Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (2026-27 / New NCERT)

Chapter 8: Aldehydes, Ketones and Carboxylic Acids

Class 12th Chemistry — Organic Chemistry — The Carbonyl Family

What you will master in this chapter

The carbonyl group $>$ **C**$=$**O** is the single most tested functional group in Class 12 organic chemistry. In this chapter you will (i) name aldehydes, ketones and carboxylic acids in both common and IUPAC systems; (ii) prepare them by nine industrial and laboratory routes; (iii) understand the planar, polar geometry that makes the carbonyl carbon electrophilic; (iv) work through every named reaction the syllabus tests — HCN, $NaHSO_3$, ammonia derivatives, alcohols, Grignard, $NaBH_4$/$LiAlH_4$, Clemmensen, Wolff-Kishner, Tollens, Fehling, Cannizzaro, Aldol, Cross-aldol, Hell-Volhard-Zelinsky and esterification — with mechanisms for the high-yield ones; and (v) handle the pKa-acidity arguments that JEE Main and NEET ask every single year.

Contents

1 The Carbonyl Group and Its Family

The carbonyl group $>$ **C**$=$**O** joins almost everything organic: fragrances, fabrics, plastics, medicines and the energy currency of living cells. When the carbonyl carbon is bonded to (at least one) hydrogen, the compound is an **aldehyde**; when it is bonded to two carbons, it is a **ketone**; and when it carries a hydroxyl group ($-OH$) as well, it is a **carboxylic acid**. Replace the $-OH$ of an acid with $-NH_2$, halogen, $-OR$ or $-OOCR$ and you get amides, acyl halides, esters and anhydrides — the so-called *acid derivatives*.

1.1 The Carbonyl Family Tree

General formulas of the carbonyl family

Aldehyde: $R-CHO$ (carbonyl carbon bears at least one H)
Ketone: $R-CO-R'$ (carbonyl carbon bears two C groups)
Carboxylic acid: $R-COOH$
Acyl halide: $R-COX$
Acid amide: $R-CONH_2$
Ester: $R-COOR'$
Acid anhydride: $R-CO-O-CO-R$

Where carbonyls meet you every day

Vanillin (vanilla), cinnamaldehyde (cinnamon) and salicylaldehyde (meadowsweet) are aldehydes that gift the kitchen and perfume industry their signature smells. Acetone is the nail-polish remover sitting in every cosmetic kit. Formaldehyde, as 40% formalin, preserves biological specimens. Vinegar is 6–10% aqueous ethanoic acid. Soaps and detergents are sodium and potassium salts of higher fatty acids (C_{12}–C_{18}).

1.2 Nomenclature of Aldehydes and Ketones

There are two parallel naming systems — the older **common names** (still used in industry and in mnemonics) and the modern **IUPAC** names that you must master for the exam.

Aldehydes:

- *Common name:* replace the ending "-ic acid" of the corresponding carboxylic acid with "-aldehyde". Acetic acid → acetaldehyde. Formic acid → formaldehyde.
- *IUPAC name:* replace the "-e" of the parent alkane by "-al". CH_3CHO = ethan**al**; HCHO = methan**al**.
- The aldehyde carbon is always C-1.
- When the $-CHO$ group is attached to a ring, the suffix is "-carbaldehyde" (e.g.

cyclohexane**carbaldehyde**).

Ketones:

- *Common name:* name the two alkyl/aryl groups bonded to C=O followed by the word “ketone”. $CH_3-CO-CH_3$ = dimethyl ketone (a.k.a. **acetone**); $C_6H_5-CO-CH_3$ = methyl phenyl ketone (a.k.a. **acetophenone**).
- *IUPAC name:* replace the “-e” of the parent alkane by “-one”. The longest chain containing C=O is numbered so that the carbonyl carbon receives the lowest locant. $CH_3COCH_2CH_3$ = butan-2-one.

Common vs IUPAC — four must-know examples

Structure	Common	IUPAC
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3COCH_3	Acetone	Propan-2-one
C_6H_5CHO	Benzaldehyde	Benzenecarbaldehyde

Spot the longest-chain trap

For ketones, the longest carbon chain need not pass through the carbonyl carbon trivially — but the chain you choose must *contain* the carbonyl carbon. Locant set must give C=O the lowest number. For $CH_3CH_2COCH_2CH(CH_3)_2$, the answer is **5-methylhexan-3-one**, not “4-methyl-something”.

1.3 Structure of the Carbonyl Group

The carbonyl carbon is sp^2 hybridised: it forms three σ bonds (to two substituents and to oxygen) lying in one plane with bond angles of $\approx 120°$, while the unhybridised p-orbital overlaps sideways with a p-orbital of oxygen to form a π-bond. The oxygen retains two lone pairs.

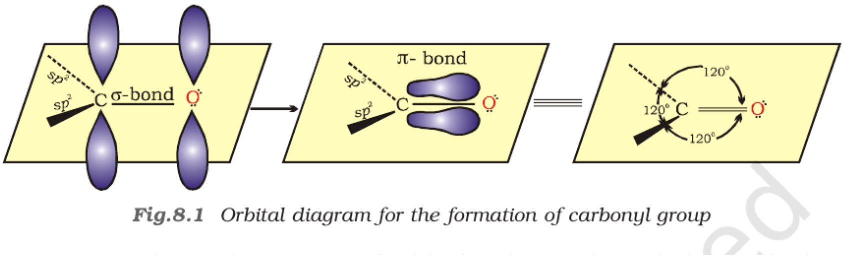


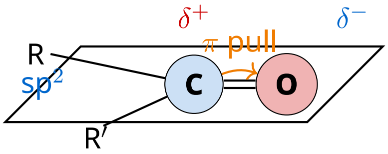
Fig. 8.1 (NCERT): Orbital diagram showing the formation of the carbonyl group — sp^2 planar geometry, one σ-bond and one π-bond between C and O.

Because oxygen is more electronegative than carbon ($\chi_O = 3.5$, $\chi_C = 2.5$), the π-electrons spend more time on oxygen. The C–O bond is therefore strongly polarised, with a partial positive charge (δ^+) on carbon and a partial negative charge (δ^-) on oxygen.

Carbonyl resonance and dipole

$$\underset{\text{(A) neutral}}{R_2C{=}O} \longleftrightarrow \underset{\text{(B) dipolar}}{R_2C^+{-}O^-}$$

$\mu(R_2C{=}O) \approx 2.3$ – 2.7 D, much larger than ethers (~ 1.2 D). The carbonyl carbon is therefore *electrophilic* (a Lewis acid), and oxygen is *nucleophilic* (a Lewis base).



The carbonyl: sp^2 trigonal planar at C, polar π-bond, δ^+ at C and δ^- at O.

