

Total Pages—15

UG/III/CHEM/H/VI/18 (New)

2018

CHEMISTRY

[Honours]

PAPER – VI

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use separate scripts for Group – A and Group – B

[NEW SYLLABUS]

GROUP – A

(*Organic*)

Group – A (a)

Answer any one question : 15 × 1

1. (a) What is latent polarity ? "Convergent strategy of synthesis is more ideal than *linear strategy*" – Explain. 1 + 2

(Turn Over)

(b) Draw the conformation you predict to be the most stable for – 1 + 1

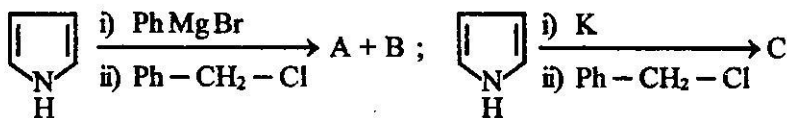
(i) β -D-Allopyranose

(ii) β -L-glucopyranose.

(c) Acetyl acetone shows λ_{\max} value in water at 274 nm (t, 2000) and in isooctane at – 272 nm (t, 12000). Explain the observation. 2

(d) Give the steps of the reaction of coumarin with 2-mol of the Grignard Reagent (Ph Mg Br), followed by heating with H_2SO_4 . 2

(e) Predict the product(s) in each case and explain the difference : 2



(f) How can lysine (PI = 9.6) be separated from glycine (PI = 5.97) by electrophoresis ? 2

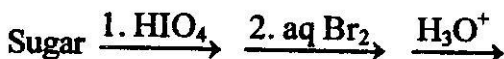
(g) Write the role of m-RNA and t-RNA in protein synthesis. 2

2. (a) "Broad signals are often observed in $^1\text{H-NMR}$ spectra associated with $-\text{OH}$ and $-\text{NH}_2$ resonances" – Explain. 2

- (b) What is the finger print region in the IR spectrum of organic compound? Why is it so called? 1 + 1

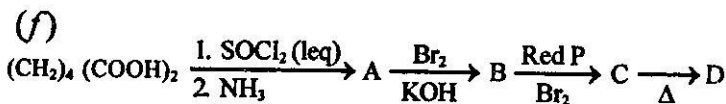
- (c) Synthesize alanylglycine Me-ester using DCC. 3

- (d) How can the sequence –



Show if a methylglucoside has a pyranose or furanose ring? 3

- (e) How do epimers and anomers differ? 1



Find out the structure of A \rightarrow D. 2

- (g) The O – H stretching frequency is 3600 cm^{-1} . Calculate the O – D stretching frequency? 2

(4)

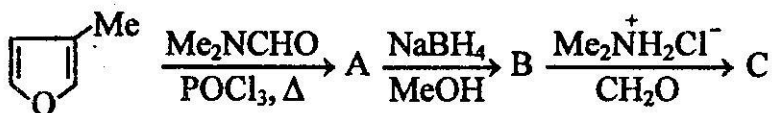
Group – A (b)

Answer any two questions : 10 × 2

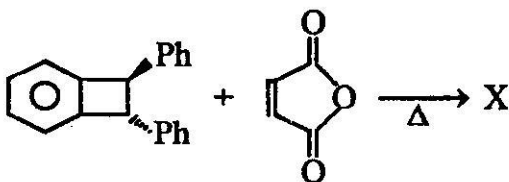
3. (a) Toluene can be oxidised to benzaldehyde or benzoic acid. How it can be confirmed that oxidation produces benzoic acid not benzaldehyde by H^1 -NMR spectroscopy ? 2
- (b) "RNA is hydrolyzed 3-billion times faster than DNA" in alkaline medium" – Explain. 2
- (c) Write the retrosynthetic path of 2, 4, 6-Tribromobenzoic acid using FGA and FGI strategy with out disturbing – COOH group. Also write the forward synthetic route from benzoic acid. $1\frac{1}{2} + 1\frac{1}{2}$
- (d) Show that $[H_2S + H_2S]$ cycloaddition is photochemically allowed by FMO approach. 3
4. (a) Guanosine is hydrolysed more rapidly than adenosine in acid medium – Explain with proper reason. 2

(5)

