Signature of Invigilators

1. .....

2. .....

Roll No. | | | | | |

(In figures as in Admit Card)

CHEMICAL SCIENCE

Paper III

Roll No. .....

.....

(In words)

D/03/3

Name of Areas/Section (if any) .....

Time Allowed : $2\frac{1}{2}$ Hours] [Maximum Marks : 200

Instructions for the Candidates

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 calculator or any other Electronics Devices are 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 માટે સૂચનાઓ :

૧. આ પૃષ્ઠના ઉપલા ભાગે આપેલી જગ્યામાં તમારી ક્રમાંક સંખ્યા (રોલ નંબર) લખો.

૨. તમે જે વિકલ્પનો ઉત્તર આપો તેનો સ્પષ્ટ નિર્દેશ કરો.

૩. ટૂંક નોંધ કે નિબંધ પ્રકારના પ્રશ્નોના ઉત્તર દરેક પ્રશ્નની નીચે આપેલી જગ્યામાં જ લખો. વધારાના કોઈ કાગળનો ઉપયોગ કરશો નહીં.

૪. અંદર આપેલી સૂચનાઓ ધ્યાનથી વાંચો.

૫. આ ઉત્તરપોથીને અંતે આપેલું પૃષ્ઠ કાચા કામ માટે છે.

૬. આ ઉત્તરપોથીમાં કયાંય પણ તમારી ઓળખ કરાવી દે એવી રીતે તમારું નામ કે કોઈ ચોકકસ નિશાની કરી હશે તો તમે આ પરીક્ષા માટે ગેરલાયક સાબીત થશો.

૭. કેલકયુલેટર અથવા ઈલેકટ્રોનિકસ સાધનો જેવા ઉપયોગ કરવો નહીં.

૮. નકારાત્મક ગુણાંક પદ્ધતિ નથી.

૯. પ્રશ્નપત્ર લખાઈ રહે એટલે આ ઉત્તરપોથી તમારા નિરીક્ષકને આપી દેવી. પરીક્ષાખંડની બહાર કોઈપણ પ્રશ્નપત્ર લઈ જવું નહીં.

FOR OFFICE USE ONLY
Marks Obtained

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			
8		33			
9		34			
10		35			
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25					

Total Marks Obtained.....

Signature of the co-ordinator.....
(Evaluation)

SEAL

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).

General Physical Constants :

Speed of light C = 2.998×10^8 ms^{-1}

Avogadro constant N = 6.023×10^{23} mol^{-1}

Faraday F = 96500 coulombs mol^{-1}

Planck constant h = 6.626×10^{-34} Js

Boltzmann constant k = 1.381×10^{-23} JK^{-1}

Gas constant R = 8.314 JK^{-1} mol^{-1} or 1.987 cal K^{-1} mol^{-1}

1. Attempt any *four* of the following : 10×4

(*a*) Find out hyperfine coupling constant for benzene anion radical.

(*b*) Derive relation for recoil energy in Mössbauer spectroscopy. Mössbauer spectra are almost always obtained on solids employing solid sources. Explain.

(*c*) Calculate the atomic specific heat of Aluminium and Copper at 10 K. The Debye characteristic temperature (θ) for Al and Cu are 398 and 315 K respectively.

(*d*) The magnetic susceptibility of O_2 is 4.08×10^{-8} m^3 mol^{-1} at room temperature. Calculate the number of unpaired electrons in O_2 molecule.

(*e*) Deduce the structural formulae of the compounds that are consistent with the given data.

(*i*) Mol. formula : $C_9H_6O_2$

UV : 260 nm

IR : 3000-2700, 2200, 1690, 1500, 700 cm^{-1}.

NMR : 7.5 δ, complex, 5H; 11.0 δ, 1H.

(*ii*) Mol. formula : $C_7H_{14}O$

IR : 2900, 1710, 1470, 1380, 1150 cm^{-1}

NMR : 2.3 δ, septet, 1H; 1.1 δ, *d*, 6H.

2. Explain the mechanism involved in the solvent extraction separations of :

(*a*) Alkali metals by crown ether;

(*b*) Iron (III) from manganese from hydrochloric acid with diethyl ether;

(*c*) Cobalt and nickel by Trioctylamine in chloride media;

(*d*) Uranium (VI) and thorium (IV) with oxine. 16

3. What factors are responsible for the retention of the solute on stationary support in the following chromatographic techniques ?

