

M.Sc. 2nd Semester Examination, 2010

CHEMISTRY

(Organic)

PAPER—CH-1202

Full Marks : 40

Time : 2 hours

Answer any **five** questions taking at least **two** from each Group where **Q. Nos. 6 or 7** are compulsory

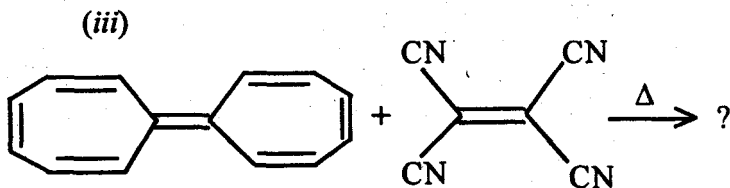
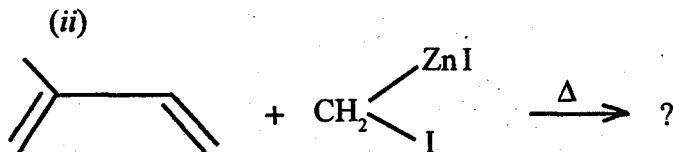
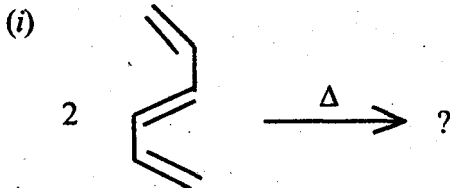
The figures in the right-hand margin indicate marks

Candidates are required to give their answers in their own words as far as practicable

GROUP—A

1. (a) Distinguish between site selectivity and periselectivity with specific example and explain. 2 + 2

(b) Predict the product/s of the following reactions with reason (attempt any two): 2 × 2

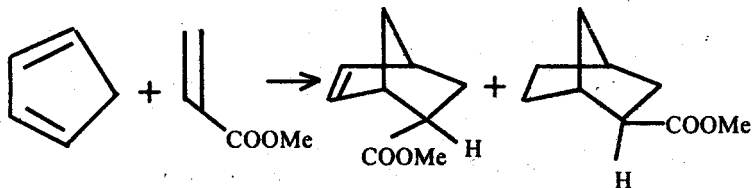


2. (a) What is Chelotropic reaction? Explain with an example. 2

(b) The following reaction gives different products ratios as shown below in different conditions.

Indicate the reason behind this :

2



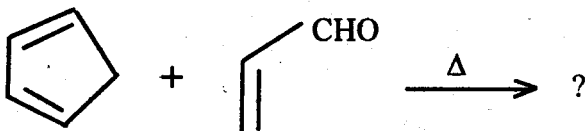
(i) At 0°C without catalyst : 88% 12%

(ii) 0°C / AlCl₃ : 96% 4%

(iii) -80°C / AlCl₃ : 98% 2%

(c) What is secondary interaction ? Explain what could be the effect of rate of the following reaction with Lewis acid and without Lewis acid ?

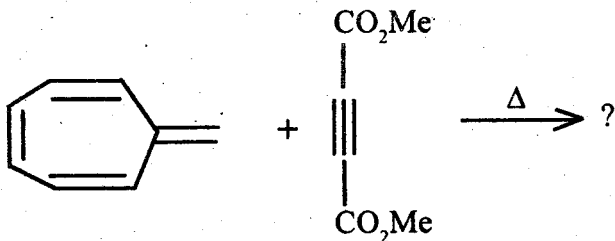
4



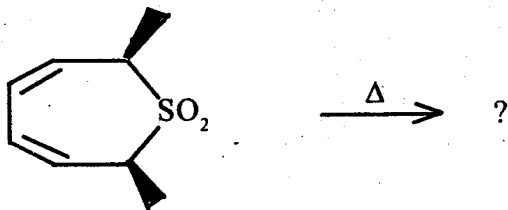
3. Predict the product/s of the following reactions indicating frontier orbital interaction (F.O.I) in each case (attempt any *four*):

2 x 4

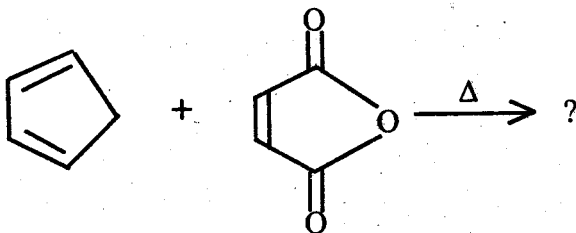
(i)



