[This question paper contains 6 printed pages.]

Your Roll No.....

B

Sr. No. of Question Paper : 730

Unique Paper Code : 32171201

Name of the Paper : Organic Chemistry – I

Name of the Course : B.Sc. (H) Chemistry

Semester : II

Duration : 3 hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. All questions carry equal marks.

1. Give reasons for the following statements. Attempt any **five** :

   (a) Methyl group in Toluene is ortho-para directing.

   (b) Chair conformation of cyclohexane is more stable than boat conformation.

   (c) Both racemic mixture and meso compound are optically inactive.

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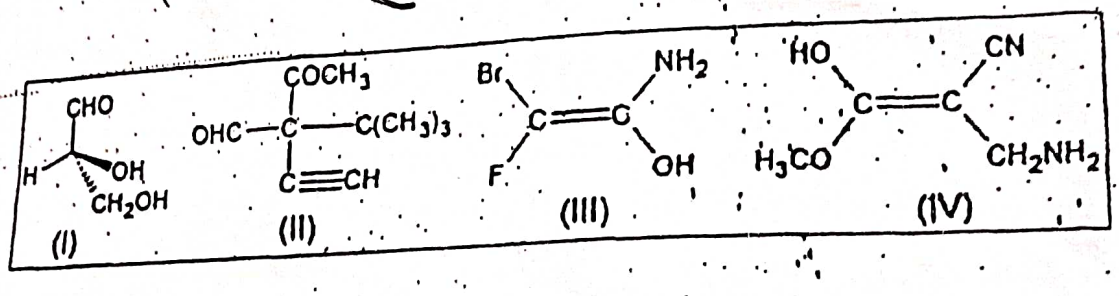
(d) Phenols are less acidic than carboxylic acids.

(e) Terminal alkynes are acidic in nature.

(f) Alkenes are more reactive than alkynes towards electrophilic addition reactions. (2.5×5=12.5)

2. (a) Assigning priorities, determine the configuration (E/Z or R/S) for the following compounds



(b) An alkene on reductive ozonolysis yields a mixture of two isomers with molecular formula C_3H_6O. Identify the structure of the alkene and the products. Write the product of the reaction between alken e with HBr. (8,4.5)

3. (a) Comment on the aromaticity of the following compounds

(i) Naphthalene

(ii) Cyclopentadienyl cation

(iii) Cycloheptatriene

(iv) Pyridine

(b) A compound (4.25 g in 100 mL)'s solution in chloroform was taken in a polarimeter tube of length 5 cm and its optical rotation (at 25°C) was observed to be −1.2°. Calculate the specific rotation. (8,4.5)

4. (a) Carry out the following conversions :

(i) Propane to 2,3-Dimethyl butane

(ii) Propyne to Pent-2-yne

(iii) But-1-yne to Butan-2-one

(iv) But-1-ene to But-2-ene

(b) Write down the mechanism involved in Friedel Craft's alkylation of benzene with propyl chloride. (8,4.5)

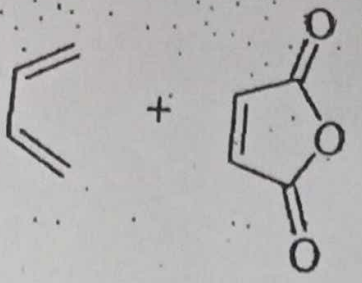
5. (a) Draw the Fischer projection for all the possible stereoisomers of butane-2,3-diol. State the correlation among these stereoisomers? Comment on the optical activity of these isomers.

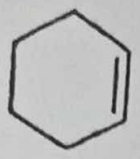
(b) In halogenation of alkanes why chlorination is more reactive but less selective than bromination?

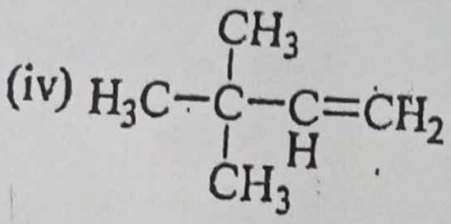
(c) Why peroxide effect is observed in case of addition of HBr? (5,4,5,3) 7.

6. (a) Complete the following reaction with product(s) (including stereochemistry wherever applicable)

(i) $H_3CC{\equiv}CCH_3 \xrightarrow[\text{Liq. } NH_3]{Na}$

(ii)  $\xrightarrow{\text{Heat}}$

(iii)  $\xrightarrow[\text{Cold}]{\text{dil. aq. } KMnO_4}$

(iv)  $\xrightarrow{HCl}$

(b) Calculate the percentage of isomers formed on monochlorination of n-butane. Relative rates of hydrogens 3°:2°:1° towards chlorination at room temperature are 5.0:3.8:1. (8,4.5)

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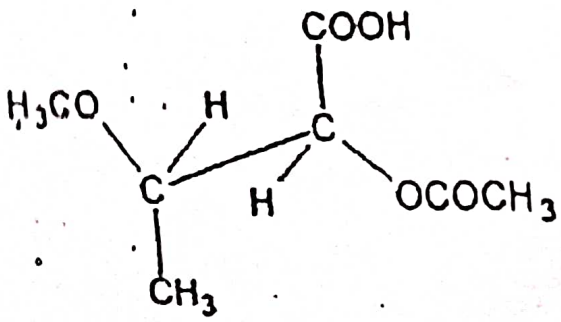
7. (a) Comment on the stereochemistry of the products formed when cis and trans isomers of but-2-ene reacts with bromine solution. Explain the reaction with mechanism.

(b) State limitations of Wurtz reaction. How Corey-House synthesis overcomes these limitations? Give with suitable examples.

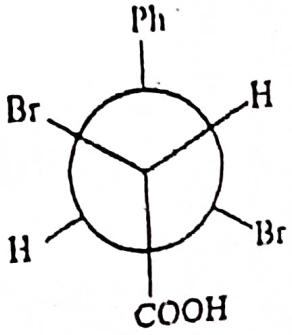
(c) Which is more acidic, p-nitrophenol or o-nitrophenol? Give reasons. (5,4.5,3)

8. (a) How will you chemically distinguish between 1-butyne and 2-butyne?

