

**2021**  
**CHEMISTRY**  
**[HONOURS]**  
**Paper : VIII**

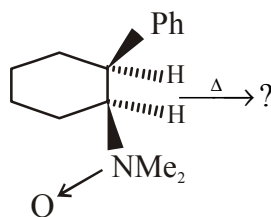
Full Marks : 80

Time : 4 Hours

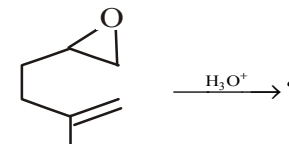
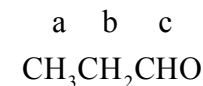
*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.***GROUP-A****(Marks : 40)**1. Answer any **two** questions from the following:

1×2=2

a) Indicate the major product of the following reaction:

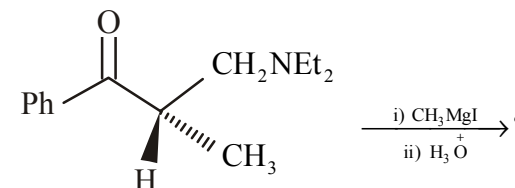
b) Comment on the position of  $\text{C} \equiv \text{N}$  stretching band of nitrile compounds in IR spectrum.

c) Identify the major product of the following reaction:

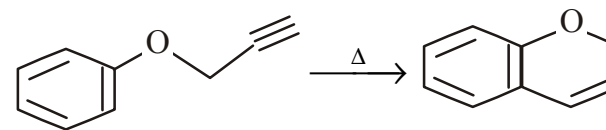
d) Arrange the following labelled hydrogens in order of increasing chemical shift value in  $^1\text{H}$  NMR:2. Answer any **two** questions from the following:

2×2=4

a) Use Cram's rule to predict the major product of the following reaction:



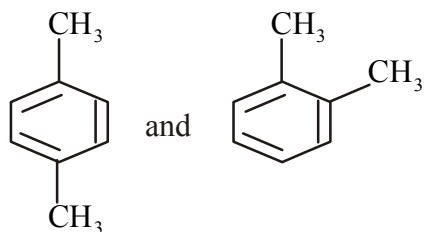
b) Suggest mechanism for the following reaction:



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- c) 2, 3-Di-tert-butyl-1, 3-butadiene is reluctant to give Diels-Alder reaction with an alkene. Explain.

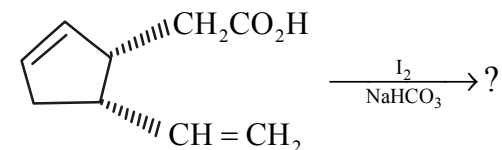
- d) How would you distinguish the following pair by  $^1\text{H-NMR}$ ?



3. Answer any **four** from the following:  $6 \times 4 = 24$

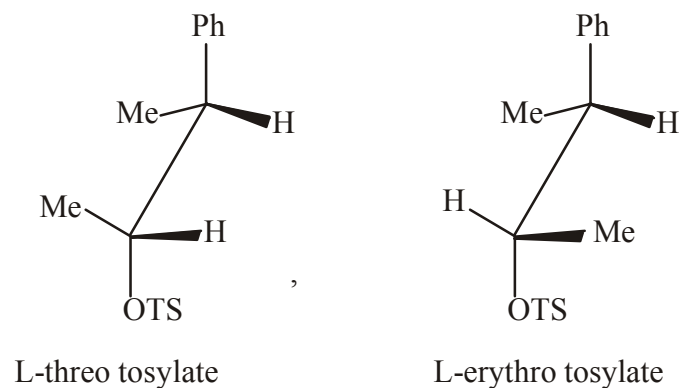
- a) i) An organic compound with molecular mass 69 is transparent above 200nm. The absorption bands in IR spectrum are  $2941\text{cm}^{-1}(\text{m})$ ,  $2273\text{cm}^{-1}(\text{m})$  and  $1460\text{cm}^{-1}(\text{m})$ . In  $^1\text{H-NMR}$ , two signals are observed. One is septet at 2.72ppm and another is doublet at 1.33ppm. Deduce the structure of organic compound.

