

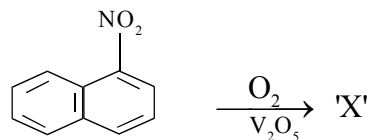
2021
CHEMISTRY
[HONOURS]
Paper : X

Full Marks : 100

Time : 4 Hours

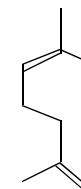
*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.***GROUP-A****(Marks : 50)**1. Answer any **five** questions: 2×5=10

- a) Between pyrrole and furan, which one has higher dipole moment? Give the direction of (+)ve and (-)ve poles in each case.
- b) What is 'X' in the following reaction:

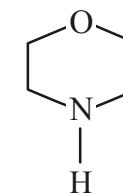


- c) Explain why D-fructose reduces Fehling's solution although it is a ketohexose.

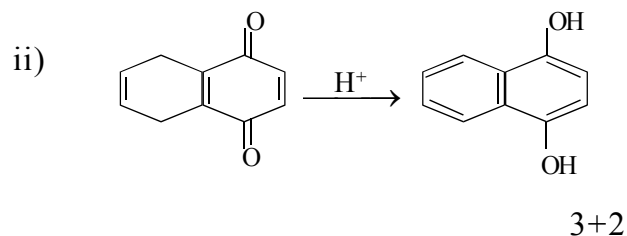
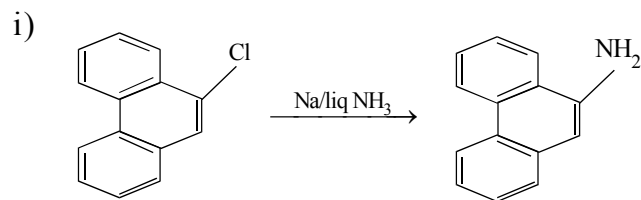
- d) Write down the Fischer projection and Howarth structure of β -D-Glucopyranose.
- e) Pyridine-N-oxide is more reactive towards both electrophilic and nucleophilic reaction. Why?
- f) Write down all the products of ozonolysis of the following compound:



- g) What products would you expect to get by the application of Hofmann's exhaustive methylation to the following compound?

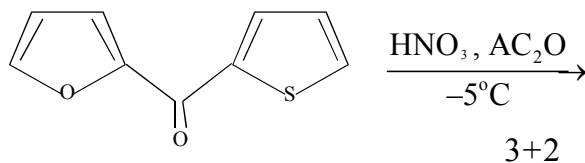


- h) Compare the reaction of benzoic acid and 2-furoic acid to heating to $\approx 200^\circ\text{C}$.
2. Answer any **four** questions: 5×4=20
- a) Write a reasonable mechanism for the following reactions:



b) i) Draw the more and less stable chair conformations of β -D-manno-pyranose and β -L-Glucopyranose.

ii) Write the products of the following reaction:



c) i) Why is periodic acid rather than lead tetraacetate used for oxidative cleavage of carbohydrates?

ii) Distinguish the terms 'anomers' and 'epimers' by taking suitable aldohexoses as examples.

2+3

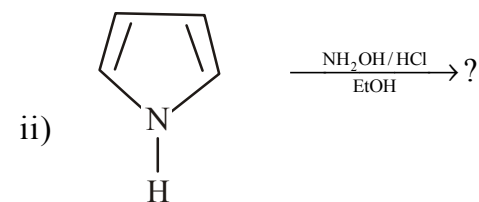
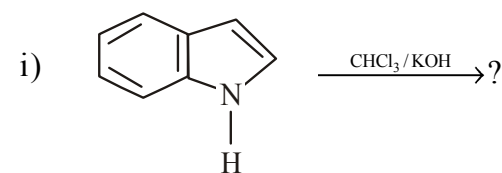
d) i) D-Glucose reacts with excess of PhNHNH₂ to form a compound called glucosazone. Give the mechanism of reaction.

ii) How would you detect and then separate the presence of trace amount of thiophene in benzene? 3+2

e) i) Starting from DEM and any other compounds of your choice synthesize cyclohexane-1, 4-dicarboxylic acid.

ii) How can you, convert furan to α -Naphthol using Diels-Alder reaction? 2.5+2.5

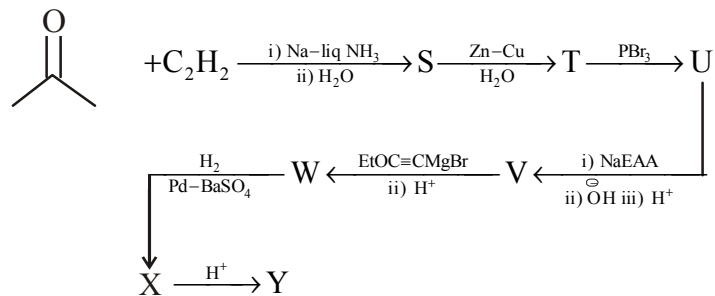
f) Give product(s) of the following reaction:



