

Signature of Invigilators

Roll No.

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(In figures as in Admit Card)

CHEMICAL SCIENCES

Paper III

Roll No.

(In words)

—0302

Name of Areas/Section (if any)

Time Allowed : 2½ Hours]

[Maximum Marks : 200

Instructions for the Candidates

FOR OFFICE USE ONLY Marks Obtained

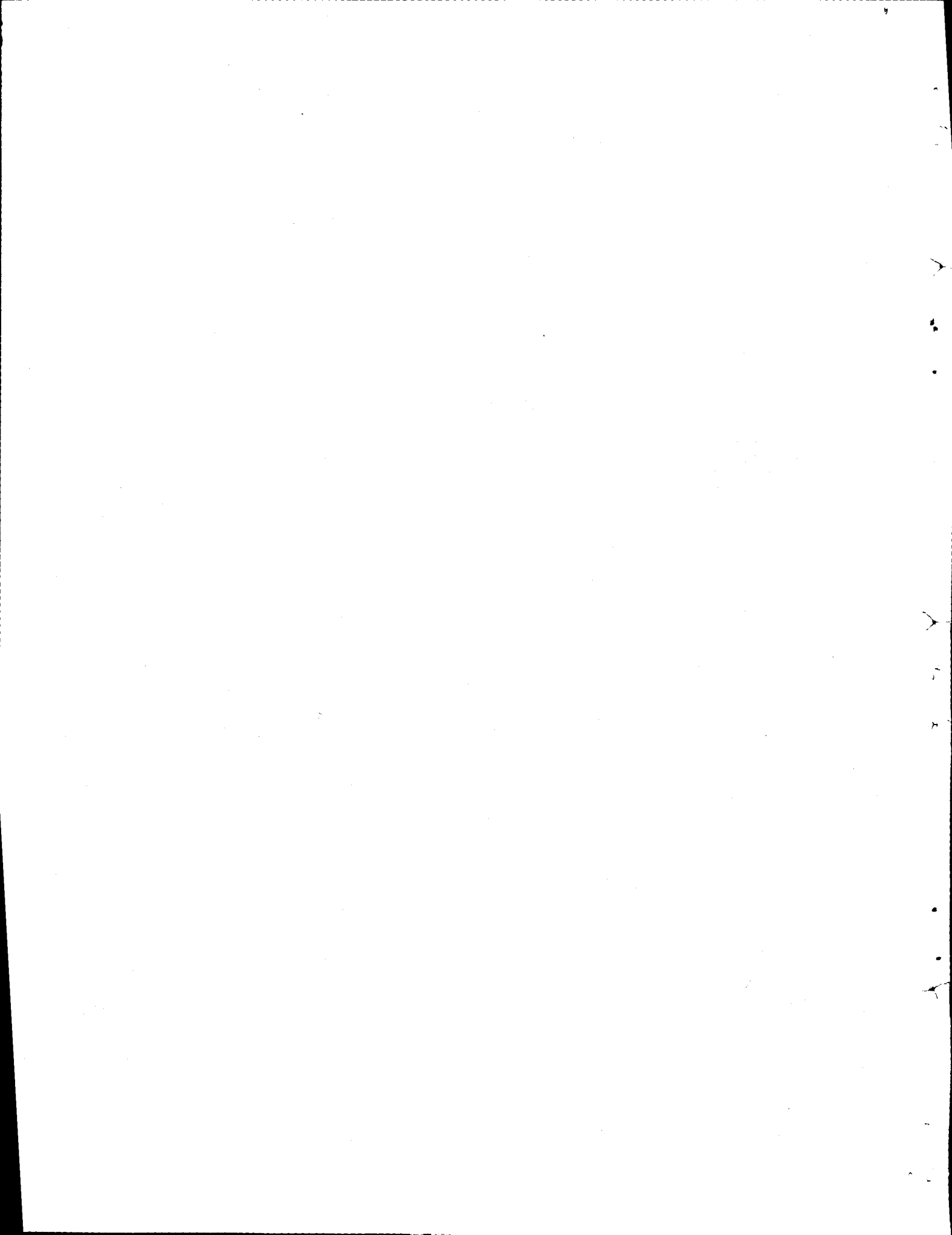
1. Write your Roll number in the space provided on the top of this page.
2. Write name of your Elective/Section if any.
3. Answer to short answer/essay type questions are to be written in the space provided below each question or after the questions in test booklet itself. No additional sheets are to be used.
4. Read instructions given inside carefully.
5. Last page is attached at the end of the test booklet for rough work.
6. If you write your name or put any special mark on any part of the test booklet which may disclose in any way your identity, you will render yourself liable to disqualification.
7. Use of any calculator is prohibited.
8. There is no negative marking.
9. You should return the test booklet to the invigilator at the end of the examination and should not carry any paper outside the examination hall.

