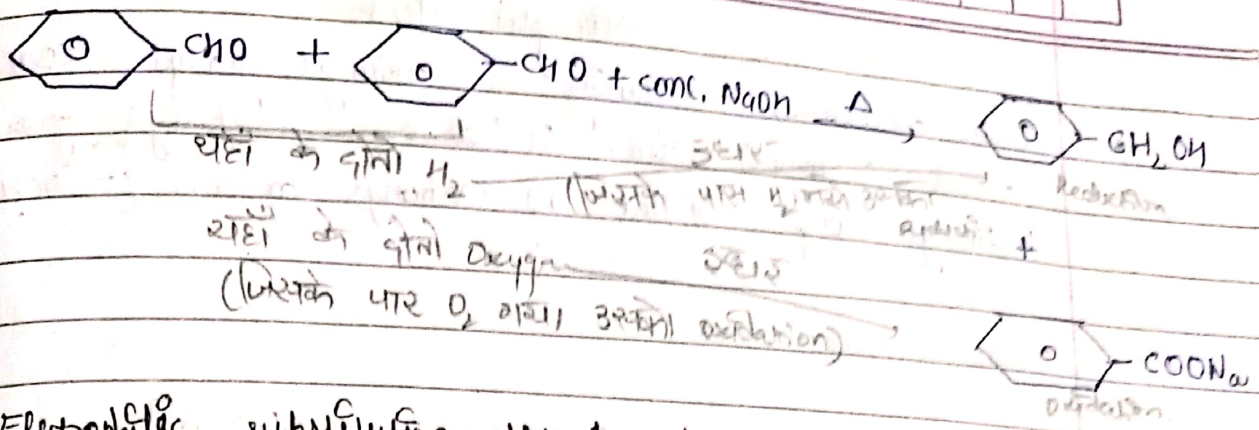
$CH_3-\underset{CH_3}{\underset{|}{C}}-CH_2OH$ (Reduction)

+

$CH_3-\underset{CH_3}{\underset{|}{C}}-COONa$ (Oxidation)

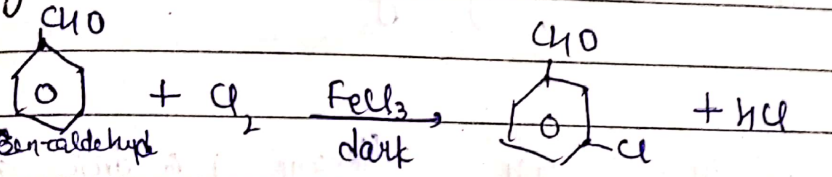
यहाँ के दोनों H_2 इधर

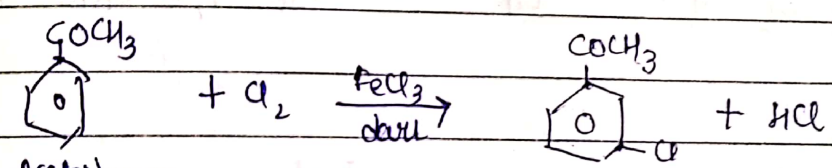
यहाँ के दोनों Oxygen इधर



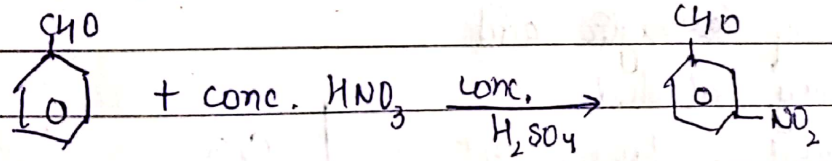
ii) Electrophilic substitution rxn due to Benzene Ring: Aldehydes & ketones are meta directing deactivating groups.

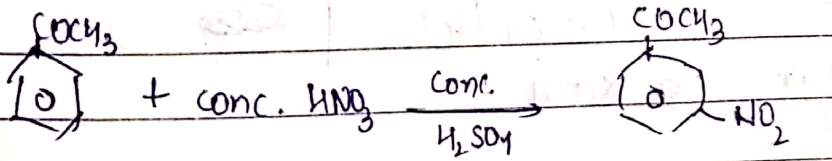
- Halogenation:



