[This question paper contains 4 printed pages]

Roll No.	

ASME-23B-CHEM-II

CHEMISTRY (Paper-II)

Time Allowed : Three Hours	Maximum Marks: 100

QUESTIONS PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions:

1. Question paper consists of **EIGHT** questions printed in English.
2. Candidate has to attempt **FIVE** questions in all.
3. **Question No. 1 is compulsory.**
4. Out of the remaining **SEVEN** questions, **FOUR** questions are to be attempted.
5. All questions carry equal marks, i.e. **20 marks**.
6. Each question has **FOUR** parts (**a, b, c, d**). Marks carried by each part (**a, b, c, d**) of a question are equally distributed.
7. Each part of the question must be answered in sequence and in the same continuation.
8. Write answer in legible handwriting.
9. Unless otherwise mentioned, symbols and notations carry their usual standard meanings.
10. Assume suitable data, if considered necessary, and indicate the same clearly.
11. Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partially.
12. Any page or portion of the page left blank in answer book must be clearly struck off.
13. Re-evaluation / Re-checking of an
14. Answer book of the candidate is not allowed.

1. (a) An organic compound with molecular formula $C_9H_{10}O_2$ gave following spectral informations. Predict the structure of the compound.

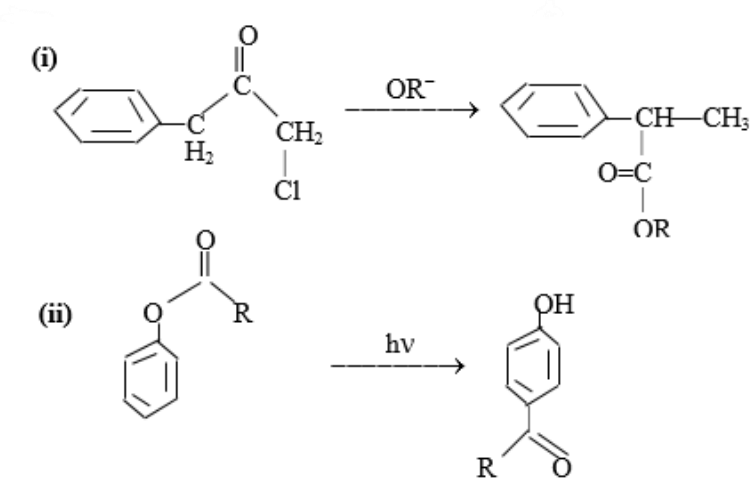
^1H NMR ($CDCl_3$): δ7.22, S(5); δ 5.0, S(2); δ 1.96, S(3).

IR (CCl_4) bands at 1745 cm^{-1} (Inst); large broad band at 1225 cm^{-1}; two intense bands at 749 and 697 cm^{-1}.

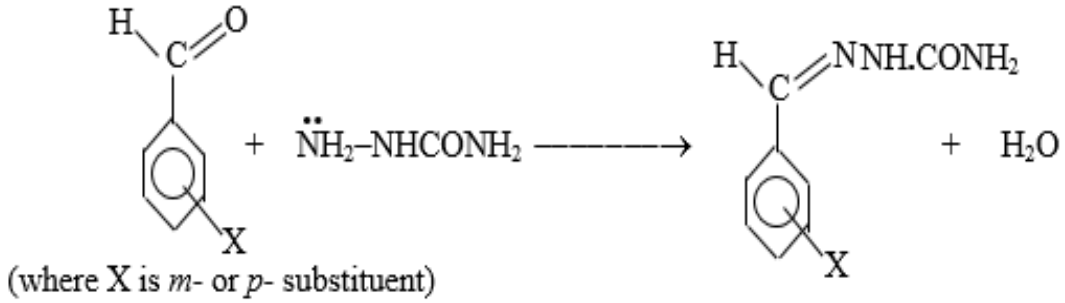
Mass spectrum (M/Z) 150 (29); 108 (100); 91 (75); 43 (72).

UV λ_{max} EtOH, 264 E_{max} 158; 257 E_{max} 194.

