



EASTERN UNIVERSITY, SRI LANKA

THIRD YEAR EXAMINATION IN SCIENCE-2020/2021 (2024)

HONOURS DEGREE IN CHEMISTRY

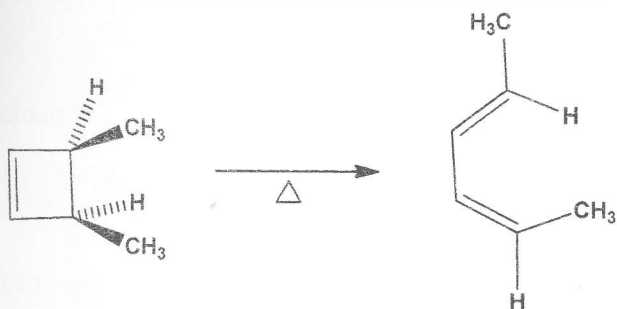
CH4022 Advanced Organic Chemistry I

Answer **all** questions

Time Allowed: **Two** hours

1. a) *Apply* Frontier Molecular Orbital theory to determine the preferred mode (conrotatory or disrotatory) of thermal and photochemical cyclisation of 1,3-butadiene. (30 marks)

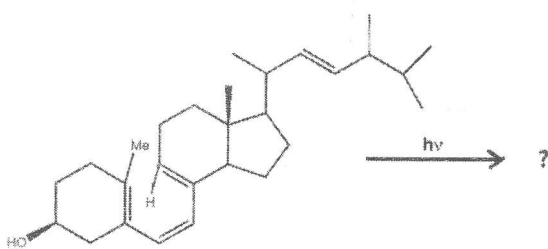
- b) *Explain* the following reaction and the stereochemistry with the help of the molecular orbitals involved at the terminal carbon atoms.



(25 marks)

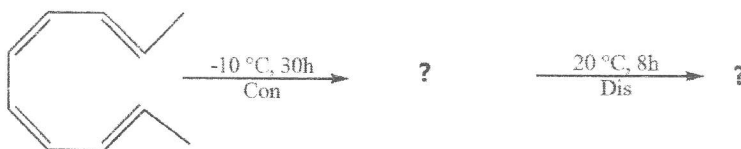
- c) *Predict* the product/s including stereochemistry of the following electrocyclic/cycloaddition reactions.

i)

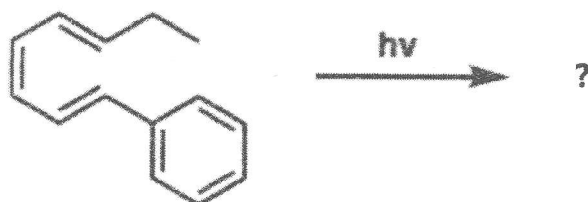


(10 marks)

ii)



iii)



(20 marks)

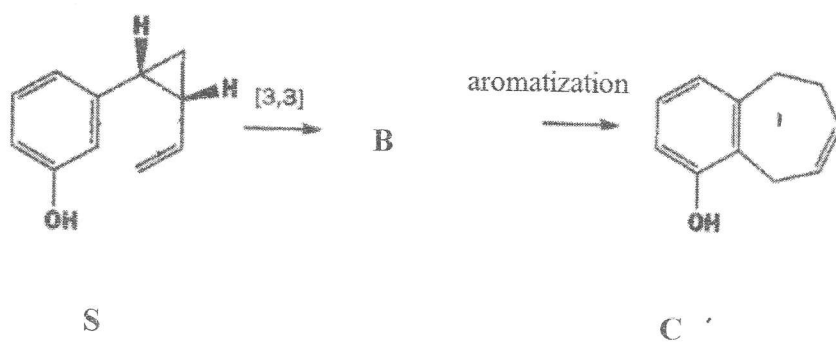
(15 marks)

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2. a) Compound **S** undergoes [3,3]-sigmatropic rearrangement to give **B**. Compound **B** undergoes aromatization to give the product **C**. It was proved that the aromatization of six-membered ring occurs by losing a proton from the ring junction and not by [1,3]-[1,7] hydrogen shift.

