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PEPERIKSAAN AKHIR TAHUN 2009

T6A

Kertas 2
Paper 2 **Chemistry**
(Kimia)
2 jam 30 min **Kertas 2** **962/2**

Ínstructions to candidates

Answer all the questions in Section A in the spaces provided. All working must be shown. For numerical answers, units must be quoted wherever they are appropriate.

Answer any four questions from Section B. For this section, write your answer in your exam pad.. Begin each answer on a fresh sheet of paper and arrange your answers in numerical order. Staple/tie your answers.

This paper consists of 9 printed pages

For examiners use	
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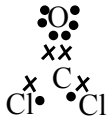
Total	

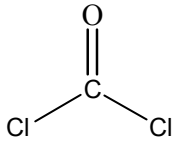
Section A[40m] – Answer all the question in this section

1. Carbonyl chloride, $COCl_2$ is a highly poisonous gas manufactured from the reaction between carbon monoxide and chlorine

i) Draw the Lewis structure of $COCl_2$. [1]



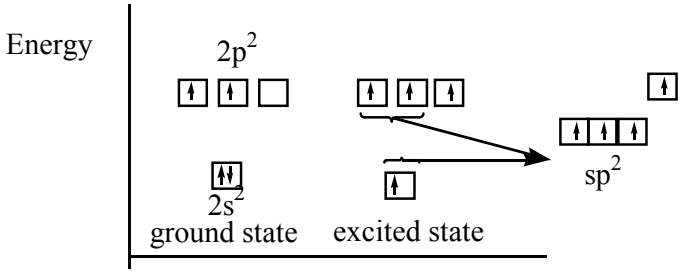
ii) Draw the molecular structure of $COCl_2$. [1]



iii) Name the type of type of hybridization undergone by the carbon atom in carbonyl chloride. [1]

sp^2

iv) Explain the hybridisation process undergone by carbon. [3]



In the ground state the electron config is 1s2 $2s^2p^2$, the atom is excited and one s electron moves to the empty p-orbital. One s-orbital and two p-orbital combines to form sp^2

iv) Compare the molecular shape of $COCl_2$ with that of $SOCl_2$, thionyl chloride. Give reasons for any similarities or differences between them in the table provided. [4]

	$COCl_2$	$SOCl_2$
Similarites	**2 single bonds and one double bond**	**2 single bonds and one double bond**
Differences	**Trigonal planar**	**pyrmidal**
	Angle between bonds 120^o	**Angle less that 109.7^o**
	Bond-bond pair repulsion only	**Lone-pair –bond pair and bond pair bond pair repulsion**

2. The Calomel electrode , a secondary reference electrode, is far easier and safer to use than a hydrogen electrode. The standard electrode potential of a Calomel electrode potential is +0.334V when its electrolyte concentration is 0.1M .

Its half equation is $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$

The emf of a cell when Ag^+/Ag electrode is connected to the Calomel electrode is 0.466V.

i) What is the standard electrode potential of $Ag^+(aq)/Ag(s)$ if $Ag^+(aq)/Ag(s)$ is the positive electrode and the calomel electrode is the negative electrode.[1]

E_{Ag+Ag} **- 0.334 = 0.466, therefore** E_{Ag+Ag} **=0.8V**

ii) What would be the emf of a cell when a standard zinc electrode is connected to the calomel electrode. [1]

1.094V

iii) How would the E^o value of the Calomel change if the electrolyte used were saturated [4]

$$E = E^o + \frac{RT}{nF} \ln \frac{1}{[Cl^-]^2}$$ **Nernst's equation**

Concentration of the Cl^- ions in saturated solution is higher, therefore the E value decreases.

b) A Cr^{3+} solution is electrolysed using a current. What is the current needed to deposit 0.25mol Cr from Cr^{3+} solution in a period of 8 hours. [4]

Cr^{3+} + 3e → Cr

n= 0.75mol n=0.25 mol

Q= 0.75 mol x 96500C mol^{-1}
I x t = 0.75 x 96500

I x 8 x 60 x 60 = 0.75 x 96500
I = 2.51A

3. The mechanism for the reaction between alkanes and halogen proceeds by a number of steps.

a) What is the name of the mechanism.? [1]

free radical substitution

b) There are two possible ways for the formation of radicals in the initiation step.

