Total Pages : 9

End Semester Examination of Semester–I, 2015
Subject : CHEMISTRY (PG)
Paper : CEM–101 (Theory)
Full Marks : 40
Time : 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

Illustrate the answers wheeever necessary.

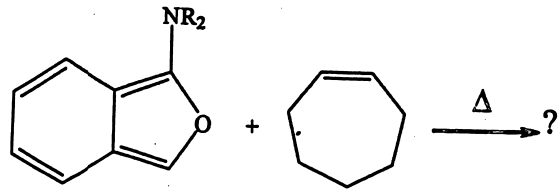
Group A

Answer **any one** questions

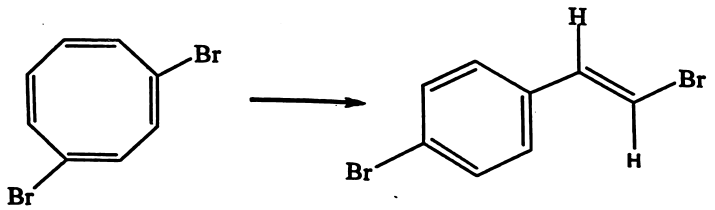
1. a) Draw the correlation diagram of an electrocyclic ring opening/ring closing reaction between cyclohexadiene and 1,3,5–hexantriene in presence of light.

Justify the above transformation in terms of fundamental rules of conservation of orbital symmetry as proposed by Woodward and Hoffmann. 4

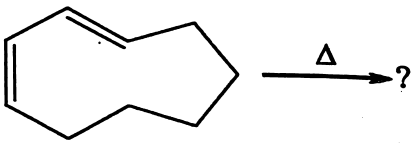
b) Using Hückel-Mobius (H–M) method or perturbation molecular orbital (PMO) method, explain the following cycloaddition reaction with proper stereochemistry: 3



c) 1,4–dibromocyclo octatetraene rearranges on heating to 180°C to produce a 92% yield of para β-dibromostyrene. Suggest a suitable mechanism for this reaction. 2



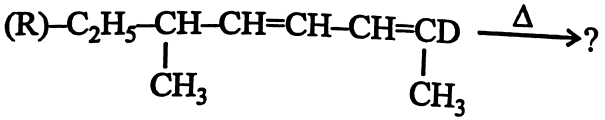
d) Write down the product with appropriate stereochemistry.

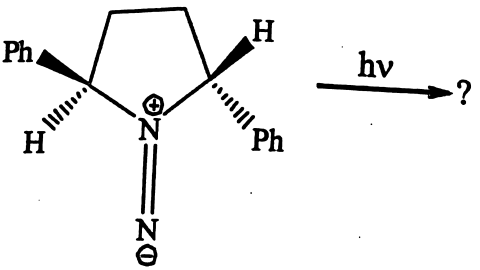


1

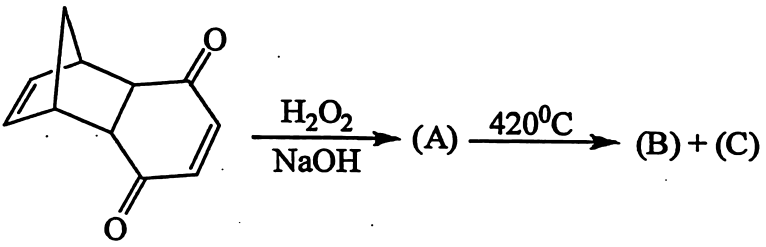
2. a) Benzidine is an example of [9, 9] sigmatropic rearrangemen. Rationalize the fact within the frame work of pericyclic rules. 2

b) Write down the product(s) for the following reactions:

i) 