પરીક્ષાર્થીઓ માટેની સૂચનાઓ :

1. આ પાનાની ટોચમાં દર્શાવેલી જગ્યામાં તમારો રોલ નંબર લખો.
2. જો કોઈ વિકલ્પ/વિભાગ પસંદ કર્યા હોય તો તે યોગ્ય જગ્યાએ દર્શાવો.
3. ટૂંકા પ્રશ્નો/નિબંધ વિષેના જવાબો એ પ્રશ્નની નીચે અથવા બાજુમાં આપેલી જગ્યામાં લખો. વધારાના કોઈ પાનાનો ઉપયોગ કરશો નહીં.
4. અંદર આપેલી સૂચનાઓ કાળજીપૂર્વક વાંચો.
5. બુકલેટની પાછળ આપેલું છેલ્લું પાનું રફ કામ માટે છે.
6. બુકલેટ કોઈપણ ઠેકાણે તમારું નામ કે કોઈ ચોક્કસ સંજ્ઞા કરવી નહીં કે જે તમારી ઓળખ પૂરી પાડે. આ તમને પરીક્ષા માટે ગેરલાયક ઠેરવશે.
7. કેલ્ક્યુલેટર નો ઉપયોગ કરાશે નહીં.
8. નકારાત્મક માર્કીંગ નથી.
9. પરીક્ષા સમય પૂરો થઈ ગયા પછી આ બુકલેટ જે તે નીરીક્ષકને સોંપી દેવી. કોઈપણ પેપર પરીક્ષા રૂમની બહાર લઈ જવું નહીં.

Question Number	Marks Obtained	Question Number	Marks Obtained	Question Number	Marks Obtained
1		26			
2		27			
3		28			
4		29			
5		30			
6		31			
7		32			
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Total Marks Obtained.....
Signature of the co-ordinator.....
(Evaluation)



ANTILOGARITHMS

Table of anti-logarithms with columns labeled 0 through 9 and a final column for the mantissa (e.g., 1000, 1001, 1002, etc.).

ANTILOGARITHMS

Table of anti-logarithms with columns labeled 0 through 9 and a final column for the mantissa (e.g., 3162, 3163, 3164, etc.).

LOGARITHMS

Table of logarithms for numbers 10 to 99. Columns represent the integer part (0-9) and the decimal part (0-9). Rows are labeled with numbers 10 through 99.

LOGARITHMS

Table of logarithms for numbers 60 to 99. Columns represent the integer part (0-9) and the decimal part (0-9). Rows are labeled with numbers 60 through 99.

CHEMICAL SCIENCE
PAPER III

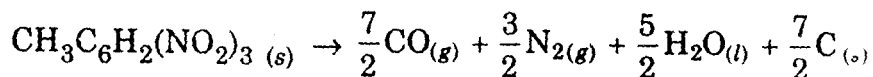
Note :—(i) Question no. 1 is compulsory (40 marks). Answer it in 800 words (8 pages).

(ii) Attempt any *ten* questions out of the remaining 35 questions (16 marks each). Answer each question in 300 words (3 pages).

1. (A) Answer any *three* of the following :

(a) By improving the instrument design the resolving power can be improved. However, a minimum width called 'natural line width' is inherent to all atomic and molecular transitions. What factors contribute to this ?

(b) TNT on detonation decomposes as



In a constant volume calorimeter, 454 mg of TNT at 25°C on detonation evolved 1.64 kcal. Neglecting volumes of solids and liquids, calculate ΔH and ΔU for the detonation. (MW of TNT = 227)

(c) Neatly sketch the possible fundamental modes of vibration for CO_2 molecule. Which of them are IR or Raman active vibrations ?

(d) The first rotational absorption of $^{12}\text{C}^{16}\text{O}$ is at 3.84235 cm^{-1} while that of $^{13}\text{C}^{16}\text{O}$ is at 3.67337 cm^{-1} . Taking the mass of oxygen to be 15.9994 and that of ^{12}C to be 12.00, calculate the atomic mass of ^{13}C .

12

(B) Write briefly on any *three* of the following :

(a) Superconducting Heterometal Oxides;

(b) Structural features of ZEOLITES make them fascinating materials in catalysis;

(c) Fischer-Tropsch process for Synthetic Gasoline;

(d) Unique behaviour Fluorine.

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(C) Attempt any *three* of the following :

(a) A 100 MHz (23, 846 gauss) spectrometer observes a proton that absorbs at a field 0.20 gauss downfield from TMS. Determine its chemical shift and express this shift as a frequency.

(b) Propose a structure for compound that has the molecular formula $C_{10}H_{14}$ and shows the proton NMR signals at $7.1 \delta(m, 5H)$ and $1.2(s, 9H)$.

(c) Deduce structural formula of compound X which shows : $M^+ = 117$, $\lambda_{max} = 234 \text{ nm}$, ^{13}C -NMR shows six lines, IR— 2230 cm^{-1} . The 1H NMR signals are seen at $7.5 \delta(d, 2H)$, $7.2 \delta(d, 2H)$, $2.4 \delta(s, 3H)$.