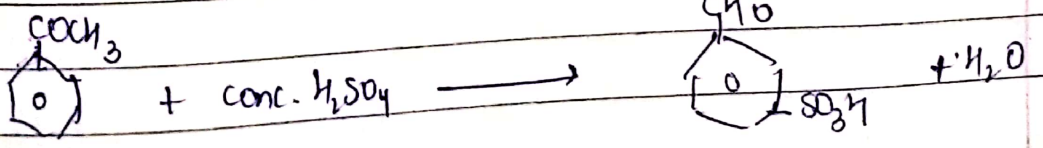


- Nitration:





- Sulphonation:



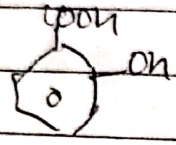
carbonyl + hydroxyl

Carboxylic Acid

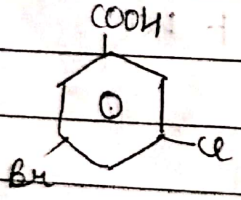
- Carbon compounds containing a carboxyl group, -COOH are called carboxylic acid. It has one carbonyl group & a hydroxyl group attached to carboxyl carbon [-COOH]

- Nomenclature

⇒ $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-COOH$ 3-Hydroxybutanoic acid

⇒  2-hydroxy benzoic acid

⇒ $HOOC-CH_2-CH_2-CH_2-CH_2-COOH$ Hexane-1,6-dioic acid.

⇒  3-Bromo-5-chloro Benzoic acid.

* Preparation of carboxylic acid.

① From primary alcohol

Oxidising agent : $KMnO_4/H^+$ | CrO_3
$K_2Cr_2O_7/H^+$

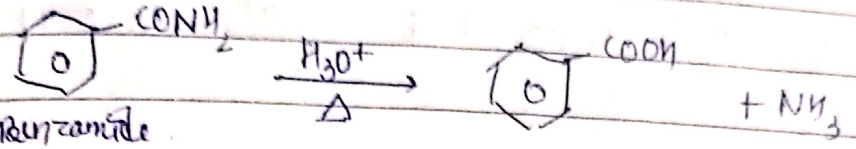
- $RCH_2OH \xrightarrow[2.\ H_3O^+]{1.\ alkaline\ KMnO_4} RCOOH$

- $CH_3(CH_2)_8CH_2OH \xrightarrow{CrO_3-H_2SO_4} CH_3(CH_2)_8COOH$

② By complete hydrolysis of nitriles & amides.

$$R-C\equiv N + H_2O \xrightarrow{H^+} \underset{\text{amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[\Delta]{H^+} RCOOH$$

$$\underset{\text{ethanamide}}{CH_3CONH_2} \xrightarrow[\Delta]{H_3O^+} CH_3COOH + NH_3$$



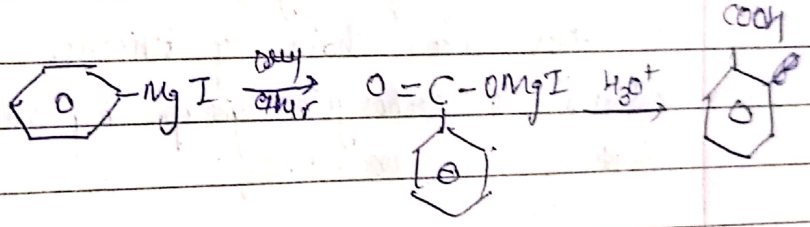
Benzamide

③ From Grignard Reagent.

$$O=C=O + R-MgX \xrightarrow[\text{ether}]{\text{Dry}} O=C(R)-OMgX \xrightarrow{H_3O^+} RCOOH$$

carbon dioxide

$$O=C=O + C_2H_5-MgBr \xrightarrow[\text{ether}]{\text{Dry}} O=C(C_2H_5)-OMgBr \xrightarrow{H_3O^+} C_2H_5COOH$$

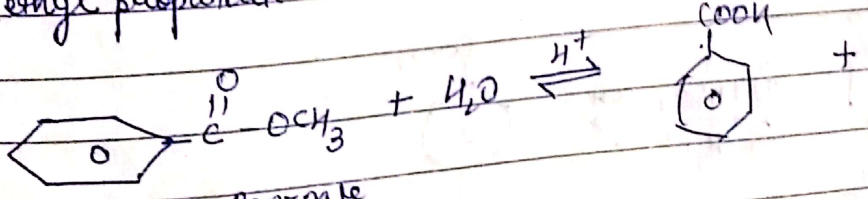


④ From esters.

$$\underset{\text{OH}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OH + R'-OH$$

$$C_2H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O \overset{H^+}{\rightleftharpoons} C_2H_5-COOH + C_2H_5OH$$

ethyl propanoate



methyl Benzoate

(5) From Acyl halides

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2O \longrightarrow RCOOH + HCl$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + H_2O \longrightarrow C_6H_5COOH + HCl$$

OR

$$RCOCl \xrightarrow[H_2O]{OH^-} RCOO^- + Cl \xrightarrow{H_3O^+} RCOOH$$

(6) From Anhydrides.

