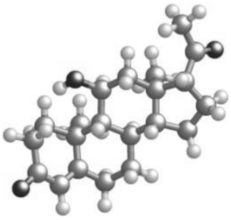

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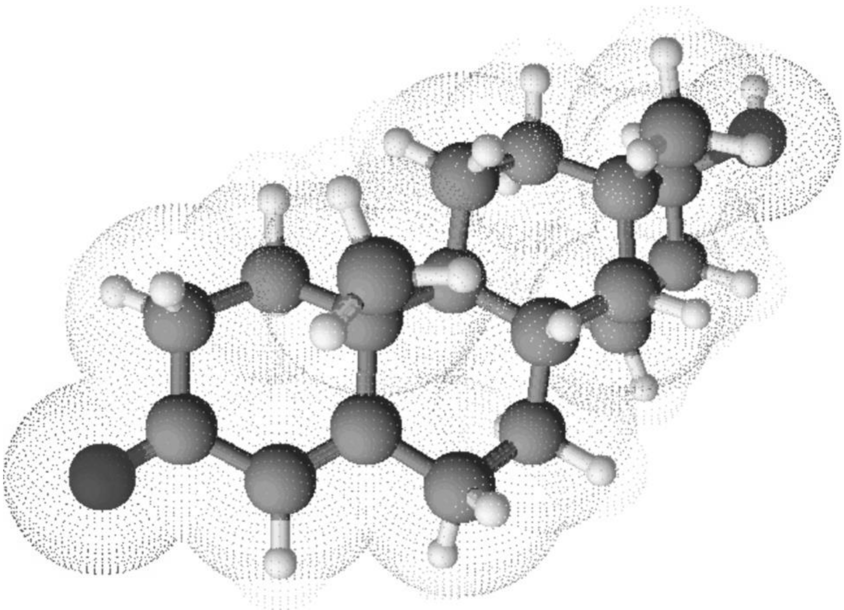
The Chemistry of Aldehydes and Ketones

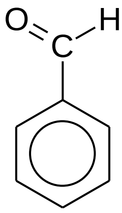
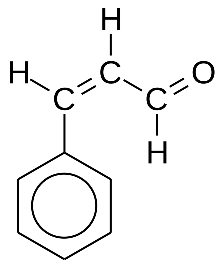
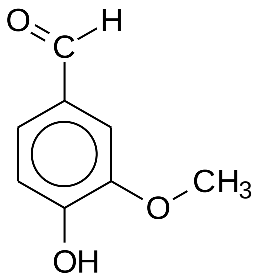
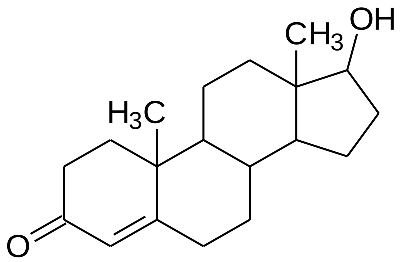


This booklet covers the essential chemistry of aldehydes and ketones. It is presented in an open learning format which students can work through at their own pace during private study or as part of a formal lesson. Contained in this booklet is a mixture of information, questions and model answers.

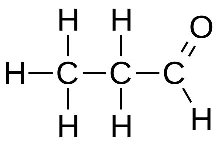
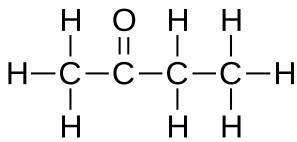
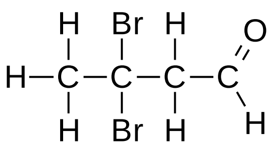
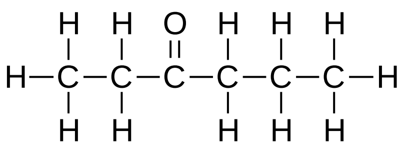
Contents

The Chemistry of Aldehydes and Ketones

● **Question One – Introduction:** Study the structural formulae of the aldehydes and ketones presented below. By using a highlighter pen, or some other suitable method, identify the different functional groups belonging to the homologous series of aldehydes and the homologous series of ketones. Which other functional groups can you identify?

