

2022
CHEMISTRY
[HONOURS]
Paper : VIII

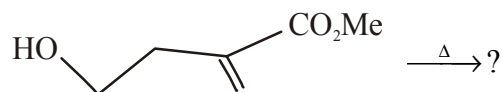
Full Marks : 80

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:

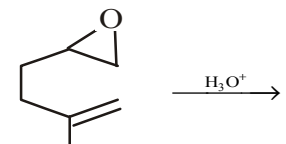
1×2=2

a) Indicate the major product of the following reaction:

b) Identify the geometrical isomer of stilbene from their λ_{\max} values of 294 nm and 278 nm.c) Arrange the following labelled hydrogens in order of increasing chemical shift value in ^1H NMR:*[Turn over]*

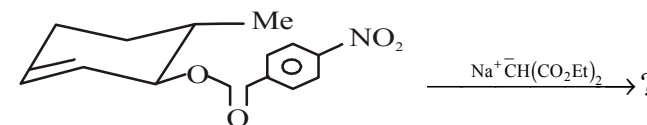
a b c
 $\text{CH}_3\text{CH}_2\text{CHO}$

d) Identify the major product of the following reaction:

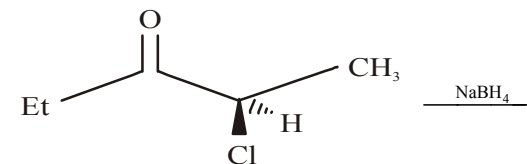
2. Answer any **two** questions from the following:

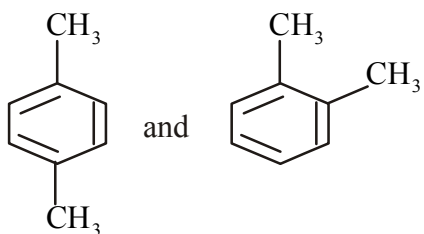
2×2=4

a) Predict the product of the following reaction with mechanism. Hence comment on the stereochemical course of the reaction.

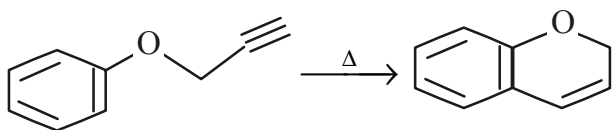


b) Use Cram's rule to predict the major product of the following reaction:

c) How would you distinguish the following pair by ^1H -NMR?



d) Suggest mechanism for the following reaction:



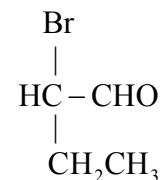
3. Answer any **four** from the following: $6 \times 4 = 24$

a) i) A liquid with molecular formula $C_6H_7NO_2$ shows characteristic IR absorptions at 2240 cm^{-1} and 1730 cm^{-1} and $^1\text{H-NMR}$ peaks at 2.7 (s, 4H), 3.8 (s, 3H). Assign the structure.

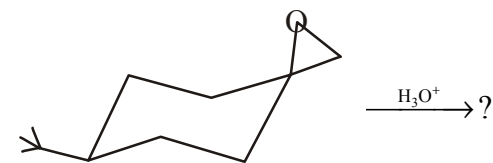
ii) Discuss on Lewis acid catalysis in Diels-Alder reaction. $3+3=6$

b) i) Is Ester of o-chlorobenzoic acid shows two $\text{C}=\text{O}$ stretching frequencies? Explain.

ii) Draw tentative sketch of $^1\text{H NMR}$ spectrum of

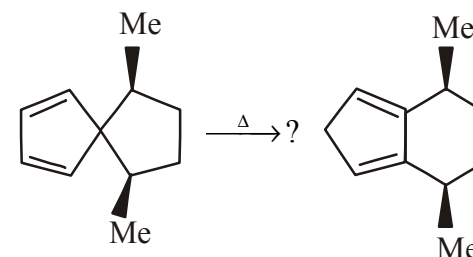


iii) Predict the major product obtained in the following reaction:

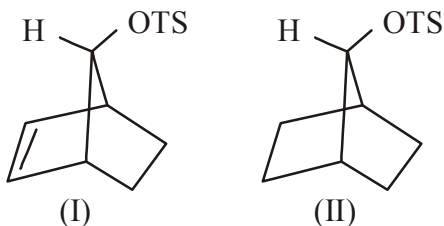


Give reason against the formation of the product. $2+2+2=6$

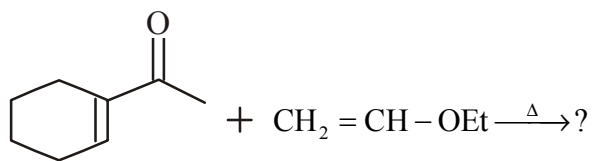
c) i) Indicate the type of Sigmatropic shifts involved in the following transformation. Rationalize mechanistically.



