# 2016

## CHEMISTRY

( Major )

Paper : 5.3

*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) Why does colourless aniline on storage turn brown?

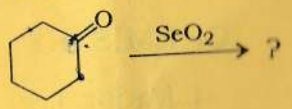
(b) What is 'reductive amination'?

(c) What happens when acetylene and $H_2S$ are passed over alumina at 400 °C?

(d) Why does diethyl malonate undergo alkylation?

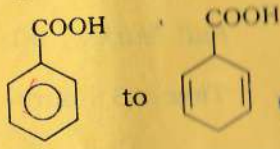
(e) Why is naphthalene less aromatic than benzene?

(f) Give the product (with name) of the following reaction :




(g) Define 'conrotatory ring closure'.

(h) Write the appropriate reagent to convert

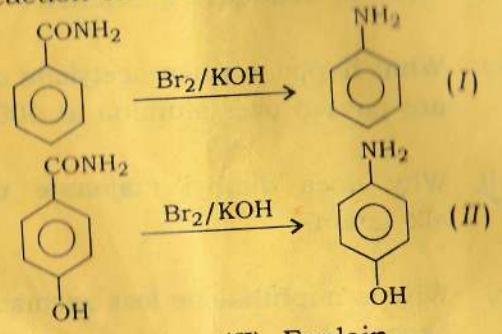



**2.** Answer the following questions (any *four*) : 2×4=8

(a) What is enolate anion and how can it be prepared?

(b) What happens to α-diazoketone when it is heated thermally in presence of $Ag_2O$? Give the reaction.

(c) Reaction rate of




(*I*) is more than (*II*). Explain.

( Continued )



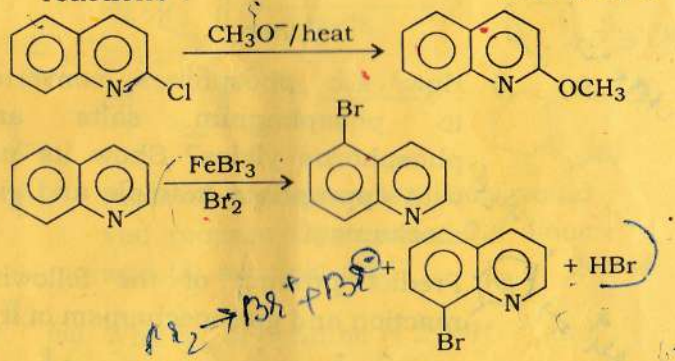


(d) Pyridine is basic. Explain.

(e) Explain the acidic behaviour of nitroalkane.

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

(a) Write Skraup synthesis of quinoline. What is the role of $FeSO_4$ in this reaction? Explain the reactivity of quinoline with the help of following reactions : 2½+½+2=5




(b) Define pericyclic reaction. Explain, why electrocyclic reactions are stereospecific, with appropriate examples. 1+4=5

(c) Convert benzophenone oxime to benzanilide in the presence of $PCl_5$ and give equation with mechanism. What is the driving force for the 1,2-shift in this reaction? 1+3+1=5



( Turn Over )

(d) Write Nakabayashi mechanism of Clemmensen reduction. Explain why in this reaction amalgamated zinc is used instead of pure zinc. 4+1=5

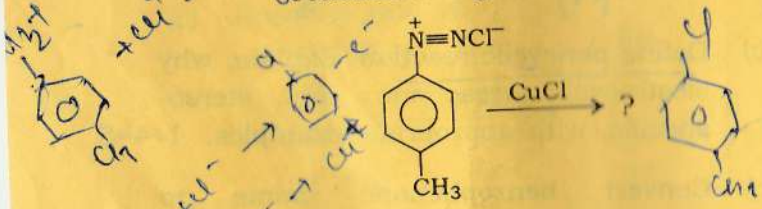
(e) Why do aliphatic nitrocompounds dissolve in aqueous alkali? How can $CH_3CN$ and $CH_3NC$ be prepared? What do you get when they are subjected to acid hydrolysis? 1+2+2=5

**4.** Answer the following questions :

*Either*

(a) (i) How are phosphines converted to phosphonium salts and phosphorus ylides? Show its use with appropriate example and give mechanism. 3+2=5

