

**OLD**

**2016**

**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.*

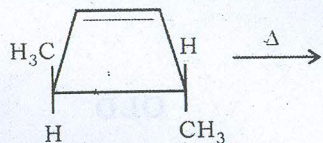
**(Organic Chemistry)**

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

**Group-A**

1. (a) Write the structures of the products expected from both ways of electrocyclic transformation and tell which one is preferred and why?

*(Turn Over)*

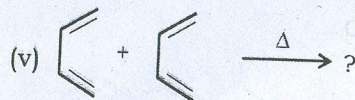
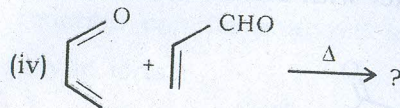
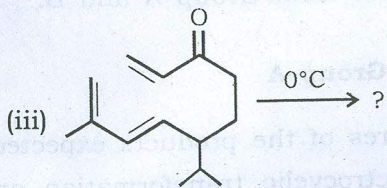
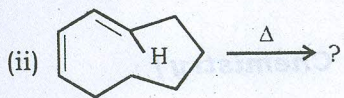
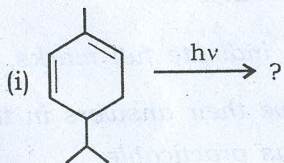


3

(b) Draw a correlation diagram for the transformation of butadiene  $\rightleftharpoons$  Cyclobutene under thermal condition.

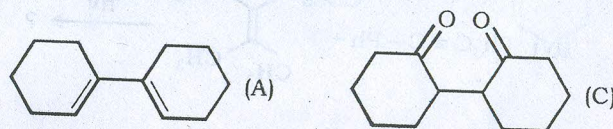
4

(c) Predict the product of the given reactions showing FMO interaction. (any four)



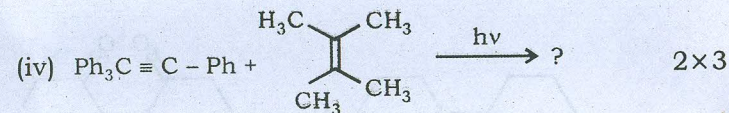
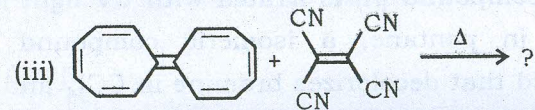
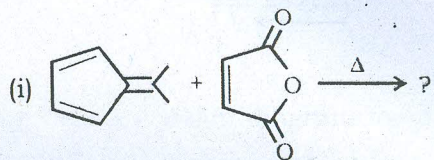
4x2

2. (a) When compound (A) is irradiated with UV light for 115 hours in pentane, a isomeric compound (B) is obtained that decolorizes bromine in  $\text{CCl}_4$  and reacts with ozone to give a compound (C).

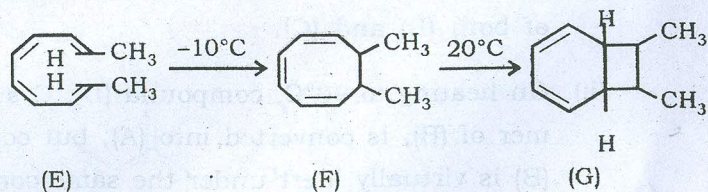


- (i) Give the structure of (B) and the stereochemistry of both (B) and (C). 3
- (ii) On heating to  $90^\circ\text{C}$ , compound (D), G stereoisomer of (B), is converted into (A), but compound (B) is virtually inert under the same conditions. Identify compound (D) and account for these observations. 3

(b) Predict the product with stereochemistry (any three):