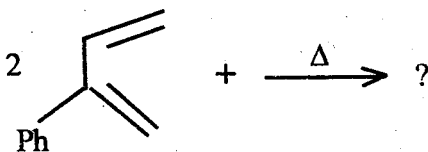
(ii)



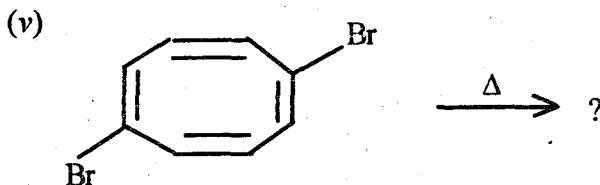
(iii)



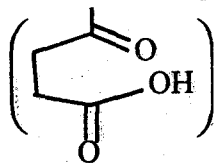
(iv)



(5)

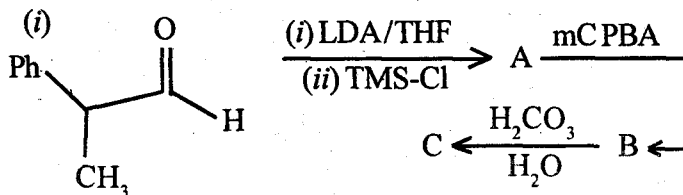


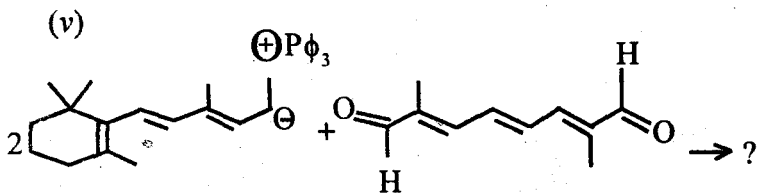
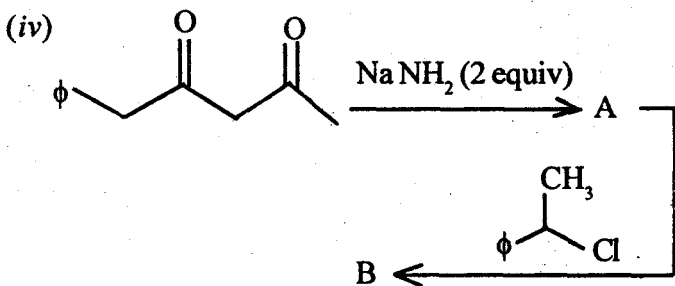
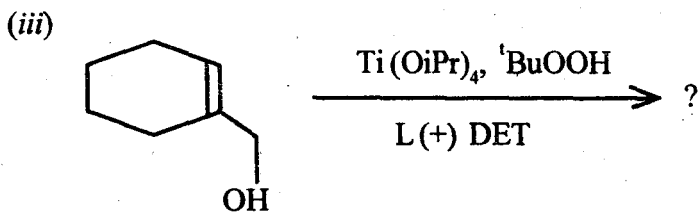
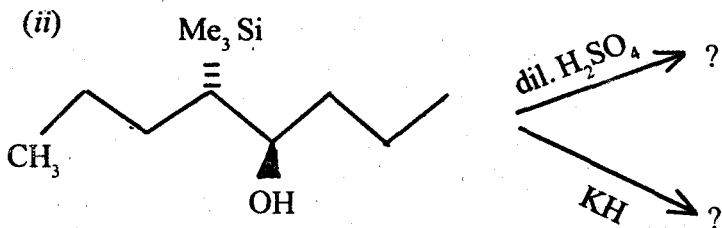
4. An acyclic monoterpene, molecular formula $C_{10}H_{18}O$ (A) on treating Ni/H_2 gives $C_{10}H_{22}O$ (B) and on acetylation yields monoacetyl derivative. On Vigorous $KMnO_4$ oxidation compound (A) yields Laevulinic Acid



and oxalic acid. Further compound (A) on treating with dil. H_2SO_4 yields geraniol through isomerisation reaction. Identify compound (A) and confirm its structure through synthesis. 6 + 2

5. Predict the products (any *four*, with Plausible mechanism): 8





GROUP – B

6. (a) Answer any two :

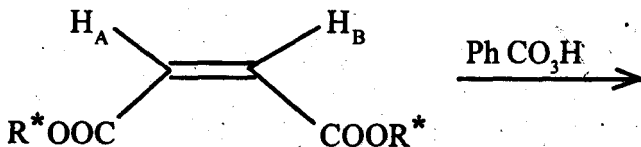
 $1\frac{1}{2} \times 2$

(i) Give an example of a molecule having diastereotopic faces and designate them. Explain by symmetry and addition criteria.