(b) Convert the following structures to standard Fischer projections :



(I)



(II)

(c) Explain why 1,3-pentadiene is more stable than 1,4-pentadiene?

(d) Why nitration of toluene is faster than nitration of benzene? (2.4,3,3.5)

9. Write short notes on the following : (any four).

(a) E1 and E2 reactions (including mechanism)

(b) D,L system of configuration (including limitations)

(c) Oxymercuration – Demercuration Reaction (including mechanism)

(d) Allylic Halogenation using NBS (including mechanism)

(e) Nucleophilic addition reactions in alkynes (3.5,3,3,3)

[This question paper contains 8 printed pages.]

Your Roll No.....

A

Sr. No. of Question Paper : 1142

Unique Paper Code : 32171401

Name of the Paper : Inorganic Chemistry – III

Name of the Course : **B.Sc. (H) Chemistry**

Semester : IV

Duration : 3.5 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **Six** questions in all.
3. **All** questions carry equal marks.

1. (a) Name of the following complexes according to the IUPAC system of nomenclature :

(i) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

(ii) $[(NH_3)_5Cr(NH_2)\ Cr(NH_3)_4(H_2O)]Cl_5$

(iii) $[Co(NH_3)_6]_3[Co(CN)_6]_2$

P.T.O.

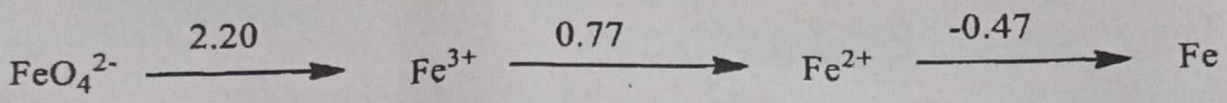
(b) Write the formulae of the following complexes :

(i) Sodium bis(thiosulphato)argentate(I)

(ii) Triamminechlorocyanonitrocobalt(III)

(iii) Potassium diaquatetrabromovanadate(III)

(c) Given below is the Latimer diagram for Fe in acidic medium :



(i) Why FeO_4^{2-} is strong oxidising agent?

(ii) Is there any tendency of Fe^{2+} to reduce to Fe. Give reasons.

(d) A strong oxidizing agent(A) on heating with KCl and conc. H_2SO_4 gives red coloured gas B which on passing through potassium hydroxide solution gives yellow solution C. C may also be obtained on heating A on treatment with conc. H_2SO_4 gives a red product D which decomposes on heating to give a product. Identify A, B, C, D.

(3,3,3,3.5)

2. (a) Which of the following is more stable :

$[Co(en)_3]^{3+}$, $[Co(dien)_3]^{3+}$

(b) Justify the presence of copper in the transition series.

(c) Explain $d_\pi - p_\pi$ bonding in complexes.

(d) Explain Jahn Teller effect.

Which of the following complex have all equal bond length and why?

$[CrF_6]^{3-}$ and $[MnF_6]^{3-}$ (3,3,3,3.5)

3. (a) Identify A, B, C, D in the following reactions :

(i) $[PtCl_4]^{2-} \xrightarrow{NH_3} [A] \xrightarrow{NH_3} [B]$

(ii) $[Pt(NH_3)_4]^{2+} \xrightarrow{Cl^-} [C] \xrightarrow{Cl^-} [D]$

(b) What happens when

(i) KI is added to $KMnO_4$ in acidic medium.

(ii) SO_2 is passed through acidified $K_2Cr_2O_7$ solution.

(c) +3 is the most common oxidation state of lanthanides. Explain.

(d) Fe_3O_4 is inverse spinel while Mn_3O_4 is normal spinel. Explain on the basis of CFT.

(3,3,3,3.5)

4. (a) The pairing energy (P) for the $[Cr(H_2O)_6]^{2+}$ ion is 23000 cm^{-1} and crystal field splitting (Δ_0) is 14000 cm^{-1}. Calculate the crystal field stabilization energy in high spin and low spin state. Which state is more stable?

(b) 4d and 5d elements usually form low spin complexes. Justify.

(c) Tetrahedral complexes are high spin. Explain

(d) Using the valence bond theory method, work out following for $[Cr(CN)_6]^{3-}$

(i) Assign the electronic configuration to the central metal ion,

(ii) predict the type of hybridization involved,

(iii) geometry, and

(iv) the magnetic moment (3,3,3,3.5)

5. (a) What are differences between valence bond theory and crystal field theory?

(b) Explain Spectrochemical series.

(c) Higher Oxidation states of transition elements are stabilized by small anions like F^-, O^{2-}. Explain.

(d) For Cr^{2+} octahedral complexes in strong and weak field, determine the (i) configuration in terms of $t_{2g}^{\ x}\ e_g^{\ y}$, (ii) number of unpaired electrons, and (iii) crystal field stabilization energy. (3,3,3,3.5)

6. (a) Write three differences between the characteristic features of lanthanides and actinides.

(b) Ce^{4+} ion is coloured whereas Ce^{3+} ion is colourless. Why?

(c) Work out the number of unpaired electrons in the following ions :

$$Eu^{2+},\ Tb^{4+},\ Lu^{3+}$$

(Atomic number of Eu = 63, Tb = 65, Lu = 71)

(d) What is lanthanide contraction? What are the major consequences of lanthanide contraction on the chemistry of d block elements? (3,3,3,3.5)

P.T.O.

7. (a) The compound $CoCl_3.4NH_3$ gives one Cl^- ion on the addition of Ag^+ ion. Draw the structure of the compound on the basis of Werner's coordination theory.

(b) Explain the following with suitable examples :

(i) Ionisation isomerism

(ii) Linkage isomerism

(c) Using valence bond theory, discuss hybridization and structure of the following :

(i) $[Cr(NH_3)_6]^{3+}$

(ii) $Ni(CO)_4$

(d) $[Fe(CN)_6]^{4-}$ ion is diamagnetic but $[Fe(CN)_6]^{3-}$ ion is paramagnetic in nature. Explain using V.B.T.