2.5+2.5

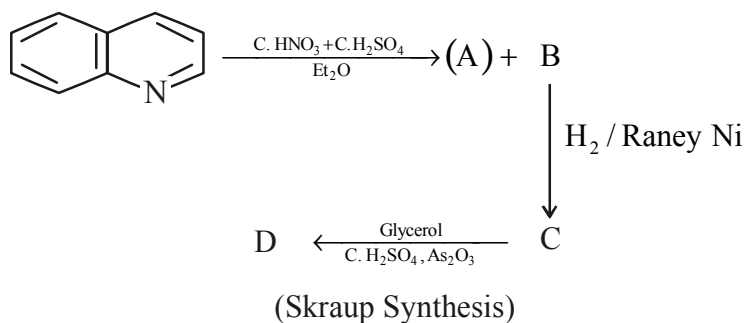
3. Answer any **two** questions: $10 \times 2 = 20$

a) i) Write structures for S to Y in the following reaction scheme:



ii) Write down the structure of geometrical isomers of citral. How would you differentiate them by NMR spectroscopy? $7+3$

b) i) Write structures for A to D for the following reaction scheme:



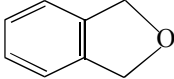
Give mechanism for the conversion of C to D.

ii) Di-O-isopropylidene derivative of D-Glucose but not that of D-Galactose can be alkylated at C-3-position. Give reason. $(4+3)+3$

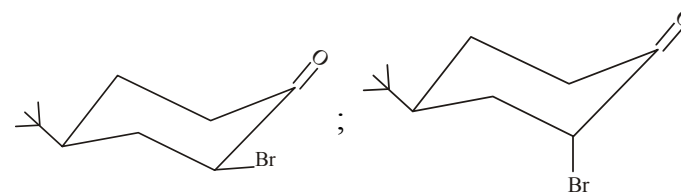
c) i) Give the product and mechanism of hydramine fission reaction of Ephedrine with hydrochloric acid.

ii) Give a total synthesis of D(-) Ephedrine.

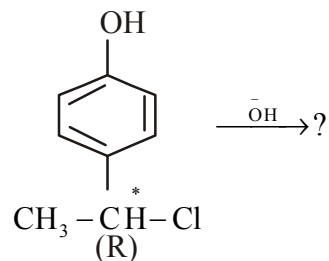
iii) Draw the stereochemical structure of piperine.

iv) Prepare  from quinoline. $3+3+2+2$

d) i) Which one is the most stable conformation and why among the following?



- ii) Write down the product of the following reaction:



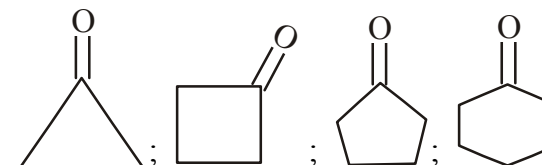
- iii) What happens when cis- and trans-isomers of 3-Hydroxycyclohexanecarboxylic acid are heated separately?
- iv) How would you prove that coniine contains n-propyl group as side chain and not isopropyl group at 2-position of piperidine nucleus? 2+3+3+2

GROUP-B

(Marks : 50)

4. Answer any **five** questions: 2×5=10
- a) What is a chromophore? Identify the chromophoric group in cyclopentene and toluene.
- b) Give the structure of Lysine in its isoelectronic point.

- c) Aniline in neutral/basic medium and acidic medium show different UV spectra. Explain the fact.
- d) Arrange the following cyclic ketones in order of increasing C=O stretching frequency:



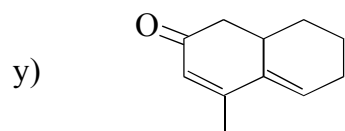
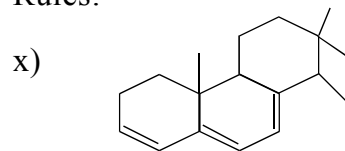
- e) Define the term 'chemical shift' used in NMR-spectroscopy.
- f) Draw the HOMO of 1, 3, 5-cycloheptatriene in its first excited state.
- g) What is the difference between nucleoside and nucleotide?
- h) What is 'Isoprene rule'?
5. Answer any **four** questions: 5×4=20
- a) i) Write a detailed mechanism of the reaction between an α -amino acid and ninhydrin.
- ii) Give one method of determination of C-terminal amino acid in a peptide molecule. 3+2

b) i) In an electric field, towards which electrode an α -amino acid migrate at a (x) $\text{pH} < \text{pI}$ (y) $\text{pH} > \text{pI}$ and (z) $\text{pH} = \text{pI}$. Explain your answer.

