

NEW / OLD

2015

M.Sc. Part-I Examination

CHEMISTRY

PAPER—II

(Organic Chemistry)

The figures in the right-hand margin indicate full marks.

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

Illustrate the answers wherever necessary.

New Syllabus

Answer questions of Group—A and B and C.

Answer *five* questions taking at least *two* from Group—A and B.

Full Marks : 100

Time : 4 Hours

Old Syllabus

Answer questions of Group—A and B.

Answer *five* questions taking at least *two* from each group.

Full Marks : 75

Time : 3 Hours

(Turn Over)

Group—A
(New & Old Syllabus)

1. (a) Cite an example to explain the exception of Woodward Hoffmann selection rule from electrocyclic reactions.

$2\frac{1}{2}$

- (b) Construct a correlation diagram for the following transformations :

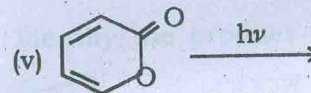
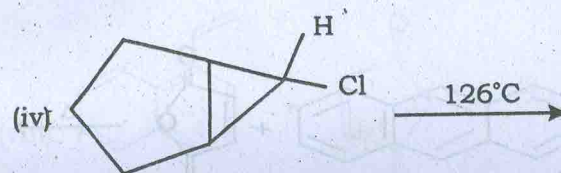
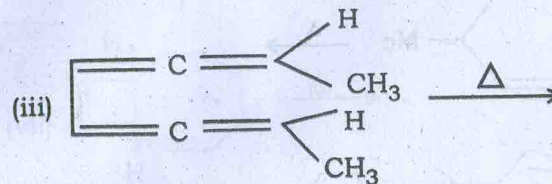
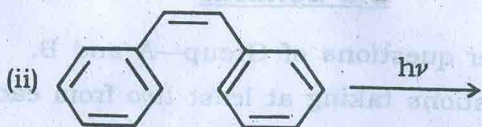
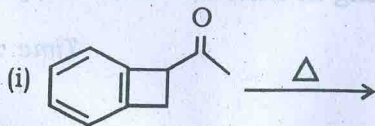
$3+1\frac{1}{2}+2$



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

- (c) Predict the product (s) of the following reactions indicating FMO interactions. (attempt any three)

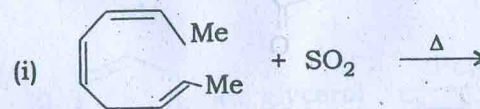
2×3

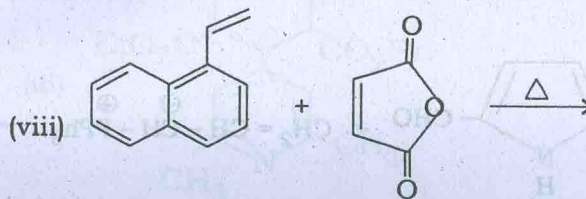
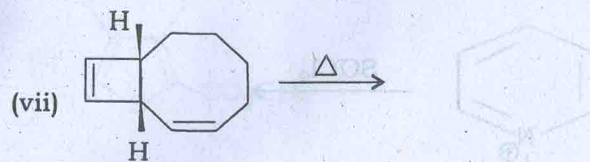
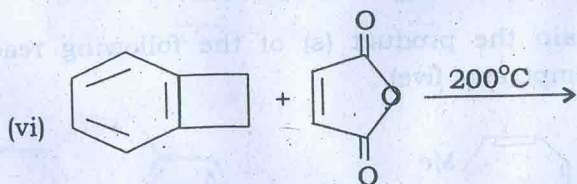
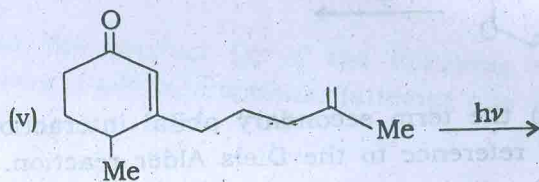
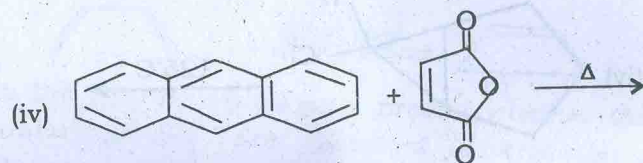
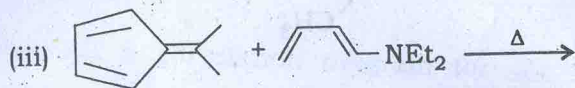
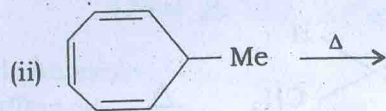