(3,3,3,3.5)

8. (a) Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium.

(b) $K_2Cr_2O_7$ is a good oxidising agent in acidic medium.

Explain.

(c) Write down the number of 3d electrons in each of the following ions :

(i) Cr^{3+}

(ii) Fe^{3+}

(iii) Cu^{2+}

(d) Transition elements and their compounds are generally found to be good catalyst in chemical reaction. Discuss. (3,3,3,3.5)

9. (a) Give the reasons for the following **(any two)** :

(i) Mn(II) ion shows maximum magnetic character among the bivalent ions of first transition series.

(ii) Cu(I) is diamagnetic while Cu(II) is paramagnetic.

(iii) Zn^{2+} salts are white while Cu^{2+} salts are blue.

(b) Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of

Cr^{3+} is 3.87 B.M. and that of Co^{2+} is 4.87 B.M. Explain.

(c) Explain why Fe(II) and Fe(III) form complexes with CN^- ions but not with NH_3. (6,3,3.5)

B.Sc (H) Chemistry

[This question paper contains 8 printed pages.]

Your Roll No.....

A

Sr. No. of Question Paper : 1387

Unique Paper Code : 32171403

Name of the Paper : Physical Chemistry – IV

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : IV

Duration : 3½ Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **six** questions in all.
3. Use of scientific calculator is permitted.

1. (i) Comment on the following :

(a) Elementary reaction with molecularity greater than three are unknown.

(b) In the steady state, the concentration of the reactive intermediate though small remains the same for an appreciable time.

(2+2)

(ii) Predict the overall order of reaction for which half-life period depend inversely on the concentration and derive the expression for its half-life. (4)

(iii) The rate constant for a certain reaction is found to be tripled when the temperature is increased from 288K to 323K. If the enthalpy of reaction is 80 kJ/mol, calculate the activation energy of the reaction. (4.5)

2. (i) Differentiate the following **(any two)** :

(a) Stationary and non-stationary chain reaction

(b) Order and molecularity

(c) Average rate and Instantaneous rate of reaction (2+2)

(ii) Under what conditions a given catalytic reaction may be classified into a general acid catalysis and a specific hydrogen-ion catalysis, if the acid catalysed reaction follows the mechanism :

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$ (4)

(iii) Derive the Michaelis - Menten equation for enzyme catalysed reactions. The mechanism involves the following steps :

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} ES$$

$$ES \xrightarrow{k_2} P + E$$

Show that the enzyme catalysed reaction is first-order and zero-order with respect to S at low and high concentrations of S, respectively. (4.5)

3. (i) Explain the role of catalyst with the help of potential energy diagram? (4)

(ii) Hydroxide ion is involved in the mechanism but not consumed in this reaction in aqueous solution.

$$OCl^-(aq) + I^-(aq) \xrightarrow{OH^-} OI^-(aq) + Cl^-(aq)$$

(a) From the data in the table, determine the order of reaction with respect to OCl^-, I^-, and OH^-, and the overall order.

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[OCl⁻] /(M)	[I⁻] /(M)	[OH⁻] /M	Rate of formation of OI^- (mol L^{-1} s^{-1})
0.004	00.0020	1.00	4.8×10^{-4}
0.002	00.0040	1.00	5.0×10^{-4}
0.002	00.0020	1.00	2.4×10^{-4}
0.002	00.0020	0.50	2.4×10^{-4}
0.002	00.0020	0.25	9.4×10^{-4}

(b) Write the rate law. (4)

(iii) The following mechanism has been suggested for the decomposition of O_3

$$O_3 \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

(a) Assuming $k_{-1}[O_2] > k_2[O_3]$, show that the rate of the all-overall reaction is

$$-\frac{d[O_2]}{dt} = \frac{k[O_3^2]}{[O_2]}.$$

(b) What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation?

(4.5)

4. (i) Derive the relation between Arrhenius activation energy E_a and the minimum energy E_0 of the collision theory of bimolecular reaction theory. (4)

(ii) (a) What are the two conditions that are necessary for effective collisions?

(b) Why the value of steric factor p is usually less than 1 ? (2+2)

(iii) Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times the time for 50.0% completion. (4.5)

5. (i) Write a short note on **any three** :

(a) Effect of temperature on Photochemical Reactions

(b) Activated Complex Theory

(c) Conductometric titration of mixture of HCl and CH_3COOH against NaOH

(d) Kohlrausch Law of Independent Migration of Ions (3×3)

(ii) Why does the transport number of Cd^{2+} ions in concentrated solutions of CdI_2 is negative? (3.5)

6. (i) State and derive Lambert-Beer's Law. (4)

(ii) 2.0×10^{-3} m thickness of a certain glass transmits 10% of the incident light of wavelength 300 nm. What percentage of light of the same wavelength will be absorbed by a 1.0×10^{-3} m thickness of the glass? (4)

(iii) The proposed mechanism of photochemical reaction between H_2 and Br_2 is

$$Br_2 \xrightarrow{h\nu} 2\,Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

Derive the quantum yield of reaction. (4.5)

7. (i) Explain, giving reasons : **(any two)**

(a) Specific conductance decreases while equivalent conductance increase on dilution.

(b) Molar conductance values for alkali metal cations are in the order $Rb^+ > K^+ > Na^+ > Li^+$.

(c) ADC current cannot be used for conductance measurements. (2+2)

(ii) What are the various factors affecting the conductance of a solution? How do you account for the increase in conductance of solutions at high field strength and at high frequency? (4)

(iii) A conductance cell when filled with 0.05 M solution of KCl records the resistance of 410.0 ohm at 25°C. When filled with $CaCl_2$ solution (11g $CaCl_2$ in 500 mL) it records 990 ohm. If the specific conductance of 0.05 M KCl solution is 0.00189 mho/cm, calculate (a) Cell constant, (b) specific conductance and (c) Molar conductance of $CaCl_2$. (4.5)

8. (i) Discuss **(any two)** applications of conductance measurements :

(a) Solubility and solubility product of a sparingly soluble salt.

(b) Determination of Ionic product of water.

