

Duration: 2 ½ Hrs.

Total Marks: 60

Instructions:

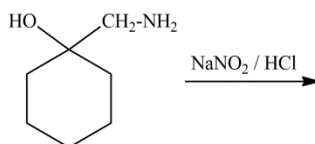
(1) All questions are compulsory.

(2) Figures to the right indicate full marks.

Q. 1 (a) Attempt any two of the following: 08

(i) Explain molecular orbital basis for the  $\alpha$ -effect.

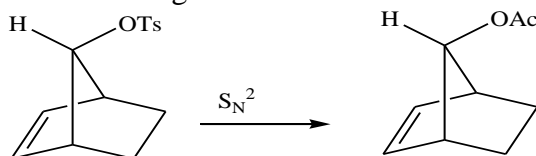
(ii) Predict the product formed in the following reaction and suggest a possible mechanism.



(iii) Give reaction for generating aryne from (I) Phthalic anhydride (II) 1-aminobenzotriazole  
What is the action of the following on benzyne?

(I) Anthracene (II) Furan

(iv) Explain the following reaction with mechanism:



(b) Attempt any one of the following: 04

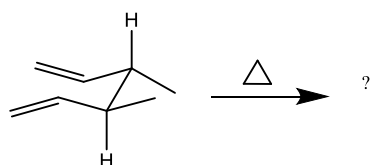
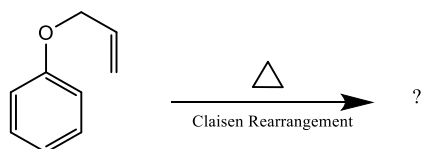
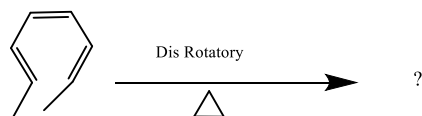
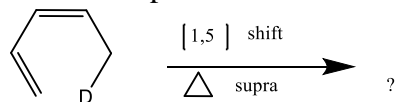
(i) Explain any four features of Pericyclic reactions with suitable examples.

(ii) Draw the molecular orbitals of 1,3,5-hexatriene and comment upon their symmetry properties.

Q. 2 (a) Attempt any two of the following: 08

(i) What are the ENE-reactions? Explain with any two suitable examples.

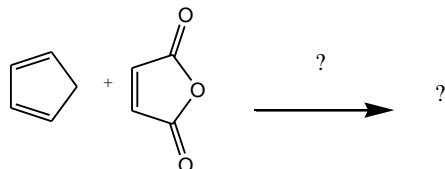
(ii) Predict the products in following reaction:



- (iii) Explain regioselectivity & Peri-selectivity in pericyclic reactions with suitable examples.
- (iv) Explain symmetry approach in the ring closer reaction of 1,3 – Butadiene using correlation diagram approach.

(b) Attempt any one of the following: 04

- (i) Complete the following reaction & explain the stereochemistry involved.



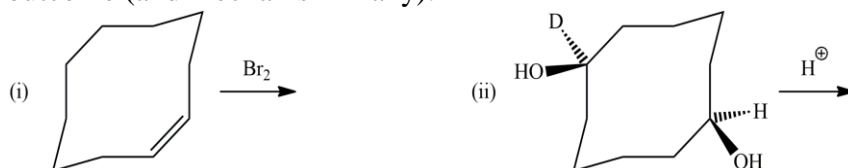
- (ii) Give the synthesis of Citral using pericyclic reactions.

Q. 3 (a) Attempt any two of the following: 08

- (i) Assign the point groups to the following molecules:  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_4$ , staggered ethane and  $\text{CHCl}_3$
- (ii) Discuss the conformational features of cyclodecane ring system.
- (iii) Explain the stereochemistry and stability of hydrindane.
- (iv) “Dehydrochlorination of menthyl chloride is slower than neomenthyl chloride.” Explain this observation.

(b) Attempt any one of the following: 04

- (i) Complete the following reactions with their appropriate stereochemical outcome (and mechanism if any): -



- (ii) Draw all the diastereomers of perhydroanthracene and comment on optical activity of each diastereomer.

Q. 4 (a) Attempt any two of the following: 08

- (i) What are photochemical quenchers? Discuss the principle involved in photoquenching process.
- (ii) Discuss the cleavage of a bond  $\beta$  to the carbonyl group in photochemical reactions of ketones with a suitable example.
- (iii) Explain the mechanism of di- $\pi$  methane rearrangement.
- (iv) Explain the two examples of the following reactions with mechanism: -  
I) photodimerisation reaction  
II) 1, 4 addition reaction of arenes

(b) Attempt any one of the following: 04

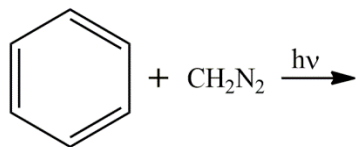
- (i) What is Paterno-Buchi reaction? Give its mechanism and stereochemical consequences.
- (ii) Explain the process of chemiluminescence with examples.

Q. 5

Attempt any four of the following:

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- (i) Draw the molecular orbitals of allyl system and ethylene. Comment upon their symmetry properties.
- (ii) Explain structure of carbene. Predict the product/s of following reaction.



- (iii) What are Chelotropic reactions? Explain with suitable examples.
- (iv) Define Retro – Diels-Alder reaction. Explain the effect of substituents in Diels-Alder reaction.
- (v) Explain I strain concept with examples.
- (vi) Explain Bredt's rule with two examples.
- (vii) What is Photo-Fries rearrangement? Give examples.
- (viii) Write a note on photo-oxygenation reactions.

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