

**M.Sc. 2nd Semester Examination, 2013**

**CHEMISTRY**

( *Organic* )

PAPER—CEM-202

*Full Marks : 40*

*Time : 2 hours*

**Answer any five questions taking at least two  
from each Group where Q. No. 6 or  
Q. No. 7 is compulsory**

*The figures in the right-hand margin indicate marks*

**GROUP – A**

1. (a) Define Diels-Alder reaction of 'Reverse electron demand' with a proper example, showing the energy diagram. 3

( *Turn Over* )

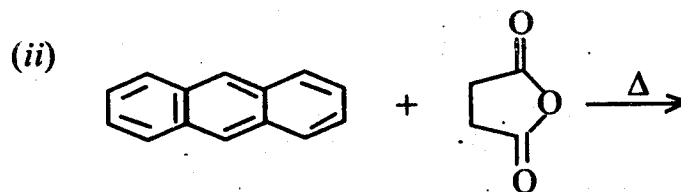
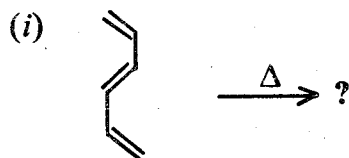
- (b) Predict the products of the following reaction under different conditions indicating Frontier-Orbital interactions; 5

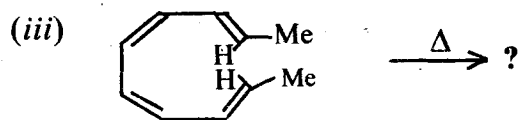


Without catalyst : 88% 12%

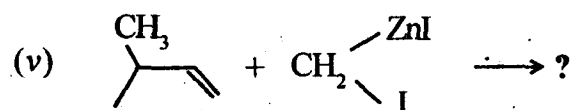
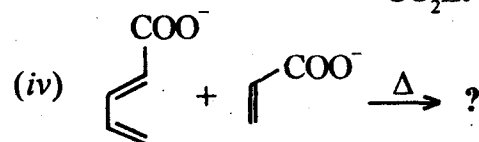
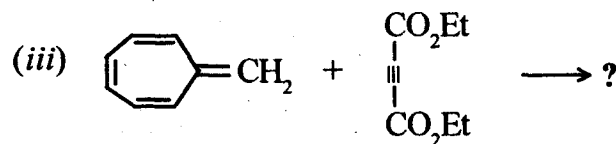
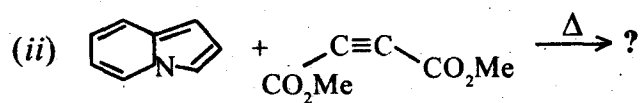
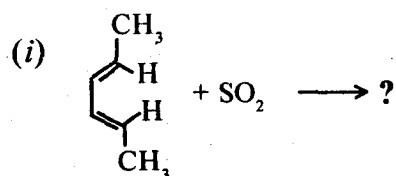
With catalyst : 96% 4%

2. Differentiate between 'Site Selectivity' and 'periselectivity' and hence predict the products of the following reactions specifying mode of reaction in each case, showing Frontier Orbital Interactions (F.O.I.); (attempt any two) 2+2+2×2

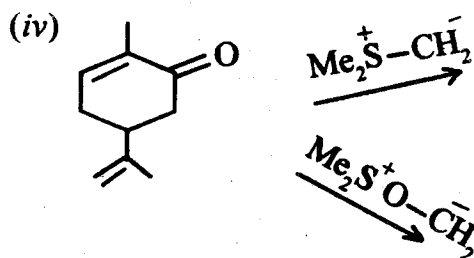
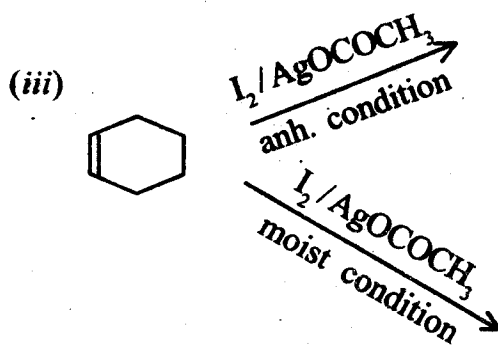
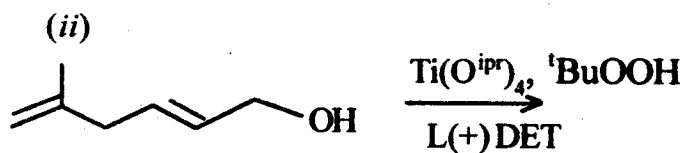
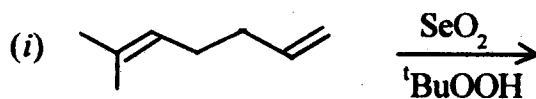