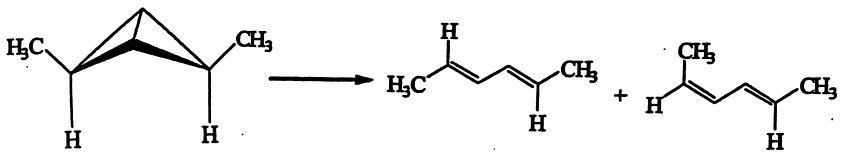
ii) 

c) Write down the product(s) (A), (B) and (C): 2



d) Explain the dimerization of hexatriene in terms of orbital co-efficient, regioselectivity and energy of activation. 2

e) Account for the following thermal rearrangement in two different conditions: 2



(A) (B) (C)

Condition	*% Yield*	*% Yield*
i) 200°C, uncatalysed	3.9	93.2
ii) Ag(I), Catalysed, 26°C	77.0	23.0

Group B

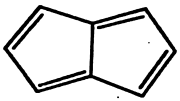
Answer **any one** question

3. a) Calculate the energy of each M.O.'s of butadiene by constructing secular determinant. 4

   b) Define with examples alternant and non-alternant hydrocarbons. 3

   c) Calculate the Hückel Delocalization energy of benzene. 3

4. a) Predict whether the following compound is aromatic or pseudoaromatic by applying Craig's rules. 2



   b) Define "pseudo-Jahn-Teller" effect in case of cyclobutadiene molecule. 3

   c) Synthesize : 1, 6-methano-[10]-annulene. 2

   d) Prove by taking help of ^1H NMR spectroscopy that homotropylium cation is a "non classical carbocation". 3

Group C

Answer **any one** question

5. Answer **any two**:

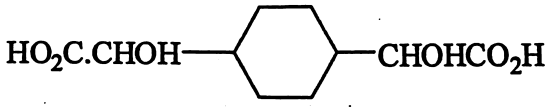
   a) Maleic acid is first esterified with (–)-menthol and then the resultant diester is reacted with Fe(CO)4. How

many products would be formed? Comment on the ^1H NMR signals of the olefinic protons of the diester and the final products. 5

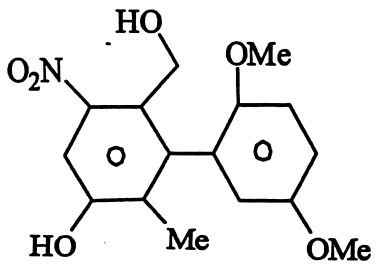
b) Write all the stereisomers having the molecular formula $MeCHCl.CH(CHOHMe)_2$. Designate the configurations of the 'Central' C and comment on its stereogenicity in all the isomers.

c) Write the structure of the following compounds: 1+2+2

i) $PhCOCHBrCHPhCO_2H$ (One Part isomer in sawhorse projection)

ii) 

(meso isomer)

iii) 

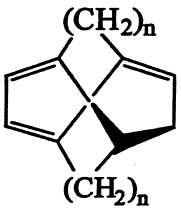
(isomer with R-configuration)

6. Answer (a), (b) and **any one** of (c) and (d).

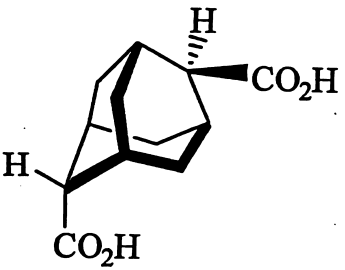
a) Explain the term 'butressing effect'. Illustrate with example. 3

b) Illustrate 'pseudoasymmetry' with examples. 3

c) Delineate the symmetry elements and designate the configuration in R/S. 2+2



(A)



(B)

d) Justify or criticize the following statements: $1+1\frac{1}{2}+1\frac{1}{2}$

i) An enantiomer can never show 0^0 optical rotation.

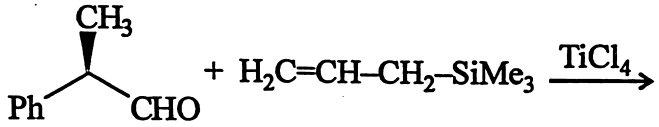
ii) All achival diastereoisomers are meso compounds.

iii) Rigid molecules which belong to Cn or Dn point groups cannot have enantiotopic ligands.