(*a*) Adsorption chromatography;

(*b*) Partition chromatography;

(*c*) Exclusion chromatography;

(*d*) Electrochromatography. 16

4. (*a*) Mention various sources of radiation used in the atomic absorption spectroscopy. What are the advantages of hollow cathode lamp ?

(*b*) Why is it essential to use cold vapour atomic absorption spectroscopy for the analysis of mercury ?

How is tin analysed by atomic absorption spectrometry ? 16

5. (*a*) A solution containing the complex of bismuth (III) with thiourea has molar absorptivity of 9.50×10^3 at 470 nm. Calculate the absorbance of 6.2×10^{-5} M solution of the complex measured at 470 nm in 1 cm cell. What should be the value of absorbance if optical path is doubled ? What is the percentage transmittance of solution with the concentration of 6.20×10^{-5} M ? 10

(*b*) Calculate the percentage of calcium oxalate if the thermogram of 0.1257 gm of the sample containing a mixture of $CaC_2O_4\ H_2O$ (M.W. = 146.2) and stable salt had a mass loss due to water being 6.98 mg at 140°C. 6

6. Explain briefly for the following observations : 16

(*a*) The half wave potential varies with the supporting electrolyte in polarographic analysis.

(*b*) It is essential to flush the analyte with nitrogen in DME in polarographic analysis.

(*c*) The scattering of radiation in nephelometry is not same as scattering in Raman spectroscopy.

(*d*) In coulometry of copper solution it is necessary to apply more negative potential with SCE as the reference electrode.

7. (*a*) Complete the following nuclear equations : 8

(*i*) $^{11}_{5}B + ? \rightarrow {}^{8}_{4}Be + {}^{4}_{2}He$

(*ii*) $^{239}_{94}Pu + {}^{4}_{2}He \rightarrow {}^{241}_{96}Cm + ?$

(*iii*) $^{9}_{4}Be + {}^{1}_{1}p \rightarrow ? + {}^{4}_{2}He$

(*iv*) $^{63}_{29}Cu + {}^{1}_{1}p \rightarrow {}^{24}_{11}Na + ? + {}^{1}_{0}n$

(*b*) A sample of buried wood with a mass of 152 mg was found to have an activity of 61.2 Bq. Calculate the age of this specimen (to two significant figures). 8

8. (*a*) What is polymorphism ? Discuss the polymorphism of phosphorus. 4

(*b*) Describe *two* synthetic methods for each of the following : 12

(*i*) $OsCl_2$

(*ii*) ClF

(*iii*) XeO_3

9. Discuss the structure of the following : 16

(*a*) B_4H_{10}

(*b*) $C_2B_4H_8$

(*c*) $P_4(NMe)_6$

(*d*) S_2N_2.

10. (*a*) Discuss the splitting of *d*-orbitals in (*i*) square planar (D_{4h}) (*ii*) square pyramidal (C_{4v}) and (*iii*) trigonal bipyramidal (D_{3h}) ligand fields. 9

(*b*) Calculate spin-orbit coupling constant for $\left[Ni(H_2O)_6\right]^{2+}$ complex ion using μ_{eff} = 3.23 B.M. at 300°K, 10 D_q = 8500 cm^{-1}. 7

11. (*a*) Explain why spectrochemical series cannot be justified by CFT. 4

(*b*) Consider the following electronic spectral data : 12

$\left[CrF_6\right]^{3-}$ 34400, 22700, 14900 cm^{-1}

$\left[Ni(H_2O)_6\right]^{2+}$ 8500, 15400, 26000 cm^{-1}

$\left[Ni(NH_3)_6\right]^{2+}$ 10750, 17500, 28200 cm^{-1}

Assign the bands and calculate 10 D_q and B parameters.

12. (*a*) The nephelauxetic factor (ratio) β is always less than one. 4

(*b*) What is quenching of orbital angular momentum contributions to magnetic moment ? Show that for A and E terms there is no orbital angular momentum contributions to magnetic moment while it remains for T terms. 12

13. (*a*) In contrast to the *d-d* transitions of transition metal complexes, the broadening effect of the *f-f* transitions in lanthanide and actinide complexes is minimized. Explain. 8

(*b*) Discuss the magnetic properties of lanthanides. 8

14. Explain the following : 16

(*a*) The CO stretching frequency of a variety of metal carbonyl complexes is appreciably lower than that of free carbon monoxide.

(*b*) $W(CO)_5[C(OMe)Me]$ is far more stable than $[W(CO)_5(CMe_2)]$.

(*c*) The C = C double bond character of ethylene decreases on complexation with metal.

