Carbonyl compounds

Making aldehydes and ketones, reduction, nucleophilic addition of hydrogen cyanide, tests with 2,4-DNPH, Fehling's and Tollens' reagents, and the tri-iodomethane test.

17.1 Aldehydes and ketones

Both contain the **carbonyl group** C=O. In an **aldehyde** (R–CHO) the carbonyl carbon is at the end of the chain and bonded to a hydrogen; in a **ketone** (R–CO–R′) it is bonded to two carbon atoms.

Preparation

- **Primary alcohol** → aldehyde: acidified $K_2Cr_2O_7$ or $KMnO_4$, **distil** off the aldehyde as it forms.
- **Secondary alcohol** → ketone: the same reagents, heated (a ketone is not oxidised further, so reflux is fine).

Reduction

$NaBH_4$ or $LiAlH_4$ reduce aldehydes to primary alcohols and ketones to secondary alcohols: $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$. ($NaBH_4$ is used in water or ethanol; $LiAlH_4$ in dry ether.)

Nucleophilic addition of hydrogen cyanide

With **HCN and KCN as catalyst** (and gentle warming) aldehydes and ketones form **hydroxynitriles**: $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$ (2-hydroxypropanenitrile) and $CH_3COCH_3 + HCN \rightarrow (CH_3)_2C(OH)CN$.

Mechanism:

1. The nucleophile CN^- attacks the $\delta+$ carbon of C=O (arrow from the lone pair on carbon of CN^- to the carbon of C=O), and the C=O π bond breaks (arrow to oxygen), giving an **anion intermediate** with O^-.
2. O^- takes a proton from HCN (or from water), giving the hydroxynitrile and regenerating CN^-.

HCN is a weak acid, so KCN supplies the CN^- needed. A new C–C bond is formed, so this lengthens the chain by one carbon. The product from an unsymmetrical carbonyl (an aldehyde other than methanal, or an unsymmetrical ketone) is a **racemic mixture**, because the planar carbonyl is attacked equally from both faces.

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Tests

Test	Aldehyde	Ketone
2,4-DNPH (2,4-dinitrophenylhydrazine)	orange precipitate	orange precipitate
Tollens' reagent (ammoniacal silver nitrate, warm)	**silver mirror**	no reaction
Fehling's reagent (warm)	**brick-red precipitate** of Cu_2O	no reaction

2,4-DNPH shows that a **carbonyl** group is present (aldehyde or ketone); the melting point of the crystalline derivative can identify the compound. Tollens' and Fehling's reagents are mild **oxidising agents** that oxidise only aldehydes, to carboxylic acids (or their salts); the Ag^+ is reduced to Ag.

$$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O$$

The tri-iodomethane test

Warming with **alkaline aqueous iodine** gives a **yellow precipitate of** CHI_3 if the compound contains a CH_3CO- group, CH_3COR (ethanal and methyl ketones such as propanone). The other product is the carboxylate ion RCO_2^-.

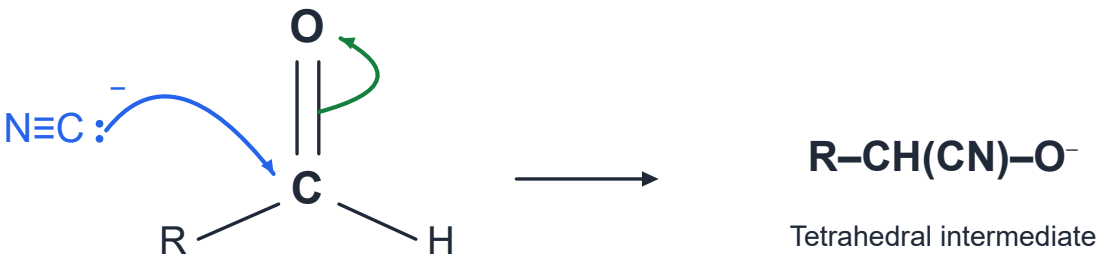
> **TRY IT**
>
> A compound C_4H_8O gives an orange precipitate with 2,4-DNPH, no silver mirror, and a yellow precipitate with alkaline iodine. Identify it.

It is a ketone (no Tollens' reaction) with a CH_3CO group: **butanone**, $CH_3COCH_2CH_3$.

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Carbonyl polarity explains nucleophilic attack

Nucleophilic addition: follow two electron pairs



1 Cyanide lone pair → carbonyl carbon

2 Carbonyl π-bond pair → oxygen

Protonation of O^- gives the hydroxynitrile R–CH(OH)–CN.