$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' + H_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$$

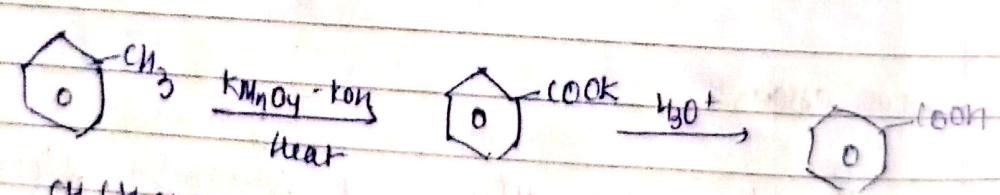
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \longrightarrow CH_3COOH + CH_3COOH$$

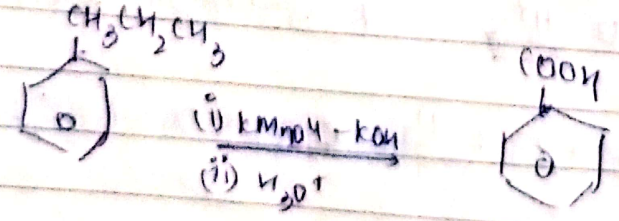
OR

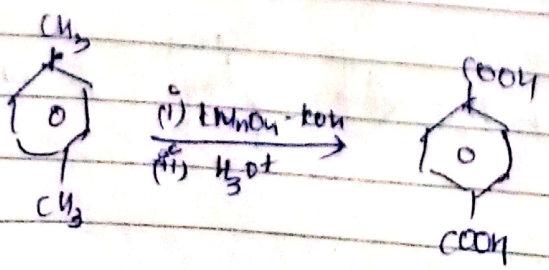
$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5COOH$$

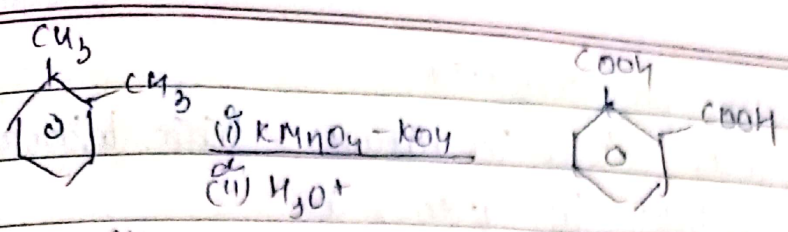
(7) From oxidation of alkylbenzenes.

The alkyl side chain of benzene ring can be easily oxidises to carboxylic group by alkaline $KMnO_4$ or chromic anhydride or conc. HNO_3.

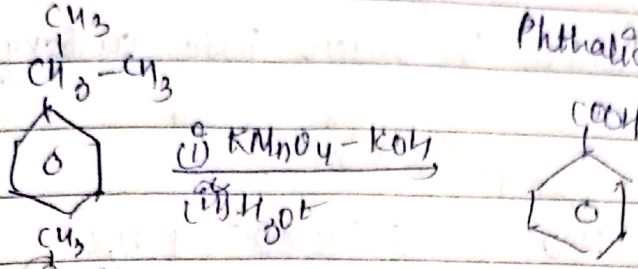


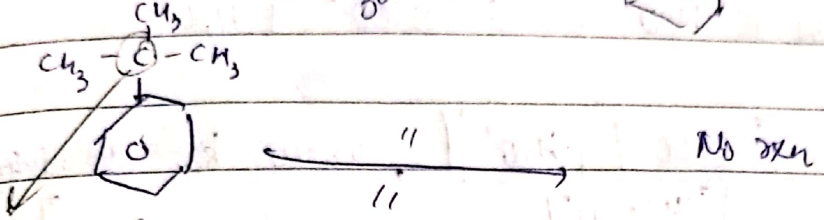






Phthalic acid





because this carbon don't have any hydrogen.

* Physical properties of carboxylic acid.

