2018

CHEMISTRY

(Major)

Paper : 5.3

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions (any *seven*) : 1×7=7

(a) Write one reaction of Pd used as dehydrogenating agent.

(b) Define 'ketonic hydrolysis'.

(c) Write name and formula of an antidot compound.

(d) Write the structure of benzilic acid anion.

(e) What is Adam's catalyst?

(f) What is the limited importance of Lossen rearrangement reaction?

(g) Write the structure and name of a quinolinium salt.

(h) Fill in the blank of the following statement :

"Pericyclic reactions are _____."

2. Answer the following questions (any *four*) : 2×4=8

(a) Give symmetry properties of π-orbitals of ethylene.

(b) What is Hinsberg's test?

(c) How can CH_3CH_2SH be prepared from thiourea? Write with reactions.

(d) How do you get adipic acid from diethyl malonate?

(e) Give one reaction each to distinguish acetonitrile and methyl isonitrile.

3. Answer the following questions [any *one* from *(a)* and *(b)* and *two* from *(c)*, *(d)* and *(e)*] : 5+(5×2)=15

(a) How do the following reagents take part in reaction? 1×5=5

(i) Lead tetraacetate in oxidative decarboxylation

(ii) SeO_2 in oxidation of allylic C—H fragments

(iii) $LiAlH_4$ in hydride transfer

(iv) Pyridinium chloromate with 2° alcohol

(v) CrO_3 with aq. H_2SO_4 to cleave $\rangle C=C\langle$

(b) (i) What happens when $C_6H_5CH_2CON_3$ is heated? Give the mechanism of this reaction. 1+2=3

(ii) Identify *A* and *B* in the following reactions (give structure and name of each) : 2

(1) $C_2H_5-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{P_2O_5} A$

(2) $C_2H_5-I + AgCN \xrightarrow[\text{heat}]{\text{Aq. EtOH}} B$

(c) Write the mechanism of the following reaction

$$Ph_2C=N-OH \xrightarrow[2)\ H_2O^{18}]{1)\ PCl_5} PhCO^{18}NHPh$$

and establish that *(i)* original oxygen atom of oxime is lost, *(ii)* carbonium ion is formed as intermediate and *(iii)* it does not proceed by intramolecular exchange. 2+1+1+1=5

(d) What is Woodward-Hoffmann rule of an electrocyclic reaction? Explain the rule with orbital symmetry of 1,3-butadiene. 5

(e) What is a keto-quarternary ammonium salt? How does it react with strong base? Write the reaction and its mechanism. 5

4. Answer the following questions :

Either

(a) (i) Discuss relative reactivity of pyridine, thiophene, pyrrole and furan towards Friedel-Crafts acylation reaction reflected in the Lewis acid catalyst. 5

(ii) Write desulphurization reaction of $CH_3—S—CH_3$ takes part by Raney Ni. 1

(iii) "Birch reduction is regioselective." Justify with appropriate example. 3

(iv) How can thiophene be obtained from *n*-butane? 1

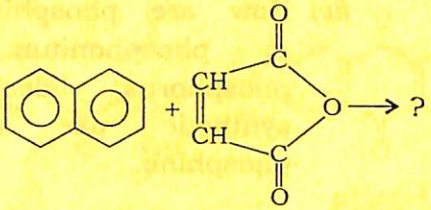
Or

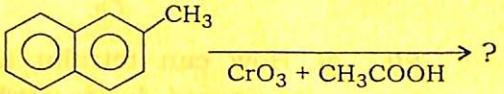
(b) (i) How can nitrobutane be converted to butanal? Give the reaction and write the mechanism. 3

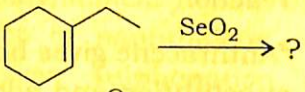
(ii) With the help of a reaction, prove that pyridine ring is present in quinoline. 1

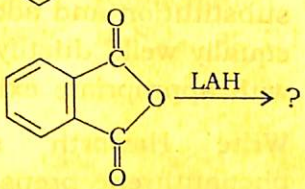
(iii) Prepare sulphone from thioether. 1

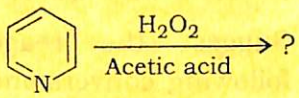
(iv) Give the product in each of the following reactions (give formula and name of each product) : 1×5=5

(1) 

(2) 

(3) 

(4) 

(5) 

Either

(c) *(i)* How is cyanoacetic ester prepared? 1

(ii) How do α-diazoketones undergo rearrangement with elimination of N_2? Give the reaction with mechanism. 1+2=3

(iii) Why does pyrrole give electrophilic substitution reaction with mild reagent? 1

(iv) How are phosphines converted to phosphonium salts and phosphorus ylides? Show one synthetic use of triphenyl-phosphine. 5

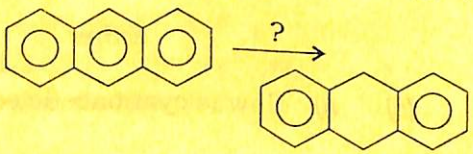
Or

(d) (i) How can tetralin and decalin be prepared from naphthalene? Give reaction. 2

(ii) "Anthracene gives both electrophilic substitution and addition reactions equally well." Justify the statement with appropriate example. 1½+1½=3

(iii) Write Haworth synthesis for phenanthrene preparation. 3

(iv) Suggest the reagents for the following conversions : ½×4=2

(1) 

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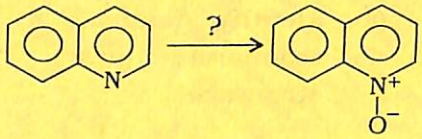
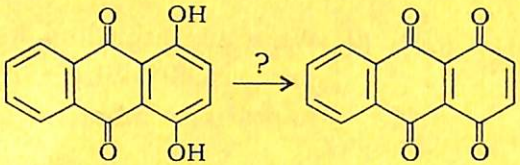
(2) 

(3) $CH_3CH_2CH_2NO_2 \xrightarrow{?} CH_3CH{=}CH_2 + HNO_2$

(4) 

Either

(e) *(i)* Discuss about kinetically and thermodynamically controlled product of naphthalene, when it undergoes sulphonation reaction with conc. H_2SO_4 at 80 °C and 160 °C. 3

(ii) Show that indole undergoes electrophilic substitution reaction at C-3 regioselectively. 3

(iii) How can 'yellow oil' be prepared from $CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}H$? Give reaction. 2

(iv) Identify *A* and *B* in the following reactions (give names and structures) : 1×2=2

(1) $C_2H_5ONO_2 + H_2O \xrightarrow{H^+} A$

(2) $CH_3NO_2 + 3Cl_2 + 3NaOH \longrightarrow B$

Or

(f) *(i)* What are suprafacial and antafacial processes? Why are suprafacial migrations more common? (1+1)+2=4

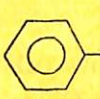
(ii) Prepare pentanone from acetoacetic ester. 2

(iii) Identify *A*, *B*, *C* and *D* in the following reactions (give structure and name of each) : 1×4=4

(1) $C_2H_5SH + HgO \longrightarrow A$

(2)  $\xrightarrow{HCN,\ HCl} B$

(3)  $\xrightarrow[Al_2O_3]{NH_3,\ steam} C$

(4)  $+ Cl-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow D$

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