

Total number of printed pages-15

14 (CHM-2) CH 202

2019

CHEMISTRY

Paper : CH 202

(Organic Chemistry-2)

Full Marks : 80

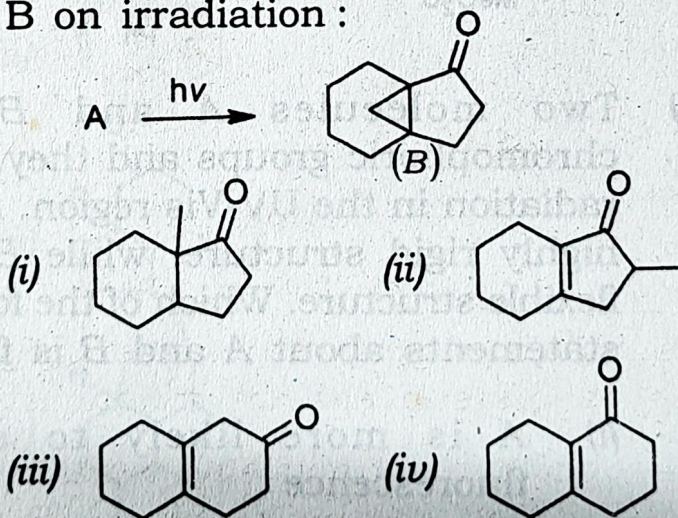
Time : Three hours

The figures in the margin indicate full marks for the questions.

Answer Question No. 1 and
any three from Question Nos. 2-5.

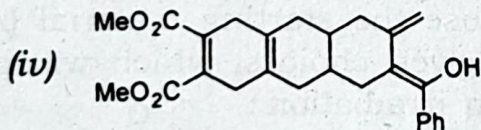
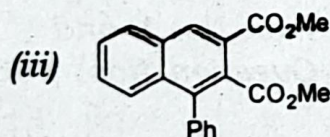
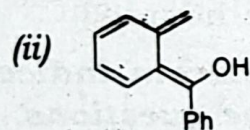
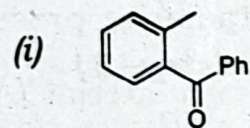
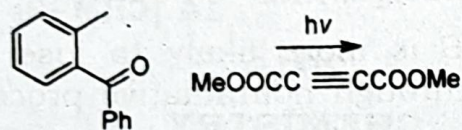
$$5+5\times 3=20$$

1. (a) Choose the starting material (A) from the given choices, which will produce B on irradiation:



Contd.

- (b) Which one of the following products will form in the reaction given below?



- (c) Two molecules *A* and *B* have chromophoric groups and they absorb radiation in the UV-Vis region. *A* has a highly rigid structure, while *B* has a flexible structure. Which of the following statements about *A* and *B* is false?

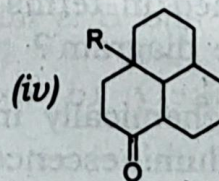
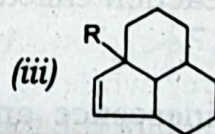
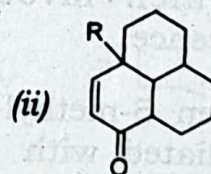
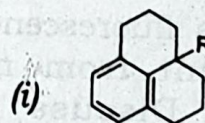
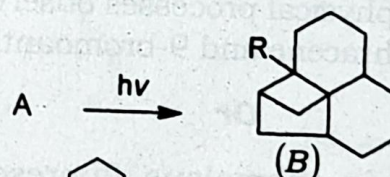
- (i) *A* is more likely to exhibit fluorescence

- (ii) *B* is more likely to exhibit fluorescence

- (iii) *B* is more likely to lose energy through nonradiative processes

- (iv) *A* is less likely to lose energy through nonradiative processes

- (d) Identify the starting material (*A*) from the given choices which forms (*B*) on irradiation with UV-Vis light:



- (e) A compound (A) having a chromophoric group undergoes a transition from S_0 to S_1 state. The λ_{max} for the transition is 320 nm and ϵ value is 100. With these information fill in the blank given below :

The transition from S_0 to S_1 is an example of _____ transition. $1 \times 5 = 5$

2. (a) Compare and discuss the radiative photophysical processes observed in case of anthracene and 9-bromoanthracene. 3