(*d*) PMe_3 ligand is relatively better σ-donor and π-acceptor than $P(OMe)_3$.

15. (*a*) Describe *two* methods for the synthesis of transition metal-σ-alkyl complexes. 8

(*b*) Draw the structure of : 8

(*i*) $\left[PtCl_3\left(\eta^2 - C_2H_4\right)\right]^-$;

(*ii*) $\left[Pt\left(PPh_3\right)_2\left(PhC \equiv CPh\right)\right]$;

(*iii*) $\left[\left(\eta^5 - C_5H_5\right)_2 Fe\right]$; and

(*iv*) $\left[\left(\eta^5 - C_5H_5\right)TiCl_2\right]$.

16. Answer the following : 16

(*a*) What proteins are responsible for oxygen storage and transport, respectively, in humans ? Without drawing structures, show how is iron bound within them ?

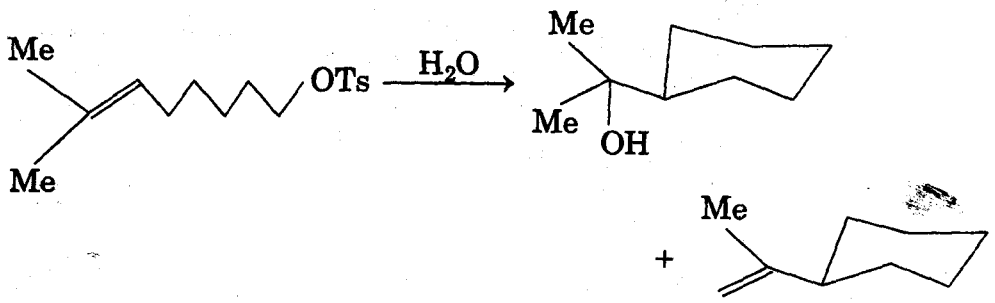
(*b*) How does hemoglobin use ligand field theory to make iron pucker out of the porphyrin ring when oxygen dissociates ?

(*c*) What metal is applied in oxaloacetate decarboxylase and what property of this metal makes it best suited for this enzyme ?

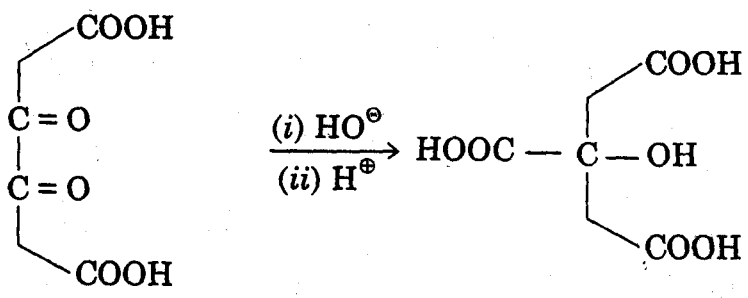
(*d*) What role do cytochrome P-450 enzymes play in humans and how do they do this ? (mechanism not necessary).

17. (*a*) Propose reasonable mechanisms for the following conversions : 8

(*i*)

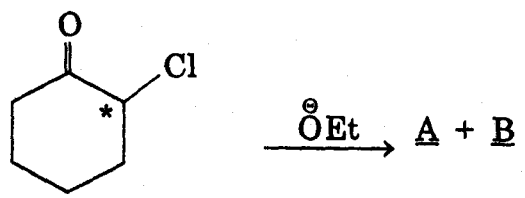


(*ii*)



(*b*) Identify the products and suggest possible mechanisms for each of the following reactions : 8

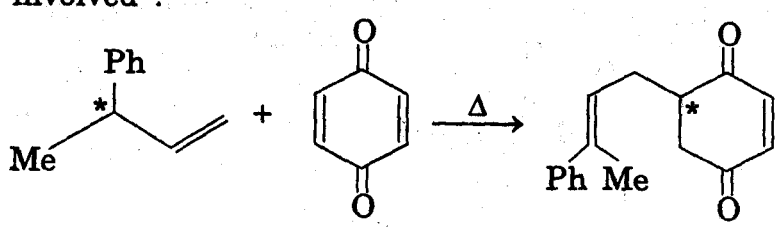
(*i*)



