

2013

DDE

M.Sc. Part-I Examination

CHEMISTRY

PAPER—II

Full Marks : 75

Time : 3 Hours

The figures in the margin indicate full marks.

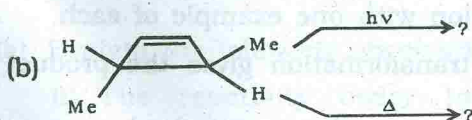
Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

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

## Group—A

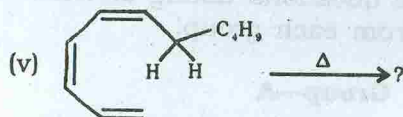
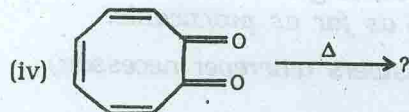
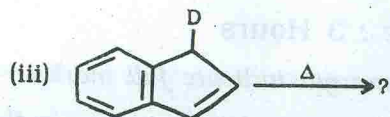
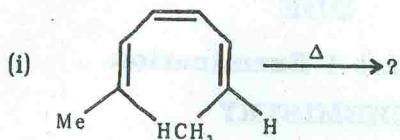
1. (a) What is electrocyclic reaction? Explain with suitable examples. 2



In what pathway of the above ring opening reaction takes place? Indicate the most favoured path in each case. 2×2

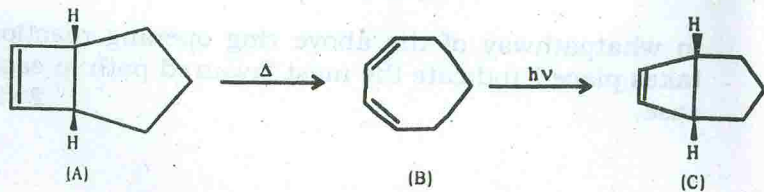
(Turn Over)

- (c) predict the product(s) of the following reactions showing Frontier Orbital Interactions (attempt any three) : **3×3**



2. (a) Write down the Woodward-Hoffman selection rule for electrocyclic reaction in case of photochemical and thermal condition with one example of each. **4**

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

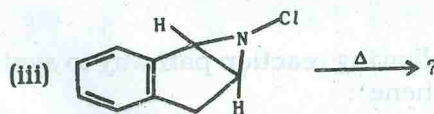
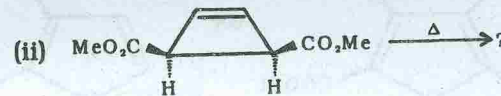
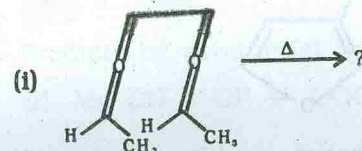


Explain, whether  $A \longrightarrow B$  and  $B \longrightarrow C$  follow Woodward-Hoffman Rule and reverse reaction

$C \longrightarrow B$  is at all possible. Indicate mechanism and show frontier orbital interactions whenever necessary. Comment on 'principle of microscopic reversibility' for the above transformation.

6+1

- (c) Write down the product(s) of the following reactions with mechanism stating frontier orbital interactions in each case (any two) : **2×2**



3. (a) Explain the following observations :

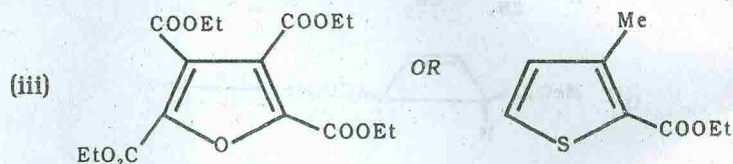
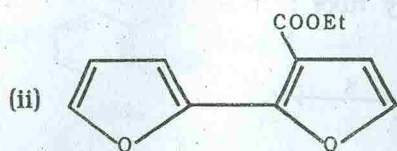
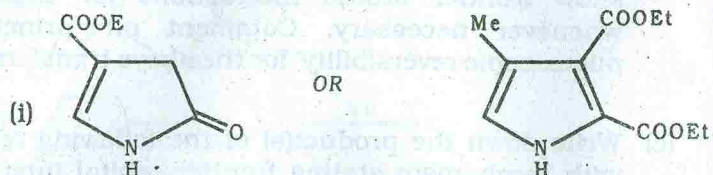
(i) The reactivity order towards electrophilic substitution reaction —

