

UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL I) SEMESTER- I
EXAMINATION JULY 2 016

SUBJECT : CHEMISTRY

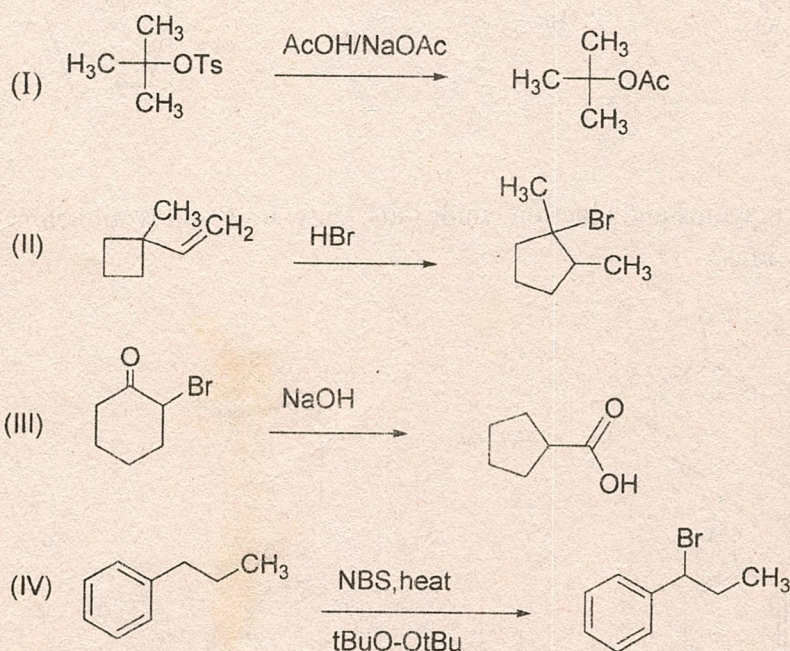
COURSE UNIT : CHE 4123

TIME : Three (03) hours

Answer all questions.

01. Answer all parts

(a) Consider the chemical transformations given below

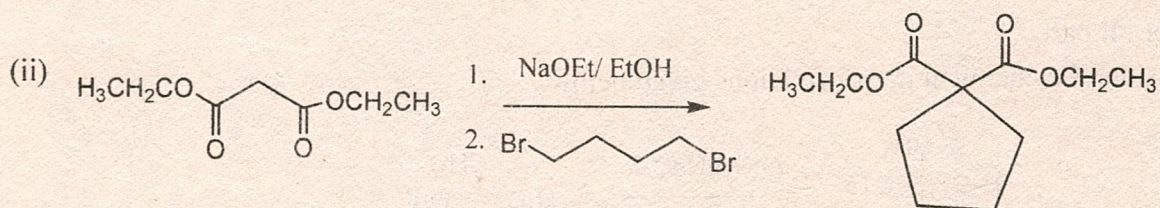
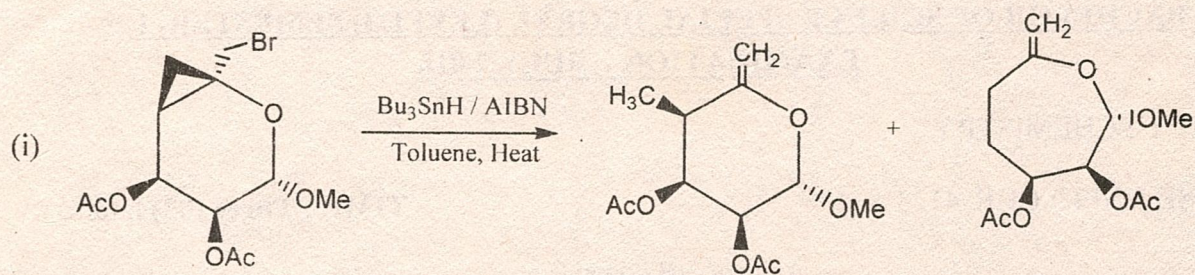


(i) Draw the structure of the intermediate formed in each of the above reactions.

(ii) Giving necessary structures, explain the stability of each intermediate mentioned in (i).

