NEW

2017

M.Sc. Part–I Examination

CHEMISTRY

PAPER—II

Full Marks : 100

Time : 4 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

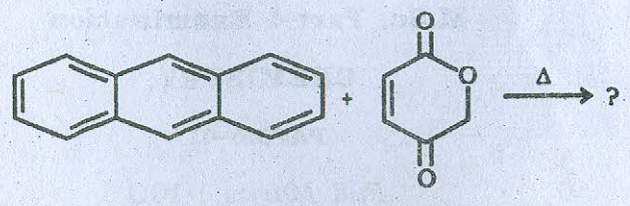
(Organic)

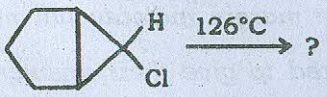
Answer any *five* questions,
taking at least *two* from Group–A and B
and *one* from Group–C.

Group–A

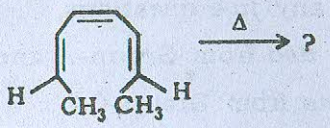
1. (a) Cite an example to explain the exception of Woodward Hoffmann selection rule from electrocyclic reactions. $2\frac{1}{2}$

(b) Predict the product(s) of the following reactions showing frontier orbital interaction.
(attempt any *four*)

(i) 

(ii) 

(iii) 

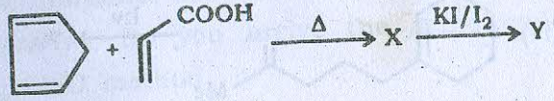
(iv) 

3×3

(c) Explain the term secondary orbital interaction with special reference to the Diels Alder reaction.

$2\frac{1}{2}$

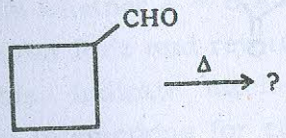
(d) Identify the product X and Y.

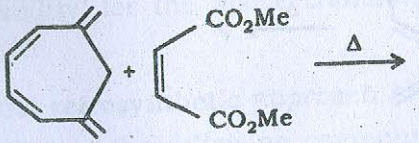


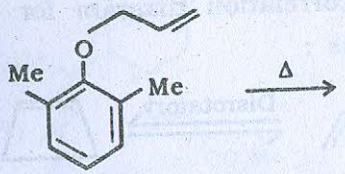
1

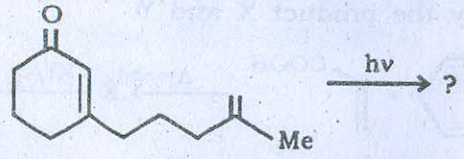
2. (a) State the principle of 'Microscopic Reversibility' whether is it applicable or not to an electrocyclic reaction ? Explain. 3

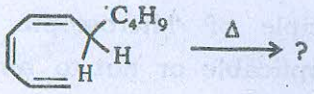
(b) Explain the product(s) of the following reactions (attempt any *six*) :

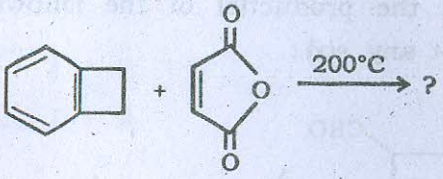
(i) 

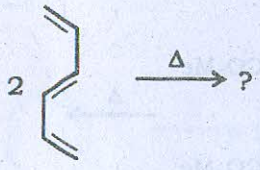
(ii) 

(iii) 

(iv) 

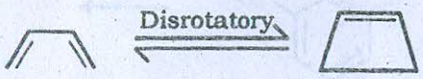
(v) 

(vi) 

(viii) 

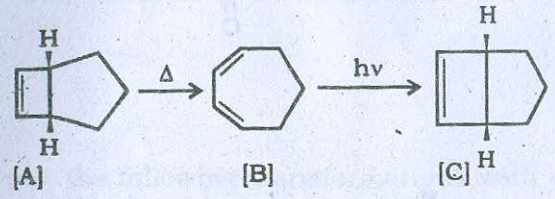
6×2

3. (a) Construct a correlation diagram for the following transformations :



