

Carbonyl compounds

AS

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Last checked 30 September 2026

Read first: [An introduction to AS Level organic chemistry](#), [Hydroxy compounds](#)

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What you need to know

By the end of this topic you should be able to:

1. **Recall how aldehydes and ketones are made** (reagents and conditions):
 - (a) oxidising a **primary alcohol** with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$, **distilling** the product off, gives an **aldehyde**;
 - (b) oxidising a **secondary alcohol** in the same way gives a **ketone**.
2. **Describe two reactions of aldehydes and ketones:**
 - (a) **reduction** to alcohols with $NaBH_4$ or $LiAlH_4$;
 - (b) **addition of HCN**, with KCN as a catalyst and heat, giving **hydroxynitriles** (ethanal and propanone are the examples).
3. **Describe the mechanism of that HCN reaction:** nucleophilic addition, with curly arrows.
4. **Use 2,4-dinitrophenylhydrazine (2,4-DNPH reagent)** to show that a compound contains a carbonyl group.
5. **Decide whether an unknown carbonyl compound is an aldehyde or a ketone** from simple tests: Fehling's reagent, Tollens' reagent, and how easily it is oxidised.
6. **Deduce a CH_3CO- group** in an aldehyde or ketone, CH_3COR , from its reaction with alkaline $I_2(aq)$: a yellow precipitate of tri-iodomethane, CHI_3 , and an ion RCO_2^- .

Understand it

Aldehydes and ketones

Both contain the **carbonyl group**, $C=O$. What is attached to the carbonyl carbon decides which family a compound is in:

Family	Carbonyl carbon carries	General formula	Name ending	Examples
Aldehyde	at least one H (the $C=O$ is at the end of the chain)	$RCHO$	-al	ethanal CH_3CHO , propanal CH_3CH_2CHO

Family	Carbonyl carbon carries	General formula	Name ending	Examples
Ketone	two carbon groups (the C=O is inside the chain)	RCOR'	-one	propanone CH ₃ COCH ₃ , butanone CH ₃ COCH ₂ CH ₃

The aldehyde carbon is always C1, so it needs no number (butanal, 2-methylpropanal). A ketone needs a number once there is a choice: pentan-2-one, CH₃COCH₂CH₂CH₃, is a different compound from pentan-3-one, CH₃CH₂COCH₂CH₃. Aldehydes and ketones with the same number of carbons are isomers: propanal and propanone are both C₃H₆O. Simple aldehydes and ketones have the general formula C_nH_{2n}O.

Oxygen is much more electronegative than carbon, so the C=O bond is **polar**: C^{δ+}=O^{δ-}. The δ+ carbon is what attacking species go for. C=O molecules cannot hydrogen-bond to each other (there is no O-H), so aldehydes and ketones boil **lower** than the alcohols they come from, which is what lets you distil them off.

Making them: oxidising alcohols

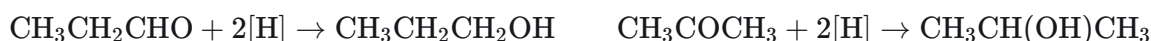
This was met in Hydroxy compounds. Warm the alcohol with acidified potassium dichromate(VI) (K₂Cr₂O₇ and dilute H₂SO₄) and the orange solution turns **green**. [O] stands for an oxygen atom from the oxidising agent.

- **Primary alcohol** → **aldehyde**. Distil the aldehyde off as it forms, so it cannot be oxidised further to a carboxylic acid: CH₃CH₂OH + [O] → CH₃CHO + H₂O Heating under reflux instead takes it on to the acid: CH₃CHO + [O] → CH₃COOH.
- **Secondary alcohol** → **ketone**. Ketones are not oxidised further, so distillation or reflux gives the same product: CH₃CH(OH)CH₃ + [O] → CH₃COCH₃ + H₂O
- **Tertiary alcohols** are not oxidised: no aldehyde or ketone, and the dichromate stays orange.

Acidified KMnO₄ does the same job (purple to colourless).

Reduction back to alcohols

Sodium tetrahydridoborate, NaBH₄, or lithium tetrahydridoaluminate, LiAlH₄, reduces the C=O to CH-OH. Write [H] for a hydrogen atom from the reducing agent; each C=O needs 2[H]:



So an **aldehyde gives a primary alcohol** and a **ketone gives a secondary alcohol**, with the same carbon skeleton. It is the reverse of the oxidation above. The reducing agent delivers a **hydride ion**, H⁻, which is a nucleophile: it adds to the δ+ carbon, and the O then picks up H⁺ from water. So this reduction is also a **nucleophilic addition**. NaBH₄ does not touch C=C bonds; LiAlH₄, the stronger reagent, also reduces COOH groups (Hydroxy compounds), but not C=C either.

Adding HCN: hydroxynitriles

Heat an aldehyde or ketone with HCN and a little KCN (or NaCN). HCN adds across the C=O: the H goes to the oxygen and the CN to the carbon. The product has an OH and a CN on the old carbonyl carbon: a **hydroxynitrile**.



