

M.Sc 1st Semester Examination, 2009

CHEMISTRY

PAPER—CH-1102

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

**Write the answers questions of each Group
in separate books**

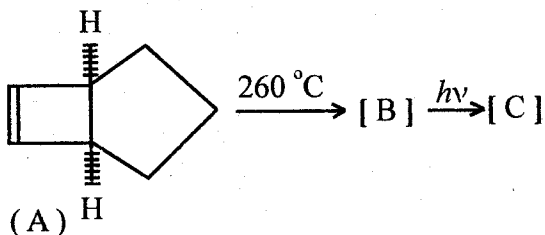
(Organic)

GROUP—A

1. (a) Write Woodward-Hoffmann Rules for electrocyclic ring closure reaction. 2

(Turn Over)

- (b) Define principle of 'microscopic reversibility'? Predict the product of the following reaction sequence,

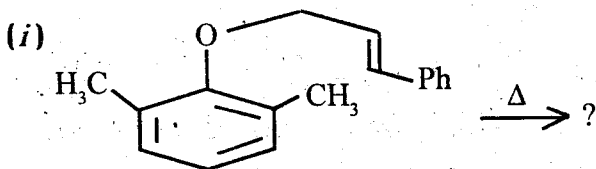


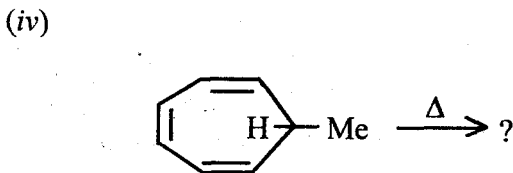
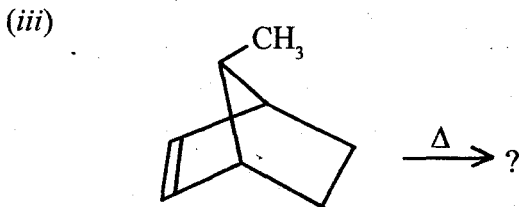
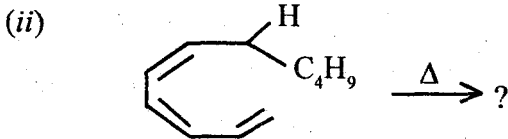
Identify 'B' and 'C' and indicate whether 'principle of microscopic reversibility' as well as Woodward-Hoffmann Rule of the reaction sequence is obeyed or not.

6

2. (a) What is meant by sigmatropic shift of (*i*, *g*) order? Define supra and antarafacial process in sigmatropic reaction and hence predict the product of the following reactions with F.O.I. (attempt any two) :

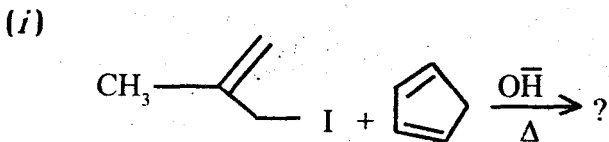
$$2 + \left(1\frac{1}{2} \times 2\right)$$



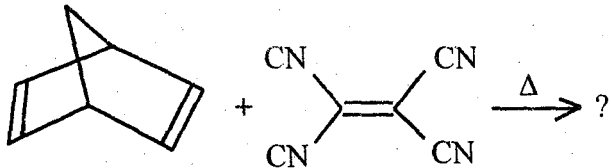


(b) Predict the product of the following reaction indicating frontier orbital interaction in each case ; (attempt any two) :

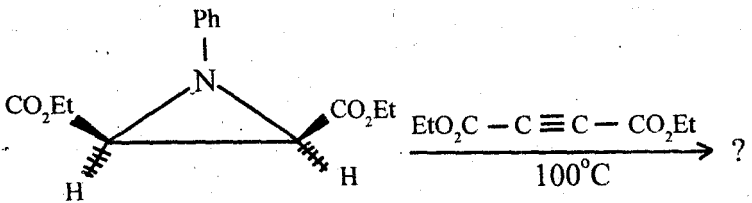
$1\frac{1}{2} \times 2$



(ii)



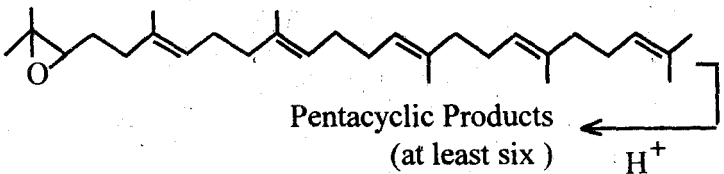
(iii)