• Solubility:

- Among aliphatic acids, the first four members are very soluble in water because of formation of hydrogen bonding with water molecule.
- The solubility goes on decreasing with increase in alkyl chain, because the hydrophobic alkyl group increases & tendency to form hydrogen bond decreases.
- All these carboxylic acids are soluble in organic solvent like alcohol, ether & benzene etc.

• Boiling point:

- Carboxylic acids have highest b.pt than corresponding alcohol of comparative molecular masses because they form dimers due to double hydrogen bonding as well as -OH in acids is more polar & so H-bonding is more stronger.
- While alcohol do not form such double hydrogen bonding

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Chemical properties of -COOH acid

- Carboxylic acids are acidic in nature. Acidic behaviour is due to production of H_3O^+ in aqueous soln
- Carboxylic acids ionise in water into carboxylate ion & hydrogen ion.

pure liquid concentration = 1 mole

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

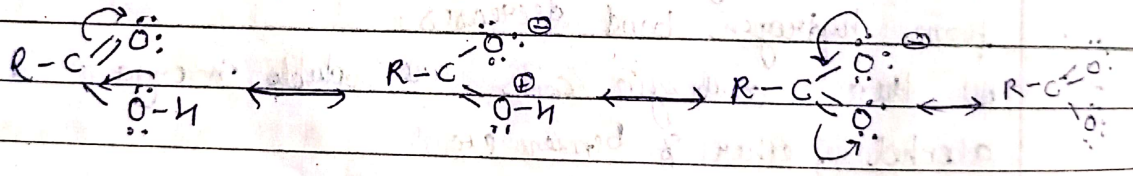
$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$, where K_a = dissociation constant of acid

⇒ Larger the value of 'K_a' more stronger is the acid

- For acids $pK_a = -\log K_a$
⇒ So smaller the value of 'pK_a', more stronger is the acid

$$\text{Acid strength} \propto K_a \propto \frac{1}{pK_a}$$

- Carboxylic acids are acidic in nature because it exist in two resonating forms



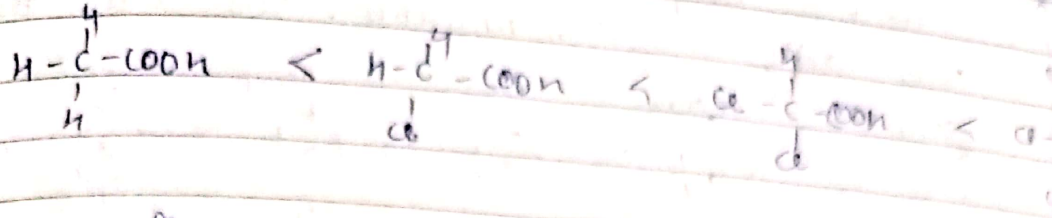
- Among aliphatic carboxylic acids, the size of alkyl group increases, the acidic strength decreases.

$HCOOH > CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

- Electron releasing groups like alkyl group decreases the acidic strength due to its +I effect

- e^- withdrawing group like $-NO_2$, $-CN$, $-F$ increase the acidic strength of carboxylic acid due to -I effect

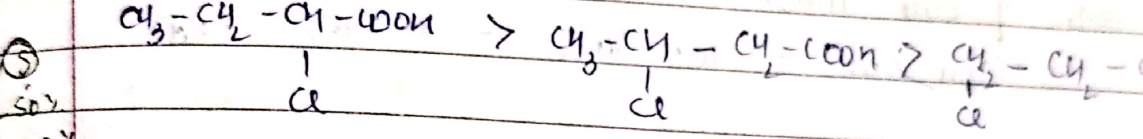
- Larger the no. of halogen atom, more is -I effect, so more stronger is the acid



- More is the electronegativity of halogen, more is -I effect & more is acidic strength.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

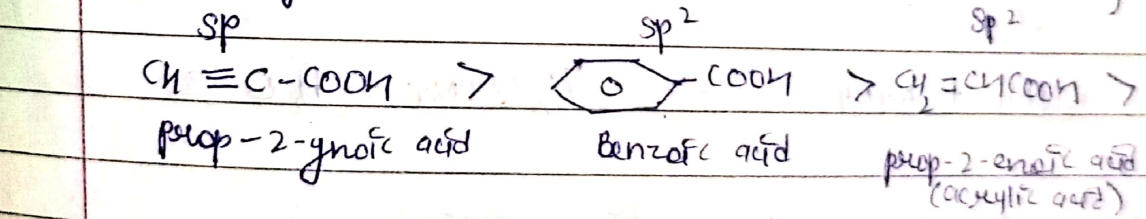
- As the distance of halogen from carboxylic acid increases, -I effect decreases so acidic strength of acid also decreases



