PG/IIS/CEM-202/15

M.Sc. 2nd Semester Examination, 2015

CHEMISTRY

(*Organic*)

PAPER – CEM - 202

Full Marks : 40

Time : 2 hours

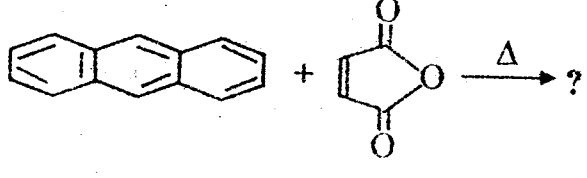
Answer any **five** questions taking at least **two** from each Group where **Q. No.8** or **Q. No. 9** is compulsory

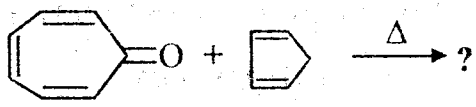
The figures in the right-hand margin indicate marks

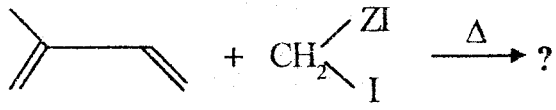
GROUP–A

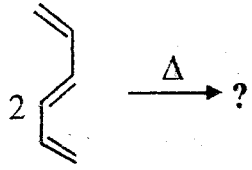
1. Distinguish between 'Site selectivity' and 'periselectivity' and hence predict the product/s of the following reactions indicating the kind of 'selectivity' occuring in each case (Attempt any *three*) : $2 + (2 \times 3)$

(*i*)



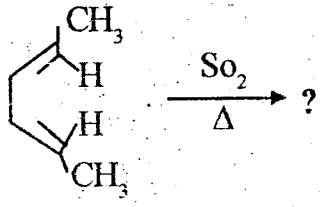
(*ii*) 

(*iii*) 

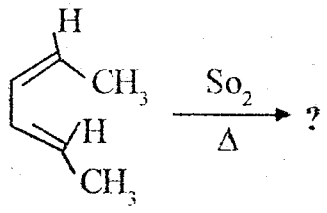
(*iv*) 

2. (*a*) What is chelotropic reaction ? Show the mechanistic path of insertion of Carbene to olefin. Indicate the Frontier orbitals taking part during insertion. 4

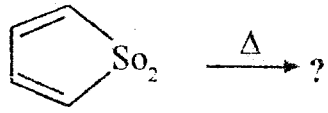
(*b*) Predict the product/s of the reaction indicating frontier orbital interaction (F.O.I) in each case (attempt any *two*) : 2 × 2

(*i*) 

(*ii*)

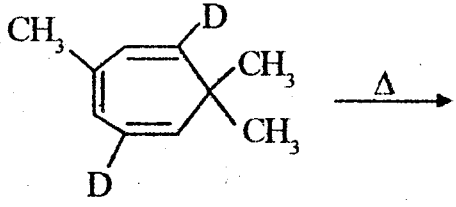


(*iii*)

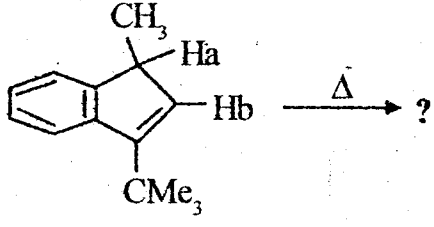


3. (*a*) Predict the product/s of the following reaction indicating F.O.I (attempt any *two*) : 2 × 2

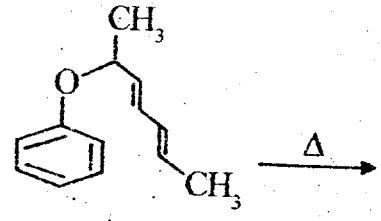
(*i*)