3. Predict the product/s of the following reactions indicating F.O.I. in each case : 4 × 2

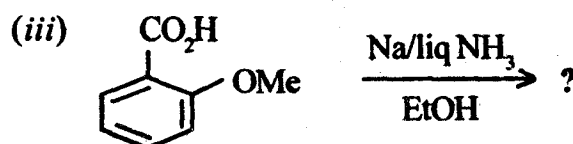
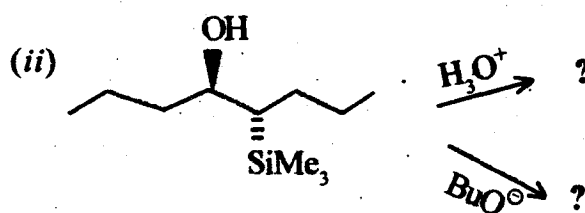
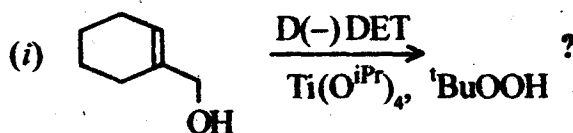


4. (a) Predict the product/s (any *three*) with plausible mechanism : 2 x 3



(b) What is 'Asymmetric-Dihydroxylation' mixture? Give an example of asymmetric transformation using 'Asymmetric Dihydroxylation' mixture. 2

5. (a) Predict the product/s with plausible mechanism: 2 x 2



(b) What are cheletropic reactions? Delineate HOMO & LUMO of a cheletropic species. Show linear and non-linear approach of a carbene towards ethylene for cyclo addition reaction. 4

## GROUP – B

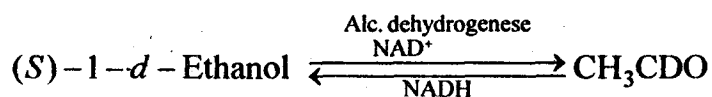
6. (a) Comment on the following statements (answer any two) : 3

(i) The two  $-\text{CHOHCO}_2\text{H}$  groups in *meso*-tartaric acid are enantiotopic to each other.

(ii) Compounds with point symmetry  $C_s$  and  $C_i$  cannot have a set of enantiotopic ligands exceeding two.

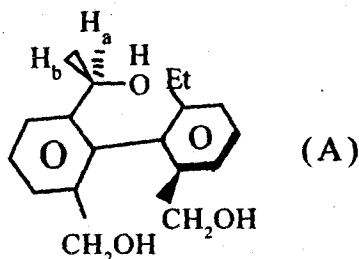
(iii) When a molecule possesses homotopic ligands it must have  $C_n$  ( $n > 2$ ).

(b) From the following observations determine whether *pro-R* or *pro-S* *H* is eliminated when undeuterated ethanol undergoes dehydrogenation in the presence of alcohol dehydrogenase to yield acetaldehyde : 2