2. (a) Explain the term secondary orbital interaction with special reference to the Diels Alder reaction. 2

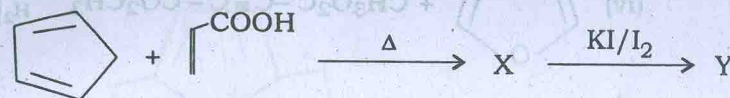
- (b) Why the reactivity of the diene is increased by electron releasing substituents? 1

- (c) Explain the product (s) of the following reactions: (Attempt any five) 5×2



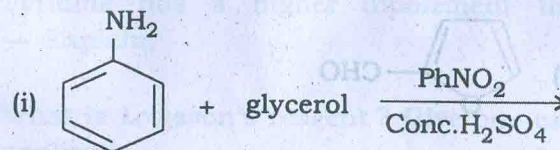


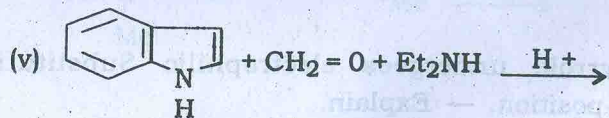
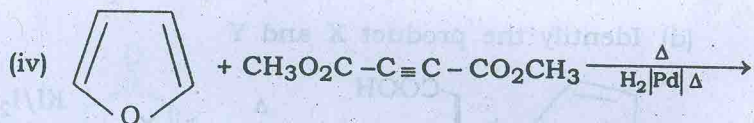
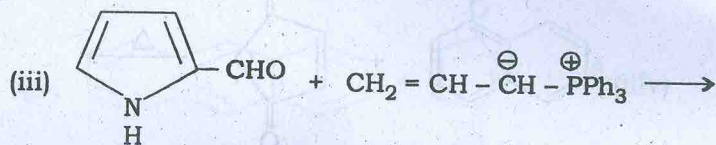
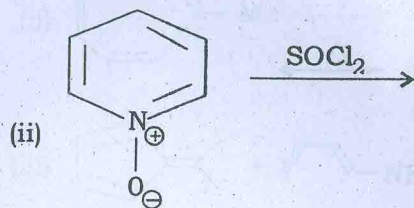
(d) Identify the product X and Y



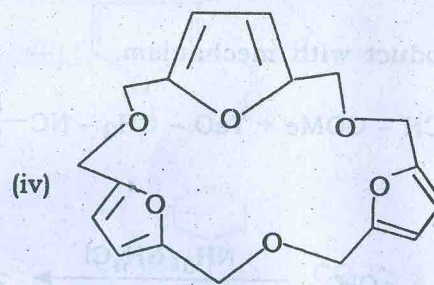
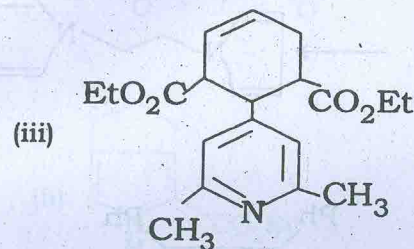
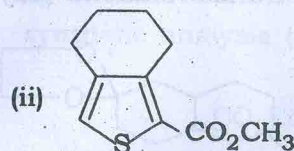
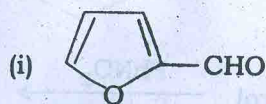
3. (a) Pyrrole undergoes electrophilic Substitution at 2-position. — Explain.

(b) Predict the product(s) in each of the following reactions and suggest mechanism. (any four) : $1\frac{1}{2} \times 4$





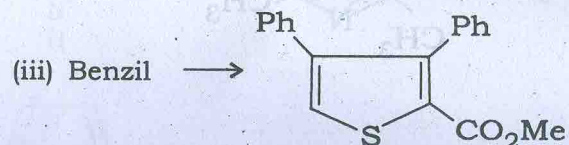
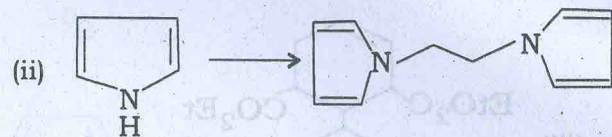
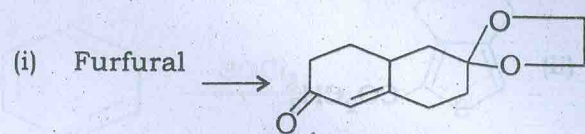
(c) Logically develop the synthesis of the following compounds. (any three) : 3×2



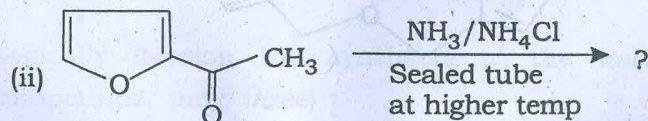
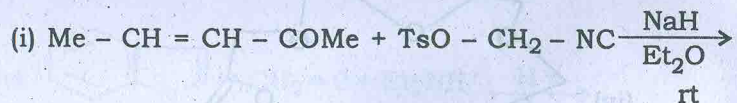
(d) Pyridine has a higher dipole moment than pyrrole. — Explain.