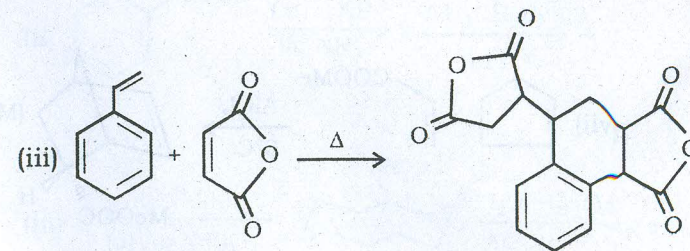
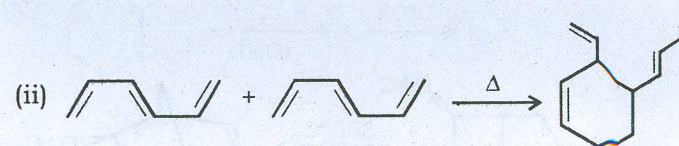
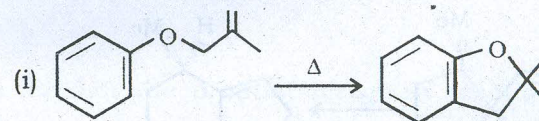
(c) Predict the stereochemistry of compounds (F) & (G).

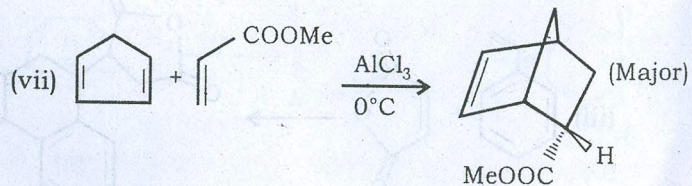
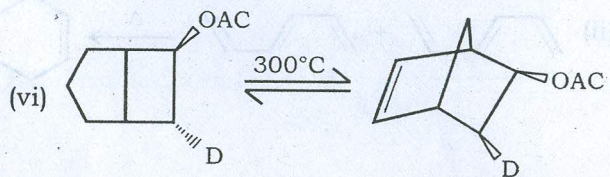
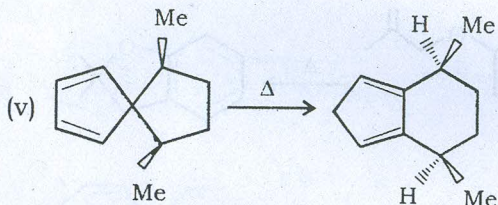
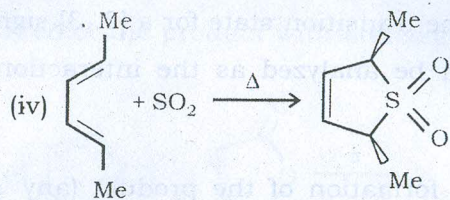


What stereoisomer of (E) also gives compound (G) on heating? 3

3. (a) Show how the transition state for a [3, 3] sigmatropic reaction can be analyzed as the interaction of two allylic ions. 2

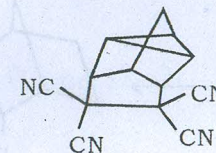
(b) Explain the formation of the product (any six):





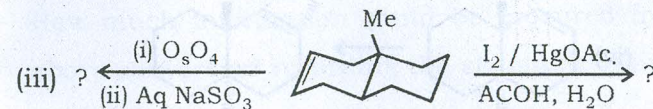
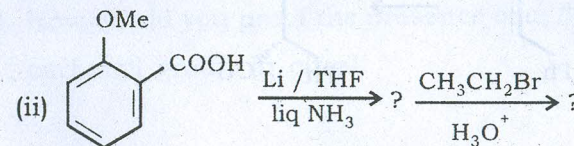
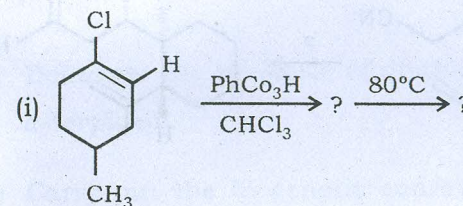
2×6

(c) How would you employ pericyclic reaction in the synthesis of the following :



