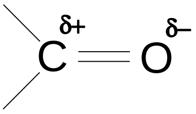
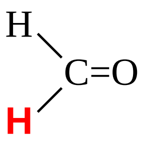
CARBONYL COMPOUNDS - Aldehydes and Ketones

Structure

- carbonyl groups consists of a **carbon-oxygen double bond**
- the bond is **polar** due to the difference in electronegativity
- aldehydes / ketones differ in what is attached to the carbon



ALDEHYDES - at least one H attached to the carbonyl group



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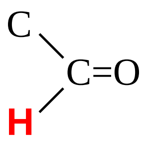
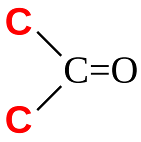


HCHO
CH_3CHO
C_6H_5CHO

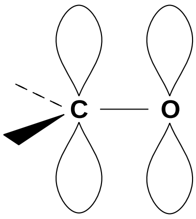
KETONES - two carbons attached to the carbonyl group

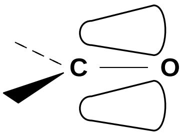


CH_3COCH_3
$C_2H_5COCH_3$
$C_6H_5COCH_3$

Bonding

- the carbonyl carbon is sp^2 hybridised and three sigma (σ) bonds are planar
- the unhybridised 2p orbital of carbon is at 90° to these
- it overlaps with a 2p orbital of oxygen to form a pi (π) bond
- as oxygen is more electronegative than carbon, the bond is polar





Naming

- aldehydes end in **AL**
- ketones end in **ONE**
- pick the longest chain of carbon atoms which includes the C=O
- substituent positions are based on the carbon with the O attached

$CH_3CH_2CH_2CH_2CH_2CHO$	$CH_3COCH_2CH_2CH_2CH_3$
hexanal	*hexan-2-one*

Q.1 *Draw structures for, and name, all the carbonyl compounds with molecular formulae;*

a) C_4H_8O *b)* $C_5H_{10}O$ *c)* $C_6H_{12}O$

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Formation of carbonyl compounds from alcohols

Aldehydes
- Oxidation of primary (1°) alcohols - **risk of oxidation to acids**

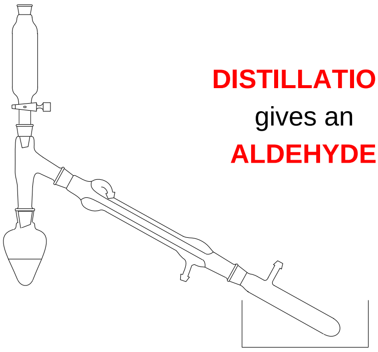
eg $CH_3CH_2OH(l) + [O] \longrightarrow CH_3CHO(l) + H_2O(l)$

ethanol *ethanal*

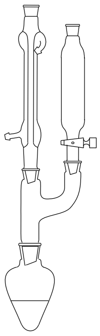
however, this can happen $CH_3CHO(l) + [O] \longrightarrow CH_3COOH(l)$

ethanal *ethanoic acid*

- it is essential to **distil off the aldehyde** before it gets oxidised to the acid
- the alcohol is dripped into a warm solution of **acidified $K_2Cr_2O_7$** ($Cr_2O_7^{2-}$ / H^+)
- the **orange $Cr_2O_7^{2-}$** [dichromate(VI)] is **reduced** to the **green Cr^{3+}**
- the **aldehyde has a low boiling point** - no hydrogen bonding - it distils off
- if it didn't distil off it would be oxidised to the equivalent carboxylic acid
- to oxidise an alcohol straight to the acid you would reflux the mixture



DISTILLATION
gives an
ALDEHYDE



REFLUXING
gives a
CARBOXYLIC ACID

Ketones
- Oxidation of secondary (2°) alcohols.

eg $CH_3CHOHCH_3(l) + [O] \longrightarrow CH_3COCH_3(l) + H_2O(l)$

propan-2-ol *propanone*

Q.2 *Which alcohol would you use to make the following?*

- C_2H_5CHO
- $C_2H_5COCH_3$
- *hexanal*
- *3-methylhexan-2-one*
- *3-methylpentanal*

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CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

OXIDATION

- provides a way of differentiating between aldehydes and ketones
- mild oxidising agents are best
- aldehydes are easier to oxidise
- powerful oxidising agents oxidise ketones to carboxylic acid mixtures

