2019

Part - II

**CHEMISTRY** 

(Honours)

Paper-III

[New Syllabus]

Full Marks - 90

Time: 4 Hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

[Use separate answer script for Group-A and Group-B]

Group—A (Organic)

Answer any one question:

15×1

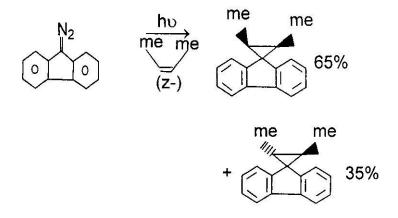
1.(a) Explain the observed diastereoselectivity in the following reaction.

$$z - 2$$
 - butene  $\xrightarrow{Br_2}$  Me  $\xrightarrow{Br}$  Me

syndibromise

-00 100/0000 00000

- (b) Why tetra -t-butylallene is inert to ozonolysis? 2
- (c) Which one between cis-and trans 4-tbutylcyclohexane carboxylic acid will act as a stranger acid and why?
- (d) Explain the following observation.



(e) Predict the product(s) with suitable explanation.

$$\frac{\text{KNH}_2}{\text{liq-NH}_3}?$$

$$\frac{\text{LiAIH(Ot-B4)}_3}{\text{LiAIH}(Ot-B4)_3}?$$

(f) Convent : CH
CH<sub>3</sub> - CH<sub>2</sub> - C ≡ CH → CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO 2

2. (a) Predict the product(s) with mechanism (any two)  $2\frac{1}{2} + 2\frac{1}{2}$ 

(i) 
$$(CH_2)_3 - NH - CH_3 \xrightarrow{KNH_2} (IIq.-NH_3) ?$$

(ii) 
$$\bigcirc$$
 + MI<sub>3</sub>CCH<sub>2</sub>CI  $\xrightarrow{\text{Anhy}}$  ?

(iii) 
$$CONMe_2$$
  $\xrightarrow{LiAIH_4}$  ?

- (b) O-Hydroxybenzoic acid and P-hydroxyden-zoic acid offer same product upon bromination reaction in water. Expalin.
- (c) Methylbenzoate and methyl-4-Nitrobenzoate are hydrolysed at almost same rate by dilute mineral acid. Justify.

(d) Predict the product with plausible mechanism (any two) 2½+2½=5

(i) 
$$\sim NH_2 \xrightarrow{H_2 SO_4} ?$$

(ii)

Ph - CH - 
$$CH_2$$
 -  $CON_3 \xrightarrow{\Delta}$ ?

OH

(iii) 
$$CH_3CI \rightarrow ?$$
(Excess)
AICl<sub>3</sub> (ash)

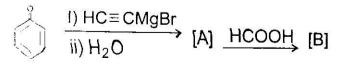
(e) Draw the stable Conformation of 1-methyl-1phenylcyclohexane.

## Group-A (b)

Answer any two questions

10×2

3.(a) Identify [A] and [B] in the following transformation and give the mechanism of formation of [B] from [A].



(b) Explain the following observations.

$$CN \xrightarrow{NaOH} CO_2Na$$

me

me

 $CN \xrightarrow{NaOH} me$ 

me

 $CONH_2$ 

me

me

- (c) Acetamilide undergo nitroation by Ac<sub>2</sub>O-HNO<sub>3</sub> Predominantly at the sterically hindered orthoposition. Explain.
- (d) Write down the product(s) with mechanism. 21/2

4.(a) Predict the major product and explain the diastareo selectivity.

Ph 
$$\xrightarrow{\text{Dial}H_4}$$
 ?

(b) Write down the product (s) with stereochemistry of the following reactions (Give mechanism) (any two) 2½+2½=5

(i) me 
$$O$$
 NaBH<sub>4</sub> ?

(ii)

(c) can you prepare the following compound by williamison synthesis? Explain your answer and suggest an effective synthetic route.

5.(a) convert (any two):

(b) How do you separate 1-pentene and 2-pentene from their mixture by using a boron containing reagent?

(c) Predict product(s) with mechanism

MeOH 
$$CH_3$$
  $CH_2$   $CH_2$   $HBr,?$ 

6.(a) carry out the following transformations: (any three) (mechanism is not necessary) 3×2

(i) 
$$CH_3 \longrightarrow CH_3 COPh$$

$$(ii) \bigcirc \longrightarrow \bigcirc$$

$$(iii) \bigcirc OH \longrightarrow OH \\ Br$$

(iv) 
$$\longrightarrow$$
  $\longrightarrow$ 

(b) Predict the product with mechanism: 2×2

(ii) 
$$\begin{array}{c} 50\% \text{ ags.} \\ \hline \text{KOH} \\ \text{heat} \end{array} \begin{array}{c} \Theta_{\text{OH}} \\ \hline \end{array}$$

7. Answer any five question

5×2

 (i) Predict the product and explain its formation mechanistically

(ii) How can you carryout the following transformation.

$$\begin{array}{c|c}
OH & O & OH \\
? & ? & ?
\end{array}$$

$$CH_2 & \frac{Hg(CAC)_2}{NaBH_4}$$

(iv) Write down the product with mechanism.

$$CH_3$$
 $O$ 
 $CH_3$ 
 $Me_2S$ 

(v) Identify the products [A] and [B].

(vi) Convert : 
$$CH_2$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

(vii) Suggest a mechanism for the following conversion.

(viii) 
$$CH_3$$
  $SO_2N(CH_3)NO \xrightarrow{ad. KOH} ?$ 

Shows mechanism.