(d) In the mass spectrum of ethyl butanoate an intense peak at $M/2 = 88$ is seen. Explain its formation.

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(D) Draw a block diagram of a double beam spectrophotometer. Name the source and the detectors used in uv, visible and IR regions.

4

2. (a) The lowest pH recorded experimentally so far is -0.3 even in solutions with acid concentrations of greater than 10 N . Briefly give reasons.

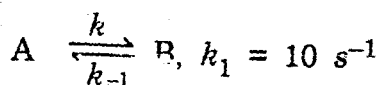
(b) What is the function of Temperature control knob in a pH-meter ?

(c) For H_3PO_4 , $K_1 = 7.5 \times 10^{-3}$, $K_2 = 5.2 \times 10^{-8}$ and $K_3 = 1.0 \times 10^{-12}$. If equal volumes of 0.1 N solutions of H_2NaPO_4 and HNa_2PO_4 solutions are mixed, what will be the pH of the mixture ?

3. (a) When common salt and crushed ice are mixed the temperature falls to -21°C . Briefly explain this on the basis of phase rule.

(b) Draw Temperature composition diagram for Ethylalcohol-water system.

(c) For the reaction :



and the equilibrium constant is 20. Calculate the relaxation time for the reaction.

4. (a) Show that for a crystalline solid, the absolute entropy is given by

$$S_T = \int_0^T C_p d(\ln T)$$

- (b) A steam engine operates between 27°C and 100°C . Calculate its maximum possible efficiency. If the boiling point of water at a pressure of 50 atm is taken as 267°C (Superheated steam), what will be the efficiency of the engine? In both cases the temperature of the sink is 27°C .
- (c) Carbonated beverages are bottled with CO_2 under high pressure. Why does the mixture fizz when the container is suddenly opened to the atmosphere? Use Le Chatelier's principle to describe what happens?
5. (a) Given $du = T.ds - P.dv$, do a Legendre transformation to get the thermodynamic quantity A.
- (b) Critical micelle concentration of an aqueous solution of sodium dodecyl sulfate is 10^{-3} mol. lit^{-1} at 25°C . What is ΔG° for micellization?
- (c) (i) Which will have higher aggregation number: Lithium dodecyl sulfate or sodium dodecyl sulfate?
- (ii) Which will show higher CMC: CTAB or PEO having equal number of carbon atoms?
6. (a) 'Stern model for electrical double layer is superior to Gouy-Chapman model'. Give reasons.
- (b) Draw Evans' diagram to show inhibition of corrosion.
- (c) The standard reduction potential of Cu and Ag are + 0.34 V and + 0.79 V respectively. Calculate the e.m.f. of the cell formed by their combination. Indicate how the cell can be represented. Write the electrode and cell reactions.
7. (a) A finely divided metal shows high catalytic activity but it is difficult to handle it. Suggest an alternative to maintain high activity and name characterization techniques you may use.
- (b) Write BET equation, draw BET plot and show how monolayer volume can be determined from it.
- (c) Why physisorption has no catalytic application?

8. (a) The resonance reabsorption of γ -rays is difficult to observe. What conditions Mössbauer used to realize it ?
- (b) State the conditions for molecules to be microwave active and infrared active.
- (c) What are magnetogyric ratio and the g_N factor of the ^{31}P nucleus, the magnetic moment of which is $1.1305 \mu_N$. (Given $\mu_N = 5.051 \times 10^{-27} \text{ J} \cdot \text{T}^{-1}$ and $h = 6.626 \times 10^{-34} \text{ Js}$).
9. (a) In what respect high temperature fuel cell is better than low temperature fuel cell ?
- (b) Give important differences between step growth polymerization and chain growth polymerization.
- (c) In a given space there are 20 particles. If an imaginary wall divides space into two parts, compute the probability that all the 20 particles are on the same side of the wall.

10. (a) The entropy is defined as

$$S = -k \sum_i P_i \ln P_i$$

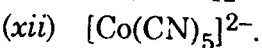
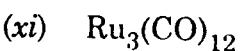
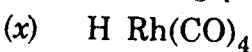
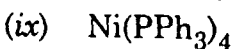
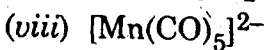
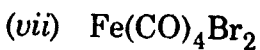
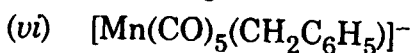
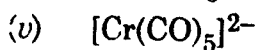
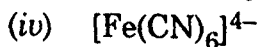
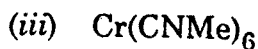
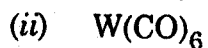
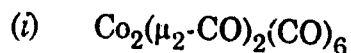
where $P_i = e^{-\beta E_i} / Q$ and $Q = \sum_i e^{-\beta E_i}$. Explain S in terms of Q.

