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Level: CIE A & AS Level Chemistry (9701)

Subject: Chemistry

Topic: A & AS Chemistry

Type: Mark Scheme

2002

XVIII

1583

Chemistry CIE A & AS Level
To be used for all exam preparation for 2025+

CHEMISTRY

A & AS

Key skills



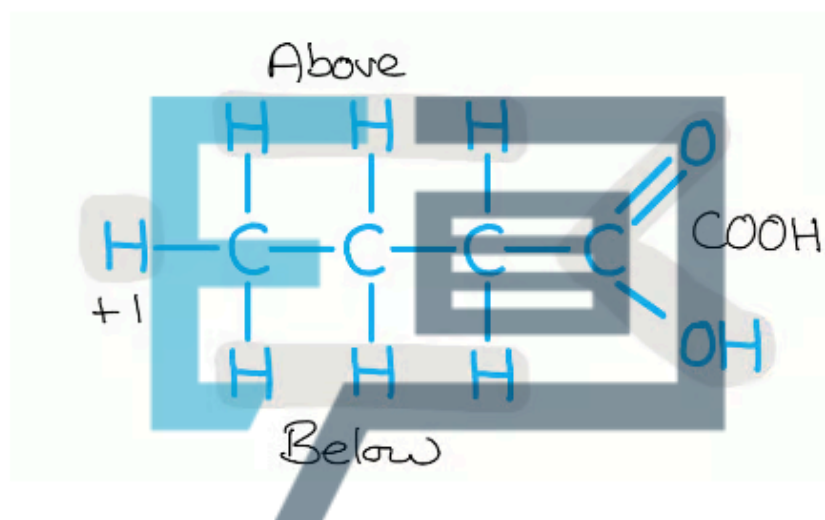
Mark Scheme

Answer 1.

a) The general formula of a carboxylic acid is:

- $C_nH_{2n+1}COOH$; [1 mark]

[Total: 1 mark]



- For every carbon in the hydrocarbon chain
 - There is a hydrogen above
 - There is a hydrogen below
 - There is also one hydrogen at the end of the chain
 - This means we have $2n+1$ hydrogen for n carbons
 - This is the C_nH_{2n+1} portion of the general formula
- There is also the COOH at the other end of the chain
 - So, overall we have $C_nH_{2n+1}COOH$

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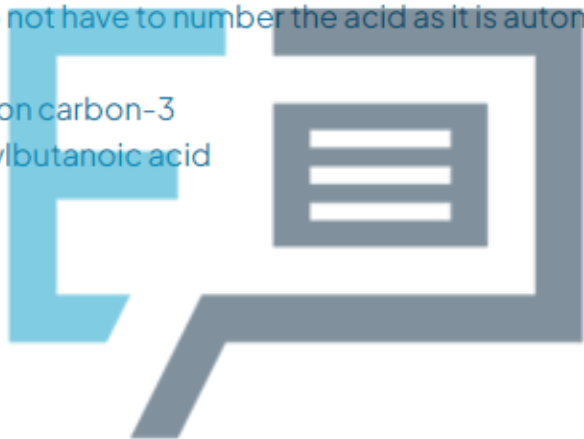


b) The carboxylic acid shown in Fig.1.1 is:

- 3-methylbutanoic acid; [1 mark]

[Total: 1 mark]

- The longest carbon chain is 4 carbons long
 - Therefore, butan- stem
- There is a carboxylic acid
 - Therefore, butanoic acid
 - **Remember:** You do not have to number the acid as it is automatically carbon-1, as this is the priority group
- There is a methyl group on carbon-3
 - Therefore, 3-methylbutanoic acid



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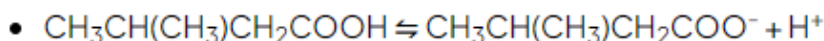
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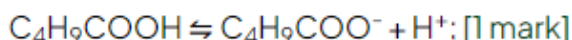


c)

i) The equation to show the dissociation of the acid is:



OR



ii) The position of the equilibrium lies:

- To the left; [1 mark]
- (This tells us that it is a) weak acid; [1 mark]

[Total: 3 marks]