Or

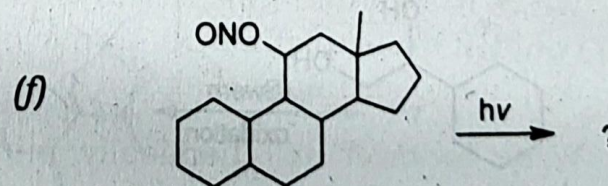
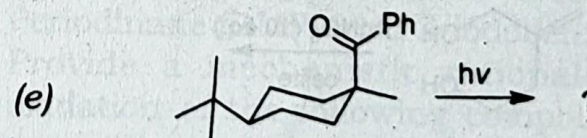
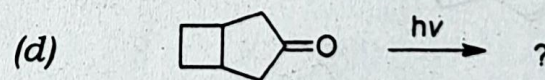
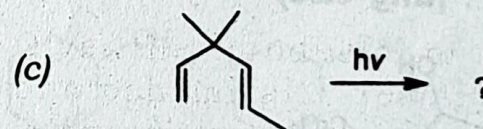
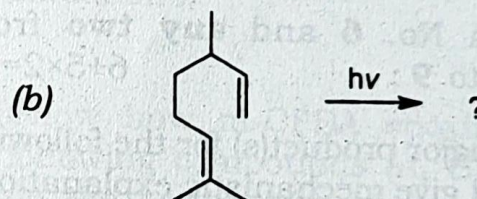
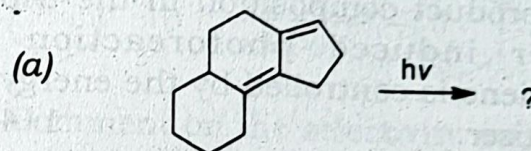
What is anomalous fluorescence and how is it different from normal fluorescence? Discuss the circumstances which favour the anomalous fluorescence.

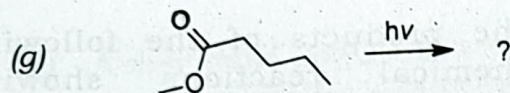
- (b) What happens when 5-methyl-hex-3-ene-2-one is irradiated with UV-Vis light? Why is this reaction called a case of optical pumping? 2

3. (a) What is chemiluminescence and how could it be explained in terms of the reaction coordinate diagram? 2

- (b) Write in brief on chemically initiated electron exchange luminescence. 3

4. Give the products of the following photochemical reactions showing intermediates wherever applicable :
(any five) $1 \times 5 = 5$

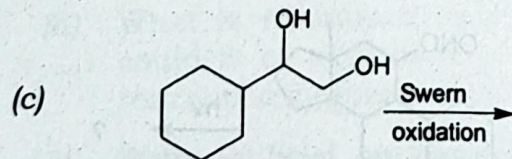
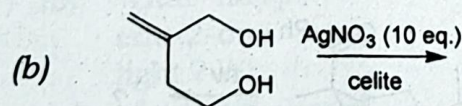
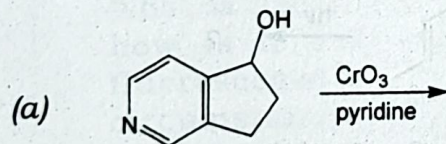




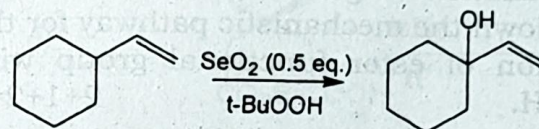
5. What is a photosensitized reaction? Discuss how the product composition in the triplet sensitizer induced photoreaction of 1,3-butadiene is controlled by the energy of the sensitizer. 1+4=5

Answer Question No. 6 and **any two** from Question Nos. 7 to 9: 6+5×2=16

6. Identify the major product(s) for the following reactions and give mechanistic explanations for the same: (**any two**) 3×2=6

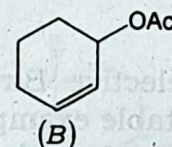
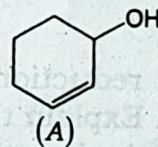


7. Provide a mechanistic rationale for the following oxidation reaction:

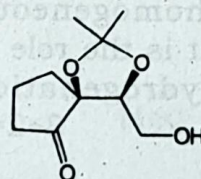


Comment on the selectivity aspects for SeO_2 oxidations. 3+2=5

8. Show how m-CPBA epoxidations for the following compounds (A, B) are dependent on the nature of substituent(s): 5



9. How do you synthesise Dess-Martin Periodinane (DMP) from 2-iodobenzoic acid? Provide a mechanistic rationale for the oxidation of the following compound: 3+2=5



10. Describe the stereochemistry of reduction of carbonyl compounds with transfer hydrogenation reagents. What is DIBALH? Write down the mechanistic pathway for the reduction of ester functional group with DIBALH. 2+1+2=5