(b) Write name and mechanism of the following reactions:



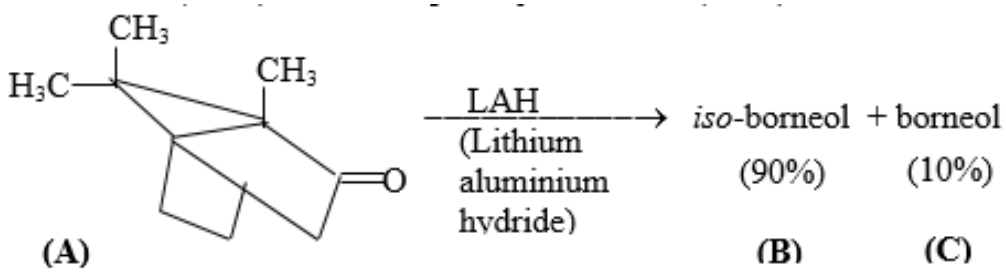
(c) **(i)** Substituted benzaldehyde reacts with semicarbazide to form the corresponding semicarbazone:



(where X is *m*- or *p*- substituent)

This reaction undergoes in two steps and rate was found to vary with pH. Find out the rate determining and rate limiting steps in the above reaction. Justify answer with reaction mechanism.

(ii) In the reduction of camphor (A) with LAH as reagent, why the product is predominantly *iso*-borneol (90 %) with little quantity of borneol (10 %)?



(d) Explain how do you account for the following facts:

(i) Cryptate salts are good phase transfer catalyst as compared to simple salts.

(ii) Of thermal cycloaddition [4+2] is easy and [2+2] is difficult, whereas [2+2] photochemical cycloaddition is easy.

2. (a) Predict the sequence of steps and mechanism involved in the conversion of 3-chloroaniline to 5-chloroquinoline by Skraup's synthesis.

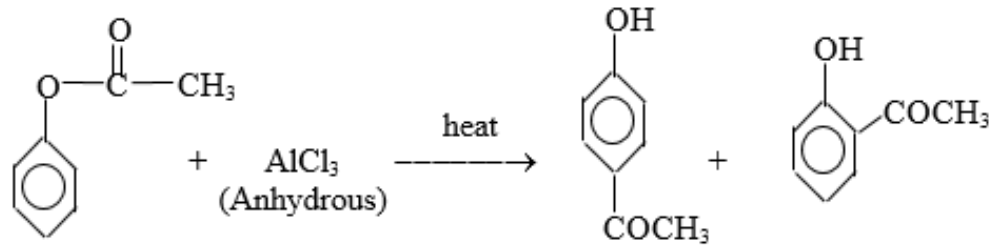
(b) Provide an explanation for the following statements:

(i) Cyclooctatetraene is a tub shaped molecule.

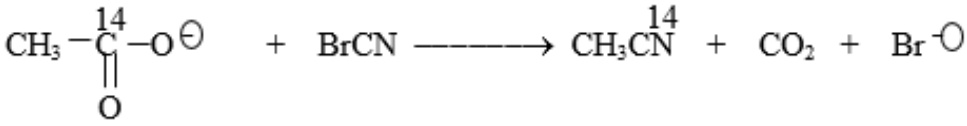
(ii) Dipole moment of Azulene ($C_{10}H_8$) is 1.08D, whereas Naphthalene ($C_{10}H_8$) has zero dipole moment.

(c) Rationalise the formation of the product(s) and explain the mechanism of the following reactions:

(i)



(ii)

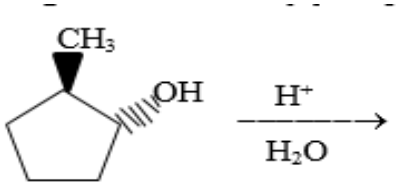


(Carbon is isotopically labelled)

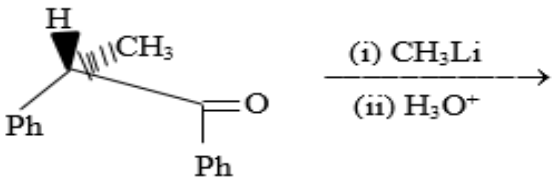
(d) Explain Woodword-Hoffmann rules and the terns – symmetry allowed and symmetry forbidden – associated with it.

3. (a) Predict the stereochemistry of the major product (wherever applicable) in the following reactions. Justify your prediction.

(i)



(ii)



(b) Explain and substantiate the followings:

(i) Pyridine is less reactive than benzene towards electrophiles.