ii) What is DCC? What is its use in peptide synthesis? 3+2

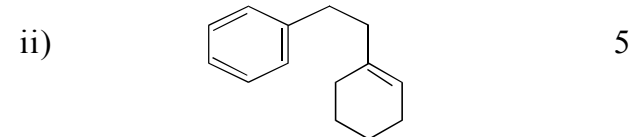
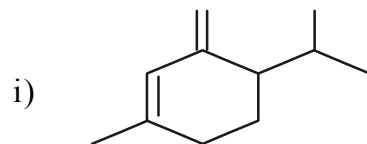
c) i) The position of absorption of acetone shift in different solvents. 279 nm (hexane) and 264nm (water)—Explain.

ii) Calculate λ_{max} for the following compound according to Woodward Fieser Rules:

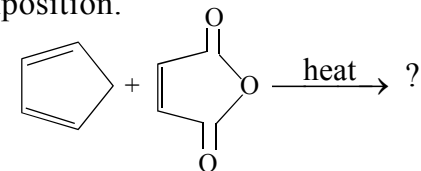


2+3

d) Synthesise the following compounds showing proper retrosynthetic analysis:



e) i) Discuss secondary interaction in the following reaction with FMO-diagram of the T.S. and hence the product composition.

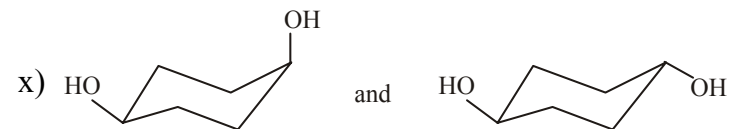


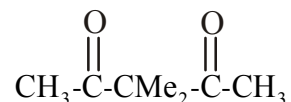
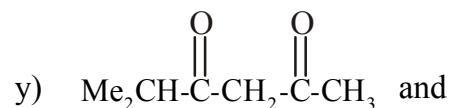
ii) Predict the approximate chemical shifts of the protons of acetaldehyde.

$$3\frac{1}{2} + 1\frac{1}{2}$$

f) i) Summarize the relationship between the hybridisation state of the carbon of the C–H bond and the expected frequencies of the C–H vibration.

ii) How can you differentiate between the following isomeric compounds by IR-spectroscopy?

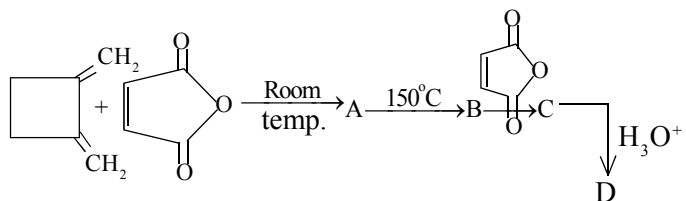




2+3

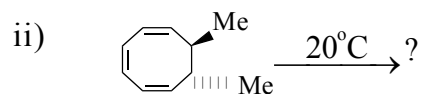
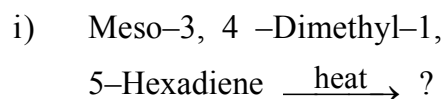
6. Answer any **two** questions: $10 \times 2 = 20$

a) i) What are A to D in the following reaction scheme:



ii) What are the selection rules for sigmatropic reactions?

iii) Give product(s) with mechanism



4+2+(2+2)

b) i) Explain why benzoyl group can not be used as a N-protecting group in peptide synthesis?

ii) Write the complete reaction mechanism of cyanogenbromide method for the cleavage of peptide chains having methionine unit.

iii) What are the five different nitrogenous bases found in DNA and RNA-molecules? Draw their structures.

iv) What are the functions of t-RNA and r-RNA? $2+3+3+2$

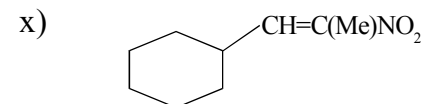
c) i) Draw the specific base pairing in a double helix structure of a DNA molecule.

ii) Synthesize (\pm) -Proline using diethylmalonate and potassium-phthalimide.

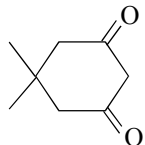
iii) Define coenzyme.

iv) What is the function of chymotrypsin, a proteolytic enzyme? $3+3+2+2$

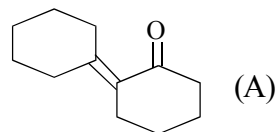
d) i) Synthesise the following compounds showing proper retrosynthetic analysis:



y)



- ii) Treatment of A with aqueous acid gives a single compound $C_6H_{10}O(B)$, which forms an oxime and is oxidised to $HOOC(CH_2)_4COOH$. Give the structure of B. Outline the steps in the transformation.



- iii) Give the product (P) from the acid catalysed reaction of cyclopentanone with pyrrolidine. To what class of compound P belong?

$$2+2\frac{1}{2}+3+2\frac{1}{2}$$