 **a)** *Benzaldehyde*: A derivative of this compound gives almonds their characteristic flavour.	 **b)** *3-phenylpropenal*: This compound is partly responsible for the characteristic flavour of cinnamon.
 **c)** *Vanillin*: This compound is partly responsible for the characteristic flavour of vanilla.	 **d)** *Testosterone*: This steroidal hormone is responsible for the development of secondary sexual characteristics in men.

● **Question Two – Nomenclature:** Name the aldehydes and ketones whose structural formulae are given below:

 **a)** Name: ………………………………………………	 **b)** Name: ………………………………………………
 **c)** Name: ………………………………………………	 **d)** Name: ………………………………………………

● **Question Three – Preparation of Aldehydes:** Aldehydes are synthesised in the laboratory by oxidising *primary alcohols* using acidified potassium dichromate(VI) as the oxidising agent.

a) What do you understand by the term *primary alcohol*?

………

………

b) Complete the ionic half-equation shown below to describe how the acidified dichromate(VI) ion functions as an oxidising agent:

$$Cr_2O_7^{2-}{}_{(aq)} \ + \ \ldots\ldots\ldots\ldots \ + \ \ldots\ldots\ldots\ldots \ \rightarrow \ 2Cr^{3+}{}_{(aq)} \ + \ \ldots\ldots\ldots\ldots$$

c) Complete the ionic half-equation shown below to describe the oxidation of ethanol to ethanal:

$$CH_3CH_2OH_{(aq)} \ \rightarrow \ CH_3CHO_{(aq)} \ + \ \ldots\ldots\ldots\ldots \ + \ \ldots\ldots\ldots\ldots$$

d) Combine your answers to **Question Three a)** and **b)** together to create an ionic equation that accurately describes the oxidation of ethanol to ethanal using acidified dichromate(VI) ions:

………

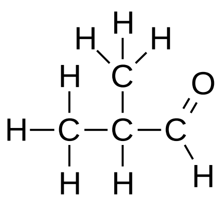
e) Aldehydes can be oxidised further to form carboxylic acids. Identify at least *two* different precautions that can be taken in the laboratory to ensure that, once the ethanol has been oxidised to ethanal, it is not oxidised further to form ethanoic acid:

● ……

● ……

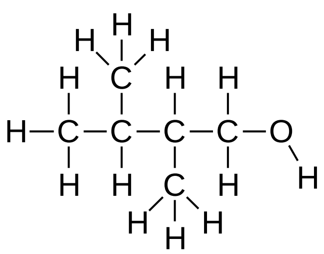
f) Give the structural formula and systematic name of the primary alcohol that can be oxidised to produce 2-methylpropanal as the reaction product:

→



Name: ………………………………… 2-methylpropanal

g) Give the structural formula and systematic name of the aldehyde that is produced when 2,3-dimethylbutan-1-ol is oxidised using acidified potassium dichromate(VI) as the oxidising agent:



→

2,3-dimethylbutan-1-ol Name: …………………………………

● **Question Four – Preparation of Ketones:** Ketones are synthesised in the laboratory by oxidising *secondary alcohols* using acidified potassium manganate(VII) as the oxidising agent.

a) What do you understand by the term *secondary alcohol*?