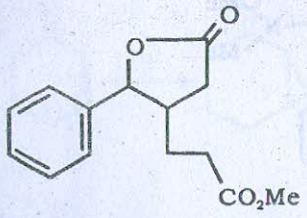
With the help of the diagram predict whether these transformations are allowed thermally or photochemically ? Do you arrive the same conclusions using PMO method. 3+2+2

(b) The following transformation gives the product as follows :

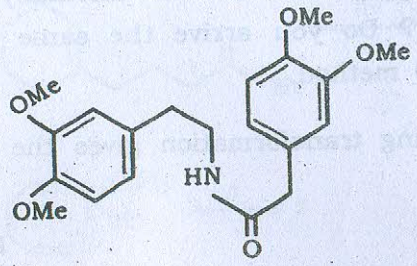


Explain whether A → B and B → C follow Woodward-Hoffmann Rule and reverse reaction C → B is at all possible. Indicate mechanism and show frontier orbital interactions for each steps whenever necessary. Comment or 'Principle of microscopic reversibility' for the above transformation. 7+1

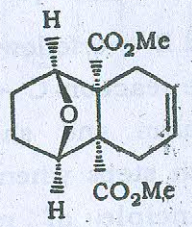
4. (a) Give the retrosynthetic approach and their synthetic strategies of the following compounds (any *four*) :

(i) 

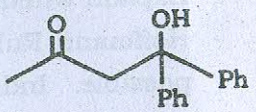
(ii)



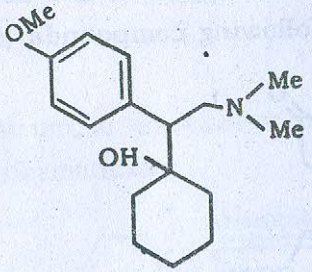
(iii)



(iv)

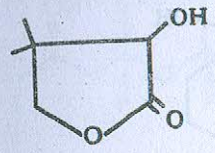


(v)



(Continued)

(vi)



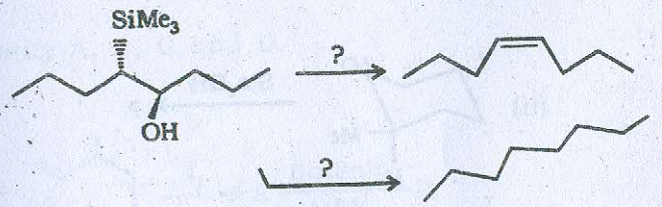
4×3

(b) Define with example (i) Disconnection and synthon.

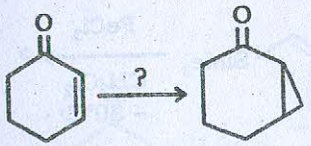
$1\frac{1}{2}+1\frac{1}{2}$

5. (a) Carry out the following transformations with mechanism : (any *two*)

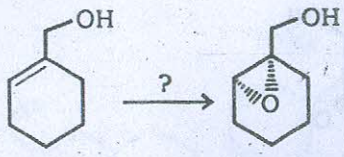
(i)



(ii)

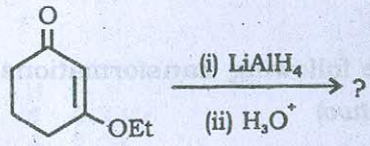


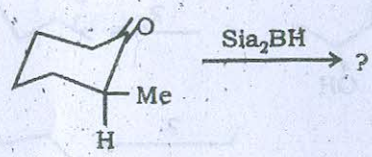
(Turn Over)

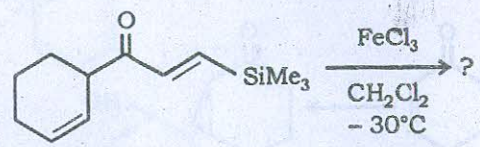
(iii) 

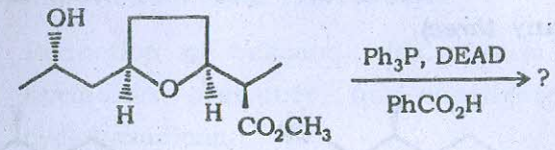
3x2

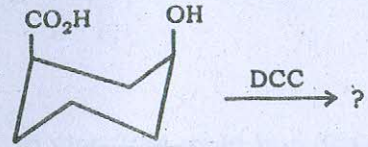
(b) Predict the product(s) with mechanism : 3x3
(any *three*)

(i) 

