M.Sc. 2nd Semester Examination, 2012

CHEMISTRY

(*Organic*)

PAPER– CEM-202

Full Marks : 40

Time : 2 hours

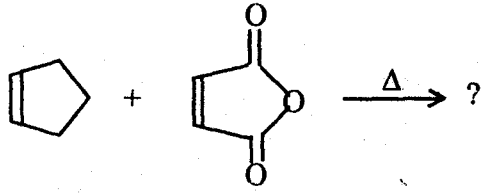
Answer any **five** questions taking at least **two** questions from each Group where **Q. No. 6** or **Q. No. 7** is compulsory

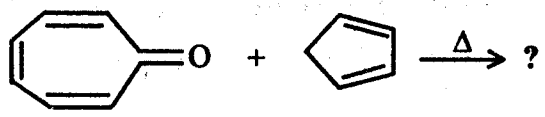
The figures in the right-hand margin indicate marks

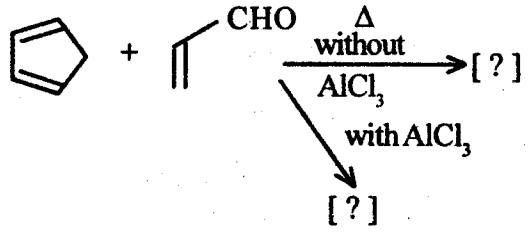
GROUP – A

1. What is 'Secondary interactions' in pericyclic reactions and hence predict the products of the following reactions indicating frontier orbital interactions (attempt any *two*) : $2 + 2 \times 3$

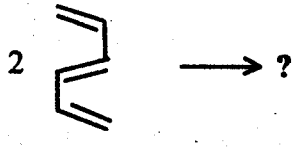
(*i*)



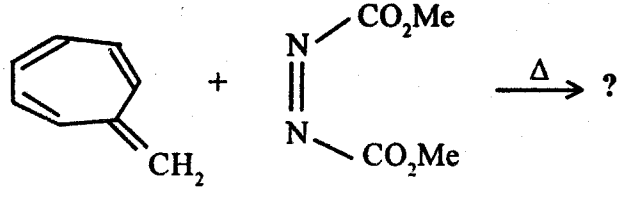
(*ii*) 

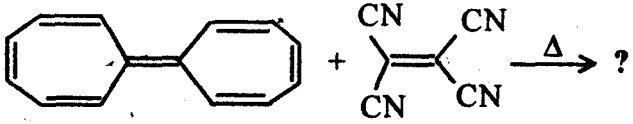
(*iii*) 

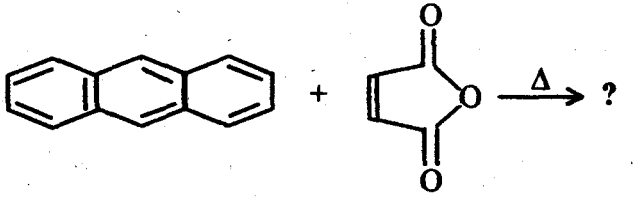
2. Predict the product/s of the following reactions indicating frontier orbital interactions with proper explanation (attempt any *four*) : 2 × 4

(*i*) 

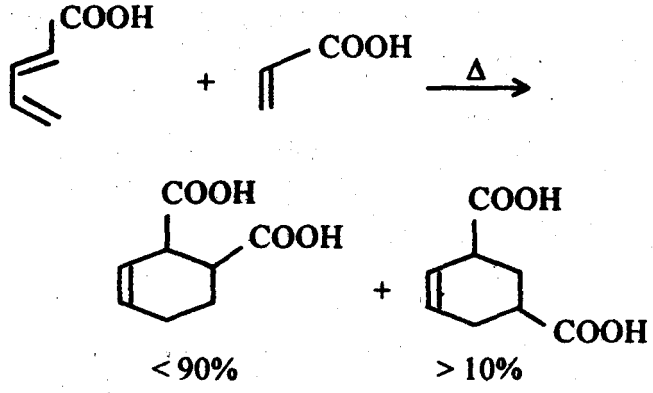
(*ii*) 

(*iii*) 

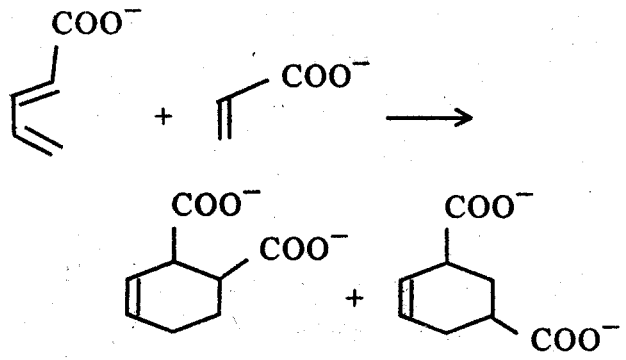
(*iv*) 

(*v*) 

3. **The following set of reaction give the product ratios as follows :** **4 + 4**

(*i*) 

(*ii*)

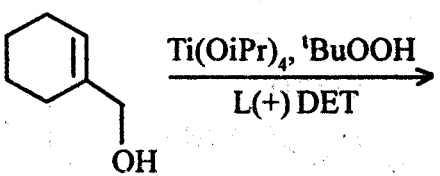


(1 : 1)

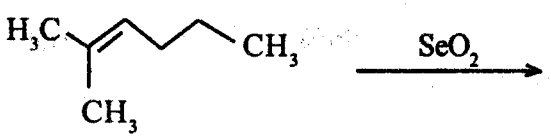
Explain the formation of the products in each case with proper reasoning.

