

2018

M.Sc.

Part-I Examination

CHEMISTRY

PAPER—II

Full Marks : 100

Time : 4 Hours

The figures in the right-hand 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 Chemistry)

Answer questions from Group-A, B and C

Answer any five questions,

taking at least two from Group-A and B

Group-A

1. Explain with examples :

(a) (2+2) Cycloaddition is photochemically allowed process. 3

(b) (4+2) Cycloaddition is thermally allowed process. 3

(Turn Over)

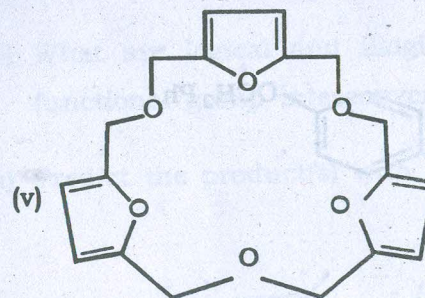
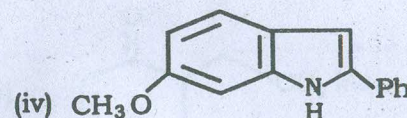
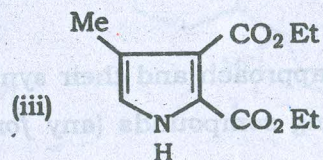
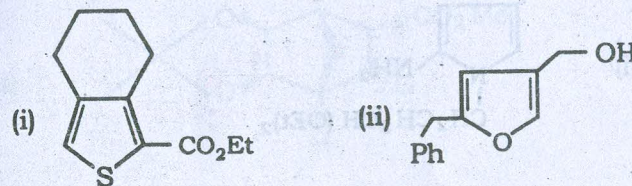
- (c) Cope reaction is a Sigmatropic process. 3
- (d) Alder ene reaction follows frontier molecular orbitals. 3
- (e) $4n$ thermal electrocyclic reactions follow conrotatory motions. 3

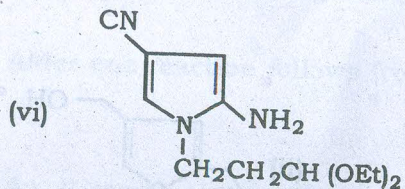
2. Explain the followings :

- (a) Cyclopentadiene dimerises under thermal condition explain with MO diagrams. 3
- (b) 1,3-butadiene cyclises to cyclobutene under thermal and also photo chemical condition Explain. 3
- (c) Is it possible to do (2 + 2) thermal cycloaddition reaction? If so, explain with example. 3
- (d) Explain S-S or A-A matching in pericyclic reaction. 3
- (e) Conservation of orbital symmetry. Explain with Woodward's concept. 3
3. (a) Pyridine undergoes nucleophilic substitution at α and γ position—Explain. 2

(b) Synthesize the following compounds (any four) :

3×4

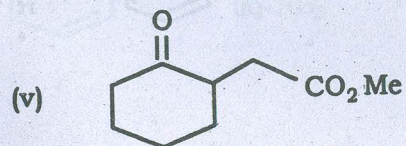
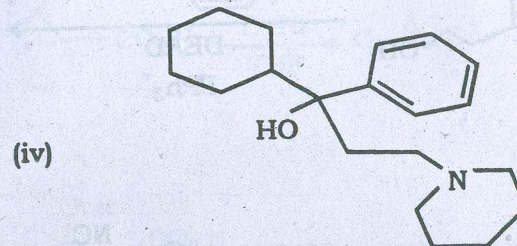
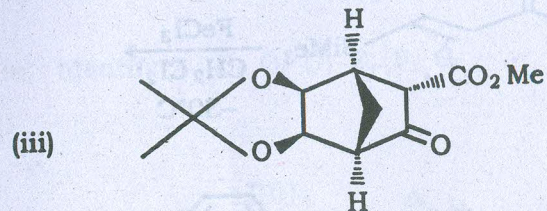
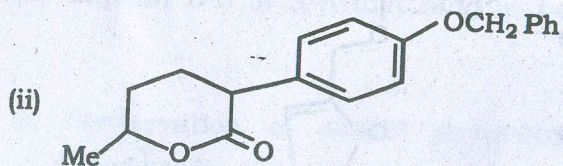
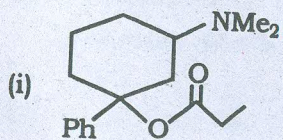




(c) Write down the structure of Lawesson's reagent. 1

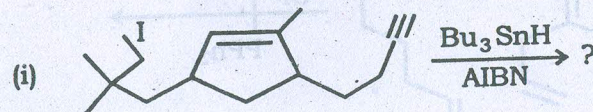
4. (a) Give the retrosynthetic approach and their synthetic strategies of the following compounds (any four) :