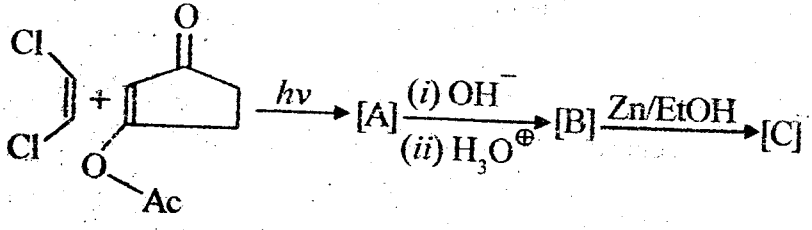
(*ii*)



(*iii*)



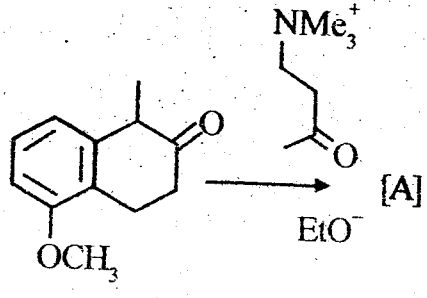
(*b*) Complete the following transformation : 4



Indentify A, B and C.

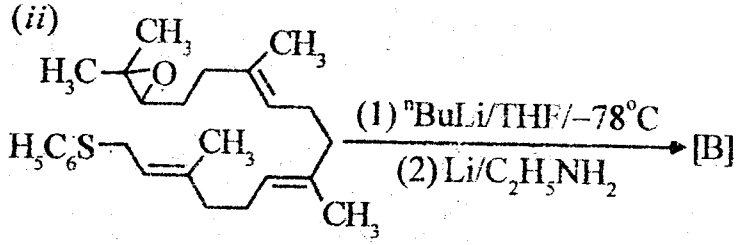
4. **Predict the products (any *four* with plausible mechanism) :** 2 × 4

(*i*)

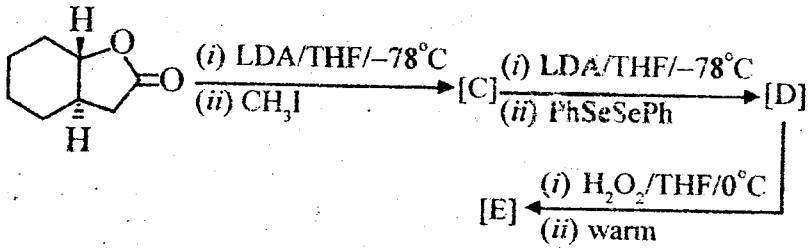


(*Continued*)

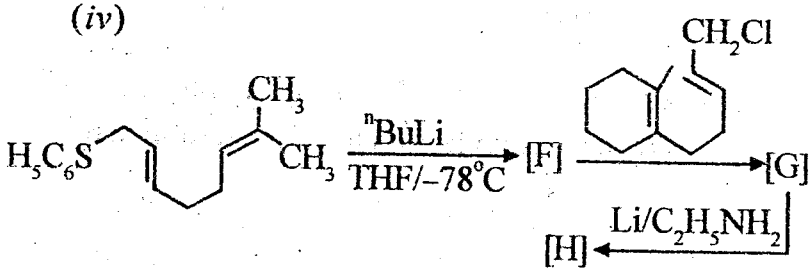
(*ii*)


CH3
H3C
O
CH3
H5C6S
CH3
CH3
(1) nBuLi/THF/–78°C
(2) Li/C2H5NH2
[B]

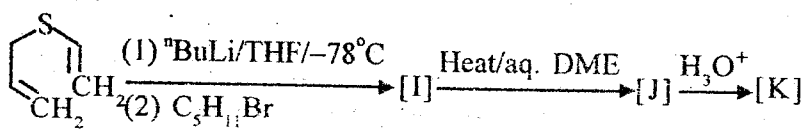
(*iii*)


H
O
O
H
(i) LDA/THF/–78°C
(ii) CH3I
[C]
(i) LDA/THF/–78°C
(ii) PhSeSePh
[D]
(i) H2O2/THF/0°C
(ii) warm
[E]

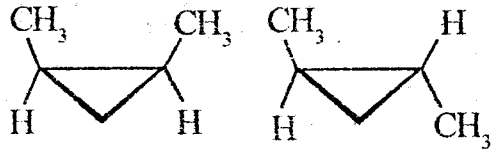
(*iv*)