(ii) 

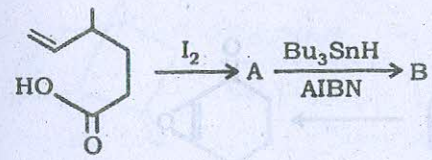
(iii) 

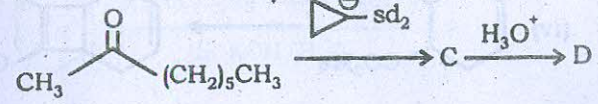
(iv) 

(v) 

Group–B

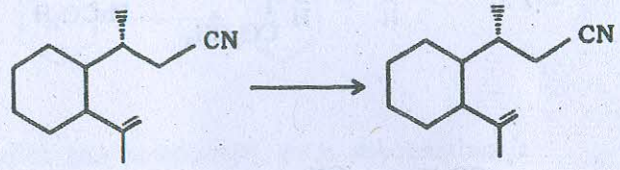
6. (a) Identify A, B, C and D.

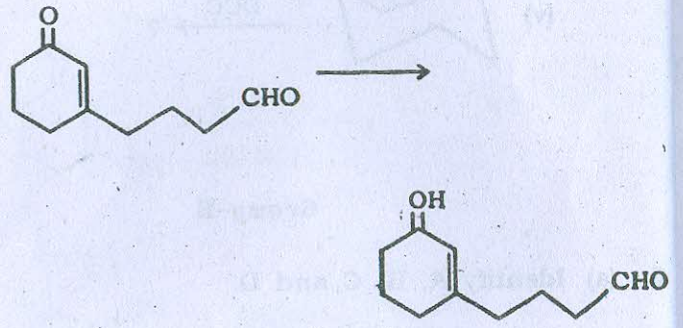
(i) 

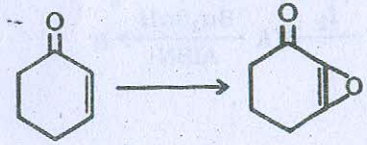
(ii) 

4

(b) Indicate appropriate reagent in each case : (any *three*)

(i) 

(ii) 

(iii) 

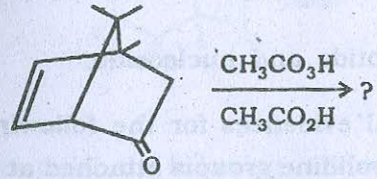
(iv) 

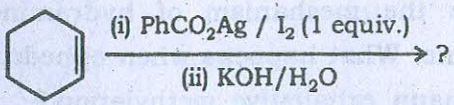
(c) Explain the following observations :

(i) Reduction of benzene with sodium in liquid ammonia produces non-conjugated 1, 4-cyclohexadiene.

(ii) $(EtO)_2\overset{\overset{O}{\|}}{P}-\overset{\ominus}{C}H-COOEt$ reacts with cyclohexanone to give 70% yield but $(EtO)_3\overset{+}{\underset{\underset{O}{\|}}{P}}-\overset{\ominus}{C}H-COOEt$ gives 25% yield.

(d) Write down the structure of the major product

(i) 

(ii) 

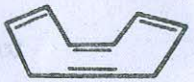
1×2

7. (a) Show that owing to delocatization benzene is stabilised an amount of energy is equal to 2β.

(b) Define Homoaromaticity. With an example.

(c) Account for the instability of [10] annulene, although it obey Huckel's rule.

(d) Arrange the stability order with proper explanation

(i)  (ii)  (iii) 

(e) [18] annulene is more stable then [18] annulene dianion. Explain with M.O. diagram.

4+3+2+3+3

8. (a) Define Nucleotide and nucleoside. 2+2

(b) Give chemical evidences for the following point : N-methyl pyrrolidine groupis attached at position 2(α) to the pyridine nucleus in nicotine. 3

(c) Discuss the mechanism of hydramine fission of ephedrine. What happens when ephedrine subjected to Hofmann exhaustive methylation ? 3+2