(ii) 2-bromoaniline reacts with amide ion in ammonia but 2-bromo-3-methylanisole does not.

(c) A compound 'A' with molecular formula C_8H_8O on reduction with $NaBH_4$ gives compound 'B' which on treatment with $KHSO_4$ / Cu powder gives compound 'C'. Identify these compounds on the basis of the spectral data given below:

Compound 'A':- IR: 1690, 1600, 1585 cm^{-1}

UV: 246, 278, 310 nm

Mass spectrum (m/z peak): 51, 77, 105 (base peak),

120 (molecular ion peak)

Compound 'B':- IR: 3640, 1486, 1080 cm^{-1}

NMR: 7.16 (5H, s), 4.62 (1H, quartret)

1.25 (3H, d)

Compound 'C':- UV: 248, 282, 291 nm

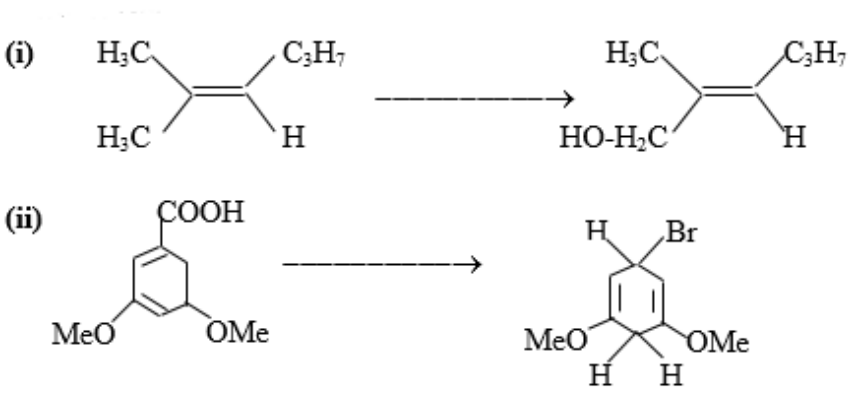
NMR: 7.0 (5H, d), 6.14 (1H, quartret) 5.97 (2H, triplet)

(d) Explain the types of bonding involved in supramolecules. What types of guest would crown ether be able to bind? Justify answer with appropriate illustrations.

4. (a) A catalogue of scientific equipment stated as – "Plastic Tubing: Polythene. Natural grade, medium wall, tough and flexible. Can be manipulated by softening in hot water."

Does this mean that polythene is a thermosetting polymer? What does it suggest about the glass transition temperature of polythene?

(b) Indicate the reagent(s) and reaction conditions for carrying out the following transformations:



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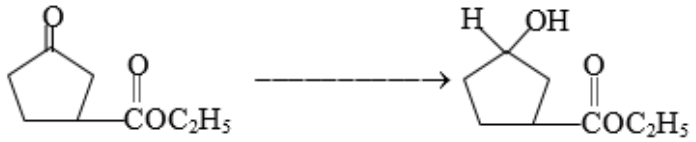

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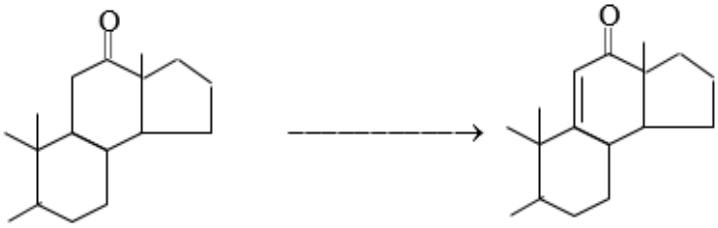