- All acids dissociate
 - Strong acids can fully dissociate into their component ions and the equilibrium lies to the right
 - For sulfuric acid, this is a two-step process
 - Step 1 is the full dissociation of the sulfuric acid to HSO_4^-
 - $\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}^+$
 - Step 2 is an equilibrium as the HSO_4^- acts as a weak acid
 - $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$
 - Carboxylic acids such as CH_3COOH are weak acids - they do **not** fully dissociate and the equilibrium lies to the left

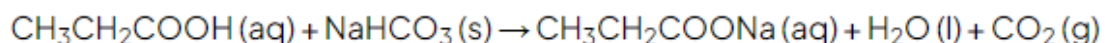


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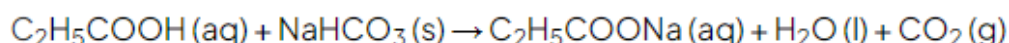
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d) The balanced symbol equation, including state symbols, for the reaction of propanoic acid with sodium hydrogen carbonate powder is:



OR



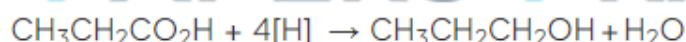
- Correct formulae of reactants; [1 mark]
- Correct formulae of products; [1 mark]
- Correct state symbols; [1 mark]

[Total: 3 marks]

- **Remember:** The reaction of an acid with a carbonate/hydrogen carbonate forms the salt plus water plus carbon dioxide
- You would be expected to know or deduce the chemical formulae and state symbols for all of the chemicals in this reaction

Answer 2.

a) An equation for reaction 1, using [H] to represent the reducing agent is:



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- Correct reactants; [1 mark]
- Correct products; [1 mark]

[Total: 2 marks]

- Reaction 1 shows the reduction of propanoic acid
- The reduction of this alcohol will produce propanol and water



b)

i) Reaction 2 is:

- Oxidation; [1 mark]

ii) A suitable reagent and conditions for reaction 2 is:

- Acidified potassium dichromate(VI) $K_2Cr_2O_7$ / acidified potassium manganate(VII) / $KMnO_4$; [1 mark]
- Reflux; [1 mark]

[Total: 3 marks]

- You can see that oxygen has been gained in the formula for the propanoic acid compared to propanol
- Acidified potassium dichromate(VI) and acidified potassium manganate(VII) are common oxidising agents you should be aware of
- They will be reduced as they oxidise the propanol

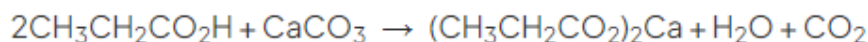
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c) An equation for the reaction of propanoic acid with calcium carbonate, CaCO_3 is:



- Correct equation; [1 mark]
- Correctly balanced; [1 mark]

[Total: 2 marks]

- Propanoic acid reacts like any other acid
 - Acid + metal carbonate \rightarrow salt + water + carbon dioxide
 - The salt formed is calcium propanoate

d)

i) A suitable reagent and conditions for reaction 3 is:

- $\text{CH}_3\text{CO}_2\text{H}$; [1 mark]
- Warm / hot / higher temperature / heat / reflux **AND** concentrated sulfuric acid; [1 mark]

ii) The other product of reaction 3 is:

- Water; [1 mark]

[Total: 3 marks]

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• Reaction 3 shows propanol forming propyl ethanoate, an ester

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- An ester is formed when an alcohol reacts with a carboxylic acid
 - The first part of the name comes from the alcohol, and the second part from the carboxylic acid
 - To form propyl ethanoate, ethanoic acid is therefore the reagent needed
 - Esterification reactions are known as condensation reactions as they lose a molecule of water when the ester linkage forms



Answer 3.

a)

i) The molecular formula of 2-ethyl-3-methylbutanoic acid is:

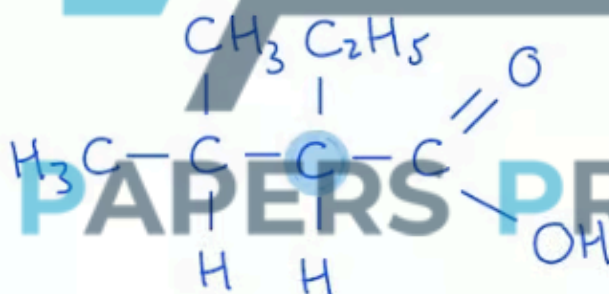
- $C_7H_{14}O_2$; [1 mark]

ii) The number of chiral carbon atoms present in a molecule of 2-ethyl-3-methylbutanoic acid is:

- One; [1 mark]

[Total: 2 marks]

- A chiral carbon is one attached to four different atoms / groups of atoms
- It is useful to draw the displayed formula for the structure so you can identify chiral carbons more clearly:



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b)

i) The reagents used and the colour change that would be seen is:

Alternative 1:

- Acidified $K_2Cr_2O_7$ / acidified potassium dichomate (VII); [1 mark]
- From orange; [1 mark]
- To green; [1 mark]

Alternative 2:

- Acidified $KMnO_4$ / potassium manganate (VI); [1 mark]
- From purple; [1 mark]
- To colourless; [1 mark]

ii) The main organic impurity present in the sample of the acid could be:

- 2-ethyl-3-methylbutanal / $(CH_3)_2CHCH(C_2H_5)CHO$; [1 mark]
- Because partial oxidation of alcohol will form an aldehyde; [1 mark]

iii) The apparatus used should be:

- Reflux
AND

Because the alcohol must be fully oxidised; [1 mark]

[Total: 6 marks]

- **Remember:** The oxidising agents used to convert the alcohol to a carboxylic acid, are themselves reduced which results in the colour changes
- Questions about these colour changes occur frequently so make sure you learn them the right way around

c) The colour change you would see if this were heated with the reagents you have given in (b)(i) is:

- None / no colour change; [1 mark]
- (Because) the alcohol is tertiary; [1 mark]
- So cannot be oxidised; [1 mark]

[Total: 3 marks]

- The -OH group is bonded to a carbon atom that is bonded to three other alkyl groups so it is a tertiary alcohol



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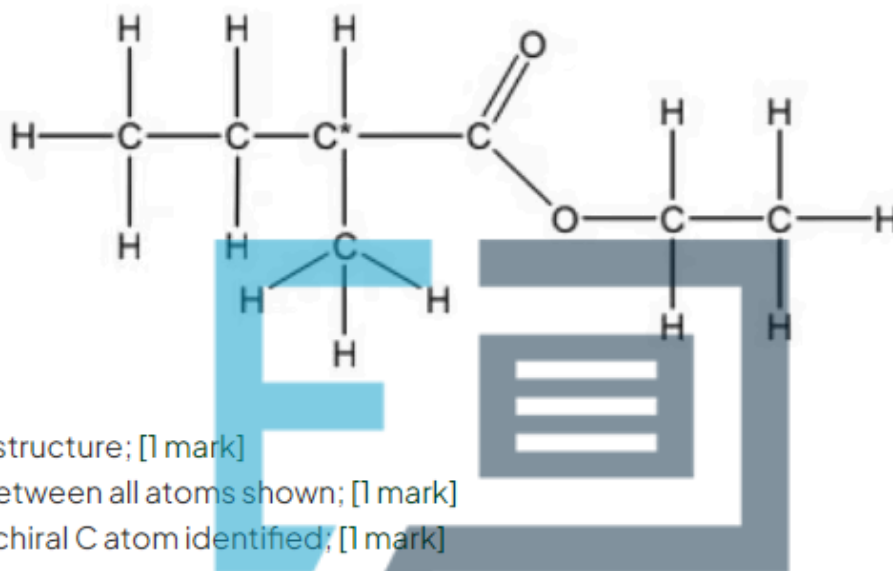
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d)

i) The displayed formula of this ethyl ester and chiral carbon atom is:



- Correct structure; [1 mark]
- Bonds between all atoms shown; [1 mark]
- Correct chiral C atom identified; [1 mark]

[Total: 3 marks]

- The molecular formula of 2-ethyl-3-methylbutanoic acid is $C_7H_{14}O_2$
- Start by drawing the $-COO-$ group
- You are told that it is an ethyl ester, so the chain connected to the oxygen in the $-COO-$ group is C_2H_5
- This leaves four carbons and nine hydrogen atoms
- You know that the remaining four carbons should not be straight chained, but branched
- Draw a chain of three carbon atoms on the left hand side of your ester, and play around moving the location of the methyl group until it is in a position that there is a chiral carbon
- You can achieve marking point 1 if you have not shown the bonds between all atoms
- If you have made an error in drawing the structure, you can still score mark 3 for identifying a correct chiral carbon



Answer 4.

a) The intermediate formed during this oxidation is:

- Propanal; [1 mark]

[Total: 1 mark]