The key takeaway

A carbonyl group is a **permanent dipole with a polarisable π cloud**. Every reaction in this chapter follows from two facts: (1) nucleophiles attack the δ^+ carbon; (2) electrophiles (H^+, Lewis acids) attack the δ^- oxygen.

Why aldehydes win on dipole moment

In aldehydes, an H sits on the carbonyl carbon. H is small and only weakly donating, so it cannot dilute the δ^+. In ketones, two alkyl groups push electron density toward the carbonyl carbon and *reduce* the dipole. Mnemonic: **"Aldehydes lack a defender"** — no alkyl group to shield the δ^+, so aldehyde dipole $>$ ketone dipole, and aldehyde reactivity $>$ ketone reactivity.

2 Preparation of Aldehydes and Ketones

This section organises the dozen preparations the NCERT covers into three groups: *(a)* routes that give either aldehydes or ketones (oxidation/dehydrogenation of alcohols, ozonolysis, hydration of alkynes), *(b)* aldehyde-specific routes (Rosenmund, Stephen, DIBAL, Etard, Gattermann-Koch, side-chain Cl_2 hydrolysis), and *(c)* ketone-specific routes (from acyl chloride with dialkylcadmium, Friedel-Crafts acylation, nitrile $+$ Grignard).

2.1 Common Routes: Oxidation, Ozonolysis, Hydration

1. Oxidation/dehydrogenation of alcohols. Primary alcohols give aldehydes (which are vulnerable to over-oxidation to acids unless removed), secondary alcohols give ketones (stable end-point).

$$R{-}CH_2OH \xrightarrow{[O]} R{-}CHO \xrightarrow{[O]} R{-}COOH \qquad R_2CH{-}OH \xrightarrow{[O]} R_2C{=}O$$

The mild reagent **PCC** (pyridinium chlorochromate, $C_5H_5N \cdot HCl \cdot CrO_3$) in CH_2Cl_2 *stops at the aldehyde*. Cu/573 K dehydrogenation is used industrially; tertiary alcohols cannot be oxidised this way (no α-H on C-1).

Two clean conversions

$$\mathrm{CH_3CH_2OH} \xrightarrow{Cu,\ 573\,K} \mathrm{CH_3CHO + H_2}$$

$$\mathrm{CH_3CH(OH)CH_3} \xrightarrow{Cu,\ 573\,K} \mathrm{CH_3COCH_3 + H_2}$$

2. Ozonolysis of alkenes. Reductive ozonolysis ($O_3/Zn,\ H_2O$) cleaves C=C to give two carbonyls.

$$\mathrm{R{-}CH{=}CH{-}R'} \xrightarrow{(i)\ O3\quad (ii)\ Zn/H2O} \mathrm{R{-}CHO + R'{-}CHO}$$

Disubstituted on both ends ⇒ two ketones. One end CH_2 ⇒ one is formaldehyde.

3. Hydration of alkynes (Markovnikov). Dilute H_2SO_4 with $HgSO_4$ adds water across $-C{\equiv}C-$ via an enol intermediate that tautomerises to a carbonyl.

$$\mathrm{HC{\equiv}CH} \xrightarrow{H2SO4,\ HgSO4} \mathrm{[CH_2{=}CHOH]} \rightarrow \mathrm{CH_3{-}CHO}$$

$$\mathrm{R{-}C{\equiv}CH} \xrightarrow{H2SO4,\ HgSO4} \mathrm{R{-}CO{-}CH_3} \quad \text{(Markovnikov)}$$

Acetaldehyde — the only "terminal alkyne → aldehyde" case

Only acetylene ($HC{\equiv}CH$) gives an aldehyde on Markovnikov hydration. Every other terminal alkyne ($R{-}C{\equiv}CH$) gives a methyl ketone. JEE love to test this exception.

2.2 Aldehyde-Specific Preparations

Rosenmund reduction — acyl chloride to aldehyde

$$\mathrm{R{-}COCl + H_2} \xrightarrow[quinoline\ +\ S]{Pd/BaSO4} \mathrm{R{-}CHO + HCl}$$

The Pd is *poisoned* with $BaSO_4$ and quinoline-S so that the aldehyde is *not* further reduced to alcohol.

Stephen reaction. An alkyl/aryl nitrile is reduced to an imine salt with $SnCl_{2/}HCl$, then hydrolysed.

$$\mathrm{R{-}C{\equiv}N} \xrightarrow{SnCl2/HCl} \mathrm{[R{-}CH{=}NH \cdot HCl]} \xrightarrow{H2O} \mathrm{R{-}CHO}$$

DIBAL-H reduction. Di*iso*butylaluminium hydride [$(iBu)_2AlH$] reduces both nitriles *and* esters to aldehydes (stops there because of the bulky H-donor):

$$R{-}C{\equiv}N \xrightarrow[(ii)\ H2O]{(i)\ AlH(iBu)2} R{-}CHO \qquad R{-}COOR' \xrightarrow[(ii)\ H2O]{(i)\ AlH(iBu)2} R{-}CHO$$

From hydrocarbons (aromatic aldehydes):

Etard reaction: chromyl chloride attacks the methyl group of toluene to give a chromium complex, hydrolysed to benzaldehyde.

$$C_6H_5CH_3 \xrightarrow[CS2]{CrO2Cl2} [\text{complex}] \xrightarrow{H3O+} C_6H_5CHO$$

Gattermann-Koch reaction: benzene with CO + HCl in presence of anhydrous $AlCl_3/CuCl$ gives benzaldehyde — a formylation.

$$C_6H_6 + CO + HCl \xrightarrow[CuCl]{anhyd.\ AlCl3} C_6H_5CHO$$

Side-chain chlorination + hydrolysis: $C_6H_5CH_3 \rightarrow C_6H_5CHCl_2$ (boiling Cl_2, light or heat) $\rightarrow C_6H_5CHO$ (aqueous base or acid).

> **Six paths to benzaldehyde — "REGT-OS"**
>
> **R**osenmund (from benzoyl chloride), **E**tard (from toluene + CrO_2Cl_2), **G**attermann-Koch (from benzene + CO/HCl), **T**oluene $+Cl_2$ hydrolysis, **O**xidation of benzyl alcohol, **S**tephen (from C_6H_5CN). REGT-OS will give you marks every year.

2.3 Ketone-Specific Preparations

1. Acyl chloride + dialkylcadmium. Grignard's RMgX is *too* reactive and converts acyl chlorides past the ketone all the way to tertiary alcohols. Cadmium reagents are tamer: they stop at the ketone.

$$2\ R{-}COCl + R'_2Cd \rightarrow 2\ R{-}CO{-}R' + CdCl_2$$

2. Friedel-Crafts acylation. Aromatic ketones in one step from arenes:

$$C_6H_6 + R{-}COCl \xrightarrow{anhyd.\ AlCl3} C_6H_5{-}CO{-}R + HCl$$

Works equally well with an anhydride $(RCO)_2O$ as the acylating reagent.