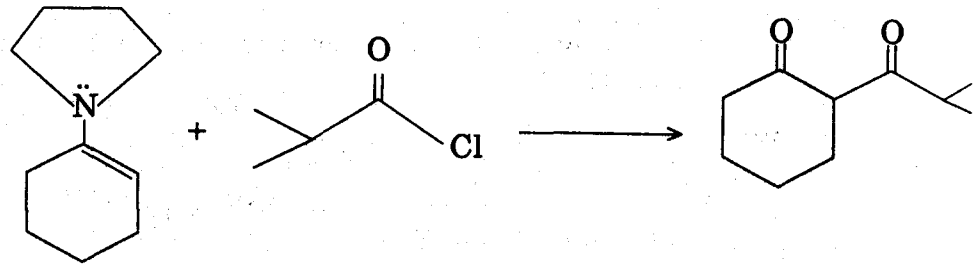
(*ii*)

18. (*a*) For the following transformations identify the reaction, give mechanism involved : 12

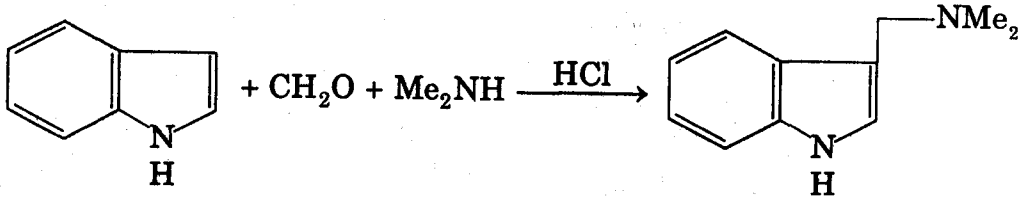
(*i*)



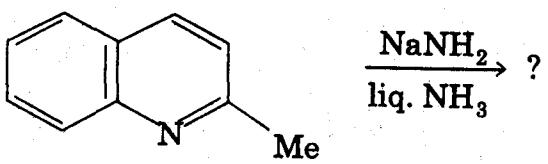
(*ii*)



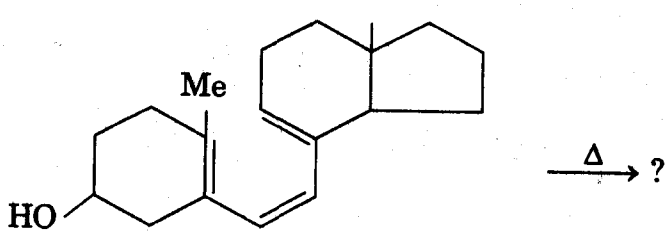
(*iii*)



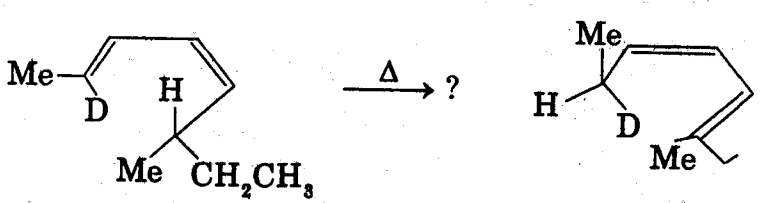
(*b*) Predict the product and name the reaction involved : 4



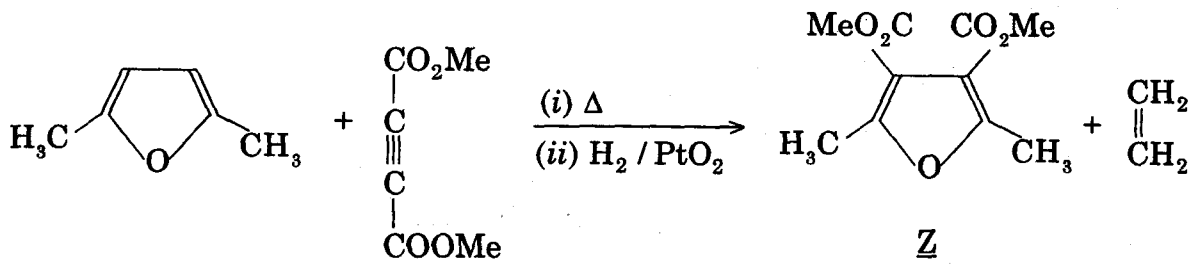
19. (*a*) For the following concerted reaction predict the product and its stereochemistry, quote the necessary selection rule. 4



(*b*) Classify the following concerted reaction, giving necessary selection rule. 4



