

UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL I) SEMESTER- I  
EXAMINATIONS APRIL/MAY 2021

SUBJECT: CHEMISTRY

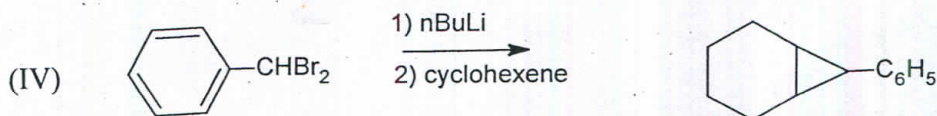
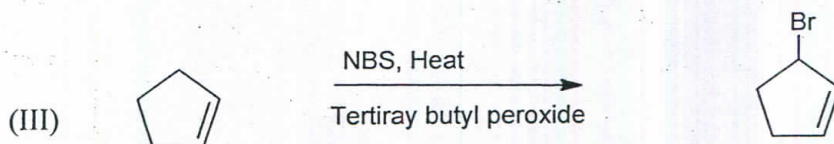
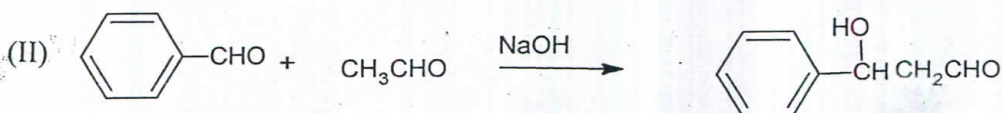
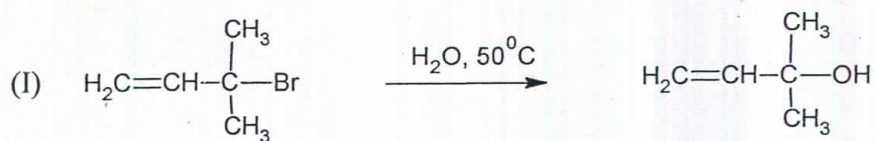
COURSE UNIT: CHE 4123 : Reactive Intermediates &  
Advanced Organic Reaction Mechanisms

TIME: Three (03) hours

Answer all questions.

01. Answer all parts

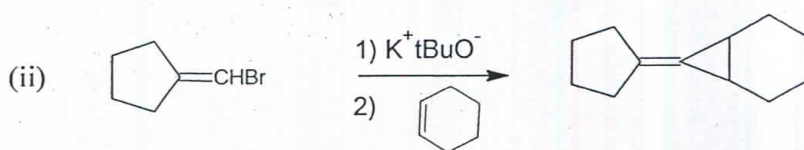
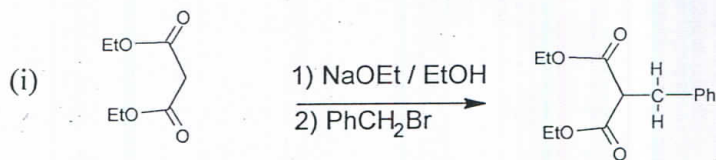
(a) Consider the reactions given below,



- (i) Draw the structure of the intermediate formed in each of the reaction.  
(ii) Explain the stability of the intermediate proposed using appropriate structures.

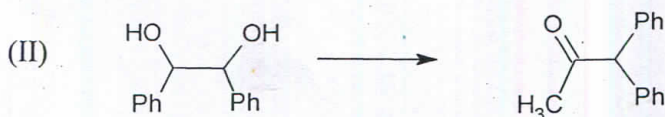
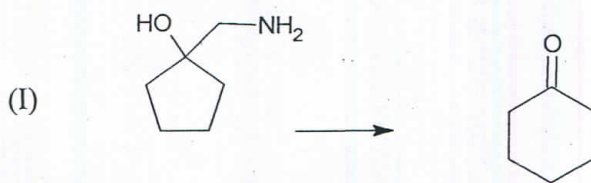
( 40 marks)

(b) Give a plausible mechanism for each of the following transformations.  
 (note: reactive intermediate of each reaction need to be highlighted)



(28 marks)

(c) Consider the reactions given below.



(i) What is the structure of the reactive intermediate(s) required to generate in order to perform each of the above transformation?