(5) sp - 50%, sp^2 - 33%, sp^3 - 25%

- sp hybridised carbon is more electronegative than sp^2 hybridised carbon atom which is more electronegative than sp^3 hybridised

- More is the electronegativity of α-carbon, more is electron withdrawing nature & so more is acidic strength



prop-2-ynoic acid | Benzoic acid | prop-2-enoic acid (acrylic acid) | ethanoic acid

Benzoic acid is stronger acid than acrylic acid because benzoate ion is more resonance stabilised due to dispersal of -ve charge on benzene ring.

Effect of Electron withdrawing group [E.W.G]

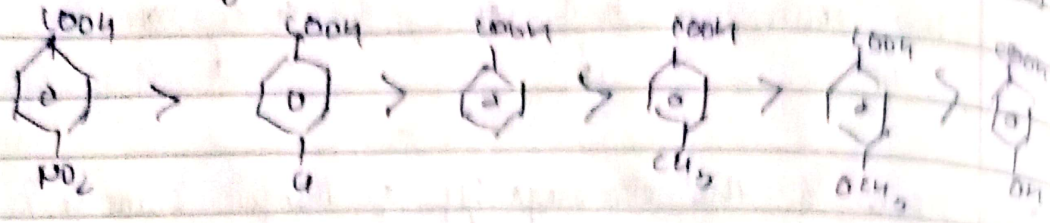
E.W.G disperse the -ve charge of carboxylate ion to stabilize thus increase acidic strength

$C_6H_5 < I < Br < Cl < F < CN < NO_2 < CF_3$

order of E.W.G

Effect of e⁻ releasing groups

e⁻ releasing groups increase the electron carboxylate ion & thus make it more unstable. Thus acidic decreases



Decreasing order of acidic strength

Rxn showing acidic behaviour of carboxylic acids

1) Action of Blue litmus.

-COOH acid + Blue litmus ⟶ turns red

2) Rxn with Active metals:

$2CH_3COOH + 2Na \longrightarrow 2CH_3-COONa + H_2 \uparrow$

$2CH_3COOH + 2Zn \longrightarrow 2CH_3-COO)_2Zn + H_2 \uparrow$

3) Rxn with Alkalies.

Carboxylic acids neutralise alkalies & forms salt & water

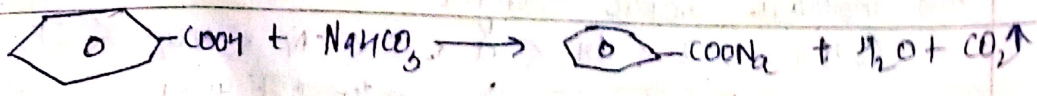
$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

4) Action with carbonates & Bicarbonates.

Carboxylic acids react with metal carbonates & metal bicarbonates & form salt & evolve CO_2 gas.

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

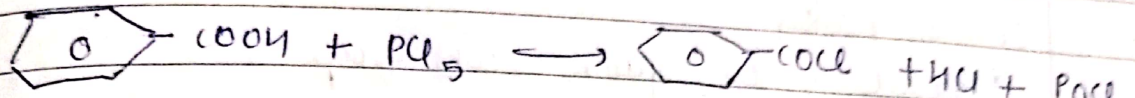
$2.\ CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 \uparrow + H_2O$



NOTE: The CO_2 gas is evolved with brisk effervescence so these rxns are used to distinguish phenols & carboxylic acids. Phenols do not react with metal carbonates & metal hydrogen carbonates.

* Reactions due to $-OH$ groups.

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



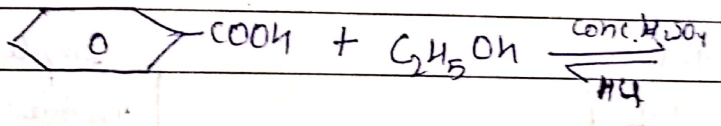
$3\,RCOOH + PCl_3 \longrightarrow 3\,RCOCl + H_3PO_3$

$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$

* Esterification

Carboxylic acids on heating with alcohol in the presence of conc. H_2SO_4 form esters.