4. (a) What is Lowson's reagent? Give one example of its application. 1+2

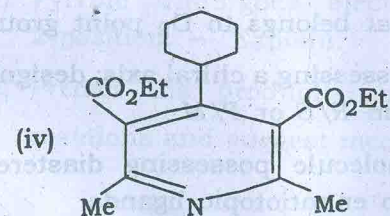
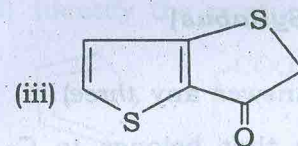
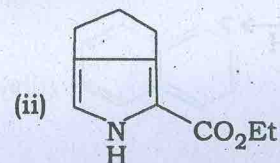
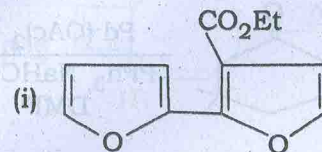
(b) Carry out the following transformations (any two) :



(c) Predict the product with mechanism.

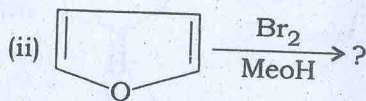
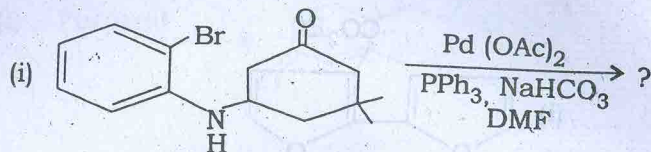


5. (a) Synthesize the following compounds using retro synthetic analysis (any three) : 3×4



(b) Write down the product of the following reactions.

3



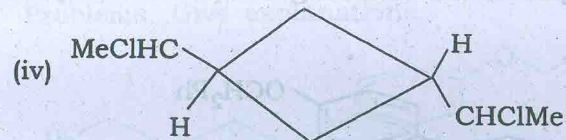
Group—B

(New & Old Syllabus)

6. (a) Give an example each (Answer any three) 6

- An organic molecule that belongs to C_3 point group.
- A molecule that belongs to D_2 point group.
- A molecule possessing a chiral axis; designate its configuration in R/S or P/M .
- An achiral molecule possessing diastereotopic ligands but no enantiotopic ligands.
- An achiral molecule possessing both enantiotopic and diastereotopic ligands.

(b) How many stereoisomers are possible with the following constitutional structure? Comment on the symmetry elements present in each and the chirality of each isomer. (Answer any two) 8



(c) Define *meso*-isomer. 1

7. (a) State whether the following statements are true or false. Give reasons in support of your answer. (Attempt any two) : 6

- A molecule belonging to C_s point group cannot have enantiotopic ligands exceeding two in a set.
- Rigid molecules that belong to C_n or D_n point group cannot have enantiotopic ligands.
- Enantiomerism always embraces a pair, but the enantiomerism is not necessarily so.
- A *meso* isomer is an achiral diastereomer.

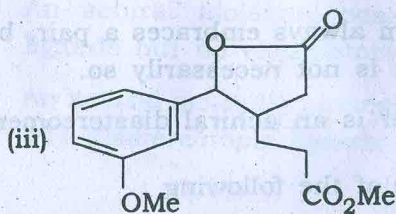
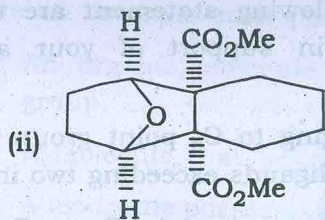
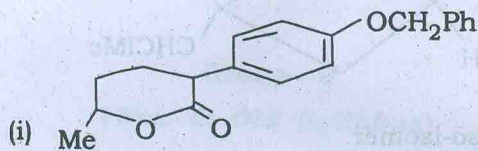
(b) Answer any three of the following :

- What is atropisomerism? Explain with examples.