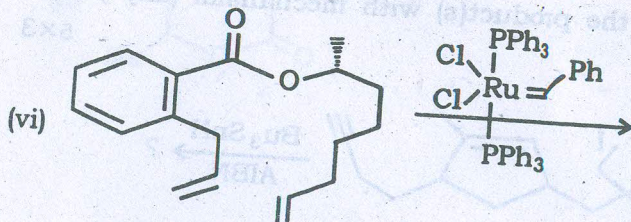
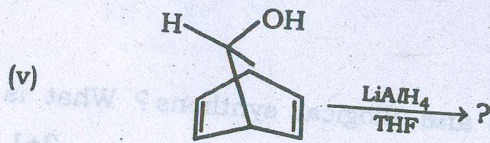
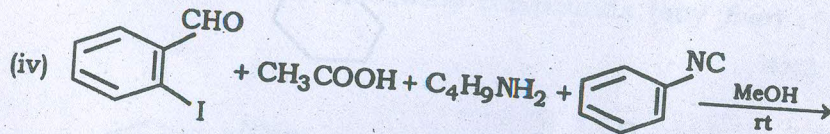
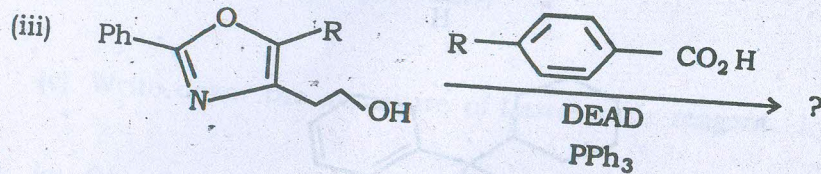
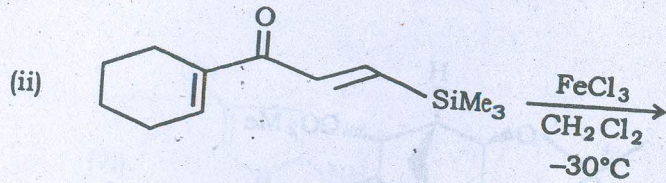
4×3



(b) What are logical and illogical synthons? What is functional group interconversion? 2+1

5. (a) Predict the product(s) with mechanism (any five) : 5×3

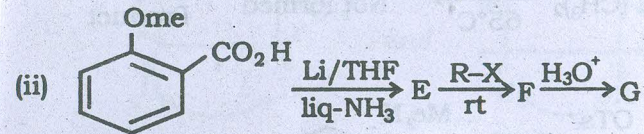
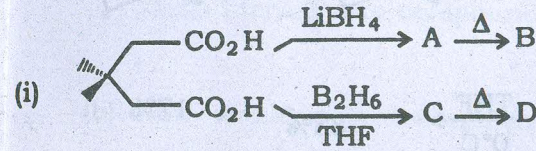




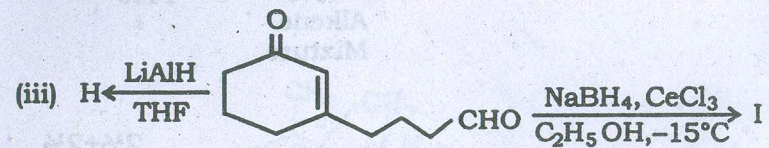
Group-B

6. (a) Identify A, B, C, D, E, F, G.

2

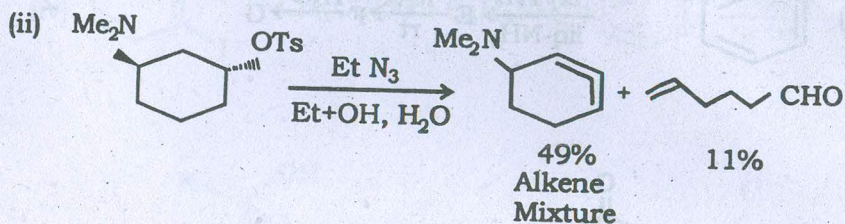
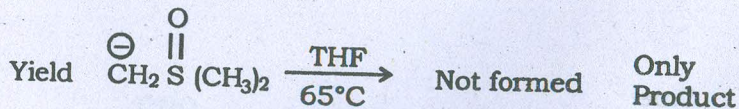
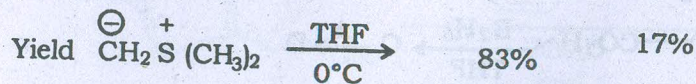
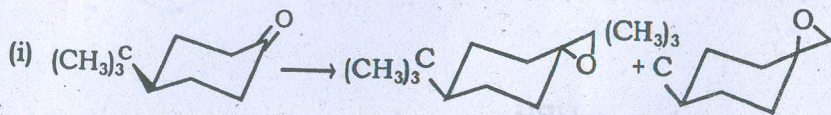


2



2

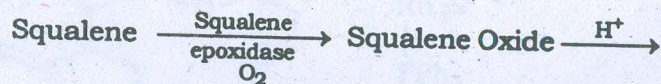
(b) Explain the following observations.