3. From nitriles via Grignard.

$$R{-}C{\equiv}N + R'{-}MgX \rightarrow R{-}C({=}NMgX){-}R' \xrightarrow{H3O+} R{-}CO{-}R' + NH_3$$

Why cadmium and not magnesium?

R_2Cd has weaker C–M polarity than RMgX (Cd has higher electronegativity than Mg, so the carbanion character is reduced). The kinetic product — the ketone — survives because the cadmium reagent is too gentle to attack it a second time.

Don't write Grignard $+$ acyl chloride $\rightarrow$ ketone

A common trap. RMgX *will* add twice to acyl chlorides, giving a tertiary alcohol after work-up. To stop at the ketone you must switch to R_2Cd *or* use a Weinreb amide (advanced). For NCERT problems, write R_2Cd.

3 Physical Properties of Aldehydes and Ketones

3.1 State, Smell and Boiling Points

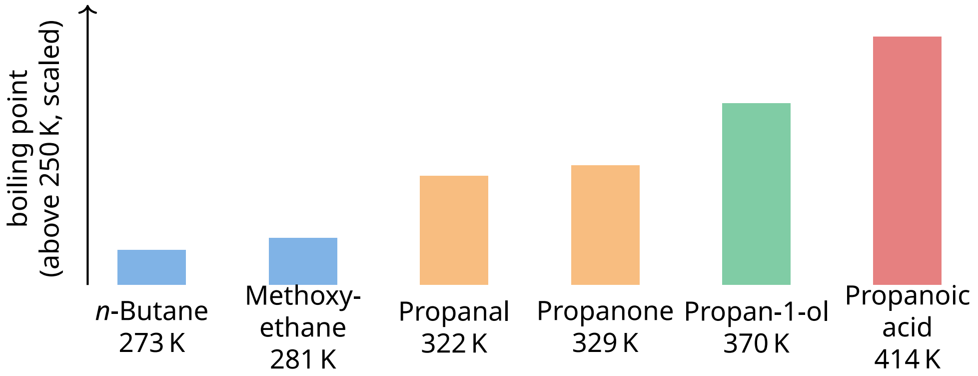
Methanal is a gas; ethanal is a low-boiling volatile liquid (b.p. 294 K); other aldehydes and ketones with up to 11 C atoms are liquids; higher members are solids. Lower aldehydes have a sharp, pungent odour while higher ones (e.g. vanillin, cinnamaldehyde) smell pleasant and are used in perfumery.

Boiling-point ladder for comparable molecules

For molecules of similar molar mass:

$$\text{alkane} < \text{ether} < \text{aldehyde} \approx \text{ketone} < \text{alcohol} < \text{carboxylic acid}$$

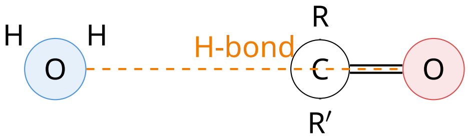
Reason: dipole-dipole attractions in C–O$=$ are stronger than London forces (alkane, ether) but weaker than H-bonding networks (alcohol, acid).



Boiling-point comparison for C_3/C_4 molecules of similar molar mass (58–74 g mol^{-1}): dispersion (alkane) $<$ weak dipole (ether) $<$ dipole-dipole (carbonyl) $<$ single H-bond (alcohol) $<$ dimeric H-bond (acid). Source: NCERT Tables (Section 8.3, 8.8).

3.2 Solubility

Carbonyl compounds form H-bonds with water through the lone pair on oxygen, so lower aldehydes and ketones (up to C_4) are reasonably soluble. Solubility falls sharply as the hydrocarbon tail grows — the hydrophobic part dominates. All carbonyl compounds dissolve readily in less polar organic solvents (ether, benzene, $CHCl_3$).



H-bonding between water and the carbonyl oxygen explains the solubility of methanal, ethanal and acetone in water.

Why nail-polish remover is acetone

Acetone dissolves both water-loving and oil-loving compounds in a single liquid: its C=O accepts H-bonds from water while its methyl groups dissolve nitrocellulose and resins. This dual character makes it the cheapest universal solvent in the cosmetic industry.

4 Chemical Reactions of Aldehydes and Ketones

Because aldehydes and ketones share the same >C=O, they share most reactions. Five broad reaction types account for almost every named transformation in the syllabus:

1. Nucleophilic addition reactions (HCN, $NaHSO_3$, alcohols, Grignard, ammonia derivatives).
2. Reduction to alcohols ($NaBH_4$, $LiAlH_4$, H_2/Ni) and to hydrocarbons (Clemmensen, Wolff-Kishner).
3. Oxidation — aldehydes only to acids; ketones cleave under harsh conditions.
4. α-Hydrogen reactions (Aldol, cross-aldol, halogenation).
5. Cannizzaro disproportionation (only for aldehydes without α-H) and electrophilic substitution on aromatic carbonyls.

4.1 Mechanism of Nucleophilic Addition

A nucleophile attacks the δ^+ carbonyl carbon perpendicular to the sp^2 plane (Bürgi-Dunitz trajectory). The carbon switches from sp^2 to sp^3 and a tetrahedral alkoxide forms; this is then protonated by the medium to give a neutral product.

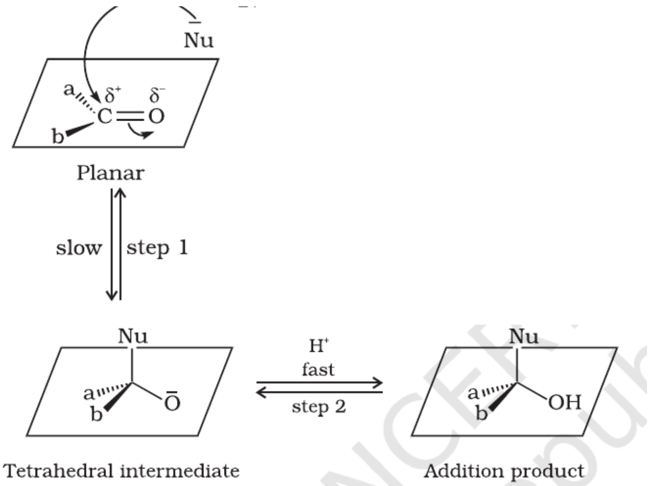


Fig.8.2: Nucleophilic attack on carbonyl carbon

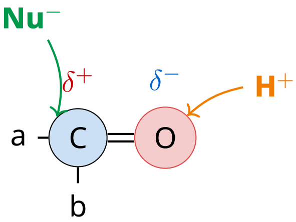
(ii) Reactivity

Fig. 8.2 (NCERT): Two-step nucleophilic addition. Step 1 (slow): Nu⁻ attacks C=O, *giving a tetrahedral alkoxide. Step 2 (fast):* H^+ *protonates the alkoxide to give the neutral addition product.*

Reactivity order: aldehyde vs ketone

$$\text{HCHO} > \text{R-CHO} > \text{R-CO-R}' \text{ (aliphatic ketone)} > \text{Ar-CO-R} > \text{Ar-CO-Ar}$$

Why? Steric crowding (two large R groups in ketones block nucleophile approach) *and* electronic donation (alkyl/aryl groups push electrons into C=O, reducing δ^+). For aromatic ketones the ring donates by resonance, lowering reactivity further.



