2019

CHEMISTRY

(Major)

Paper : 5.3

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

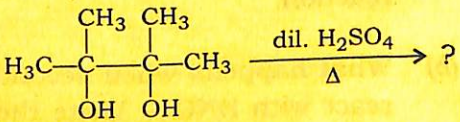
The figures in the margin indicate full marks for the questions

1. Answer any *seven* of the following : 1×7=7

(a) What is the name of the following reaction?

$$RCOOH + HN_3 \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$$

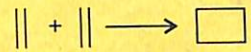
(b) Complete the following reaction :



(c) Complete the following reaction :

$$CH_3CH_2COCH_2CH_3 \xrightarrow{?} CH_3CH_2CH(OH)CH_2CH_3$$

(d) Name the type of the following reaction :



(e) What is the full form of HOMO?

(f) Which one is more acidic RSH or ROH?

(g) Why is furan least aromatic than thiophene?

(h) Which position of pyridine undergoes electrophilic substitution reaction?

(i) Why is nitromethane acidic?

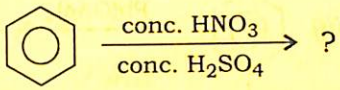
2. Answer any *four* of the following questions : 2×4=8

(a) What happens on boiling an aqueous solution of sodium nitrite with an α-halogen carboxylic acid? Write the reaction.

(b) What happens when secondary amines react with HNO_2? Write the reaction.

(c) What happens when aryldiazonium salt is treated with β-naphthol? Write the reaction.

(d) Complete the following reaction :



Give the mechanism.

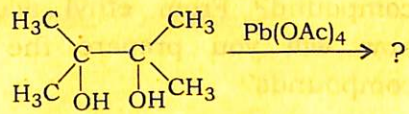
(e) Draw the tautomers of acetoacetic ester. Which one is more stable and why?

3. Answer any *three* of the following questions : 5×3=15

(a) How does phenyl acetate undergo intra-molecular rearrangement reaction in the presence of $AlCl_3$? Give mechanism of this reaction. What are the factors on which relative amount of product depends? 1+3+1=5

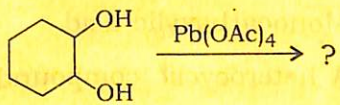
(b) Complete the following reactions : 1×5=5

(i)



Pinacol

(ii)



Cyclohexane -1,2-diol

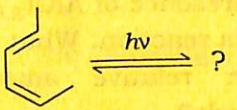
(iii) 

$\xrightarrow{Pb(OAc)_4}$?

(iv) $CH_3(CH_2)_4CHO \xrightarrow{?} CH_3(CH_2)_4CH_2OH$

(v) $CH_3COCl \xrightarrow{LAH}$?

(c) Which cycloaddition reaction is known as Diels-Alder reaction? Write the product of the following reaction and justify the stereochemistry of the product using FMO method : 1+4=5



(d) What do you mean by active methylene compound? From ethyl acetoacetate, how will you prepare the following compounds? 1+4=5

(i) Cinnamic acid

(ii) Monocarboxylic acid

(iii) A heterocyclic compound

(iv) Butanone

4. Answer the following questions : 10×3=30

Either

(a) (i) What happens when ethanal treated with nitroethane in the presence of a base? Write the reaction and give the mechanism. Write the Mannich reaction. 1+3+1=5

(ii) What are the different products you obtain when nitrobenzene undergoes reduction in alkaline medium? Write the reactions. 5

Or

(b) (i) What is exhaustive methylation of amines and Hoffmann's elimination? Discuss with a suitable example. 5

(ii) Explain the following : 1+1+1+2=5

1. Aniline is less basic than N-methyl aniline.
2. Diphenyl amine is a much weaker base than aniline.
3. 2,4,6-trinitroaniline is termed Picramide even though it contains no amide linkage.

4. Triphenyl amine and N,N-dimethyl aniline are both tertiary amines. Triphenyl amine is insoluble in HCl but N,N-dimethyl aniline readily dissolves in HCl.

Either

(c) (i) Explain why the electrophilic substitution takes place preferably at α-position in furan, thiophene and pyrrole. 3

(ii) Pyrrole is acidic in character like phenol. Explain. 2

(iii) Describe the mechanism of nitration of pyridine and justify that substitution takes place at position 3. 5

Or

(d) (i) What are polynuclear hydrocarbons? What are the different types? 1+2=3

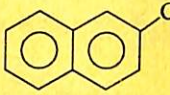
(ii) Write the Haworth's synthesis of naphthalene. 3

(iii) Give the product with name of the following : 1×4=4

1.  $\xrightarrow{\text{Acidic } KMnO_4}$?

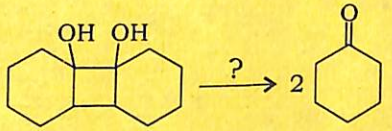
2.  $\xrightarrow[289°]{CrO_3,\ AcOH}$?

3.  $\xrightarrow[[O]]{Na_2Cr_2O_7/H_2SO_4}$?

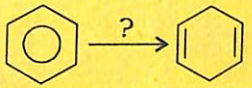
4.  $\xrightarrow{[O]}$?

Either

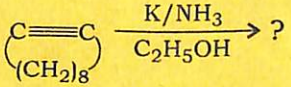
(e) Complete the following, specifying the transformation as oxidation or reduction : 2×5=10

(i) 

(ii) $Ph—CH=CH—COOEt \xrightarrow{AlH_3}$?

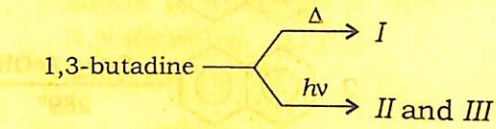
(iii) 

(iv) ? $\xrightarrow{Pd/H_2}$ RCHO

(v) 

Or

(f) *(i)* Predict the structures for compounds *I*, *II* and *III* : 3



(ii) What is sigmatropic rearrangement? What do you mean by the order $[i, j]$ of a sigmatropic rearrangement? Give example. 1+1+1=3

(iii) Discuss the FMO method of (4 + 2) cycloaddition reaction. 2

(iv) Write down the Woodward-Hoffmann rules for electrocyclic reaction. 2

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