Carbonyl compound	Hydroxynitrile	Chiral centre?
ethanal, CH_3CHO	2-hydroxypropanenitrile, $\text{CH}_3\text{CH}(\text{OH})\text{CN}$	yes (H, OH, CN, CH_3)
propanone, CH_3COCH_3	2-hydroxy-2-methylpropanenitrile, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$	no (two CH_3)
propanal, $\text{CH}_3\text{CH}_2\text{CHO}$	2-hydroxybutanenitrile, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$	yes
butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$	2-hydroxy-2-methylbutanenitrile, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CN}$	yes

Three things to notice:

- **The chain gains a carbon.** Name the product as a nitrile: the CN carbon is C1, and the OH is on C2. This is why HCN is useful in synthesis.
- **Chiral centres.** A **chiral centre** is a carbon atom bonded to four different atoms or groups. The new carbon carries OH and CN plus the two groups that were on the carbonyl carbon. It is chiral if those two groups are different from each other (and neither is OH or CN). So every aldehyde except methanal gives a chiral product, and every ketone gives one unless its two groups are the same (propanone, pentan-3-one).
- **The same test for reduction.** After reduction the carbon carries H and OH plus the two old groups. An aldehyde's product has two H on that carbon, so it is never chiral there; an unsymmetrical ketone's product is.

Why you get a mixture of two optical isomers. The C=O group and the two groups on its carbon all lie in one flat plane. The nucleophile (CN^- with HCN, or H^- from NaBH_4) can attack the carbon from above or below that plane, and each side is equally likely. When the product has a chiral centre, attack from one side gives one optical isomer and attack from the other side gives its mirror image, so the product is a mixture of the two optical isomers in equal amounts (a racemic mixture). Ethanal with HCN, and butanone with NaBH_4 , both give such a mixture.

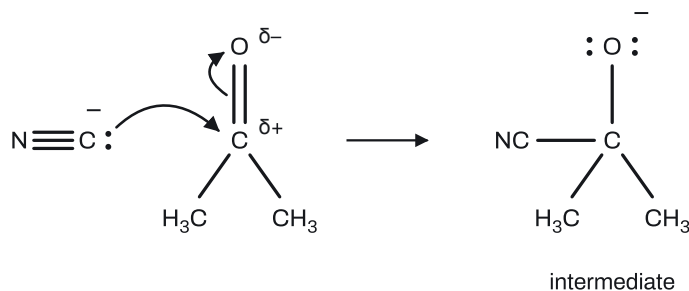
The mechanism: nucleophilic addition

HCN is a very weak acid, so it hardly ionises and there are very few CN^- ions. KCN supplies CN^- , which is the species that attacks: a **nucleophile**, with a lone pair on its **carbon** atom and a negative charge.

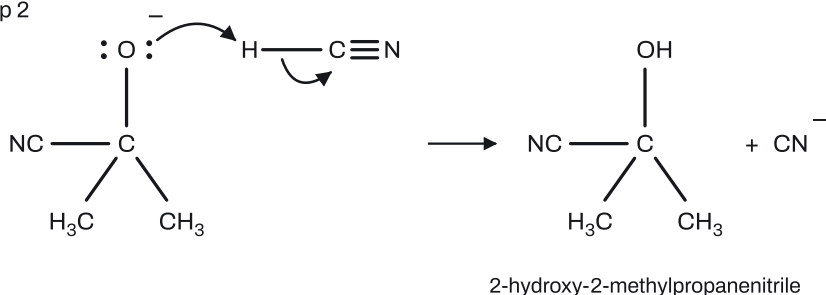
Step 1. The lone pair on the C of CN^- forms a bond to the δ^+ carbonyl carbon. At the same time the π bond of C=O breaks and its electron pair moves onto the oxygen. The intermediate is an **anion**: the oxygen now carries a negative charge and lone pairs.

Step 2. A lone pair on the negative oxygen takes an H^+ from an HCN molecule. That makes the OH group and gives back a CN^- ion.

Step 1



Step 2



Because the CN^- used in step 1 is made again in step 2, KCN is a **catalyst**. The overall change is **addition** (two molecules become one), started by a **nucleophile: nucleophilic addition**. Compare alkenes: a $\text{C}=\text{C}$ bond has no δ^+ end and is rich in electrons, so it is attacked by electrophiles instead (electrophilic addition).

Testing for a carbonyl group: 2,4-DNPH

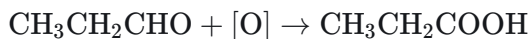
2,4-Dinitrophenylhydrazine (2,4-DNPH reagent, Brady's reagent) reacts with the $\text{C}=\text{O}$ of **every** aldehyde and ketone to give a **yellow-orange (orange or red) precipitate**. It is the general test for a carbonyl group. It does **not** react with the $\text{C}=\text{O}$ in carboxylic acids or esters, and it does not tell aldehydes from ketones. (The precipitate's melting point can identify the exact compound.)