CH3
H5C6S
CH3
nBuLi
THF/–78°C
[F]
CH2Cl
[G]
Li/C2H5NH2
[H]

(*v*)

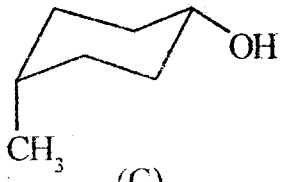

S
CH
CH2
(1) nBuLi/THF/–78°C
(2) C5H11Br
[I]
Heat/aq. DME
[J]
H3O+
[K]

5. (*a*) Which of the following molecules is chiral ? What is the relationship between (A) and (B) and (D) and (E) ? 4

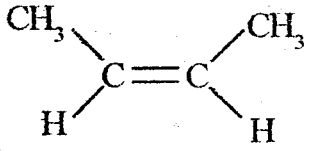


(A)

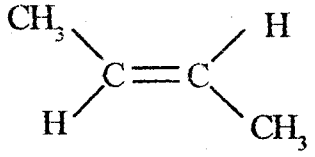
(B)



(C)

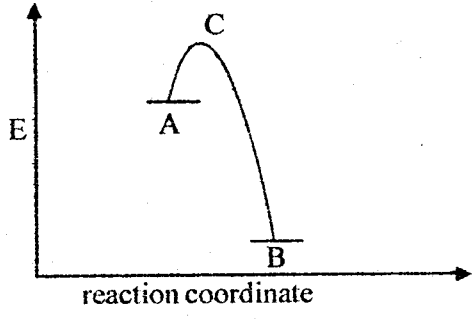


(D)



(E)

(*b*) According to the following energy profile, the rate of reaction from A to B is determined by ? 2



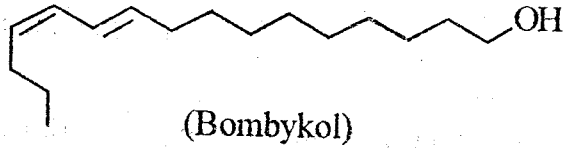
(*Continued*)

(*c*) Draw Fisher projections for (2R, 3S)-2-bromo -3-chlorobutane and (2S, 3R)-2-bromo-3 -chlorobutane. 2

GROUP – B

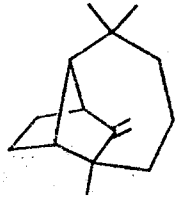
6. (*a*) Synthesize the following from easily available starting material (any *one*) : 4

(*i*)



(Bombykol)

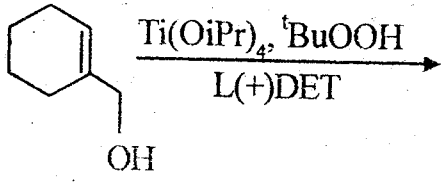
(*ii*)



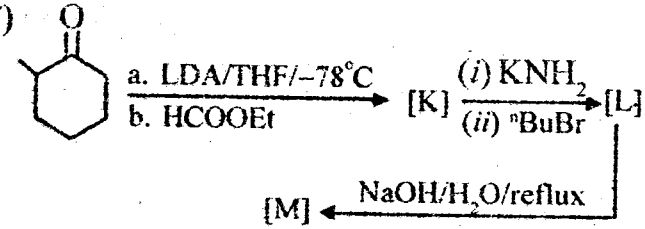
(Longifolene)

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

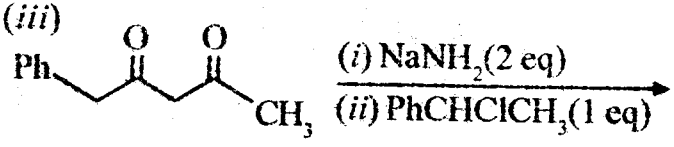
(*i*)



(*ii*)

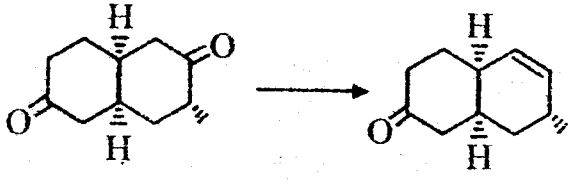


(*iii*)