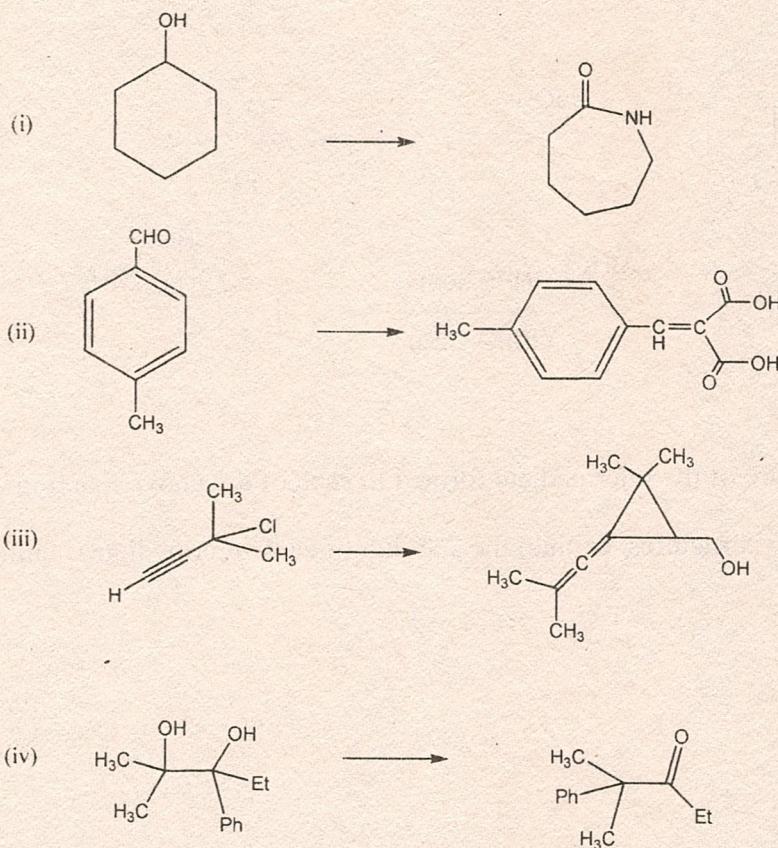
(32 marks)

(b) Give plausible mechanism(s) for the following chemical transformations



(36 marks)

(c) Giving necessary reagents and reaction conditions, show how you would carry out following conversions.

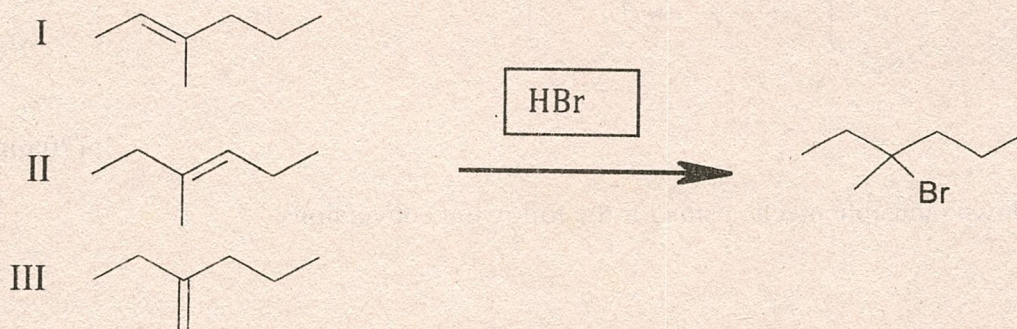


(32 marks)

02. Answer all parts

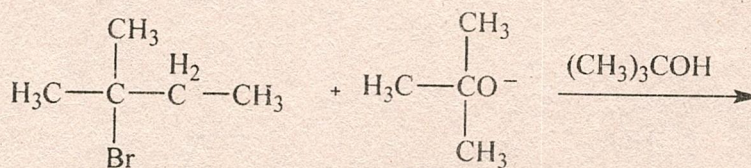
(a)

(i) All three reactants produce the same product with HBr as shown below. Justify this giving necessary intermediate structures.



(15 marks)

(ii) Give the structures of the product(s) formed in the following reaction. Explain the formation of the predicted product(s).



2-bromo-2-methylbutane

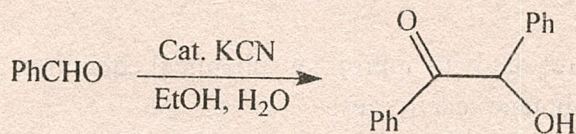
tert-butoxide ion

Write down the mechanism for the above reaction.

(20 marks)

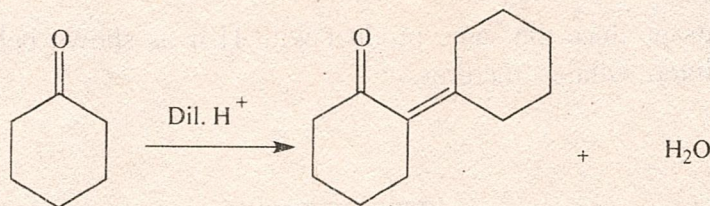
(b)

(i) An aldol reaction is one of the key steps in the benzoin condensation, which requires a catalytic amount of -CN to proceed. Draw a reasonable mechanism for the reaction below.