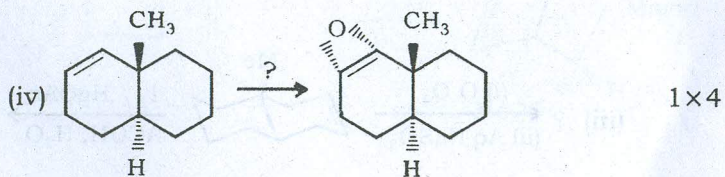
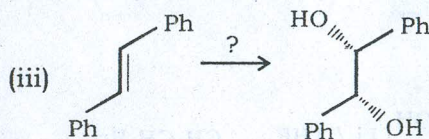
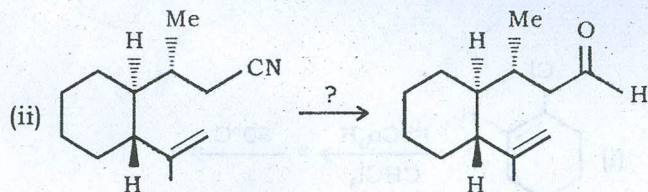
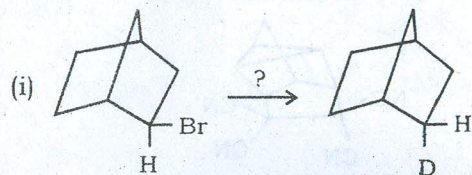
1

4. (a) Predict the product for given reactions.



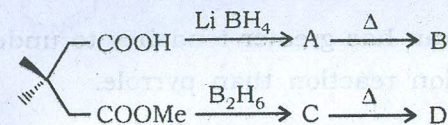
1×6

(b) Supply appropriate reagents in each case.



(c) Phosphonium ylide on reaction with cyclohexanone gives alkene while sulphonium ylide gives an epoxide. Explain. 3

(d) Identify A, B, C and D :



5. (a) Delineate the presence of double bond in the ring of  $\alpha$ -terpineol. 3

(b) Carry out the biogenetic conversion

(i) IPP to Citral (ii) Acetyl CoA  $\longrightarrow$  IPP 3×2

(c) How would you proof the presence of  $\alpha, \beta$  unsaturated carbonyl group in citral. 3

(d) Linalool  $\xrightarrow{H_3O^+}$  Geraniol.

How much information could be procured from the above conversion regarding the structure of linalool? 3

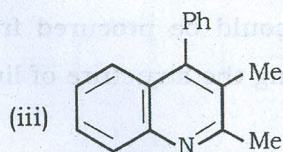
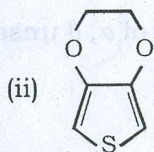
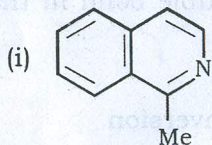
## Group-B

6. (a) Explain the following observation :  $2\frac{1}{2} \times 2$

(i) Indole undergoes electrophilic substitution reaction at 2-position.

(ii) Furan has greater tendency to undergo cycloaddition reaction than pyrrole.

(b) Logically develop the synthesis of the following compounds (any two) :

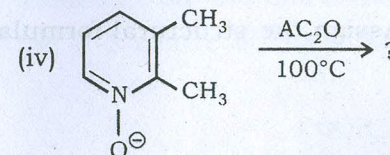
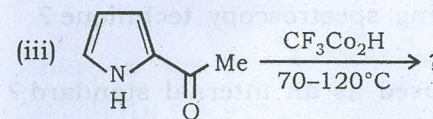
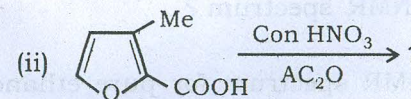
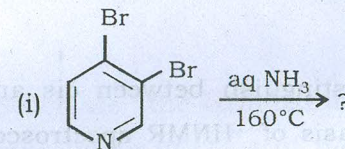


$2 \times 2$

(c) Predict the product(s) with plausible mechanism.

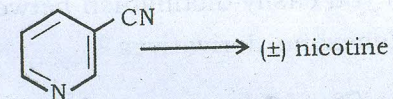
(any three) :

$2 \times 3$

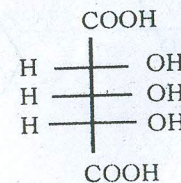


7. (a) Explain why the aromatic protons are more deshielded than the ethylenic protons although both the types of protons are attached to  $sp^2$  hybridised carbon? 2
- (b) How would you distinguish between cis and trans stilbenes on the basis of  $^1\text{H NMR}$  spectroscopy? 2
- (c) Explain why the aldehydic proton appears much down field in the  $^1\text{H NMR}$  spectrum? 2
- (d) Explain the  $^1\text{H NMR}$  spectrum for pure ethanol. 3
- (e) How will you distinguish between p-xylene and mesitylene using spectroscopy technique? 2
- (f) Why TMS is used as an internal standard? 2
- (g) A compound having molecular formula  $\text{C}_{10}\text{H}_{14}$  gave the following  $^1\text{H NMR}$  data : (i) 0.88 (9H, s) and (ii) 7.28 (5H, s). Assign the structural formula to the compound. 2
8. (a) Give an experimental evidence in favor of erythro configuration of ephedrine and threo configurations of  $\psi$ -ephedrine. 4