………

………

b) Complete the ionic half-equation shown below to describe how the acidified manganate(VII) ion functions as an oxidising agent:

$MnO_4^-{}_{(aq)}$ + ………… + ………… → $Mn^{2+}{}_{(aq)}$ + …………

c) Complete the ionic half-equation shown below to describe the oxidation of propan-2-ol to propanone:

$CH_3CH(OH)CH_{3(aq)}$ → $CH_3(CO)CH_{3(aq)}$ + ………… + …………

d) Combine your answers to **Question Three a)** and **b)** together to create an ionic equation that accurately describes the oxidation of propan-2-ol to propanone using acidified manganate(VII) ions:

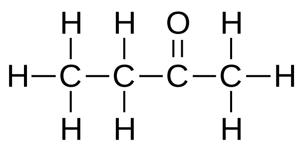
………

e) Explain why it is *extremely difficult* for a ketone to be oxidised to form a carboxylic acid:

………

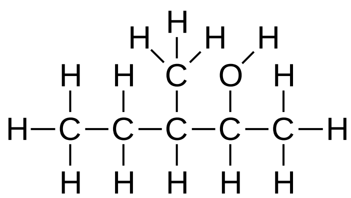
………

f) Give the structural formula and systematic name of the secondary alcohol that can be oxidised to produce butanone as the reaction product:

→ 

Name: ……………………………… Butanone

g) Give the structural formula and systematic name of the ketone that is produced when 3-methylpentan-2-ol is oxidised using acidified potassium manganate(VII) as the oxidising agent:

 →

3-methylpentan-2-ol Name: ………………………………

● **Question Five – Qualitative Test for Aldehydes and Ketones:** Aldehydes and ketones both react with the reagent *2,4-dinitrophenylhydrazine* to form an orange precipitate known as a *hydrazone*. This can be used as a qualitative test to distinguish aldehydes and ketones from other homologous series of organic compounds. In **Figure 1**, the ketone *propanone* reacts with 2,4-dinitrophenylhydrazone to form an orange precipitate of the hydrazone *propanone 2,4-dinitrophenylhydrazone*:

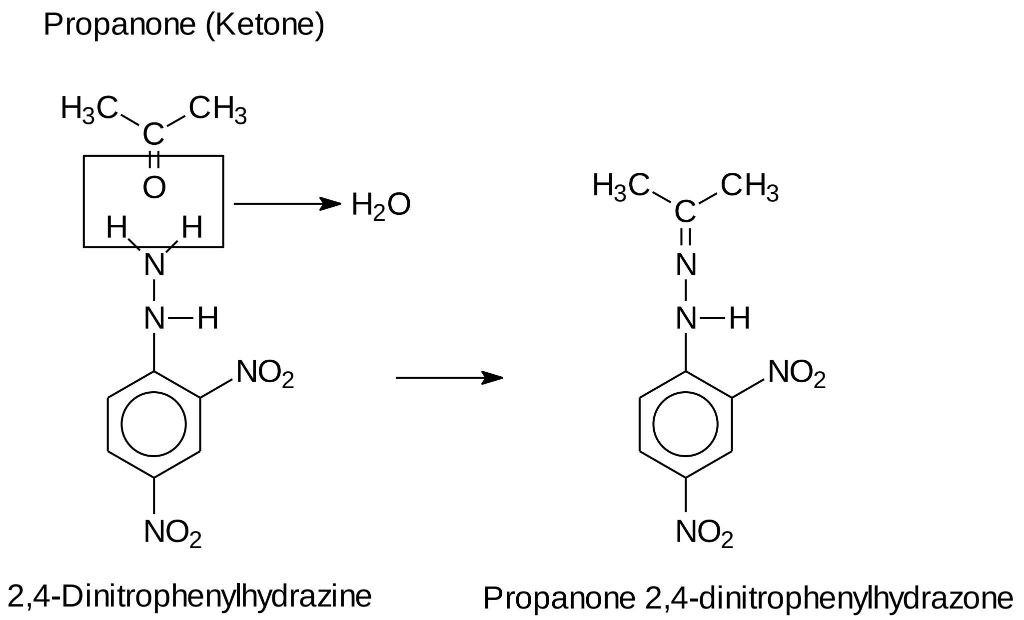


Figure 1: The formation of an orange precipitate upon the addition of 2,4-dinitrophenylhydrazine allows for the qualitative identification of aldehydes and ketones.

