M.Sc. 1st Semester Examination, 2012

CHEMISTRY

(*Organic*)

PAPER—CEM-102

Full Marks : 40

Time : 2 hours

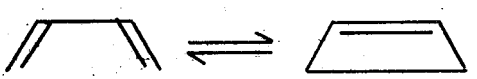
Answer any **five** questions taking at least **two** from each Group where **Q. No. 6** is compulsory

The figures in the right-hand margin indicate marks

Write the answers to questions of each Group in separate books

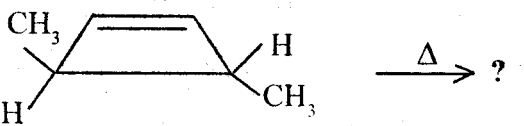
GROUP – A

1. (*a*) Draw the correlation diagram for the following interconversion under thermal condition; 4



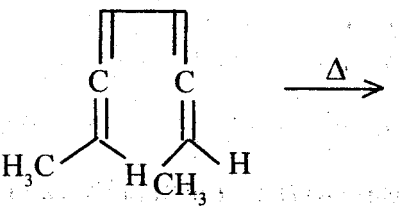
and indicate the symmetry allowed path for the reaction.

(*b*) Explain the path way of the following ring opening reaction and indicate the observed product: 4

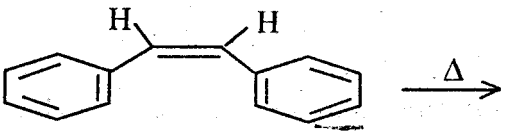


2. (*a*) Predict the product of the following reactions indicating Frontier-Orbital interactions (F.O.I) (Attempt any *two*) : 2 × 2

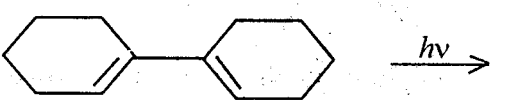
(*i*)



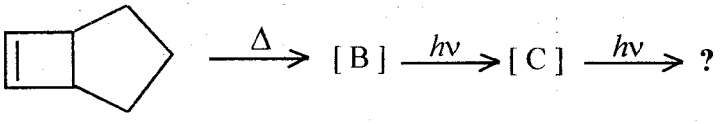
(*ii*)



(*iii*)



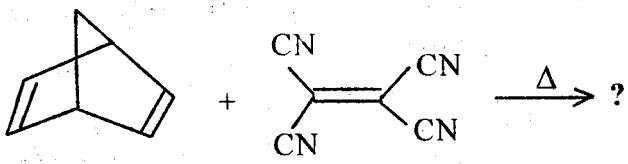
(*b*) Predict the product/s of the following reaction sequence indicating F.O.I. State and explain whether Woodward-Hofmann rule and principle of microscopic reversibility is maintained : 4



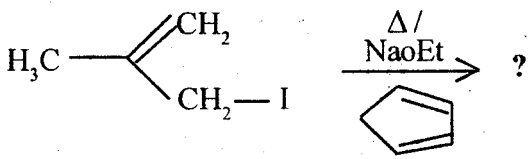
(A)

3. Write the selection rules for cycloaddition reactions and hence predict the products of the following reactions indicating F.O.I. (attempt any *three*) : 2 + 3 × 2

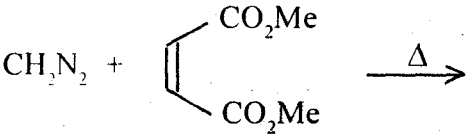
(*i*)



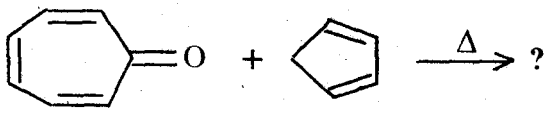
(*ii*)



(*iii*)



(*iv*)

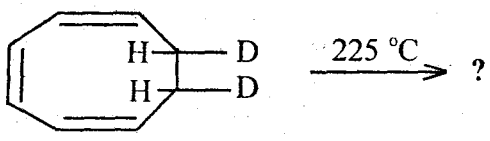


4. (*a*) What is [*i*, *j*] sigmatropic shift. Explain with example.

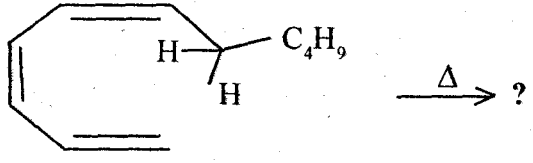
(*b*) "1, 3 - H migration is difficult to occur but 1, 3 - C migration occurs with inversion of configuration under thermal condition" – Explain.