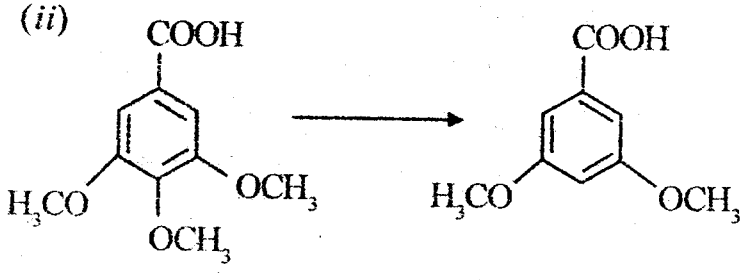


7. Carry out the following transformation (any *four*) with plausible mechanism : 2 × 4

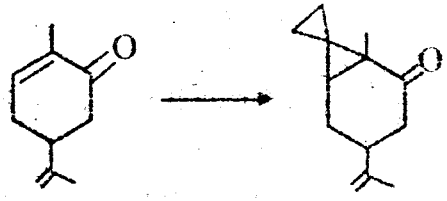
(*i*)



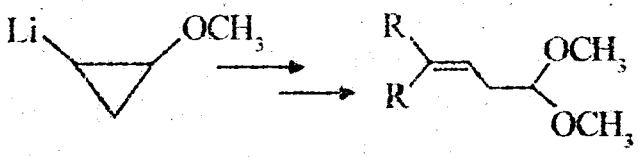
(*ii*)



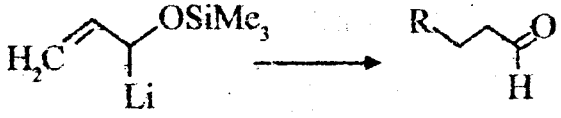
(*iii*)



(*iv*)



(*v*)



8. (*a*) How many chiral centers are there in 9, 10-dimethyl decalins ? Write 3d structures of those conformers and show in them the *gauche-butane* interactions, and comment on their chiralities. 4

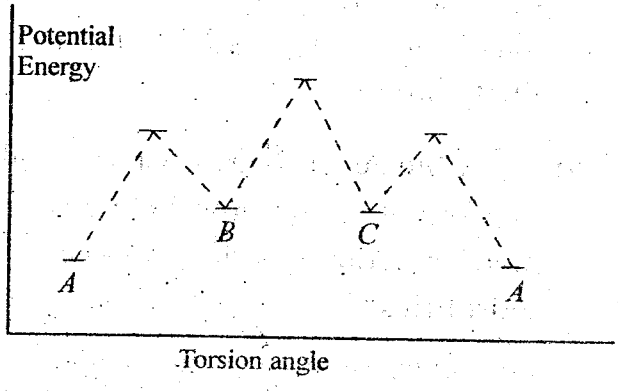
(*b*) Draw the 3d structures for the following conformers and show in them different steric interactions and comment on their chiralities: 4

(*i*) *cis*-transoid-*cis* perhydroanthracene.

(*ii*) *trans*-cisoid-*cis* perhydrophenanthrene.

9. (*a*) The observed rotation of a 0·3 g of cholesterol in 15 ml of $CHCl_3$ contained in 10 cm long polarimeter tube is $-0{\cdot}78^{\circ}$. Calculate specific rotation of cholesterol. When (+)-cholesterol was mixed to the above (−)-cholesterol, the mixture had a specific rotation of -13°. What is the fraction of the (+)-cholesterol ? 4

(*b*) The following is the energy profile drawing of 1,1-dibromo-2-methylpropane, draw the appropriate Newman conformations of A, B and C. 4



10. Discuss in brief with one example in each case (attempt any *four*) : 2×4

(*a*) 2-alkylketone effect

(*b*) 3-alkylketone effect

(*c*) Allylic 1, 3 strain

(*d*) Cieplak Model

(*e*) Cram's model.