- **Remember:** Primary alcohols partially oxidise to form aldehydes and fully oxidise to form carboxylic acids
- The difference in oxidation depends on the reaction conditions

b)

i) The colour of the chromium species after the potassium dichromate(VI) has reacted is:

- Green; [1 mark]

ii) The conditions used to ensure that propanoic acid is obtained in a high yield are:

- Excess acidified potassium dichromate(VI); [1 mark]
- Reflux; [1 mark]

[Total: 3 marks]

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- To convert a primary alcohol to a carboxylic acid, you can reflux the alcohol with excess acidified potassium dichromate(VI)
- The reaction can be observed as potassium dichromate(VI) will change from orange to green



c) A chemical test and observation to confirm the presence of a carboxyl functional group is:

- Add a Group 1 carbonate / Na_2CO_3 , etc
OR
Add a Group 1 bicarbonate / NaHCO_3 , etc; [1 mark]
- Effervescence / fizzing / bubbling; [1 mark]

[Total: 2 marks]

- The chemical test for a carboxylic acid is the addition of a carbonate / hydrogen carbonate
- The observation for this test is the production of (carbon dioxide) gas, which is seen as effervescence / fizzing / bubbling

Answer 5.

a) The white precipitate is:

- Aluminium hydroxide / $\text{Al}(\text{OH})_3$; [1 mark]

[Total: 1 mark]

- You are told that lithium hydroxide is formed
- It is logically to deduce that the other metals in the LiAlH_4 will also react with water to form a hydroxide, $\text{Al}(\text{OH})_3$

From GCSE you should know that aluminium ions form a white precipitate in sodium hydroxide, and that in excess NaOH the precipitate should redissolve

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b)

i) The reagents and conditions required for reaction 1 are:

- Potassium dichromate (VI); [1 mark]
 - Acid(ified)
- AND**
- Heat under reflux; [1 mark]

ii) Identify which of **Q** or **R** is 2-hydroxybutanoic acid and explain the difference between reactions 2 and 3:

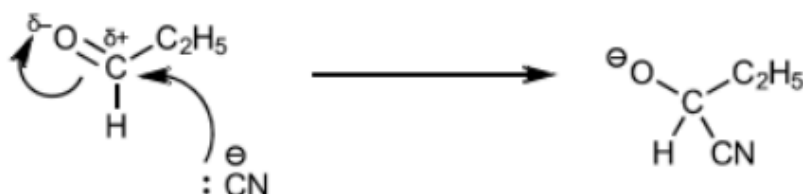
- **R** is 2-hydroxybutanoic acid
- AND**
- (Because) Only the C=O / ketone is reduced; [1 mark]
- NaBH₄ cannot reduce the COOH / carboxylic acid; [1 mark]

[Total: 4 marks]

- In reaction 1, a diol is being oxidised (shown by [O]) so the reagent must be an oxidising agent
- You would also score the mark for potassium manganate (VII)
- **P** contains a carbonyl group and a carboxylic acid group
- When the compound is reduced using LiAlH₄, both carbonyl and carboxylic acid group would gain hydrogen
- When the compound is reduced using NaBH₄ only the carbonyl group will gain hydrogen
- LiAlH₄ is stronger reducing agent than NaBH₄
- You are expected to know that an aldehyde / ketone can be reduced using both of these substances, but only LiAlH₄ is the reducing agent for a carboxylic acid



c) The mechanism for the reaction of propanal with the mixture of NaCN and HCN to form **S** is:



- Presence of :CN^- ; [1 mark]
- Curly arrow from :CN^- lone pair to carbonyl carbon; [1 mark]
- Correct dipole **AND** curly arrow from double bond to oxygen; [1 mark]
- Correct intermediate drawn; [1 mark]

[Total: 4 marks]

- If you show the bonds within the cyanide ion, it must clearly be a triple bond or you will not score the mark
- NaCN acts as catalyst in the reaction whilst the HCN provide the nucleophile, :CN^- for the reaction
- You will score the marks if your negative charges are not circled

d) The equation for the reaction in step 2, when **S** is heated under reflux with HCl (aq) is:

- $\text{C}_2\text{H}_5\text{CH}(\text{OH})\text{CN} + \text{HCl} + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{CH}(\text{OH})\text{COOH} + \text{NH}_4\text{Cl}$; [1 mark]