Or

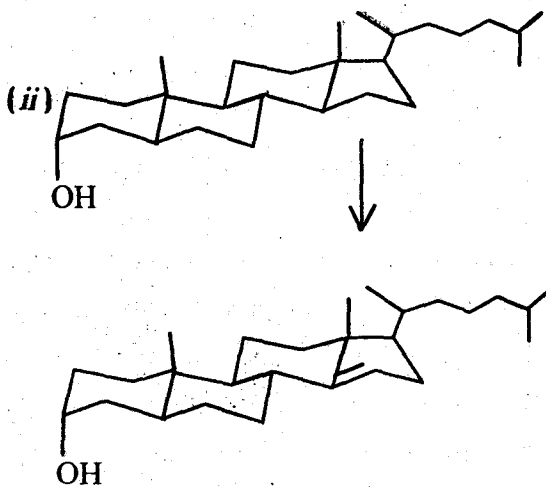
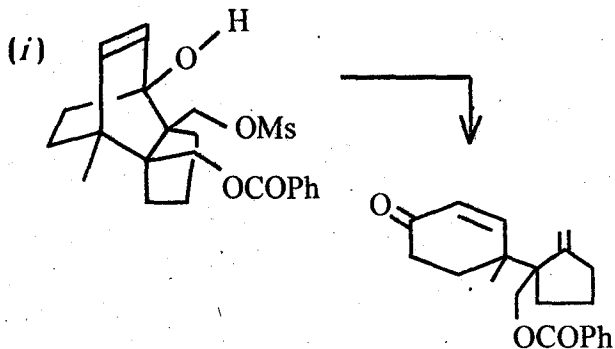
(b) What is the necessary condition for nuclear magnetic resonance? How is this condition maintained? 3

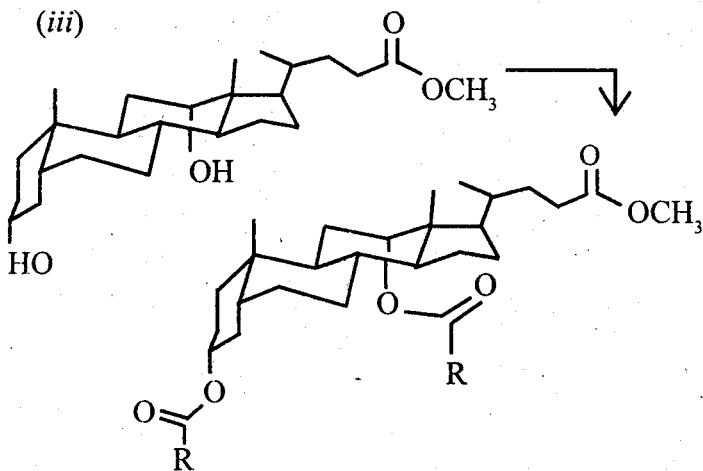
3. (a)



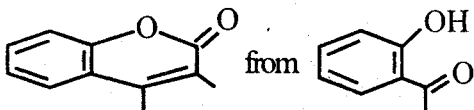
(b) Carry out the following transformations (any two, with plausible mechanism) :

3





(c) Synthesize



via Ring-Closing-Metathesis reaction.

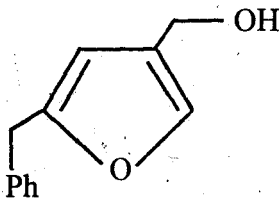
2

4. What are the limitations of Hückels rule? What is meant by the term homoaromaticity and explain the phenomenon with homotropylium cation? How homotropylium cation is synthesised? Explain why the hydrocarbon with an acceptable Hückel number of 10 ($n=2$) is not aromatic.

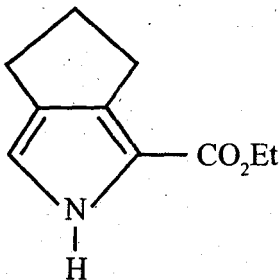
2 + 4 + 2

5. (a) How would you synthesize the following compounds [any two]. 2x2

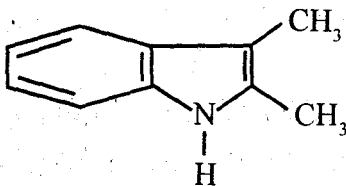
(i)



(ii)



(iii)