$Cl_2 \rightarrow 2Cl\cdot$

$CH_4 \rightarrow CH_3\cdot + H\cdot$

i) Which is the preferred radical in the initiation step. [1]
Cl ·

ii) Give your reason.[1]

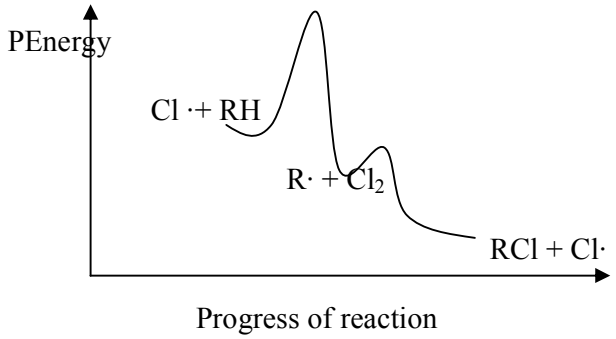
Cl_2 has a lower bond dissociation energy

c) The propogation steps are shown below

$Cl\cdot + RH \rightarrow R\cdot + HCl$

$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot$

The reaction mechanism for the propogation steps are shown below



i) Which step is the rate controlling step. [1]

step 1

ii) Give a reason for your answer. [1]

higher activation energy

d) Give two reactions that occur in the termination step. [2]

$Cl\bullet + Cl\bullet \longrightarrow Cl_2$

$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$

$CH_3\bullet + CH_3\bullet \longrightarrow CH_3CH_3$

e) The propogation step for the thermal cracking of butane may occur in two ways

$CH_3\cdot + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_4 + \cdot CH_2CH_2CH_2CH_3$

Or

$CH_3\cdot + CH_3CH_2CH_2CH_2CH_3 \rightarrow CH_4 + CH_2CH_2CH_2CH_3$.

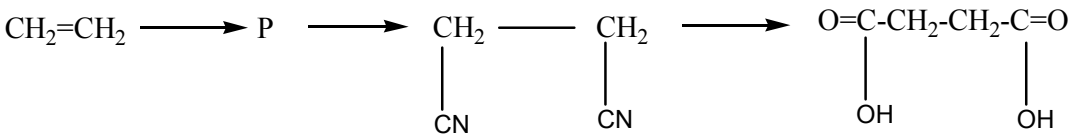
i) which is the more likely reaction.[1]
rxn 2

ii) Give a reason for your answer. [2}

secondary radical is more stable than primary radical , alkyl groups stabilize the radicals.

4. Succinic acid(butandioic acid) is a colourless crystalline solid with a melting point of 185 -187^{o}C. It occurs naturally in plant and animal tissues.

a)The scheme below shows how succinic acid, $C_4H_6O_4$ can be prepared from ethene



Q

i) Identify compound P. [1]

1,2 dichloroethane or 1,2 dibromaethane

ii) Suggest how compound P can be prepared . [1]

Ethene vapour is passed through Bromine /Chlorine in an insert solvent.

iii) Name the mechanism. [1]

Electrophilic addition

iv) Suggest how succinic acid can be prepared from compound Q. [2]

Q is boiled with mineral acid, HCl

v) Write a balanced equation for the reaction in (iv). [1]

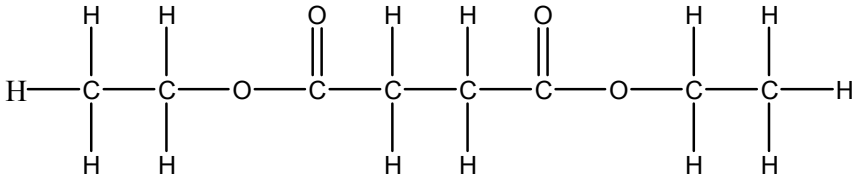
$CNCH_2CH_2CN + 4H_2O + 2HCl \rightarrow HOOCCH_2CH_2COOH + 2NH_4Cl$

b) Explain the solubility of succinic acid in water. [1]

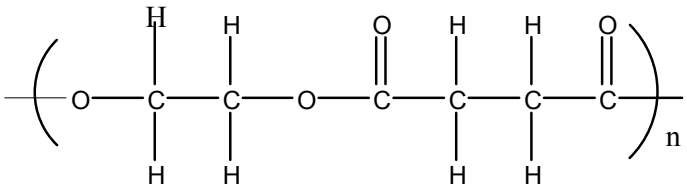
Very soluble due to the formation of hydrogen bonds with water.

