UG/II/CHEM/H/III/17 (New)

2017

CHEMISTRY

[Honours]

PAPER – III

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

[NEW SYLLABUS]

GROUP – A

(*Organic*)

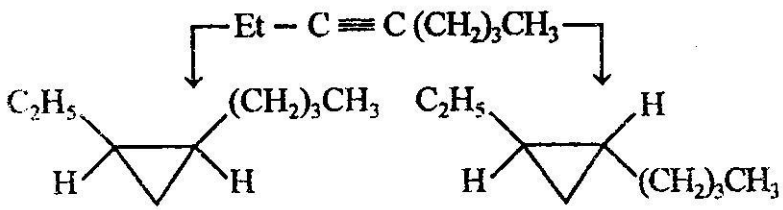
GROUP – A (a)

Answer any **one** question :

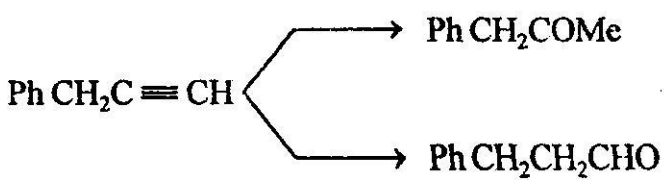
1. (*a*) Reaction of $Cl_2C = CHCl$ with NaOD in D_2O affords $Cl - C \equiv C - Cl$. When the

reaction is stopped before completion, the recovered alkene contains deuterium. Suggest a mechanism of the reaction consistent with this observation. 3

(*b*) Give the appropriate reagents to carry out the following transformation : 2



(*c*) How would you carry out the following transformations ? Give mechanism : 3



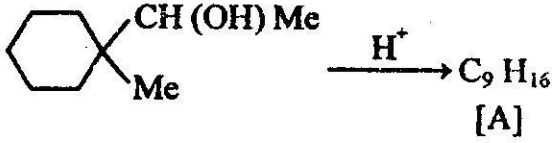
(*d*) Arrange the following carboxylic acid derivatives in order of increasing reactivity

towards hydrolysis reaction and justify your answer. 2

$RCOOR^1$, $RCONH_2$, RCOCl

(*e*) Predict the product of the following reaction and give mechanism : 2

(*f*) Write the structure of [A] which on ozonolysis gives nonane 2, 8-dione. Suggest a mechanism for its formation. 3



2. (*a*) Outline a general mechanism for the radical addition of HBr to $CH_3CH = CH_2$. Explain why peroxide effect is shown by HBr only ? 3

(*b*) Explain the role of $Li^{\oplus}$ ion in the reduction of carbonyl compounds with $LiAlH_4$. Give the mechanism of the reaction. 3

(*c*) Addition of HBr to 1, 3-butadiene yields two products and the product composition dependes very much on the reaction temperature. Write the structures of the products and account for the observation. 3

(*d*) "Heat of combustion and not heat of hydrogenation is more suitable to compare the stabilities of 1-butene, *cis*-2-butene, *trans*-2-butene and isobutene." Explain. 3

(*e*) 2, 4, 6-Trimethylbenzoic acid does not undergo esterification with methanol under ordinary acid catalysed condition whereas when dissolved in conc. H_2SO_4 and then the solution is poured into methanol it undergoes nearly quantitative esterification. Explain. 3

GROUP – A (b)

Answer any **two** questions :

3. (*a*) Predict with reasons, which one of the

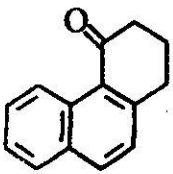
following pair of alcohols will under go faster oxidation with chromic acid. 3

trans-4-tert-butyl cyclohexanol and
cis-4-tert-butyl cyclohexanol

(*b*) In the Kolbe-Schmidt reaction sodium phenate gives salicyclic acid as the predominant product while p-hydroxybenzoic acid is the major product if potassium phenate is used. Account for the observation. 3

(*c*) Tertiary amines of the type $R^1R^2NCH_3$ can be prepared using HCHO and HCOOH as the reagents. Show the mechanistic step(s) involved. 2

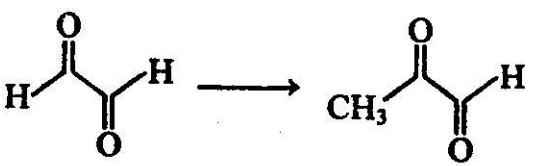
(*d*) Complete the following sequence of reactions : 2

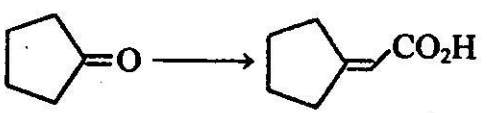


$$\xrightarrow[\text{ii) } CH_3I]{\text{i) } KH, THF} (X) \xrightarrow[\text{glycol, } \Delta]{N_2H_4, KOH} (Y) \xrightarrow[\Delta]{Se} (Z)$$

4. (*a*) Explain the fact that *trans*-4-tert-butylcyclohexyltosylate undergoes bimolecular elimination with thiophenate, but not with much stronger base ethoxide. 3

