

Carbonyl Compounds

01 · THE CARBONYL GROUP

$C=O$ is trigonal planar at 120° , one σ plus one π bond. Oxygen is far more electronegative, so the bond is **strongly polar** with $\delta+$ carbon.

That $\delta+$ carbon is attacked by **nucleophiles** — the opposite of an alkene, whose electron-rich $C=C$ attracts electrophiles.

02 · ALDEHYDE OR KETONE?

Aldehyde $RCHO$ — the carbonyl is at the end of the chain, so it carries a hydrogen and is easily oxidised.

Ketone $RCOR'$ — the carbonyl is inside the chain with no hydrogen attached, so it resists oxidation. That single difference drives every test below.

03 · TESTS TO KNOW

Reagent	Aldehyde	Ketone
2,4-DNPH	orange ppt	orange ppt
Tollens'	silver mirror	none
Fehling's	brick-red ppt	none
$K_2Cr_2O_7 / H^+$	orange $\rightarrow$ green	stays orange

2,4-DNPH detects any carbonyl; the melting point of the purified orange derivative identifies which one. Tollens' and Fehling's then separate aldehyde from ketone.

04 · REDUCTION

Reagent: $NaBH_4$ in aqueous methanol, or $LiAlH_4$ in dry ether.

$RCHO + 2[H] \rightarrow RCH_2OH$ (primary alcohol)
 $RCOR' + 2[H] \rightarrow RCH(OH)R'$ (secondary alcohol)

Exactly the reverse of alcohol oxidation, so the two reactions run a loop you can use in synthesis.

05 · OXIDATION

$RCHO + [O] \rightarrow RCOOH$ with acidified $K_2Cr_2O_7$ under reflux. Ketones do not react — there is no hydrogen on the carbonyl carbon to remove.

Methanal is the exception among aldehydes in being oxidised all the way to CO_2 under vigorous conditions.

06 · ADDITION OF HCN

Reagent: $NaCN$ with dilute acid — HCN itself is a toxic gas, and the cyanide must be generated in situ.

The product is a **hydroxynitrile**: $RCHO + HCN \rightarrow RCH(OH)CN$. This **lengthens the carbon chain by one**, and the nitrile can then be hydrolysed to a hydroxy acid.

07 · NUCLEOPHILIC ADDITION MECHANISM

- CN^- attacks the $\delta+$ carbonyl carbon; the π electrons shift onto the oxygen.
- An intermediate with a negatively charged oxygen forms.
- That oxygen takes H^+ from HCN or water, giving the $-OH$ and regenerating CN^- .

Two curly arrows in step 1: one from the lone pair on CN^- to the carbon, one from the $C=O$ π bond to the oxygen.

08 · RACEMIC PRODUCTS A2

The carbonyl is planar, so the nucleophile attacks either face with equal probability. If the product has a chiral carbon the two enantiomers form in equal amounts — a **racemic mixture**, optically inactive.

09 · THE TRI-iodomETHANE TEST

I_2 with $NaOH(aq)$, warm $\rightarrow$ pale yellow CHI_3 precipitate.

Positive for **ethanal and any methyl ketone** (CH_3CO-), and for alcohols oxidisable to them. Propanone gives it; propanal does not — a fast way to separate the two.

10 · WORKED EXAMPLE — IDENTIFY THE COMPOUND

C_3H_6O gives an orange precipitate with 2,4-DNPH, no silver mirror with Tollens', and a yellow precipitate with alkaline iodine.

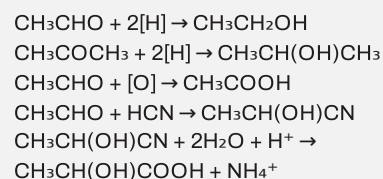
2,4-DNPH $\rightarrow$ a carbonyl compound
 No mirror $\rightarrow$ ketone, not aldehyde
 Yellow $CHI_3 \rightarrow$ contains CH_3CO-
 $\rightarrow$ **propanone**, CH_3COCH_3

11 · MAKING CARBONYLS

Aldehyde — oxidise a primary alcohol with acidified $K_2Cr_2O_7$ and **distil the product off** as it forms, before it is oxidised further.

Ketone — reflux a secondary alcohol with the same reagent; no over-oxidation is possible, so reflux is safe.

12 · EQUATIONS TO KNOW



13 · REAGENTS AT A GLANCE

Reagent	What it contains
Tollens'	$[Ag(NH_3)_2]^+$ in aqueous ammonia
Fehling's	Cu^{2+} complexed in alkali
2,4-DNPH	2,4-dinitrophenylhydrazine
tri-iodomethane	I_2 with $NaOH(aq)$

Both Tollens' and Fehling's work by the aldehyde **reducing** the metal ion: $Ag^+ \rightarrow Ag$ as a mirror, $Cu^{2+} \rightarrow Cu_2O$ as a brick-red solid.

14 · WHERE CARBONYLS SIT IN SYNTHESIS

They are the junction between alcohols and acids: reduce to go one way, oxidise to go the other.

Adding HCN is one of only two ways in the syllabus to lengthen a carbon chain, and the hydroxynitrile it makes can be hydrolysed to a hydroxy acid such as 2-hydroxypropanoic acid.

15 · WORKED EXAMPLE — CHAIN LENGTHENING

Convert propanone into 2-hydroxy-2-methylpropanoic acid.

- $NaCN$ with dilute acid $\rightarrow (CH_3)_2C(OH)CN$
- dilute HCl , reflux $\rightarrow (CH_3)_2C(OH)COOH$

The nitrile carbon becomes the $-COOH$, so the product has one carbon more than the ketone. The product here is achiral, but a similar route from an aldehyde would give a racemic mixture.

MARKS LOST HERE

- Saying 2,4-DNPH distinguishes aldehydes from ketones; it detects both.
- Calling the HCN reaction electrophilic addition. The carbonyl carbon is $\delta+$, so the attack is nucleophilic.
- Forgetting that the hydroxynitrile has one more carbon than the starting material.
- Missing the racemic outcome when a chiral centre is created.