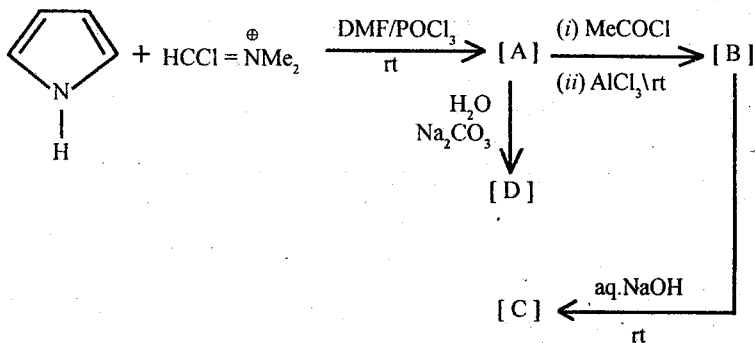
(b) Give the product(s) with mechanism of the reaction of 2-acyl furan with $\text{NH}_3/\text{NH}_4\text{Cl}$ when heated in a sealed tube.

2

(8)

(c) Identify [A] to [D] :

2



GROUP—B

Q.No.6 or 7 is compulsory

6. (a) Identify the following statements as *true* or *false* with justification. Answer any *three*: 3

(i) The two forms of gauche butane are conformational enantiomers whereas *cis*- and *trans*-1, 3-dimethylcyclohexanes are configurational diastereomers.

(ii) A molecule may have an achirotopic but stereogenic center. Explain with an example.

(iii) The symmetry point group of the boat form of cyclohexane is D_2 .

(iv) The molecule $C_{ab} = C = C_{aa}$ possesses a chiral axis.

(v) The molecule MeCOEt is chiral in 2-dimension and pro-chiral in 3-dimension.

(b) Answer any two of the following :

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

(i) Indicate by (R, S)-notation the absolute configuration of each diastereomer of $*CA_2B_2$, where A and B are different chiral ligands and indicate the chirotopicity and stereogenicity of $*C$ in each diastereomer.

(ii) The two isomers of 1, 2-dibromocyclohexane exhibit dipole moments 3.12 D and 2.11 D. characterize the isomers and comment on their optical activity.

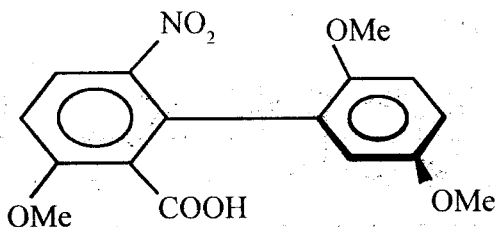
(iii) Explain the relative rates of saponification of the two isomers of ethyl 4-*t*-butylcyclohexane carboxylate with the help of an energy diagram.

7. (a) Draw correctly the chair conformation (showing all bonds) and the Newman projection formula of trans-1,4-dimethylcyclohexane, and state its relation with its flipped form. How one should view the cyclohexane ring to get its projection as the usual chair conformation? How can you find out the torsion angle signs in the ring across C1—C2 and C4—C5 bonds from its Newman projection formula, or directly from its chair conformation. Comment on its optical activity.

$$3 + \frac{1}{2} + 2 + \frac{1}{2}$$

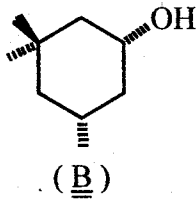
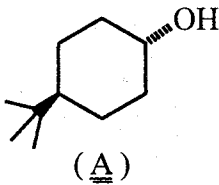
- (b) Name the following biphenyl compound according to the new convention of the CIP nomenclature.

2

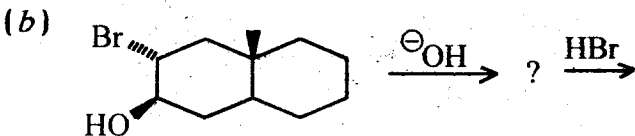
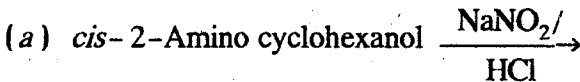


Or

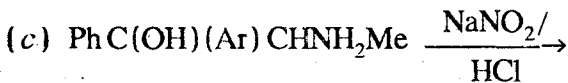
- (c) The relative rates of CrO_3 oxidations of (A) and (B) are 1.00 and 62.7 respectively. Explain. 2



8. Indicate the plausible mechanism of the following reactions leading to the product(s). Name the product(s) showing the predominant product, if any. Attempt any *four*: 2 x 4



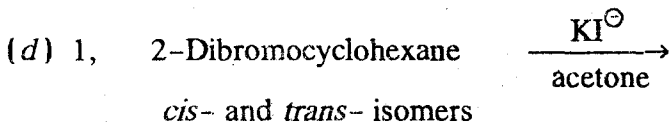
Comment on the rates of each step.