The Bürgi-Dunitz attack: Nu⁻ *approaches the carbonyl carbon from above the* sp^2 *plane while* H^+ *neutralises the alkoxide.*

4.2 Important Nucleophilic Addition Reactions

(a) Addition of HCN. Base-catalysed; the free CN⁻ ion (stronger Nu than HCN) attacks C=O to give a **cyanohydrin**, a synthetically valuable bifunctional molecule.

$$\text{R}_2\text{C=O} + \text{HCN} \xrightarrow{trace\ OH^-} \text{R}_2\text{C(OH)(CN)}$$

(b) Addition of $NaHSO_3$**.** Sodium hydrogensulphite adds across C$=$O to give a white crystalline salt, the **bisulphite addition product**.

$$R_2C{=}O + NaHSO_3 \rightleftharpoons R_2C(OH)(SO_3Na)$$

The reaction is reversed by warming with dilute acid or alkali — useful for separating aldehydes from non-reactive components in a mixture.

(c) Addition of alcohols — hemi/acetals. Dry HCl catalyses two successive additions of R'OH to an aldehyde:

$$\mathrm{R{-}CHO + R'{-}OH} \xrightarrow{dry\ HCl} \underset{\text{hemiacetal}}{\mathrm{R{-}CH(OH)(OR')}} \xrightarrow{R'OH} \underset{\text{acetal}}{\mathrm{R{-}CH(OR')_2}} + \mathrm{H_2O}$$

Ketones with ethylene glycol form cyclic **ketals**. Acetals/ketals hydrolyse back to the carbonyl under aqueous acid — they are valuable as *protecting groups*.

(d) Addition of ammonia derivatives (H_2N**-Z).** The amine adds, then water is eliminated to give a C$=$N-Z product. The choice of Z determines the name:

Reagent (H_2N-Z)	**Z**	**Product class**
Ammonia	–H	Imine (C$=$NH)
Primary amine	–R	Schiff's base (substituted imine)
Hydroxylamine	$-OH$	Oxime
Hydrazine	$-NH_2$	Hydrazone
Phenylhydrazine	$-NHC_6H_5$	Phenylhydrazone
2,4-DNP	$-NH-C_6H_3(NO_2)_2$	2,4-DNP-hydrazone (orange-red solid)
Semicarbazide	$-NHCONH_2$	Semicarbazone

2,4-DNP — a colour-coded carbonyl detector

2,4-Dinitrophenylhydrazine (**2,4-DNP** or Brady's reagent) forms yellow, orange or red solids with aldehydes and ketones. The sharp melting points of these derivatives are characteristic of the parent carbonyl — generations of qualitative-analysis labs have used the colour test to identify unknown carbonyls.

4.3 Reduction Reactions

To alcohols. $NaBH_4$, $LiAlH_4$ or catalytic $H_2/Ni, Pd, Pt$ reduces aldehydes to primary alcohols and ketones to secondary alcohols.

$$\mathrm{R{-}CHO} \xrightarrow{NaBH4} \mathrm{R{-}CH_2OH} \qquad \mathrm{R_2C{=}O} \xrightarrow{NaBH4} \mathrm{R_2CH{-}OH}$$

To hydrocarbons — two named reactions.

Clemmensen reduction

$$R_2C{=}O + 4\,[H] \xrightarrow{Zn(Hg),\ conc.\ HCl} R_2CH_2 + H_2O$$

Use it when the substrate is acid-stable. Strongly acidic medium, hence not for acid-sensitive groups.

Wolff-Kishner reduction

$$R_2C{=}O + NH_2NH_2 \rightarrow \underset{\text{hydrazone}}{R_2C{=}N{-}NH_2} \xrightarrow[\Delta]{KOH,\ \text{ethylene glycol}} R_2CH_2 + N_2$$

Use it when the substrate is base-stable. Strongly basic, hot — not for base-sensitive groups.

Clemmensen vs Wolff-Kishner — pick by pH

If the molecule has an acid-sensitive group (an acetal, an enol ether), go basic: **Wolff-Kishner**. If it has a base-sensitive group (an ester, a β-keto-ester), go acidic: **Clemmensen**. Same product, opposite pH path — this single rule will let you choose correctly every time.

4.4 Oxidation Reactions

Aldehydes oxidise easily to carboxylic acids with mild reagents like nitric acid, $KMnO_4$, $K_2Cr_2O_7$ *and* the very mild Tollens and Fehling reagents (which ketones do not respond to). This is the basis of the standard chemical distinction between aldehydes and ketones.

Ketones require harsh conditions (concentrated HNO_3, hot $KMnO_4$); the reaction cleaves a C-C bond, giving a mixture of shorter-chain acids. Predict the cleavage by **Popoff's rule:** the bond preferentially cleaves between the carbonyl and the more substituted α-carbon (so that the more stable carbocation-like intermediate forms).

Three tests that distinguish aldehydes from ketones

Tollens' test (silver-mirror test): aldehydes reduce $[Ag(NH_3)_2]^+$ to metallic Ag.

$$R{-}CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \rightarrow R{-}COO^- + 2\,Ag\,(s)\downarrow + 4\,NH_3 + 2\,H_2O$$

Fehling's test: aldehydes reduce Cu^{2+} (deep-blue complex) to red Cu_2O.

$$R{-}CHO + 2\,Cu^{2+} + 5\,OH^- \rightarrow R{-}COO^- + Cu_2O(s)\downarrow + 3\,H_2O$$

Iodoform test (methyl ketones *and* ethanal): yellow CHI_3 from any compound with a $CH_3{-}CO^-$ or $CH_3{-}CH(OH)^-$ group:

$$CH_3{-}CO{-}R + 3\,NaOI \rightarrow CHI_3\downarrow + R{-}COONa + 2\,NaOH$$

Fehling fails on aromatic aldehydes

Benzaldehyde gives Tollens but NOT Fehling. The aromatic ring stabilises the δ^+ carbon by resonance, so the milder Cu^{2+} reagent cannot oxidise it. Don't write a Fehling reaction for C_6H_5CHO in the exam — you will lose the mark.

