CARBONYL COMPOUNDS - Aldehydes and Ketones

Q.1 *Carbonyl compounds are formed by oxidation of alcohols;*

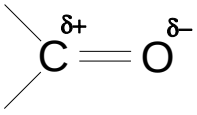
a) Which type of alcohol is oxidised to an aldehyde?

b) Which type of alcohol is oxidised to a ketone?

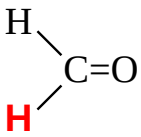
c) What compounds are formed when aldehydes are oxidised?

Structure

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



ALDEHYDES - attached to



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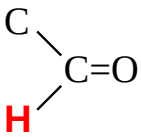


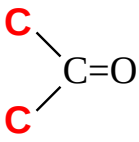
group

HCHO

CH_3CHO

C_6H_5CHO

KETONES - two carbons



e carbonyl group

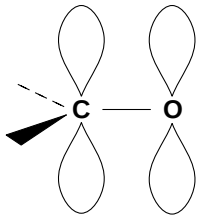
CH_3COCH_3

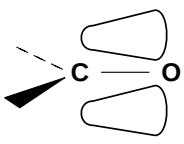
$C_2H_5COCH_3$

$C_6H_5COCH_3$

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





Formation

Aldehydes

- Oxidation of primary (1°) alcohols - **beware of further oxidation to acids**
- Reduction of carboxylic acids

Ketones

- Oxidation of secondary (2°) alcohols.

IDENTIFYING A CARBONYL COMPOUND

Methods

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

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

Differentiating between Aldehydes and Ketones

Differentiation

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

Tollen's Reagent

- **ammoniacal silver nitrate** - 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

  $$\mathbf{Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}}$$

- the test is known as THE SILVER MIRROR TEST

Fehling's Solution

- **contains copper(II) ions** complexed with tartrate ions giving a blue solution
- on warming, it will oxidise aliphatic (but not aromatic) aldehydes
- copper(II) is reduced and a **red precipitate** of copper(I) oxide, Cu_2O, is formed

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

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

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 can oxidise ketones to a mixture of carboxylic acids

ALDEHYDES **easily oxidised to acids** *e.g.*

$$\mathbf{RCHO_{(l)} + [O] \longrightarrow RCOOH_{(l)}}$$

$$\mathbf{CH_3CHO_{(l)} + [O] \longrightarrow CH_3COOH_{(l)}}$$

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

e.g. $\mathbf{C_2H_5COCH_2CH_{3(l)} + 3\,[O] \longrightarrow C_2H_5COOH_{(l)} + CH_3COOH_{(l)}}$

NUCLEOPHILIC ADDITION REACTIONS

Mechanism

- occurs with **both aldehydes and ketones**
- involves addition to the **polar** C=O double bond (oxygen has a greater electronegativity)
- attacked by nucleophiles at the positive carbon centre
- alkenes are non-polar and are attacked by electrophiles

Summary

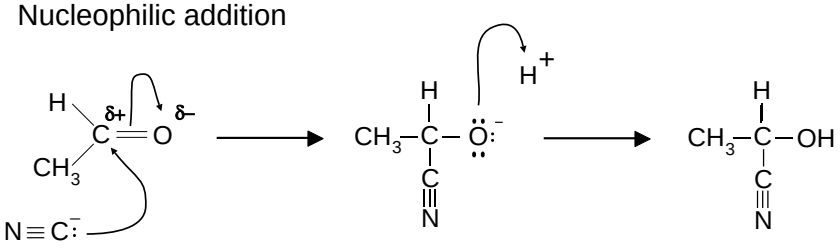
	Bond	*Polarity*	*Attacked by*	*Result*
Carbonyl	C=O	Polar	Nucleophiles	Addition
Alkene	C=C	Non-polar	Electrophiles	Addition

HCN

Reagent hydrogen cyanide - HCN (in the presence of KCN)
Conditions reflux in alkaline solution
Nucleophile cyanide ion CN^-
Product(s) hydroxynitrile (cyanohydrin)

Equation **CH_3CHO + HCN ——> $CH_3CH(OH)CN$** *2-hydroxypropanenitrile*

Mechanism Nucleophilic addition



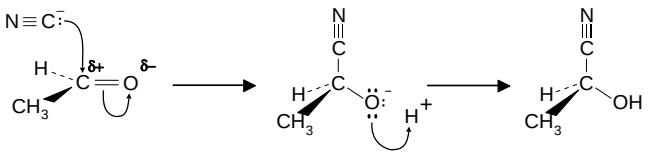
Step 1 CN^- acts as a nucleophile and attacks the slightly positive C
One of the C=O bonds breaks; a pair of electrons goes onto the O

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

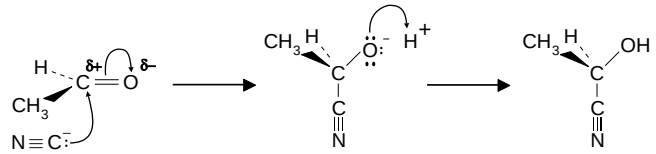
Notes

- HCN is a **weak acid ; HCN $\rightleftharpoons$ H^+ + CN^-** **few CN^- ions** produced
- the reaction is catalysed by alkali which helps produce more of the nucleophilic CN^-
- watch out for the possibility of **optical isomerism in hydroxynitriles**

CN^- attacks from above



CN^- attacks from below



- hydrolysis of the CN group to COOH is possible

Q.2 *Write out equations for the reactions between HCN and...*

- C_2H_5CHO + HCN ——>
- CH_3COCH_3 + HCN ——>
- hexanal + HCN ——>

Indicate which reactions give rise to optically active organic compounds?

