ABC-4 (Carboxylic acid & Carbonyl compounds)

(A) CARBOXYLIC ACID

> Compounds containing the carboxyl group (–COOH) are distinctly acidic and called carboxylic acid.

Compound	Common name	IUPAC name	Occurrence
НСООН	Formic acid	Methanoic acid	Ants, bees & other stinging insects.
CH₃COOH	Acetic acid	Ethanoic acid	Grapes, Vinegar & pickle
CH3-CH2-COOH	Propionic acid	Propanoic acid	Animal fats, vegetables fats (coconut oil.)
CH ₃ –(CH ₂) ₂ –COOH	Butyric acid	Butanoic acid	Rancid butter
соон І соон	Oxalic acid	Ethanedioic acid	Kidney stone [Ca(C ₂ O ₄)], Cabbage
COOH CH2 COOH	Malonic acid	Propanedioic acid	Plants (Leaves of lucerne)
СН ₂ –СООН I CH ₂ –СООН	Succinic acid	Butanedioic acid	Amber, Lignite and many plants
Соон	Benzoic acid	Benzene carboxylic acid	Cranberries, fruit juice, soft drink, plum

Preparation of carboxylic acid (3-Methods)



HYDROCARBON



Chemical reactions of carboxylic acid [5-Reactions]



HYDROCARBON

	$\begin{array}{c} O \\ H \\ R-C-OH \end{array} \xrightarrow{R'OH, H^{*}} R-C-OR' + H_{2}O \\ Carboxylic acid reacts with excess alcohol in the presence of an acid catalyst produce ester. This reaction is called fisher esterification reaction. \\ \end{array}$	$\begin{array}{c} & & & \\ & & & \\ & & & \\ (i) & & CH_{2}-C-OH + C_{2}H_{5}OH \\ (i) & & CH_{3} & & \\ & & \\ & & \\ & & \\ CH_{3}-CH-CH_{2}-C-OC_{2}H_{5} + H_{2}O \\ & & \\ & & \\ & & \\ & CH_{3} & \\ & & \\ $
3	 Hunsdiecker reaction: (i) A carboxylic acid can be decarboxylated if a heavy metal salt of the carboxylic acid is heated with bromine. (ii) The product is an alkyl halide with one less carbon than the starting carboxylic acid. (iii) The heavy metal can be silver ion or mercuric ion. R-COOH (i) Ag₂O (i) Br₂, ∆ R-Br+CO₂+AgBr(Precipitate) 	$(i) CH_{3}-CH_{2}-CH_{2}-C-OH \xrightarrow{(i) Ag_{2}O} CH_{3}-CH_{2}-CH_{2}-Br$ $(i) CH_{3}-CH_{2}-CH_{2}-C-OH \xrightarrow{(i) Ag_{2}O} + CO_{2} + AgBr$ $(ii) Ph-CH_{2}-CH_{2}-C-OH \xrightarrow{(i) Ag_{2}O} + CO_{2} + AgBr$ $(iii) Ph-CH_{2}-CH_{2}-CH_{2}-C-OH \xrightarrow{(i) Ag_{2}O} + CO_{2} + AgBr$
4	Sodalime decarboxylation: $R - C - OH$ $\xrightarrow{NaOH + CaO} A$ $R - H + CO_2$ (i) Sodalime: NaOH + CaO (ii) Decarboxylation simply means removal of CO ₂ . Kolbe's electrolysis: Electrolysis	$(i)CH_{3}-CH_{2}-C-OH \xrightarrow{NaOH+CaO} CH_{3}-CH_{3}+CO_{2}$ $(ii) \xrightarrow{COOH} \xrightarrow{NaOH+CaO} + CO_{2}$ $(iii)Ph - CH_{2} - COOH \xrightarrow{NaOH+CaO} Ph - CH_{3} + CO_{2}$ $(i) 2CH_{3}-COOK + 2H_{2}O \xrightarrow{Electrolysis} OH - CH_{3} + CO_{2}$
	$2\text{RCOOK} + 2\text{HOH} \xrightarrow{\text{Leconorysis}}$ R-R + 2CO ₂ + H ₂ + 2KOH If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n–1) carbon atoms.	$CH_{3}-CH_{3} + 2CO_{2} + H_{2} + 2KOH$ $CH_{2}-COOK \qquad CH_{2}$ $(ii) CH_{2}-COOK_{+2H_{2}O} \xrightarrow{Electrolysis} CH_{2} + 2CO_{2}+H_{2} + 2KOH$ $(iii) 2CH_{3}-CH_{2}-COOK + 2H_{2}O \xrightarrow{Electrolysis} CH_{3}-CH_{2}-CH_{3} + 2CO_{2} + H_{2} + 2KOH$

