2016

M.Sc. 2nd Seme. Examination

CHEMISTRY

PAPER—CEM-202

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

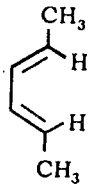
(*Organic*)

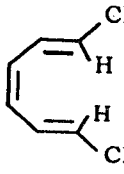
Answer any *five* questions,
taking at least *two* from each group.

Group—A

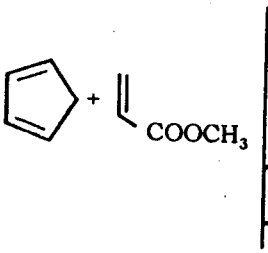
1. (a) Define Chelotropic reaction. Cite the mechanism of insertion of carbene to olefin.

(b) Predict the product of the following reaction indicating Frontier Orbital Interactions (F.O.I).

(i)  $+ SO_2 \longrightarrow (?)$

(ii)  $+ SO_2 \longrightarrow (?)$ 4+(2×2)

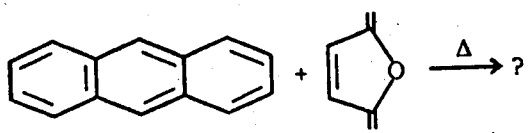
2. (a) The following reaction yields both *endo* and *exo* products in different concentrations with variation of conditions ;

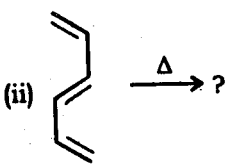


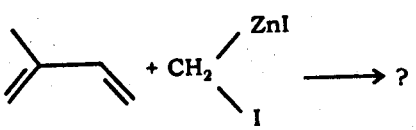
	endo	+ Exo products
0°C	88%	12%
with catalyst	96%	4%
0°C / $AlCl_3$	98%	2%
–80C/$AlCl_3$		

Explain the reason of rate enhancement by adding Lewis acid.

(b) Define site selectivity and hence predict the products of the following reaction indicating reason in each case (attempt any *two*) :

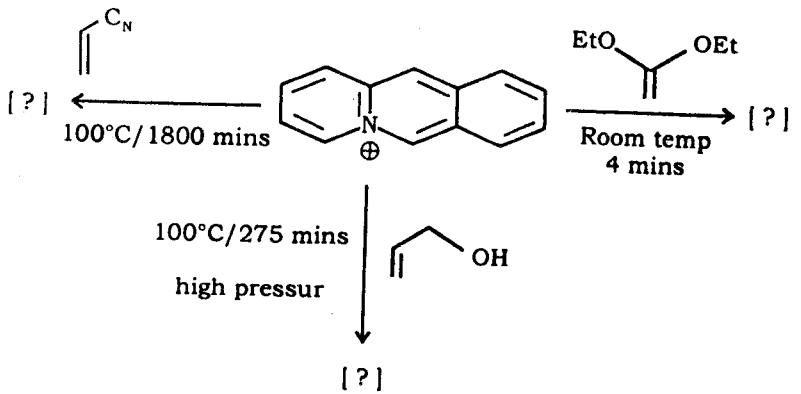
(i) 

(ii) 

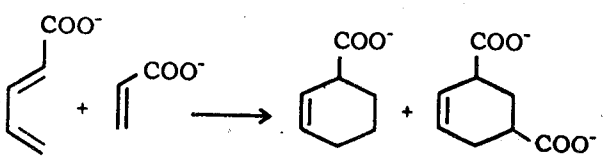
(iii) 

4+(2×2)

3. (a) Predict the product of the following reaction indicating why different conditions are needed to carry out the Diels-Alder reaction ; and explain.

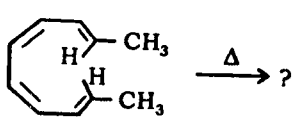


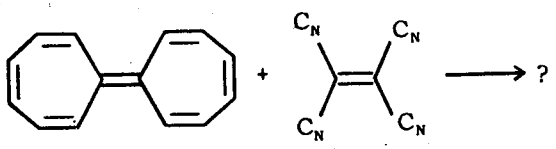
(b) Define 'Regioselectivity' with an example and also explain the formation of the products of the following reaction :