Oxygen attracts the C=O bonding electrons more strongly than carbon, leaving an electrophilic carbon and a partially negative oxygen. A nucleophile donates a pair to carbon while the pi-bond pair moves to oxygen. The carbon changes from approximately trigonal planar to tetrahedral as a new bond forms. Addition, rather than ordinary substitution, is possible because the pi bond can open without needing a leaving group.

Worked example: ethanal plus HCN gives $CH_3CH(OH)CN$. Cyanide forms a new C–C bond, while oxygen is protonated to become OH. Count the nitrile carbon: the product has three carbons although ethanal has two. Its name is 2-hydroxypropanenitrile. A mechanism should show the oxygen anion intermediate rather than jumping straight from reactants to neutral product without accounting for proton transfer.

When the oxygen anion is protonated by HCN, the H–CN bond pair returns to carbon of cyanide, regenerating the nucleophile. HCN is weakly ionised, so a cyanide salt provides a useful concentration of the attacking species. These are theoretical reaction descriptions; cyanide chemistry requires specialist handling and is not a home practical.

> **TRY IT**
>
> Give the structural formula of the product from propanone and HCN. Is its newly formed centre chiral?

Answer: $(CH_3)_2C(OH)CN$. It is not chiral because the central carbon has two identical methyl groups. Adding a new tetrahedral carbon does not automatically create a chiral centre.

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Planarity and racemic products

An achiral planar carbonyl can be approached from either face by cyanide. If addition creates a carbon with four different groups, the two approaches produce enantiomers in equal amounts under achiral conditions. Methanal does not create such a centre because its product has two hydrogens on the reacting carbon. A symmetrical ketone likewise retains two identical carbon groups.

Worked example: ethanal gives a carbon attached to OH, H, methyl and CN, so it becomes chiral. The racemic product contains both mirror-image forms. Butanone can also give a chiral hydroxynitrile because methyl and ethyl differ. Draw the actual four substituents before deciding.

> **TRY IT**
>
> Why is “the product is racemic because the nucleophile can attack anywhere” too vague?

Answer: Attack occurs at the electrophilic carbonyl carbon, from either face of its planar group. The resulting tetrahedral centre must have four different groups for the two products to be enantiomers.

Reduction and selective oxidation

Aldehyde reduction gives a primary alcohol; ketone reduction gives a secondary alcohol. The carbon count is unchanged. A simplified $2[H]$ equation represents addition of hydrogen equivalents to the carbonyl group, not necessarily molecular hydrogen gas as the actual reagent. Sodium borohydride is useful for aldehydes and ketones under suitable aqueous/alcoholic conditions, whereas lithium aluminium hydride requires dry conditions followed by an appropriate work-up.

Worked route: butanone $+2[H] \longrightarrow$ butan-2-ol. The product carbon may become chiral because it has methyl, ethyl, H and OH groups. Reduction from an achiral carbonyl with an achiral reagent can therefore give a racemic alcohol. Oxidising that secondary alcohol returns the ketone without changing the carbon skeleton.

Mild aldehyde tests oxidise the aldehyde group, while ordinary ketones do not respond under those conditions. In alkaline Tollens' or Fehling's mixtures the organic product is a carboxylate, not a free acid unless acidification follows. Fehling's is particularly appropriate to aliphatic aldehydes; some aromatic aldehydes do not give the same response, so later aromatic chemistry requires care.

Combining carbonyl tests as evidence

2,4-DNPH indicates aldehyde/ketone functionality by a yellow/orange precipitate; it does not by itself distinguish which. Tollens' identifies many aldehydes through silver formation. Alkaline iodine identifies ethanal and methyl ketones, but also certain alcohol precursors. Test separate portions so one reagent does not change the compound before another test is interpreted.

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Worked identification: C_3H_6O gives DNPH precipitate and a silver mirror. It is propanal rather than propanone. A separate C_3H_6O sample gives DNPH, no Tollens' response and positive iodoform: these observations identify propanone. The molecular formula restricts possibilities, while the tests discriminate among them.

An isolated DNPH derivative's melting point can be compared with reference data after purification. A narrow melting range supports purity; a mixed or impure product can give a depressed/broadened range. Treat a match as evidence alongside the reaction observations, not permission to ignore contradictory data.

> **TRY IT**
>
> A compound gives a silver mirror and a yellow iodoform precipitate. Which simple aldehyde is indicated?

Answer: Ethanal, CH_3CHO. It has both an aldehyde group and the methyl-carbonyl arrangement required for the iodoform reaction. Other simple aldehydes normally fail the latter test.

Chapter check: state the carbonyl polarity, show arrows and intermediate charge, count any added cyanide carbon, and use the complete set of tests to justify a structure rather than naming it from a single observation.

References and further reading

Scope follows section 17 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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