Lab test of carboxylic acid [3-Tests]

1	Sodium bicarbonate (NaHCO ₃) test :	
	All carboxylic acids & sulphonic acids give.	(i) Ph–COOH + NaHCO3 → PhCOONa + H2CO3
	R -COOH + NaHCO ₃ \longrightarrow R -COONa + H ₂ CO ₃	H₂O + CO₂↑

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	H₂O + CO₂↑	(ii)CH ₃ –SO ₃ H + NaHCO ₃ → CH ₃ SO ₃ Na + H ₂ CO ₃
	R–SO ₃ H + NaHCO ₃ \longrightarrow R–SO ₃ Na + H ₂ CO ₃ ↓ $H_2O + CO_2^{\uparrow}$	H₂O + CO₂↑
	Exception :	
	Picric acid gives NaHCO ₃ test.	
	Note : Phenol does not give NaHCO3 test.	
2	Litmus test: Acid converts blue litmus into red litmus.	
3	Esterification of acid: When carboxylic acid reacts	$H^* \rightarrow RCOOR' + H_2O$
	with alcohol then ester forms, which are sweet (fruity)	(sweet smelling liquid)
	smelling liquids.	

(B) CARBONYL COMPOUNDS Preparation of carbonyl compounds (4-Methods)





Chemical reactions of carbonyl compounds (3-Reactions)

1.	Cannizzaro reaction:	
	Simple Cannizzaro reaction Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.	$H \rightarrow C=O + Conc. KOH \rightarrow H - C \rightarrow OK$ H - C - OH + H - C - OK Formaldehyde Methanol Potassium formate
	Crossed Cannizzaro reaction On using two types of carbonyl compounds not having α -hydrogen atom, acid salt will be corresponding to that aldehyde or ketone which is less sterically crowded and another will give alcohol.	$\begin{array}{c} H \\ H \\ H \\ - C \\ (A) \end{array} + C_0H_0 \\ (B) \\ \hline O^- \end{array} + C_0H_0CH_2OH \\ \hline O^- + C_0H_0CH_2OH \\ \hline O^- \\ \hline O^- \end{array}$ $\begin{array}{c} H \\ - C_0H_0CH_2OH \\ \hline O^- \\ O^- \end{array}$ $\begin{array}{c} H \\ - C_0H_0CH_2OH \\ \hline O^- \\ O^- \end{array}$
2.	Aldol condensation (or aldol reaction): Aldehydes and ketones with atleast one α- hydrogen undergo a reaction in the presence of dilute alkali as catalyst.	$\begin{array}{c} H \\ H \\ CH_{3}-C=CH-C-H \\ H \\ CH_{3}-C=CH-C-H \\ H \\ CH_{3}-C=CH-C-H \\ H \\ CH_{3}-C=CH-C-H \\ H \\ CH_{3}-C=CH-C-CH_{3} \\ H \\ CH_{3}-C=CH-C-C-CH_{3} \\ CH_{3}-C=CH-C-C-C-CH_{3} \\ CH_{3}-C=CH-C-C-C-CH_{3} \\ CH_{3}-C=CH-C-C-C-CH_{3} \\ CH_{3}-C=CH-C-C-C-CH_{3} \\ CH_{3}-C=CH-C-C-C-CH_{3} \\ CH_{3}-C=CH-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-$
	Prediction of reactant	$ \begin{array}{c} \searrow C = O + CH_3 - C - H \\ \bigcup \\ O \\ (ii) \Delta \end{array} \xrightarrow{\beta + C + C} H \\ (i) dil. NaOH \\ (ii) \Delta \end{array} \xrightarrow{\beta + C + C} H \\ O \\ O$
3.	Reaction with NH_2OH	$\overset{CH_{3}}{H}C=O \xrightarrow{H} H^{2}OH \xrightarrow{A} H^{2}C=N \xrightarrow{OH} $
	$\begin{array}{c} \searrow C = \underbrace{IO + H_2} N - OH \\ Aldehyde / Ketone \end{array} \xrightarrow{\Delta} -H_2O \end{array} \xrightarrow{Aldehyde \rightarrow Aldoxime} Ketone \rightarrow Ketoxime \end{array}$	$\xrightarrow{\text{PhCo}}_{X=\frac{\text{PhCo}}{\text{HCO}}} \xrightarrow{\text{Y=PhCH}} (X) \xrightarrow{\Delta}_{-\text{CaCO}_3} (Y) \xrightarrow{\text{NH}_2\text{OH}} \stackrel{\text{Ph}}{} C=N \xrightarrow{\text{OH}}$