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(c) Degree of hydrolysis and hydrolysis constant of a hydrolysable salt. (4+4)

(ii) A solution of HCl acid is electrolysed in a transport cell using platinum electrodes. 20.175 g of the cathode solution contained 0.175g of Cl^- ion before electrolysis and 18.466 g of the cathode solution contained 0.146 g Cl^- ion after electrolysis. A silver coulometer connected in series had a deposit of 0.2508 g Ag. Calculate the transport number of Cl^- and H^+ ions. (4.5)

9. (i) Describe Hittorf's method or Moving boundary method employed in determining the transport number of an ion. (4)

(ii) Which of the following pairs will have higher molar conductance and why?

(a) LiCl or NaCl

(b) Cl^- ion in HCl or in NaCl (2+2)

(iii) The resistance of a 0.02 mol/dm^3 solution of acetic acid in a cell having cell constant 0.2063 cm^{-1} was found to be 888ohm. What is the degree of ionization of the acid at this concentration? (Given Λ_m^0 for acetic acid = 387.9 $\times 10^{-4}$ $Smol^{-1}m^2$). (4.5)

(1500)

[This question paper contains 8 printed pages.]

Your Roll No.....

A

Sr. No. of Question Paper : 1107

Unique Paper Code : 32171601

Name of the Paper : Inorganic Chemistry IV: Organometallic Chemistry and Bio-inorganic Chemistry

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : VI

Duration : 3 hours 30 minutes Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **six** questions out of nine.
3. **All** questions carry equal marks **(12.5)**.

1. (i) What are Metalloenzymes and Metal Activated Enzymes? Give the name and the mechanism of action of the enzyme transporting CO_2 from the tissues to the lungs.

P.T.O.

(ii) What are interfering anions? How do they interfere in the cation analysis? Why do they interfere only after the second group cation analysis and not before?

(iii) Predict whether the following compounds obey EAN rule or not.

(a) $[Fe(CO)_2(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)]$

(b) $[Fe(CO)_2(NO)_2]$ (5,5,2.5)

2. (i) The Heam group in Haemoglobin cannot function as an oxygen carrier in the absence of the globin chain. Explain. Give the Hill's equation for the oxygenation of Haemoglobin.

(ii) What is Zeise's salt? Discuss the bonding in Zeise's salt on the basis of Dewar-Chatt-Duncanson model and IR studies. How is M-C bonding in Zeise's salt different from that in metal carbonyl complexes?

(iii) Explain the steps involved in the identification of NO_2^- and NO_3^- ions when present together in a salt mixture. (5,5,2.5)

3. (i) A mixture of anions gives brown vapours with concentrated H_2SO_4, which are intensified on adding copper turnings. A rod dipped in ammonia solution gives white dense fumes when brought near the mouth of the test tube. The sodium carbonate extract gives a white precipitate with silver nitrate after acidification, which is completely soluble in ammonium hydroxide solution. Explain with reactions how will you confirm the anions present.

(ii) How are organometallic compounds classified on the basis of type of bonding? Explain giving examples.

(iii) State what special features of Zn(II) make it an excellent biocatalyst? (5,5,2.5)

4. (i) State how does cis-platin block cell proliferation? Explain.

(ii) What is Bohr Effect? Draw the oxygen saturation curves for haemoglobin and myoglobin. Why do their shapes differ?

(iii) What is meant by the term hapticity? Give an example where the same ligand can show varying hapticity. (5,5,2.5)

5. (i) Give examples of metal containing biomolecules which perform the following functions. (Give the name of the metal and the biomolecule which contains the metal)

(a) Oxygen storage

(b) Metal storage

(c) Electron carrier

(d) Photoredox

(e) Prevention of disease

(ii) Ferrocene on acetylation with excess of reagent shows heteroannular substitution while on alkylation with excess of reagent shows homoannular substitution. Give reason.

(iii) Which alkaline earth metal is also involved in the sodium - potassium pump? What is the source of energy for this pump? (5,5,2.5)

6. (i) Explain the functioning and mechanism of action of the enzymes: Carbonic anhydrase and Carboxypeptidase A?

(ii) Define the following terms with reference to Catalysis :

(a) Catalytic cycle

(b) Tolman catalytic loop

(c) Lifetime of a catalyst

(d) Turnover number

(e) Poison

(iii) How will you detect potassium ion in presence of ammonium ions? (5,5,2.5)

7. (i) Name the metal with oxidation state involved in following biomolecules.

(a) Ferritin

(b) Vitamin B12

(c) Haemoglobin

(d) Chlorophyll

(e) Transferrin

(ii) What is Zieglar Natta Catalyst? Explain the active form of this catalyst which is involved in the oligomerization of olefin.

(iii) Write the formulae and draw the structures of two organometallic compounds having multicentre bonding. What is the reason of their multicentre bonding? (5,5,2.5)

8. (i) An unknown salt A, when heated with NaOH solution, produced a pungent smelling gas B. B turned red litmus blue and gave dense white fumes of C when a glass rod dipped in HCl was held at the mouth of the test tube. A, on heating with concentrated sulphuric acid, gave a mixture of two odourless gases D and E. D burnt with a blue flame while E turned lime water milky. An aqueous solution of A gave a white precipitate with calcium chloride solution, the acid

extract of which discharged the colour of acidified potassium permanganate solution. Identify A, B, C, D and E giving the reactions involved.

(ii) What do you mean by reductive carbonylation? Give a suitable example for this. The symmetric CO stretching frequencies in isoelectronic series of $[V(CO)_6]^-$, $Cr(CO)_6$ and $[Mn(CO)_6]^+$ are 1860 cm^{-1}, 2000 cm^{-1} and 2090 cm^{-1} respectively. Explain these observations.

(iii) In what form iron is stored in the human body? How is it taken from the storage site for the incorporation into haemoglobin? (5,5,2.5)

9. (i) Both carbon and oxygen have one lone pair of electron but in metal carbonyls, bonding is through carbon and not through oxygen. Explain with help of Molecular orbital diagram.