(d) Give example sesquiterpene. 1

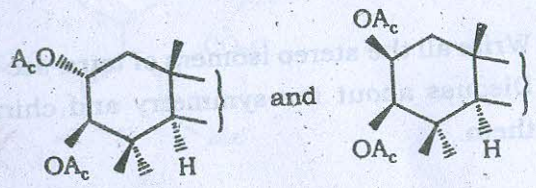
(e) Predict the product with mechanism

Glutaraldehyde + Ammonia + N-methyl pyrolinium chloride

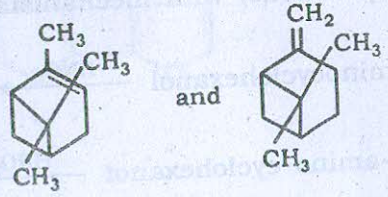
$$\xrightarrow[\text{pH = 10/air}]{\text{Phosphate buffer}} ?$$ 2

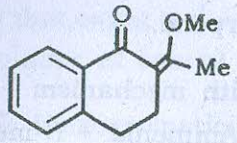
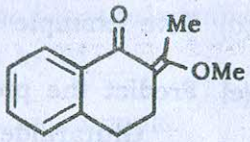
9. (a) A compound A, C_8H_6, showed ^1H NMR signals at $\delta_{7.2}$ (5H, m) and $\delta_{3.08}$ (1H, S). Identify the compound.

(b) How would you distinguish between the following isomeric compound using the Karplus equation :



(c) Distinguish the following compounds with explanation :

(i) 

(ii)  and 

(d) Compound $C_6H_{10}O_2$ characterised by ^1H NMR spectram which contains $\delta_{2.2}$ (6H, S) and $\delta_{2.7}$ (4H, S) peak. Identify the compound.

(e) Compound $C_6H_{12}O$ shows in its ^1H NMR spectrum two signals at $\delta_{1.1}$ (9H) and 2.1 (3H) both as singlets. Identify the compounds.

$2\frac{1}{2}+2\frac{1}{2}+(2\frac{1}{2}\times2)+2+2\frac{1}{2}$

Or

(a) Write all the stereo isomers of tetra-sec-butylmethane. Discuss about the symmetry and chirility of each of them. 5

(b) What is atropisomerism ? Explain with examples. 3

(c) Predict the product(s) with mechanism

(i) cis-2-aminocyclohexanol $\xrightarrow{HNO_2}$?

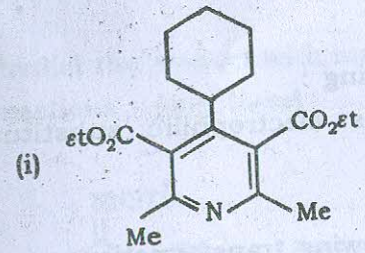
(ii) trans-2-amino cyclohexanol $\xrightarrow{HNO_2}$? 3

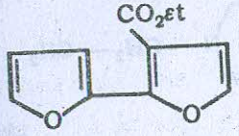
(d) State whether the following statement are true or false. Give reasons.

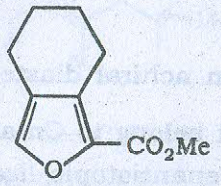
(i) A meso isomer is an achiral diaste reomer.

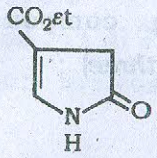
(ii) Rigid molecules that belong to Cn and Dn point group cannot have enantiotopic ligands. 2+2

10. (a) Synthesize the following compounds using retrosynthetic analysis (any *three*) :

(i) 

(ii) 

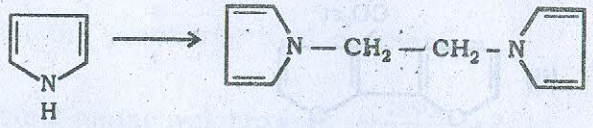
(iii) 

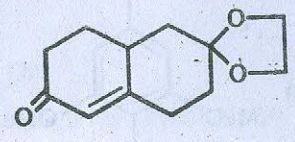
(iv) 

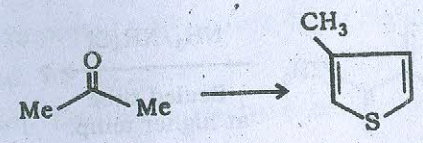
3×3

(b) Explain the following :
Pyrrole undergoes electrophilic substitution at 2 position. 2

(c) Carry out the following transformations :
(any *two*)

(i) 