Or

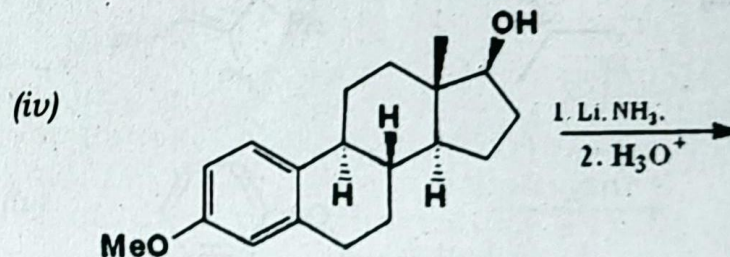
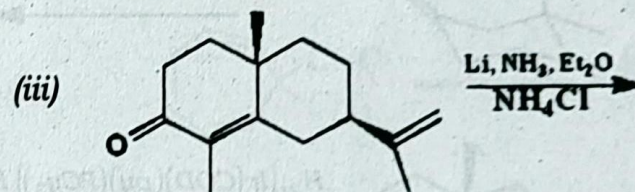
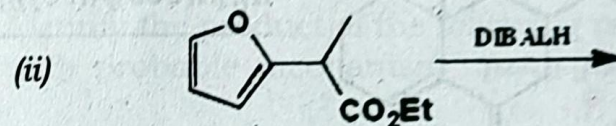
What is Lindlar's catalyst? Describe the stereochemistry of reduction of alkynes with Lindlar's catalyst. How can you stereoselectively reduce alkynes to trans olefins? 1+2+2=5

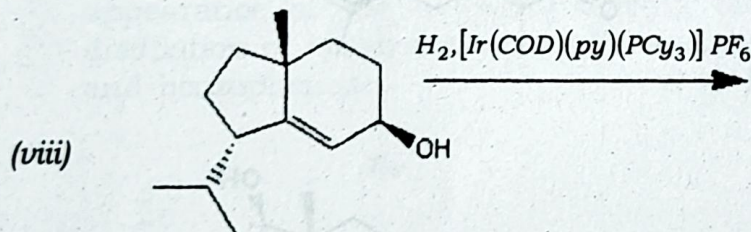
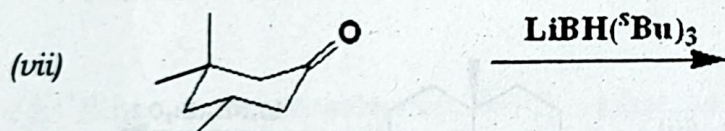
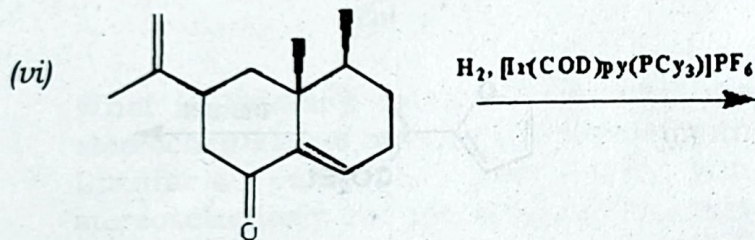
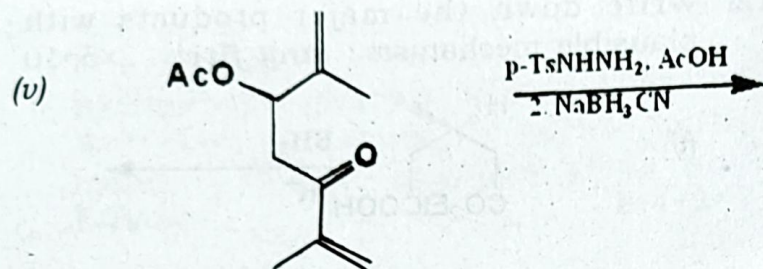
11. What is stereoselective Birch reduction? Describe with suitable example. Explain the appearance of purple colour during the distillation of tetrahydrofuran with sodium and benzophenone. 3+2=5

Or

Explain the structure and mechanism of reduction of important homogeneous hydrogenation catalyst. What is the role of BINAP in asymmetric hydrogenation reaction? 3+2=5

12. Write down the major products with plausible mechanism: (*any five*) 2×5=10



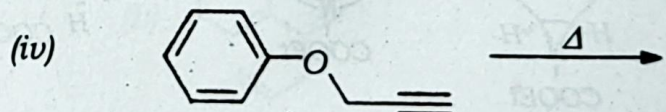
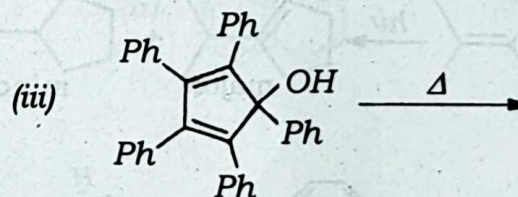
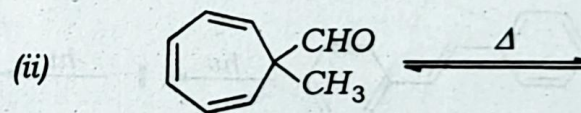
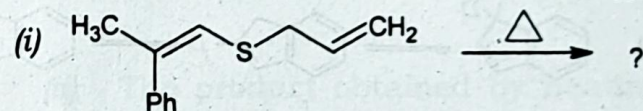


