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

2018

CHEMISTRY

[Honours]

PAPER – III(A+B)

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

[NEW SYLLABUS]

GROUP – A

(*Organic*)

GROUP- A(a)

Answer any **one** question : 15 × 1

1. (*a*) Isobutene in the presence of H_2SO_4 forms a

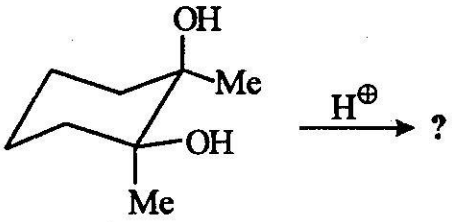
mixture of two isomeric alkenes C_8H_{16}. Formulate the reaction. 3

(*b*) What are singlet and triplet carbene ? Triplet carbenes add to *E* or *Z* alkenes with loss of stereochemical integrity. Explain with an example. 4

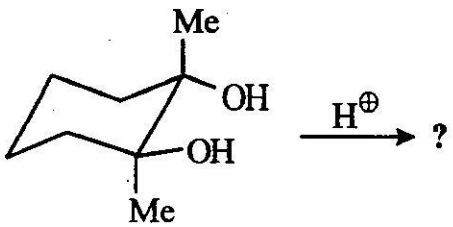
(*c*) Cis-4-hydroxy cyclohexane carboxylic acid is easily lactomized on heating but the trans-isomer does not.– Explain. 2

(*d*) Predict the product with mechanism 3

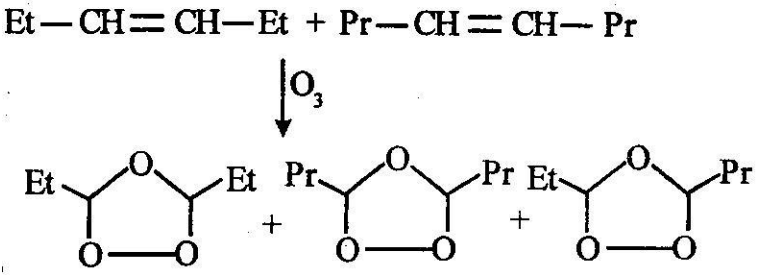
(*i*)



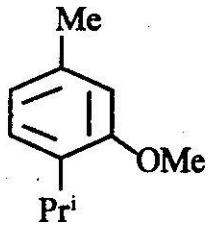
(*ii*)



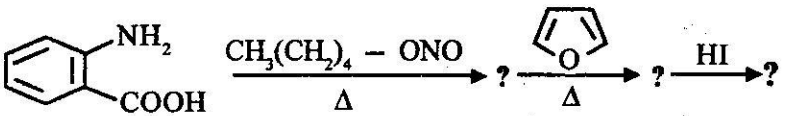
(*e*) Explain the following observation 3



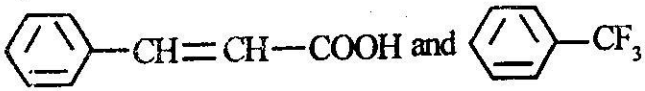
2. (*a*) When the following compound is treated with mixed acid a single product of the molecular formula $C_8H_8N_2O_5$ is obtained. Identify the compound. 3



(*b*) Complete the reaction with mechanism 3



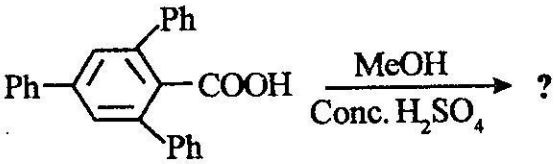
(*c*) Predict the favoured position of electrophilic substitution and justify your answer. 3



(*d*) $R^1 - CH = CH - COR^2 + R^3MgX \longrightarrow ?$

How would the ratio of the products change in this reaction if R^2 = Et, ^{i}Pr and ^{t}Bu ? 3

(*e*) Predict the product with plausible mechanism. 2

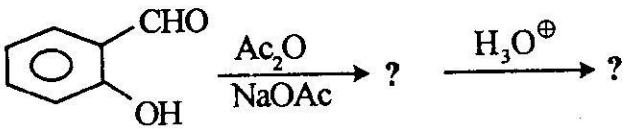


(*f*) What happen when benzophenone in ether dissolves sodium metal ? 1

GROUP- A(b)

