FREE NOTES · NCERT + JEE/NEET LEVEL

Aldehydes, Ketones & Carboxylic Acids

Carbonyl group, preparation, nucleophilic addition, oxidation and reduction, aldol and Cannizzaro reactions, tests, carboxylic acids: preparation, acidity and reactions, with all named reactions in one table.

01 Carbonyl group & naming
02 Preparation of aldehydes & ketones
03 Nucleophilic addition
04 Reduction, oxidation & tests
05 Reactions due to α-hydrogen
06 Carboxylic acids: preparation
07 Acidity of carboxylic acids
08 Reactions of carboxylic acids
09 All named reactions in one place
10 JEE Extra + Tricks
11 Solved questions, mistakes & practice
12 Quick revision

01 Carbonyl group & naming

C=O carbon is **sp²**, trigonal planar (120°). The bond is polar: C δ+ (attacked by nucleophiles), O δ− (attacked by electrophiles).

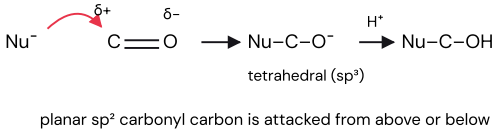
Formula	Common	IUPAC
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3COCH_3	Acetone (dimethyl ketone)	Propanone
C_6H_5CHO	Benzaldehyde	Benzenecarbaldehyde
$C_6H_5COCH_3$	Acetophenone	1-Phenylethanone
HCOOH / CH_3COOH	Formic / acetic acid	Methanoic / ethanoic acid

Boiling points: alkane < ether < aldehyde/ketone (dipole) < alcohol < carboxylic acid (dimer by H-bonding).

02 Preparation of aldehydes & ketones

Method	Gives
Oxidation of 1° alcohol (PCC) / 2° alcohol (CrO_3, $K_2Cr_2O_7$)	Aldehyde / ketone
Dehydrogenation (Cu, 573 K)	Aldehyde / ketone
Ozonolysis of alkenes (O_3, then Zn/H_2O)	Aldehydes/ketones
Hydration of alkynes ($HgSO_4$, H_2SO_4)	Ethyne → ethanal; others → ketones
Rosenmund: RCOCl + H_2, $Pd/BaSO_4$	Aldehyde
Stephen: RCN + $SnCl_2$/HCl, then H_3O^+	Aldehyde
RCN + DIBAL-H, then H_2O	Aldehyde (also from esters)
Etard: toluene + CrO_2Cl_2	Benzaldehyde
Toluene + CrO_3/$(CH_3CO)_2O$, then H_3O^+	Benzaldehyde
Gatterman-Koch: benzene + CO + HCl, $AlCl_3$/CuCl	Benzaldehyde
2RMgX/R_2Cd + R′COCl	Ketone
RCN + R′MgX, then H_3O^+	Ketone
Friedel-Crafts acylation: ArH + RCOCl/$AlCl_3$	Aryl ketone

03 Nucleophilic addition



Nucleophilic addition to C=O

Aldehydes are more reactive than ketones: (1) less crowding (steric), (2) ketone's two alkyl groups reduce the δ+ on C (electronic). Aromatic carbonyls are less reactive (resonance).

Reagent	Product
HCN (base catalysed)	Cyanohydrin
$NaHSO_3$	Bisulphite adduct (crystalline; used to separate/purify)
RMgX, then H_3O^+	Alcohols
R′OH / dry HCl	Hemiacetal → acetal; ketone + ethylene glycol → ketal
NH_3 derivatives ($H_2N–Z$)	C=N–Z (addition-elimination, pH ~3.5)

$H_2N–Z$	Product
NH_2OH	Oxime
NH_2NH_2	Hydrazone
$C_6H_5NHNH_2$	Phenylhydrazone
2,4-DNP	2,4-Dinitrophenylhydrazone (orange/yellow ppt: test for C=O)
$NH_2NHCONH_2$	Semicarbazone

04 Reduction, oxidation & tests

- $NaBH_4$/$LiAlH_4$ or H_2/Ni ⇒ alcohols.
- **Clemmensen:** Zn-Hg/conc. HCl ⇒ C=O → CH_2.
- **Wolff-Kishner:** NH_2NH_2, then KOH/ethylene glycol, heat ⇒ CH_2.

Test	Aldehyde	Ketone
Tollens' (ammoniacal $AgNO_3$)	Silver mirror	No reaction
Fehling's (Cu^{2+} tartrate)	Red-brown Cu_2O ppt (aliphatic only; benzaldehyde doesn't)	No reaction
Iodoform (NaOI)	Yellow CHI_3 for CH_3CO- group (ethanal, methyl ketones) and $CH_3CH(OH)-$	

Ketones are oxidised only by strong oxidants, breaking C–C bonds (Popoff's rule: the C=O stays with the smaller alkyl group).

05 Reactions due to α-hydrogen

α-H is **acidic** because the carbanion (enolate) is stabilised by resonance with C=O.

ALDOL CONDENSATION

Aldehydes/ketones **with α-H** + dilute NaOH ⇒ β-hydroxy aldehyde (aldol) or β-hydroxy ketone (ketol), which on heating loses water ⇒ α,β-unsaturated carbonyl. $2CH_3CHO$ → $CH_3CH(OH)CH_2CHO$ → $CH_3CH{=}CHCHO$ (but-2-enal). Two different carbonyls ⇒ **cross aldol** (4 products).

CANNIZZARO REACTION

Aldehydes **without α-H** (HCHO, C_6H_5CHO) + conc. NaOH ⇒ disproportionation: one molecule is oxidised to acid salt, another reduced to alcohol. 2HCHO → CH_3OH + HCOONa.