Iodoform-positive list

"**All ethanols and ketols with methyl pendants**": ethanol, ethanal, propan-2-ol, propan-2-one, butan-2-ol, butan-2-one, acetophenone — and many more bearing the CH_3CO^- or $CH_3CH(OH)^-$ unit. Methanol, propan-1-ol and propanal give a NEGATIVE iodoform test.

4.5 α-Hydrogen Reactions — Aldol Condensation

The α-hydrogen of a carbonyl is unusually acidic (p$K_a \approx 20$, vs ~ 50 for methane). Two reasons: (i) the carbonyl is strongly electron-withdrawing, stabilising the α-carbanion; (ii) the resulting enolate has the negative charge delocalised onto the more electronegative oxygen.

Enolate resonance — the source of α-H acidity

$$\mathrm{R{-}CH_2{-}C({=}O){-}R'} \overset{OH^-}{\rightleftharpoons} \mathrm{R{-}CH^-\text{-}C({=}O)\text{-}R'} \leftrightarrow \mathrm{R{-}CH{=}C(O^-){-}R'}$$

The negative charge resides on the more electronegative O in the right-hand contributor, making the enolate the dominant form.

Aldol reaction. In the presence of dilute alkali, an aldehyde or ketone with at least one α-H undergoes self-addition: the α-carbanion of one molecule attacks the carbonyl carbon of another.

$$2\ \mathrm{CH_3CHO} \xrightarrow[273-283\,K]{dil.\ NaOH} \mathrm{CH_3{-}CH(OH){-}CH_2{-}CHO} \xrightarrow{\Delta} \mathrm{CH_3{-}CH{=}CH{-}CHO} + \mathrm{H_2O}$$

The β-hydroxyaldehyde formed is called an **aldol** (from **ald**ehyde+alcoh**ol**). On warming, water is lost to give the α,β-unsaturated aldehyde — the **aldol condensation** product.

For ketones, the analogous product is a β-hydroxyketone (**ketol**), which similarly dehydrates.

Step 1: OH⁻ removes α-H

$$CH_3-CHO \xrightarrow{OH^-} {}^-CH_2-CHO$$

Step 2: carbanion attacks C=O

$${}^-CH_2-CHO + CH_3CHO \rightarrow CH_3-CH(O^-)-CH_2-CHO$$

Step 3: protonation and dehydration

$$\underset{\text{(aldol)}}{CH_3-CH(OH)-CH_2-CHO} \xrightarrow{\Delta} \underset{\text{(but-2-enal)}}{CH_3-CH=CH-CHO}$$

The three steps of an aldol condensation: enolate formation, C–C bond formation, dehydration to the conjugated enone.

Cross-aldol condensation. When two *different* carbonyls (each with α-H) react, four products form. The reaction is synthetically useful only when one partner has *no* α-H — e.g. benzaldehyde or formaldehyde — because then a single β-hydroxy/α,β-unsaturated product dominates:

$$C_6H_5CHO + CH_3CHO \xrightarrow{dil.\ NaOH} C_6H_5-CH=CH-CHO \quad (\textbf{cinnamaldehyde})$$

Plan your cross-aldol

The α-H-bearing partner becomes the nucleophile; the α-H-free partner (C_6H_5CHO, HCHO) becomes the electrophile. Always draw the enolate-attacks-aldehyde arrow flow; the answer reveals itself.

4.6 Other Reactions — Cannizzaro and Ring Substitution

Cannizzaro reaction (only for aldehydes *without* α-H, e.g. HCHO, C_6H_5CHO, $(CH_3)_3CCHO$): on heating with concentrated alkali, one molecule is oxidised to the acid and another is reduced to the alcohol — a *disproportionation*.

$$2\ HCHO \xrightarrow[\Delta]{conc.\ NaOH} HCOONa + CH_3OH$$

$$2\ C_6H_5CHO \xrightarrow[\Delta]{conc.\ NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

Electrophilic substitution on aromatic carbonyls. The $-$CHO and $-$COR groups are deactivating (they withdraw electrons by resonance) and *meta-directing*. So benzaldehyde nitrates and brominates predominantly at the *m*-position.

$$C_6H_5CHO + HNO_3 \xrightarrow{H2SO4} m\text{-}NO_2C_6H_4CHO$$

Cannizzaro requires NO α-H

If the aldehyde has even one α-H, it preferentially undergoes the aldol reaction, not Cannizzaro. Acetaldehyde, propanal, butanal — all aldols, never Cannizzaro. Only HCHO, C_6H_5CHO, $(CH_3)_3CCHO$ (pivalaldehyde) and similar are Cannizzaro candidates.

4.7 Uses of Aldehydes and Ketones

- **Formaldehyde** (40% formalin): preservative for biological specimens; bakelite (phenol-formaldehyde resin); urea-formaldehyde glues.
- **Acetaldehyde**: starting material for acetic acid, ethyl acetate, vinyl acetate.
- **Benzaldehyde**: perfumery, dye industry.
- **Acetone, MEK** (butan-2-one): industrial solvents for paints, varnishes, plastics.
- **Vanillin, camphor, butyraldehyde**: flavouring and fragrance.

5 Carboxylic Acids

A **carboxyl group** ($-$COOH) combines a carbonyl with a hydroxyl on the *same* carbon. The geometry around the carboxyl carbon is trigonal planar (sp^2) with $\approx 120°$ bond angles. Resonance among three structures spreads the π-electrons over both oxygens, making the C–O bond lengths nearly equal and the carboxyl carbon *less* electrophilic than a simple carbonyl carbon.

5.1 Nomenclature of Carboxylic Acids

Common names are Latin or Greek words for the natural source: formic acid (Latin *formica*, ant), acetic acid (Latin *acetum*, vinegar), butyric acid (Latin *butyrum*, butter).

IUPAC names replace the “-e” of the parent alkane with “-oic acid”. The carboxyl carbon is always C-1. Multiple $-$COOH groups: number the parent chain (without the $-$COOH) and use “-dicarboxylic acid” suffix. For aromatic acids: *benzenecarboxylic acid* (a.k.a. benzoic acid).