(ii) Predict product of the following reaction and give mechanism of it : 3




(iii) Why aniline cannot undergo (1) Friedel-Crafts reaction and (2) nitration reaction with $HNO_3$ ? 1+1=2



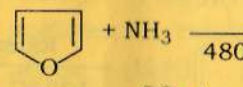
( Continued )

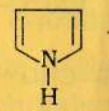


*Or*

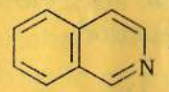
(b) (i) Write products and the names of the products (wherever possible) for the reactions given below : 1×5=5

(1) $ROH + H_2S \xrightarrow[400\ °C]{ThO_2} ?$

(2)  $+ NH_3 \xrightarrow[480\ °C–490\ °C]{Al_2O_3} ?$

(3)  $\xrightarrow[\text{Pyridine}]{SO_3 +} ?$

(4)  $\xrightarrow[SnCl_4]{CH_3COCl +} ?$

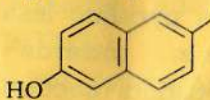
(5)  $\xrightarrow{Pt–H_2} ?$

(ii) From ethyl acetoacetate, how would you prepare (1) pentane-2,4-dione and (2) succinic acid? 2+2=4

(iii) Why $K_b$ of pyridine is $2{\cdot}3\times10^{-9}$ and that of pyrrole is $2{\cdot}5\times10^{-4}$? 1

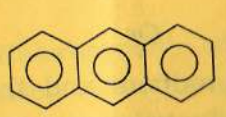
*Either*

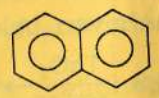
(c) (i) Identify *A*, *B*, *C*, *D* and *E* in the following reactions (write name of each product) : 1×5=5

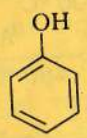
(1)  $\xrightarrow{Pb(OAc)_4} A$



( Turn Over )

(2)  $\xrightarrow[\Delta]{Na + EtOH} B$

(3)  $\xrightarrow[CH_3COOH]{CrO_3} C$

(4)  $+ H_2 \xrightarrow[120\ °C–150\ °C]{Raney\ Ni}$ 

(5) $C_6H_5CH{=}CH{-}CHO \xrightarrow{LAH} E$

(ii) Write about frontier molecular orbital analysis of a [4 + 2] cyclo-addition reaction. 5

*Or*

(d) (i) Explain 'ion pair mechanism in a solvent cage' with appropriate example of a rearrangement reaction. 5

(ii) How can you obtain butanoic acid from diethyl malonate? Write the reaction. 2

(iii) How can benzene be converted to anthracene with phthalic anhydride? Give reaction. 2

(iv) Why is pyridine less reactive than benzene towards electrophilic substitution reaction? 1

*( Continued )*





*Either*

(e) (i) How can you obtain (give reaction)—

(1) dimethyl amine from methyl isocyanide;

(2) methyl propyl ketone from acetoacetic ester;

(3) acetic acid from methyl cyanide? 1×3=3

(ii) Write Haworth synthesis of naphthalene. 2

(iii) How does hydride transfer reduction of propanone take place with $NaBH_4$ in alcohol? Why is hydride transfer of carboxylic group difficult? 2+1=3

(iv) What is the role of C in following conversion reaction? Give product of the reaction

$$CH_3CH_2\underset{\underset{Cl}{|}}{C}{=}O \xrightarrow[Pd\text{-}C]{H_2} \ ?$$

*Or*

(f) (i) What happens when (give reactions)—

(1) *m*-dinitrobenzene reacts with $(NH_4)_2S$;

(2) N-methyl aniline reacts with HONO;

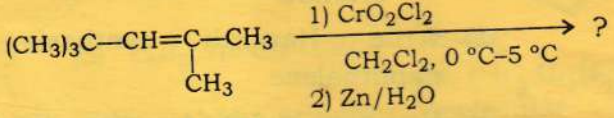
(3) ethyl bromide is heated with potassium sulphide? 1×3=3

*( Turn Over )*

(ii) Give an example to show the application of benzilic acid rearrangement. 2

(iii) How is primary amine diazotized? Show the mechanism with aniline. 1+2=3

(iv) Complete the following reaction : 1




(v) How is the strong acidity of the reagent, pcc, generally controlled? 1

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