- (b) Show that statistical mechanical partition function has same property as quantum mechanical wave function.
- (c) Air consists of a mixture of 21% of oxygen and 79% N_2 by volume. Calculate the entropy of mixing of the elements of air.
11. (a) Show that an oscillating dipole has frequency components $\nu \pm \nu_{\text{vib}}$ as well as the exciting frequency ν .
- (b) From the following data comment on the molecular structure of nitrous oxide and assign the observed lines to specific molecular vibrations :

$\bar{\nu} (\text{cm}^{-1})$	IR	Raman
589	strong, PQR Contour	—
1285	very strong, PR	very strong, polarized
2224	very strong, PR	strong, depolarized

- (c) What do you mean by 'hot bands' in spectroscopy ?

12. (a) Give the valence electron count for the following species. Which one/s conforms to the E.A.N. rules ?



(b) Name each one of the above species.

(c) Using Wilkinson's Complex, discuss the Homogeneous Catalytic Hydrogenation of Propene.

13. Write briefly on :

(a) Structure and Role of Biological Membranes during ion transport.

(b) Biological Nitrogen Fixation.

(c) Icosahedral structure of $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion.

(d) Structural features and Correlation between the structures of Heme group proteins.

14. (a) (i) Sketch π bonding orbitals that result from the combination of the following orbitals on separate atoms : p_x and p_z ; p_z and d_{xz} ; and d_{xz} and d_{xz} .

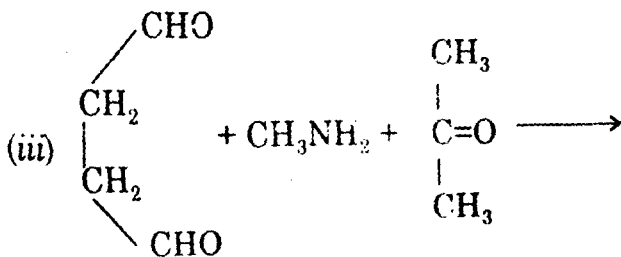
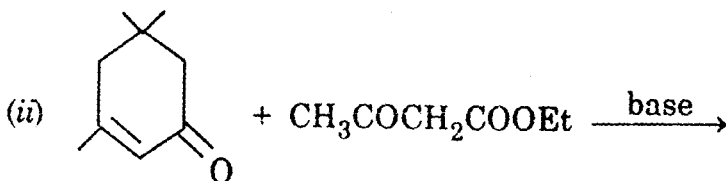
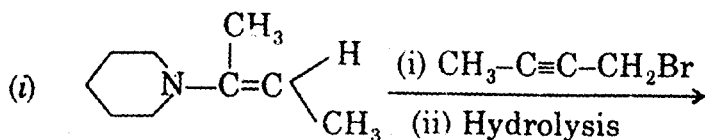
(ii) Write the molecular orbital configuration diagrams and give the bond order of NO^+ ; NO_2 and NO^- . Which one/s of these species should be paramagnetic ?

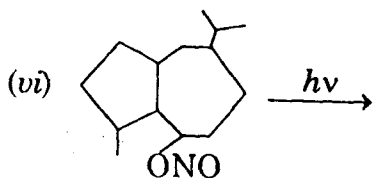
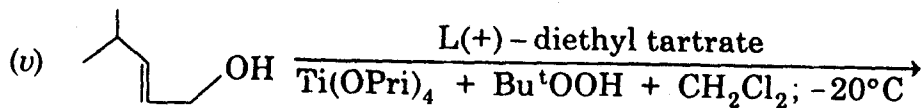
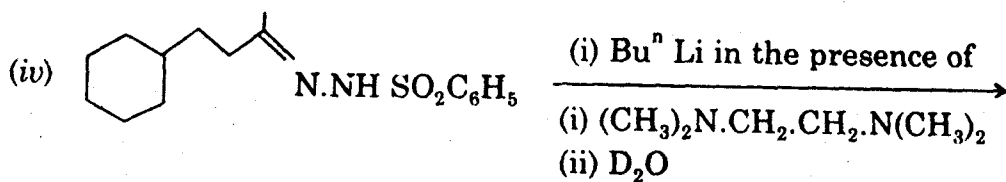
(b) Give molecular orbital diagram of COBALTOCENE and explain its magnetic behaviour.

15. (a) How one can distinguish between the following isomers ?
- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
 - $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$
 - Cis-and Trans $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
 - Cis-and Trans $[\text{Pt}(\text{glycine})_2]$
 - Cis-and Trans $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$
- (b) Cite one example each of the following types of isomerism :
- Hydration Isomerism;
 - Coordination Isomerism;
 - Linkage Isomerism;
 - Ionization Isomerism;
 - Geometrical Isomerism;
 - Optical Isomerism.
- (c) Measurement of $10 Dq$ and discuss the factors responsible for the magnitude of $10 Dq$.
16. Write briefly on :
- Ziegler-Natta Catalysed Polymerization of ethylene.
 - Water gas shift reaction using Homogeneous catalyst.
 - Fluxional behaviour of Pentacoordinated molecule.
 - ZSM-5, its nature and applications.
17. (a) Arrange the following in the increasing order of property given in each case :
- Oxidizing capacity of CrO_4^{2-} , FeO_4^{2-} and $[\text{VO}_4]^{3-}$
 - First ionization energy of S, Al, P and Mg
 - N-N bond order in N_2 , N_2F_2 and N_2H_4
 - Ionic radii O^{2-} , N_3^- and O_2^- .
- (b) (i) In solid state CuF_2 , the Cu—F distance is found at 1.93 Å (four bonds) and two bonds of Cu—F at 2.27 Å.
- (ii) Magnetic properties of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, give their comparison.
- (iii) Explain why solid ferrocene exhibit staggered conformation. While ferrocene in vapour form possesses Eclipsed conformation.
- (iv) Back donation in metal alkene and metal alkyne complexes stabilize these compounds. Discuss in brief.

