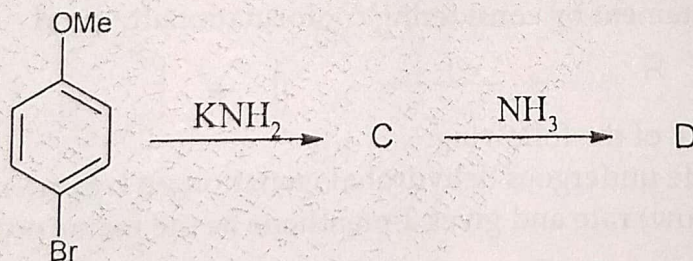
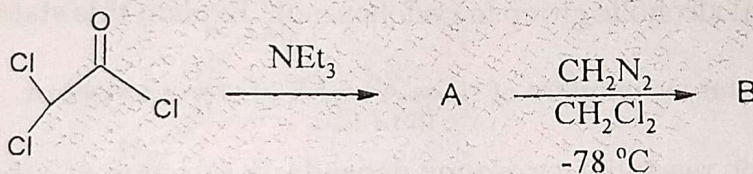


[Time: 2½ Hours]

[ Marks: 60]

- N. B. 1. All Questions are compulsory.  
2. Figures to the right indicate maximum marks.

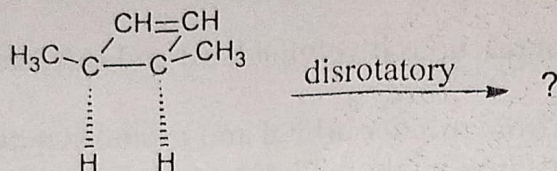
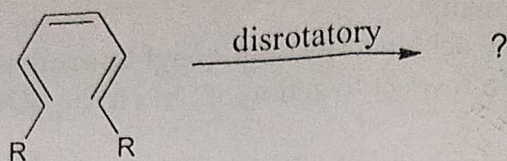
1. (a) Attempt any two of the following: 08
- (i) Stability of carbocation is also achieved through neighbouring group effect. Explain the above with respect to action of  $\text{SbF}_5$  in liq  $\text{SO}_2$  on  $p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Cl}$ .
- (ii) Write mechanism of any rearrangement which involves nitrene intermediate.
- (iii) Explain the role of FMO in reactions involving hard and soft nucleophiles and electrophiles.
- (iv) What do you understand from frontier orbital and orbital symmetry? Explain with diagrammatic presentation. Illustrate what happens when a molecule/ion is exposed to suitable wavelength of light?
- (b) Attempt any one of the following: 04
- (i) Complete the following reactions by identifying A, B, C and D. Give the reaction intermediates generated.



- (ii) Explain molecular orbital basis for the  $\alpha$ -effect. 08
2. (a) Attempt any two of the following:
- (i) Discuss site selectivity of Diels-Alder reaction.
- (ii) Explain FMO approach towards cyclization of  $4n\pi$  system.
- (iii) Account for 1,3-dipolar cycloaddition with a suitable example.
- (iv) What is oxy-Cope and aza-Cope rearrangement reactions? Explain with mechanism the preparation of carbonyl compounds from Cope rearrangement.



- (b) Attempt any **one** of the following:
- (i) Explain the synthesis of citral using pericyclic reaction.
- (ii) On the basis of FMO method, explain the following reactions -



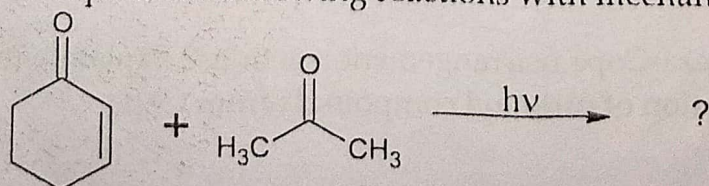
- Q. 3 a) Attempt any **two** of the following:
- i) Draw the conformations of cyclooctane and discuss the evidences in favour of its most stable conformation.
- ii) 'Chromic acid oxidation of an axial alcoholic group is faster than that of an equatorial alcoholic group in cyclohexanol.' Explain this statement.
- iii) Explain the stereochemistry of rings A and B of steroid system.
- iv) Conformation reactivity correlation depends on selection of substrate. Explain this statement by considering conformationally rigid diastereomers.

- b) Attempt any **one** of the following:
- i) Menthyl chloride undergoes dehydrohalogenation on treatment with base at a sluggish (slow) rate and gives 2-menthene as the major product. Explain.

Acetolysis of cis-4-tert. butylcyclohexyltosylate is faster than trans-isomer under  $S_N1$  conditions. Explain.