- (b) Explain the formation of product when ephedrine was subjected to Hoffmann exhaustive methylation. What information was obtained from this experiment. 3+1
- (c) Elucidate the configuration of C-2 of N-methyl pyrrolidine nucleus of nicotine. 4
- (d) Carryout the transformation :

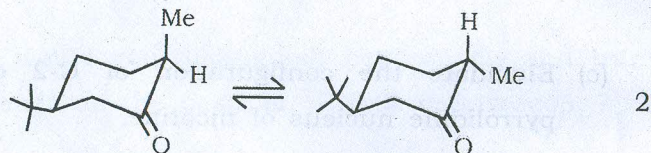


9. (a) What is the designation of erythro isomer of  $\text{CH}_3\text{CH}(\text{D})\text{CHBrCH}_3$  according to pref-part system of nomenclature? 2
- (b) Comment on the chirotopicity and stereogenicity of the C-3 centre of the following compound :

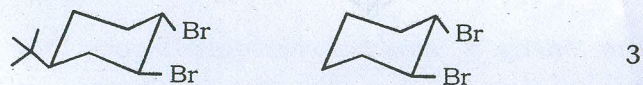


2

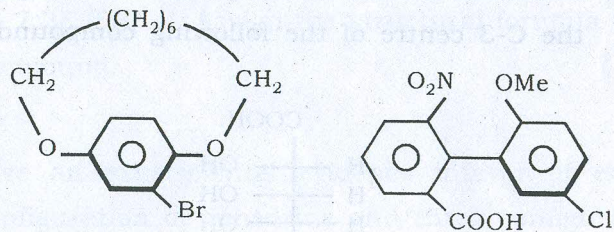
- (c) The energy barrier for following epimerisation is lower in comparison to that in the case of corresponding cyclohexanes. Explain



- (d) How can you easily distinguish between the following two cyclohexane derivatives?



- (e) Explain whether the following compound is chiral or not. Assign 'P' or 'M' descriptor of the following compounds.



2×3

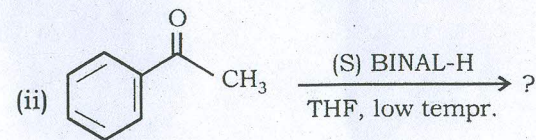
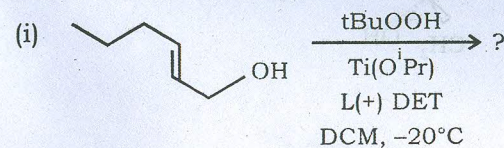
10. (a) Write down the major and minor products in the reaction between PhMgBr and the ester formed by pyruvic acid and (R)-2-octanol. Show proper transition state.

3

- (b) Write down the condition for atropisomerism.

2

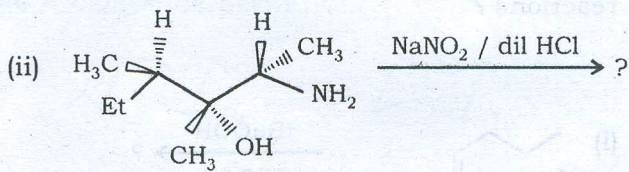
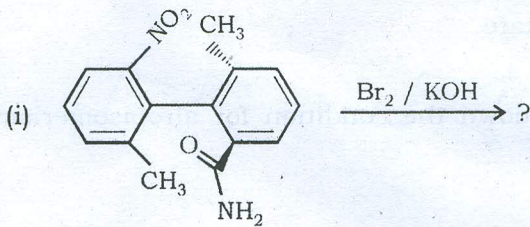
- (c) What is the major product in the following reactions?



2×2



- (d) Write the products of the following reactions and give plausible mechanism in each case.



2×3