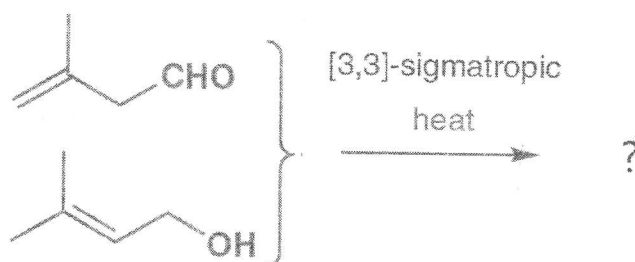
i. Predict the structure of product **B** by showing suitable mechanism.

ii. Explain how the aromatization occurs in compound **B** to give **C**.



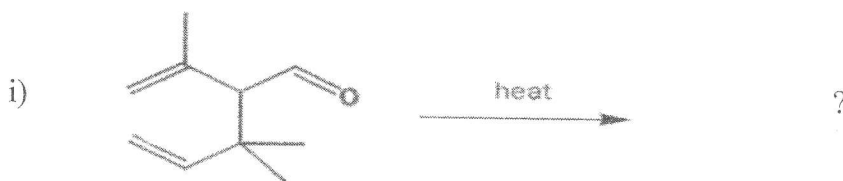
(30 marks)

- b) Draw the product of the following reaction and explain.



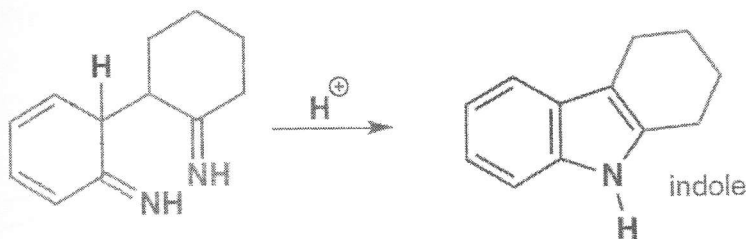
(20 marks)

- c) The following reactions Draw the structures of the Products including stereochemistry wherever possible.



Contd....

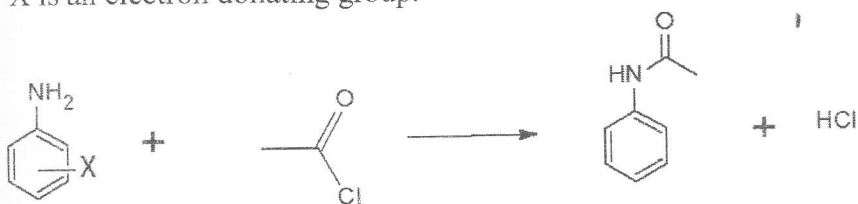
- d) The reactant is a highly unstable double imine. But aromaticity is immediately restored, and a series of proton shifts and C–N bond formation and cleavage reactions give the aromatic indole. *Explain the observations by means of plausible mechanisms.*



(30 marks)

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

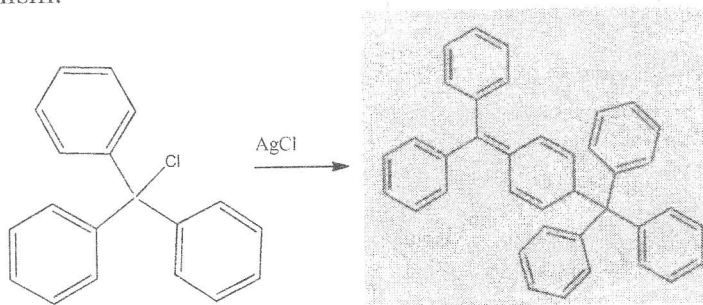
- i. X is an electron withdrawing group.
- ii. X is an electron donating group.



(30 marks)

- b) The pKa values of p-chlorobenzoic acid and benzoic acid are 3.98 and 4.19 respectively. *Calculate* substituent constant (σ) for p-Cl. (20 marks)

- c) Triphenyl radical is relatively stable but reacts with itself reversibly in solution. The product of the dimerization of triphenylmethyl was for 70 years believed to be hexaphenyl ethane but, in 1970, NMR showed that it was, in fact, an unsymmetrical dimer. *Propose* a plausible radical mechanism.