Pyrrole > furan > thiophene. **2**

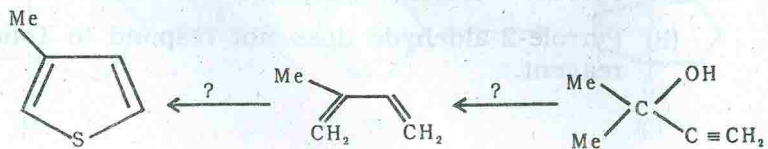
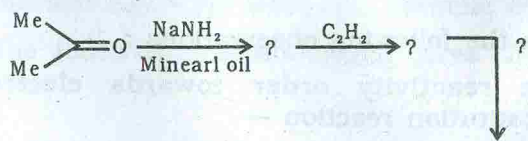
(ii) Pyrrole-2-aldehyde does not respond to Tollens reagent. **2**

(b) What is Lawesson's reagent? Give one example of its application. 1

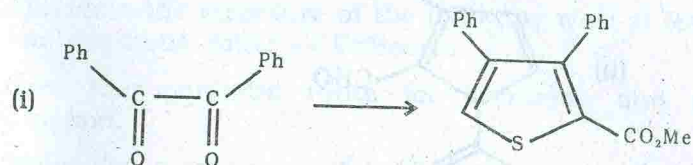
(c) Synthesise the following compounds using retrosynthetic pathway : 3+4+3



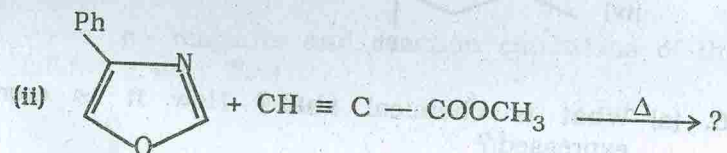
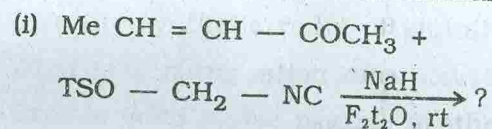
4. (a) Complete the following reaction pathway to synthesise 3-methyl thiophene : 3



(b) Carry out the following transformations : 3+3

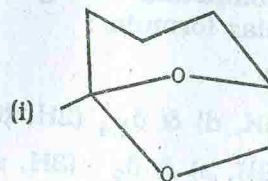


(c) Predict the product(s) with mechanism : 3+3

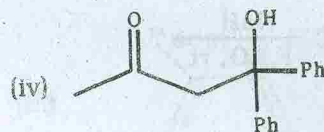
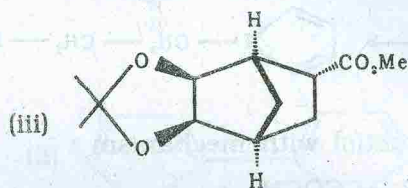
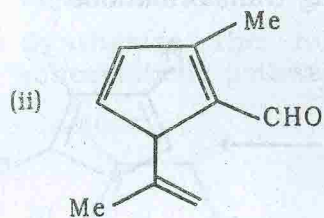


5. (a) Define with example — (i) disconnection and (ii) synthon.  $1\frac{1}{2} \times 2$

(b) Give the retrosynthetic approach and their synthetic strategies of the following (any three) :  $4 \times 3$



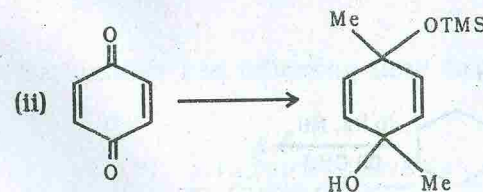
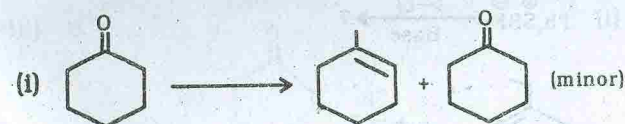