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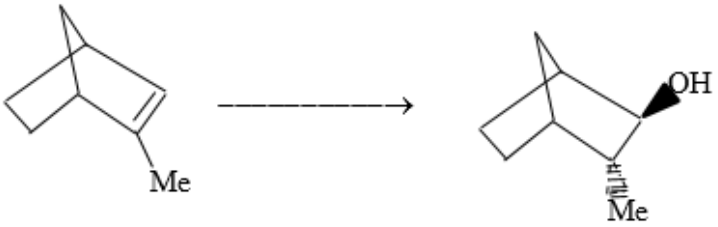
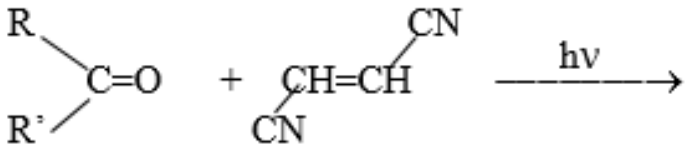
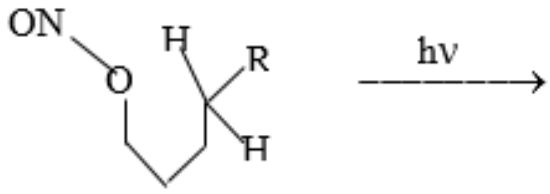


(c) Identify the product(s) and the name of the following photochemical reactions. Write the reaction mechanism also.

(i)



(ii)



(d) Describe the principle of phase transfer catalysis (PTC) with suitable examples.

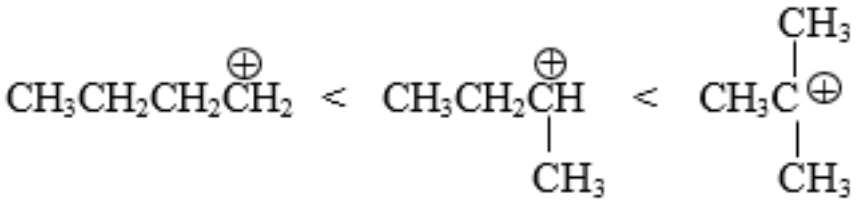
5 **(a)** Explain the mechanism of the following rearrangements:

(i) Beckmann (rearrangement) reaction

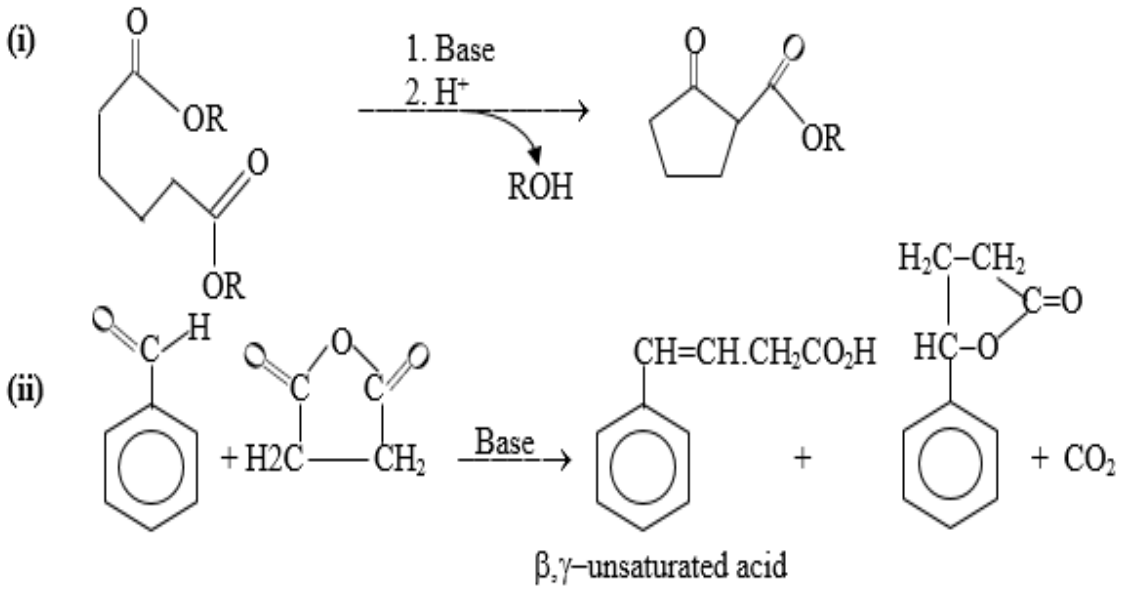
(ii) Baeyer-Villiger (rearrangement) reaction

(b) **(i)** How would you distinguish position isomers: 2-pentanone and 3-pentanone using mass spectroscopy and NMR?