(ii) Giving necessary reagents show how you would carryout each of the transformations through the intermediate you proposed (note: highlight main steps of the mechanism).

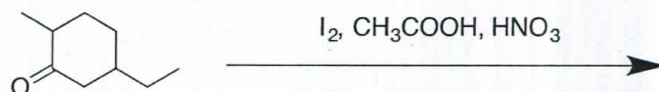
(32 marks)

02. Answer all parts.

- (a) "S<sub>N</sub>2 or S<sub>N</sub>1 type mechanisms does not work for nucleophilic aromatic substitutions"
- Explain the above statement by drawing appropriate intermediates of benzene.
  - Name the two mechanisms possible for nucleophilic aromatic substitution reactions.
  - Draw the appropriate reactive intermediates forming in the two mechanisms mentioned in the part (ii).

(22 marks)

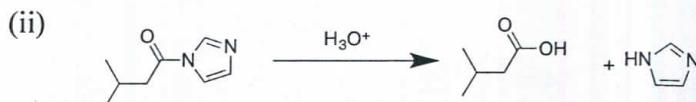
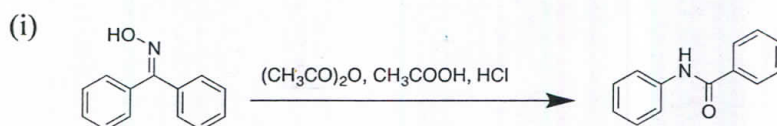
- (b) Consider the halogenation reaction of the following compound with the given reagents.



- Give the two possible reaction intermediates and the products formed during the reaction with the given set of reagents.
- Giving reasons, predict the major product formed with the given reagents.
- If the reaction happens under strong basic conditions (using LDA as the base) draw the possible reaction intermediates form.
- Giving reasons state whether the major product remains the same or different when the medium is acidic.

(30 marks)

- (c) Write the detailed mechanisms for the following reactions. You may abbreviate the substituents when necessary.



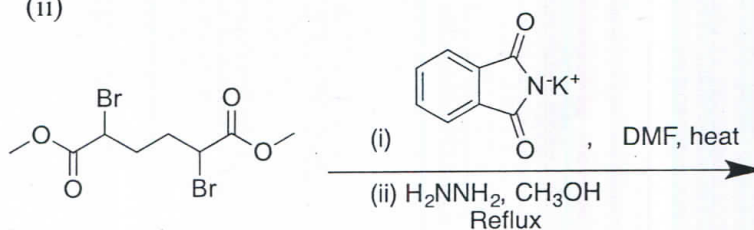
(32 marks)

- (d) Consider the reactants, reagents and reaction conditions given below and predict the major product formed in each reaction.

(i)



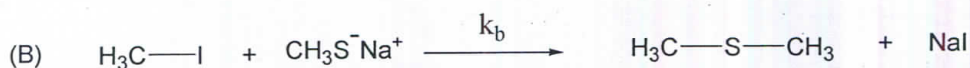
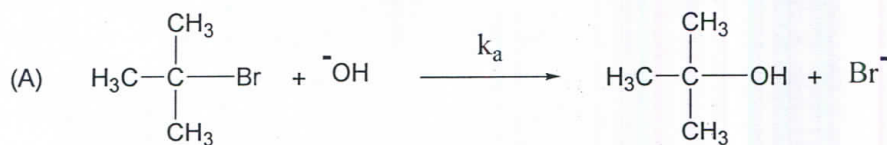
(ii)