18. (a) Write the highest coordination number exhibited by the following ligands :
- (i) Acetyl acetone;
 - (ii) Porphyrin;
 - (iii) 18 Crown-6 ether;
 - (iv) Diethylene triamine;
 - (v) Diethylene triamine penta-acetic acid;
 - (vi) Valinomycin;
 - (vii) Schiff base Salen;
 - (viii) EDTA;
 - (ix) Triphenyl phosphine;
 - (x) Tripeptide glutathione (γ L glutamyl Lcysteinyl glycine)
- (b) Discuss the electronic configuration of lanthanides and lanthanide contraction.
19. (a) (i) Give the structural formulae of two metallocenes with bent structures
- (ii) Structure of σ bonded metal alkyne and metal allylene compounds.
 - (iii) Factors governing the Ionization energy should be discussed in brief.
 - (iv) Give four points of differences between Boron and Aluminium.
 - (v) Why CO_2 is a gas while SiO_2 is solid ?
- (b) What are Silicones ? How are these prepared and discuss in brief their application ?
20. (a) Give Schematic representation of Homogeneously Catalysed Hydroformylation of Ethylene using Cobalt Carbonyl.
- (b) A black substance (X) when heated in presence of KNO_3 and KOH produced a green mass (Y). On extraction with water Y gave a green solution. The green solution turned purple (Z) when a current of chlorine was passed through it.
- (c) What are porphyrins and discuss in brief the Biogenesis of Porphyrin ?

21. (a) What are Ionophores and what role these play in understanding the biochemistry of alkali metals ?
- (b) Discuss critically but in brief the reversibly binding of dioxygen to Haemoglobin.
- (c) General structure of chlorophyll and discuss how chlorophyll facilitate photosynthesis.
22. (a) A classical method of synthesizing α -amino acids is based upon modified phthalimido malonic ester method. Utilizing this concept suggest a synthesis of glutamic acid. 8
- (b) Allose is an aldohexose with a structure similar to glucose except for the opposite stereochemical configuration at C_3 . Draw Haworth structure for a β -anomer of D-allose. 4
- (c) Treatment of 3-chlorocyclopropene with $SbCl_5$ yields a stable crystalline solid (I) of formula $C_3H_3SbCl_6$. I is insoluble in non-polar solvents but soluble in polar solvents. The 1H NMR shows three exactly equivalent protons. Give most likely structure of I and show how this structure accounts for the various observations. 4
23. Predict the product and name the reactions involved wherever possible (any four) :



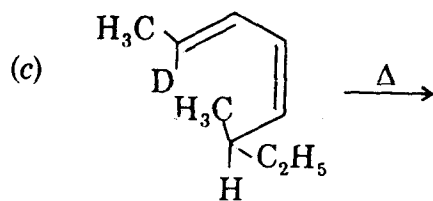
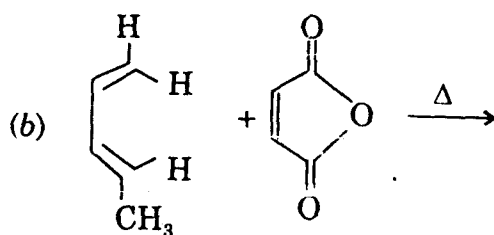
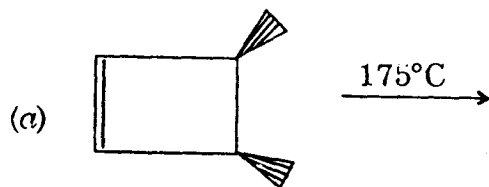


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24. (A) In the following pericyclic reactions :

(i) Predict the product and its stereochemistry; and

(ii) Name the reaction type and give selection rules (attempt any two) :