Test for carbonyl compounds

1.	2,4-DNP1/42,4-Dinitrophenyl hydrazine+1/2Test :	H^{CH_3} C=O + H ₂ N-NH - O - NO ₂
	Carbonyl compouds (all aldehydes and ketones) give yellow–orange precipitate with 2,4-DNP. It is also knwon as Brady's reagent . General Reactions	\dot{NO}_2 2, 4-DNP \downarrow CH_3 C=N-NH- O -NO ₂ H O_2 (yellow-orange precipitate of Hydrazone)

	$C=O + H_2N-NH - O - NO_2$	CH_3 C=O + H_N-NH \rightarrow O - NO			
	NOa	CH ₃			
	2, 4-DNP	2. 4-DNP			
	Ţ	_,			
	$C = N - NH \rightarrow O$				
	NO_2 (yellow–orange precipitate of Hydrazone)	NO ₂			
	Test for Alde	ehydes			
1.	I olien's reagent [AgNO ₃ + NH ₄ OH or $\{A_{\alpha}(NH_{2})_{2}\}_{2}$ OH ₂] ·	AgNO₄+NH₄OH			
	Tollen's Reagent gives silver mirror or Black	$CH_3-CH=O \qquad \qquad$			
	precipitate with aldehydes.				
	General reactions				
		$PhCHO \longrightarrow Ph-C-O^{\circ} + Ag \downarrow$			
	$R-CH=O \longrightarrow R-C-O^{\circ} + Ag \downarrow$				
	Note: HCOOH also gives this test.	HCOOH \longrightarrow H-C-O ^{\vee} + Ag \downarrow silver mirror			
2.	Fehling or Benedict test (Cu ₂₊ in basic				
	medium) %	Θ			
	Aliphatic aldehyde gives red precipitate of Cu_2O with Febling/Benedict solution. Cu ₂ , reduced into	$CH_{3}-CH=O+Cu^{2+} \xrightarrow{OH} CH_{3}-\overrightarrow{C}-O^{\Theta}+Cu_{2}O\downarrow$			
	Cu₁₊and aldehyde oxidised into acid salt.	red precipitate			
	General reactions	e O			
		$C_2H_5-CH=O+Cu^{2+} \xrightarrow{OH} C_2H_5-C-O^{\Theta}+Cu_2O\downarrow$			
	red precipitate	red precipitate			
	* Aromatic aldehydes do not give this test.				
	aldehydes only.				
	Iodoform Test				
	Reagents : I_2 + NaOH or NaOI (Where R = H,				
	Acetaldehyde, all methyl ketones & ethyl alcohol	CH –C–CH – ^{I₂+NaOH} →CH –C–ONa + CHL ↓			
	give lodoform test.	$ _{H^{-}}$ yellow ppt.			
	Q Q	¢ CH_COOH			
	R–C–CH₃ – ^{I₂+NaOH} R–C–ONa + CHI₃ ↓				
	J _H ⁻ yellow ppt.				
	R-COOH				
	(Acid of 1 carbon less)	H H H H H H H H H H			
		сн_соон			
	$R - C - C - C R + C H_3 \downarrow$ $ _{H}, \qquad \text{yellow ppt.}$				











(D) (CH₃)₃COONa and HCOO- Na+.





	Answers								
1.	(C)	2.	(B)	3.	(C)	4.	(D)	5.	(/
6.	(C)	7.	(D)	8.	(C)	9.	(C)	10.	((
11.	(B)	12.	(B)	13.	(C)	14.	(C)	15.	(
16.	(B)	17.	(B)	18.	(B)	19.	(C)	20.	(
21.	(A)	22.	(C)	23.	(A)	24.	(A)	25.	(
26.	(A)	27.	(A)	28.	(D)	29.	(C)	30.	(/
31.	(D)	32.	(A)	33.	(B)	34.	(D)	35.	(
36.	(C)	37.	(C)	38.	(A)	39.	(C)	40.	(
41.	(D)	42.	(C)	43.	(C)	44.	(C)		