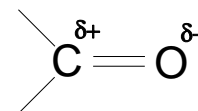


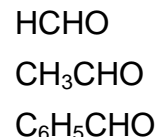
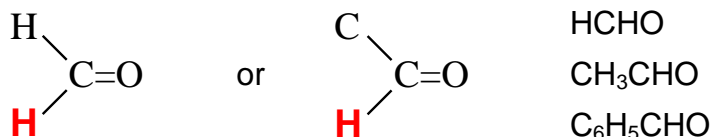
## CARBONYL COMPOUNDS - Aldehydes and Ketones

### Structure

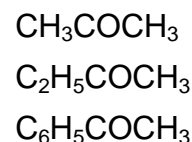
- carbonyl groups consists of a **carbon-oxygen double bond**
- the bond is **polar** due to the difference in electronegativity
- aldehydes / ketones differ in what is attached to the carbon



**ALDEHYDES** - at least one H attached to the carbonyl group



**KETONES** - two carbons attached to the carbonyl group



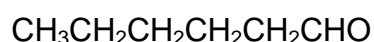
### Bonding

- the carbonyl carbon is sp<sup>2</sup> 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

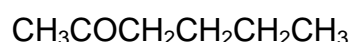


### Naming

- 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



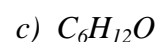
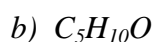
*hexanal*



*hexan-2-one*

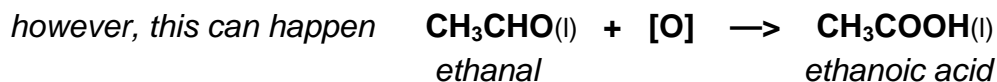
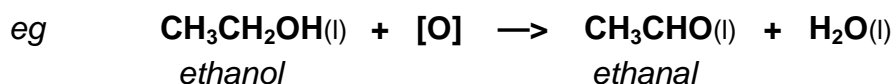
### Q.1

Draw structures for, and name, all the carbonyl compounds with molecular formulae;

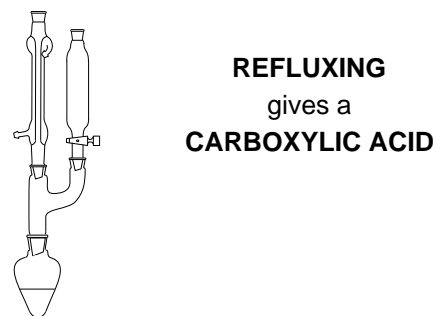
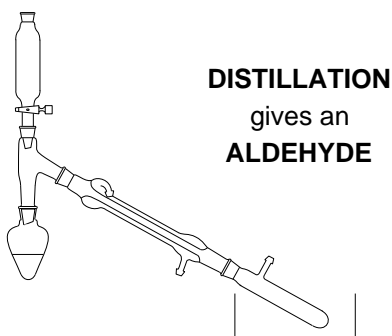


## Formation of carbonyl compounds from alcohols

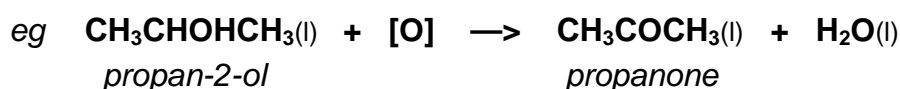
**Aldehydes** • Oxidation of primary (1°) alcohols - **risk of oxidation to acids**



- 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  $\text{K}_2\text{Cr}_2\text{O}_7$**
- 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



**Ketones** • Oxidation of secondary (2°) alcohols.



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

- $\text{C}_2\text{H}_5\text{CHO}$
- $\text{C}_2\text{H}_5\text{COCH}_3$
- hexanal
- 3-methylhexan-2-one
- 3-methylpentanal

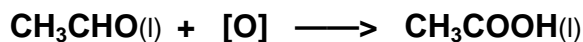
## CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

### 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.  $\text{RCHO(l)} + [\text{O}] \longrightarrow \text{RCOOH(l)}$



### KETONES

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



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

- $\text{C}_2\text{H}_5\text{CHO}$
- $\text{C}_2\text{H}_5\text{COCH}_3$
- *hexanal*
- *3-methylhexan-2-one*
- *3-methylpentanal*
- *cyclohexanone*

## IDENTIFYING A CARBONYL COMPOUND

- Methods*
- characteristically **strong peak at 1400-1600 cm<sup>-1</sup>** 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**
  - contains the diammine silver(I) ion -  $[\text{Ag}(\text{NH}_3)_2]^+$
  - acts as a mild oxidising agent and will oxidise aldehydes but not ketones
  - the silver(I) ion is reduced to silver  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$
  - the test is known as THE SILVER MIRROR TEST

- 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,  $\text{Cu}_2\text{O}$

The silver mirror test is the better alternative as it works with all aldehydes.

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

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

- $\text{C}_2\text{H}_5\text{OH}$
- $\text{C}_2\text{H}_5\text{COCH}_3$
- hexanal
- 3-methylhexan-2-one
- cyclohexanol
- 3-methylpentan-1-ol

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

- $\text{C}_2\text{H}_5\text{CHO}$
- $\text{C}_2\text{H}_5\text{COCH}_3$
- hexanal
- 3-methylhexan-2-one
- cyclohexanone
- 3-methylpentanal