(ii) Write an achiral molecule having enantiotopic ligands and designate the ligands. Explain by symmetry and substitution criteria.

(iii) A center of a molecule may be prochiral but prostereogenic. Explain with an example.

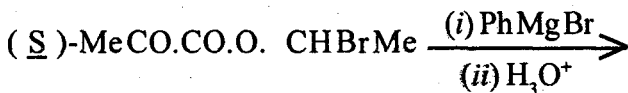
(b) Write down the product of the following reaction :



R^* is a chiral ligand

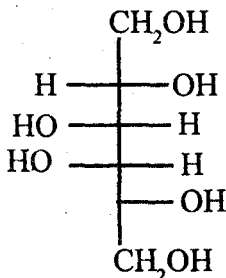
Comment on the ^1H NMR signals of H_A and H_B for both the starting material and the product/s explaining in terms of their topicity as revealed by their symmetry criteria. 2 $\frac{1}{2}$

(c) Explain the mechanism of the following reaction :



Assign the π -face undergoing predominant attack and the pref/parf nomenclature to the predominant product. 2 $\frac{1}{2}$

7. (a) Comment on the optical activity of galactitol (A). Explain the topicity of the CH_2OH groups by application of their symmetry and selective oxidation criteria. 3

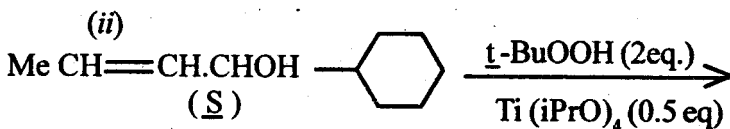


Galactitol (A)

- (b) Indicate the plausible mechanism of the following reactions and name the predominant product, if any. Attempt any *two* : $2\frac{1}{2} \times 2$

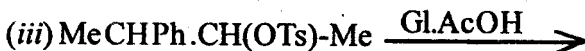


Apply Felkin model with justifications



(R), (R)-(+)-Diethyl tartarate

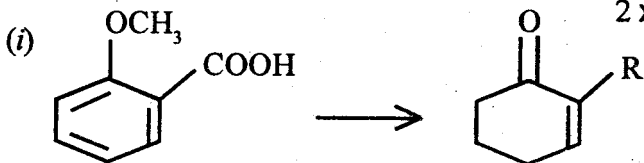
(Sharpless epoxidation)

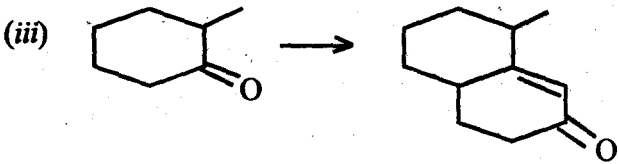
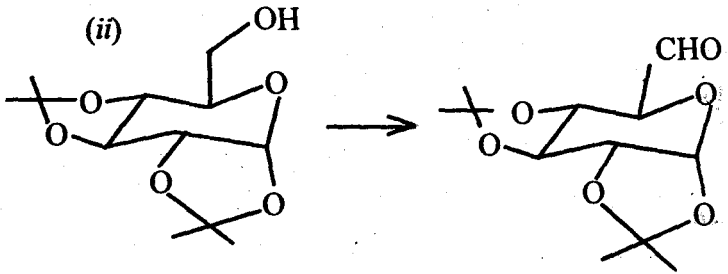


Active threo and active erythro isomers.

Comment on the optical activity of the product(s) in each case.

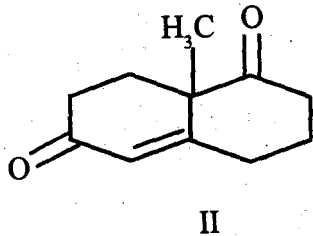
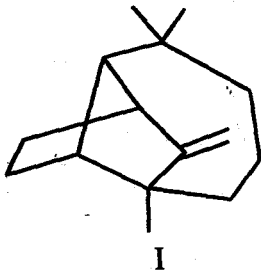
8. (a) Carry out the following transformations (any *two*) : 2×2





(b) Synthesize Longifolene (I) from Wieland Mischer 4

Ketone (II) :



9. Describe in detail the reactions involved in the determination of structure and stereochemistry of nicotine.

8