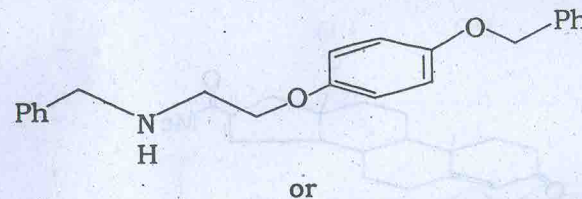
- (ii) What is buttressing effect? Discuss with an example.
- (iii) Define 'pseudorotation'. Illustrate with an example.
- (iv) Give an example and illustrate 2-alkyl ketone effect.

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

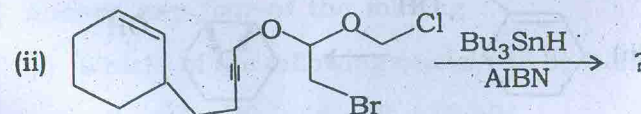
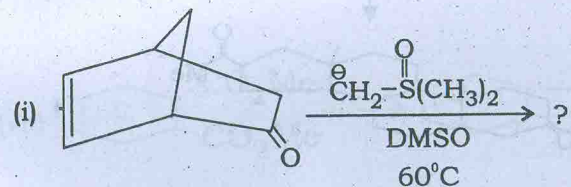
4×3

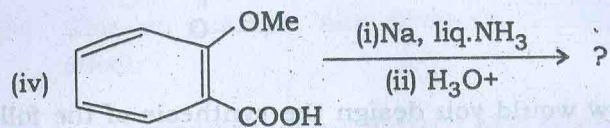
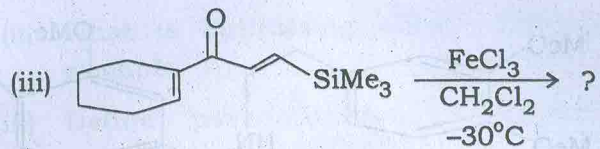


(b) How would you design the synthesis of the following compound avoiding that causes chemoselective. Problems. Give explanations. 3



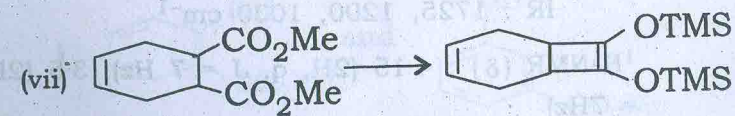
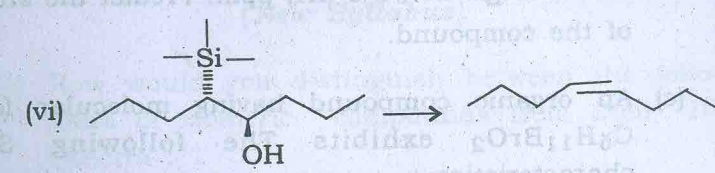
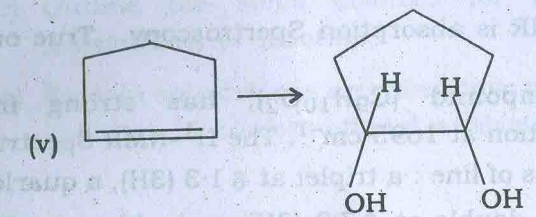
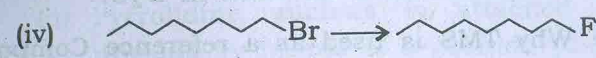
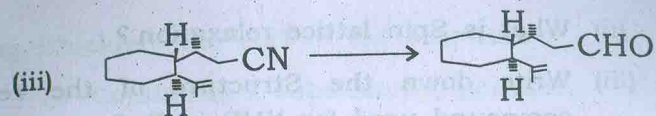
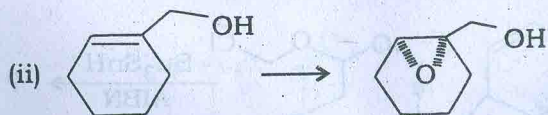
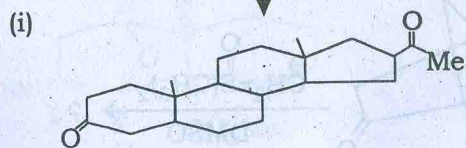
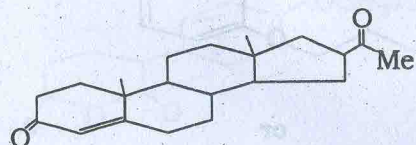
(a) Predict the product with mechanism. (any *three*):