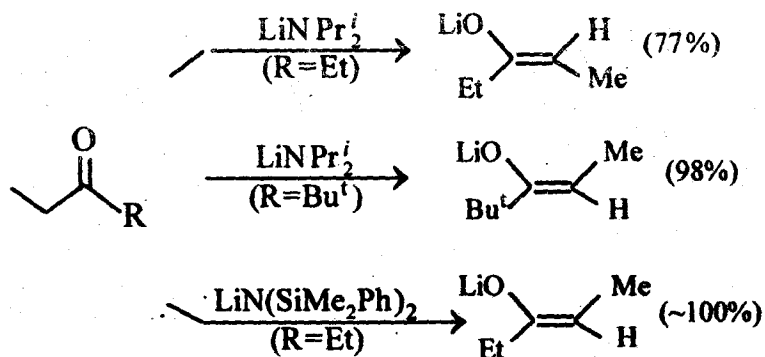
- (c) Comment on the chirality of the molecule (A) and the topic relationship between  $H_a$  and  $H_b$ . Now comment on the expected multiplicity of the  $^1\text{H-NMR}$  signal of  $H_a$  and  $H_b$ .

1 + 2

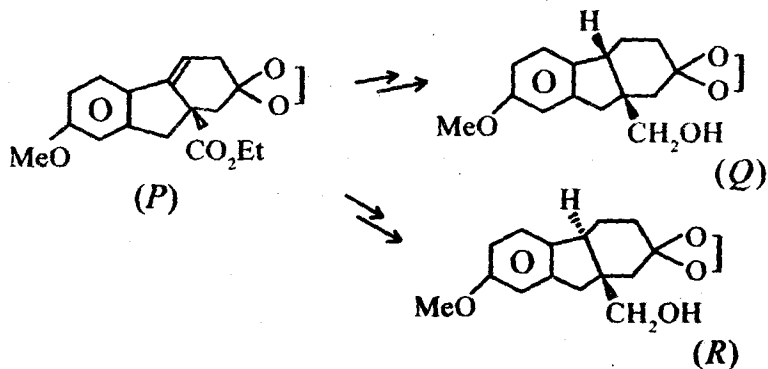


7. Attempt any *two* of the following : 4 × 2

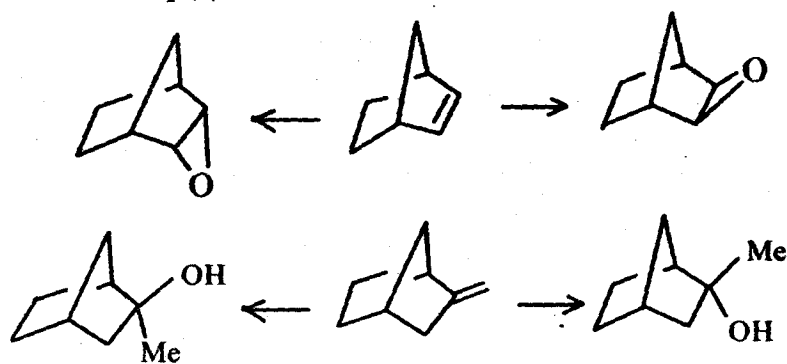
- (a) Explain the stereoselective formation of (*E*)-/(*Z*)-enolates in the following reactions :



(b) What is a haptophilic group ? How do you obtain stereoselectively (*Q*) and (*R*) from (*P*) ? Explain your answer.

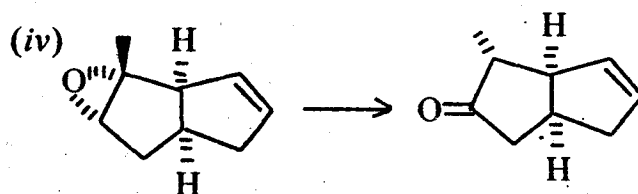
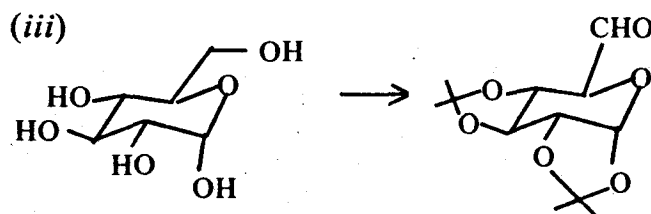
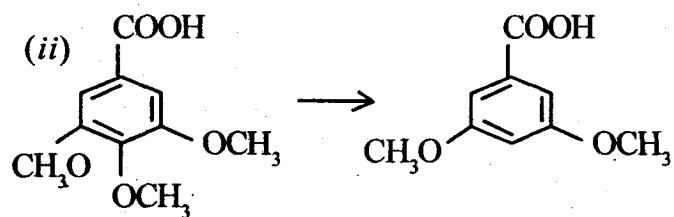
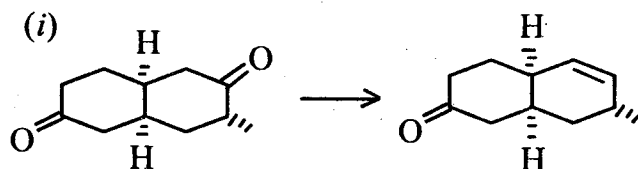