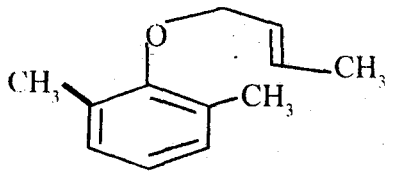
(*c*) Predict the product/s of the following with F.O.I. (any *two*) :

(*i*)

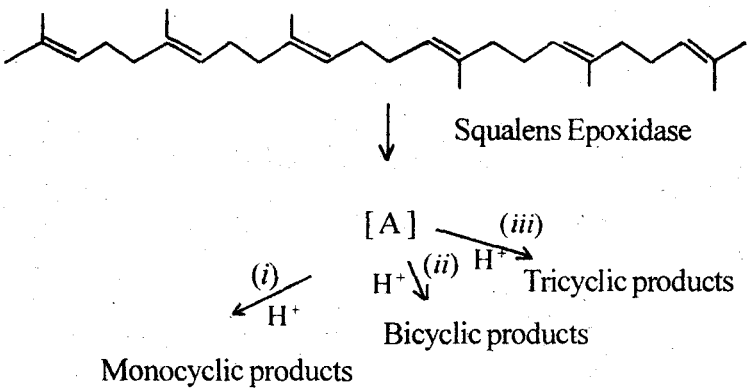


(*ii*)



(*iii*) 

5. Write the structure of [A] and predict the products :



1 + 2 + 2 + 3

GROUP – B

6. (*a*) Write the structures of the following (attempt any *four*) : 4

(*i*) 2R, 4R-2, 3, 4-Tribromopentane (in Fischer projection)

(*ii*) Meso-trans-2, 5-dichlorohex-3E-ene (in flying wedge formula)

(*iii*) (S)-Cyclooctene

(*iv*) (R)-4-Phenylcyclohexylidene acetic acid

(*v*) $PhCOCHBrCHPhCO_2H$ (one *parf* isomer in Newman projection formula)

(*b*) Answer *true* or *false*. Cite an example or explain in support of your answer (attempt any *four*) : 4

(*i*) A stereogenic center may be a non-material point.

(*ii*) All optically inactive stereoisomers are meso-isomers.

(*iii*) Any homofacial change preserves the configuration of a stereocenter and the stereodescriptor (*R*/*S*) of the latter remains unchanged.

(*iv*) An S_4 axis is always a C_2 axis though the reverse is not true.

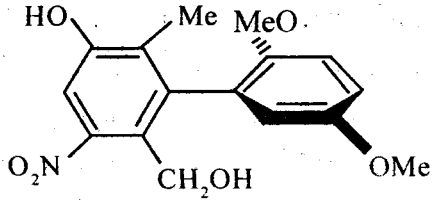
(*v*) Each and every point within an achiral molecule, material or non-material, is achirotopic.

(*vi*) An achiral molecule must not have any chiral conformation.

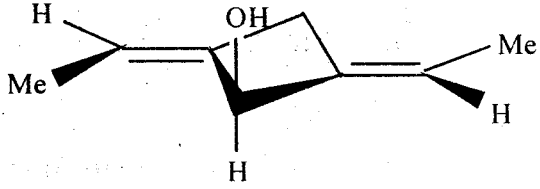
Or

(*a*) Answer any *two* of the following : 2 × 2

(*i*) Designate the absolute configuration of the following molecules as directed :



(in *aR*/*aS*)



(stereocenter in R_n / S_n)

(*ii*) Dipole moment of 1, 2-dichloroethane increases with rise in temperature but that of ethane-1, 2-diol decreases in such a change. Explain the observations.

(*iii*) IR spectrum of a synthetic sample of 2-chlorobutane shows three signals for C—Cl bond, but polarimeter records two different rotations (of course after resolution) for the compound. Explain the facts.

(*b*) How many isomers for each of the following structures are possible ? Draw all of these and comment on the asymmetry, Chirotopicity and stereogenicity of the 'central' carbon. Give configurational notation to this center in *R/S* or *r/s* as appropriate.

(*i*) CHA^RA^SCl

(*ii*) CHA^RA^SB

[A^R and A^S are two enantiomorphic groups; B = — CHClMe and is different from A]. 4

7. (*a*) Answer any *two* of the following : 2 × 2

(*i*) Explain the terms with an example; (*I*) pseudorotation, and (*II*) topomerisation.