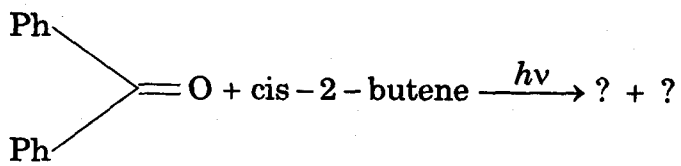
(*c*) In the formation of compound Z a pericyclic reaction and its reverse process is involved. Explain the formation of Z. Identify the reaction involved. 8



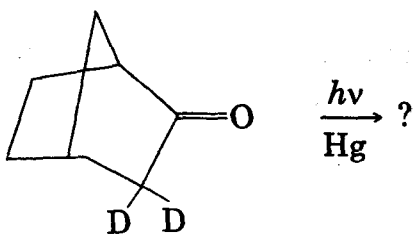
Z

20. (*a*) Predict the product(s) of the following photochemical reactions. Identify the reaction involved : 12

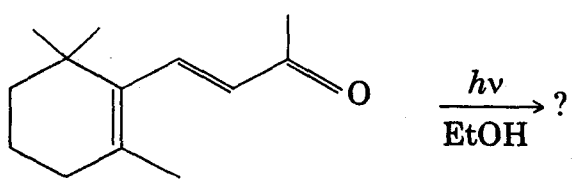
(*i*)



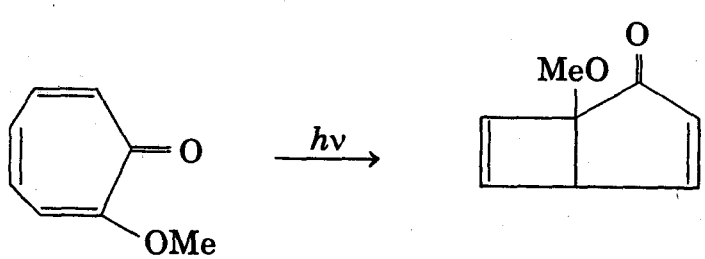
(*ii*)



(*iii*)



(*b*) Propose mechanisms for the following photochemical reaction : 4



21. (*a*) Deduce the structure of the compound from the given spectral data : 6

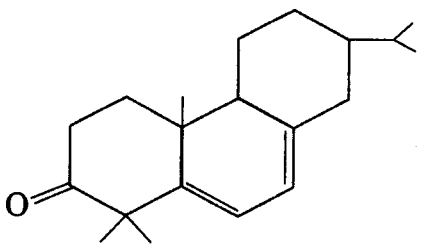
Mol. For. : C_3H_7ON

IR : 3500, 3400, 3000, 1670, 1600, 1400 cm^{-1}

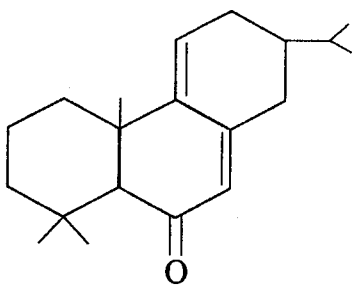
Mass : 73 (M+), 57, 44 (base peak), 29

NMR : 1.2 δ, *t*, J = 6 Hz, 3 H; 2.1 δ, *q*, J = 6 Hz, 2 H; 6.4 δ, *bs*, 2 H.

(*b*) Following the Woodward's rule, calculate the λ_{max} for the compounds given below : 6

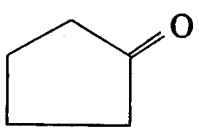


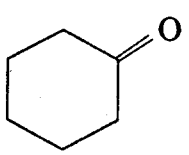
I



II

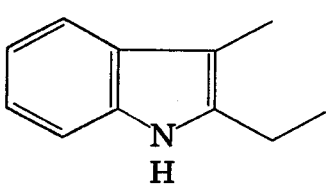
(*c*) How can the following pair of molecules be differentiated spectroscopically ? 4

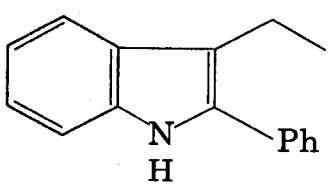
(*i*) 

and 

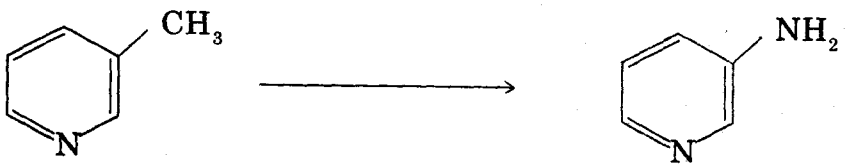
(*ii*) PhC ≡ N and PhC ≡ CH.