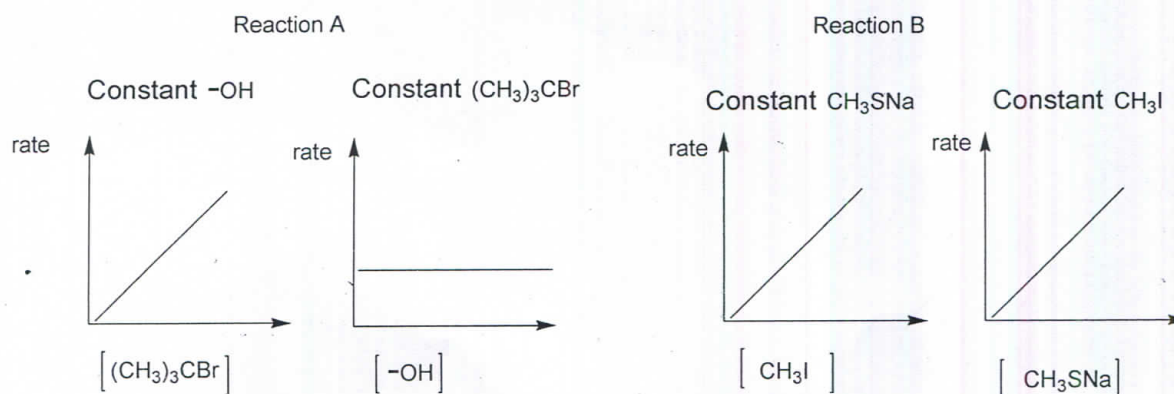
(16 marks)

03. Answer all parts

- (a) Consider the following substitution reactions (A) and (B).



The initial rate method was applied to determine the order of the reactions with respect to each reactant species and the observations made were given below.

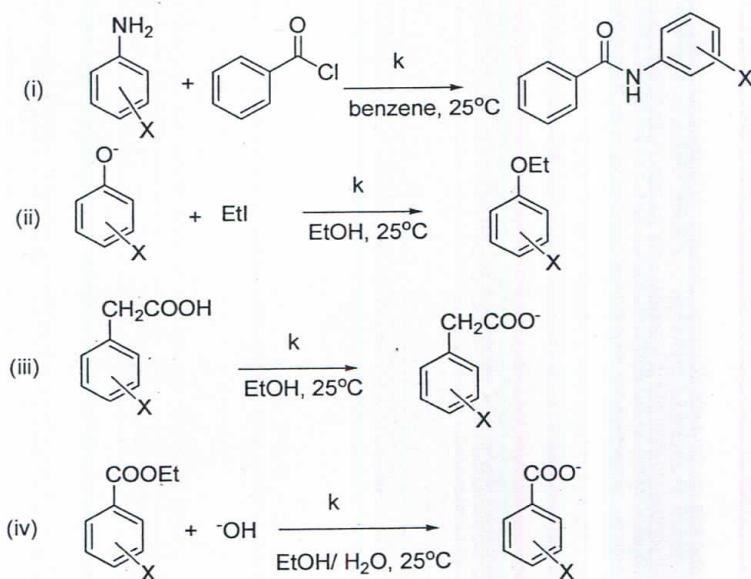


- (i) Determine the order of each reaction with respect to each reactant involved based on the above experimental results.
- (ii) Write the elementary steps for the reaction (A) and (B)
- (iii) Giving assumptions you made derive an expression for the rate of each reaction (A) and (B).

(40 marks)

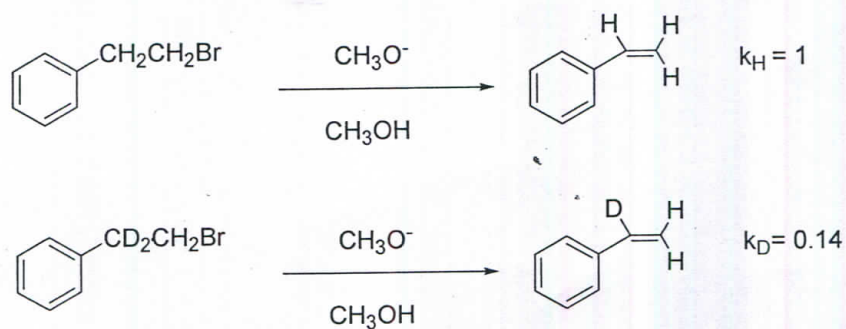
(b) Giving reasons assign the correct  $\rho$  value to the reactions (i)-(iv) from the values given below.

$$\rho : -2.69, -0.99, +0.47, +2.51$$



(40 marks)

(c) Using Isotope substitution effects, determine the mechanism for the following transformation.



