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PG CBCS

M.Sc. Semester-IV Examination, 2022

CHEMISTRY

PAPER: CEM 403 (SPL PAPER)

(ADVANCED ORGANIC CHEMISTRY-IV)

Full Marks: 40 **Time: 2 Hours**

GROUP – A

1. Answer any four questions from the following questions: 2×4 = 8

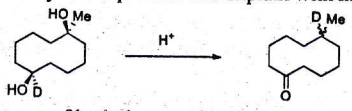
a) State with reasons which of the following phenathren-9-ones will epimerise and which do not in the presence of base?

(i) *cis*-c-*trans* (ii) *cis*-t-*trans*

b) Depict the gauche-butane interactions present in *cis*-decalin (in either steroidal or non-steroidal conformation).

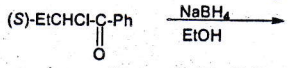
c) What happens when *cis*-4-tert-butyl-6-nitro-1-phenylcyclohexene is treated with base? Explain your answer.

d) Mention the stereochemistry of the product and explain with mechanism:

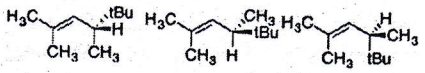


e) Write down the conformers of both the enantiomers of *cis*-1-decalone

f) Predict the major product of the following reaction and justify:



g) Rank the following compound according to their stability.



A B C

GROUP - B

2. Answer any four questions from the following questions: 4×4 = 16

a) Write short notes on (i) and (ii) or (iii)

(i) Felkin-Anh model (ii) Burgi-Dunitz trajectory 3 + 1

(iii) Various strains present in large rings.

b) Compare and contrast *trans*-decalin and *trans*-1,2-dimethylcyclohexane in respect of (i) symmetry and chirality and (ii) relative stability of the conformers.

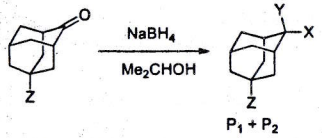
c) (-)-Menthone having 2*R*, 5*R* configuration, shows only a positive Cotton effect CD Curve in water, but exhibits a strong negative Cotton effect in isooctane. Explain these observations.

(P.T.O.)

d) Calculate ΔG at 25 °C for *cis*-4-methylcyclohexanol from the given rates of acetylation as follows:

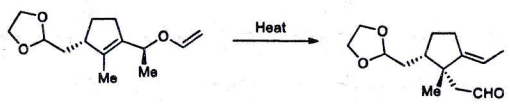
i. Cyclohexanol : 3.76 units
ii. *cis*-4-*tert*-Butylcylcohexanol : 2.89 units
iii. *trans*-4-*tert*-Butylcyclohexanol : 10.65 units

e) Explain with the help of Cieplak model, giving orbital interpretation, the diatereomeric composition of the products in the following reactions when substituent (Z) is varied as shown:



Z	Percentage of P1 (*E*-isomer)	P2 (*Z*-isomer)
-Cl	59	41
4-Cl-C_5H_4	60	40
4-HO-C_5H_4	44	56

f) In the following thermal rearrangement a particular diastereomer (as shown) is formed. Identify at which face of the olefin (*Re* or *Si*) the migration takes place. Offer an explanation why the other diastereomer is not formed.



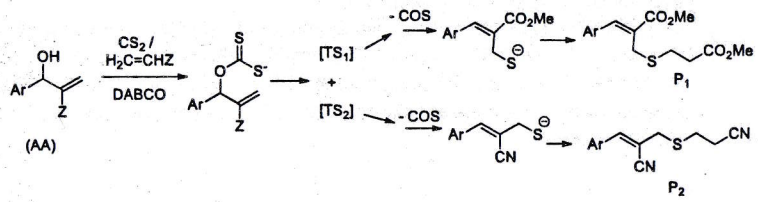
GROUP - C

3. Answer any <u>two</u> questions from the following questions: 8×2 = 16

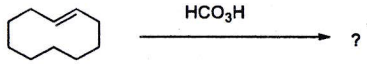
a) (i) (-) *trans*-10-Methyl-2-decalone exhibits negative Cotton effect in the ORD curve. Deduce its absolute configuration by the application of octant rule and specify its stereocenters in terms of (*R, S*) nomenclature. 4 + 1

(ii) Give an application of axial haloketone rule. 3

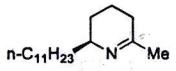
b) (i) Allylic alcohol (AA: Z = CO_2Me) undergoes a three-component reaction on being treated with methyl acrylate and CS_2 in the presence of a tertiary amine to yield product P_1. Replacing methyl acrylate with acrylonitrile product P_2 is obtained from AA (Z = CN). P_1 and P_2 differ in the configuration of the double bond. Account for this difference on the basis of preferred T. States in the two cases. 5



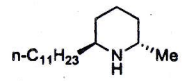
(ii) Predict the product of the following reaction and explain with mechanism 3



c) (i) Give a synthesis of Solenopsin A starting from (I). Explain the sequence of reactions in the synthesis. 3



(I)



Solenopsin A

State the principle of Curtin-Hammett principle. Mention the conditions under which the principle is valid. 2+3

d) Write configurational names of all the diastereomers of perhydrophenanthrene. Draw one planar structure for each diastereomer depicting the angular β-H by heavy dot. Now answer the following:

(i) Mention the axial/equatorial bonds of the central ring that are incorporated into the side rings.
(ii) Which diastereomer cannot have central ring in chair conformation?
(iii) Which diastereomer is most stable and which is the least?
(iv) Which diastereomer can undergo ring reversal? 4 + 4

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