ALDEHYDES **easily oxidised to acids** *e.g.* $\mathbf{RCHO}(l) + [O] \longrightarrow \mathbf{RCOOH}(l)$

$\mathbf{CH_3CHO}(l) + [O] \longrightarrow \mathbf{CH_3COOH}(l)$

KETONES **only oxidised under vigorous conditions** to acids with fewer carbons.

e.g. $\mathbf{C_2H_5COCH_2CH_3}(l) + 3\,[O] \longrightarrow \mathbf{C_2H_5COOH}(l) + \mathbf{CH_3COOH}(l)$

Q.3 *What product (if any) is formed when the following undergo* ***mild*** *oxidation?*

- C_2H_5CHO
- $C_2H_5COCH_3$
- *hexanal*
- *3-methylhexan-2-one*
- *3-methylpentanal*
- *cyclohexanone*

IDENTIFYING A CARBONYL COMPOUND

Methods
- characteristically **strong peak at 1400-1600 cm^{-1}** in the **infra red spectrum** *or*
- formation of **orange crystalline precipitate** with **2,4-dinitrophenylhydrazine**

BUT to narrow it down to an aldehyde or ketone you must do a second test

Differentiation • to distinguish an aldehyde from a ketone you need a **mild** oxidising agent ...

Tollens' Reagent
- **ammoniacal silver nitrate** solution
- contains the diammine silver(I) ion - $[Ag(NH_3)_2]^+$
- acts as a mild oxidising agent and will oxidise aldehydes but not ketones
- the silver(I) ion is reduced to silver $Ag^+(aq) + e^- \longrightarrow Ag(s)$
- the test is known as THE SILVER MIRROR TEST

Q.4 *Which of the following produce an orange precipitate with 2,4-dinitrophenylhydrazine?*

- C_2H_5OH
- $C_2H_5COCH_3$
- *hexanal*
- *3-methylhexan-2-one*
- *cyclohexanol*
- *3-methylpentan-1-ol*

Q.5 *Which of the following produce a silver mirror with Tollens' reagent?*

- C_2H_5CHO
- $C_2H_5COCH_3$
- *hexanal*
- *3-methylhexan-2-one*
- *cyclohexanone*
- *3-methylpentanal*

Fehling's Solution
- **contains copper(II) ions** complexed with tartrate ions
- on warming, **it will oxidise aliphatic (but not aromatic) aldehydes**
- copper(II) is reduced to a **red precipitate** of copper(I) oxide, Cu_2O
- **Tollens' reagent is better as it works with all aldehydes.**

Ketones do not react with Tollens' Reagent or Fehling's Solution.

NUCLEOPHILIC ADDITION REACTIONS

Mechanism
- occurs with **both aldehydes and ketones**
- involves addition to the **polar** C=O double bond
- attack is by nucleophiles at the positive carbon centre
- alkenes are non-polar and are attacked by electrophiles

	Bond	*Polarity*	*Attacked by*	*Result*
Carbonyl	C=O	Polar	Nucleophiles	Addition
Alkene	C=C	Non-polar	Electrophiles	Addition

REDUCTION

Reagent	sodium tetrahydridoborate(III) (sodium borohydride), $NaBH_4$
Conditions	aqueous or alcoholic solution
Mechanism	Nucleophilic addition (also reduction as it is addition of H^-)
Nucleophile	H^- (hydride ion)

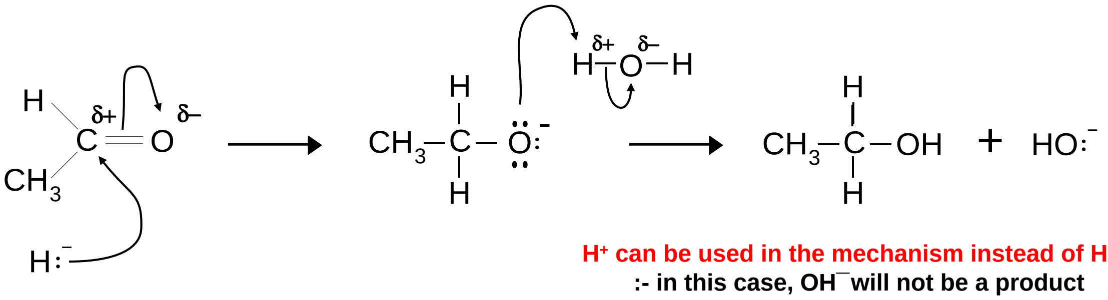
Product(s)