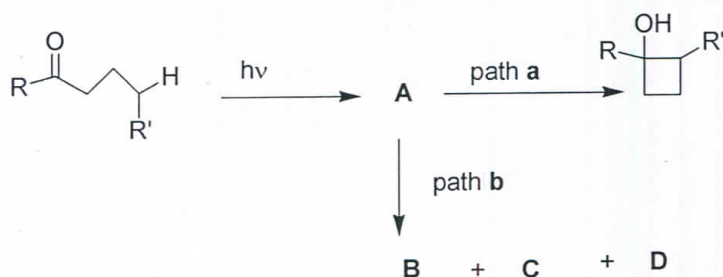
(20 marks)

04. Answer all parts

- (a) Draw the structures of major radicals formed by Norrish Type I reaction of ethylmethylketone .

(10 marks)

- (b) Consider the following photochemical reaction to answer the questions given below.

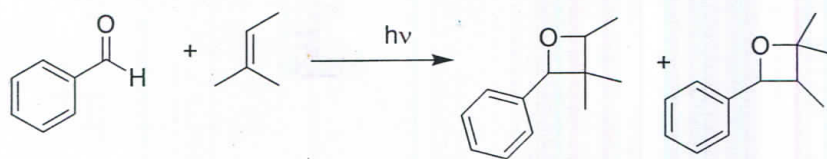


- (i) Draw the structure of intermediate (A) formed in above reaction.
- (ii) What step facilitate for this reaction?
- (iii) Identify the reactions happening in **path a** and **path b**.
- (iv) Write down structures of **B, C, and D**.

(35 marks)

(c)

- (i) Write down the plausible mechanism for the following photochemical conversion.

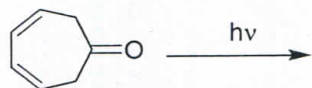


- (ii) What is the major product that you would expect from the above reaction? Explain your answer.

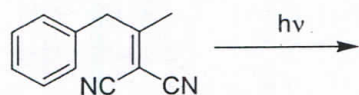
(25 marks)

(d) Give the structure(s) of the product(s) formed in the reactions below.

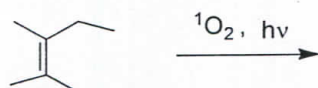
(i)



(ii)



(iii)



(30 marks)

05. Answer all parts

(a)

(i) Draw the products you would expect from conrotatory and disrotatory cyclizations of (2Z, 4Z, 6Z)-2, 4, 6-octatriene and state which path follows the thermal reaction.



(ii) What are the products you expect to obtain from the photochemical cyclization of the following compounds?



(25 marks)

(b) Emphasizing the stereochemistry predict the structure of the product of the Diels - Alder reaction between (2E, 4E)-2,4-hexadiene and ethylene. State the stereochemical change occur if the starting diene is changed to (2E, 4Z)-2,4-hexadiene.

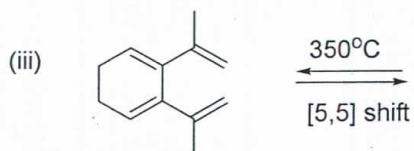
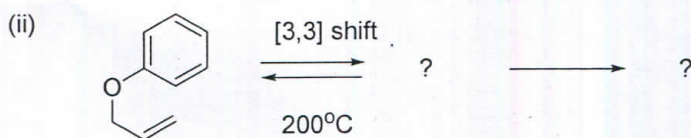
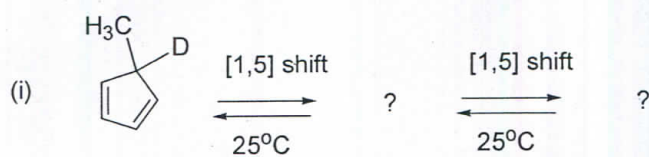
(15 marks)

(c) Ultraviolet irradiation of polyenes causes change in HOMO and LUMO symmetries and hence stereochemistry of their reactions. Considering the **photochemical** cyclization of 2,4-hexadiene and 2,4,6-octatriene answer the following questions.

- (i) Draw the array of orbitals for the ground state HOMO of each reactant.
- (ii) Draw the array of orbitals for the excited state HOMO of each reactant.
- (iii) Determine the cyclization path (conrotatory or disrotatory) for the cyclization of each reactant using above orbital diagrams.

(30 marks)

(d) Write down the products of the following reactions.



(30 marks)

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