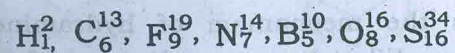
(b) Indicate appropriate reagent in each case. (any six)

6 × 1



9. (a) Answer any four of the following : 4 × 2

(i) Which of the following nuclei will be NMR active :



- (ii) What is Spin lattice relaxation ?
- (iii) Write down the Structure of the reference compound used for NMR in D_2O .
- (iv) Why TMS is used as a reference Compound in NMR ?
- (v) NMR is absorption Spectroscopy - True or false?
- (b) A Compound ($C_9H_{10}O_2$), has strong infrared absorption at 1695 cm^{-1} . The H^1 -NMR Spectrum has five sets of line : a triplet at $\delta\ 1.3$ (3H), a quartet $\delta\ 4.1$ (2H), a doublet at $\delta\ 7.0$ (2H), a doublet at $\delta\ 7.8$ (2H) and a single at $\delta\ 9.8$ (1H) ppm. Predict the structure of the compound. 4
- (c) An organic compound having molecular formula $C_6H_{11}BrO_2$ exhibits The following Spatial characteristics :

IR : $1725, 1200, 1030\text{ cm}^{-1}$

H^1 -NMR (δ) : 4.15 (2H, q, $J = 7\text{ Hz}$), 3.5 (2H, t, $J = 7\text{ Hz}$)

$2.0 - 2.7$ (4H, m), 1.25 (3H, t, $J = 7\text{ Hz}$)

Deduce the structure of the compound. 3

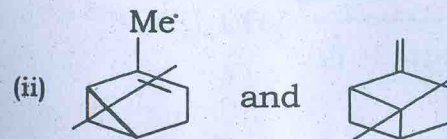
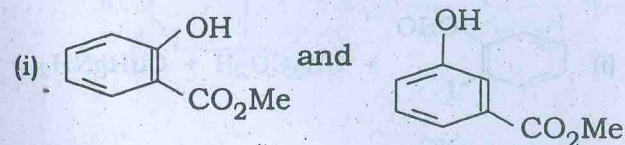
10. (a) Discuss the mechanism of hydramine fission of ephedrine. What happens when ephedrine subjected to Hofmann exhaustive methylation? 2+2

- (b) Elucidate the part of the structure :
- (i) Coniine is 2-substituted piperidine.
- (ii) Pyrrolidine nucleus is attached to pyridine nucleus by means of α -position (C-2). 2+2
- (c) Outline the steps involved for the biosynthesis (biosynthex) of nicotine.
- (d) Explain ephedrine is a weaker base than ψ -ephedrine in terms of conformational analysis.

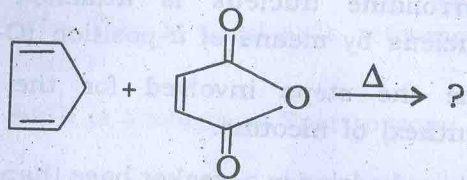
Group—C

(New Syllabus)

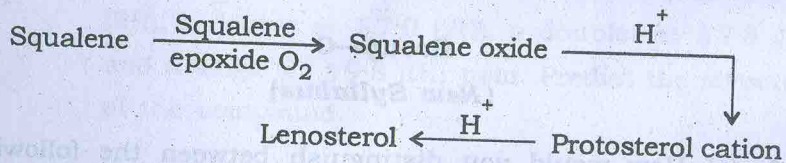
11. (a) How would you distinguish between the following pairs of isomeric compounds from their H^1 NMR Spectra : 2x2



- (b) Write down the expected product from the following reactions. Which of them will be the major product. Example your and answer : *4

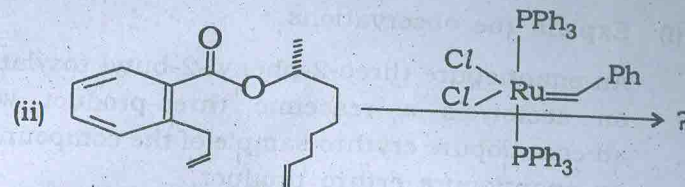
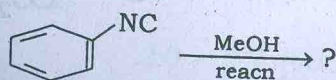
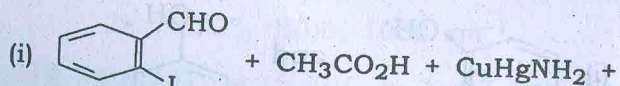


- (c) Write down the product structure with mechanism :



- (d) What is multicomponent reaction ?

Predict the product of the following reactions :



1+(1½×2)

- (e) Predict the product with mechanism (any two) :
3×2