(ii) Account for the order of stability of carbonium ions:

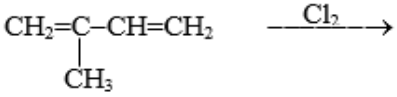


(c) Write name of the following reactions and explain the reaction mechanism:



(d) **(i)** What are the sigmatropic changes? Explain giving one example each.

(ii) Predict product(s) with their structural formula in the reaction of isoprene with chlorine. Explain the reaction mechanism.

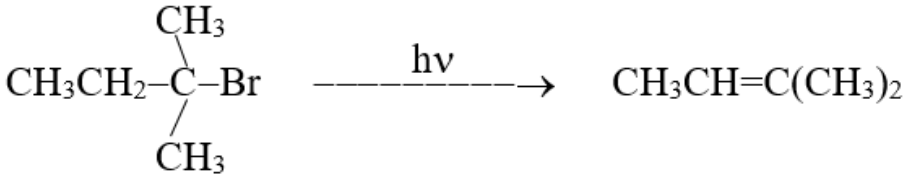


6. **(a)** **(i)** Show diagrammatically the Frontier–Orbital (FMO) and Hückel–Möbius (PMO) methods of cycloadditions.

(ii) Explain which of the two is a better leaving group – phenoxide ion or ethoxide ion?

(b) Write mechanism of the following reactions and indicate which rule – Saytzeff or Hoffmann – is followed by the substrate in these reactions?

(i)



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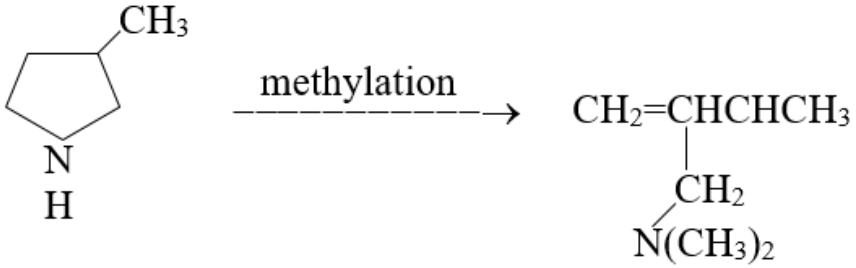
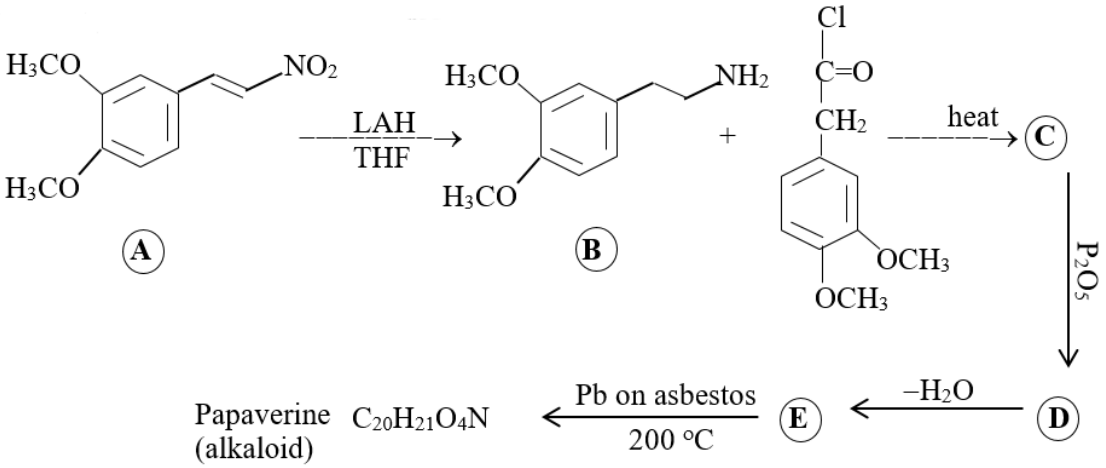


(c) Complete the following reaction of an alkaloid (papaverine) synthesis. Explain the mechanism and write name of the reaction.

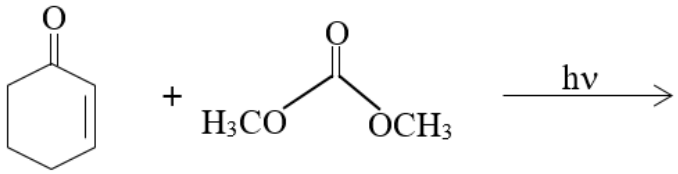


(d) With reference to commercial polymers, what are silicons and fire retardant polymers? Explain their synthesis.