Aldehyde or ketone? Ease of oxidation

An aldehyde still has an H on its carbonyl carbon, so it is easily oxidised to a carboxylic acid. A ketone has no such H and is **not easily oxidised**. Mild oxidising agents therefore react with aldehydes only.

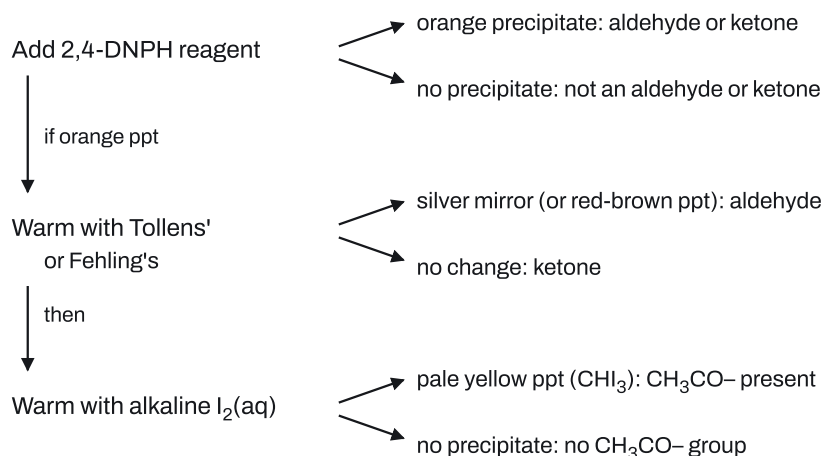
Test (warm with...)	Aldehyde	Ketone
Tollens' reagent (silver nitrate in aqueous ammonia, $[\text{Ag}(\text{NH}_3)_2]^+$)	silver mirror on the tube (or grey-black precipitate): Ag^+ reduced to Ag	no change
Fehling's reagent (alkaline, blue copper(II) complex)	blue solution gives a red-brown precipitate (Cu_2O): Cu(II) reduced to Cu(I)	stays blue
Acidified $\text{K}_2\text{Cr}_2\text{O}_7$	orange $\rightarrow$ green	stays orange

In each positive test the aldehyde is **oxidised** to the carboxylic acid (in the alkaline Tollens' and Fehling's reagents it ends up as the carboxylate ion), and the reagent is **reduced**, so the reagent acts as the **oxidising agent**:



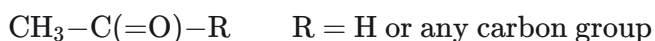
Watch the dichromate test: primary and secondary **alcohols** turn it green too, so on its own it only shows "something oxidisable". Tollens' and Fehling's do not react with alcohols.

Identifying a carbonyl compound



The tri-iodomethane (iodoform) test

Warm the compound with iodine solution and sodium hydroxide (**alkaline** $\text{I}_2(\text{aq})$). A **pale yellow precipitate** of **tri-iodomethane**, CHI_3 (antiseptic smell), shows a **methyl carbonyl group**:



The three H atoms of the CH_3 are replaced by I, then the CI_3 group breaks off as CHI_3 . What is left, the carbonyl carbon with R, becomes a **carboxylate ion**, RCO_2^- , which has **one carbon fewer** than the starting compound:



Compound	R	Products
ethanal, CH_3CHO	H	CHI_3 + methanoate, HCO_2^-
propanone, CH_3COCH_3	CH_3	CHI_3 + ethanoate, CH_3CO_2^-
butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$	CH_2CH_3	CHI_3 + propanoate, $\text{CH}_3\text{CH}_2\text{CO}_2^-$

Positive: ethanal (the only aldehyde) and every **methyl ketone** (propanone, butanone, pentan-2-one, 3-methylbutan-2-one). **Negative:** methanal, every other aldehyde (propanal, butanal), and ketones without a CH_3 next to the $\text{C}=\text{O}$ (pentan-3-one). Adding acid afterwards turns the carboxylate into the carboxylic acid: butanone ends up as propanoic acid.

Alcohols with a $\text{CH}_3\text{CH}(\text{OH})-$ group (ethanol, propan-2-ol, butan-2-ol) are positive too, because the alkaline iodine first oxidises them to $\text{CH}_3\text{CO}-$ (Hydroxy compounds). So a positive test on a compound that gives no precipitate with 2,4-DNPH points to a $\text{CH}_3\text{CH}(\text{OH})-$ alcohol.

Key facts and formulas

"Given" means it is printed in the 9701 Data Booklet. "Learn it" means you must remember it. Reagents, conditions, colours and equations are never printed.