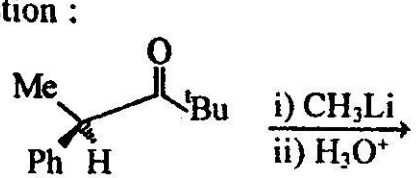
(*b*) Carry out the following conversions : 2 × 2

(*i*) 

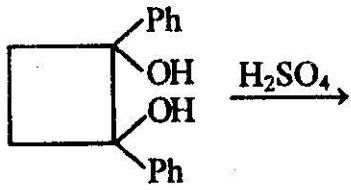
(*ii*) 

(*c*) Explain why anthracene can not be prepared from naphthalene by Friedel-Crafts reaction with succinoylation reaction. 3

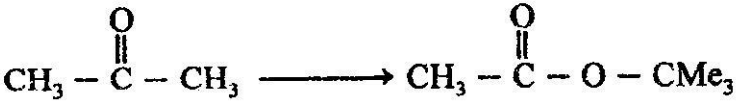
5. (*a*) Use Felkin-Anh model to explain the formation of major product in the following reaction : 3



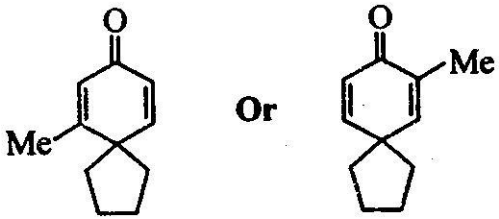
(*b*) Predict the product with Plausible mechanism 2



(*c*) How would you carry out the following transformation : 2

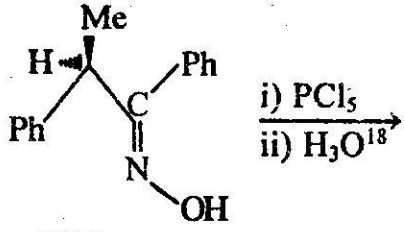


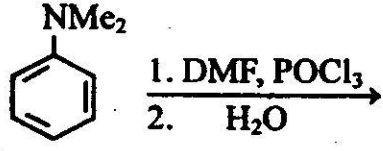
(*d*) Which member of the following pair will undergo Dienone-Phenol rearrangement more rapidly and why ? 3



6. (*a*) How can you separate a mixture of primary, secondary and tertiary aliphatic amines by Hinsberg method ? 3

(*b*) Predict the product and give mechanism : 2 × 2

(*i*) 

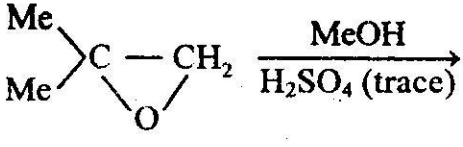
(*ii*) 

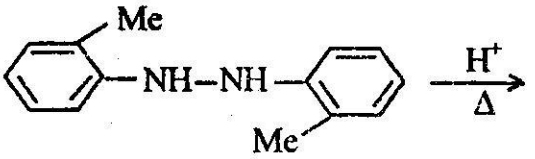
(*c*) What happens when diisopropyl ketone is allowed to react with $(^{i}Pr)_2CHMgBr$? Give the mechanism. Do you expect to get the same product. if diisopropyl ketone is allowed to react with $(^{i}Pr)_2CHLi$. Explain. 3

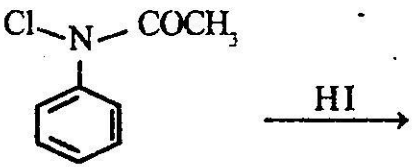
GROUP – A (c)

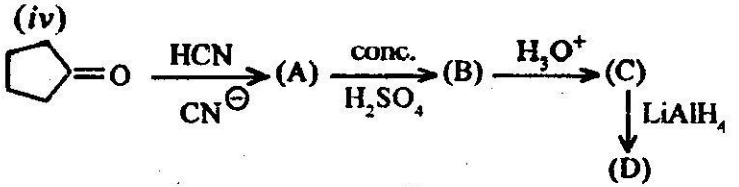
7. Answer any *five* questions : 2 × 5

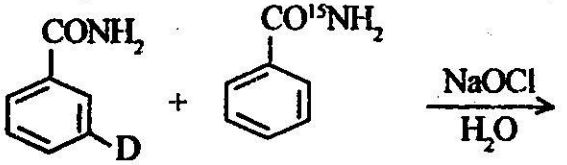
Complete the following giving mechanism :

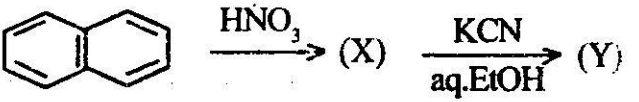
(*i*) 

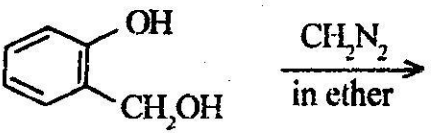
(*ii*) 

(*iii*) 

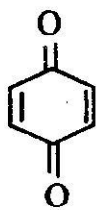
(*iv*) 

(*v*) 

(*vi*) 

(*vii*) 