a) Explain why the reaction shown in **Figure 1** can be considered to be a *condensation reaction*:

……

……

b) Give the structural formula and name of the hydrazone that is formed when 2,4-dinitrophenylhydrazine reacts with each one of the following aldehydes and ketones:

Butanal:	Cyclopentanone:	2-methylpentanal:
Name: ……………………………	Name: ……………………………	Name: ……………………………

● **Question Six – Qualitative Test for Aldehydes:** Aldehydes can be oxidised to form carboxylic acids.

a) Complete the ionic half-equation shown below to describe the oxidation of propanal to propanoic acid:

$$CH_3CH_2CHO_{(aq)} + \ldots\ldots\ldots\ldots \rightarrow CH_3CH_2COOH_{(aq)} + \ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots$$

b) Using either acidified dichromate(VI) ions (**Question Three b**) or acidified manganate(VII) ions (**Question Four b**) as the oxidising agent for the reaction, write an ionic equation that accurately describes the oxidation of propanal to propanoic acid:

……

● The fact that aldehydes can be oxidised to form carboxylic acids, while ketones cannot, can be used to distinguish between aldehydes and ketones in qualitative analysis. There are two important reagents that function as mild oxidising reagents in organic chemistry; *Fehling's Reagent* and *Tollen's Reagent*. During the redox reaction that converts the aldehyde into a carboxylic acid, the mild oxidising agent undergoes an obvious change in its appearance, thus indicating that a chemical reaction is taking place, which in turn infers that an aldehyde is present in the reaction mixture.

c) Fehling's Reagent: The test reagent is a complex of copper(II) ions (Cu^{2+}) in an aqueous solution of ammonia. When warmed with an aldehyde, the blue solution of copper(II) ions is reduced to form a brick red precipitate of copper(I) oxide while the aldehyde is oxidised to a carboxylic acid. No reaction is observed when Fehling's reagent is warmed with a ketone. Because ketones cannot be oxidised, the copper(II) ions are not reduced to copper(I) ions.

i) Write an ionic half-equation to describe the oxidation of ethanal to ethanoic acid in an alkaline medium:

……

ii) Write an ionic half-equation to describe the reduction of copper(II) ions to copper(I) oxide in an alkaline medium:

……

iii) By combining the previous two half-equations together, write the ionic equation for the redox reaction that takes place between ethanal and ammoniacal cooper(II) ions in an alkaline medium:

……

d) Tollen's Reagent: This is also known as the *Silver Mirror Test*. The test reagent is a complex of silver ions (Ag^{+}) in an aqueous solution of ammonia. When warmed with an aldehyde, the silver ions are reduced to elemental silver while the aldehyde is oxidised to a carboxylic acid. As a consequence, a layer of silver is deposited on the inside of the test tube (*i.e.* a silver mirror is formed). No reaction is observed when Tollen's reagent is warmed with a ketone. Because ketones cannot be oxidised, the silver ions are not reduced to elemental silver.

i) Write an ionic half-equation to describe the oxidation of butanal to butanoic acid in an alkaline medium:

……

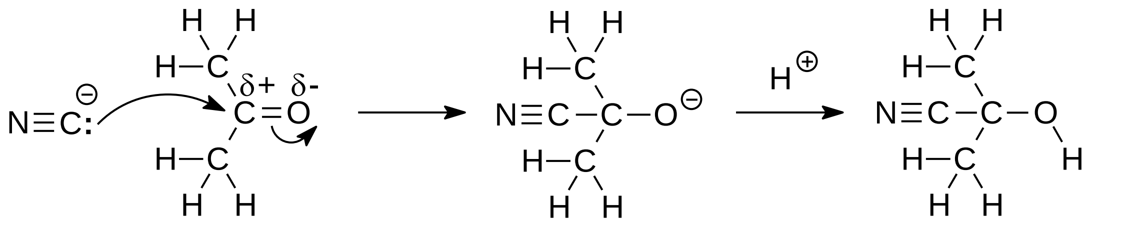
ii) Write an ionic half-equation to describe the reduction of silver ions to elemental silver:

……

iii) By combining the previous two half-equations together, write the ionic equation for the redox reaction that takes place between butanal and ammoniacal silver ions in an alkaline medium:

……

● **Question Seven – Essential Reactions:** Due to a difference in electronegativity values between carbon (2.5) and oxygen (3.5) the carbonyl group of both aldehydes and ketones is *polar*: $^{\delta+}C{=}O^{\delta-}$. As a consequence, aldehydes and ketones are both susceptible to attack by *nucleophiles*, undergoing *addition reactions* which are of great use in organic synthesis. **Figure 2** shows propanone undergoing nucleophilic addition with a cyanide anion, forming 2-hydroxy-2-methylpropanenitrile as the reaction product:



Cyanide Anion | Propanone | Intermediate | 2-hydroxy-2-methyl-propanenitrile

Figure 2: Propanone undergoes nucleophilic addition with the cyanide anion to form 2-hydroxy-2-methylpropanenitrile as the reaction product.

a) Give the structural formulae and names of the reaction products that are formed when butanal reacts with each one of the following nucleophiles:

Cyanide anion C≡N:⁻ (From KCN)	Hydride anion H:⁻ (From NaH)	Methylmagnesium iodide $H_3C^{\delta-}{-}Mg^{\delta+}{-}I^{\delta-}$
Name: ………………………………	Name: ………………………………	Name: ………………………………

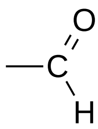
b) Give the structural formula and name of the reaction product that is formed when ethylmagnesium bromide, $H_3CH_2C^{\delta-}{-}Mg^{\delta+}{-}Br^{\delta-}$, reacts with carbon dioxide:

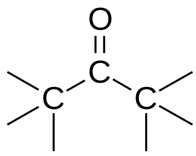
c) Methylmagnesium iodide and ethylmagnesium bromide are known a *Grignard reagents* in honour of the French Chemist, Victor Grignard, who was awarded the Nobel Prize for Chemistry in 1912 for their discovery. Briefly explain why Grignard reagents are of great importance in organic synthesis:

……

<u>**Answers to Questions**</u>

• Question One:

The aldehyde functional group is: 

The ketone functional group is: 

• Question Two:

a) Propanal. **b)** Butanone. **c)** 3,3-dibromobutanal. **d)** Hexan-3-one.

• Question Three:

a) In a *primary alcohol*, the carbon atom to which the –OH group is bonded is *directly* bonded to only *one* other carbon atom, *e.g.* propan-1-ol, $CH_3CH_2CH_2OH$.

b) $Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$

c) $CH_3CH_2OH_{(aq)} \rightarrow CH_3CHO_{(aq)} + 2H^+{}_{(aq)} + 2e^-$ (×3)

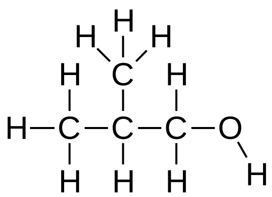
d) $Cr_2O_7^{2-}{}_{(aq)} + 3CH_3CH_2OH_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} + 3CH_3CHO_{(aq)} + 7H_2O_{(l)} + 6H^+{}_{(aq)} + 6e^-$

$Cr_2O_7^{2-}{}_{(aq)} + 3CH_3CH_2OH_{(aq)} + 8H^+{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3CH_3CHO_{(aq)} + 7H_2O_{(l)}$

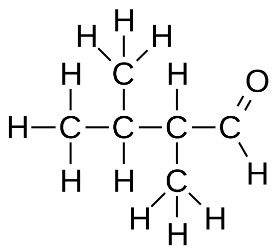
e) → Use a mild oxidising agent, *e.g.* acidified potassium dichromate(VI).

→ Use an excess of the alcohol, *i.e.* ensure that the oxidising agent is the limiting reagent.