- ii) Which one of the following compounds will undergo faster acetolysis and why? 3+3=6



- d) 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.

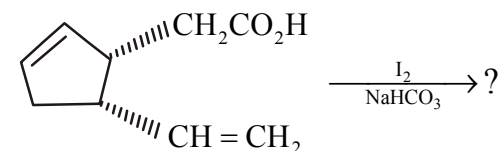


3+3=6

- e) i) An organic compound with molecular mass 69 is transparent above 200nm. The absorption bands in IR spectrum are 2941cm⁻¹(m), 2273cm⁻¹(m) and

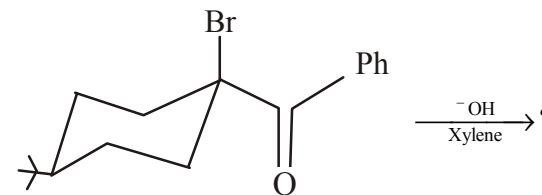
1460cm⁻¹(m). In ¹H-NMR, two signals are observed. One is septet at 2.72ppm and another is doublet at 1.33ppm. Deduce the structure of organic compound.

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

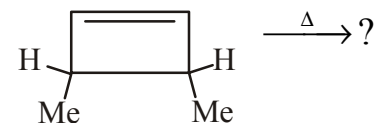


3+3=6

- f) 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?

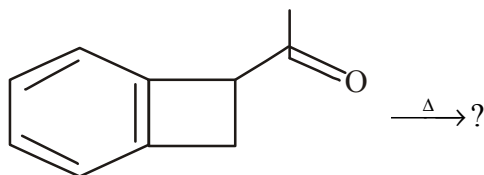
2+2+2=6

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

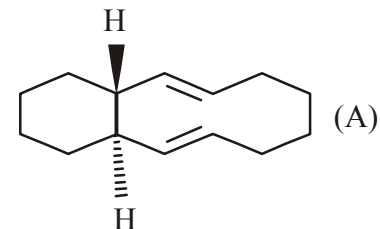
10×1=10

- a) i) The acid catalysed dehydration of 1-methyl cyclohexanol yields a mixture of two alkenes. How would you use $^1\text{H-NMR}$ to distinguish between the two?
- ii) A compound ($\text{C}_7\text{H}_8\text{O}$) exhibits proton NMR signals at $\delta=7.3(5\text{H})$, $4.4(2\text{H})$ and $3.7(1\text{H})$ ppm. Deduce the structure of the compound.
- iii) Draw the HOMO and LUMO of allyl cation.
- iv) Indicate the product of the following reaction:

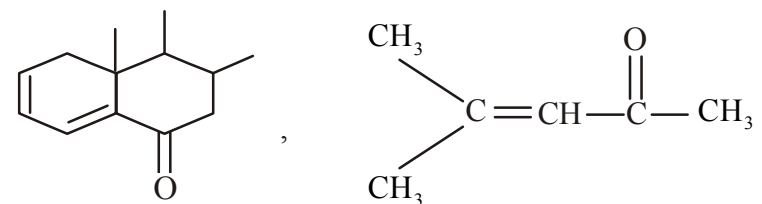
3+3+3+1=10



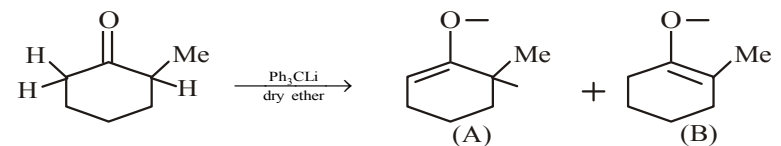
- b) i) Optically active 'A' racemises on heating at 50°C with a half-life of 24hr. Rationalize this observation:



- ii) Calculate the λ_{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?



| | | |
|------------|-----|-----|
| | (A) | (B) |
| at - 78 °C | 90% | 10% |
| at 25 °C | 10% | 90% |

$3+(1+1)+2+3=10$

GROUP-B

5. Answer any **two** questions from the following:

$1 \times 2 = 2$

- a) Give one synthetic use of trimethyl silyl iodide.
- b) Give an example of cationic dye.
- c) Assign the correct wittig salt for the following reaction:



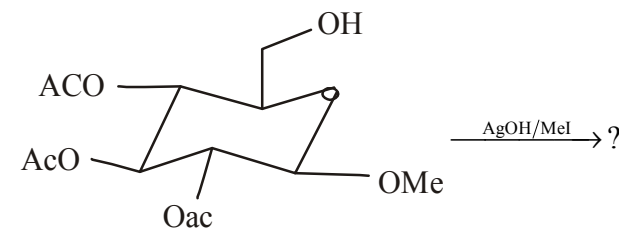
- d) Give one synthetic use of DDQ.