c) Draw the structural formula of the products formed when succinic acid is reacted with each of the following reagents

i) ethanol [1]



ii) ethane-1,2- diol [1]

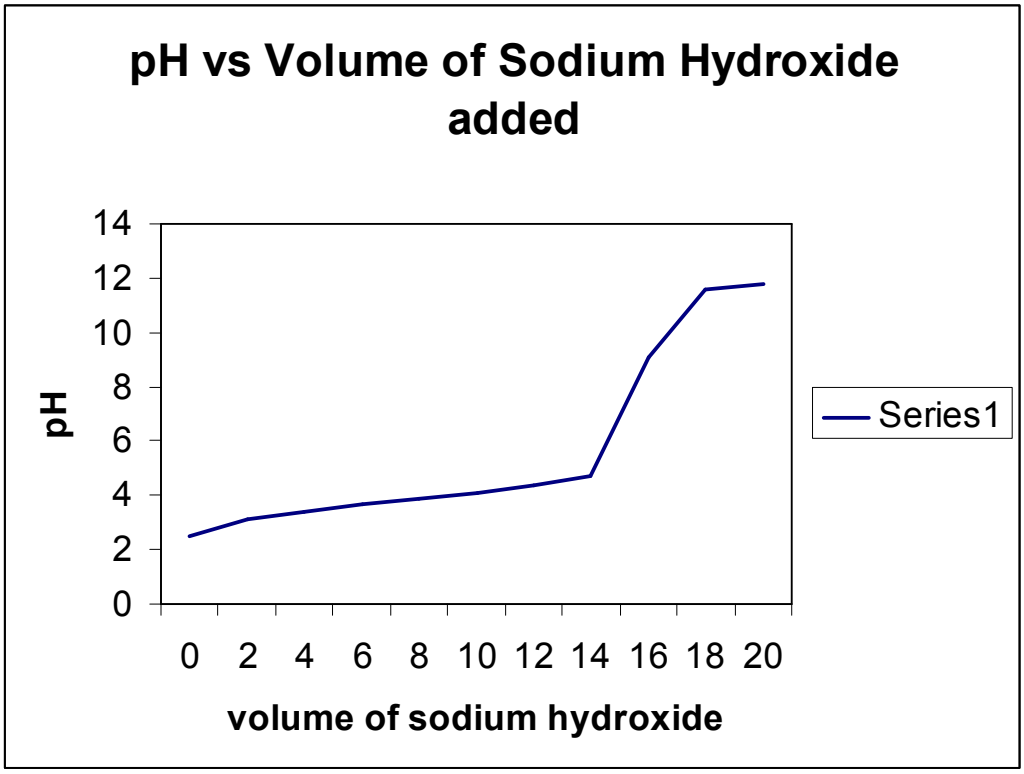


iii) State the physical difference between the products obtained in c(i) dan c(ii). [1]

ci) pleasant smelling liquid cii) colourless solid

Section B[60m] – answer any four question from this section

5. 10 cm^3 of a solution of lactic acid was titrated against 0.05M sodium hydroxide. A plot of pH against volume of sodium hydroxide is shown below



There are three points and three regions marked on the graph.

a) Name a suitable indicator for the above titration. Give your reasons. [2]
Phenolpthalein
pKIn = 9.3 for pH range 8.2 – 10.00
Equivalent point is within this range

b)i) Identify the buffer region on the graph. [1]
Region 1

ii)Name the weak acid and salt of the weak acid which will make up this buffer. [2]

Sodium Lactate and Lactic acid

iii) Explain how this buffer can resist changes in pH when small amounts of acid and alkali are added.[4]
Na^+Lac^-
Lac^- anion reacts with added H^+ ions to form lactic acide molecules, HLac. Thus resists the change in pH ddue to acid.

