EASTERN UNIVERSITY, SRI LANKA

THIRD EXAMINATION IN SCIENCE-2010/2011 (2016)

SPECIAL DEGREE IN CHEMISTRY

CHS 02 Organic Chemistry I

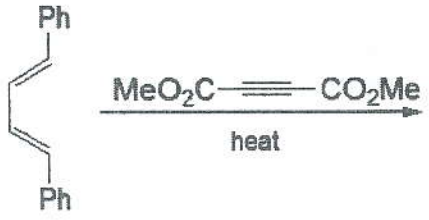
ver all questions **Time Allowed: Two hour**

) *Apply* frontier molecular Orbital theory to determine the preferred mode (suprafacial or antarafacial) of [2+2] cycloaddition reaction of two ethylene molecules under thermal and photochemical condition.

(40 marks)

) *Draw* the structure including stereochemistry of the product / products of the following reactions.

1.



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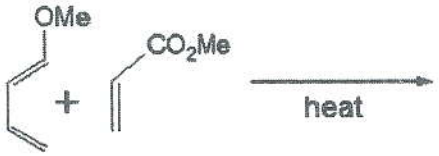
2.



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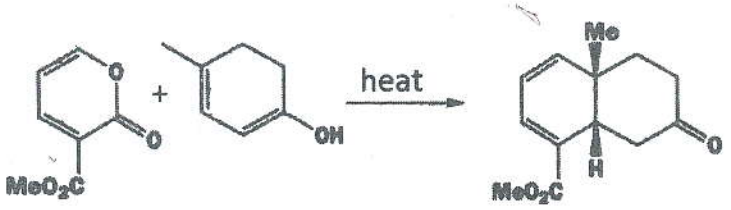
(30 marks)

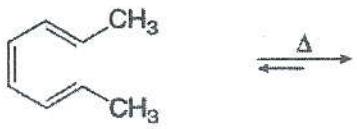
) *Explain* the following reaction including the stereochemistry of the product given below by a plausible mechanism.



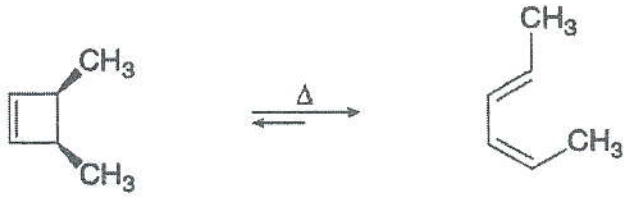
(30 marks)

Contd....

2. a) *Explain* why ring closure of (2E,4Z,6E)-2,4,6-octatriene yields only a single product v cis methyl groups on the ring, while ring opening reaction of cis-3,4-dimethylcyclobut forms a single conjugated diene with one Z alkene and one E alkene as shown below.



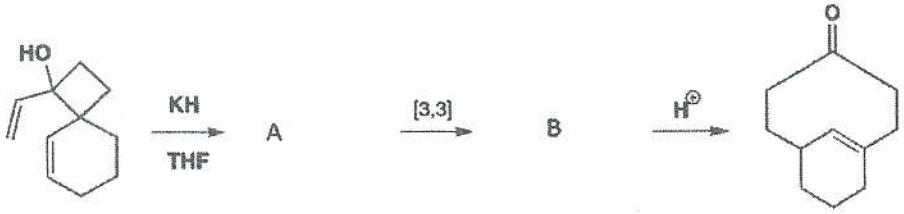
(2*E*,4*Z*,6*E*)-2,4,6-octatriene *cis*-5,6-dimethyl-1,3-cyclohexadiene



cis-3,4-dimethylcyclobutene (2*E*,4*Z*)-2,4-hexadiene

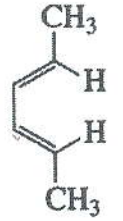
(30 mark

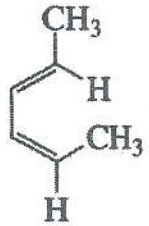
b) Compound S was treated with potassium alkoxide (base) in THF to get **A** which th undergoes [3,3]-sigmatropic rearrangement to give **B**. The compound **B** was allowed react with acid to obtain the product **P**. Give reasons and *draw* the structures of t compounds **A** and **B**.