→ Once it has been formed, remove the aldehyde from the reaction vessel by distillation.

f) 

2-methylpropan-1-ol

g) 

2,3-dimethylbutanal

• Question Four:

a) In a *secondary alcohol*, the carbon atom to which the –OH group is bonded is *directly* bonded to *two* other carbon atoms, *e.g.* butan-2-ol, $CH_3CH(OH)CH_2CH_3$.

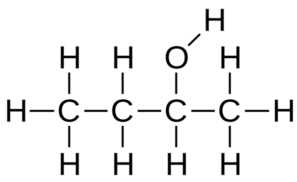
b) $MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$ (×2)

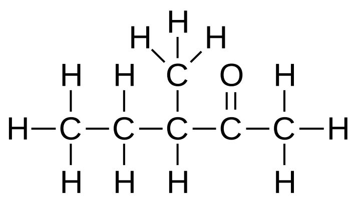
c) $CH_3CH(OH)CH_{3(aq)} \rightarrow CH_3(CO)CH_{3(aq)} + 2H^+{}_{(aq)} + 2e^-$ (×5)

d) $2MnO_4^-{}_{(aq)} + 5CH_3CH(OH)CH_{3(aq)} + 16H^+{}_{(aq)} + 10e^- \rightarrow 2Mn^{2+}{}_{(aq)} + 5CH_3(CO)CH_{3(aq)} + 8H_2O_{(l)} + 10H^+{}_{(aq)} + 10e^-$

$2MnO_4^-{}_{(aq)} + 5CH_3CH(OH)CH_{3(aq)} + 6H^+{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 5CH_3(CO)CH_{3(aq)} + 8H_2O_{(l)}$

e) The oxidation of a ketone to a carboxylic acid requires fission of a carbon-to-carbon single covalent bond. Due to the relatively high C–C bond enthalpy (348 kJ mol^{-1}), fission of the carbon-to-carbon single covalent bond is difficult, and so the ketone is resistant to oxidation.

f) 

g) 

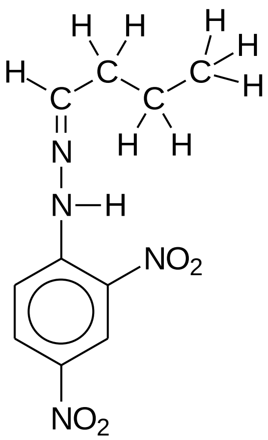
Butan-2-ol

3-methylpentan-2-one

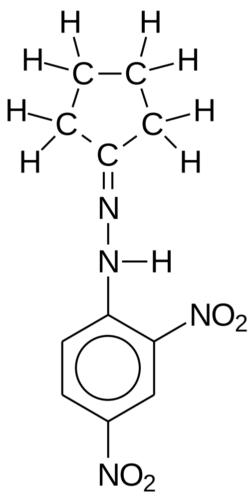
- **Question Five:**

a) In organic chemistry, any reaction that results in the formation of a simple inorganic compound (*e.g.* HCl, H_2O or NH_3) as a side-product is considered to be a condensation reaction.

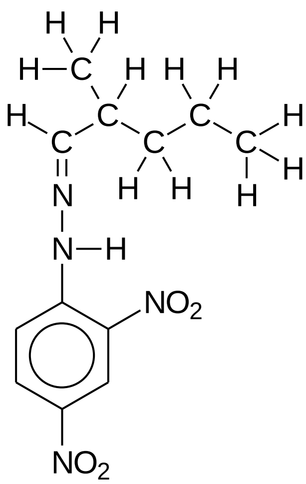
b)



Butanal 2,4-dinitrophenylhydrazone



Cyclopentanone
2,4-dinitrophenylhydrazone



2-methylpentanal
2,4-dinitrophenylhydrazone

- **Question Six:**

a) $CH_3CH_2CHO_{(aq)} + H_2O_{(l)} \rightarrow CH_3CH_2COOH_{(aq)} + 2H^+_{(aq)} + 2e^-$