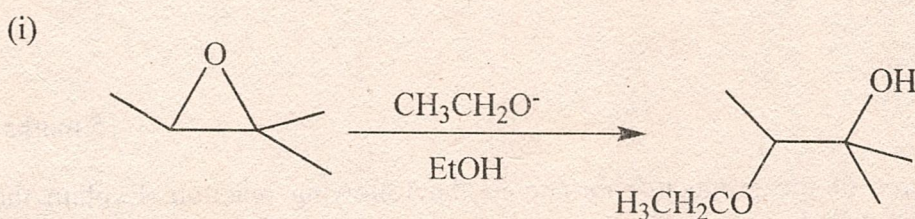
(20 marks)

(ii) Following reaction is the acid catalyzed aldol condensation of cyclohexanone. Give mechanism for this reaction.

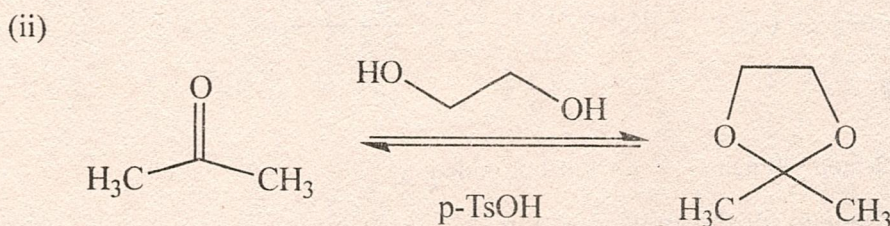


(20 marks)

(c) Write down plausible mechanisms for the following conversions.



(10 marks)



(15 marks)

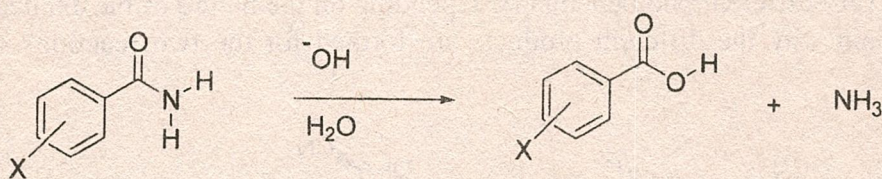
03. Answer all parts

(a) The rate of solvolysis (substitution) of 2-halo-2-methylbutanes in aqueous methanol depends on the halogen (Br, Cl, I) present. However all halobutanes give the same mixture of 2-methoxy-2-methylbutane and 2-methyl-2-butanol as the only products.

- (i) Explain these experimental results with appropriate chemical equations.
- (ii) Predict the order of the halobutane reactivities.

(30 marks)

(b) Substituted benzamides hydrolyze to substituted benzoic acids in the presence of base as shown below.



Experimental data for hydrolysis of various substituted benzamides in water at 100 °C is given below. Use the data to answer the questions (i) –(iv).

Substituent	Substituent constant	Relative rate (k_x/k_H)
	σ	
<i>m</i> -I	0.35	2.6
<i>p</i> -I	0.28	1.69
<i>p</i> -Br	0.23	1.91
<i>m</i> -NO ₂	0.71	5.6
H	0	1
<i>p</i> -CH ₃	-0.17	0.65
<i>p</i> -OCH ₃	-0.27	0.49
<i>m</i> -NH ₂	-0.16	0.93
<i>m</i> -OH	+0.12	0.19

(i) Explain whether these experimental data are correlated by the Hammett Equation.

(35 marks)

(ii) Determine the reaction constant (ρ)

(05 marks)

(iii) What do you deduce from the sign of the reaction constant (ρ)?

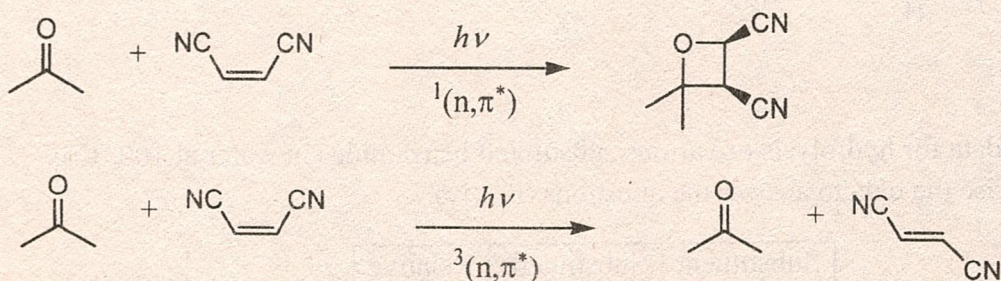
(10 marks)

(iv) Determine whether there is any substituted benzamide deviated from Hammett Equation and if so explain the reason for the deviation.