2½+2½

(c) Write down the product structure with mechanism.

4

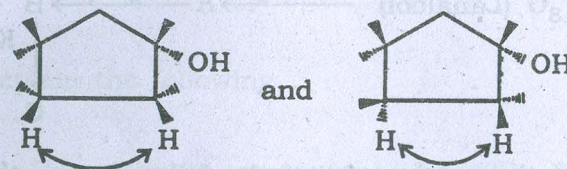


A + B + C + D + E (All are four member ring product)

7. (a) A compound $\text{C}_4\text{H}_8\text{O}_2$ showed IR absorption band at $\gamma_{\text{max}} = 1735 \text{ cm}^{-1}$. The $^1\text{H NMR}$ spectrum of the compound exhibited signals at $\delta_{1.97}(3\text{H, S})$, $4.1(2\text{H, q, } J = 7\text{ Hz})$ and $1.13(3\text{H, t, } J = 7\text{ Hz})$. Identify the compound.

3

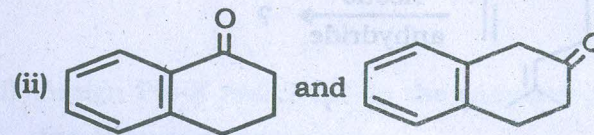
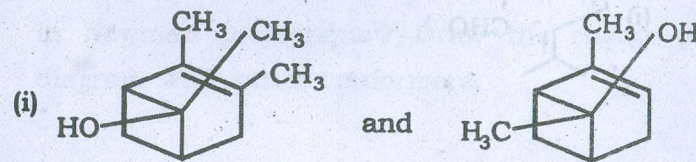
(b) How would you distinguish between the following isomeric compound using the Karplus equation.



3

(c) Distinguish the following compounds with explanation

2½×3

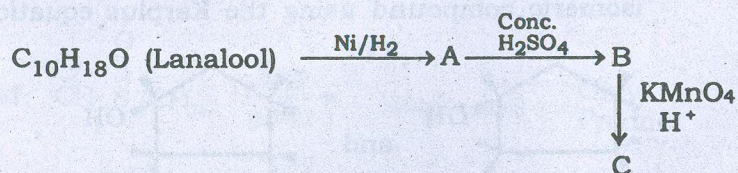


(iii) cis and trans stilbene.

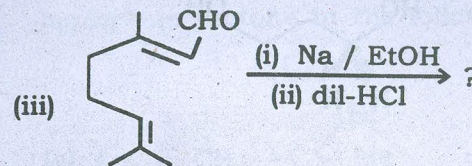
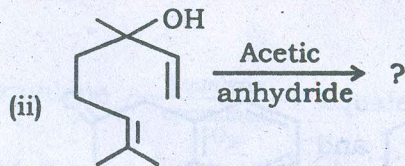
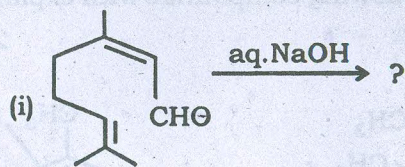
- (d) A compound with M.F. C_5H_5O , shows a characteristic band at 1745 cm^{-1} (s) in IR spectrum. Suggest structure for it. 1½

8. (a) Define Isoprene rule. 2

(b) Identify the product A to C 3



(c) Predict the product (s) of the following reactions. 2+2+2



(d) How many isomers are possible from Citral ($C_{10}H_{16}O$). Confirm the structure by NMR evidence. 4

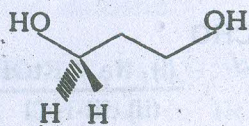
9. Explain the following :

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

(b) Write the most stable conformation of $(Cl)_2CH-CH(Cl)_2$ in Newman projections? Draw the energy profile diagram with other conformers. 3

(c) Explain why ethane is more stable in staggered form. 3

(d) Assign Pro-R and Pro-S to the enantiotopic protons of the following compound. 3



- (e) Write the most stable conformer of 2-isopropyl cyclohexanone with explanation. 3

10. Draw the 3d structures for the following conformers and show in them different steric interactions and comment on their optical properties.