Formula or fact	Status
Relative atomic masses: C 12.0, H 1.0, N 14.0, O 16.0, I 126.9	Given
Primary alcohol $\xrightarrow{[\text{O}], \text{distil}}$ aldehyde; secondary alcohol $\xrightarrow{[\text{O}]}$ ketone (acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4)	Learn it
$\text{RCH}_2\text{OH} + [\text{O}] \rightarrow \text{RCHO} + \text{H}_2\text{O}$; $\text{RCH}(\text{OH})\text{R}' + [\text{O}] \rightarrow \text{RCOR}' + \text{H}_2\text{O}$	Learn it
$\text{RCHO} + 2[\text{H}] \rightarrow \text{RCH}_2\text{OH}$; $\text{RCOR}' + 2[\text{H}] \rightarrow \text{RCH}(\text{OH})\text{R}'$ (NaBH_4 or LiAlH_4)	Learn it
$\text{RCOR}' + \text{HCN} \rightarrow \text{RC}(\text{OH})(\text{CN})\text{R}'$, KCN catalyst, heat; nucleophilic addition	Learn it
2,4-DNPH: orange precipitate with any aldehyde or ketone	Learn it
Tollens': silver mirror; Fehling's: blue to red-brown precipitate; both with aldehydes only	Learn it
$\text{RCHO} + [\text{O}] \rightarrow \text{RCOOH}$ (aldehydes are easily oxidised, ketones are not)	Learn it
$\text{CH}_3\text{COR} + 3\text{I}_2 + 4\text{OH}^- \rightarrow \text{CHI}_3 + \text{RCO}_2^- + 3\text{I}^- + 3\text{H}_2\text{O}$: yellow precipitate	Learn it
Hydroxynitrile has one more carbon than the carbonyl compound; M_r rises by 27.0 (HCN)	Learn it
Reduction raises M_r by 2.0 (two H atoms)	Learn it

How to do it

We have tagged 101 questions on this topic from 2021–2025 (87 different, since some papers share questions). 18 of them mix more than one type, so the counts add up to more than 101.

Question type	Questions
Predict the products of HCN addition and reduction	31
Identify an unknown compound from test results	26
State test observations or choose a distinguishing reagent	26
Describe the HCN nucleophilic addition mechanism	22
Apply the tri-iodomethane reaction	15
Give reagents, conditions and oxidation routes	9

1. Predict the products of HCN addition and reduction (31 questions)

1. **Find the C=O** and write down the two groups on its carbon.
2. **HCN (with KCN):** put OH and CN on that carbon. The product has one more carbon; name it as a 2-hydroxy...nitrile, counting the CN carbon as C1.
3. **NaBH₄ or LiAlH₄:** put H and OH on that carbon. Aldehyde → primary alcohol, ketone → secondary alcohol. Equation: add 2[H] for each C=O.
4. **Chiral centre?** A chiral centre is a carbon atom bonded to four different atoms or groups. List the four groups on the old carbonyl carbon; if all four differ, it is chiral, and the product forms as a mixture of two optical isomers.

Variations you will meet:

- **Work backwards.** From a hydroxynitrile, remove HCN: the carbon bearing OH and CN was the C=O carbon, and the CN carbon is the extra one. 2-hydroxybutanenitrile, CH₃CH₂CH(OH)CN, came from propanal. From an alcohol after reduction: a primary alcohol came from an aldehyde, a secondary from a ketone.
- **Multi-step chains.** "Primary alcohol, dichromate, distil, then HCN": first the aldehyde, then its hydroxynitrile. Propan-1-ol → propanal → 2-hydroxybutanenitrile.
- **Which carbonyl gives a chiral product with both HCN and NaBH₄?** It must be an unsymmetrical **ketone**: an aldehyde's reduction product has two H on that carbon. Butanone works; propanone and propanal do not.
- **M_r clues.** A hydroxynitrile's M_r is the carbonyl compound's plus 27.0; a reduction product's is plus 2.0. So a product of M_r 85.0 from HCN came from a carbonyl compound of M_r 58.0, C₃H₆O. A percentage rise of $\frac{2.0}{M_r} \times 100$ on reduction gives the ketone's M_r.
- **Molecules with other groups.** NaBH₄ reduces only C=O in aldehydes and ketones; C=C, COOH and esters are left alone. LiAlH₄ also reduces COOH, not C=C. HCN adds to each aldehyde or ketone C=O, so a molecule with two such groups can take two HCN if there is an excess.
- **Other nucleophiles.** Any nucleophile adds the same way: its lone pair (or negative carbon) bonds to the carbonyl carbon, and the O becomes OH after protonation. The hydride from NaBH₄ is one example; an unfamiliar one such as CH₃[−] adds a CH₃ group to that carbon.
- **"Why is a mixture of two products formed?"** The C=O group is planar, so the nucleophile (CN[−] or H[−]) can attack from either side of the plane with equal chance. The product has a chiral centre, so the two directions of attack give the two optical isomers, in equal amounts.
- **"State the type of reaction":** HCN, **nucleophilic addition**; NaBH₄, **reduction** (also a nucleophilic addition). **"Role of NaBH₄":** reducing agent.