Aldehydes	REDUCED to **primary (1°) alcohols**
Ketones	REDUCED to **secondary (2°) alcohols**

Equation(s)

$$\mathbf{CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH}$$

$$\mathbf{CH_3COCH_3 + 2[H] \longrightarrow CH_3CHOHCH_3}$$



H^+ can be used in the mechanism instead of H_2O
:- in this case, OH^- will not be a product

Step 1 — *H^- is a nucleophile and attacks the $C^{\delta+}$*
An electron pair from the C=C moves onto O making it -ive

Step 2 — *A lone pair on oxygen removes a proton from water*
Overall, there is addition of hydrogen (reduction)

Q.6 *Draw a diagram to indicate the bonding in $NaBH_4$.*

Alternative Method

Reagent	hydrogen
Conditions	catalyst - nickel or platinum
Reaction type	Hydrogenation, reduction (NOT NUCLEOPHILIC ADITION)

Equation(s)

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

$$CH_3COCH_3 + H_2 \longrightarrow CH_3CHOHCH_3$$

Note **Hydrogen also reduces C=C bonds**

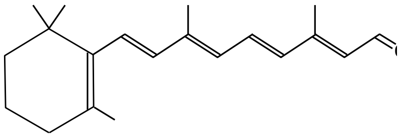
e.g. $CH_2{=}CHCHO + 2H_2 \longrightarrow CH_3CH_2CH_2OH$

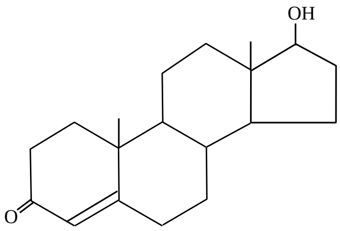
Q.7 *Why are C=C double bonds NOT reduced when $NaBH_4$ is used?*

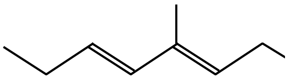
Q.8 *Draw structures of the organic products formed when the following are reduced using...*

$NaBH_4$ *H_2*

$CH_2=CHCH_2CHO$





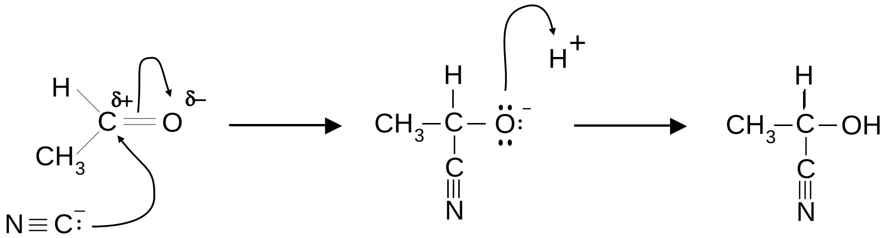


HCN	*Reagent*	potassium cyanide (HAZARDOUS) - followed by dilute acid
	Conditions	reflux
	Nucleophile	cyanide ion CN^-
	Product(s)	hydroxynitrile (cyanohydrin)

Equation $\mathbf{CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN}$

2-hydroxypropanenitrile

Mechanism Nucleophilic addition



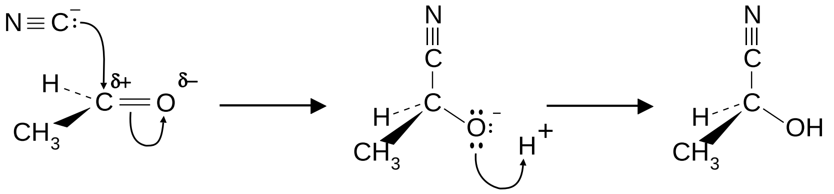
Step 1 CN^- acts as a nucleophile and attacks the slightly positive C
One of the C=O bonds breaks; a pair of electrons goes onto the O

Step 2 A pair of electrons is used to form a bond with H^+
Overall, there has been addition of HCN