- ii) Draw the chair conformers of decalin and discuss their symmetry.

- Q. 4 (a) Attempt any **two** of the following:
- (i) Complete the following reactions with mechanism.

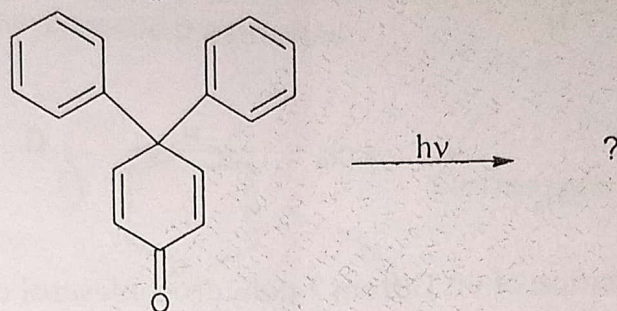




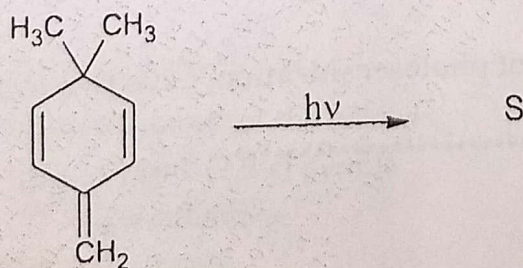
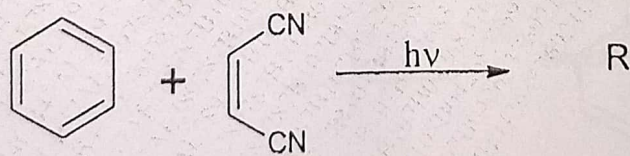
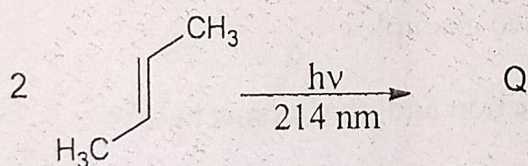
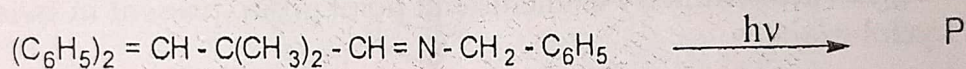
- (ii) Explain the photochemistry of Barton reaction.
- (iii) What are photochemical quenchers? Explain the principle involved in photoquenching.
- (iv) Discuss the cleavage of a bond  $\beta$  to the carbonyl group in photochemical reactions of ketones. Give mechanism.

(b) Attempt any **one** of the following:

- (i) Predict the products and give the mechanism-



(ii) Complete the following reactions and identify the products:



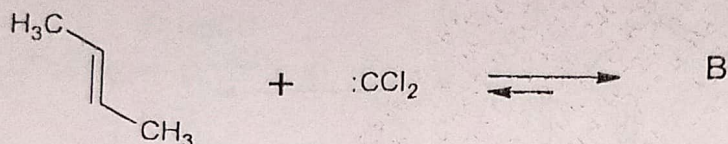
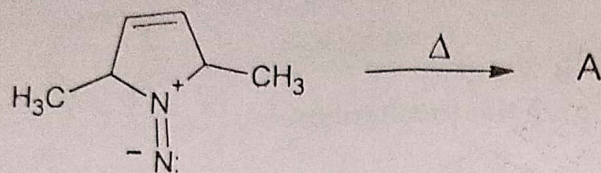
Q. 5

Attempt any **four** of the following:

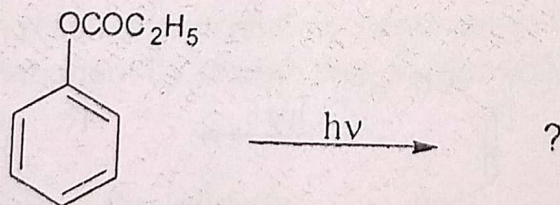
- (a) Write a note on periselectivity with suitable examples.
- (b) The rate of solvolysis (acetolysis) of the cis and trans - isomers of 2-acetoxycyclohexyl fosylate differ by a factor of about 700, the trans-compound being more reactive, explain.



- (c) What is cheletropic reactions?  
Complete the following reactions and identify A and B.



- (d) Discuss formation of vit D from 7-dehydrocholesterol using pericyclic reaction.
- e) Suggest the symmetry elements and point group present in twist-boat cyclohexane.
- f) Explain Brecht's rule with two examples.
- g) Complete the following reaction and give its mechanism.



- h) Define and give mechanism of photosensitization. Give two examples.

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