2. Identify an unknown compound from test results (26 questions)

1. **Read each result as a fact:**

Result	Means
Orange precipitate with 2,4-DNPH	aldehyde or ketone
Silver mirror (Tollens') or red-brown precipitate (Fehling's)	aldehyde
No change with Tollens' or Fehling's, but DNPH positive	ketone
Yellow precipitate with alkaline I ₂	CH ₃ CO– (or CH ₃ CH(OH)–)
Acidified K ₂ Cr ₂ O ₇ orange → green	aldehyde, or primary or secondary alcohol
Acidified K ₂ Cr ₂ O ₇ stays orange	not an aldehyde, not a 1° or 2° alcohol
Fizzing with Na	an OH group

2. **Draw every candidate** that fits the formula or the options, then cross out any that fails a result.

3. **Give exactly what is asked:** a name, a structural formula or the functional group ("carbonyl").

Variations you will meet:

- **Three bottles, three names.** Propanal, propanone and ethanal all give the DNPH precipitate. Tollens' picks out the two aldehydes; alkaline I₂ picks out ethanal and propanone. The one positive in both is ethanal, Tollens' only is propanal, iodine only is propanone.
- **A data clue picks the formula.** Percentage of carbon (divide by 12.0 as usual), moles of CO₂ from combustion (moles of C per molecule = $\frac{\text{mol CO}_2}{\text{mol compound}}$, using 24.0 dm³ mol⁻¹ at room conditions), or an *M_r*, after HCN addition or reduction.
- **Extra structural clues:** "shows cis/trans isomerism" means a C=C with two different groups on each end; "has a chiral centre"; "unbranched chain".
- **Counting isomers that fit.** Draw all the aldehydes and ketones of the formula, keep those that pass the tests, and if the question says so, count stereoisomers too: a chiral carbon doubles the count, as does a C=C with cis/trans forms. For C₄H₈O there are three carbonyl compounds: butanal, 2-methylpropanal and butanone.
- **Two carbonyl groups in one molecule** (such as CH₃COCHO): each group behaves on its own. The CHO end gives Tollens' and Fehling's; the CH₃CO end gives the iodine test; DNPH is positive.

3. State test observations or choose a distinguishing reagent (26 questions)

1. **Find the groups** in the compound: CHO, ketone C=O, CH₃CO–, CH₃CH(OH)–, OH, C=C, COOH.
2. **Go through each reagent** with the tables in "Understand it" and write what you would **see**: "orange precipitate", "silver mirror", "red-brown precipitate", "yellow precipitate", "orange to green".
3. **Where nothing happens, say so**: "no visible change", "stays blue", "no precipitate".

Choosing a reagent for a pair: find a group that one compound has and the other lacks. Give the reagent, what is seen, and **which** compound gives it.

- Aldehyde vs ketone: Tollens' (silver mirror with the aldehyde) or Fehling's (red-brown precipitate with the aldehyde).

- Carbonyl compound vs alcohol or ester: 2,4-DNPH (orange precipitate with the carbonyl).
- Methyl ketone vs other ketone (propanone vs pentan-3-one), or ethanal vs propanal: alkaline I_2 .
- Ketone vs secondary alcohol: 2,4-DNPH, or acidified $K_2Cr_2O_7$ (the alcohol turns it green).

"Why does Fehling's not react with propanone?" Ketones are not easily oxidised (there is no H on the carbonyl carbon), and Fehling's is a mild oxidising agent.

4. Describe the HCN nucleophilic addition mechanism (22 questions)

On Paper 2 you complete a diagram. Each of these earns a mark:

1. **Dipole** on $C=O$: $\delta+$ on C, $\delta-$ on O.
2. **Curly arrow from the lone pair on the C of** : CN^- to the carbonyl carbon (the lone pair and the negative charge must be on carbon, not nitrogen).
3. **Curly arrow from the $C=O$ double bond** to the O.
4. **Intermediate**: the carbon now bonded to CN, with O^- (negative charge and a lone pair).
5. **Curly arrow from a lone pair on O^- to the H of $H-CN$** (an arrow from the H–C bond to C in HCN completes it and regenerates CN^-).

Variations you will meet (multiple choice):

- **Name the mechanism**: nucleophilic addition, not electrophilic addition and not nucleophilic substitution (nothing leaves).
- **The first step**: CN^- attacks the carbon. The first step is **not** H^+ attacking the oxygen.
- **The intermediate** is negatively charged; a **proton from HCN** is then transferred to it.
- **The catalyst** is CN^- (from KCN or NaCN); it is used then made again. Acid conditions are not used: they would remove CN^- .
- **Which compounds can undergo nucleophilic addition?** Aldehydes and ketones (a polar $C=O$). Alkenes undergo electrophilic addition; halogenoalkanes undergo nucleophilic substitution.