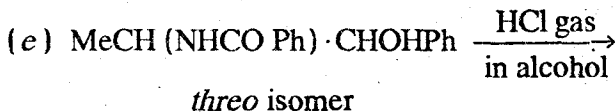
Parf diastereomer.

(any enantiomer)

Here, Ar = P-Anisyl.

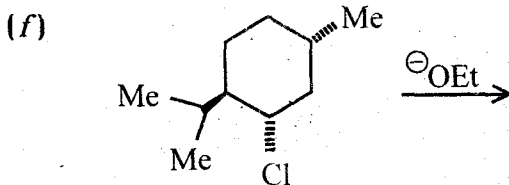


Comment on the rates.



N-Benzoyl-nor- ψ -ephedrine

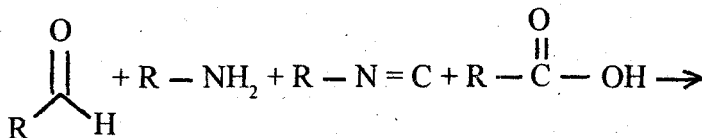
(any enantiomer).



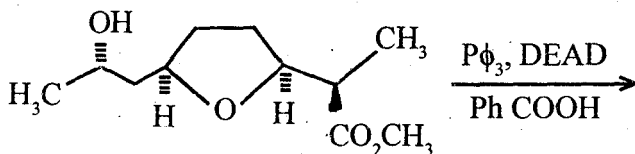
Neomenthyl chloride

9. Predict the product(s) with plausible mechanism (any four) : 2 x 4

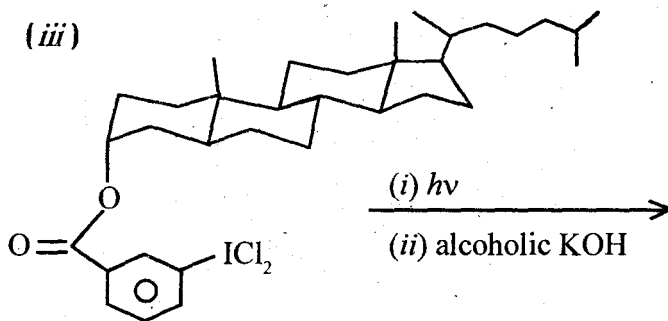
(i).



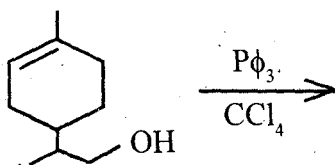
(ii)



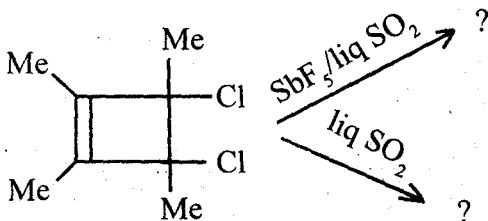
(iii)



(iv)

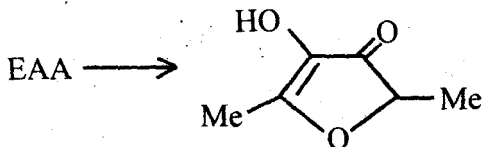


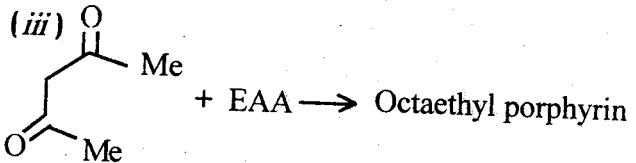
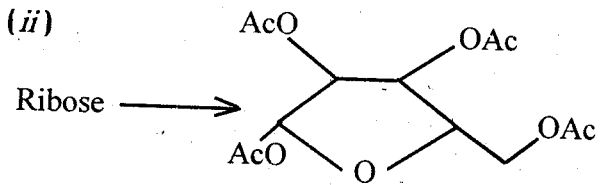
(v)



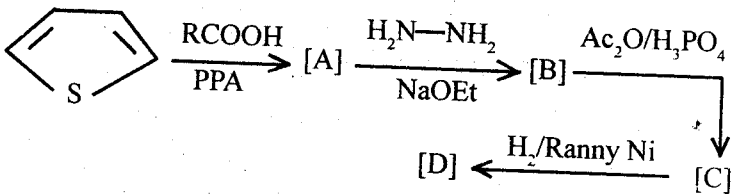
10. (a) Carry out the following transformations (any two): 2 x 2

(i)





(b) Identify [A] to [D] :



(c) Explain the following observations :