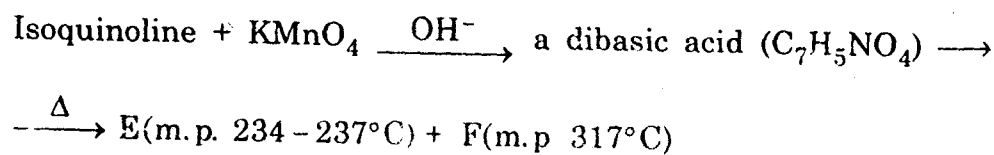
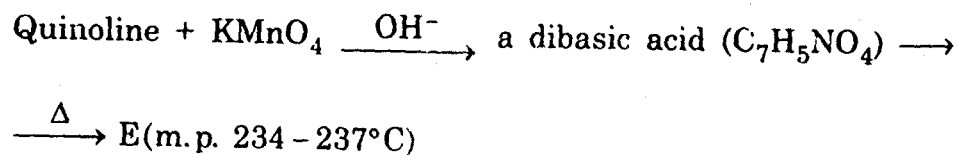


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(B) There are three isomeric pyridine mono-carboxylic acids :

D, m.p. 137°C, E, m.p. 234–237°C, F, m.p. 317°C

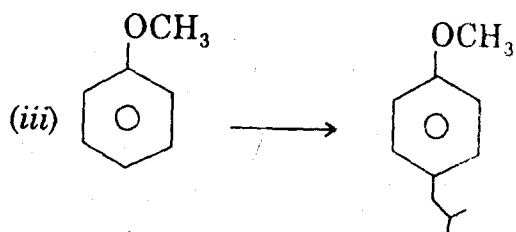
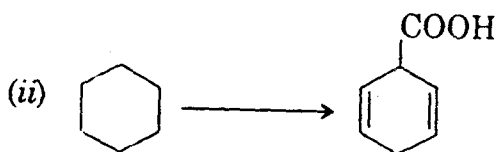
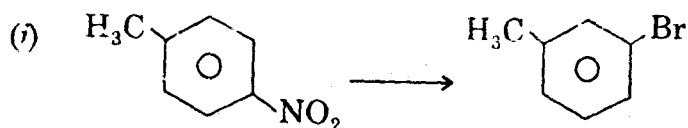
Their structures were proved as follows :



What structure should be assigned to D, E and F ?

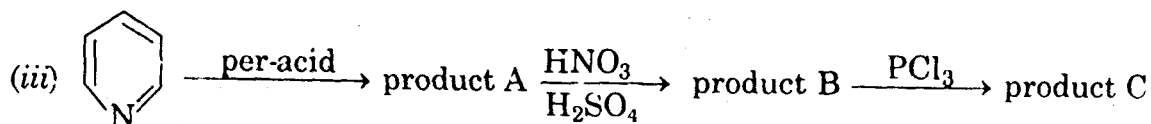
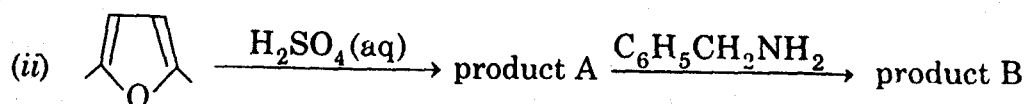
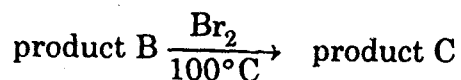
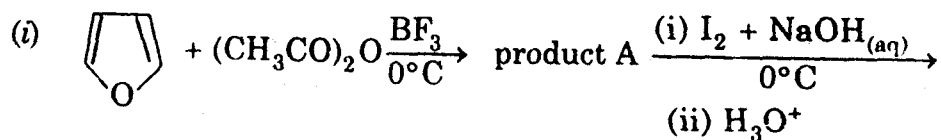
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25. Describe the reagents and the intermediates required for each of the following conversions (more than one step may be required). Attempt any two :



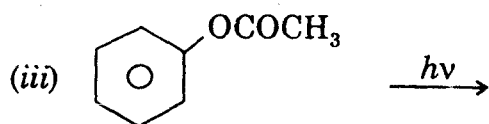
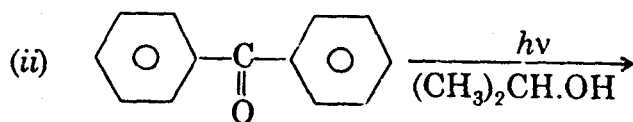
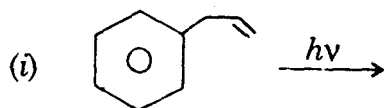
16

26. Predict the product of the following reactions (any two) :



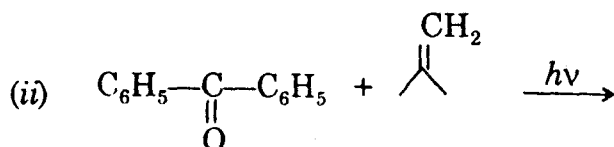
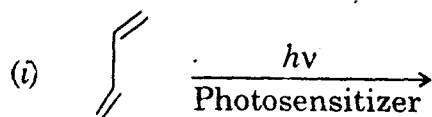
16

27. (a) Predict the product and suggest a mechanism of the following photochemical transformations (any two) :