4. Predict the product(s) (*any four*, with plausible mechanism) : 2 × 4

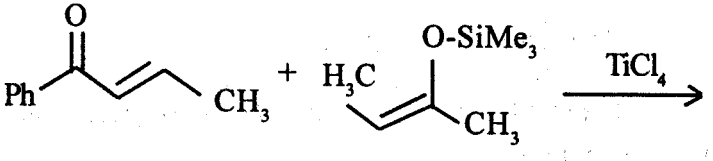
(*i*)



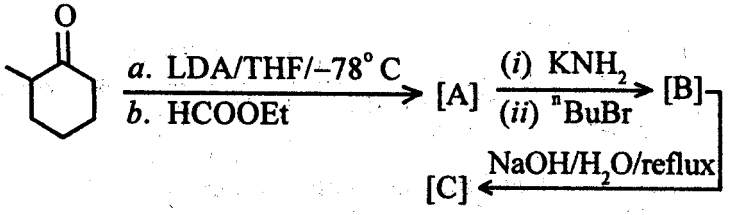
(*ii*)



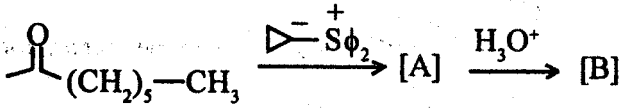
(*iii*)



(*iv*)



(*v*)



5. Answer (*a*) or (*b*), and (*c*) :

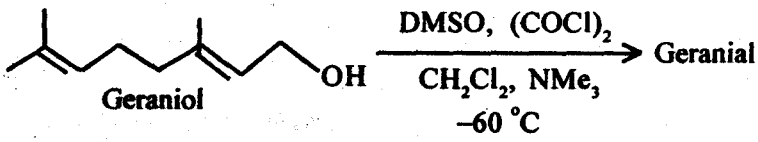
(*a*) Show the biogenetic relationship of geranyl pyrophosphate with neryl pyrophosphate, linalyl pyrophosphate, camphor, α-pinene and β-pinene. 4

(*b*) Explain the biosynthesis of geranyl pyrophosphate (GPP) from one molecule of isopentenyl pyrophos-

phate (IPP) and one molecule of *r*, *r*-dimethylallyl pyrophosphate (DMAPP) from kinetic and mechanistic view points. 4

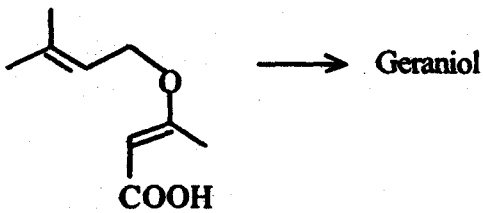
(*c*) Explain mechanistically the following conversions. Attempt any *two* : 2 × 2

(*i*)

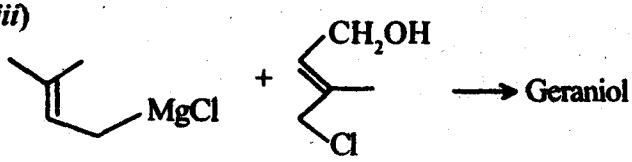


Name the oxidation reaction

(*ii*)



(*iii*)



GROUP – B

6. (*a*) Answer any *two* : $1\frac{1}{2} \times 2$

(*i*) A center of a molecule may be prostereogenic but not prochiral. Explain with an example.

(*ii*) Write a Fischer projection formula of an active isomer of 2, 4-dihydroxypentane. Explain why C3 is a prochirotopic but not a prostereogenic center, by substitution criterion and hence designate the hydrogen atoms at C3.

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

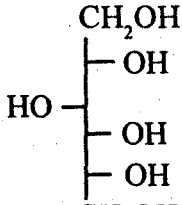
(*b*) Explain the mechanism of the following reaction and name the predominant product, if any :

$$(S)\text{-MeCOC(OH)MePh} \xrightarrow{\text{PhMgBr}}$$

Apply Cram's chelate model. Indicate the product that will be predominant if Cram's open chain model is applied. 3

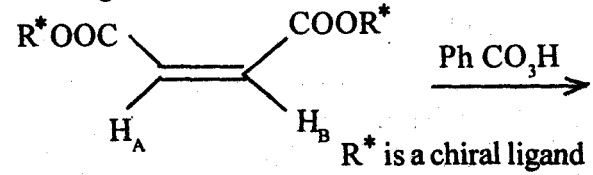
(*c*) Comment on the optical activity and topicity of the CH_2OH groups of the following compounds

(A), named glucitol, by application of symmetry and selective oxidation criteria. 2



(A)

7. (*a*) Write down the product or products of the following reaction 3



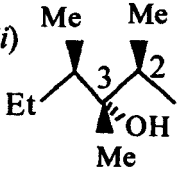
Comment on the ^1H NMR signals of H_A and H_B of both the starting material and the product/s. Explain in terms of their topicity as revealed by the symmetry criteria.