Answer any **two** questions : 10 × 2

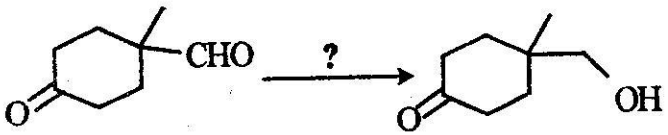
3. (*a*) Complete the following reaction sequence 2



(*b*) Draw the mechanistic path of the following reaction and name the reaction

$$R-CHO \xrightarrow{Al(OEt)_3} R-COOHCH_2R$$ 2

(*c*) Convert : 2



(*d*) *p*-Toluidine react with benzenediazonium chloride forms a compound which on heating with dil H_2SO_4 gives four products (excluding nitrogen). Write the products with appropriate mechanism. 4

4. (*a*) Predict the major product and explain the reaction using Cram-model.

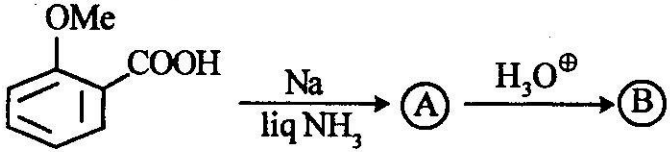
$$\text{(S)-Benzoin} \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ CH_3MgI} ?$$ 3

(*b*) Draw the stable conformation of the following compound. 2

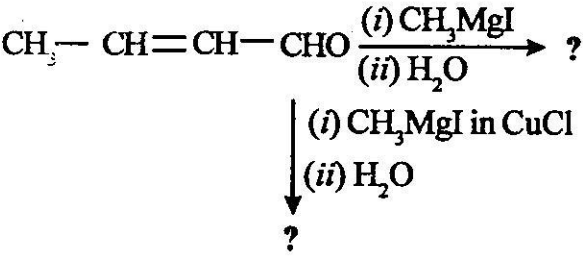
(*i*) trans-1, 3-di-tert-butylcyclohexane

(*ii*) trans-cyclohexane 1, 3-diol.

(*c*) Identify the compound Ⓐ and Ⓑ: 2



(*d*) Predict the product (s) with plausible mechanism -

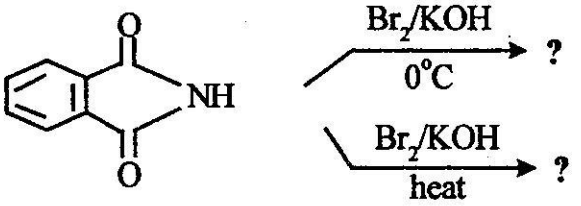


3

5. (*a*) Hoffmann and Lossen rearrangements are mechanistically allied. Justify. 3

(*b*) Write a concerted and step-wise mechanism for conversion of $PhCH_2CH_2Br$ to $PhCH=CH_2$ using NaOEt in EtOH. How would you establish the actual process taking place ? 3

(*c*) Predict the product with mechanism

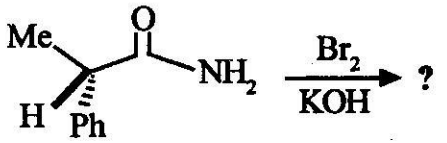


3

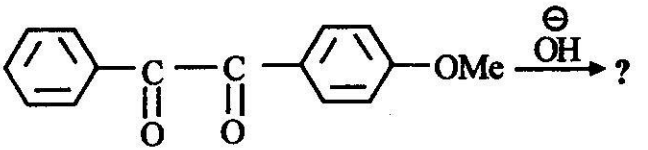
(*d*) What is ipso substitution ? 1

6. Predict the product with mechanism : $2\frac{1}{2} \times 4$

(*i*)

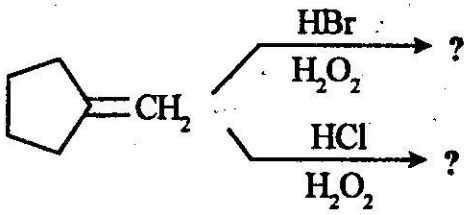


(*ii*)



(*iii*)

(*iv*)