Why is the addition of HCN such a useful reaction?

REDUCTION

Reagent sodium tetrahydridoborate(III) (sodium borohydride), $NaBH_4$

Conditions aqueous or alcoholic solution

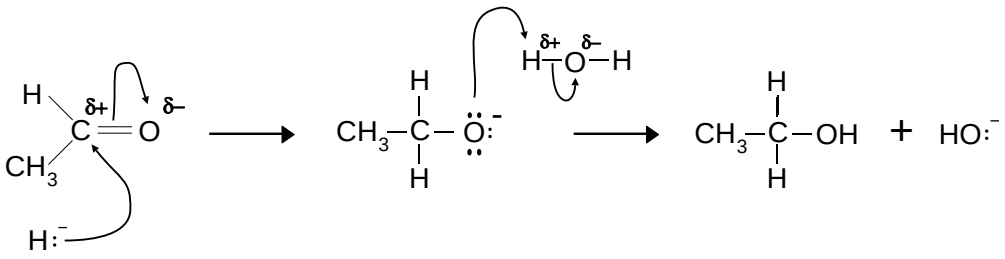
Mechanism Nucleophilic addition (also reduction as it is addition of H^-)

Nucleophile H^- (hydride ion)

Product(s) Alcohols :- Aldehydes are REDUCED to primary (1°) alcohols.
Ketones are REDUCED to secondary (2°) alcohols.

Equation(s) **$CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$**

$CH_3COCH_3 + 2[H] \longrightarrow CH_3CHOHCH_3$



Notes The water provides a proton

$NaBH_4$ doesn't reduce C=C bonds. WHY?

e.g. **$CH_2 = CHCHO + 2[H] \longrightarrow CH_2 = CHCH_2OH$**

Q.3 *Draw a diagram to indicate the bonding in $NaBH_4$.*
What shape is it ?

Alternative Method

Reagent hydrogen

Conditions catalyst - nickel or platinum

Reaction type Hydrogenation, reduction

Product(s) Alcohols :- Aldehydes are REDUCED to primary (1°) alcohols.
Ketones are REDUCED to secondary (2°) alcohols.

Equation(s) $CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$

$CH_3COCH_3 + H_2 \longrightarrow CH_3CHOHCH_3$

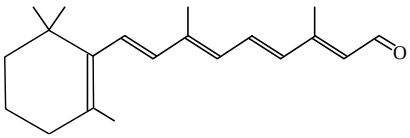
Note Hydrogen also reduces C=C bonds

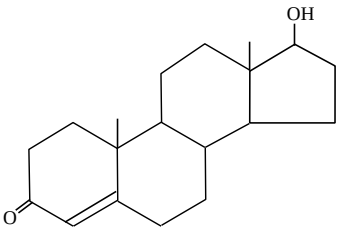
e.g. $CH_2 = CHCHO + 2H_2 \longrightarrow CH_3CH_2CH_2OH$

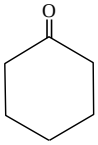
Q.4 *Draw structures of the organic products formed when the following are reduced using...*

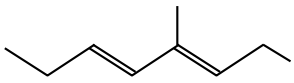
$NaBH_4$ H_2

$CH_2 = CHCH_2CHO$



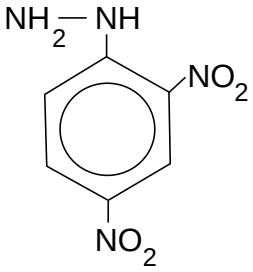






2,4-DINITROPHENYLHYDRAZINE

$C_6H_3(NO_2)_2NHNH_2$



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**.

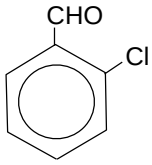
Identification

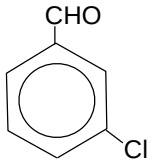
A simple way of characterising a compound (finding out what it is) is to measure...

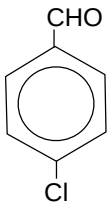
- the **melting point of a solid**
- the **boiling point of a liquid**

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



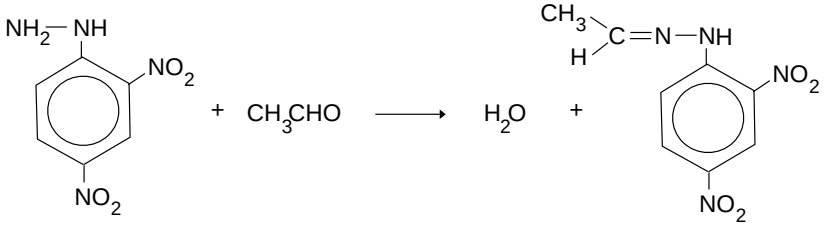




Boiling point of compound	213°C	214°C	214°C
Melting point of 2,4-dnph derivative	209°C	248°C	265°C

By forming the 2,4-dinitrophenylhydrazone derivatives and taking the melting point of the crystalline product, it will be easy to identify the unknown original carbonyl compound.

Typical equation



Mechanism

ADDITION-ELIMINATION