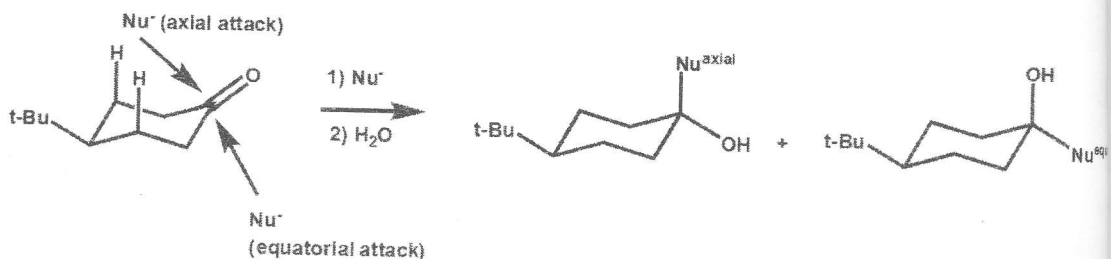
(20 marks)

- d) i) Write a plausible radical mechanism for a pinacol dimerization of acetone (ketyl radical reaction in hydrocarbon solvent)
- ii) *Explain* why the above method (i) is not a suitable method to prepare a single diastereomer of a pinacol.

(30 marks)

Contd....

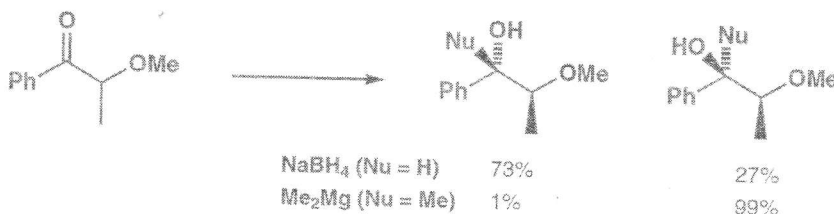
4. a) Explain how this reaction gives two different diastereomers as the products, as shown in the table below



Nu ⁻	% axial attack	% equatorial attack
LiAlH ₄	90	10
<i>t</i> -BuMgBr	0	100

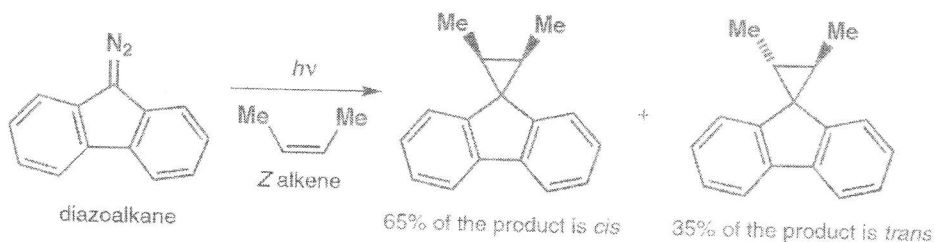
(30 marks)

- b) Explain the percentage yield of the diastereomers formed using a nonchelated / chelated Felkin-Anh model when NaBH₄ / Me₂Mg is used as reagents as shown below.



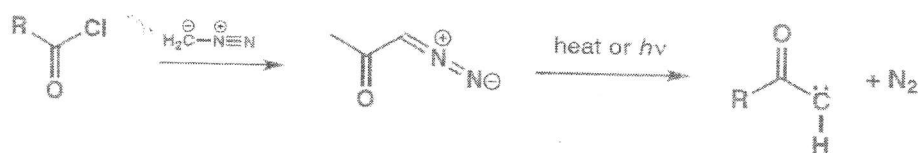
(30 marks)

- c) i) The alkene insertion reaction is non-stereospecific for triplet carbenes and hence it gives a mixture of cyclopropane diastereomers from a pure *Z* alkene.



(20 marks)

- ii) Write plausible mechanism/s for the following reaction given below.



(20 marks)