(c) How do you achieve the following stereoselective synthesis is one or more step(s) ?

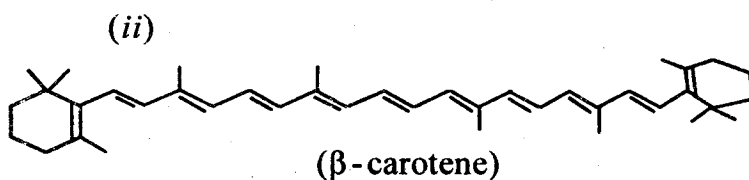
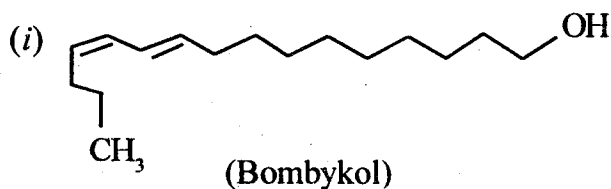




8. (a) Carry out the following transformations (any three) with plausible mechanism:  $2 \times 3$

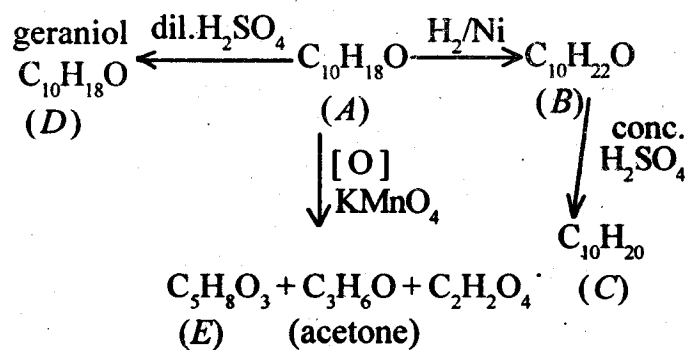


(b) Synthesize any *one* of the following from easily available starting material : 2



9. (a) State the isoprene rule and explain with an example.

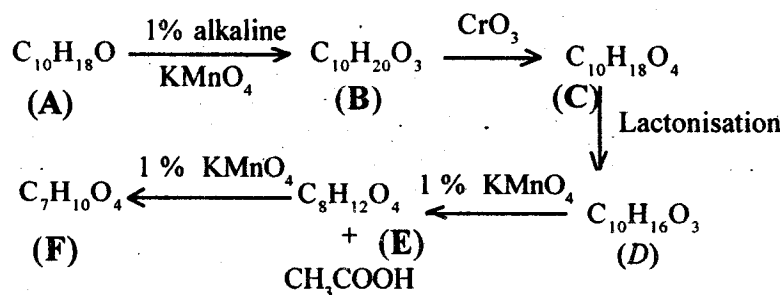
(b) The following monoterpene penoid (A) undergoes the following transformations :



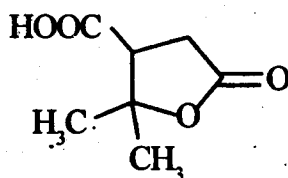
Identify (B), (C), (D) and (E) and from the results elucidate the structure of (A) and confirm the structure of (A) from its synthesis. 2 + 6

Or

10. The following compound 'A' undergoes the oxidative degradation reaction as follows :



Compound (F) was identified as terebic acid with the structure,



Draw backwards and write the structures of the intermediate products **B**, **C**, **D**, **E** and identify the structure of **A** and confirm the structure through its synthesis.

8

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