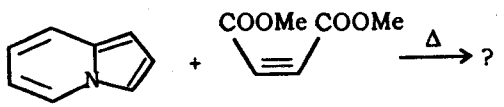
3+1+4

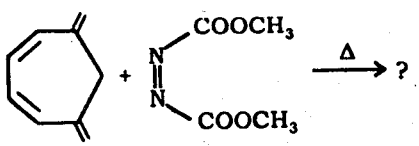
4. (a) Define 'periselectivity' and hence predict the product of the following reaction :

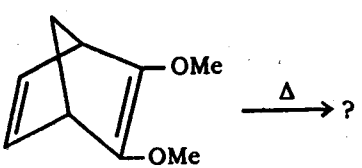
(i) 

(ii) 

(b) Predict the product of the following reaction indicating F.O.I (Attempt any two) :

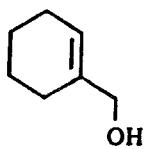
(i) 

(ii) 

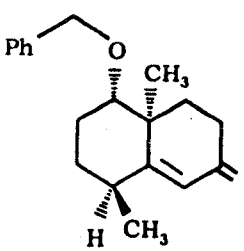
(iii) 

$1+2\times2+1\frac{1}{2}\times2$

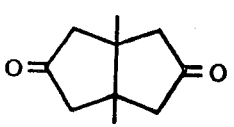
5. Predict the product(s) (any *four*, with plausible mechanism) :

(a) 

$\xrightarrow[\text{L(+) DET}]{\text{Ti(OiPr)}_4,\ {}^t\text{BuOOH}}$

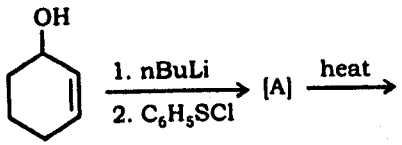
(b) 

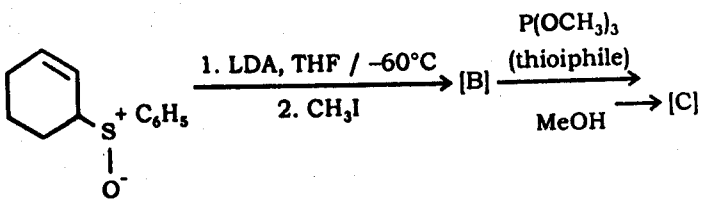
$\xrightarrow[\text{b. } {}^n\text{BuLi, c. } H^+]{\text{a. } ArSO_2NHNH_2}$

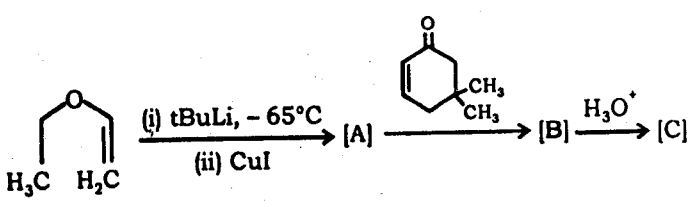
(c) 

$\xrightarrow[\text{2. } (EtO)_2POCl]{\text{1. LiN(SiMe}_3)_2\text{, THF, } -30^\circ C}$ [A]

$\xrightarrow{H_2 \text{ / Pd-C}}$ [B]

(d) 

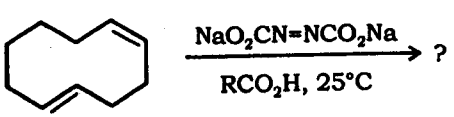


(e) 

4×2

Group—B

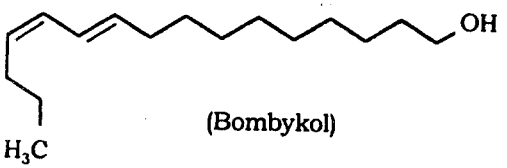
6. **(a)** **Write the product with plausible mechanism :**



2

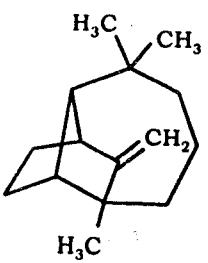
(b) Synthesize the following (any two) :

(i)



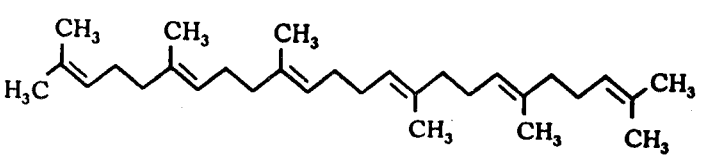
(Bombykol)

(ii)



(Longifolene)