- ii) Predict the major product of the following reaction with mechanism:

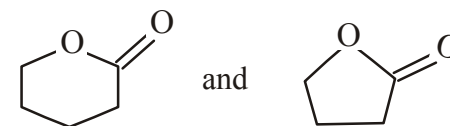


$3+3=6$

- b) i) What happens when the following tosylates are separately subjected to acetolysis? Explain the reactions and comment on optical activity of the products.

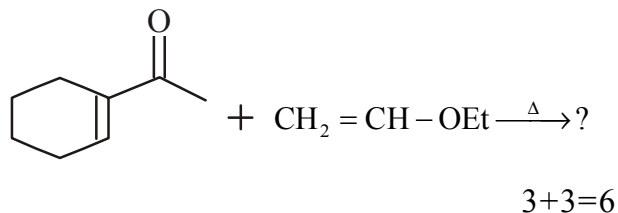


- ii) How can you distinguish the following pair by IR spectroscopy?

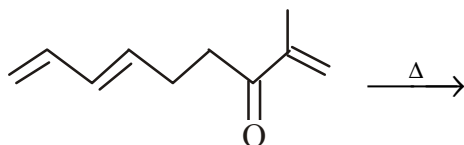


$4+2=6$

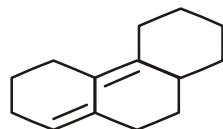
- c) i) Using frontier orbital overlap, explain the preferred mode of Diels-Alder reaction between butadiene and ethylene.
- ii) Predict the major product of the following thermal reaction and give the plausible mechanism.



- d) i) Identify the product with mechanism in the following reaction:

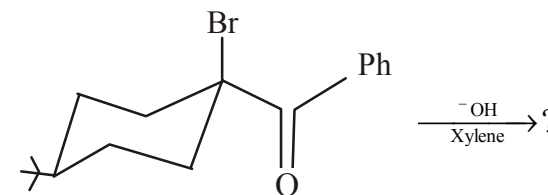


- ii) Based on Woodward rule calculate  $\lambda_{\max}$  of the following compound:

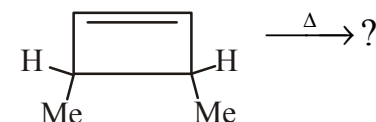


- iii) Explain why [1, 5]-sigmatropic H-shift in penta-1,3-diene is very facile but [1, 3]- sigmatropic H-shift is not observed.
- 2+2+2=6

- e) i) Give product with mechanism of the following reaction:



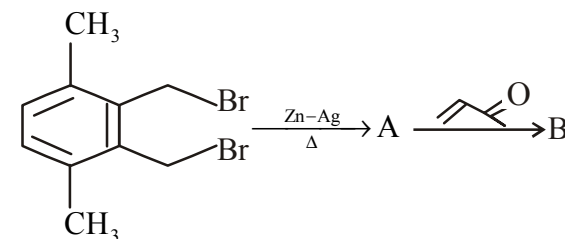
- ii) Based on FMO interaction predict the product(s) of the following reaction:



- iii) Although a wet sample can be used for UV spectral analysis, a dry sample is necessary for IR analysis. Why?

2+2+2=6

- f) i) Identify 'A' and 'B' in the following conversions and explain their formation with mechanism.



- ii) What happens when *cis*-4-*t*-butylcyclohexylamine is treated with nitrous acid? Give justification. 4+2=6

4. Answer any **one** of the following questions:

10×1=10

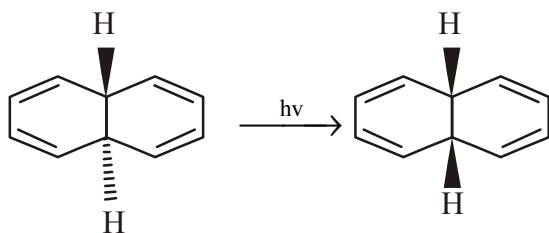
- a) i) A compound has a molecular formula  $C_{10}H_{13}Cl$ . Assign its structure with the help of the following proton NMR data:

singlet 1.57 $\delta$  6H

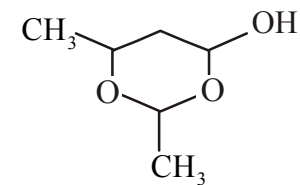
singlet 3.07 $\delta$  2H

singlet 7.27 $\delta$  5H

- ii) Rationalise the following observation:



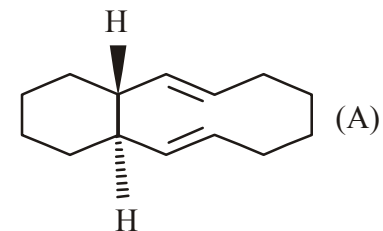
- iii) Aldols as such are not always isolated from the condensation. For example, acetaldehyde readily forms the following cyclic hemiacetal during aldol reaction.