5. Apply the tri-iodomethane reaction (15 questions)

1. **Look beside each $C=O$** . Is there a CH_3 on the carbonyl carbon (or the compound ethanal)? Also check any $CH_3CH(OH)-$ group.
2. **Observation**: pale yellow precipitate. **Name**: tri-iodomethane, CHI_3 (write it in that order).
3. **Other product**: RCO_2^- , where R is the group on the other side of the $C=O$; it has one carbon fewer. After acidifying, $RCOOH$.

Variations you will meet:

- **Counting positive compounds** in a list or among isomers: tick each one with CH_3CO- or $CH_3CH(OH)-$. Of the aldehydes, only ethanal counts.

- **Diols and diones.** Each $\text{CH}_3\text{CH}(\text{OH})-$ or $\text{CH}_3\text{CO}-$ end reacts. A molecule with one at **each** end, such as hexane-2,5-dione $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$, loses both CH_3 groups and gives a **dicarboxylate**, $^-\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2^-$; acid turns it into butanedioic acid, $\text{HOOCCH}_2\text{CH}_2\text{COOH}$. A diol such as hexane-2,5-diol does the same, since each $\text{CH}_3\text{CH}(\text{OH})-$ is oxidised first.
- **Suggest a non-carbonyl compound that also gives the precipitate:** an alcohol $\text{CH}_3\text{CH}(\text{OH})\text{R}$, with $\text{R} = \text{H}$ or an alkyl group.
- **Redox:** iodine is reduced to I^- ; the organic compound is oxidised.

6. Give reagents, conditions and oxidation routes (9 questions)

1. **To make an aldehyde:** primary alcohol, acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (or KMnO_4), warm, **distil off the aldehyde** as it forms.
2. **To make a ketone:** secondary alcohol, the same reagent, heat (distil or reflux).
3. **Aldehyde $\rightarrow$ carboxylic acid:** acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat under **reflux**. Equation $\text{RCHO} + [\text{O}] \rightarrow \text{RCOOH}$.
4. **Carbonyl $\rightarrow$ hydroxynitrile:** HCN with KCN , heat. **Carbonyl $\rightarrow$ alcohol:** NaBH_4 or LiAlH_4 .

Variations you will meet: "which single reaction makes propanoic acid?" (oxidising propanal, or propan-1-ol under reflux); "the role of Tollens' reagent" (oxidising agent); "is the organic compound oxidised?" (yes with Tollens' or Fehling's; no with LiAlH_4 , which reduces it).

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

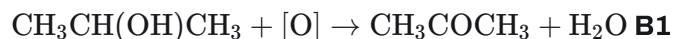
Example 1

Propanone, CH_3COCH_3 , can be made from propan-2-ol.

- (a) Give the reagents and conditions, and write an equation using $[\text{O}]$. **[3]**
- (b) Propanone is reduced by NaBH_4 . Write an equation using $[\text{H}]$ and name the product. **[2]**
- (c) Propanone reacts with HCN in the presence of KCN . Give the structural formula and name of the product, and explain why it has no chiral centre. **[3]**

(d) State what you would see when propanone is warmed separately with 2,4-DNPH reagent and with Tollens' reagent. **[2]**

(a) Acidified potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$ and dilute H_2SO_4) **B1**, heat (distil). **B1**



(b) $\text{CH}_3\text{COCH}_3 + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ **B1**; propan-2-ol. **B1**

(c) $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$ **B1**, 2-hydroxy-2-methylpropanenitrile. **B1** The carbon bonded to OH and CN also carries **two identical** CH_3 **groups**, so it is not bonded to four different groups. **B1**

(d) 2,4-DNPH: orange precipitate. **B1** Tollens': no visible change, because a ketone is not easily oxidised. **B1**

Example 2

Ethanal reacts with hydrogen cyanide in the presence of a small amount of potassium cyanide.

(a) Name the type of mechanism. **[1]**

(b) Describe the mechanism, including dipoles, lone pairs, charges and curly arrows. **[4]**

(c) Explain the role of the potassium cyanide. **[2]**

(d) Name the product and identify its chiral centre. **[2]**

(a) Nucleophilic addition. **B1**

(b) Draw ethanal with $\text{C}^{\delta+}=\text{O}^{\delta-}$, and $:\text{CN}^-$ with its lone pair and charge on carbon.

- Curly arrow from the lone pair on the C of CN^- to the $\delta+$ carbon, **and** the dipole shown. **M1**
- Curly arrow from the $\text{C}=\text{O}$ bond to the O. **M1**
- Intermediate $\text{CH}_3\text{CH}(\text{O}^-)\text{CN}$ with the negative charge on O. **M1**
- Curly arrow from a lone pair on O^- to the H of H-CN , giving $\text{CH}_3\text{CH}(\text{OH})\text{CN}$ and CN^- . **M1**

The diagram in "Understand it" shows the same steps for propanone.