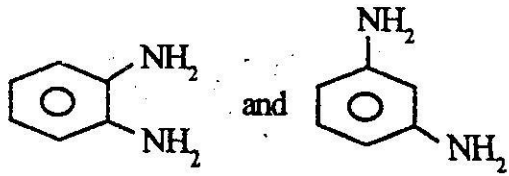


GROUP- A(c)

7. Answer any *five* questions : 2 × 5

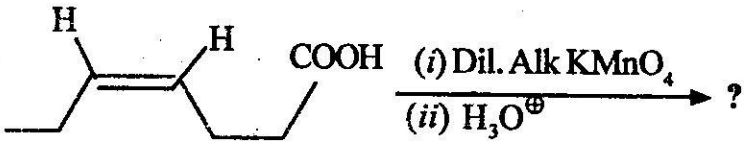
(*i*) Acetals are stable towards alkali but readily hydrolysed in presence of acid. Explain.

(*ii*) How can you distinguish the following compounds using chemical reaction ?

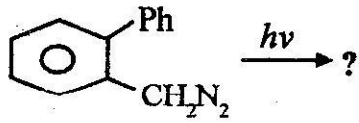


(*iii*) What happen when m-bromoanisole is treated with $NaNH_2$ and liq.NH_3 ?

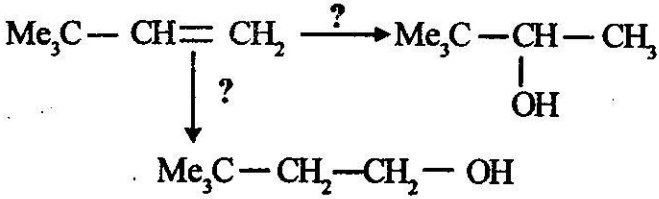
(*iv*) Predict the product



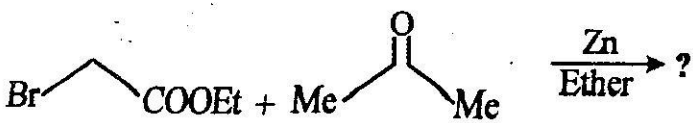
(*v*) Write down the product obtained for the following reaction



(*vi*) How can you carry out the following transformation

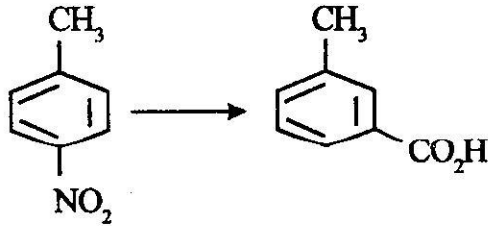


(*vii*) Write down the product and name the reaction



(*viii*) Excess diazomethane is used in Arndt Eistert synthesis. – Explain.

(*ix*) Convert :



GROUP – B

GROUP- B(a)

Answer any **one** question : 15 × 1

8. (*a*) Using group displacement law assign the position in periodic Table after releasing of 8α and 6β particle from $^{238}_{92}U$. Write Radioactive disintegration series. 3

(*b*) Following n/p ratio principle explain nuclear instability of $^{14}_{6}C$ $^{13}_{7}N$ and $^{133}_{53}I$. 3

(*c*) By radiotracer technique explain redox nonequivalence character of S in $S_2O_3^{=}$. 2

(*d*) Calculate mass defect and binding energy per nucleon of ^4_2He. (Given : mass of proton, 1.00728 amu, mass of neutron, 1.00867 amu, 1 amu = 931 Mev) 3

(*e*) Write notes on (any *two*) : 2 × 2

(*i*) Nuclear hazard

(*ii*) Spallation

(*iii*) Transmutation

(*iv*) Nuclear medicine.

9. (*a*) Heating of $(NH_4)_2Cr_2O_7$ releases N_2. Write down the chemical reaction. Balance the chemical equation using ion-electron method. 2

(*b*) In acid medium I^- is oxidised to iodine $\left(\frac{1}{2}I_2\right)$ by Cu^{2+}. Is it appropriate from the following data ?

$E^0_{Cu^{2+}/Cu^+} = 0{\cdot}15$ V; $E^0_{(I2/I-)} = 0{\cdot}54$ V. Explain your answer. 2

(*c*) Mention the name of a redox indicator and explain its indicating features during titration. 1

(*d*) Half-Cell E^0, V

Zn^{2+}/Zn – 0.763

$Ag+/Ag$ +0.799

Fe^{2+}/Fe – 0.441.