(ii) Write the toxic effects of Pb(II). Give the reasons for its toxicity. How it can be treated?

(iii) What is Wilkinson's catalyst. Explain its structure and oxidation state of the central metal ion. (5,5,2.5)

[This question paper contains 8 printed pages.]

Your Roll No.....

A

Sr. No. of Question Paper : 1352

Unique Paper Code : 32171602

Name of the Paper : Organic Chemistry V : Spectroscopy

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : VI

Duration : 3.5 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **six** questions.
3. **All** questions carry equal marks.

1. (a) A and B are two isomers of C_3H_6O based upon peaks obtained in spectral data recorded in ^1H NMR spectrophotometer: Identify A and B, give their IUPAC names and explain :

   (i) A : ^1H NMR, (in $CDCl_3$): δ1.1(t,3H), δ2.1 (m,2H), δ 9.5 (t, 1H)

P.T.O.

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IR (in Nujol) wave number: 2720cm^{-1} (doublet, m) and 1735cm^{-1}(s)

(ii) B: ^{1}H NMR, (in $CDCl_3$) δ2.3(s,6H)

IR (in Nujol) : 1710 cm^{-1}(s)

(b) Compound A shows strong peak in IR spectrum at 1717 cm^{-1} and give positive test with DNP. on reaction with hydroxylamine and followed by a well known Beckmann rearrangement gives compound B. Compound B polymerizes to give polymer, C. Identify, give name and structural formula of the compounds A, B and C (polymer).

$$\underset{\text{A}}{C_6H_{10}O} \xrightarrow[\text{(ii) } H_2SO_4]{\text{(i) } NH_2OH} \text{B} \xrightarrow{H_2O} \text{C (Polymer)}$$

(c) λ_{max} of Acetone in hexane is 279 nm while in water is 264.5 nm. Assign the given peak and explain by drawing transitions involved showing HOMO-LUMO. (4,4,4.5)

2. (a) Using N,N-Dimethylaniline writing all necessary conditions and reagents give synthesis of :

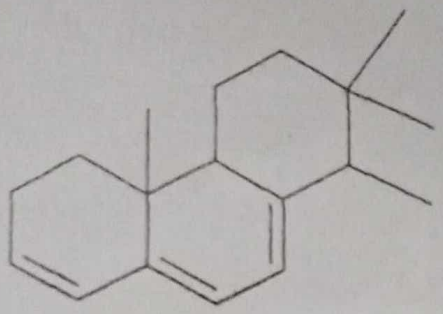
(i) Methyl orange and

(ii) Malachite green

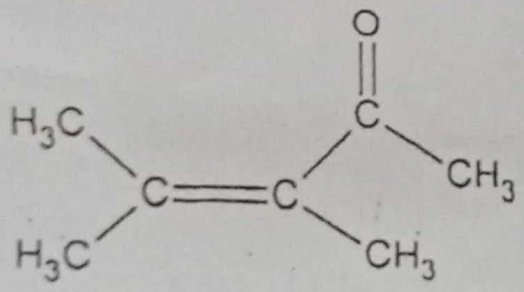
(b) Give stereochemical structure of (-)-chloramphenicol, its IUPAC name, uses and the name of species from which it is isolated.

(c) Calculate the λ max. for $\pi \rightarrow \pi^*$ in nm for the following compounds :

(i)



(ii)



Homoannular conjugated diene's base value = 253 nm

Heteroannular conjugated diene's base value = 215 nm

Increment for each substitution

Alkyl substituent or ring residue	= 5 nm
Exocyclic double bond	= 5 nm
Double bond extending conjugation	= 30 nm
Acyclic enone base value	= 215 nm

P.T.O.

α-Alkyl group or ring residue = 10 nm

β-Alkyl group or ring residue = 12 nm

γ-Alkyl group or ring residue = 17 nm

for correction in solvent :

methanol/ethanol = 0 nm

water = +8 nm

Also calculate the λ max for both of the above compounds (i) and (ii) in water and ethanol using correction appropriately. (4,4,4.5)

3. (a) Give synthesis of Alizarin from anthraquinone. Give the structure of complex with Aluminium as mordant.

(b) Give the synthesis of Congo red dye. Mention the pH at which it gives the blue colour and red and explain with structure change.

(c) What is Leuco base in a triphenylmethane dyes? Explain with appropriate reaction. Give synthesis of crystal violet dye. (4,4,4.5)

4. (a) Calculate the frequency of C-H stretching vibration from the following data :

Force Constant K = 5×10^{5} gm sec^{-2}

Mass of carbon atom = 20×10^{-24} gm

Mass of hydrogen atom = 1.6×10^{-24} gm

Velocity of the radiation(c) = 2.998×10^{10} cm sec^{-1}

(b) Attempt any **four** :

(i) What is the source of IR radiations in IR spectrophotometer

(ii) What are the Fundamental Vibrations?

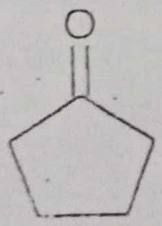
(iii) What are overtones in IR spectra?

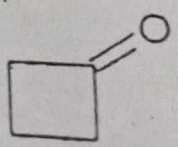
(iii) What is Fermi Resonance?

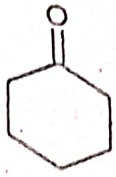
(iv) Differentiate acetamide and ethyl amine using IR spectroscopy.

(v) Differentiate in 1-Butyne and 2-Butyne using IR spectroscopy.

(c) Assign the appropriate C=O stretching frequency against the following structures. Justify the answer :

(i) 

(ii) 

(iii)  (iv) 

Stretch frequencies are

(a) 1745 cm^{-1}

(b) 1780 cm^{-1}

(c) 1815 cm^{-1}

(d) 1715 cm^{-1}

(4,4,4,5)

5. (a) Give the synthesis of Bakelite and its uses.

(b) Outline the synthesis of Nylon-6,6 and its uses.

(c) Write the mechanism involved when vinyl chloride in polymerised in presence of benzoyl peroxide?

(4,4,4.5)

6. (a) (i) Define chemical shift and coupling constant.