(ix) Give suitable reagent(s) in the following conversion.

CO <sub>2</sub> Me	MeO <sub>2</sub> C <sub>1</sub> (	СООН	г соон
	<b>←</b> \\	<b>→</b>	$\wedge \vee$
Ol	+		DH

(x) For anti-addition of HBr to alkenes the rate law is Rate = K [alkene] [HBr]<sup>2</sup>. Explain.

## Group-B (Inorganic) Group—B(a)

Answer any one question: 15×1=15

(b) coupone the coordinating properties of NO\*, Cur CO in light of MO theory.

8.(a) Mention the drawbacks of VBT.

- (c) Prepare a molecular orbital diagram for the cyanide ion. Use sketches to show clearly how the atomic orbitals interact to form MOs. 3
- (d) What is the bond order and how many unpained electron does cyanide ion has?
- (e) Which molecular orbital of CN<sup>-</sup> would you predict to intaract most strongly with a hydrogen is orbital?
   Discuss with proper reason.
- (f) How many maximum electron can be added to O<sub>2</sub> molecule. Explain with reason.

(g) What do you inter when bond order is zero	1
9.(a) What do you mean by nuclear binding energy	у?
Discuss the important features of the nucle	ar

1+2

Contd.

(b) Due to the surface energy, large and small nuclides become unstable—Justify.

binding energy curve.

- (c) Predict the mode of decay in the following nuclides in the light of  $\frac{n}{D}$  ratio
  - (i)  $^{14}_{8}$ O (ii)  $^{66}_{29}$ Cu (iii)  $^{228}_{88}$ Ra 3 (d) On analysis, an ore of uraniun shows the mass ratio for  $^{238}$ U to  $^{206}$ Pb = 6.08. All  $^{206}$ Pb atoms
  - one supposed to appear from the disintegration of  $^{238}$ U. Find the age of the ore. (Given,  $^{t}$  $_{1/2}$  for  $^{238}$ U =  $4.5 \times 10^{9}$  yr, the next longest lived nuclide  $^{234}$ U in the series shows  $^{t}$  $_{1/2}$  =  $2.5 \times 10^{5}$  yr.)
- (e) With suitable example discuss the role of radioisotope in determining organic reaction mechanism.

## Group - B(b)

Answer any two question 10×2=20

10. (a) "1(N)  $KMnO_4$  may means either 0.33M or

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(b) Draw a Frost diagram for mercury in acid solution from the given latimer diagram :

$$Hg^{2+} \xrightarrow{0.911V} Hg_2^{2+} \xrightarrow{0.796V} Hg$$
Comment on the tendency if any of the species to under go diaproportionation. 2+1

- (c) A solution of  $K_3[Fe(CN)_6]$  can not oxidise iodide to iodine but can oxidise in presence of zinc ion. Explain.
- (d) What do you mean by formal potential of a redox couple?
- 11. (a) Write IUPAC name the following specimen

(i) 
$$\left[ (H_3N)_4 CO \quad \begin{array}{cc} NH_2 \\ O_2 \end{array} \quad CO(NH_3)_4 \right]^{3+}$$

(ii) 
$$\left[ \text{Cr}_2(\mu - 0)(\text{OH})_8 (\mu - \text{OH}) \right]^{5-}$$
 2×2  
(b) Discuss the estimation of  $Zn^{2+}$  and  $Mg^{2+}$  a

- (b) Discuss the estimation of Zn<sup>2+</sup> and Mg<sup>2+</sup> a seperately from the mixterms of both by complexohetric tidration with EDTA.
- (c) cite an example of non-innocent ligard. Point

out	the	criteria	of	a	ligand	to	behave	as	non
inno	ocer	it ligant							1+2

- 12. (a) suggest probable structure of I<sub>4</sub>Cl<sup>-</sup> and ICI<sub>4</sub><sup>-</sup> with reason. Explain the differences in structures.
  - (b) What will happen when a solution of X<sub>c</sub>O<sub>3</sub> in NaOH is treated with ozone? Give the chemical reaction.
  - (c) Give the products of stepwise dehydration of H<sub>3</sub>PO<sub>4</sub> and compare the acidic properties of the products.
  - (d) A number of silicon hydrides analogous to hydrocarbous one known but there are no report for silicon analogous of Oletias or aromatics— Discuss.
- 13. (a) Write short notes on (any four): 2½×4
  - (i)  $(SN)_x$
  - (ii) Pseudohalogus
  - (iii) Nuclear hazards
  - (iv) Pourbai diagrames
  - (v) Nuclear isomerism
  - (vi) Catenation

## Group-B(c)

14. Answer any five questions:

2×5

C/19/B.Sc/Part-II(O)/Chem.-III(H) 14

Contd.

- (a) What happens when an excess of Na<sub>2</sub>SO<sub>3</sub> reacts with HIO<sub>3</sub> in acidic solution in presence of starch..
- (b) Why electrical conductivity of metal decreases with the rise in temperature?
- (c) CaO is harder and has higher melting point than KF, although both have Nacl type structure—comment.
- (d) Comment on the structure of XeF<sub>6</sub>.
- (e) show that the oxidising power of  $K_2Cr_2O_7$  depends on the pH of the medium.
- (f) H<sub>2</sub>Se can be prepared by direct combination of the elements but H<sub>2</sub>Te can not be prepared in the same way comment.
- (g)  $SO_3$  is plannar but  $SO_3^{2-}$  is pyramidal Explain.
- (h) Solubility of silver halide in water decreases from chloride to iodide— Explain.