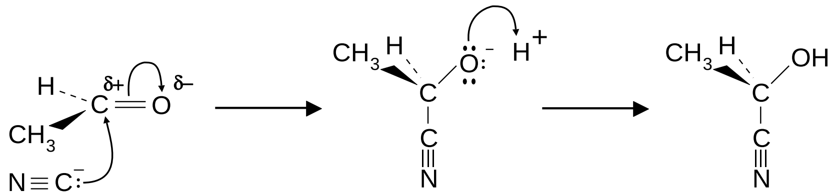
Notes

- HCN is a **weak acid ;** $\mathbf{HCN \rightleftharpoons H^+ + CN^-}$ **v. few CN^- ions** produced
- the reagent used is KCN (or NaCN) as more nucleophilic CN^- is produced
- watch out for the possibility of **optical isomerism in hydroxynitriles**

CN^- attacks from above



CN^- attacks from below



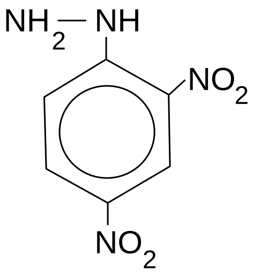
This is an excellent method for adding an extra C atom to a chain; the CN group can then be converted to carboxylic acids or amines

Hydrolysis (dilute acid) $\mathbf{C_2H_5CN + 2H_2O \longrightarrow C_2H_5COOH + NH_3}$

Reduction (H_2 / Ni cat.) $\mathbf{C_2H_5CN + 4[H] \longrightarrow C_2H_5CH_2NH_2}$

2,4-DINITROPHENYLHYDRAZINE

$C_6H_3(NO_2)_2NHNH_2$



Theory

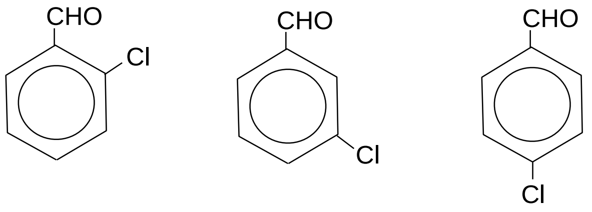
- reacts with carbonyl compounds (**aldehydes and ketones**)
- used as a **simple test for aldehydes and ketones**
- makes orange crystalline derivatives - *2,4-dinitrophenylhydrazones*
- derivatives have **sharp, well-defined melting points**
- also **used to characterise (identify) carbonyl compounds**.

Identification A simple way of characterising a compound (finding out what it is) is to measure

- the **melting point of a solid**
- the **boiling point of a liquid**

The following structural isomers have similar boiling points because of similar van der Waals forces and dipole-dipole interactions. They would be impossible to identify with any precision using boiling point determination.

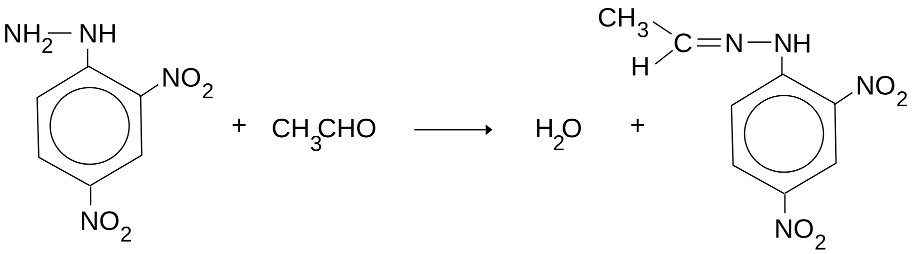
isomeric chlorophenylmethanals



Boiling point of compound	213°C	214°C	214°C
Melting point of 2,4-dnph derivative	209°C	248°C	265°C

By forming the 2,4-dinitrophenylhydrazone derivatives and taking the melting point of the **purified**, crystalline product, it is easy to identify the original compound.

Typical equation



Mechanism ADDITION-ELIMINATION

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Q.9 *Write out equations for the reactions between HCN and...*

- $C_2H_5CHO + HCN \longrightarrow$
- $CH_3COCH_3 + HCN \longrightarrow$
- *hexanal* + *HCN* ——>

Indicate which reactions give rise to optically active organic compounds?

Why is the addition of HCN such a useful reaction?

Q.10 *Suggest a method for differentiating between the following. What would be seen?*

- C_2H_5CHO *and* $C_2H_5COCH_3$
- $C_3H_7COCH_3$ *and* $C_2H_5COC_2H_5$
- *hexanal and hexanone*