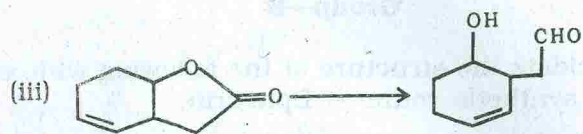


6. (a) What is chemical shift? How it is commonly expressed? 2
- (b) Indicate the multiplicity of methylene proton signal of any ethyl group in  $^1\text{H-NMR}$  spectrum and explain. 3
- (c) The chemical shift value of the ethylenic proton has higher than that of acetylenic proton. — Explain. 4
- (d) Identify the following compound using  $^1\text{H-NMR}$  spectral data and molecular formula : 2×3
- (i)  $\text{C}_{12}\text{H}_{18}$  shows  $\delta_{2.2}$  (s) ;
- (ii)  $\text{C}_6\text{H}_{14}$  shows  $\delta_{0.8}$  (12H, d) &  $\delta_{1.4}$  (2H, heptet) ;
- (iii)  $\text{C}_6\text{H}_{12}\text{O}$  shows  $\delta_{1.1}$  (9H, s) &  $\delta_{2.1}$  (3H, s).

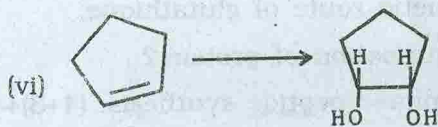
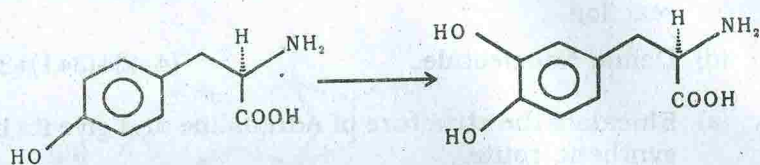
## Group—B

7. (a) Elucidate the structure of the following with at least one synthetic route — Ephedrin.
- (b) Give the synthetic route for thyroxine and its function.
- (c) Show the mechanism of DCC acid-amine coupling reaction.
- (d) Define Nucleotide. (4+2)+(3+1)+3+2
8. (a) Elucidate the structure of Adrenaline and give its biosynthetic route.
- (b) Give the synthetic route of glutathione.
- (c) What is denaturation of protein?
- (d) Explain solid phase peptide synthesis. (4+3)+4+2+2
9. (a) Write the reagents and reaction conditions of the following (any five) :

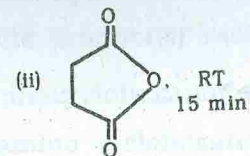
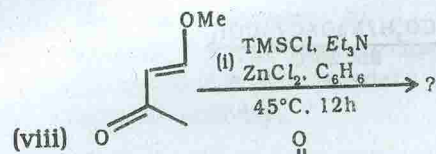
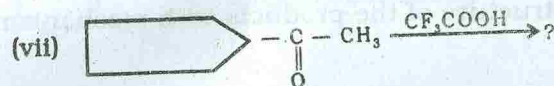
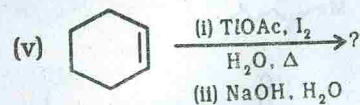
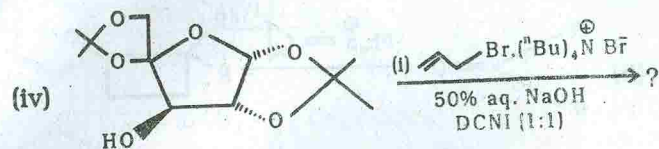
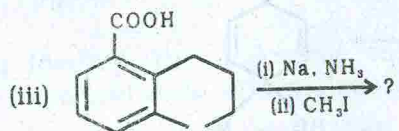
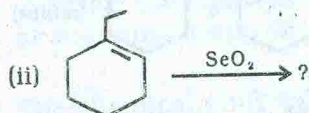




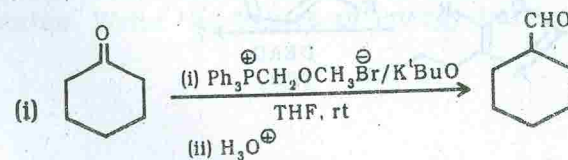
(v)