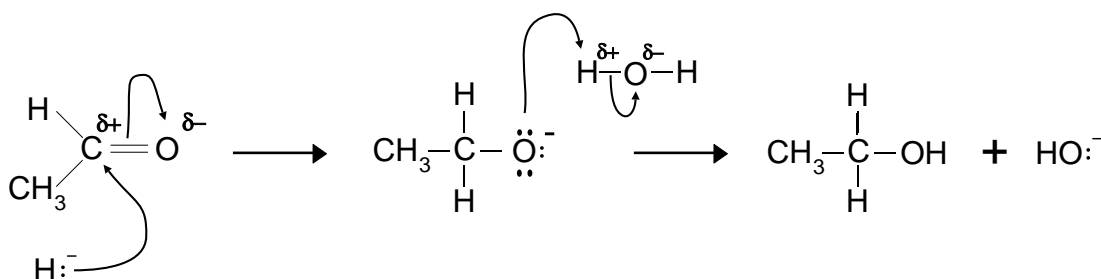
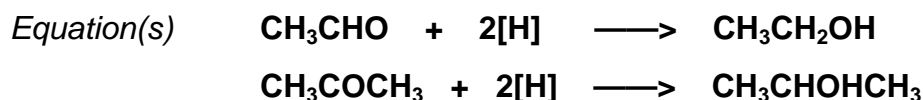
## NUCLEOPHILIC ADDITION REACTIONS

- 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

	<i>Bond</i>	<i>Polarity</i>	<i>Attacked by</i>	<i>Result</i>
Carbonyl	C=O	Polar	Nucleophiles	Addition
Alkene	C=C	Non-polar	Electrophiles	Addition

<b>REDUCTION</b>	<i>Reagent</i>	sodium tetrahydridoborate(III) (sodium borohydride), NaBH <sub>4</sub>
	<i>Conditions</i>	aqueous or alcoholic solution
	<i>Mechanism</i>	Nucleophilic addition (also reduction as it is addition of H <sup>-</sup> )
	<i>Nucleophile</i>	H <sup>-</sup> (hydride ion)

<i>Product(s)</i>	<b>Aldehydes</b>	REDUCED to <b>primary (1°) alcohols</b>
	<b>Ketones</b>	REDUCED to <b>secondary (2°) alcohols</b>

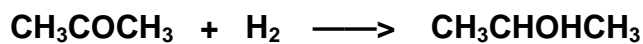


- Step 1** *H<sup>-</sup> is a nucleophile and attacks the C<sup>δ+</sup>  
An electron pair from the C=O moves onto O making it -ive*
- Step 2** *A lone pair on oxygen removes a proton from water  
Overall, there is addition of hydrogen (reduction)*

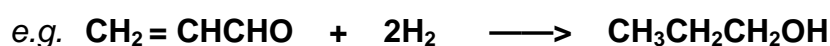
**Q.6** Draw a diagram to indicate the bonding in NaBH<sub>4</sub>.

**Alternative****Method**

<i>Reagent</i>	hydrogen
<i>Conditions</i>	catalyst - nickel or platinum
<i>Reaction type</i>	Hydrogenation, reduction



*Note*     Hydrogen also reduces C=C bonds

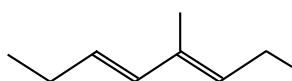
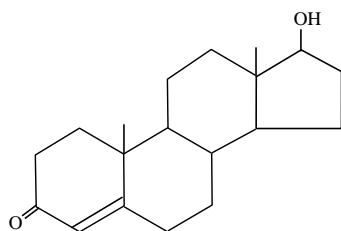
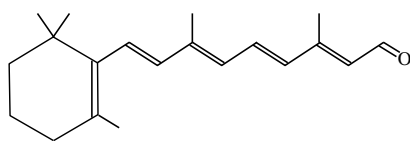


**Q.7** Why are C=C double bonds NOT reduced when  $\text{NaBH}_4$  is used?

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

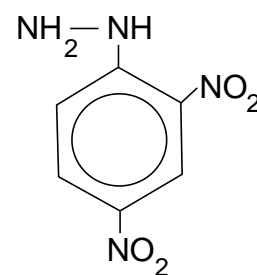
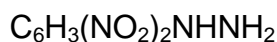
$\text{NaBH}_4$

$\text{H}_2$





## 2,4-DINITROPHENYLHYDRAZINE



### Theory

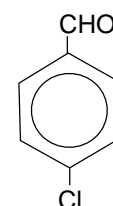
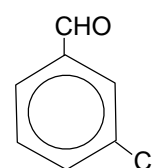
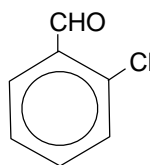
- reacts with carbonyl compounds (**aldehydes and ketones**)
- used as a **simple test for aldehydes and ketones**
- makes orange crystalline derivatives - *2,4-dinitrophenylhydrazones*
- derivatives have **sharp, well-defined melting points**
- also **used to characterise (identify) carbonyl compounds**.

*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

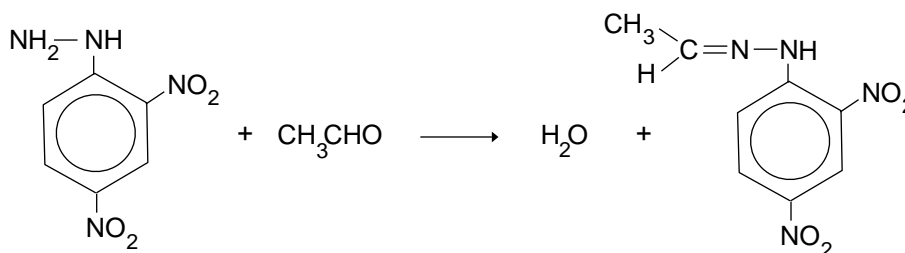
209°C

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



**Q.6** 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

**Q.5** Write out equations for the reactions between HCN and...

- $C_2H_5CHO + HCN \longrightarrow$
- $CH_3COCH_3 + HCN \longrightarrow$
- hexanal + HCN  $\longrightarrow$

Indicate which reactions give rise to optically active organic compounds?

Why is the addition of HCN such a useful reaction?