(*viii*)  + HCHO + HCl $\xrightarrow[ZnCl_2]{\text{anhy}}$

(*ix*)  $\xrightarrow[\text{conc. } H_2SO_4]{Ac_2O/H^+}$

GROUP – B

(*Inorganic*)

GROUP – B(a)

Answer any **one** questions : 15 × 1

8. (*a*) Diamond is non-conductor and extremely high melting while graphite is a conductor. However both diamond and graphite are allotropes of carbon– why ? 3

(*b*) What do you mean fissile materials and fertile materials– Give example. 2

(*c*) Give the possible crystal structure of ZnS. 2

(*d*) What happens when XeF_6 is treated with aqueous NaOH ? 2

(*e*) Calculate the redox potential values at the following three stage titration of 0·1(N) Fe^{2+} ion with 0·1 (N) $KMnO_4$ in 1(N) H_2SO_4. 3

(*i*) 25 ml Fe^{2+} + 24·9 ml $KMnO_4$

(*ii*) 25 ml Fe^{2+} + 25 ml $KMnO_4$

(*iii*) 25 ml Fe^{2+} + 25·1 ml $KMnO_4$

Given

$$E^0_{Fe^{3+}/Fe^{2+}} = 0 \cdot 77\,V \text{ and } E^0_{MnO_4^-/Mn^{2+}} = 1 \cdot 51\,V$$

(*f*) Complete the reaction and give its importance 2

$$I_2O_5 + CO \rightarrow$$

(*g*) Why S–S bond in $S_2O_4^{2-}$ is weak – Explain. 1

9. (*a*) If average energy released per fission is 196 MeV, how many fission per second are required in a reactor producing 579 MW power per day with an efficiency 27%. 3

(*b*) What are the similarities and differences between β-particle and electron. 2

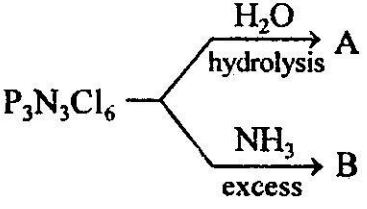
(*c*) Show stepwise hydrolysis product of P_4O_{10}. 3

(*d*) Balance by ion-electron method. 2

$$Bi_2O_3 + NaOH + NaOCl \rightarrow NaBiO_3 + NaCl + H_2O$$

(*e*) Explain why singlet oxygen is more reactive than triplet oxygen. 2

(*f*) Give the product A & B : 2



(*g*) What is ferrosilicon ? 1

GROUP – B(b)

Answer any two questions : 10 × 2

10. (*a*) Give the principal features of the Pourbaix diagram for iron. 3

(*b*) What is magic number ? Why the nuclides with magic number are extremely stable ? 1 + 2

(*c*) Explain why $SiCl_4$ is readily hydrolysed by CCl_4 does not. 2

(*d*) What is hypo ? Cite one of its use. 2

11. (*a*) What are the conditions for secular and transient radioactive equilibrium. Give example for each cases. 4

(*b*) Perchloric acid is $HClO_4$ but common form of per iodic acid is H_5IO_6 – Explain. 2

(*c*) Why $P(OH)_3$ readily rearranges itself to $HPO(OH)_2$. 2

(*d*) Write the chlorinated product of SiC and what happens when the product is hydrolysed. 2

12. (*a*) Draw the qualitative M.O energy level diagram of CN^-. Explain its ambidentate behaviour in light of MO. 4

(*b*) Why XeF_6 cannot be stored in glass vessel ? 2

(*c*) What are phosphonitrile and why are they so called ? 2

(*d*) Give example of masking and demasking agents in quantitative analysis. 2

13. (*a*) What is the composition of preventive solution used in titration of HCl acidified Fe^{2+} by $KMnO_4$ solution ? Explain its role. 3

(*b*) Differentiate nuclear fission and spallation. 2

(*c*) The $< CH_3-N-C$ angle in CH_3NCS is about 142° while $< SiH_3-N-C$ bond angle is SiH_3NCS is about 180° – Explain. 2

(*d*) Give the short account on the structure and bonding of fullerene. 2

(*e*) Complete the following equation

$$ClF + Cl_2 + AsF_5 \xrightarrow{78^\circ C} \quad 1$$

GROUP – B(c)

Answer any **five** questions : 2 × 5

14. (*a*) What is metal indicator ? With example give its role of action in complexometric titration.

(*b*) What is moderator nuclei ? Give example.

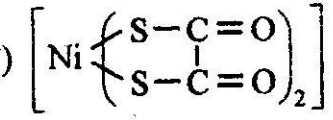
(*c*) Calculate equilibrium constant for the reaction

$$Sn(s) + Pb^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + Pb(s)$$

Predict the feasibility of this reaction.

(*d*) Write IUPAC nomenclature

(*i*) $K[PtCl_3(C_2H_4)]$

(*ii*) 

(*e*) Why interhalogens are more reactive than halogen ?

(f) Name two chelating drugs and explain its therapeutic action.

(g) What happens when iodine is added to a silver nitrate solution in presence of excess of pyridine in $CHCl_3$ medium ?