7. (a) Taking suitable example, predict the difference between addition reactions on a C=C double bond and C=O double bond. Explain the stereochemistry of addition.

(b) Predict the product(s) (major and minor – wherever applicable) of the following photochemical reactions. Write reaction steps involved in each of these reactions.

(i)



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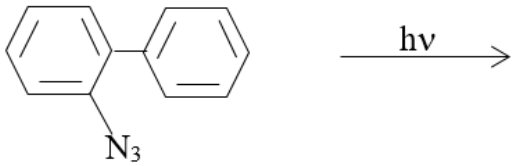

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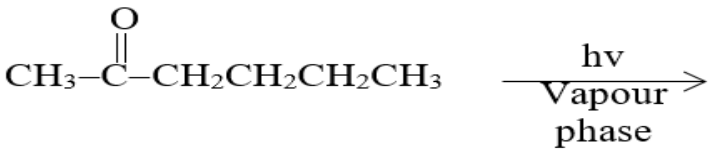

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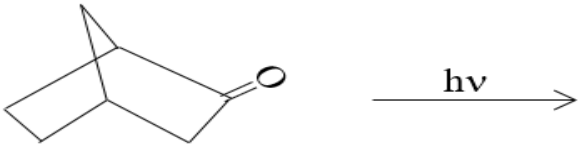

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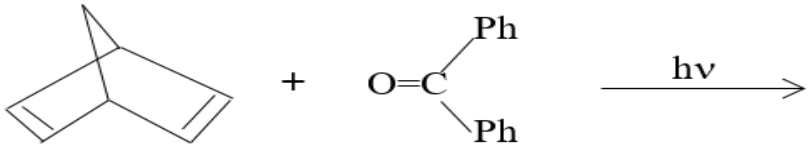
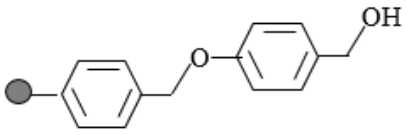


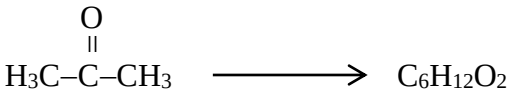
(c) **(i)** An important resin is used in combinatorial chemistry (shown below):



Identify the resin and what are the conditions used to cleave a molecule from this resin?

(ii) "Prevention of waste or by product is one of the principles of green chemistry." Explain with appropriate example.

(d) Compound 'A' was obtained by the aldol condensation of acetone on treating with NaOH and refluxing.



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The spectral data of compound 'A' are observed as:

UV: λ_{max} 283 (ε=27)

IR: 3300, 1705 cm^{-1}

^{1}H NMR: δ 1.25 (s, 6H); 2.3 (s, 3H)

2.7 (s, 1H); 3.7 (bs, exchanges with D_2O)

^{13}C NMR: 28 (q); 32(q); 54(t); 68(s) ppm

MS: shows significant ions at m/z 99, 84, 58, 43.

Interpret above data to assign structure to the compound 'A' and explain the reaction mechanism.

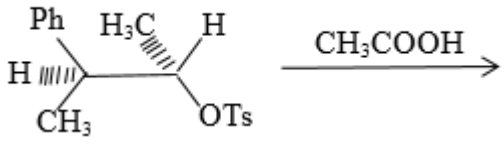
8. **(a)** Compare the radical and the ionic mechanisms of the formation of polymers.

(b) "Electrocyclic reactions are stereospecific. Their stereochemistry depends on the number of double bonds in polyethene whether the reaction is thermal or photochemical." Substantiate the statement.

(c) **(i)** Why benzophenone is a good triple sensitizer? Give at least two reasons to justify your answer.

(ii) Explain various types of electronic excitation found in most of the organic molecules which are brought about by the action of visible or ultraviolet light. Show diagrammatically also and cite examples for each type.

(d) **(i)** The acetolysis of the following tosylate affords an optically pure erythro acetate. Write structure of the product(s) and explain the mechanism of the reaction.



(ii) Write name of the following reaction and explain the reaction mechanism.