HLac racts with OH^- ions to form the $Lac^{—}$ ion thus resisting the change n pH due to the addition of OH^- ions.

c) Calculate Ka of lactic acid. [2]

$$\left(\frac{M_1 \text{ x } V_1}{M_2 \text{ x } V_2}\right) = \frac{1}{1}$$

$$\left(\frac{M_1 \text{ x } 10}{0.05 \text{ x } 15.5}\right) = \frac{1}{1}$$

$M_1 = 0.0775$

$[H^+]$ $= \sqrt{(K_a \text{ x } c)}$

$10^{-2.5} = \sqrt{(K_a \text{ x } 0.0775)}$

$K_a = 1.3 \text{ x } 10^{-4}$

d) What is the pH at which the buffer will show maximum capacity. [1]

3.5

e) Calculate the $\frac{[\text{salt}]}{[\text{weak acid}]}$ for this buffer.[3]

$pK_a = 3.88$

$$3.5 = 3.88 + \log\frac{[salt]}{[acid]}$$

$$\frac{[salt]}{[acid]} = \frac{0.42}{1}$$

6. The diagram below represents the emission spectrum of the hydrogen atom in the Lyman's series

a) Explain how the above lines spectrum of hydrogen atom is produced based on Bohr's assumptions [4]

Electrons movie in orbits.
Energies of electrons are quantized.
Electrons occpy the lowest energy level under normal conditions.
When electrons are excited when sufficient energy is provided the electrons move form lower energy level to higher energy level. The return of the excited electrons to the lower energy level results in the emission of spectral lines

b) Wave number,v = $\frac{1}{\lambda}$, determine the ionisation energy of the hydrogen atom in kJ mol^{-1} [3]

$\Delta E = h\upsilon = \frac{hc}{\lambda}$

$=6.63 \times 10^{-34} \times 10.97 \times 10^{+6} \times 3 \times 10^{8} \times 6.02 \times 10^{23}$
= 1.317kJ

c) Explain each of the following observation in terms of structure and bonding.

i) Carbon dioxide is a gas at room temperature but silicon(IV) oxide is a solid with high melting point.[2]
CO_2 – simple molecule, non polar, weak intermolar forces, VDW

SiO_2 – macromolecule, covalent bonds between atoms, infinite

ii) The boiling point of n-hexane is higher that the boiling point of the isomer 2,2 –dimethylbutane.[2]

n- hexane – straight chain hydrocarbon,greater surface area, stronger intermolecular forces.

2,2 dimethylbutane, branched chain hydrocarbon, electron cloud-spherical less surface area in contact between molecules weaker VDW forces between them.

iii) The melting point of 4-nitrophenol is higher than that of 2-nitrophenol.[2]

4-nitrophenol intermolecular hydrogen bonds

2- nitrophenol – intramolecular hydrogen bonds

iv) The sodium metal has a lower melting point than the aluminum metal.[2]

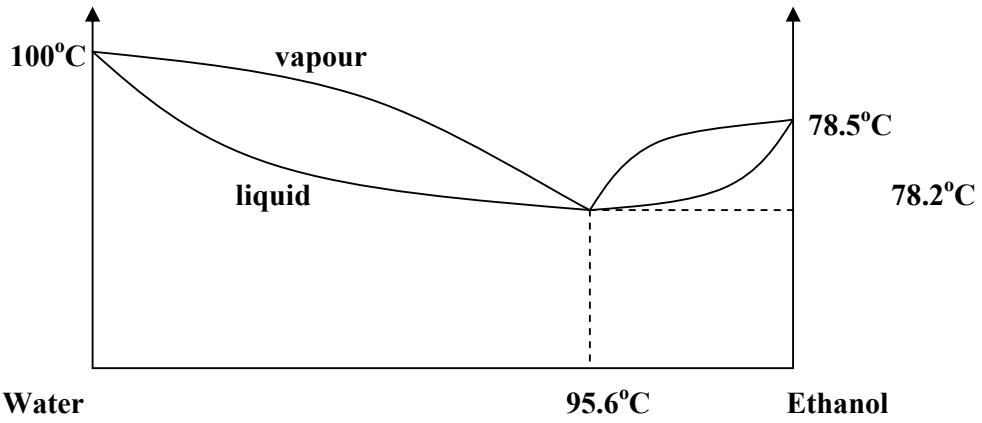
sodium metal -weaker metallic bonds due to attraction between fewer valence electrons and the +nucleus of the atom

Aluminium metal – strong metallic bond due to stronger attraction between +nucleus of the Al atom and the greater number of valence electrons.

