

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 436: ADVANCED STEREOCHEMISTRY AND REACTION MECHANISMS

STREAMS: BSC

TIME: 2 HOURS

DAY/DATE: MONDAY 22/03/2021

11.30 A.M. – 1.30 P.M.

INSTRUCTIONS:

- Answer QUESTION ONE and any OTHER TWO questions.

QUESTION ONE (30MARKS)

- a) Using an example differentiate between constitutional and stereoisomers (2 marks)
- b) Which of the following compounds have asymmetric carbons? (2 marks)
 i) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$ iii) $\text{CH}_3\text{CH}_2\text{OH}$ iv) $\text{CH}_2=\text{CHCH}(\text{NH}_2)\text{CH}_3$
- c) Draw the Newman projection for the rotation about the C-2 to C-3 bond in butane and briefly discuss the conformers obtained (5 marks)
- d) Briefly discuss three kinds of strains that can destabilize a cyclic compound (3 marks)
- e) i) Define a pericyclic reaction (1 mark)
 ii) Using a suitable example discuss the three types of pericyclic reactions. (6 marks)
- f) i) Define a carbonium ion (1 mark)
 ii) List three methods for generation of a carbonium ions (3 marks)
- g) Draw the molecular orbital description of 1,3-butadiene (4 marks)
 i) Indicate which orbitals are the HOMO and LUMO in the ground state (1 mark)
 ii) Which orbitals are the HOMO and LUMO in excited state (1 mark)

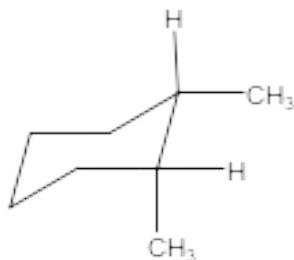
- iii) Which are the bonding orbitals and which are the antibonding orbitals (1 mark)

QUESTION TWO (20 MARKS)

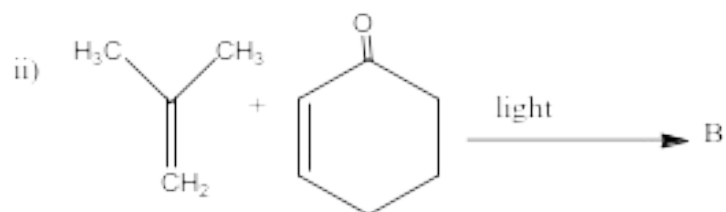
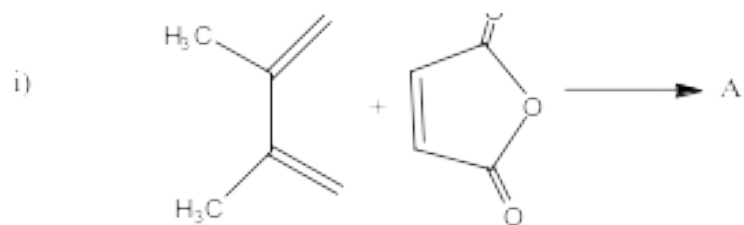
- a) Draw the cis and trans isomers of the following; (2 marks)
 i) 1-bromo-3-chlorocyclobutane
 ii) 1,4-dimethylcyclohexane
- b) Using an example differentiate between a chiral and achiral molecule (4 marks)
- c) Draw the two chair conformations of methylcyclohexane and comment on their stability. (4 marks)
- d) Using a suitable example indicate two reactions of carbonium ions (4 marks)
- e) Briefly explain the three key points of molecular orbital theory (6 marks)

QUESTION THREE (20 MARKS)

- a) Draw enantiomers for $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{OH}$ using a) Perspective formula b) Fischer projections (2mks)
- b) State with reasons if the following conformer of 1,2-dimethylcyclohexane is cis or trans isomer (3mks)



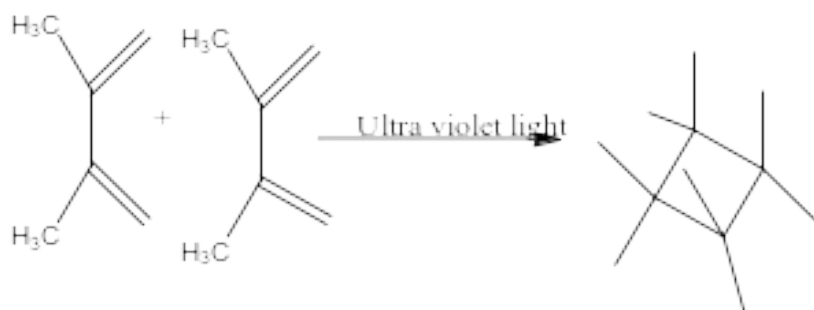
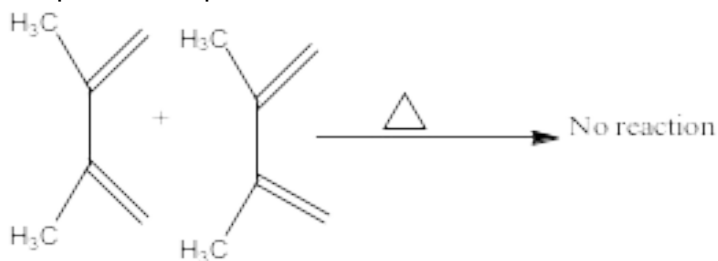
- c) Write the mechanism and give the products of the following reactants (3 marks)



d) Using a diagram differentiate between suprafacial and antarafacial (4 marks)