22. (*a*) Identify the intermediates involved in the formation of the following compounds using Fischer-indole synthesis : 4

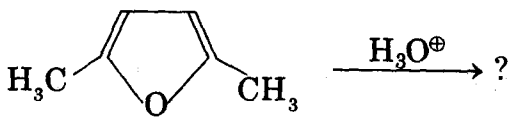
(*i*) 

(*ii*) 

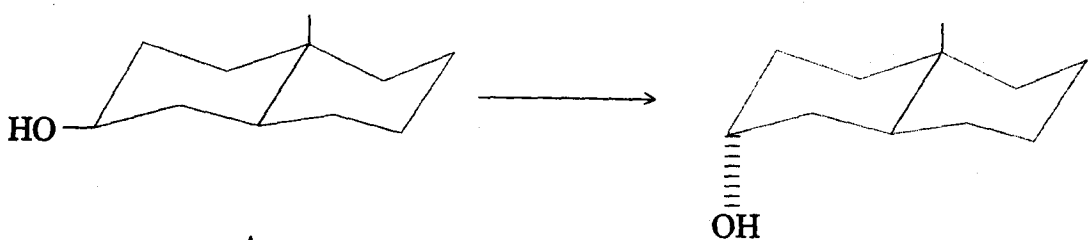
(*b*) How will you carry out the following transformation ? 8



(*c*) Predict the product and explain its formation : 4



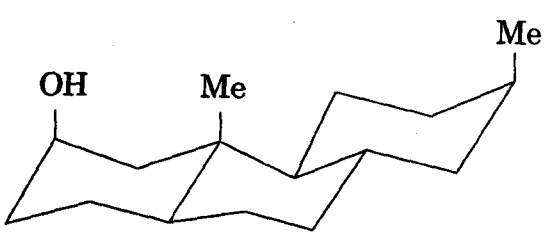
23. (*a*) In the conversion of alcohol A to alcohol B, the reagents required are Ac_2O, PBA, heat (200°), DMSO, $LiAlH_4$ and $NaBH_4$. Arrange them in appropriate order and rewrite the sequence of steps : 8



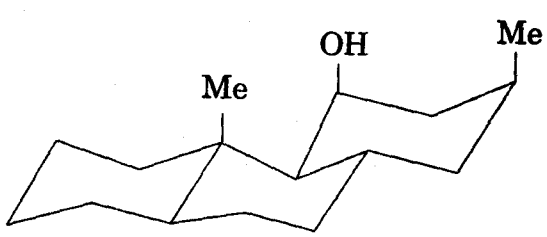
A B

(*b*) A naturally occurring alcohol $C_6H_{12}O$, was found to exhibit an optical rotation of + 49.5°. On catalytic hydrogenation the alcohol absorbed 1 mol. of hydrogen to form a new alcohol which was optically inactive. The starting alcohol on sharpless epoxidation gave a compound $C_6H_{12}O_2$. Assign structure to starting alcohol and other products. 8

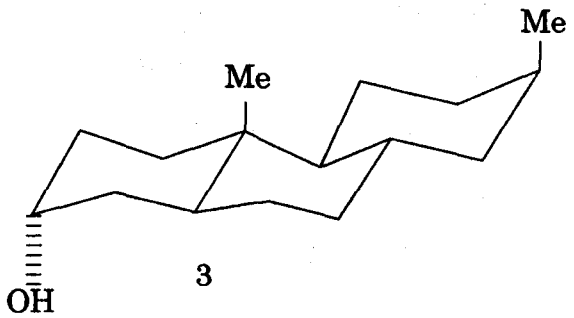
24. (*a*) Arrange the following alcohols in decreasing order of reactivity towards chromic acid oxidation : 6