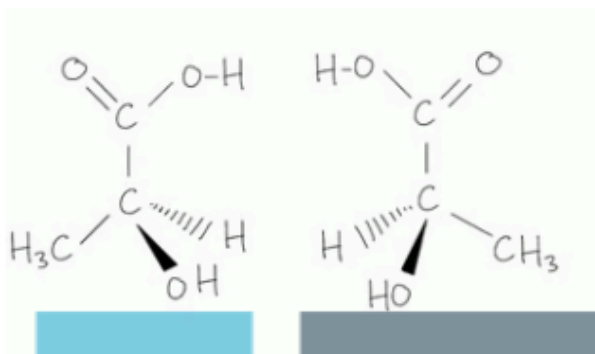
[Total: 1 mark]

- The nitrile is hydrolysed using dilute acid to form a carboxylic acid and ammonium salt
- **Careful:** The question does not indicate two more reactants are needed but both water **AND** the acid must be present
- A nitrile could also be hydrolysed using an alkali but this would produce a sodium carboxylate salt and ammonia



Answer 6.

a) The fully displayed structures of the two optical isomers of lactic acid are:



- Correct structures; [2 marks]
- Correct carbon atom labelled; [1 mark]

[Total: 3 marks]

- The optical isomers should be mirror images of each other
- Make sure you should all the bonds between the atoms in the carboxylic acid group as the question asks for the fully displayed structure
- You also need to uses dashes and wedged lines to represent the molecule as 3D
- The chiral carbon atom is the one that has four different atoms / groups of atoms attached to it
 - The C in COOH is not chiral as it only has three groups of atoms attached

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b) The reagent(s) and condition(s) for each step are:

Step 1:

- Acidified potassium dichromate (VI) / $\text{Cr}_2\text{O}_7^{2-}$
AND
 $\text{H}^+ / \text{H}_2\text{SO}_4$
OR
acidified potassium permanganate / KMnO_4
AND
 $\text{H}^+ / \text{H}_2\text{SO}_4$; [1 mark]
- Distill; [1 mark]

Step 2

- HCN in presence of CN^-
OR
 $\text{KCN} + \text{dilute H}_2\text{SO}_4$; [1 mark]
- Room temperature; [1 mark]

Step 3

- Dilute acid
OR
dilute alkali; [1 mark]

- Heat under reflux; [1 mark]

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[Total: 6 marks]

- The pathway shows:
 - ethanol \rightarrow ethanal \rightarrow 2-hydroxypropanenitrile \rightarrow 2-hydroxypropanoic acid
 - alcohol \rightarrow aldehyde \rightarrow nitrile \rightarrow carboxylic acid
 - Higher level questions expect you to know the reagents and conditions for various multi step reaction pathways
- **Remember:** In Step 1, the potassium dichromate / potassium permanganate act as oxidising agents but can only do this by being reduced themselves, hence the need for the dilute sulfuric acid which provides H^+ ions (you will get the mark for just giving H^+)
 - The aldehyde must be distilled off as it is produced otherwise full oxidation to a carboxylic acid will occur



c)

i) An equation to show this reaction using [H] to represent an atom of hydrogen from the reducing agent is:

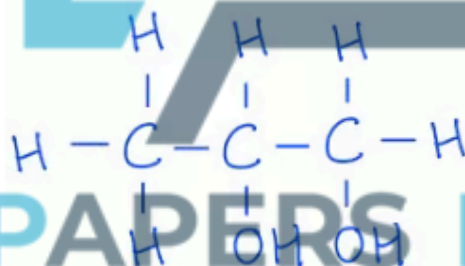


ii) The organic produced formed in this reaction is:

- Propane-1,2-diol; [1 mark]

[Total: 2 marks]

- Carboxylic acids are reduced to their corresponding primary alcohol
- The COOH group is reduced to form an OH group
- The structure of the organic compound formed is:



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- There are two alcohol groups present so the compound is a diol
- These are on the first and second carbon atoms, with three carbon atoms in total hence propane-1,2-diol



Answer 7.

a) The completed table is:

reagent	observation with glycolic acid	does a reaction occur?	functional group
Na_2CO_3	effervescence / fizzing / bubbling		COOH / carboxylic acid
2,4-DNPH	no visible reaction		no group required
acidified $\text{Cr}_2\text{O}_7^{2-}$	orange to green		-OH / alcohol