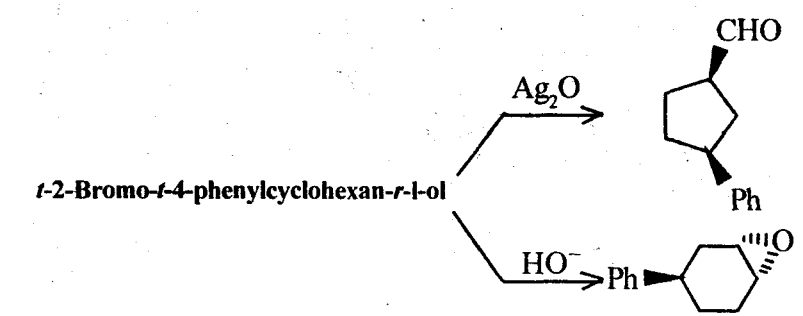
(*ii*) What is 'buttressing effect' ? Illustrate with an example.

(*iii*) Write sterostructure of a molecule each belonging to point symmetry (*a*) C_s and (*b*) C_3

(*b*) Attempt any *two* of the following : 2 × 2

(*i*) An enantiopure sample of *cis* and *trans* -isomers of 2-acetoxycyclohexyl tosylates are subjected to acetolysis separately. Compare the results.

(*ii*) Explain the reactions with mechanism :

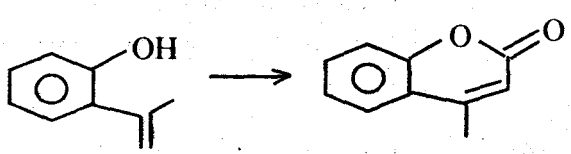


(*iii*) Give the product and explain the result :

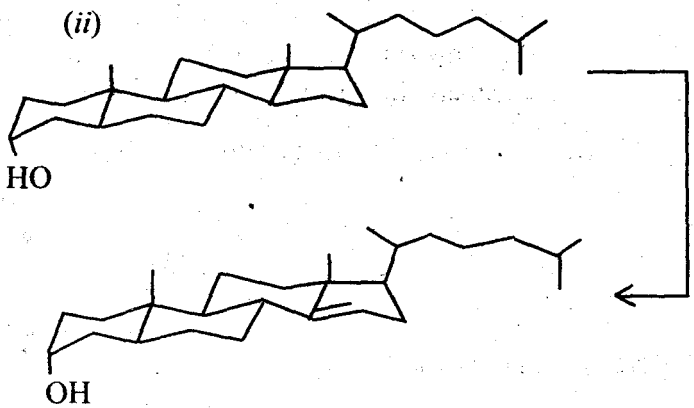
Erythro-2, 3, 4-Triphenylbutanoic acid $\xrightarrow{HF}$?

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

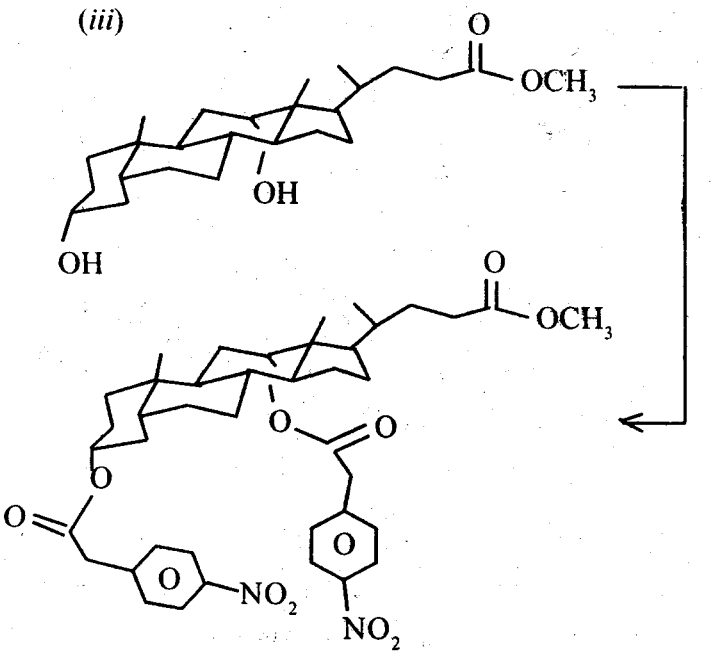
(*i*)



(*ii*)