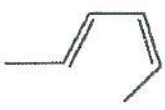


S **P** (30 marks)

c) *Predict* the product/s (including stereochemistry) of the following electrocyclic reactions.

i)  ?

ii)  ?

iii)  Heat (Δ) ?

iv)  Heat (Δ)

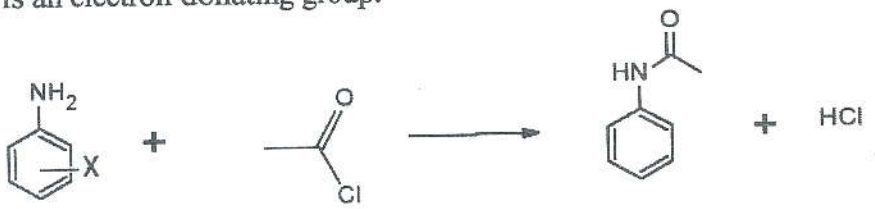
(40 marks)

Contd....

3. a) *Evaluate* the significance of rate constant of the following reaction when

i. X is an electron withdrawing group.

ii. X is an electron donating group.



(30 marks)

b) The pKa values of p-chlorobenzoicacid and benzoic acid are3.98 and 4.19 respectively. *Calculate* substituent constant (σ) for p-Cl.

(20 marks)

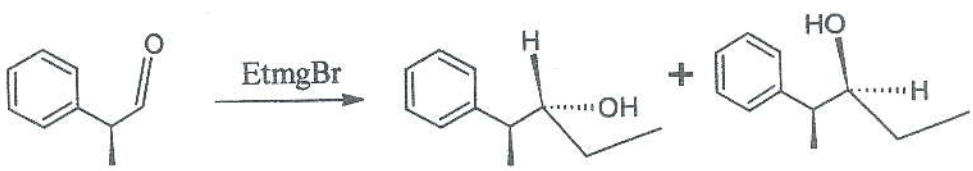
c) i) Define the term 'Kinetic isotopic effect'.

(15 marks)

ii) Nitration of benzene is found to have a deuterium isotope effect of K_H/K_D=1.0. Explain how you would *determine* the rate determining step of the reaction.

(35 marks)

4. a) Using Felkin-Ahn model *explain* how the following reaction yields different diastereoisomers of the product in 1:3 ratio.

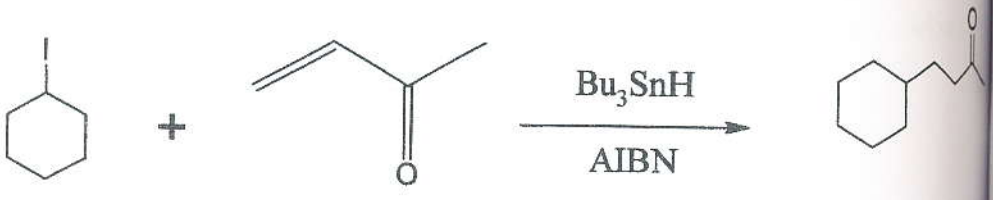


1 : 3

(40 marks)

Contd....

b) *Write* mechanism for the following radical chain reaction.

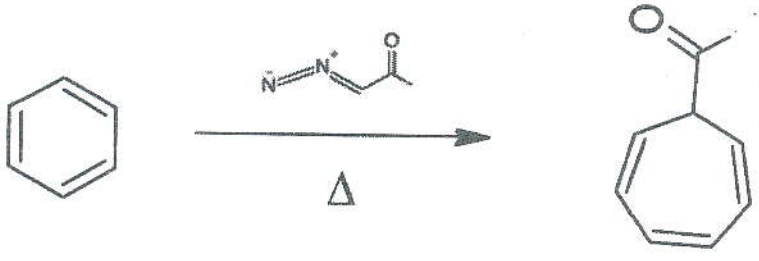


(20 marks)

c) i) Briefly *explain* the two types of carbenes.

(15 marks)

ii) *Write* mechanism of the following reaction.



(25 marks)

End of Paper