$Cr_2O_7{}^{2-}{}_{(aq)} + 3CH_3CH_2CHO_{(aq)} + 3H_2O_{(l)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 3CH_3CH_2COOH_{(aq)} + 7H_2O_{(l)} + 6H^+_{(aq)} + 6e^-$

$Cr_2O_7{}^{2-}{}_{(aq)} + 3CH_3CH_2CHO_{(aq)} + 8H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3CH_3CH_2COOH_{(aq)} + 4H_2O_{(l)}$

$2MnO_4{}^-{}_{(aq)} + 5CH_3CH_2CHO_{(aq)} + 5H_2O_{(l)} + 16H^+_{(aq)} + 10e^- \rightarrow 2Mn^{2+}_{(aq)} + 5CH_3CH_2COOH_{(aq)} + 8H_2O_{(l)} + 10H^+_{(aq)} + 10e^-$

$2MnO_4{}^-{}_{(aq)} + 5CH_3CH_2CHO_{(aq)} + 6H^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 5CH_3CH_2COOH_{(aq)} + 3H_2O_{(l)}$

b) **i)** $CH_3CHO_{(aq)} + 2OH^-_{(aq)} \rightarrow CH_3COOH_{(aq)} + H_2O_{(l)} + 2e^-$

ii) $2Cu^{2+}_{(aq)} + 2OH^-_{(aq)} + 2e^- \rightarrow Cu_2O_{(s)} + H_2O_{(l)}$

iii) $CH_3CHO_{(aq)} + 2Cu^{2+}_{(aq)} + 4OH^-_{(aq)} + 2e^- \rightarrow CH_3COOH_{(aq)} + Cu_2O_{(s)} + 2H_2O_{(l)} + 2e^-$

$CH_3CHO_{(aq)} + 2Cu^{2+}_{(aq)} + 4OH^-_{(aq)} \rightarrow CH_3COOH_{(aq)} + Cu_2O_{(s)} + 2H_2O_{(l)}$

c) **i)** $C_3H_7CHO_{(aq)} + 2OH^-_{(aq)} \rightarrow C_3H_7COOH_{(aq)} + H_2O_{(l)} + 2e^-$

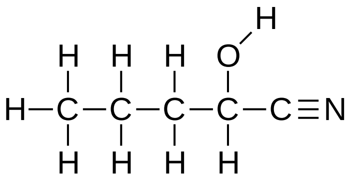
ii) $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ $(\times 2)$

iii) $C_3H_7CHO_{(aq)} + 2Ag^+_{(aq)} + 2OH^-_{(aq)} + 2e^- \rightarrow C_3H_7COOH_{(aq)} + 2Ag_{(s)} + H_2O_{(l)} + 2e^-$

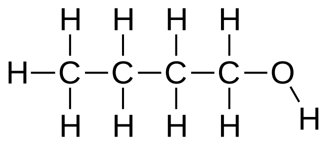
$C_3H_7CHO_{(aq)} + 2Ag^+_{(aq)} + 2OH^-_{(aq)} \rightarrow C_3H_7COOH_{(aq)} + Ag_{(s)} + H_2O_{(l)}$

• Question Seven:

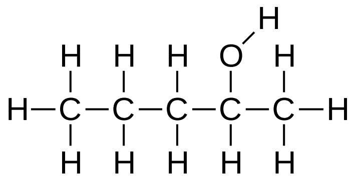
a)



2-hydroxypentanenitrile

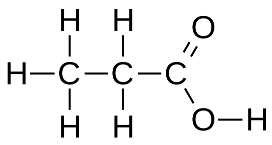


Butan-1-ol



Pentan-2-ol

b)



Propanoic acid

c) Grignard reagents allow the formation of carbon-to-carbon single covalent bonds. This is a very important process when synthesising large, complex organic molecules from relatively simple reagents.

Worksheet by Dr. Chris Slatter