Constitute most efficient and least efficient cells. Calculate ΔG for each cell reaction and explain your answer. 3

(*e*) An unit cell of cubic close packed mixed oxide is composed of O^{2-} ion; 1/4th of tetrahedal holes are occupied by A^{2+} ions and the octahedral holes are occupied by B^+ ions. Calculate the formula of oxide. 3

(*f*) Using symmetry concept define π and σ bonds and qualitatively explain their stability and reactivity. 2

(*g*) With the help of metallic bonding concept explain the origin of semiconducting properties. How can you make a semiconductor from an insulator ? 2

GROUP- B(b)

Answer any **two** questions : 10×2

10. (*a*) State the difference between radioactive equilibrium and chemical equilibrium. 2

(*b*) Using redox potential diagram explain the origin of disproportionation reaction. Give example. 2

(*c*) Following the MO concept explain the magnetic property of O_2. If you add sequentially electron to O_2 how many maximum electrons could be accommodated ? Explain the stability of species upon addition of electrons. 3

(*d*) Calculate radius ratio ($r+/r-$) range for four coordinated square plannar ionic lattice. 3

11. (*a*) Empirical formula of a complex is $COCl_3$, $5NH_3$. The conductance measurement shows that the complex is 1 : 2 type conductor and Cl^- analysis by gravimetric method determines two equivalent ion. Draw the structure of the complex and write its IUPAC name. 3

(*b*) To an aqueous solution of $CuSO_4$, ethylediamine (en) is added in dropwise and stability of the complex fromation is analysed. Explain the following observation.

$K_1([Cu(en)(H_2O)_4]^{2+}) > K_2([Cu(en)_2(H_2O)_2]^{2+}) >> K_3([Cu(en)_3]^{2+})$ 2

(*c*) Draw the structure of $[Ca(EDTA)]^{2-}$. 1

(*d*) How do you determine hardness of water ? Mention the name of indicator used in this experiment. 2

(*e*) Give examples of (*i*) perfect complex, (*ii*) imperfect complex and (*iii*) inner metallic complex. 2

12. (*a*) State basic concepts of Werner's coordination theory and mention its limitations. 3

(*b*) Give two experimental evidences of metal -ligand orbital overlap in coordination compound. 2

(*c*) Accounts on the statistical and non -statistical factors influencing the stability of complexes. 3

(*d*) Explain following data regarding stability of complexes.

$Cu(en)^{2+}$ ($\log K_1 = 11{\cdot}66$), $Cu(Pn)^{2+}$ ($\log K_1 = 10.71$), $Cu(den)^{2+}$ ($\log K_1 = 16{\cdot}02$)

en = $NH_2-CH_2-CH_2-NH_2$; pn = $NH_2-CH_2-CH_2-CH_2-NH_2$

den = $NH_2(CH_2)_2NH(CH_2)_2NH_2$ 2

13. (*a*) Using MO theory explain the cooridnating behaviour of CO with low valent metal ion through C-end although oxygen is more electronegative. 3

(*b*) Calculate bond order and hence stability of H_2^+, H_2^-, He_2 and He_2^+. 2

(*c*) What are CFCs ? How are they prepared ? 2

(*d*) Write note on pseudohalide. 2

(*e*) What happens when XeO_3 reacts with KI in presence of dil H_2SO_4. 1

GROUP– B(c)

14. Answer any *five* questions : 2 × 5

(*a*) In group-14 elements inert-pair effect is shown by Sn^{2+} and Pb^{2+} while other members remain silient.-Explain.

(*b*) Reducing activity of hydrides of Group-16 elements increases on descending the group. Explain.

(*c*) Boiling of elemental S with Na_2S develops yellow to dark red colour. Explain.

(*d*) HF cannot be stored in glass bottle. Explain.

(*e*) In group-15 elements phosphorus can form large variety of poly phosphates while other elements show very little trend. Explain.

(*f*) Draw the structure of polythionic acids and explain their reducing behaviour.

(*g*) What happen when aqueous Na_2CO_3 is saturated with SO_2 in cold condition.