7. Ethanol(bp 78.5^{o}C) and water form a constant boiling point mixture having a boiling point of 78.2^{o}C and a composition of 95.6% ethanol.

a)i) Define the term constant boiling point mixture.[2]
Mixture of two liquids that boils at constant composition which does not change on distillation because the vapour and liquid mixture has the same composition.

ii) Sketch and label the boiling-point composition diagram for ethanol and water. [4]



iii) An ethanol/water mixture shows positive deviations from Raolts Law. Explain and account for this and state the law. [2]

Positive deviation – the total vp of the liquid mixture is greater than expected from Raoult's Law. Positive deviations results in minimum boiling point.

Raoult's Law states that the partial vp of A in a solution at a given temp is equal to the vp of pure A at the same temp multiplied by the mole fraction fo A in the solution.

iv) What intermolecular changes takes place when ethanol is added to water.[2]

Intermolecular attraction between ethanol and water weaker than the intermolecular attraction between water and water and ethanol and ethanol

b) Napthalene, $C_{10}H_8$ distils in steam at a temperature of 98^{o}C. If the vapour pressure of water at this temperature is 95kPa and the atmospheric pressure is 101kPa. What is the mass of the distillate that contains 10.0g of napthalene. [5]

$$\frac{m_N}{m_w} = \frac{P_N \text{ x } M_N}{P_w \text{ x } M_w}$$

$$\frac{10}{m_w} = \frac{6 \text{ x } 128}{95 \text{ x } 18}$$

m_w = 22.26g

Mass of distillate = 32.26g

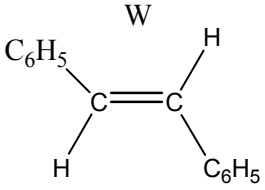
8. a) A hydrocarbon, with the empirical formula CmHn and relative molecular mass 180 contains 93.33% C and 6.67% hydrogen by mass.

i) Determine the molecular formula of the hydrocarbon [2]

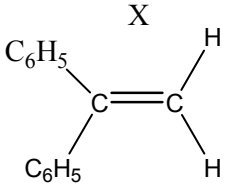
$C_{14}H_{12}$

ii) The hydrocarbon has two structural isomers W and X that contain two benzene rings respectively. W exhibits geometrical isomerism but X does not. In their reactions with HBr, W forms Y that is optically active, while X forms Z that is optically non-active. Determine the structure of W,X,Y and Z, and draw the structure for the enantiomers fo Y.[8]

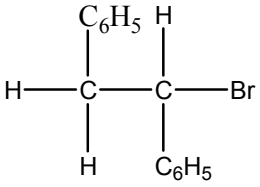
W



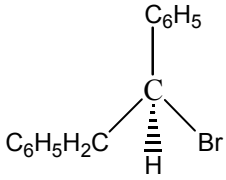
X

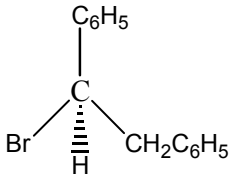


Y

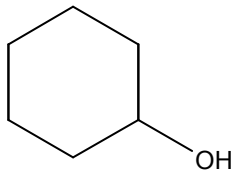
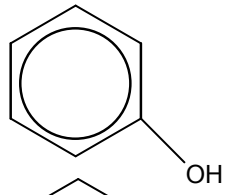
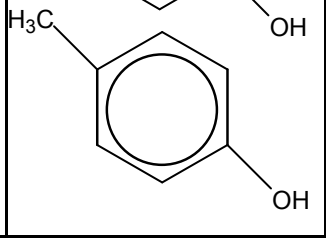


Z





b) The table below lists the acid dissociation constants, Ka, for three hydroxy compounds in aqueous solutions at 298K.

Name of compound	Formula	Ka/mol dm^{-3}
cyclohexanol		1.0×10^{-18}
Phenol		1.0×10^{-10}
4-methylphenol		$6.8 \times 10^{--11}$

i) Arrange the three compounds above in the order of increasing acidity. Explain your answer.[5]

Cyclohexanol, 4 methylphenol, phenol

Cyclohexanol – the alkyl group displaces the electrons to the oxygen atom and increases the negaaative charge density on the oxygen atom. This makes it more difficult for the hydrogen ion to dissociate front the O-H bond.

4 – methylphenol – the methyl group is an electron donating groupand enriches the benzene ring further with electrons and hence increases the negative charge dentsity on the oxygen ation and makes it more difficult for the hydrogen ion to dissociate.