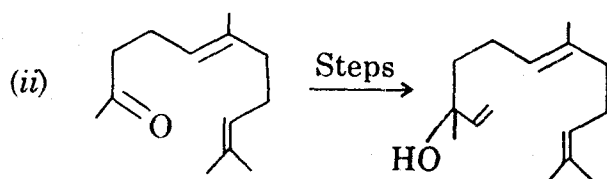
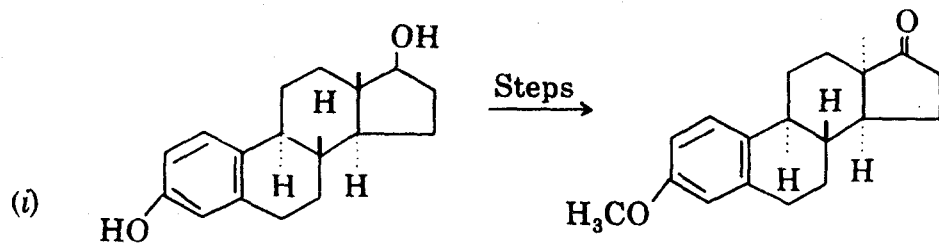
12

(b) Complete the following reactions :



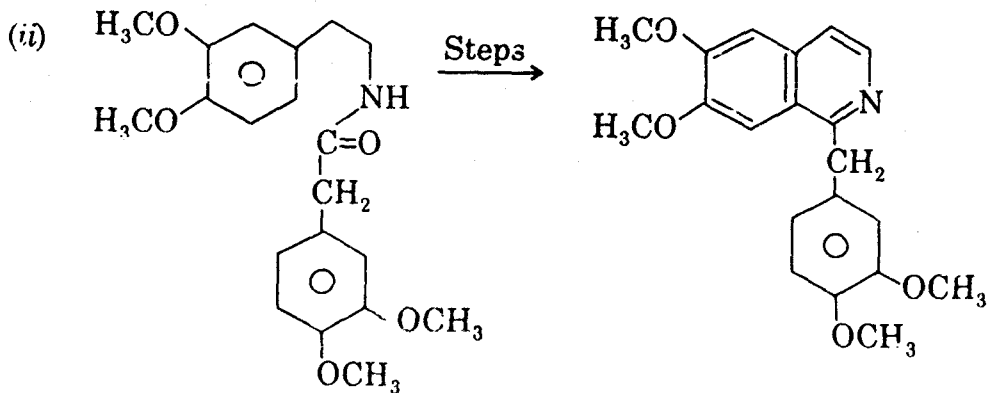
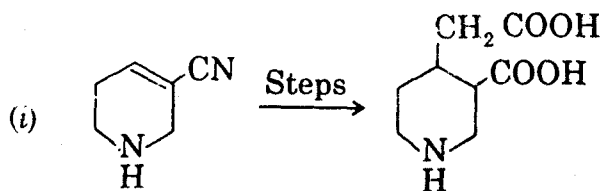
4

28. (a) How will you bring about the following conversions using appropriate reagents/reactions ?



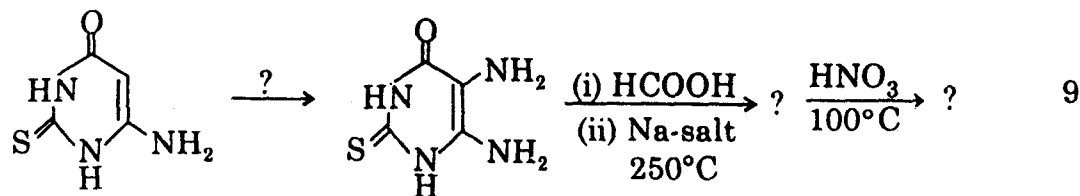
10

- (b) How will you perform the following conversions ?

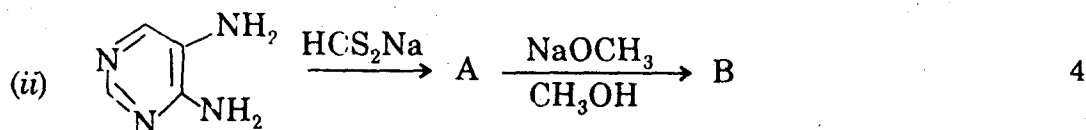
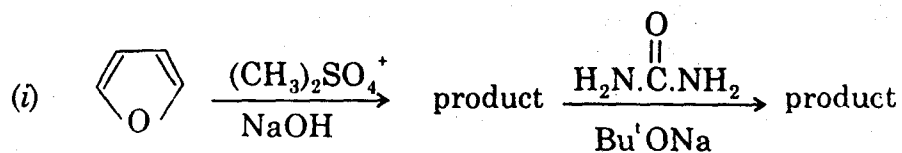


6

29. (a) Complete the following reactions :