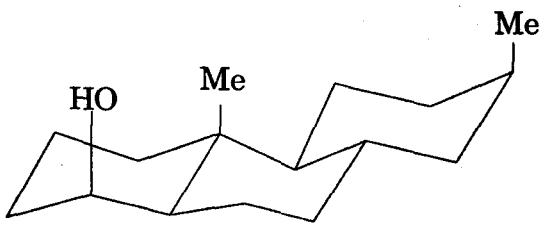
1



2



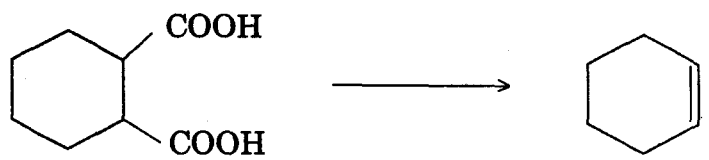
3



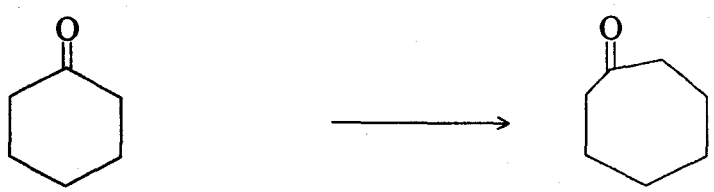
4

(*b*) Indicate suitable reagents for the following transformations : 10

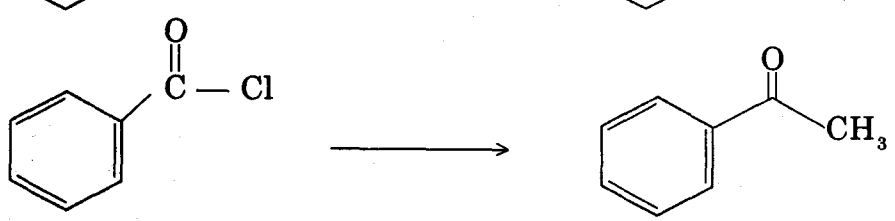
(*i*)



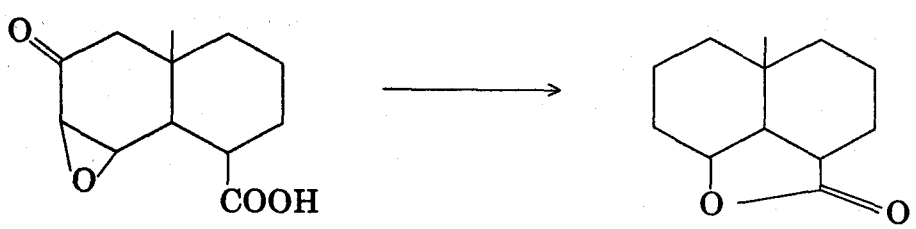
(*ii*)



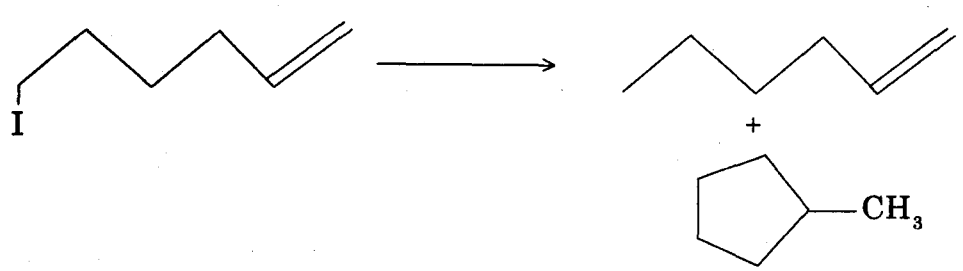
(*iii*)



(*iv*)



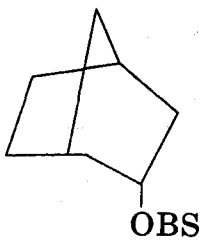
(*v*)



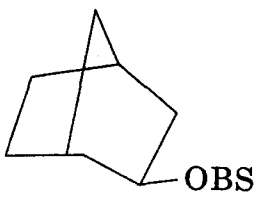
25. (*a*) Estimate 6m–NO_2 and 6m–F. Given pKa's of *m*-nitrobenzoic acid, *m*-fluorobenzoic acid and benzoic acid are 3.48, 3.85 and 4.19 respectively. 6

(*b*) Suggest a method of conversion of D-ribose to D-erythrose. 6

(*c*) Comment on the observation that acetolysis of B is several hundred times faster than A. 4



A



B

26. (*a*) Deduce the structure of a naturally occurring hydrocarbon A ($C_{15}H_{24}$) from the data given : 8

(*i*) $A \xrightarrow{H_2/PtO_2} C_{15}H_{28}$

(B)

(*ii*) $A \xrightarrow[\Delta]{Se}$ 1, 6-dimethyl-4-isopropyl naphthalene

(*iii*) In the PMR of A signals at 1.0 δ, J = 7 Hz, 6H; two singlets around 2δ each having 3H; 4.5 – 5.5 δ signals for 2H were observed

(*iv*) $A \xrightarrow[H_2O_2 / H_2O]{O_3}$ C_{15} diketo dicarboxylic acid

(*v*) $A \xrightarrow[PhCO_3H]{1 \text{ mole}}$ C (epoxide) $\xrightarrow{CH_3MgI}$ D (tertiary alcohol)

(*vi*) $D \xrightarrow[\Delta]{Se}$ 1, 5, 6-trimethyl-4-isopropyl naphthalene.