Other ring reactions: –CHO and –COOH are deactivating, **meta directing** (benzaldehyde → m-nitrobenzaldehyde).

06 Carboxylic acids: preparation

- Oxidation of 1° alcohols / aldehydes ($KMnO_4$, $K_2Cr_2O_7$).
- Alkylbenzene + $KMnO_4$ (any length side chain with benzylic H) ⇒ benzoic acid.
- Hydrolysis of nitriles (RCN + H_3O^+) and amides.
- Grignard + CO_2 (dry ice), then H_3O^+ ⇒ RCOOH (one C more).
- Hydrolysis of acyl halides, anhydrides, esters.

07 Acidity of carboxylic acids

RCOOH is more acidic than alcohols and phenols because the **carboxylate ion** has two equivalent resonance structures (charge on two O). They react with $NaHCO_3$ releasing CO_2 (test).

- Electron-withdrawing groups increase acidity: CF_3COOH > CCl_3COOH > $CHCl_2COOH$ > $ClCH_2COOH$ > CH_3COOH.
- Closer the EWG, stronger the effect: 2-chlorobutanoic > 3-chloro > 4-chloro.
- F > Cl > Br > I (electronegativity) for halo acids.
- HCOOH > C_6H_5COOH > CH_3COOH. Electron-releasing groups decrease acidity.
- Nitro-benzoic acids > benzoic acid.

08 Reactions of carboxylic acids

Reagent	Product
Metals, NaOH, $NaHCO_3$	Salts (+ H_2 or CO_2)
P_2O_5 / heat	Anhydride
R'OH / H^+	Ester (esterification)
PCl_5, PCl_3, $SOCl_2$	Acyl chloride
NH_3, then heat	Amide
$LiAlH_4$ (or B_2H_6)	1° alcohol ($NaBH_4$ doesn't reduce –COOH)
Soda lime (NaOH + CaO), heat	Alkane, one C less (decarboxylation)
Kolbe electrolysis of RCOONa	R–R
HVZ: X_2 / red P	α-halo acid (needs α-H)

09 All named reactions in one place

Name	What it does
Rosenmund	RCOCl → RCHO (H_2, Pd/$BaSO_4$)
Stephen	RCN → RCHO ($SnCl_2$/HCl)
Etard	Toluene → benzaldehyde (CrO_2Cl_2)
Gatterman-Koch	Benzene → benzaldehyde (CO, HCl)
Clemmensen / Wolff-Kishner	C=O → CH_2 (acid / base)
Aldol	α-H carbonyl + dil. base → β-hydroxy carbonyl
Cannizzaro	No α-H aldehyde + conc. base → alcohol + acid salt
HVZ	RCH_2COOH → RCHXCOOH
Decarboxylation	RCOONa + soda lime → RH

10 JEE Extra + Tricks

JEE LEVEL

- Reactivity to nucleophilic addition: HCHO > CH_3CHO > ketones (steric + electronic). Aromatic aldehydes less reactive than aliphatic.
- Aldol: needs α-H (dilute NaOH). Cannizzaro: no α-H (conc. NaOH, HCHO, PhCHO) ⇒ alcohol + acid salt. Crossed Cannizzaro: HCHO oxidised.
- Tests: Tollens' (silver mirror) and Fehling's (red Cu_2O) for aldehydes (aromatic aldehydes don't give Fehling's); iodoform test for CH_3CO- and $CH_3CH(OH)-$.
- Acidity of acids: electron-withdrawing groups increase acidity: CF_3COOH > CCl_3COOH > $ClCH_2COOH$ > HCOOH > CH_3COOH.
- HVZ reaction: α-halogenation of acids (X_2/red P). Clemmensen (Zn-Hg/HCl) and Wolff–Kishner (NH_2NH_2/KOH) reduce C=O to CH_2.
- Rosenmund (acid chloride → aldehyde, $Pd/BaSO_4$), Stephen (nitrile → aldehyde), Etard (toluene → benzaldehyde).

11 Solved questions, mistakes & practice

Q1. Distinguish ethanal and propanone.

Tollens': ethanal gives silver mirror, propanone doesn't. (Both give iodoform.)

Q2. Product of benzaldehyde + conc. NaOH?

Cannizzaro: benzyl alcohol + sodium benzoate.

Q3. Why is chloroacetic acid stronger than acetic acid?

Cl (–I) pulls electrons and stabilises the carboxylate ion.

- Applying Cannizzaro to CH_3CHO (it has α-H, it gives aldol).
- Saying benzaldehyde gives Fehling's test.
- Thinking $NaBH_4$ reduces –COOH.
- Calling –CHO ortho/para directing.

1. Reagent for the test of any C=O group?
2. Which is more reactive to HCN: HCHO or CH_3COCH_3?
3. Product of CH_3MgBr + CO_2 then H_3O^+?
4. Product of CH_3COONa + soda lime?

ANSWERS

1) 2,4-DNP · 2) HCHO · 3) CH_3COOH · 4) CH_4

12 Quick revision: 5 minutes before the exam

CARBONYL

- Aldehyde > ketone in reactivity.
- Nucleophilic addition.
- 2,4-DNP: test for C=O.

TESTS

- Tollens': aldehydes (mirror).
- Fehling's: aliphatic aldehydes.
- Iodoform: $CH_3CO–$.

A-H

- With α-H + dil. base ⇒ aldol.
- No α-H + conc. base ⇒ Cannizzaro.
- HVZ ⇒ α-halo acid.

ACIDS

- $NaHCO_3$ ⇒ CO_2 (test).
- EWG ↑ acidity; F > Cl.
- Soda lime ⇒ one C less.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.