Group D

Answer any one question

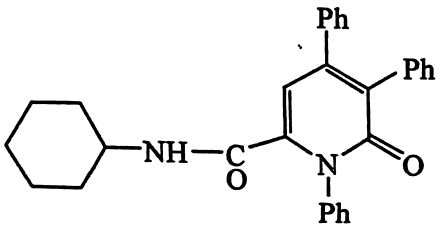
7. a) Predict the product(s) of the following reaction :



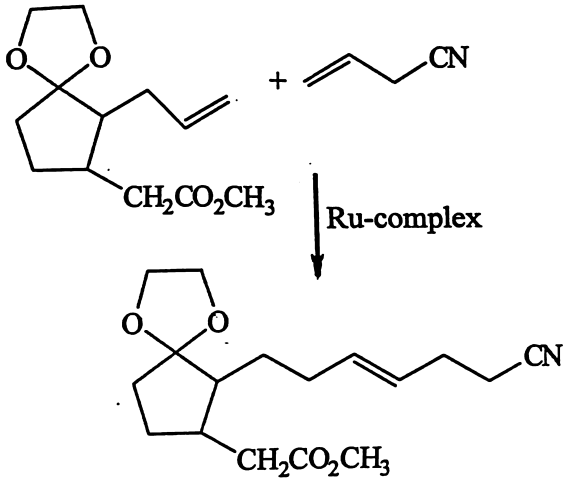
Explain the formation of major product by Felkin model. $2\frac{1}{2}$

b) Give an example of solid phase Biginelli condensation or Intramolecular Biginelli condensation. $2\frac{1}{2}$

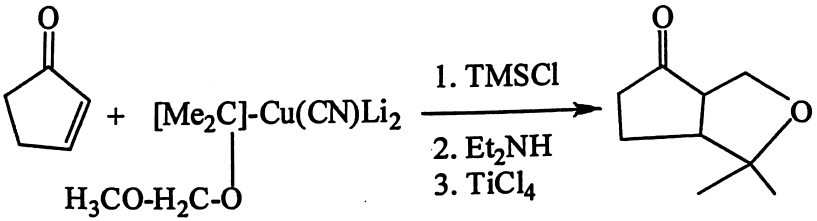
c) How can you synthesize the following compound by Ugi-4CR reaction. $2\frac{1}{2}$



d) Explain the formation of product : $2\frac{1}{2}$



OR



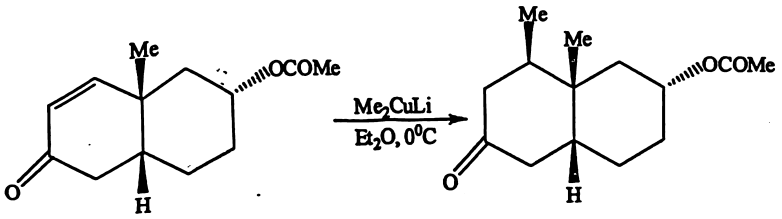
8. a) Mention a modified method of Biginelli condensation where aliphatic aldehyde can produce a good yield. $2\frac{1}{2}$

b) (S)–4–Chloro-3–pentanone $\xrightarrow{LiAlH_4}$?

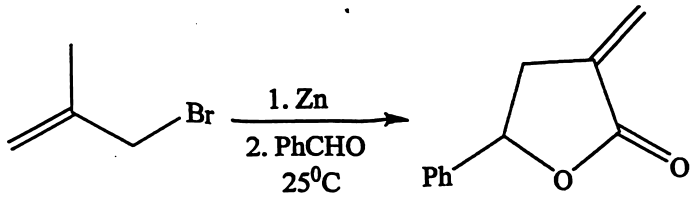
Predict the product(s). Explain the major product by Cram's rule. $2\frac{1}{2}$

c) Explain the formation of products (any **one**) : $2\frac{1}{2}$

i)



ii)



d) Carry out the synthesis of the following compound by Ugi-reaction. $2\frac{1}{2}$