(ii) How will you differentiate in between cis and trans cinnamic acid ^1H NMR spectroscopy.

(b) Give expected number of signals by ^1H NMR spectra recorded in $CDCl_3$ in each of the following compounds :

(i) 1,2-dichloroethane

(ii) Ethyl acetate

(iii) cyclohexane (at low temperature)

(iv) 2-chloroethanol

(c) A compound with molecular weight 116 gave the following spectral information :

(i) UV (in ethanol): λ_{max} = 283 nm ε_{max} = 22

(ii) IR (in Nujol): 3000-2500 (b), 1715 (s), 1342 cm^{-1} (w)

(iii) NMR (in $CDCl_3$): δ 2.12 (s, 3H)
δ 2.60 (t, 2H)
δ 2.25 (t, 2H)
δ 11.1 (t, 1H)

Find the structural formula of the compound. (4,4,4.5)

7. (a) Give the Boots synthesis of Ibuprofen and its uses.

(b) Give the synthesis of chloroquine from m-chloroaniline. Give its uses and side effects.

P.T.O.

[This question paper contains 6 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 1521 **A**

Unique Paper Code : 32177908

Name of the Paper : DSE-8: Green Chemistry

Name of the Course : **B.Sc. (H) Chemistry**

Semester : VI

Duration : 3.5 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **six** questions. **All** parts of a question should be attempted together.
3. Each question carries **12.5** marks.

1. (a) Fill in the blanks with appropriate word(s) :

   (i) Rearrangement reactions are _____% atom economical.

   (ii) _____ is an example of a green solvent.

P.T.O.

(iii) Sonication uses _____ energy.

(iv) _____ is a non-renewable feedstock.

(v) PEG stands for _____.

(vi) ISD in green chemistry stands for _____.

(b) Define the following terms :

(i) Real time analysis

(ii) Depleting feedstock

(c) Complete the formula Risk = f (hazard, ...).

(6,2×3,0.5)

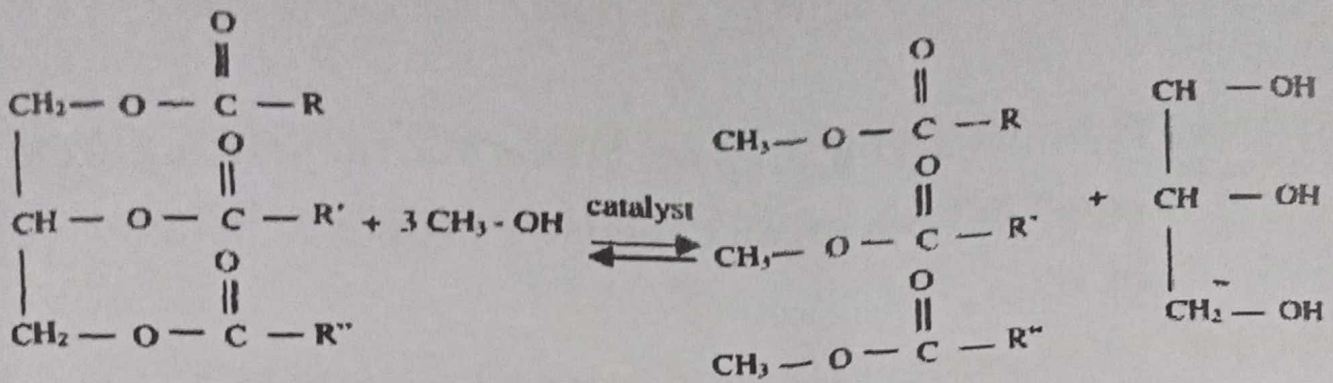
2. (a) Discuss any two Environmental laws.

(b) Name and elaborate the pollution prevention Act of 1990.

(c) Write down 12 Principles of Green Chemistry. Explain the principle of catalysis and Inherent Safer Chemicals. (3,3,6.5)

3. (a) Define atom economy.

(b) Calculate atom economy of the following reaction :



Triacylglycerol (Triglyceride) | Methanol | Fatty acid methyl esters (FAME) | Glycerol

R=CH_3

(c) Discuss the use of naturally occurring protein to stimulate plant growth and to improve crop quality. (2.5,6,4)

4. (a) Discuss two advantages of microwave assisted organic synthesis. Explain conversion of methyl benzoate to benzoic acid under microwave irradiation.

(b) What is Super-critical carbon dioxide? What are its advantages over conventional organic solvents? Why there is a need to replace PERC as a solvent for dry cleaning? (6.5,6)

5. (a) How will you prepare green plastic starting from com? Which green chemistry principle is involved in it?

(b) Explain how cradle to cradle recycling concept is applied to carpets?

(c) What is photocatalysis? How photocatalytic reactions are different from photochemical reaction? (4.5,4,4)

6. (a) Green Chemistry and sustainable development are inter-related. Explain.

(b) Explain the green synthesis of :

(i) Adipic acid and

(ii) catechol

(iii) Disodium iminodiacetate (3.5,9)

7. (a) Elaborate sonochemical Simmons-Smith reaction. What are its advantages over conventional method? Discuss how transfer of energy occurs in ultrasound assisted reactions?

(b) Discuss the advantages of combinatorial approach over conventional synthesis. (7.5,5)

8. (a) Name the Environmentally Advanced *Wood Preservative* discovered, which also won the Presidential Green Chemistry Challenge Award in 2002.

(b) Discuss the working of fluorous biphasic solvent.

(c) Why the selection of starting materials should be renewable rather than depleting? (4,4.5,4)

9. (a) Write short notes on :

(i) Combinatorial Chemistry

(ii) Co-Crystal controlled solid state synthesis

(iii) Flixiborough Accident

(iv) Biomimicry and Green chemistry

(b) Define the term Environmental Impact Factor.

(3,3,3,3,0.5)

[This question paper contains 6 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 764 **B**

Unique Paper Code : 42171205

Name of the Paper : Chemical Energetics, Equilibria & Functional Group Organic Chemistry

Name of the Course : **B.Sc. (Prog.)**

Semester : II

Duration : 3 hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Students should attempt, **Section A** and **Section B** on separate Answer sheets.
3. Attempt **three** questions from **Section A** and **three** questions from **Section B** (total **6** questions).
4. Use of non-Scientific calculator and log tables are allowed.