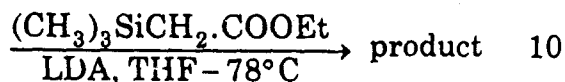
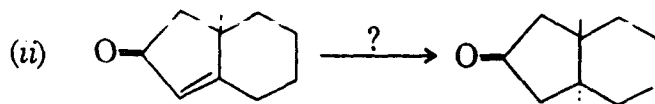
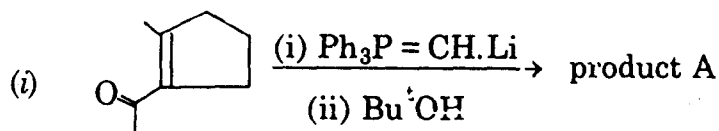


(b) Attempt any one of the two reactions :

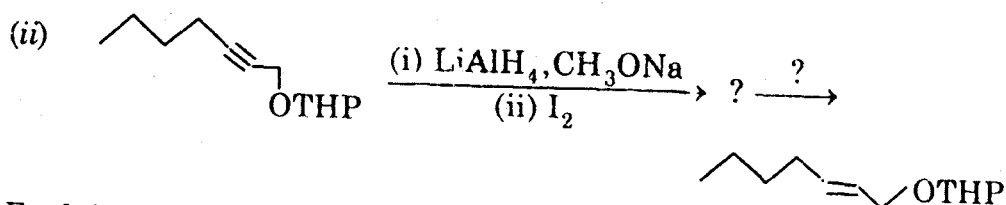
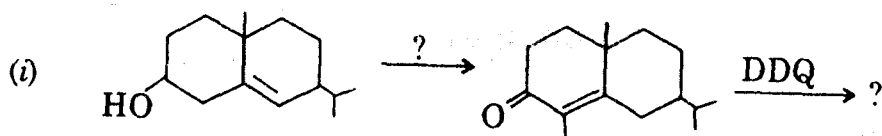


(c) Suggest the biogenesis of β -pinene starting from geranyl pyrophosphate.

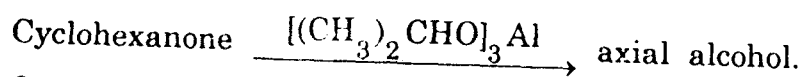
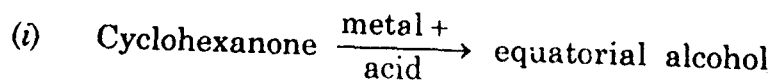
30. (a) Complete the following reaction sequences :



(b) Complete the following reactions :



31. (a) Explain the following :



(ii) On heating cis-4-hydroxycyclohexane Carboxylic acid forms a lactone; but trans-4-hydroxy cyclohexane carboxylic acid does not. Draw the stereo-structures of two carboxylic acids and lactone.

(b) Given below in column A are some common organic compounds while column B lists a possible use for each of the compound. Match the entries in the two columns by correctly identifying the use for each of the compounds :

A

- (a) Ascorbic acid
(b) Adenylic acid
(c) Anthranilic acid
(d) Salicylic acid

B

- (i) A nucleotide
(ii) A drug intermediate
(iii) A vitamin
(iv) A dye intermediate

(c) How is genetic code transcribed in protein biosynthesis ?

32. (a) Why are hollow cathode lamps less prone to self absorption than electrodeless discharge lamps ?

(b) 0.0121 g of benzoic acid (Mol wt 121) was dissolved in 100 ml of methanol water (1 : 1). If a 10 ml aliquot of this solution was further diluted to 100 ml which showed an absorbance of 0.80 at 265 nm in a 10 mm cell, what is the molar absorptivity ?

(c) Draw a schematic diagram of DTA. How is it different from DSC ?

33. (a) What could be the shape of the titration curve for the photometric titration of bismuth (III) with EDTA at 265 nm.
- (b) Why should monochromators contain as few reflecting surfaces as possible ? What is the relationship between a monochromator's bandwidth and the width of a spectral feature which ensures that it will be accurately recorded ?
- (c) What are the causes of background interferences in AAS ?
34. (a) Why are generally group V (As, Sb) elements analysed by the hydride generation method in AAS ?
- (b) When a simple digestion by heating a sample with acid or base in the hood does not dissolve the sample that is required for analysis, a digestion with a flux or microwave digestion in a closed container may solve the problem. What are the advantages of each of these techniques over simple acid digestion ?
- (c) How is thermogravimetry used for the quantitative analysis of a mixture of calcium and strontium ?
35. (a) What are the factors on which glass transition temperature of a polymer depend ? How is T_g determined ?
- (b) A sample of L-dopa is electrolysed exhaustively with $42.0 \mu\text{C}$. The process requires two electrons per molecule. The formula weight of L-dopa is 197.2. What is the mass of L-dopa in the sample ?
- (c) How is UV-visible spectrometry used for the analysis of mixtures of absorbing substances ?
36. (a) Why is linear scan voltammograms generally assume a sigmoidal curve ?
- (b) Why are stripping methods more sensitive than other voltammetric procedures ?
- (c) Why is square wave polarography of great speed and high sensitivity ?

Q. No.