9701 CHEMISTRY · TOPICS 17 & 31 · AS + A LEVEL

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 δ+ carbon.

That δ+ 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 → 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 → 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

1 CN^- attacks the δ+ carbonyl carbon; the π electrons shift onto the oxygen.
2 An intermediate with a negatively charged oxygen forms.
3 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 → 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 → a carbonyl compound
No mirror → ketone, not aldehyde
Yellow CHI_3 → contains CH_3CO–
→ **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

$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$
$CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$
$CH_3CHO + [O] \rightarrow CH_3COOH$
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$
$CH_3CH(OH)CN + 2H_2O + H^+ \rightarrow CH_3CH(OH)COOH + NH_4^+$

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.

1 · NaCN with dilute acid → $(CH_3)_2C(OH)CN$
2 · dilute HCl, reflux → $(CH_3)_2C(OH)COOH$

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 δ+, 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.