P.T.O.

Section A: Physical Chemistry

(Attempt any three questions in this section)

1. (a) What do you understand by buffer and buffer capacity? Give one example of acidic and basic buffer?

(b) Explain the term entropy and give its physical significance. Calculate the molar entropy (ΔS°_m) of $H_2O(l)$ at 298 K if S°_m of $H_2O(l)$, $H_2(g)$ and $O_2(g)$ are 69.91 J mol^{-1} K^{-1}, 130.684 J mol^{-1} K^{-1} and 205.138 J mol^{-1} K^{-1}.

(c) State the Le-Chatelier's principal. Predict the effect of increase of temperature and pressure on the following reaction :

$$H_2(g) + N_2(g) \rightleftharpoons 2NH_3 \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

What will happen if some more molecules of $N_2(g)$ introduced in the reaction? (4,4,4.5)

2. (a) The solubility of CaF_2 in water at 20°C is 15.6 mg per dm^3 of solution. Calculate the solubility product of CaF_2 (molar mass of CaF_2 = 78 g mol^{-1}).

(b) Define pH. What is the pH at 25°C for a solution which is twice as alkaline (i.e. which contains twice as many hydroxide ions) as pure water?

(c) Define Heat of Vaporization, Heat of Fusion, Heat of Sublimation. Differentiate among them by considering a suitable example. Explain Hess's law diagrammatically by considering these three enthalpy of water. ..... (4,4,4.5)

3. (a) Explain first law of thermodynamics and give the mathematical form of first law of thermodynamics.

(b) Calculate the enthalpy change for the reaction:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Data : $\Delta H^\circ_{(C=C)} = 610$ kJ mol^{-1}; $\Delta H^0_{(H-H)} = 436$ kJ mol^{-1}; $\Delta H^0_{(C-H)} = 413$ kJ mol^{-1} $\Delta H^\circ_{(C-C)} = 348$ kJ mol^{-1}.

(c) Hydrolysis of acetate ion is represented as

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Calculate the hydrolysis constant (K_h) and its degree of hydrolysis (α) in 0.1 M solution of sodium acetate. Given $K_a(CH_3COOH) = 1.8\times10^{-5}$ M and $K_w = 1 \times 10^{-14}$ M. (4,4,4.5)

P.T.O.

4. (a) Write a short note on "bond energy and bond dissociation energy".

(b) Define integral and Differential enthalpies of solution and write their expression.

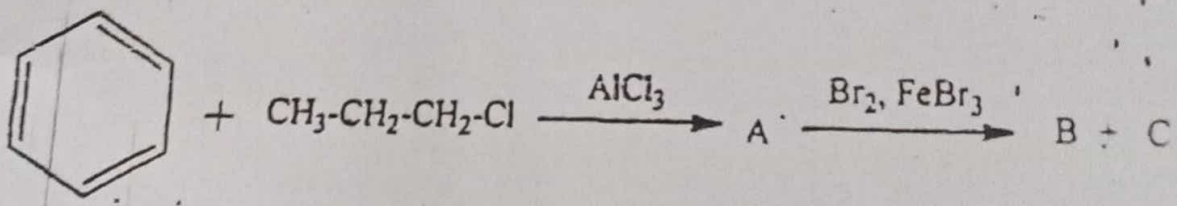
(c) Derive the expression for Kp, Kx and Kc by considering a general reaction and also find out relationship between Kp, Kx and Kc.

(4,4,4.5)

Section B: Organic Chemistry

(Attempt any **three** questions in this section)

5. (a) Complete the following reaction and draw the structures of A, B and C.



(b) How will you convert?

(i) Toluene to nitrobenzene

(ii) Benzene to diphenylmethane

(c) Explain why aromatic hydrocarbon undergoes electrophilic substitution reaction and carbonyl compound undergoes nucleophilic addition reaction. Give one example of electrophilic substitution and nucleophilic addition reaction. (4,4,4.5)

6. (a) What is the criterion of aromaticity according to Huckel's rule?

(b) Nitrophenols are more acidic than phenol: comment. Why the meta isomer has significantly low acidity?

(c) Explain why aryl halides undergo low reactivity towards nucleophilic substitution reaction (SN1 & SN2) than alkyl halides. (4,4,4.5)

7. (a) Write down the reactions involved in the industrial preparation of Phenol.

(b) Describe the benzyne mechanism for nucleophilic substitution of aryl halide by taking an example.

(c) What type of chemical reactions carbonyl compounds undergo? (4,4,4.5)

8. (a) Write a short note on **any two** of the following :

(i) Iodoform reaction

(ii) Pinacol- Pinacolone rearrangement

(iii) Wolf Kishner reduction

(b) Explain Crossed Aldol condensation via suitable example. (2×4,4.5)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 1590 **A**

Unique Paper Code : 42177926

Name of the Paper : DSE : Organometallics, Bio-inorganic Chemistry, Polynuclear Hydrocarbons and UV, IR Spectroscopy

Name of the Course : **B.Sc. (Prog.)**

Semester : VI

Duration : 3.5 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **three** questions from **Section A** and **three** from **Section B**.

SECTION A

(Attempt any **three** *questions)*

1. (a) Compound A when heated with a soluble chloride and concentrated H_2SO_4 gives orange red vapours of compound B. When an alkali is added to A it gives yellow coloured compound C which on

P.T.O.

acidifying converts back to A. Identify compounds A, B and C and write the chemical reactions involved.

(b) Draw and explain the structure of Ferrocene.

(c) What do you mean by cooperativity in haemoglobin? Discuss the role of haemoglobin and myoglobin in biological system. (4,4,4.5)

2. (a) Discuss 18-electron rule for metal carbonyls. Predict which of the following molecule does not obey 18-electron rule

(i) $[Fe(CO)_5]$

(ii) $[Cr(CO)_5]^{2-}$

(iii) $[Mn(CO)_4Cl_2]^{2-}$

(iv) $[(\eta^5\text{–}C_5H_5)_2Fe]$

(b) With reference to molecular orbital diagram explain that CO acts as both Lewis acid and Lewis base.