$R-COOH + R'OH \underset{\text{or } HCl}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} RCOOR' + H_2O$

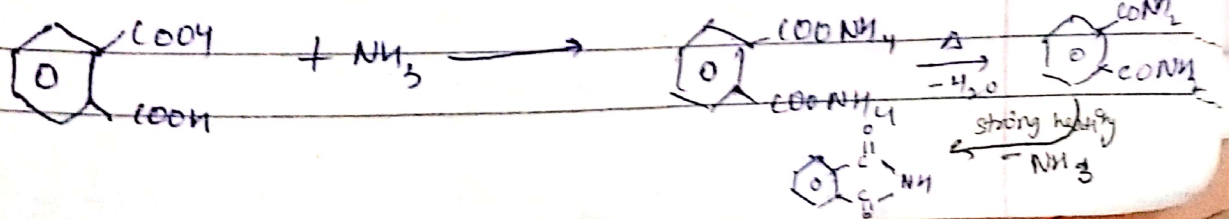


The rxn can be shift in forward dirn, by distilling water as soon as it is formed.

* Rxn with Ammonia.

$R-COOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow[-H_2O]{\Delta} RCONH_2$

$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$



* Formation of anhydride

P_2O_5 act as dehydrating agent

$$R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[\Delta]{P_2O_5} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' + H_2O$$

$$CH_3-COOH + CH_3COOH \xrightarrow[\Delta]{P_2O_5} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

* Decarboxylation

Removal of CO_2 from $-COOH$ group

$$CH_3-\overset{O}{\overset{\|}{C}}-ONa + NaOH \xrightarrow[\text{Heat}]{CaO} CH_4 + Na_2CO_3$$

(Soda lime)

Ratio $\Rightarrow$ 3 : 1

$$C_2H_5COONa \xrightarrow[\text{Heat}]{NaOH \& CaO} C_2H_6 + Na_2CO_3$$

Two types of reduction

Partial Reduction

[In the presence of $LiAlH_4$]

$$R-COOH + 4[H] \xrightarrow{LiAlH_4} RCH_2OH$$

$$C_2H_5COOH + 4[H] \xrightarrow{LiAlH_4} C_2H_5CH_2OH$$

Complete Reduction

[In the presence of $6HI$]

$$R-COOH + 6HI \xrightarrow{\text{Red Phosphorus}} R-CH_3 + 3I_2 + 2H_2O$$

$$C_2H_5COOH + 6HI \xrightarrow{\text{Red Phos.}} C_2H_5-CH_3 + 2H_2O$$

* HVZ Rxn [Hell Volhard zelinsky Rxn]

Carboxylic acid reacts with chlorine & bromine in presence of small phosphorus to give a compound in which α-hydrogen is replaced by halogen atoms.

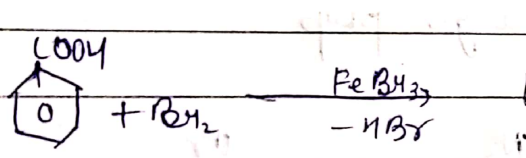
$$R-CH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2 / \text{Red Phosphorus}} R-\underset{X}{CH}-COOH$$

α-halocarboxylic acid

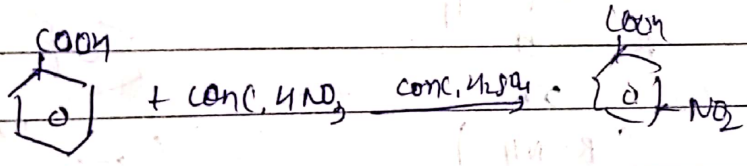
$$CH_3CH_2COOH \xrightarrow[(ii)\ "]{(i)\ Cl_2/\Delta} CH_3-\underset{Cl}{CH}-COOH$$

* Electrophilic substitution Rxn: -COOH group is a deactivating & meta directing group.

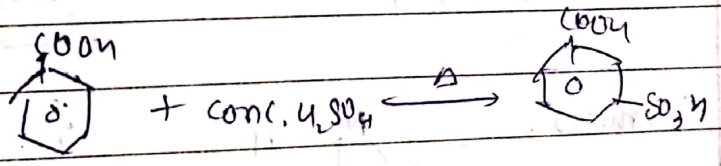
- Halogenation:



- Nitration:



- Sulphonation:



NOTE: Benzoic acid do not give Friedal Crafts rxn because carboxyl group is deactivating group.