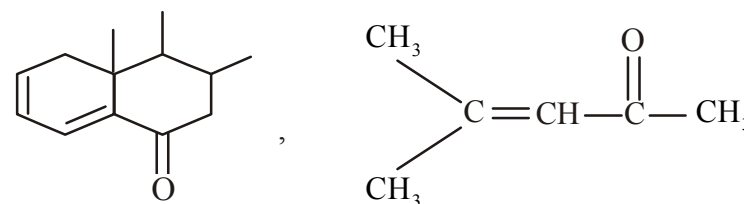
How would you explain this observation?

- iv) What do you mean by chemically non equivalent protons? Explain with example. 3+3+2+2=10

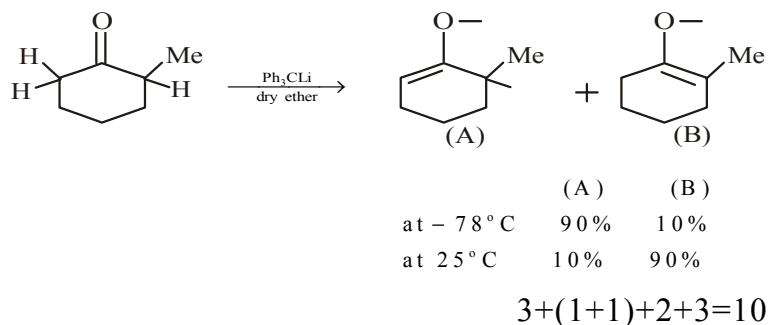
- b) i) Optically active 'A' racemises on heating at 50°C with a half-life of 24hr. Rationalize this observation.



- ii) Calculate the  $\lambda_{\max}$  values for the following compounds:



- iii) Increase in polarity of the solvent shifts  $\pi - \pi^*$  band to longer wavelength but  $n - \pi^*$  band to shorter wavelength. Comment on the statement.
- iv) How would you explain the following observations?

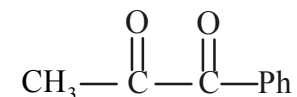


### GROUP-B

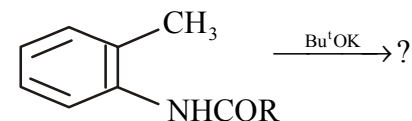
(Marks : 40)

5. Answer any **two** questions from the following:
- $1 \times 2 = 2$
- Write down the structure of malachite green.
  - Assign the correct wittig salt for the following reaction:  
 $\text{PhCHO} \xrightarrow{?} \text{PhCH}=\text{CH}(\text{OCH}_3)$
  - Give one synthetic use of DDQ.
  - Arrange the following in order of increasing aromaticity:  
 thiophene, pyrrole, furan.

6. Answer any **two** questions from the following:
- $2 \times 2 = 4$
- Give the synthesis of methyl orange.
  - Show how you would synthesize the following compound using dithiane and other chemicals.



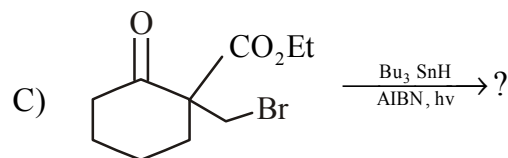
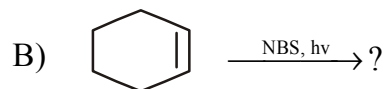
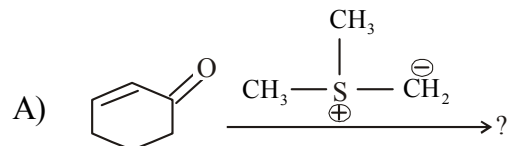
- Why does D-fructose give a positive Tollen's test?
- Predict the product of the following reaction and suggest the plausible mechanism:



7. Answer any **four** questions from the following:
- $6 \times 4 = 24$
- $\alpha$ -D-Glucose does not undergo mutarotation in pyridine alone or in phenol alone but it undergoes rapid mutarotation in a mixture of pyridine and phenol. Explain.
    - Give the synthesis of sulfadiazine. Mention its one use.  $3 + (2+1) = 6$
  - Why periodic oxidation of D-mannose is faster than that of D-glucose?