Phenol – resonance stabilization , the negative charge spreads over the benzene ring.

ii) Name the reagents used and state the expected observations and write equations for reactions that occur for a chemical test to differentiate the acidity between cyclohexanol and phenol.[2]
Sodium hydroxide

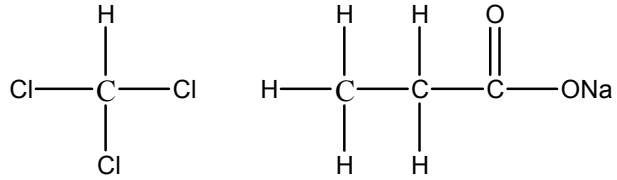
Phenols are readily soluble in aqueous sodium hydroxide at to form sodium phenoxide and water.
$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

Cyclohexanol does not react with aqueous sodum hydroxide.

9. For each carbonyl compound reaction below

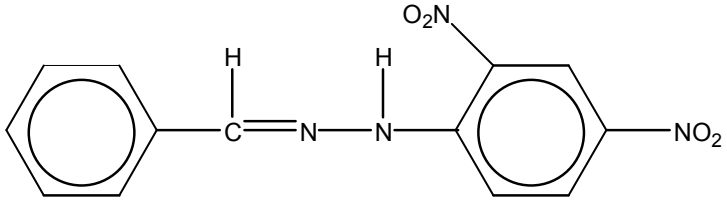
a) draw the structural formulae for the organic products formed and elaborate on the importance of the these reactions

i) $CH_3CH_2COCH_3$ with iodine in sodium hydroxide solution



importance - the formation of yellow crystals of triiodomethane , to detect the presence of CH_3CO-

ii) C_6H_5CHO in 2,4 dinitrophenylhydrazine

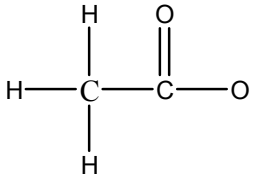


-yellow orange ppt.

-confirms the presence of a carbonyl group

-to determine the identity of the carbonyl compound by finding the mp of the 2,4 dinitrophenyhydrozone formed.

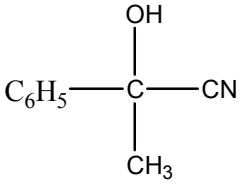
iii) CH_3CHO in Fehling's solution



Cu_2O

Brick red ppt of Cu_2O. Rxn inportant to distinguish between aldehyde and ketone. Ketones do not react with Fehling's solution.

iv) $C_6H_5COCH_3$ in HCN



Adds one carbon atom to the chain

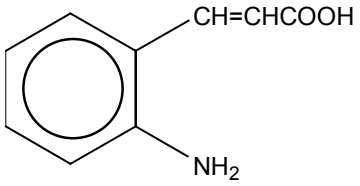
v) Bromoethane and Magnesium in eter [15]

C_2H_5MgBr Grignard's reagen

C-Mg polar bond giving the carbon atom a partial negative charge.

Grignard's reagent can be converted to 1^oalcohol with methanol, 2^oalcohol with aldehyde, 3^oalcohol with ketone, carboxylic acid with CO_2

10. How and under what conditions, would you expect a compound with the formula



To react(if possible) with
i) hydrogen

vapour of the compound and hydrogen gas passed over catalyst Ni at temperatures >150^{o}C
ii) sodium hydroxide

-COOH acid reacts readily with NaOH to form salts.

iii) HCl

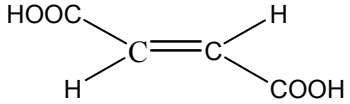
-NH_2 basic group reacts with HCl to frm ammonium chloride at rt.

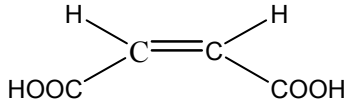
iv) nitrous acid [7]

-_NH_2 reacts with nitrous acid to form diazonium salt at tmep between 0 – 5 ^{o}C

b) i)Explain why (i) but-2-endioc acid HOOCCH=CHCOOH exist as a pair of cis-trans isomers. [4]

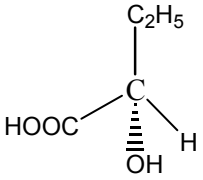
the presence of –C=C- double bond which prevents free rotation.
The –COOH groups can be on the same side of C=C double bond or on opposite side.





ii) 2-hydroxybutanoic acid $CH_3CH_2CH(OH)COOH$ exists as a pair of optical isomers. [4]

presence of a chiral carbon atom



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