Structure	Common	IUPAC
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
HOOC – COOH	Oxalic acid	Ethanedioic acid
HOOC – CH_2 – COOH	Malonic acid	Propanedioic acid
HOOC – $(CH_2)_4$ – COOH	Adipic acid	Hexanedioic acid
C_6H_5COOH	Benzoic acid	Benzenecarboxylic acid

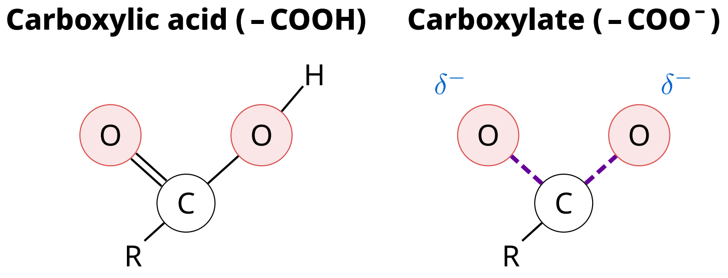
5.2 Structure of the Carboxyl Group

The –COOH group has three important resonance structures:

$$\mathrm{R{-}C({=}O){-}O{-}H} \leftrightarrow \mathrm{R{-}C(O^-){=}O^+{-}H} \leftrightarrow \mathrm{R{-}C({=}O^+H){-}O^-}$$

The middle and right contributors delocalise the lone pair on the –OH oxygen into the C=O. This makes:

- the carboxyl carbon *less* electrophilic than a simple aldehyde/ketone carbonyl (so it does *not* give standard nucleophilic-addition reactions);
- the –OH bond weaker (easier to lose H^+);
- the *conjugate base* extraordinarily stable, with the negative charge delocalised over both oxygens.


Carboxylic acid (–COOH) **Carboxylate (–COO$^-$)**

Resonance in the carboxylate ion: the negative charge is shared equally between two equivalent oxygens. The two C–O bonds are identical, intermediate in length between single and double bonds.

Why carboxylic acids are stronger acids than alcohols and phenols

The conjugate base of an **alcohol** (alkoxide RO^-) puts the negative charge on a single oxygen with no resonance stabilisation.

The conjugate base of a **phenol** (phenoxide $C_6H_5O^-$) has resonance, but the negative charge is partially delocalised onto less electronegative carbons of the ring.

The conjugate base of a **carboxylic acid** (carboxylate $RCOO^-$) delocalises the charge equally between two electronegative oxygens. Resonance stabilisation ⇒ acidity:

$$\text{alcohol } (\mathrm{p}K_a \approx 16) \ll \text{phenol } (10) \ll \text{carboxylic acid } (4\text{–}5)$$

6 Preparation of Carboxylic Acids

The NCERT lists six standard preparations.

6.1 Six Routes to a –COOH

1. From primary alcohols and aldehydes. Hot, alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ (Jones reagent: CrO_3/H_2SO_4) oxidises in one step.

$$R{-}CH_2OH \xrightarrow{Jones} R{-}COOH \qquad R{-}CHO \xrightarrow{[O]} R{-}COOH$$

2. From alkylbenzenes. Hot $KMnO_4$ or CrO_3/H^+ oxidises an alkyl side chain — whatever its length — to the carboxyl group, provided there is at least one benzylic H. Tertiary alkyl groups (no benzylic H) survive.

$$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{hot\ KMnO4} C_6H_5\text{-}COOH$$

3. From nitriles and amides. Acid- or base-catalysed hydrolysis: nitrile → amide → acid. Mild conditions stop at the amide.

$$R{-}C{\equiv}N \xrightarrow{H^+\ or\ OH^-} R{-}CONH_2 \xrightarrow{H+} R{-}COOH + NH_3$$

4. From Grignard reagents and CO_2. Grignard adds to dry-ice; protonation gives the acid with *one more C* than the alkyl halide.

$$R{-}MgX + CO_2 \rightarrow R{-}COOMgX \xrightarrow{H3O+} R{-}COOH$$

5. From acyl halides and anhydrides. Direct hydrolysis.

$$R{-}COCl + H_2O \rightarrow R{-}COOH + HCl$$

$$(RCO)_2O + H_2O \rightarrow 2\ R{-}COOH$$

6. From esters. Acidic hydrolysis is reversible; basic hydrolysis (*saponification*) is irreversible because the carboxylate end-product is stable.

$$R{-}COOR' + H_2O \xrightarrow{H+} R{-}COOH + R'{-}OH$$

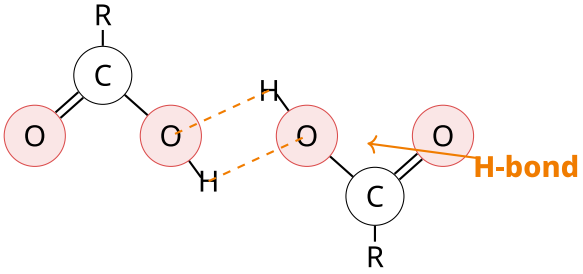
Ascending the carbon-chain ladder

To *lengthen* a chain by one carbon, use route 3 (alkyl halide → nitrile → acid) *or* route 4 (alkyl halide → Grignard → acid with CO_2). Both add a carbon. For aromatic systems, route 2 (oxidation of alkylbenzene) keeps the carbon count.

7 Physical Properties and Acidity of Carboxylic Acids

7.1 Boiling Point, Solubility and the Dimer

Carboxylic acids are higher-boiling than alcohols, aldehydes and ketones of comparable molar mass because each acid molecule forms *two* hydrogen bonds simultaneously — a **dimer** that persists even in the vapour phase or in aprotic solvents:



The cyclic carboxylic-acid dimer: two H-bonds between two molecules, persistent even in the vapour phase.

Boiling-point chart for C_2

Compound	Molar mass / g mol^{-1}	B.p. / K
CH_3CHO (ethanal)	44	294
CH_3OCH_3 (dimethyl ether)	46	248
C_2H_5OH (ethanol)	46	351
CH_3COOH (ethanoic acid)	60	391

The acid wins by ~ 100 K over the alcohol of similar mass — a vivid demonstration of dimerisation.

Aliphatic acids up to C_4 are fully miscible with water (small molecule, hydrophobic part overpowered by H-bonding). Solubility falls sharply as the alkyl chain lengthens. Benzoic acid is nearly insoluble in cold water.

7.2 Acidity — Reactions with Bases and the pKa Argument

Carboxylic acids dissolve in water to give a resonance-stabilised carboxylate plus hydronium ion:

$$\text{R–COOH} + \text{H}_2\text{O} \rightleftharpoons \text{R–COO}^- + \text{H}_3\text{O}^+ \qquad K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$\text{p}K_a = -\log K_a$. The smaller the $\text{p}K_a$, the stronger the acid.