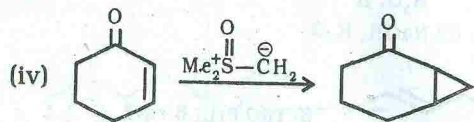
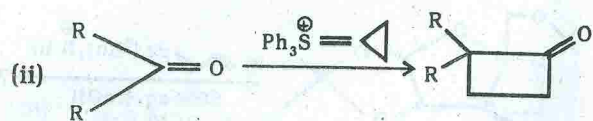
(b) Write the structure of the products (any six) :



(c) Rationalise the following (any two) :

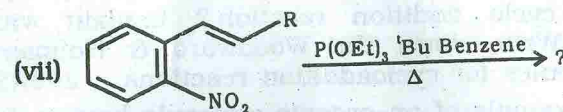
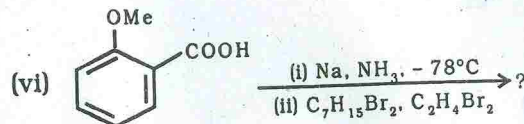
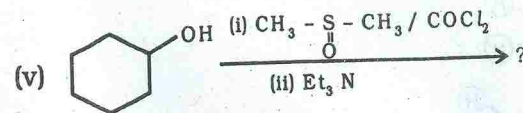
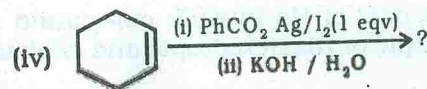
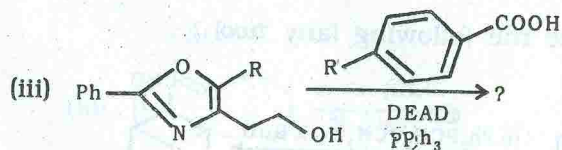
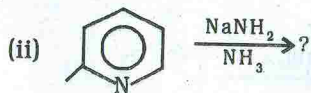
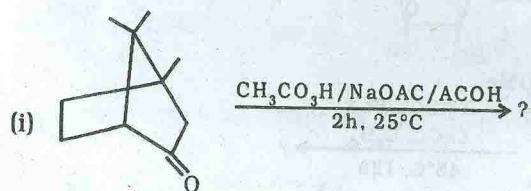






5+6+(2×2)

10. Write the structure of the products with mechanism (any five) :  
5×3



11. (a) Answer the following :

(i) The two isomers of 1, 2-dibromocyclohexane exhibit dipole moments 3.12D and 2.11D. Characterize the isomers and comment on their optical activity. 3

(ii) Predict the product(s) with mechanism : 4

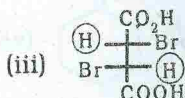
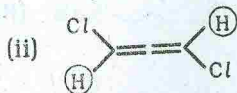
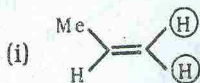
Cis-2-aminocyclohexanol  $\xrightarrow{\text{HNO}_2}$  ?

trans-2-amino cyclohexanol  $\xrightarrow{\text{HNO}_2}$  ?

(b) Draw the torsional curve for the ring reversal of cyclohexane. Show the conformers and transition states. Write the values of energy barrier. 4

- (c) Identify the marked pair of Hs in each compound as homotopic, enantiotopic or diastereotopic and explain :

3



12. (a) What is cyclo addition reaction? Explain with example. Write down the Woodward & Hofmann selection rules for cycloaddition reactions. 2+2×2

- (b) Give an example of an organic molecule having the characteristic feature stated as follows : 1+1

(i) (R) - Enantiomer having a chiral plane.

(ii) Enantiotopic faces : designate them.

- (c) Write the configurational structure of one enantiomer of each of (i) Parf- and (ii) Pref-2, 3,4-triphenylbutanoic acid. 3

- (d) Distinguish the following pairs of compounds from their <sup>1</sup>H NMR Spectra : 2×2

(i)  $\alpha$ - Pinene &  $\beta$ - Pinene ;