6. Answer any **two** questions from the following:

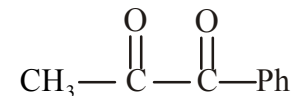
$2 \times 2 = 4$

- a) The specific rotation of α -D-mannopyranose is $+29.3^\circ$ and that of β -D-anomer is -17.0° . The equilibrium mixture of two in water has a steady specific rotation $+14.2^\circ$. Calculate the percentage of α - and β - anomers in the equilibrium mixture.

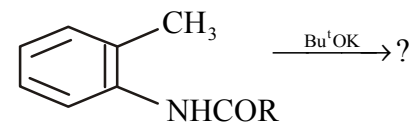
b) Indicate the product with mechanism:



c) Show how you would synthesize the following compound using dithiane and other chemicals:



d) Predict the product of the following reaction and suggest the plausible mechanism:

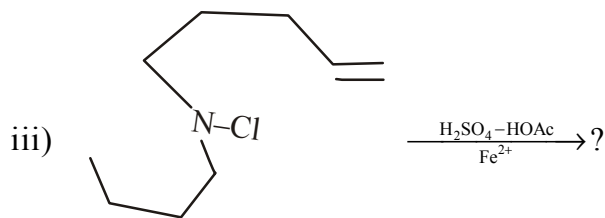
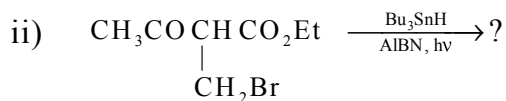
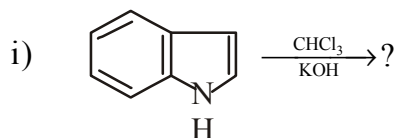


7. Answer any **four** questions from the following:

$$6 \times 4 = 24$$

a) Predict the product(s) of the following reactions with mechanism (any **two**):

$$3 \times 2 = 6$$



b) i) Write down the structures of nylon-6 and nylon-6,6 and highlight their use.

ii) How would you convert D-glucose to D-arabinose? $3+3=6$

c) i) How would you synthesize the following peptide starting from L-amino acid?

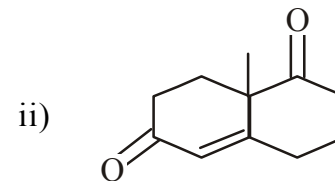
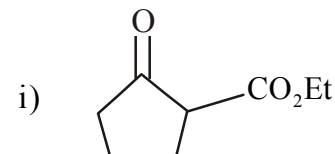
Ala-Val

ii) Why D-fructose give a positive Tollen's test? $4+2=6$

d) i) Why periodic oxidation of D-mannose is faster than that of D-glucose?

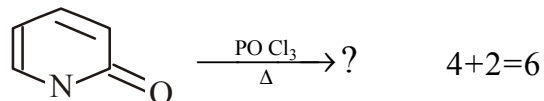
ii) The monobromination of thiophene-3-carboxylic acid gives only one product. What is its structure and why is it the only product formed? $2+(1+3)=6$

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



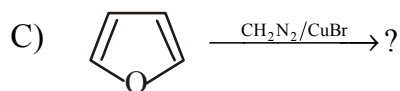
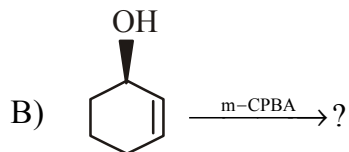
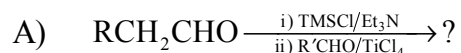
f) i) Account for the fact that position 3 of pyridine is the site for nitration and sulphonation, while positions 2 and 4 are sites for attack by sodium amide and alkyl lithium compounds.

- ii) Indicate the product of the following reaction with mechanism:



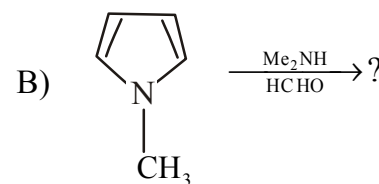
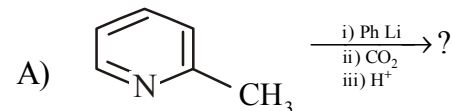
8. Answer any **one** question: 10×1=10

- a) i) Give the synthesis of congo red and mention its one use.
- ii) What is Merrifield resin? Outline the steps for the synthesis of the dipeptide gly-ala in the solid phase using this resin.
- iii) Indicate the product(s) in the following reactions (mechanism not required):



(2+1)+(1+3)+(1+1+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.