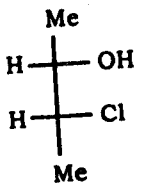
(iii)

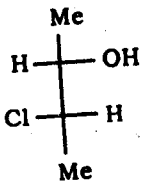


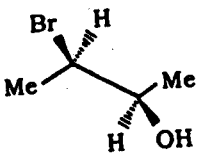
(Squalene)

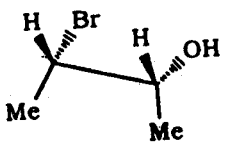
3×2

7. (a) Indicate the relationship between the compounds of the following pairs as identical or enantiomers or diastereomers. Also indicate configurations of the stereogenic centers as 'R' or 'S' showing the priority sequence at each centre.

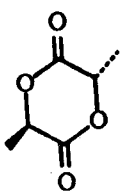


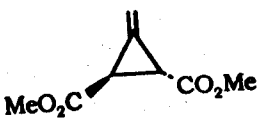




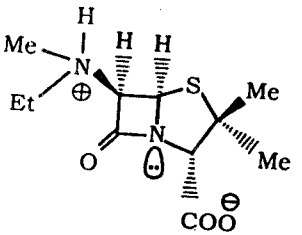


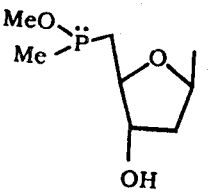
(b) Draw the stereostructure of a diastereoisomer for any *two* of the following and label them as chiral/achiral.





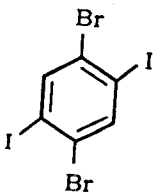
(c) How many stereogenic center(s) is (are) present in each of the following molecules ? Indicate them in the structures.

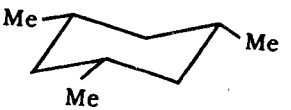


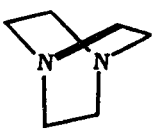


(2+2)+(1+1)+(1+1)

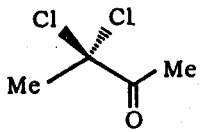
8. (a) How many planes of symmetry does each of the following molecules possess ?

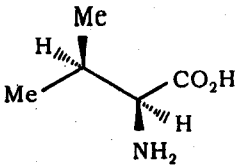




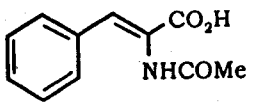


(b) Assign proR/proS configurations to the ligands as attached to the pro-stereogenic center. Also determine their topicity (enatio/diastero).





(c) A mixture of two diastereoisomeric acids A and B, on catalytic hydrogenation, gives a racemic mixture of C and D ($C_{11}H_{13}NO_3$). The mixture, on alkaline hydrolysis, gives E and F. Write the structures of B, C, D, E and F. Comment on the optical activity of final mixture of products. Also assign E/Z configuration to A and B.



+ a diastereomer

A B

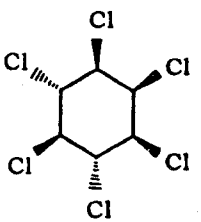
$$\xrightarrow{H_2,\ cat.} C + D\ (C_{11}H_{13}NO_3) \xrightarrow{HO^-,\ H_2O} E + F$$

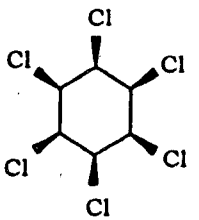
3+2+3

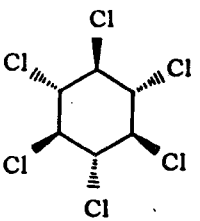
9. Draw all perferred conformations of the stereoisomers of 1, 2-dimethylcyclohexane and 1, 3-dimethylcyclohexane. Calculate their energy difference and comment on their optical activity. 8

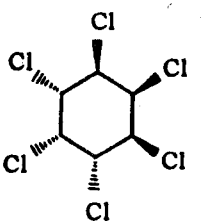
10. (a) Among 1-bromo-3-methylbutane, 2-bromo-3-methylbutane and 2-bromo-2-methylbutane, identify the one (i) that undergoes faster S_N2 with NaOMe (ii) undergoes faster S_N1 in EtOH ; (iii) that is optically active and produces an optically active compound when treated with NaN_3 in S_N2 mechanism.

(b) Which of the following hexachlorocyclohexanes is the least reactive in an E2 reaction. Explain by writing the chair for the compounds.

(i) 

(ii) 

(iii) 

(iv) 

4+4