(c) It provides CN^- ions, the nucleophile; HCN is a weak acid and gives very few. **B1** The CN^- is regenerated in the second step, so KCN is a catalyst. **B1**

(d) 2-hydroxypropanenitrile, $\text{CH}_3\text{CH}(\text{OH})\text{CN}$. **B1** The chiral centre is C2, the carbon bonded to H, OH, CN and CH_3 : four different groups. **B1**

Example 3

Three bottles, **X**, **Y** and **Z**, each contain a different compound of formula $\text{C}_4\text{H}_8\text{O}$. All three give an orange precipitate with 2,4-DNPH reagent.

	Tollens' reagent	alkaline $I_2(aq)$
X	silver mirror	no precipitate
Y	silver mirror	no precipitate
Z	no visible change	yellow precipitate

X has an unbranched chain; **Y** has a branched chain.

(a) Identify **X**, **Y** and **Z**. [3]

(b) Give the formulas of the two products when **Z** reacts with alkaline $I_2(aq)$. [2]

(c) **Y** reacts with HCN and KCN. Draw the structural formula of the product, calculate its M_r and state whether it has a chiral centre. [3]

(d) **X** is heated under reflux with acidified $K_2Cr_2O_7$. State the colour change and name the organic product. [2]

(a) All three are carbonyl compounds. **X** and **Y** are aldehydes (silver mirror). **X**, unbranched: **butanal**, $CH_3CH_2CH_2CHO$. **B1** **Y**, branched: **2-methylpropanal**, $(CH_3)_2CHCHO$. **B1** **Z** is a ketone with CH_3CO- : **butanone**, $CH_3COCH_2CH_3$. **B1**

(b) CHI_3 **B1** and the propanoate ion, $CH_3CH_2CO_2^-$ (three carbons, one fewer than butanone). **B1**

(c) $(CH_3)_2CHCH(OH)CN$ **B1**, formula C_5H_9NO :

$$M_r = 5(12.0) + 9(1.0) + 14.0 + 16.0 = 99.0$$

B1 (or $72.0 + 27.0$). Yes: the carbon bonded to OH carries H, OH, CN and $CH(CH_3)_2$, four different groups. **B1**

(d) Orange to green. **B1** Butanoic acid, $CH_3CH_2CH_2COOH$. **B1**

Example 4

Compound **W** contains 66.7% carbon, 11.1% hydrogen and 22.2% oxygen by mass, and has $M_r = 72.0$. **W** gives an orange precipitate with 2,4-DNPH reagent, does not react with Fehling's reagent, and gives a yellow precipitate with alkaline $I_2(aq)$.

(a) Show that the molecular formula of **W** is C_4H_8O . [2]

(b) Identify **W**. Explain your answer. [2]

(c) **W** is reduced with $NaBH_4$. Name the product and state how many stereoisomers it has. [2]

(d) 2.16 g of **W** is heated with an excess of HCN and a little KCN. 2.08 g of hydroxynitrile is obtained. Calculate the percentage yield. [3]

(a) $C : H : O = \frac{66.7}{12.0} : \frac{11.1}{1.0} : \frac{22.2}{16.0} = 5.56 : 11.1 : 1.39 = 4 : 8 : 1$. **M1**

Empirical formula C_4H_8O has $M_r = 48.0 + 8.0 + 16.0 = 72.0$, the same as **W**, so the molecular formula is C_4H_8O . **A1**

(b) DNPH positive and Fehling's negative: a ketone. **B1** The only C_4H_8O ketone is butanone, $CH_3COCH_2CH_3$, which has the CH_3CO- group needed for the yellow precipitate. **B1**

(c) Butan-2-ol, $CH_3CH(OH)CH_2CH_3$. **B1** C2 carries H, OH, CH_3 and C_2H_5 , so it is chiral: 2 stereoisomers (optical isomers). **B1**

(d) Amount of **W** = $2.16 \div 72.0 = 0.0300$ mol. **M1**

1 mol of **W** gives 1 mol of $CH_3CH_2C(CH_3)(OH)CN$, $M_r = 99.0$, so the theoretical mass is $0.0300 \times 99.0 = 2.97$ g. **M1**