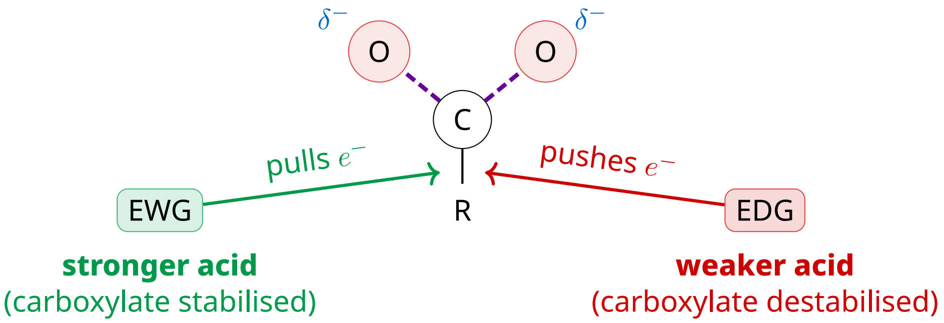
Strength scale by $\text{p}K_a$

HCl	-7
CF_3COOH (trifluoroacetic)	0.23
HCOOH (formic)	3.75
C_6H_5COOH (benzoic)	4.19
CH_3COOH (acetic)	4.76
phenol	10
ethanol	16

Unlike phenols, carboxylic acids react with the *weak* base $NaHCO_3$ to evolve CO_2. This is a clean qualitative test:

$$\text{R–COOH} + \text{NaHCO}_3 \rightarrow \text{R–COO–Na}^+ + \text{H}_2\text{O} + \text{CO}_2\uparrow$$

Effect of substituents. *Electron-withdrawing groups* (EWG: $-NO_2, -CN, -F, -Cl, -Br, -I, -CF_3$) stabilise the carboxylate by spreading the negative charge ⇒ increase acidity. *Electron-donating groups* (EDG: $-R, -OR, -NH_2, -OH$) destabilise the carboxylate by pushing electron density toward it ⇒ decrease acidity.



Substituent effects on carboxylic-acid acidity — electron pull versus push on the carboxylate ion.

Increasing-acidity order from the substituent ladder

$$\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$$

For example, on the same skeleton $X–CH_2–COOH$, the acidity rises sharply going right.

Three rules for ranking acids in seconds

1. More $-$I groups $\rightarrow$ more acidic. **2.** Closer $-$I group to $-$COOH $\rightarrow$ more acidic. **3.** For aromatic acids, $-$M substituents at o, p (e.g. $-NO_2$) increase acidity; $+$M substituents at o, p (e.g. $-OCH_3$, $-NH_2$) decrease it. The *ortho effect* is anomalous: *all* ortho substituents (whether EDG or EWG) increase acidity due to steric inhibition of resonance.

Pitfall: phenyl vs alkyl

Students sometimes write "C_6H_5COOH is weaker than CH_3COOH because phenyl donates by resonance". **Wrong.** C_6H_5COOH (pK_a 4.19) is *stronger* than CH_3COOH (pK_a 4.76) because the sp^2 carbon of the ring is *more electronegative* than the sp^3 carbon of methyl, and pulls electrons away from the carboxylate by induction. Resonance into the ring competes weakly — inductive effect wins.

8 Chemical Reactions of Carboxylic Acids

Carboxylic-acid reactions divide neatly by which bond cleaves: (a) O-H (acidity, salt and ester formation by attack on H^+), (b) C-OH (replacement of $-$OH by $-$Cl, $-$OR, $-$OCOR, $-NH_2$), (c) –COOH as a whole (reduction, decarboxylation), and (d) α-hydrogen and ring (substitution).

8.1 Reactions Involving O–H Cleavage

Salt formation.

$$2\ R-COOH + Zn \rightarrow (R-COO)_2Zn + H_2\uparrow$$

$$R-COOH + NaOH \rightarrow R-COONa + H_2O$$

$$R-COOH + NaHCO_3 \rightarrow R-COONa + CO_2\uparrow + H_2O$$

Esterification with alcohols. Acid- (or HCl-) catalysed equilibrium with a primary or secondary alcohol; water is the by-product.

$$R-COOH + R'-OH \xrightarrow{conc.\ H2SO4} R-COOR' + H_2O$$

The mechanism is **nucleophilic acyl substitution** (AAC_2): protonation activates the carbonyl, the alcohol's oxygen attacks, proton transfers, water leaves, and a final deprotonation gives the ester.

The ^{18}O-labelling proof for the mechanism

When the alcohol's oxygen is isotopically labelled ($R'-{}^{18}OH$), the label ends up in the *ester*, not in the water. This proves the bond-cleaving event is the C–O**H** bond of the *acid* (loses its –OH), not the alcohol's C–O**H** bond.

8.2 Reactions Involving C–OH Cleavage

1. Anhydride formation. Two acid molecules condense with loss of water on heating with P_2O_5 or strong acid:

$$2\ \mathrm{R{-}COOH} \xrightarrow[\Delta]{P2O5} \mathrm{(RCO)_2O} + \mathrm{H_2O}$$

2. Acyl chloride formation. Three reagents do the same job: PCl_5, PCl_3, $SOCl_2$. Thionyl chloride is preferred because the by-products (SO_2, HCl) escape as gases, leaving a pure acyl chloride.

$$\mathrm{R{-}COOH} + \mathrm{SOCl_2} \ \rightarrow\ \mathrm{R{-}COCl} + \mathrm{SO_2}\uparrow + \mathrm{HCl}\uparrow$$

3. Amide formation. Acids react with NH_3 to give an ammonium salt; pyrolysis of the salt at ~ 500 K dehydrates it to the amide.

$$\mathrm{R{-}COOH} + \mathrm{NH_3} \ \rightarrow\ \mathrm{R{-}COONH_4} \ \xrightarrow{\Delta}\ \mathrm{R{-}CONH_2} + \mathrm{H_2O}$$

8.3 Reactions of –COOH as a Whole

Reduction. $LiAlH_4$ or, even better, B_2H_6 (diborane), reduces $-$COOH to a primary alcohol. Diborane is the reagent of choice when the substrate also contains $-NO_2$, $-$COOR, halogen — groups that $LiAlH_4$ also attacks. $NaBH_4$ is too mild to touch $-$COOH.

$$\mathrm{R{-}COOH} \xrightarrow{B2H6 \text{ or } LiAlH4} \mathrm{R{-}CH_2{-}OH}$$

Decarboxylation. The sodium salt heated with soda-lime (NaOH/CaO 3:1) loses CO_2, giving the alkane:

$$\mathrm{R{-}COONa} \xrightarrow[\Delta]{NaOH/CaO} \mathrm{R{-}H} + \mathrm{Na_2CO_3}$$

This is one way to shorten a chain by one carbon (*descend the series*).

Kolbe electrolysis. Electrolysis of the aqueous sodium carboxylate gives the dimerised hydrocarbon at the anode:

$$2\ \mathrm{R{-}COONa} + 2\,\mathrm{H_2O} \xrightarrow{electrolysis} \mathrm{R{-}R} + 2\ \mathrm{CO_2} + 2\ \mathrm{NaOH} + \mathrm{H_2}\uparrow$$

8.4 Substitution Reactions on the Hydrocarbon Part

α-Halogenation (Hell-Volhard-Zelinsky). Carboxylic acids with an α-H react with Cl_2 or Br_2 in the presence of a small amount of red phosphorus to give α-halogenated acids.

$$\mathrm{R{-}CH_2{-}COOH} + \mathrm{Cl_2} \xrightarrow{red\ P} \mathrm{R{-}CHCl{-}COOH} + \mathrm{HCl}$$

Ring substitution on aromatic carboxylic acids. The $-$COOH group is deactivating and meta-directing.

$$C_6H_5COOH + HNO_3 \xrightarrow{H2SO4} m\text{-}NO_2C_6H_4COOH$$

Friedel-Crafts *does not work* on benzoic acid: $AlCl_3$ coordinates the $-$COOH group, killing the catalyst.