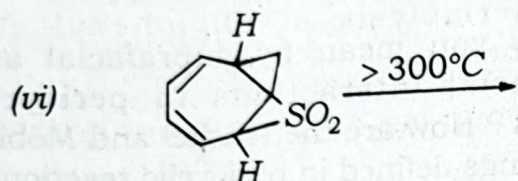
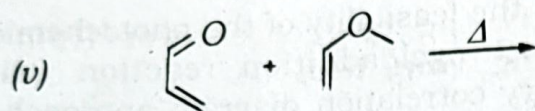
13. Discuss the feasibility of the photochemical $\pi 2S + \pi 4S$ cycloaddition reaction using symmetry correlation diagram approach. 4

14. What do you mean by suprafacial and antarafacial interactions in pericyclic reactions? How are the Hückel and Möbius type of rings defined in pericyclic reactions? Discuss using suitable examples. $2+2=4$

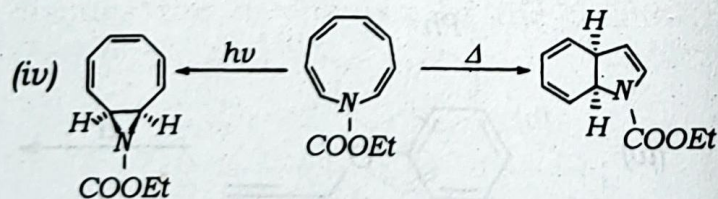
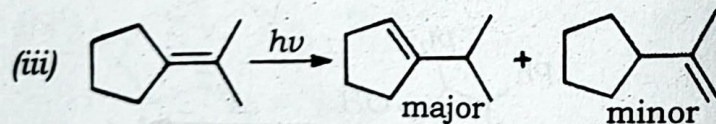
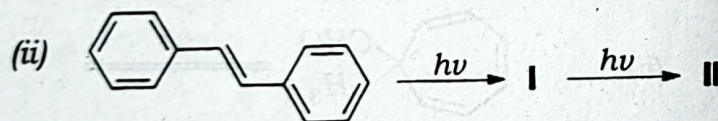
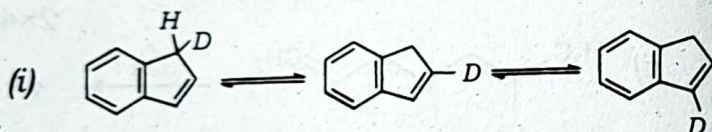
15. Identify the product of the following reactions with probable mechanism: (**any four**)

$2 \times 4 = 8$





16. Identify the product wherever applicable and discuss the mechanism of the following reactions : **(any two)** 3×2=6

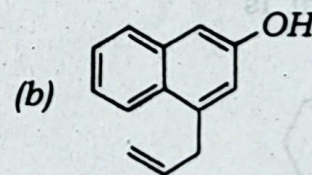
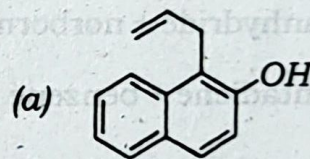


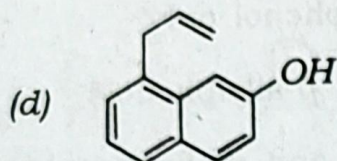
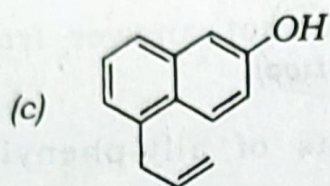
17. Identify the correct answer from the following : **(any two)** 1×2=2

(i) Thermolysis of allylphenyl ether generates

- (a) *o*-allylphenol only
- (b) *o*- and *p*-allylphenols
- (c) *o*-, *m*- and *p*-allylphenols
- (d) *m*-allylphenol only

(ii) The product obtained by heating allyl ether of 2-naphthol is





(iii) Which one of the following Diels-Alder reactions is feasible ?

- (a) Maleic anhydride + ethene
- (b) Maleic anhydride + cyclopentadiene
- (c) Maleic anhydride + norbornadiene
- (d) Cyclopentadiene + benzene

(iv) Among the following dienes, the one that undergoes a degenerate Cope rearrangement is