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

(*i*) (*S*)-*t*-BuCHMeOCOCOPh $\xrightarrow[H_3O^{\oplus}]{EtLi}$

(*ii*) 1-*p*-Anisyl-1-Phenyl-2-aminopropanol $\xrightarrow[HCl]{NaNO_2/}$

Parf diastereomer

(*iii*) 

$\xrightarrow{HNO_2}$ NH_2 (May use Newman projection formula looking through C2—C3 bond.)

Designate the absolute configuration of the chiral centers of the starting material and the product and name them.

(*iv*)

trans-2-Acetoxycyclohexyl tosylate $\xrightarrow{\text{gl. AcOH}}$ (any enantiomer)

$\xrightarrow[\text{+ small amount of water}]{\text{gl. AcOH}}$

8. (*a*) Outline the biosynthesis of the pyrrolidine ring of nicotine from (*S*)-L-ornithine, and show that it routes through a symmetrical intermediate. 4

(*b*) Explain the biosynthesis of ephedrine and ψ-ephedrine. 4

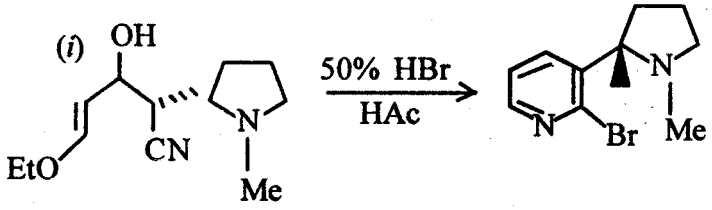
9. (*a*) Explain the following statements in terms of their conformations :

(*i*) ψ-Ephedrine and ephedrine are having *threo* and *erythro* configurations respectively. 2

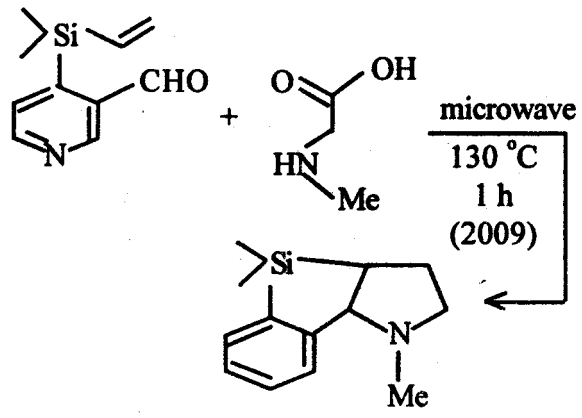
(*ii*) ψ-Ephedrine is more basic than ephedrine. 2

(*b*) Answer the following with plausible mechanism. Attempt any *one* : 2

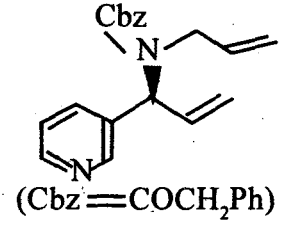
(*i*)



(*ii*)

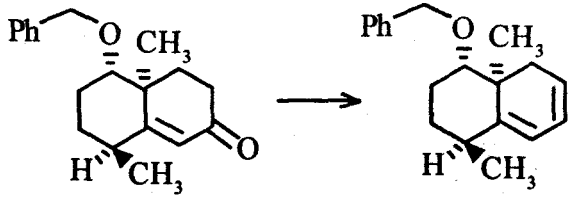


(*c*) Write down the product of the following reaction with plausible mechanism : 2

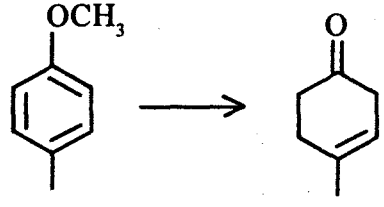


10. (*a*) Carry out the following transformations (any *two*, with plausible mechanism) : 2 × 2

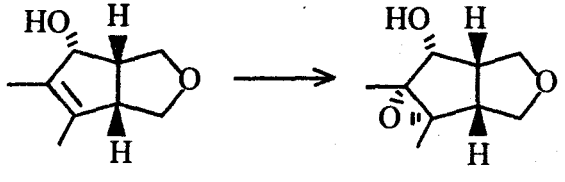
(*i*)



(*ii*)

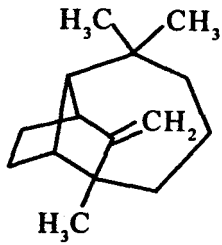


(*iii*)



(*b*) Synthesize the following from easily available starting materials (any *one*) : 4

(*i*)



(*ii*)