(20 marks)

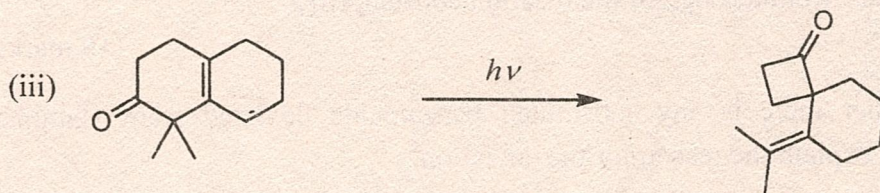
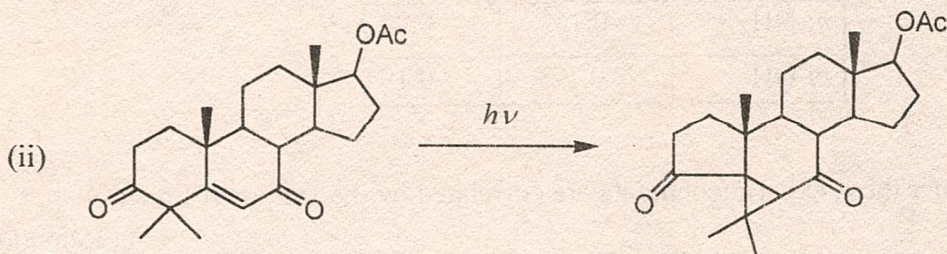
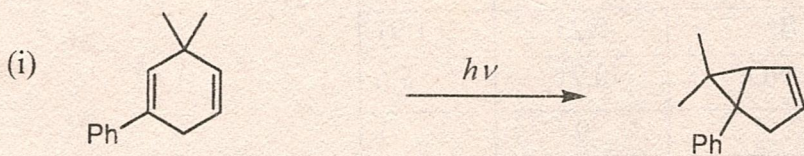
04. Answer all parts

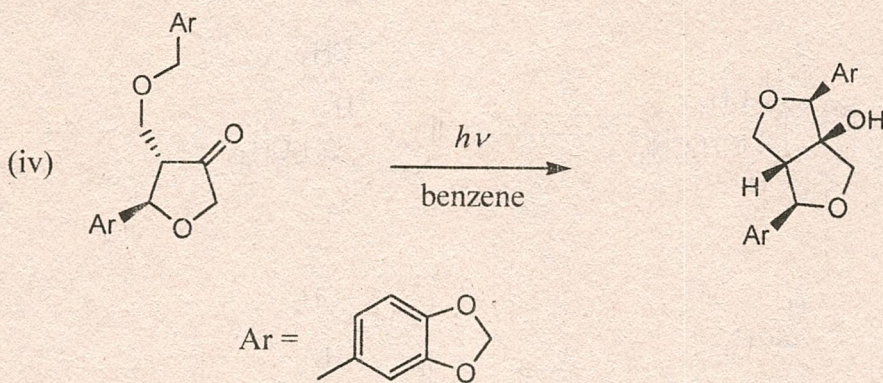
- (a) Acetone shows very different photochemistry depending on the nature of the excited state involved. Explain why the different products are formed for the two reactions shown below



(20 marks)

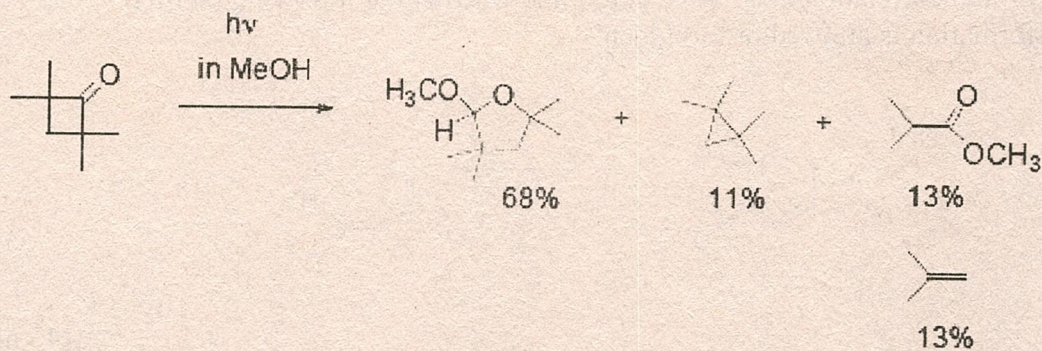
- (b) Suggest a plausible mechanism for each of the following photochemical transformations. Indicate clearly the primary photochemical process for each reaction.