- 1 mark for each correct observation; [3 marks]
- 1 mark for COOH **AND** OH; [1 mark]

[Total: 4 marks]

- You are expected to know the chemical tests for different functional groups
- Sodium carbonate can be used to test for the presence of the -COOH group
 - When it is added to glycolic acid, a salt, carbon dioxide and water will be produced
 - The carbon dioxide can be observed as bubbles / effervescence
- 2,4-DNPH is used to test for the presence of the C=O functional group found in aldehydes and ketones so will not give positive results with glycolic acid
- Acidified potassium dichromate(IV) can be used to test for the presence of the -OH group as an orange oxidising agent which will turn green when it is reduced
 - Both colours must be present to score the mark

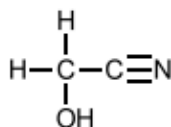
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b)

i) The structure of **X** is:



- Correct structure; [1 mark]

ii) The reagent used for reaction 2 is:

- Dilute hydrochloric / sulfuric / nitric / phosphoric acid; [1 mark]

iii) The mechanism for reaction 3 is:

- Free radical substitution; [1 mark]

iv) The essential condition for reaction 3 is:

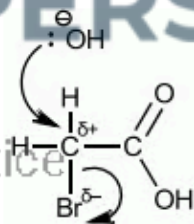
- UV / sunlight; [1 mark]

v) The diagram for the mechanism for reaction 4 is:

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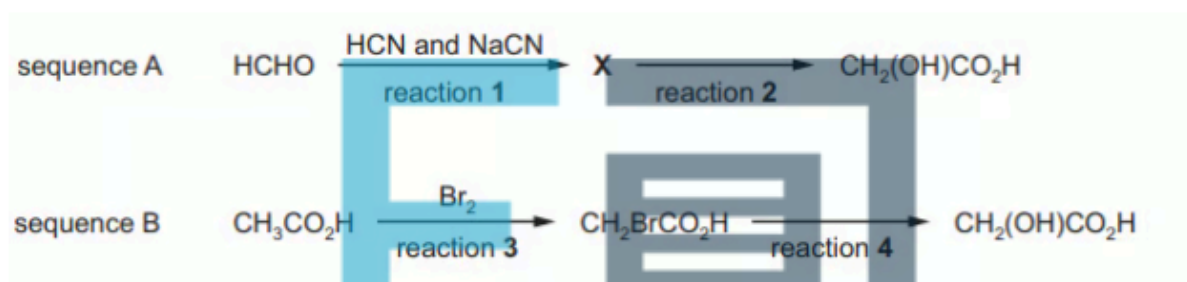
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- Lone pair on OH^-
AND
curly arrow from lone pair to C of C-Br; [1 mark]
- Correct dipole on C-Br
AND
curly arrow from bond to Br; [1 mark]

[Total: 6 marks]



- In sequence A, reaction 1, methanal undergoes nucleophilic addition to form the nitrile, 2-hydroxyethanenitrile
 - The 2-hydroxyethanenitrile then undergoes hydrolysis to form glycolic acid
 - Dilute acid is needed for this
 - 2-hydroxyethanenitrile could also undergo hydrolysis using an alkali however alkali or a named alkali is not accepted as an answer here as a carboxylate salt would be formed which would require acidification to convert it to a carboxylic acid
- In sequence B, reaction 3, hydrogen is substituted for bromine to form a halogenoalkane
 - The halogenoalkane then undergoes nucleophilic substitution to form glycolic acid
 - $\text{CH}_2\text{BrCO}_2\text{H}$ is a primary halogenoalkane so reacts via the $\text{S}_{\text{N}}2$ mechanism which is a 1 step reaction
 - Make sure your curly arrows are clear and don't forget the charge on the hydroxide ion

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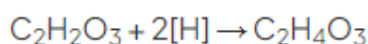


c)

i) The role of NaBH_4 in this reaction is:

- Reducing agent / reductant; [1 mark]

ii) An equation for this reaction using molecular formulae is:



- Correct molecular formulae; [1 mark]
- Correctly balanced; [1 mark]

[Total: 3 marks]

- **Careful:** The question asks for the molecular formulae to be used so writing the structural formula for glycolic acid, $\text{CH}_2(\text{OH})\text{COOH}$ and the product made (ethane-1,2-diol), $\text{CH}_2(\text{OH})\text{CH}_2\text{OH}$ would not score the marks