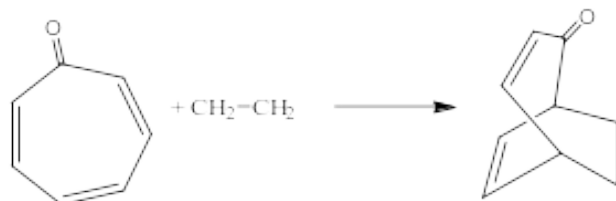
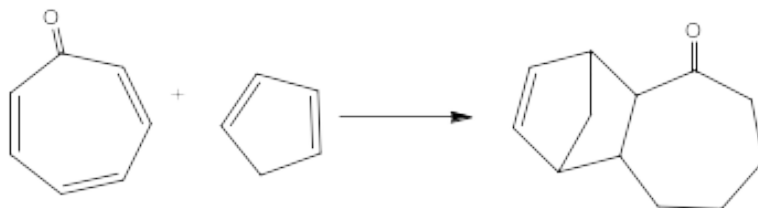
e) Explain why the compound (2E,4Z,6Z)-octatriene gives the *trans* product under thermal conditions and the *cis* product under photochemical conditions (4 marks)

f) Explain why a [2+2] cycloaddition reaction does not occur under thermal conditions but does take place under photochemical conditions (4 marks)

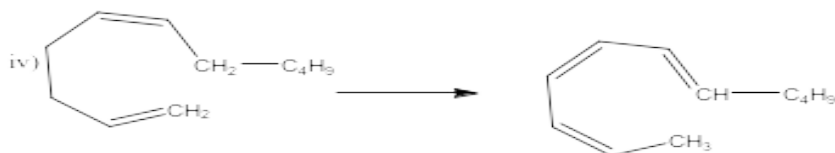
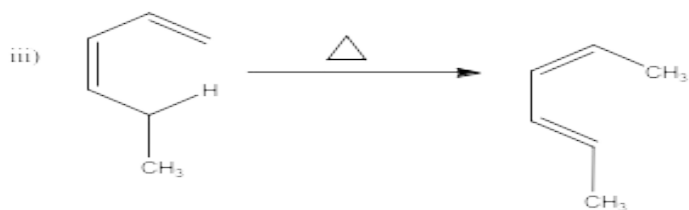
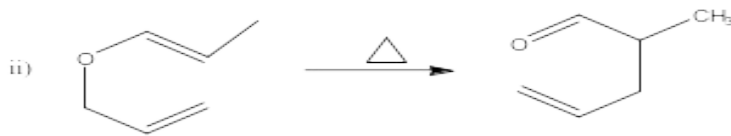
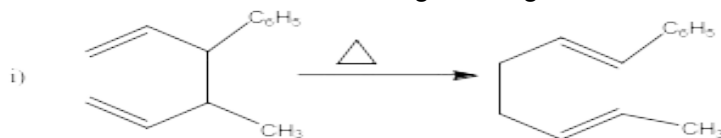


QUESTION FOUR (20 MARKS)

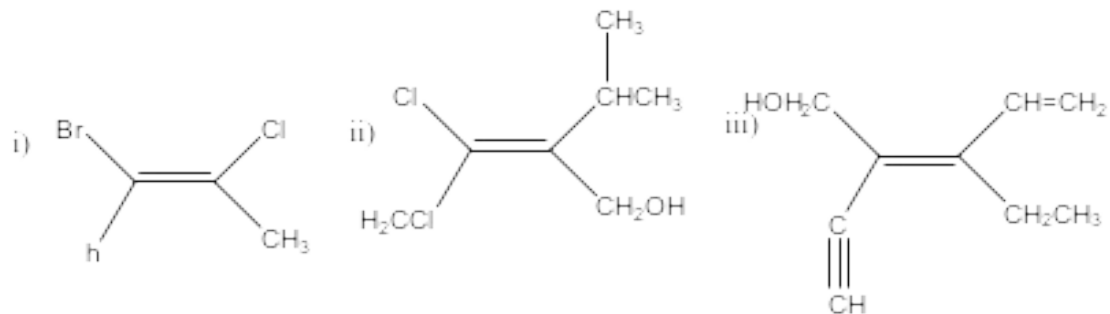
- a) Compare the reaction of 2,4,6-cycloheptatriene with cyclopentadiene to that of ethene. Why does 2,4,6-cycloheptatriene use two π electrons in one reaction and four π electrons in the other. (6 marks)



- b) Draw the mechanisms of the following rearrangement (6 marks)



c) Indicate whether the following is an *E* or *Z* isomer (3 marks)



d) 5-methyl-1,3-cyclopentadiene rearranges to give a mixture of 5-methyl-1,3-cyclopentadiene, 1-methyl-1,3-cyclopentadiene and 2-methyl-1,3-cyclopentadiene. Show the mechanism of the product formation. (5 marks)