(14 x 4 marks)

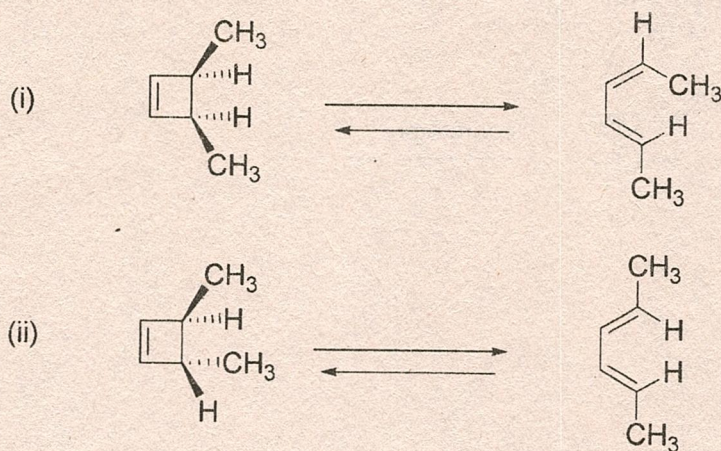
- (c) Direct irradiation of tetra methyl cyclobutanone in methanol results in different products as shown below. Giving a plausible mechanism explain the reason for this.

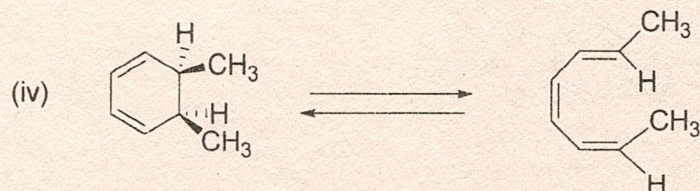
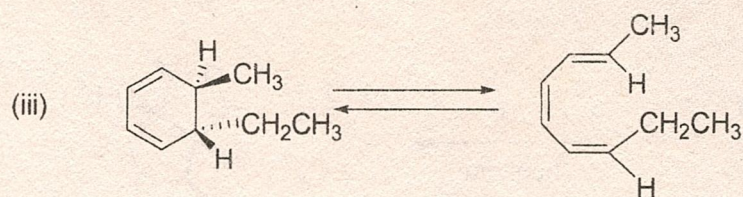


(24 marks)

05. Answer all parts

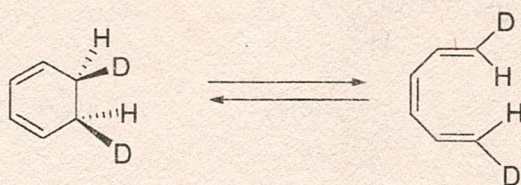
- (a) Indicate whether the following reactions are conrotatory or disrotatory with the appropriate conditions.





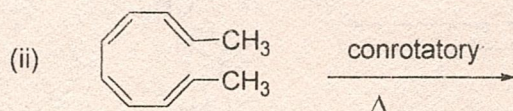
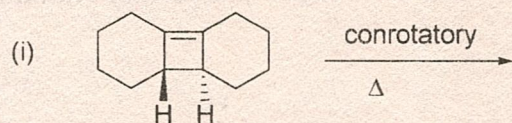
(20 marks)

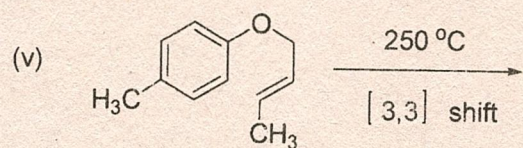
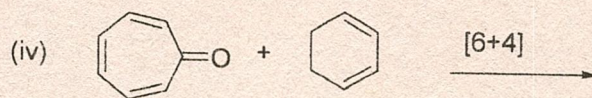
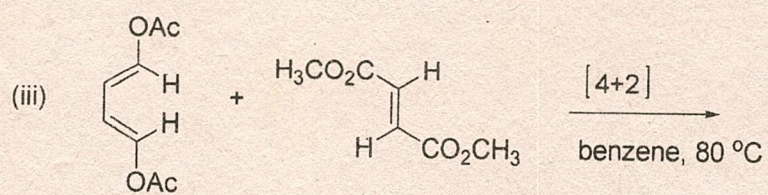
(b) Use orbital correlation diagram to determine whether the following thermal transformation is allowed or forbidden.



(45 marks)

(c) Give the structures of the products of the following reactions with their correct stereochemistry.





(35 marks)

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