(*b*) Carbon dioxide is required for the conversion of CoA into fatty acids. Yet when CO_2 labelled with 14 C is used, none of the labelled carbon appeared in the fatty acids that are formed. How do you account for these facts ? 8

27. (*a*) For benzene molecule calculate molecular orbital energy and π-electron energy using simple Huckel-π-electron theory. 8

(*b*) A particle of mass m moves along X-axis under a restoring force equal to k times its displacement. Write its Schrödinger wave equation. 4

(*c*) Consider two hypothetical spherical cells centered on H-atom nucleus with radii r and $r + dr$. What is the probability $e(r)$ that the electron will be between these shells ? For hydrogen

$$\psi = \frac{1}{\sqrt{\pi}\, a_0^{\,3}}\, e^{-\frac{r}{a_0}}.$$ 4

28. (*a*) What is Pauli's Exclusion Principle ? Explain quantum mechanically. 8

(*b*) Predict term symbol of the N_2 and O_2 molecules. 8

29. (*a*) What is the most probable distance for an electron in the 1*s* orbitals of the He^+ radical ? Wave function is

$$\frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} e^{\frac{-Zr}{a_0}}.$$ 8

(*b*) Describe bonding in tetrahedral molecule (MX_4) using molecular orbital theory. The Character Table for T_d is : 8

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6s_4$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_1	3	0	−1	−1	+1
T_2	3	0	−1	1	−1

30. (*a*) Show that :

$$C_P = C_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$ 8

(*b*) Calculate the standard free energy change ($\Delta G°$) of the following reaction :

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \Delta H° = -282.8 \text{ kJ mol}^{-1}$$

where S° for CO(g), O_2(g) and CO_2(g) are 197.9, 205.0 and 215.5 J mol^{-1} K^{-1}, respectively. Is the reaction feasible at standard state ? 8

31. (*a*) What is partial molar property ? Deduce Gibbs-Duhem equation

$$\Sigma\, n_i d\mu_i = 0.$$ 8

(*b*) The volume of a solution containing 1 kg of water and m mole of a salt at 25°C is given by :

$$V(mL) = 1003.0 + 16.62\ m + 1.77\ m^{3/2} + 0.12\ m^2.$$

Calculate the partial molal volume of salt at $m = 0.10$. 8

32. (*a*) What is H-bond ? Explain it through acetone + chloroform system. Whether solution formation will be exothermic or endothermic ? 8

(*b*) A mixture of 21.5 g of hexane and 85.5 g of octane is prepared. Calculate mole fraction of each component and free energy of mixing at 25°C assuming that it is an ideal mixture. 8

33. (*a*) Explain the terms with an example of each : 6

(*i*) Micelles;

(*ii*) Stern-double layer;

(*iii*) Micro-emulsions.

(*b*) Distinguish between :

(*i*) Physical and chemical adsorption;

(*ii*) Electrophoresis and electroosmosis. 10

34. (*a*) Deduce Bose-Einstein distribution law

$$\eta_i^* = \frac{g_i}{e^{-\alpha + \beta E_{i-1}}}.$$

Terms in the expression have their usual meaning. 6

(*b*) Calculate the translational partition function of H_2 molecule confined to a 1000 cm^3 vessel at 25°C. 10

35. (*a*) Deduce the following rate expression using transition state theory for a reaction A + B → C.

$$K = \frac{K_B T}{n} \cdot \frac{q_{\neq}}{q_A \, q_B} e^{-E_0/RT}.$$ 10

(*b*) For a photochemical reaction X-Y, 1.0×10^{-5} mol of Y was formed on absorption of 6.62×10^7 erg at 3600 Å. Calculate the quantum yield or efficiency. 6

36. (*a*) How can molecular weight of a polymer sample be determined from an osmometer ? 9

(*b*) Calculate the molecular weight of a polymer whose intrinsic viscosity [η] is 0.83 dL/g using Mark-Hownick equation. The values of K and *a* are 3.5×10^{-5} dL mol and 0.64. 7

Q. No. .....