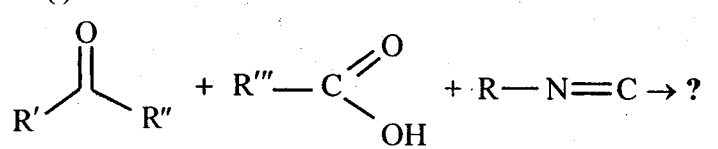


(*iii*)

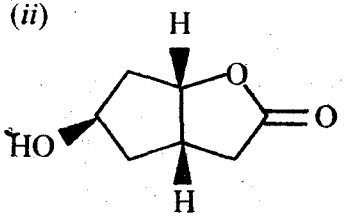


(*b*) Predict the products with plausible mechanism (any *two*) : 2 × 2

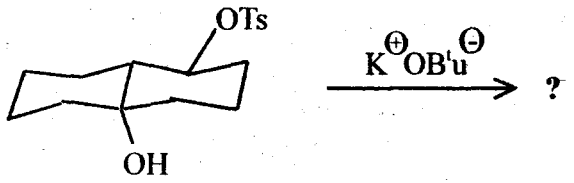
(*i*)



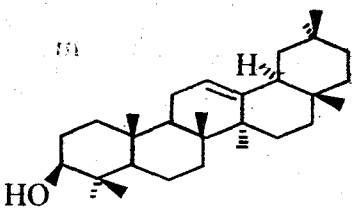
(*ii*)



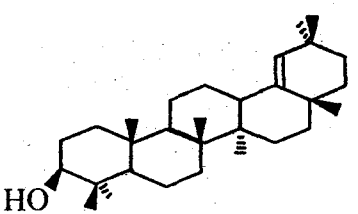
(*iii*)



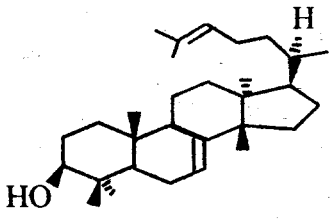
9. Synthesize β amyrin (*a*), germanicol (*b*), butyrospermeol (*c*), baccharis oxide (*d*), lupeol (*e*) (any *four*) with plausible mechanism : 2 × 4



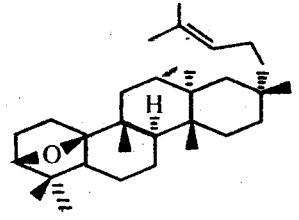
(*a*)



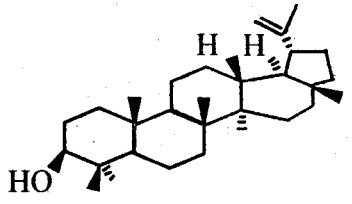
(*b*)



(*c*)



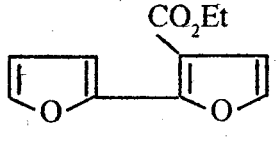
(*d*)



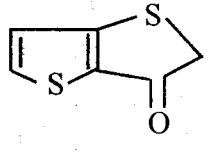
(*e*)

10. (*a*) Outline the synthesis of any *two* of the following compounds from readily available materials : 2 × 2

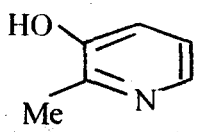
(*i*)



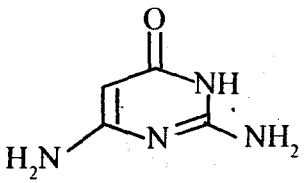
(*ii*)



(*iii*)

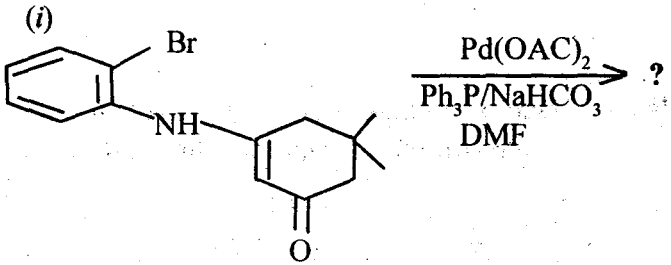


(*iv*)

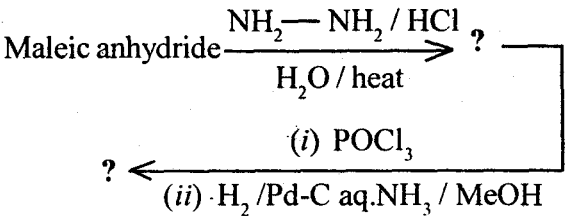


(*b*) Predict the product(s) of the following (any *one*) : 2

(*i*)



(*ii*)



(*c*) Explain the following observations : 2