(c) With the help of diagram explain the mechanism of sodium-potassium pump. Why it is considered as an active transport. What is the source of energy for its functioning? (4,4,4.5)

3. (a) Give Reasons for the followings :

(i) Nickel tetracarbonyl is a stable carbonyl but Manganese does not form stable mononuclear carbonyl.

(ii) IR stretching frequency of CO bond is different in terminal and bridging carbonyls.

(b) Discuss the role of Na^{+} and Mg^{+2} ions in biological system.

(c) Give method of preparation of potassium ferrocyanide. What is the oxidation state of iron in it? How is it used for the identification of Zn^{+2} ions present in an organic salt? Give chemical reactions. (4,4,4.5)

4. (a) What happens when (give balanced chemical equations)

(i) $KMnO_4$ reacts with a ferrous salt in acidic medium.

(ii) A solution of potassium dichromate containing dilute H_2SO_4 and ether is treated with H_2O_2.

(iii) Sulphuric acid is added to a saturated solution of K_2CrO_4.

(iv) $K_4[Fe(CN)_6]$ is treated with copper sulphate.

(b) Discuss lead-poisoning and mercury-poisoning in brief.

(c) What are organometallic compounds? Which of the followings are not organometallic compounds?

(i) Zeise's Salt

(ii) Cisplatin

(iii) Ferrocene

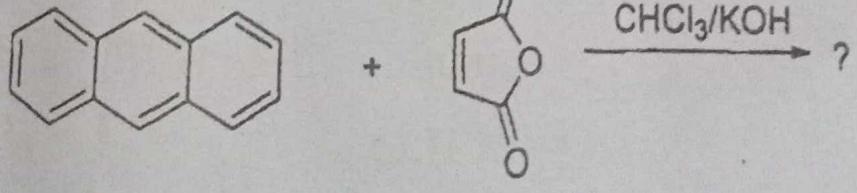
(iv) Sodium ethoxide

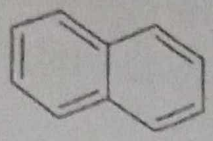
(v) Grignard Reagent (4,4,4.5)

SECTION B

(Attempt any **three** *questions)*

5. (a) What happens when :

(i) 

(ii)  + $2H_2$ $\xrightarrow{Ni/\Delta}$?

(b) Pyridine primarily undergoes nucleophilic substitution at 2- or 6- position. Explain

(c) How will you convert :

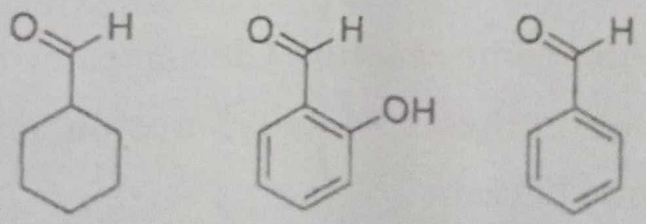
(i) Ethyl acetoacetate $\xrightarrow{\text{Ketonic hydrolysis}}$ Acetone

(ii) Ethyl acetoacetate $\xrightarrow{\text{Acidic hydrolysis}}$ Acetic acid

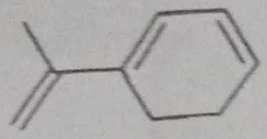
(d) Discuss the theory of electronic spectroscopy with a neat diagram showing electronic transitions in 1,3-butadiene.

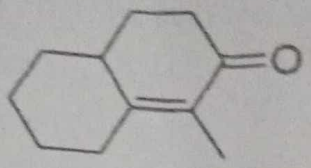
(e) Explain: chromophores. (2,2,4,2.5,2)

6. (a) Giving reasons, predict the C=O frequency shift in the given aldehydes, C=O stretching frequencies are 1665 cm^{-1}, 1700 cm^{-1} and 1730 cm^{-1}.



(b) Calculate the absorption maximum (λ_{max}) for $\pi \rightarrow \pi^*$ transition in the following compounds using Woodward-fieser rules.

(i) 

(ii) 

Parental/Base values	λ_{max} (nm)
Acyclic/ Heteroannular dienes	214
Homoannular dienes	253
α, β unsaturated Acyclic ketones	215
α, β unsaturated Aldehydes	210

Increments	(nm)
Alkyl substitution/ Ring residue	+5
Additional conjugation	+30
Exocyclic double bond	+5
α-alkyl substituent	+10
β-alkyl substituent	+12

(c) Write notes on: Bathochromic shift

(d) How will you distinguish the following pair of compounds using IR spectra?

(i) $CH_3CH_2COOCH_3$ and CH_3COCH_3

(ii) $CH_3CH_2CH_2COOH$ and $CH_3CH_2CH_2CHO$

(4,3,1.5,4)

7. (a) Write the name reaction Claisen ester condensation for the synthesis of ethyl acetoacetate. Explain with mechanism.

(b) Explain the Keto-enol tautomerism by taking active methylene compound as an example.

(c) How will you prepare the following from ethyl acetoacetate : **(Attempt any six)**

(i) Gluteric acid

(ii) Crotonic acid

(iii) Cinnamic acid

(iv) 4-methyluracil

(v) Pentane 2,4-dione

(vi) Methylisoxazolone

(vii) Cyclohexyl methyl ketone

(viii) Ethyl methyl ketone (4,2.5,6)

8. (a) How will you carry out the following conversions?

(i) Anthracene to 9-bromoanthracene

(ii) Naphthalene to Decalin

(iii) Furan to 2-nitrofuran

(iv) Pyridine to 3-pyridinesulphonic acid

(v) Pyrrole to 2-formylpyrrole

(b) How do you synthesize anthracene using Haworth synthesis?

(c) Pyridine is more basic than pyrrole. Explain

(d) Draw the resonating structure of naphthalene.

(5,3,3,1.5)

Chemistry