$$\text{percentage yield} = \frac{2.08}{2.97} \times 100 = 70.0\%$$

A1

Common mistakes

- **Putting the lone pair and charge on the N of CN^- .** Examiner reports see this often. The carbon of cyanide attacks, so the lone pair, the negative charge and the start of the curly arrow go on **C**.
- **Starting the mechanism with H^+ .** Reports describe answers where H from HCN attacks the oxygen first, or where the intermediate carries a positive charge. CN^- attacks first, the intermediate is **negative**, and the proton comes second.
- **Curly arrows from the wrong place.** The second arrow must start on the **C=O bond** and end on O, not start at the C atom. Reports also note a missing δ^+/δ^- dipole on C=O: it is a marking point.
- **Wrong hydroxynitrile.** Reports note that the product from propanone, $(CH_3)_2C(OH)CN$, is often drawn wrongly. The OH and CN go on the **same** carbon, the old carbonyl carbon, and the chain gains one carbon.
- **The wrong carboxylate in the iodoform test.** Reports say many candidates gave CHI_3 correctly but very few gave the right ion. It has **one carbon fewer**: butanone gives propanoate, not butanoate. Write CHI_3 in that order.
- **Iodine without the alkali.** The test needs **both** iodine and NaOH(aq).
- **Leaving out "precipitate".** "Orange" alone for 2,4-DNPH did not score; write "orange precipitate". Tollens' is a silver **mirror** (or grey/black precipitate), Fehling's a red-brown **precipitate**.
- **Inventing a change when nothing happens.** If a reagent does not react, write "no visible change" or "stays blue"; reports see "loses colour" or a colour change given for a negative result.
- **Using the dichromate test to tell an aldehyde from a ketone when an alcohol could be present.** Alcohols turn it green too; Tollens' or Fehling's is the specific test for aldehydes.
- **Unbalanced [H] and [O] equations.** Reduction of one C=O needs $2[H]$; do not add H_2 as a product or an extra H in the formula.

How to get the marks

- **"Reagents and conditions"** needs both: "HCN with KCN (catalyst), heat"; "acidified potassium dichromate(VI), distil"; "NaBH₄". Name the carbonyl reagent as 2,4-dinitrophenylhydrazine or 2,4-DNPH.
- **"Observation"** means what you see: colour **and** state ("orange precipitate", "silver mirror", "red-brown precipitate", "yellow precipitate", "orange to green").
- **"Complete the mechanism"**: show the δ^+/δ^- dipole, lone pairs on the attacking atoms, charges on ions and intermediates, and curly arrows that start at a lone pair or a bond and end at an atom. Each is a separate mark.
- **"Type of reaction"**: nucleophilic addition (HCN), reduction (NaBH₄), oxidation (dichromate, Tollens', Fehling's).
- **"Explain" a negative result**: give the chemical reason, such as "ketones are not easily oxidised" or "not bonded to four different groups".
- **"Identify" or "Deduce"**: give one clear answer that fits every result. A second, wrong suggestion alongside a right one can cancel the mark.
- **Equations with [O] and [H]** must balance, with the water where there is one. Use structural formulas such as CH₃CH₂CHO, not C₃H₆O, which could be propanone.
- **Multiple-choice counting questions** that say "structural and stereoisomerism should be considered" want optical and cis/trans isomers included.
- **Calculations**: show M_r , moles and the mole ratio; give 3 significant figures unless told otherwise.

Quick check

1. Name the organic product in each case: (a) propanal and NaBH₄; (b) propanal and HCN with KCN; (c) pentan-3-one and LiAlH₄; (d) butan-1-ol and acidified K₂Cr₂O₇, with the product distilled off as it forms.
2. Which of these give a yellow precipitate with alkaline I₂(aq): methanal, ethanal, propanal, pentan-2-one, pentan-3-one, 3-methylbutan-2-one? Give the carboxylate ion formed in each positive test.
3. A compound C₃H₆O gives an orange precipitate with 2,4-DNPH reagent and a red-brown precipitate with Fehling's reagent. Identify it and write an equation, using [O], for its oxidation.
4. Calculate the greatest mass of hydroxynitrile that can be made from 1.16 g of propanone.
5. Which of these carbonyl compounds give a hydroxynitrile with a chiral centre: methanal, ethanal, propanone, butanone, pentan-3-one?

Answers

1. (a) Propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$. (b) 2-hydroxybutanenitrile, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$. (c) Pentan-3-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$. (d) Butanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$.
2. Ethanal (gives methanoate, HCO_2^-), pentan-2-one (butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2^-$) and 3-methylbutan-2-one (2-methylpropanoate, $(\text{CH}_3)_2\text{CHCO}_2^-$). Methanal and propanal have no $\text{CH}_3\text{CO}-$; pentan-3-one has an ethyl group on each side of the $\text{C}=\text{O}$.
3. It is an aldehyde with three carbons: propanal, $\text{CH}_3\text{CH}_2\text{CHO}$. $\text{CH}_3\text{CH}_2\text{CHO} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$.
4. M_r of propanone = 58.0, so $1.16 \div 58.0 = 0.0200$ mol. The product, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$, has $M_r = 85.0$: $0.0200 \times 85.0 = 1.70$ g.
5. Ethanal and butanone. Methanal gives HOCH_2CN (two H on that carbon); propanone and pentan-3-one have two identical groups on the carbonyl carbon.

Past questions to try

- **9701/23/O/N/24 Q4**: the mechanism with propanone, a reduction equation, and why Fehling's does not react.
- **9701/13/M/J/24 Q38**: which carbonyl compound gives a chiral product with both HCN and NaBH_4 .
- **9701/13/O/N/24 Q34**: the iodoform reaction on a diol, giving a dicarboxylic acid.
- **9701/23/O/N/22 Q4**: choosing a different reagent to tell apart each pair of compounds.