Hell-Volhard-Zelinsky in three words

"HVZ: Halogen α-pin." Halogen replaces the α-H, with red phosphorus as the catalyst. Repeat in the exam: the bromine goes to the α-carbon, not the β-carbon, not the ring.

Aspirin — esterification at work

Salicylic acid esterified with acetic anhydride gives acetylsalicylic acid (**aspirin**), the world's most prescribed analgesic. The same ester linkage is what aspirin breaks in the body when it inhibits cyclo-oxygenase — chemistry you have just learned has a direct line to a > 15-billion-dollar pharmaceutical industry.

8.5 Uses of Carboxylic Acids

- **Methanoic acid**: rubber, textile, leather, dyeing, electroplating.
- **Ethanoic acid**: laboratory solvent; vinegar (6–10% aq.) in food.
- **Hexanedioic acid (adipic acid)**: nylon-6,6.
- **Benzoic acid esters**: perfumery; sodium benzoate is a food preservative.
- **Higher fatty acids (C_{12}–C_{18})**: soaps (Na-salts) and detergents (K-salts).

9 Quick Reference Summary

9.1 Reagent → Product cheat sheet

Reagent	Aldehyde reaction	Ketone reaction
HCN, trace OH^-	R-CHO → R-CH(OH)CN	$R_2C{=}O \rightarrow R_2C(OH)CN$
$NaHSO_3$	R-CHO → R-CH(OH)SO_3Na	$R_2C{=}O \rightarrow R_2C(OH)SO_3Na$ (less)
R′OH/dry HCl	hemiacetal → acetal	cyclic ketal with ethylene glycol
NH_2Z (Z = OH/NH_2)	oxime / hydrazone / etc.	oxime / hydrazone / etc.
$NaBH_4$ or $LiAlH_4$	primary alcohol	secondary alcohol
Zn(Hg)/HCl (Clemmensen)	R-CH_3	R_2CH_2

NH_2NH_2/KOH (Wolff-K.)	R-CH_3	R_2CH_2
Tollens $[Ag(NH_3)_2]^+$	silver mirror $\downarrow$	no reaction
Fehling solution	red $Cu_2O\downarrow$ (aliphatic only)	no reaction
NaOI / I_2+NaOH	yellow CHI_3 if CH_3-CO- present	same
dil. NaOH, 280 K	aldol $\rightarrow$ enone	ketol $\rightarrow$ enone
conc. NaOH, Δ	Cannizzaro (no α-H)	— (ketones rare)

9.2 Six routes to a carboxylic acid

1. $R{-}CH_2OH \xrightarrow{KMnO_4/H^+} R{-}COOH$ (oxidation of 1° alcohol)
2. $Ar{-}R \xrightarrow{\text{hot } KMnO_4} Ar{-}COOH$ (side-chain oxidation)
3. $R{-}X \rightarrow R{-}CN \xrightarrow{H_3O^+} R{-}COOH$ (via nitrile, $+1$ C)
4. $R{-}X \rightarrow R{-}MgX \xrightarrow{CO_2,\ H_3O^+} R{-}COOH$ (via Grignard, $+1$ C)
5. $R{-}COCl\,/\,(RCO)_2O \xrightarrow{H_2O} R{-}COOH$ (hydrolysis)
6. $R{-}COOR' \xrightarrow{H^+/H_2O} R{-}COOH$ (hydrolysis of ester)

9.3 Acidity ladder (pK_a)

$$\underbrace{\text{HCl}}_{-7} < \underbrace{CF_3COOH}_{0.23} < \underbrace{HCOOH}_{3.75} < \underbrace{C_6H_5COOH}_{4.19} < \underbrace{CH_3COOH}_{4.76} < \underbrace{\text{phenol}}_{10} < \underbrace{\text{ethanol}}_{16}$$

(smaller pK_a = stronger acid)

9.4 Named reactions you must remember

Name	What it does
Rosenmund	R-COCl + H_2 over Pd-$BaSO_4$, quinoline-S $\rightarrow$ R-CHO
Stephen	R-CN + $SnCl_2$/HCl, then H_2O $\rightarrow$ R-CHO
Etard	$ArCH_3$ + CrO_2Cl_2/CS_2, then H_3O^+ $\rightarrow$ ArCHO
Gattermann-Koch	ArH + CO + HCl/$AlCl_3$/CuCl $\rightarrow$ ArCHO
Tollens / Fehling	oxidise aldehyde $\rightarrow$ acid (test)
Clemmensen / Wolff-Kishner	C=O $\rightarrow$ CH_2 (acidic / basic)
Aldol condensation	2 carbonyls (with α-H) $\rightarrow$ α, β-unsaturated
Cannizzaro	2 ArCHO (no α-H), conc. NaOH $\rightarrow$ $ArCH_2OH$ + ArCOONa
HVZ	R-CH_2-COOH + X_2/red P $\rightarrow$ R-CHX-COOH
Hell-Volhard-Zelinsky	same as HVZ
Kolbe electrolysis	2 RCOONa, electrolysis $\rightarrow$ R-R + 2 CO_2 + 2 NaOH + H_2

9.5 Last-minute revision checklist

- Carbonyl carbon is sp^2, $120°$, δ^+. Oxygen is δ^-.
- Aldehyde $>$ ketone in reactivity (sterics $+$ electronics).
- Tollens / Fehling test for aldehydes; *Fehling fails for aromatic aldehydes*.
- Iodoform: CH_3CO^- or $CH_3CH(OH)^-$ groups (and also ethanol, ethanal).
- Aldol: needs α-H. Cannizzaro: no α-H.
- Cross-aldol *useful* only when one partner has no α-H.
- Carboxylic acids: H-bonded dimer $\Rightarrow$ high b.p.
- Acidity: EWG $\uparrow$, EDG $\downarrow$. Closer $\rightarrow$ acid carbon, stronger effect.
- HVZ halogenates α-C of an acid; ring substitution is meta-directing.
- Esterification: protonated carbonyl + ROH; ^{18}O goes into the ester.

Final word

The carbonyl chapter is the connective tissue of Class 12 organic chemistry. Master the **four moves** — nucleophile attack on δ^+ C; α-H deprotonation to a stabilised enolate; reduction; oxidation — and every reaction in this chapter, and a huge fraction of those in Chapter 9 (Amines) and Chapter 10 (Biomolecules), becomes predictable.