- ii) The monobromination of thiophene-3-carboxylic acid gives only one product. What is its structure and why is it the only product formed?  $2+(1+3)=6$

- c) i) Identify the product(s) in the following reactions (mechanism not required).

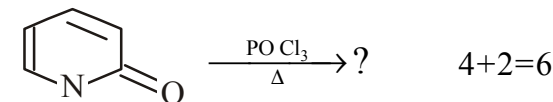


- ii) Give the structure of PVC and depict its preparation with one important use.

$$(3 \times 1) + (1 + 1 + 1) = 6$$

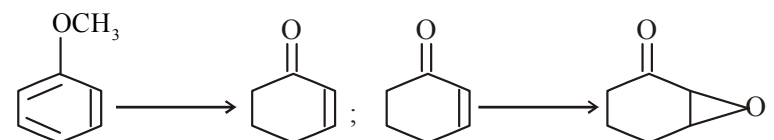
- d) i) Account for the fact that position 3 of pyridine is the site for nitration and sulphonation, while positions 2 and 4 are sites for attack by sodium amide and alkyl lithium compounds.
- ii) Indicate the product of the following

reaction with mechanism:



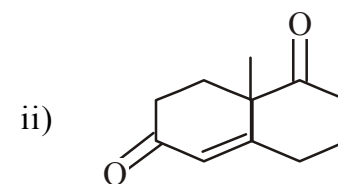
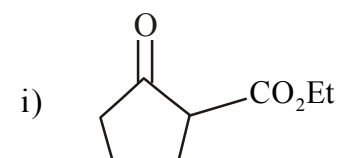
- e) i) What is meant by primary and secondary structures of polypeptide?

- ii) Carry out the following conversion with appropriate reagent. (mechanism required):



$$2 + (2 + 2) = 6$$

- f) Indicating retrosynthetic analysis give the synthetic route to the synthesis of following compounds (any **two**):



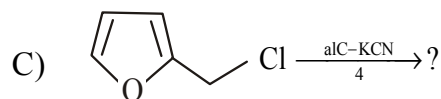
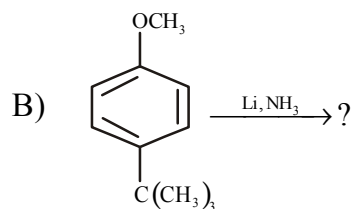
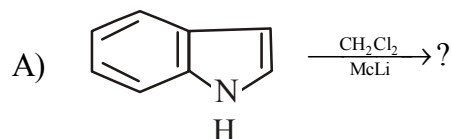


8. Answer any **one** question from the following:

$$10 \times 1 = 10$$

a) i) Prepare *cis*- and *trans*-1, 2-diols from cyclohexene by applying Prevost and Woodward reactions. Explain with mechanism.

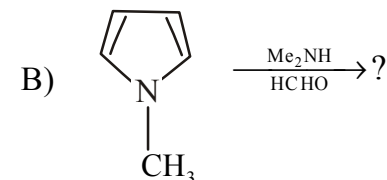
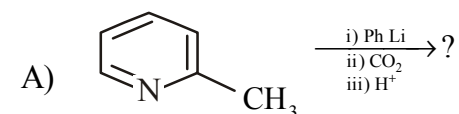
ii) Identify the product(s) with mechanism for the following reactions (any **two**):



iii) Mention one important use of 'Teflon'.

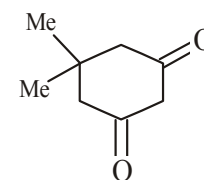
$$3 + (3 + 3) + 1 = 10$$

b) i) Indicate the product(s) of the following reactions and give plausible mechanism:



ii) Explain why primary or tertiary amines cannot be used to prepare enamines.

iii) How would you use a Michael reaction in one of the steps to prepare the following compound? Sketch the pathways with mechanism.



$$(2 \frac{1}{2} \times 2) + 2 + 3 = 10$$

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