- (a) cis-transoid-cisperhydroanthracene. 3
 (b) trans-cisoid-cisperhydrophenanthrene. 3
 (c) 9,10-dimethyl cisdecalin. 3
 (d) trans-transoid-transperhydrophenanthrene. 3
 (e) cis-cisoid-cisperhydroanthracene. 3

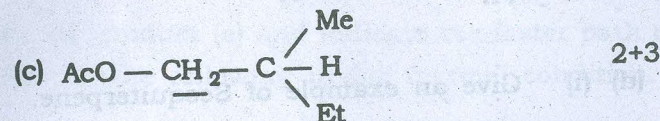
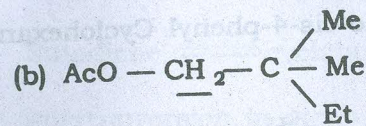
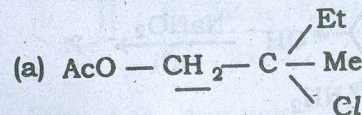
Group-C

11. Answer any five questions :

- (a) (i) Compound Z, C_8H_6 is characterized by HNMR spectrum which contains $\delta_{7.2}$ (5H, m) and $\delta_{3.08}$ (1H, S).

Suggest a possible structure for the compound.

- (ii) Predict the multiplicity of the signal of the methylene protons in the following compounds



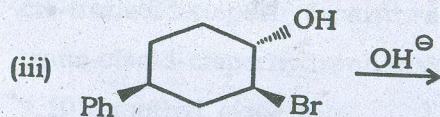
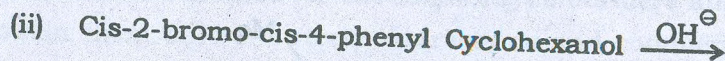
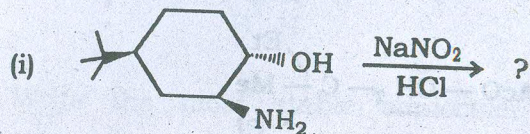
- (b) (i) Arrange the stability order of the following compounds. Explain with M.O. diagram.

[18] annulene, [18] annulene dianion, [20] annulene.

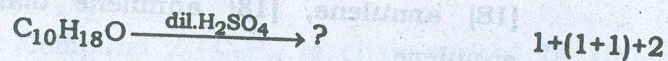
- (ii) Cyclooctatetraene is aromatic, antiaromatic or non aromatic. Explain with M.O. diagram.

2+3

- (c) Predict the product of the following reaction with mechanism (any two) : $2\frac{1}{2} \times 2$

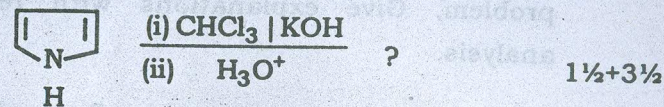


- (d) (i) Give an example of Sesquiterpene.
 (ii) Give an example of cyclic and acyclic Terpenoid.
 (iii) Predict the product of the following reaction

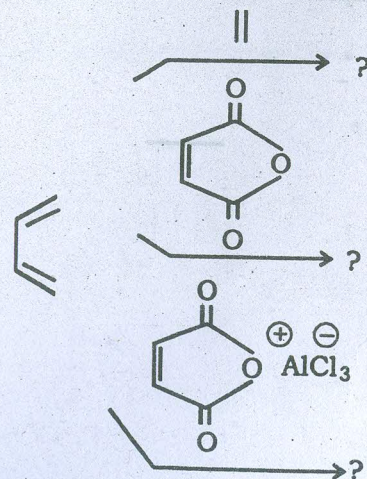


- (e) (i) Why does nucleophilic attack take place at 1-position not a 3 position of isoquinoline ?

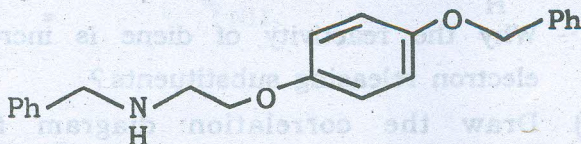
- (ii) Predict the product(s) of the following reaction with suitable mechanism.



- (f) (i) Why the reactivity of diene is increase by electron releasing substituents ?
 (ii) Draw the correlation diagram for the Butadiene \rightleftharpoons cyclobutadiene
 (iii) Interconversion in disrotatory pathway, indicate Symmetry allowed path for this conversion. $(1+2+2)$
- (g) Predict the product (s) and indicate the faster path of reaction of the following under thermal condition.



- (h) How would you design the synthesis of the following compound avoiding that causes chemoselective problem. Give explanations with retrosynthetic analysis.



- (i) (i) What is phase transfer catalyst ? Give an example.
 $1\frac{1}{2} + \frac{1}{2}$
- (ii) What is ring closing metathesis ? 1
- (iii) What is sharpless epoxidation ? Give one suitable example. 1+1