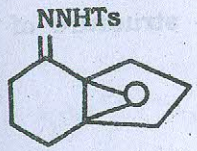
(ii) Furfural ⟶ 

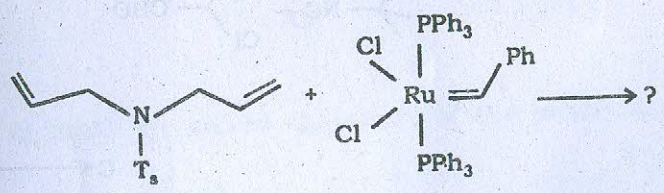
(iii) 

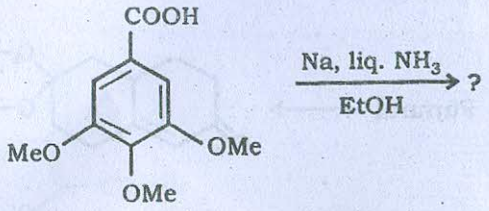
2×2

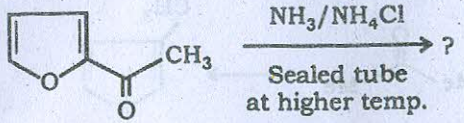
Group–C

11. (a) Predict the product with mechanism for the following reactions : (any *three*)

(i) 

(ii) 

(iii) 

(iv) 

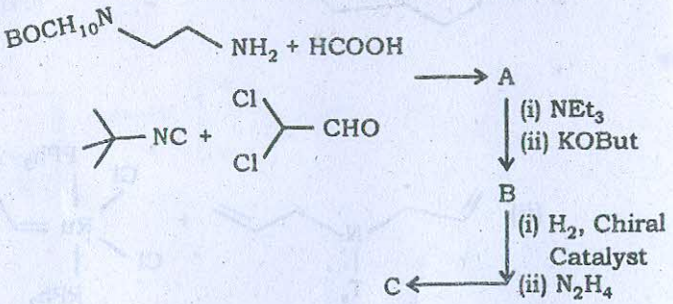
3×3

(b) Write down the product structure with mechanism

squalene $\xrightarrow[\text{epoxidase } O_2]{\text{squalene}}$ squalene oxide $\xrightarrow{H^+}$

protosterol cation $\xrightarrow{-H^+}$ Lenosterol. 3

(c) Write down the product structure of the following reactions : 3



(Continued)

(d) Define Hückel's rule. What are the limitation of Hückel's rule. 3

Or

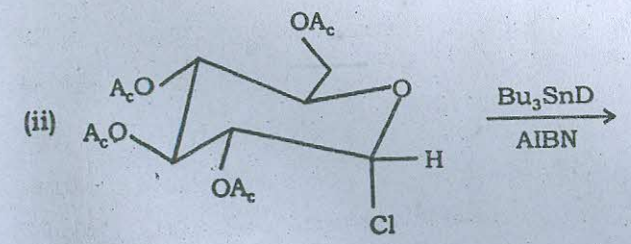
Why the $(4\eta + 2)\pi$ electron system to behave as aromatic compound. 3

(e) The important IR bands for a compound, C_3H_3N are found at $\nu_{max}(cm^{-1})$: 3050(m), 2250(s), 1620(m), 990(s). Deduce structure of the compound. 3

Or

Compound A, $C_{12}H_{18}$ is characterised by ^1H NMR spectrum which contain a single peak at $\delta_{2.2}$. Identify the compound. 3

(i) What is buttressing effect? Discuss with an example.

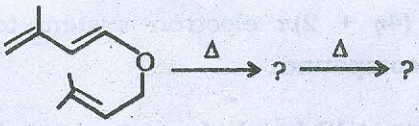
(ii) 

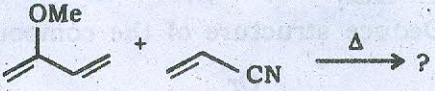
Indicate the stereo chemistry of the product(s). 2+2

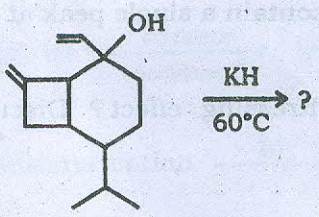
(Turn Over)

Or

Write down the products of the following reactions ;

(i) 

(ii) 

(iii) 

2+1+1