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4 SEM TDC CHM M 3

2014

(May)

CHEMISTRY

(Major)

Course : 403

(Organic)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer : 1×5=5

(a) Phthalimide on treatment with NaOH and Cl_2 gives

(i) phthalic acid

(ii) aniline

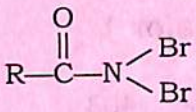
(iii) anthranilic acid

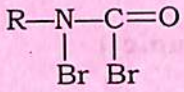
(iv) o-hydroxybenzoic acid

(b) Reaction of $RCONH_2$ with the mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediate involved in the reaction is

(i) RNHBr

(ii) $R—N=C=O$

(iii) 

(iv) 

(c) Which of the following heterocyclic skeletal units is present in both nicotine and hygrine?

(i) Quinoline

(ii) Pyridine

(iii) Pyrrolidine

(iv) Tropane

(d) What product will be formed when pyrrole undergoes reaction with dimethyl formamide and $POCl_3$?

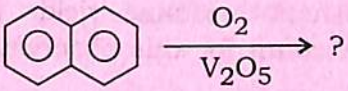
(i) 2-formyl pyrrole

(ii) 3-formyl pyrrole

(iii) 2-chloropyrrole

(iv) 2-methyl pyrrole

(e) What is the product of the following reaction?



(i) Phthalic acid

(ii) Phthalic anhydride

(iii) Anthranilic acid

(iv) Benzene

2. Answer any *five* of the following questions : 2×5=10

(a) How can primary, secondary and tertiary amines be separated from the mixture using benzene sulphonyl chloride as the main reagent? Write necessary equations.

(b) Starting from diethyl malonate, how would you prepare *n*-valeric acid?

(c) Discuss the importance of Zeisel's method in structure elucidation of alkaloids.

(d) Explain why C—N single bond is weaker and longer than the peptide C—N bond.

(e) Pyrrole shows resemblance to phenol and aromatic amines. Explain with examples.

(f) Oxidation of 1-nitronaphthalene yields 3-nitrophthalic acid while oxidation of 1-naphthylamine yields phthalic acid. Account for this observation.

UNIT—I

Answer *any* **one** question

3. (a) Give the example of an active methylene compound and write its preparation. ½+1½=2

(b) Starting from ethyl acetoacetate, how would you synthesize the following? 1+1=2

(i) Glutaric acid

(ii) Acetonyl acetone

4. (a) Starting from diethyl malonate, how would you synthesize cyclopentane carboxylic acid and then cyclopentane? 1½+½=2

(b) Draw the resonance and resonance hybrid structures of the acetoacetic ester anion. 2

UNIT—II

Answer *any* **one** question

5. (a) Give a method of preparation of diazomethane. What happens when diazomethane reacts with (i) phenol and (ii) ethylene? 1+½+½=2

(*Continued*)

(b) Give one method of preparation of (i) an alkyl cyanide and (ii) an alkyl isocyanide. Complete the following reaction : ½+½+1=2

$$RNC + HgO \longrightarrow ?$$

(c) An amine (A), $C_6H_{15}N$ on treatment with MeI and then KOH gives (B), $C_6H_{20}\overset{\oplus}{N}\overset{\ominus}{O}H$. (B) on heating produces isobutene and amine (C), $C_4H_{11}N$. What is (A)? Write necessary reactions in the form of equations. 2

6. (a) Complete the following reaction and write the plausible mechanism : 2

$$RCOCH_3 + CH_2O + (CH_3)_2NH \longrightarrow ?$$

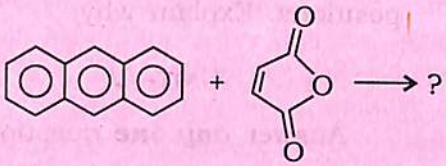
(b) Give one method of preparation of benzenediazonium chloride. Explain why aryldiazonium salts are more stable than alkyldiazonium salts. 1+1=2

(c) Complete the following reactions : 1+1=2

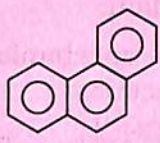
(i)  $+ CH_2N_2 \longrightarrow ?$

(ii)  $-N_2^{\oplus}Cl^{\ominus} + CuCN \longrightarrow ?$

(b) Complete the following reactions (any *two*) : 1×2=2

(i)  + ⟶ ?

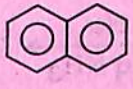
(ii)  + CH_2O + HCl ⟶ ?

(iii)  $\xrightarrow[\text{glacial AcOH}]{CrO_3}$?

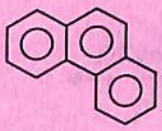
(c) Arrange benzene, naphthalene and anthracene in increasing order of reactivity giving reasons. 2

10. (a) Write all the steps involved in the synthesis of anthracene starting from benzene. 2

(b) Complete the following reactions (any *two*) : 1×2=2

(i)  $\xrightarrow[\text{isopentanol}]{Na}$?

(ii)  $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$?

(iii)  $\xrightarrow[Zn/H_2O]{O_3}$?

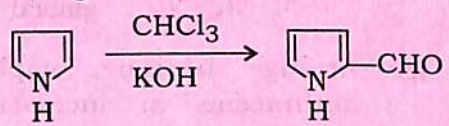
(c) Anthracene undergoes electrophilic substitution reactions at 9 and 10 positions. Explain why. 1

UNIT—V

Answer *any* **one** question

11. (a) (i) Pyridine is a strong base than pyrrole but weaker than aliphatic amines. Explain. 1½

(ii) Outline the mechanism of the following reaction : 1½

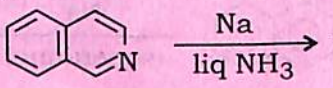


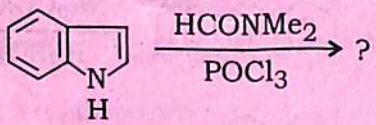
(b) Write short notes on : 2½×2=5

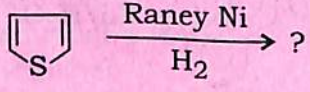
(i) Knorr pyrrole synthesis

(ii) Bischler-Napieralski synthesis of isoquinoline

12. (a) Complete the following reactions : 3

(i) 

(ii) 

(iii) 

(*Continued*)

(b) In terms of relative stability of intermediates, discuss the orientation of electrophilic substitution with furan, pyrrole and thiophene. Use the general formula C_4H_4Z. Why are these heterocycles more reactive than benzene to attack by an electrophile? 1½+1=2½

(c) Write the product resulting from heating pyridine with $NaNH_2$ followed by addition of water. Suggest a mechanism and explain the orientation of the reaction. 2½

UNIT—VI

13. (a) What are alkaloids? How are they classified? 1+1=2

(b) What is Hofmann's exhaustive methylation method? What products will be obtained when this method is applied to nicotine? 2

(c) Discuss the Ladenburg's synthesis of coniine. 1

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