(b) Find out the structure of A, B & C : 1 + 1 + 1



(c) Predict the product (X) with proper stereochemistry and explain. 3



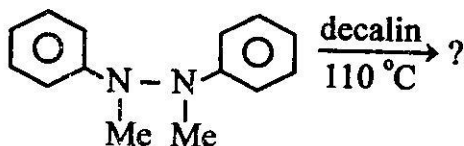
(d) How the use of TMSCl can solve the problems in ring synthesis through acyloin condensation ? 2

5. (a) Write the structure of the compound $\text{C}_5\text{H}_{11}\text{Cl}$ which shows two singlets in its $^1\text{H-NMR}$ spectrum with reasons. 2

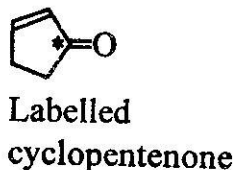
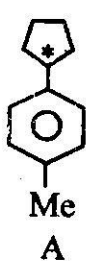
(b) Draw the structure of Uridylic acid. 2

(c) Predict the *product(s)* with mechanism : 2

(6)

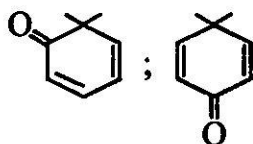


- (d) Write the retrosynthetic route and forward synthetic path of the following two compounds taking the following Labeled cyclopentenone as one of the starting material : 2 + 2



6. (a) Write down the steps involved with mechanism in Skraup Quinoline synthesis starting from aniline and acrolein. 2
- (b) Distinguish the following molecule by UV spectroscopy : 2

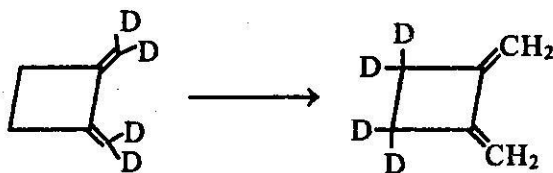
(7)



(c) An organic compound shows following spectral data :

Mass : 130 ; IR : 3082, 2862, 1825, 1755, 1455 cm^{-1} $^1\text{H-NMR}$: δ 1.30 (t, $j = 7.1$ Hz) and 2.20 (q, $j = 7.1$ Hz and ratio of peak areas = 3 : 2. Establish the structure of the compound with proper explanation. 4

(d) How would you accomplish the following conversion and explain : 2



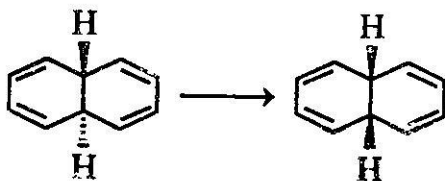
Group – A (c)

7. Answer any five questions : 2×5

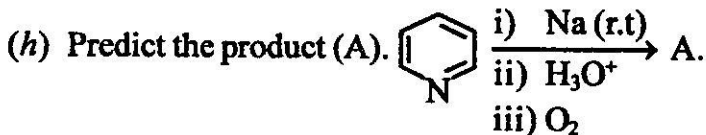
(a) Between thiophene and furan, which one

is better diene in Diels-Alder reaction and why?

- (b) Sketch the $^1\text{H-NMR}$ spectrum with integration showing relative chemical shift of isomeric dibromo ethanes.
- (c) Write three synthetic equivalent of acyl ($-\text{COCH}_3$) group.
- (d) How would you distinguish between Methylacrylate and vinylacetate by IR spectroscopy?
- (e) How can you carry out the following transformation?



- (f) What is isoelectric point? Write the significance of it.
- (g) What is end absorption? Why is it so called?



(i) Fructose can not give positive Tollen's Test
– Critisize or justify.

(j) What is vaccum UV ? Why it is so called ?

GROUP – B

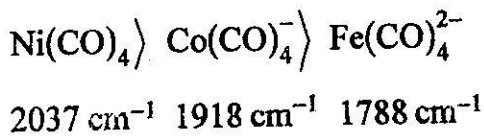
(*Inorganic*)

Group – B (a)

Answer any **one** question : 15 × 1

8. (a) What do you understand by notation Δ (delta) and Λ (lambda) for chiral complexes ? 2
- (b) Which metal ion is present in carbonic anhydrase enzyme ? Emunerate the anhydrase activity of this enzyme. 2
- (c) Draw the synergic bonding in metal carbonyls. 2

- (d) Comment on the following CO stretching frequencies : 3



- (e) Chromium acetate monohydrate is practically diamagnetic, although Cr (II) is a d^4 -system. Explain. 3

- (f) How is Ferroune Synthesized? 2

- (g) Give an example of a masking agent in complexometric titration. 1

9. (a) Sketch a catalytic cycle for the hydroformylation of $\text{RCH}=\text{CH}_2$ using an organometallic catalyst indicating steps where insertion and oxidative addition reactions occur. 4

- (b) Find the expression for CFSE for d^5 and d^6 ions in weak and strong octahedral fields in terms fo D_q and pairing energy. 2 + 2

- (c) Comment on the oxidation state of iron in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$. 2
- (d) Draw the structures of the two isomers of $\text{Co}_2(\text{CO})_8$. How can they be distinguished by IR spectroscopy? 2 + 2
- (e) What is 'Lanthanide contraction'? 1

Group – B (b)

Answer any two questions : 10 × 2

10. (a) Using Orgel diagram assign the spectral transitions of $[\text{Ni}(\text{en})_3]^{2+}$ showing broad absorptions with $\lambda_{\text{max}} \approx 325, 550$ and 900 nm. Which bands are in the visible region? 3 + 1
- (b) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ is pale pink but turns into deep blue when concentrated HCl is added in excess – why? 2
- (c) $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic – Explain. 2
- (d) Draw all the possible isomeric structures for $[\text{M}(\text{en})_2\text{Cl}_2]^+$ en = ethylenediamine. 2

11. (a) How does nature protect Fe(II) in hemoglobin from its irreversible oxidation in presence of O_2 ? What do you mean by cooperative interaction in O_2 affinity of hemoglobin? 2 + 1
- (b) What is 'linkage isomerism'? Discuss different coordination modes in $[Pt(SCN)_2(NH_3)_2]$ and $[Pt(NCS)_2(PR_3)_2]$. 2
- (c) Discuss the isolation of Au from its principal ore. Write chemical reactions. 4
- (d) Explain why $V(CO)_6$ is readily reduced to the monoanion. 1
12. (a) Calculate a value for μ_{eff} for $[Ni(en)_3]^{2+}$ taking into account spin-orbit coupling. Compare your answer with $\mu(\text{spin-only})$ and the value of $3.16 \mu_B$ observed experimentally for $[Ni(en)_3][SO_4]$.
 $\Delta_{oct} = 11500 \text{ cm}^{-1}$
 $\lambda = -315 \text{ cm}^{-1}$ 2 + 1

- (b) What is BOD₅ (five days biochemical oxygen demand)? If the BOD₅ for some waste water is 200 mg/L, and the ultimate BOD is 300 mg/L, find the reaction rate constants k (base e) and k (base 10). 1 + 2
- (c) Explain the principle of chelation therapy with reference to the removal of arsenic. 2
- (d) Low oxidation state organometallic complex tend to obey the 18-electron rule. Justify with example. 2
13. (a) NO as a 3 electron donor shows IR spectra of γ (NO) in the range 1650-1900 cm^{-1} whereas NO as 1 electron donor show γ (NO) in the range 1525-1690 cm^{-1} . Comment on the bonding mode of NO. 2
- (b) A T_d complex of Co(II) gives three absorption bands with extinction coefficients about 20 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ in the visible range. The lowest energy band is at 6000 cm^{-1} . Predict the energies of the other two bands. Given free ion value of B (Racah parameter) for Co (II) is 971 cm^{-1} . 4

- (c) Suggest why Co_3O_4 adopts a normal rather than inverse spinel structure. 2
- (d) Show that Rh in $[(\text{CO})_2\text{Rh}(\mu - \text{Cl})_2\text{Rh}(\text{CO})_2]$ does not obeys 18-electron rules. 2

Group – B (c)

14. Answer any five questions : 2 × 5

- (a) Determine the term symbol for the ground state of Ho^{3+} .
- (b) Bands arising from f - f transitions are sharp having low intensities.
- (c) Account for the observation that the color of $\text{trans-}[\text{Co}(\text{en})_2\text{F}_2]^+$ is less intense than that of $\text{cis} [\text{Co}(\text{en})_2\text{F}_2]^+$.
- (d) COD is sometimes used as a way to estimate the ultimate BOD. Comment.
- (e) Name two Zn(II)-containing enzymes.
- (f) What do you mean by masking agent ? Give an example.

(15)

- (g) What is nitrogenase ? What is its biological function ?
- (h) 'Octahedral' Cu(II) complexes are often described as having a (4 + 2) coordination pattern. Suggest the origin of this description.
- (i) Do you expect Zn^{2+} to form stable, octahedral complexes with π -acceptor ligands ? Give reasons for your answer.
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