PG Odd Semester (CBCS) Exam., December—2016

CHEMISTRY

(1st Semester)

Course No. : CHMCC–102

(Organic Chemistry—I)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, selecting **one** from each Unit

UNIT—I

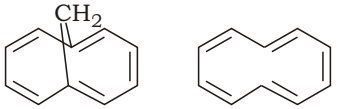
1. *(a)* *(i)* Although all C—C bonds in benzene are of equal length, C_1—C_2 bond length in naphthalene is 1·365 Å while for C_2—C_3 it is 1·404 Å. How do you account for this? 2

(ii) Explain the unusual high dipole moment (1·08D) in azulene. What is the direction of the dipole? 2

(b) Justify the following : 2×3=6

(i) 2,6-Dimethyl-4-nitrophenol is a stronger acid than 3,5-dimethyl-4-nitrophenol.

(ii) Aromatic properties are exhibited by [*A*] but not by [*B*] :



[*A*] [*B*]

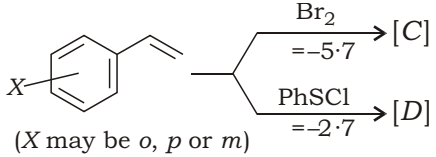
(iii) In aqueous medium, enol content of acetoacetic ester is negligible, but in toluene it is 20%.

(c) What are cyclodextrins? How are they obtained? Describe the uses of this class of compounds. 2+1+1=4

2. *(a)* *(i)* Write the mathematical form of the Hammett equation. 1

(ii) Prove that *p*-nitrophenyl acetic acid is 2·4 times more acidic than phenyl acetic acid using Hammett values. 2

(iii) Write the products and depict the mechanism of the following reactions with suitable explanation : 1½+1½=3



(*X* may be *o*, *p* or *m*)

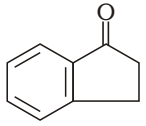
(b) What are crown ethers? State the synthesis of 18-crown-6 and 3-catenanes. 1+2+2=5

(c) Give the mechanism involved in phase transfer catalysis. 2

(d) What is purple benzene? 1

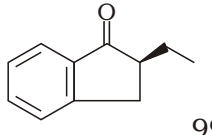
UNIT—II

3. *(a)* *(i)* BH_3 cannot reduce ketones to their corresponding alcohols. Provide a strategy to employ BH_3 to produce ee of the corresponding alcohol of the given compound [*E*] :



[*E*]

(ii) How can the compound [*E*] be alkylated to produce



99% ee

Provide mechanism for all the steps involved in the given problems. Also mention what type of asymmetric synthesis each one of them is. 3+3=6

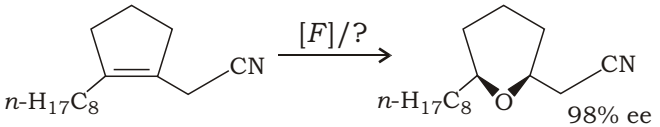
(b) Provide the structural depictions of the desired stereochemical interpretation for the following : 1+1=2

(i) *Threose*-diethyltartarate (Fischer-projections)

(ii) (R,R)-DIPAMP

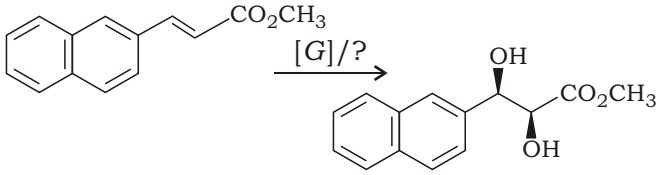
(c) Provide the substrate/reagent(s) for each of the following reactions involving an asymmetric synthesis : 1½×4=6

(i)



98% ee

(ii)



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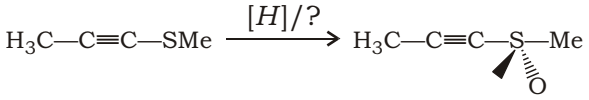
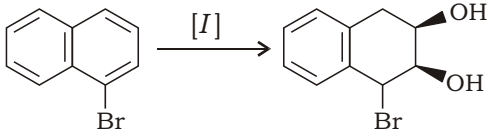
(iii)



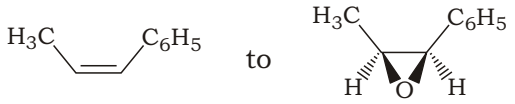
97% ee

(iv)

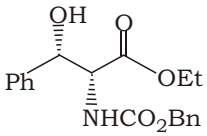


98% ee

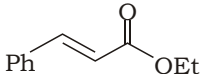
4. *(a)* Provide the catalytic cycle along with reagents for the following conversion : 3



(b) Explain how (mechanism is not required but the structure of the reagents to depict the correct stereochemistry is required along with other conditions) : 1½



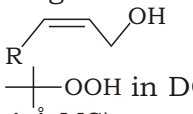
is obtained from



(c) How can (*S*)-proline be employed to convert acetophenone into its corresponding alcohol which can be optically resolved? Explain with detailed mechanism. 3

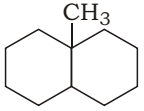
(d) Provide the structure for the following : 2+1+1+1½=5½

(i) The intermediate when (RR) DET reagents with Ti (^{i}Opr)$_4$, along with

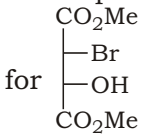


in the presence of in DCM (in the presence of 4 Å MS)

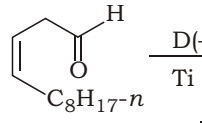
(ii) The most stable conformer of



(iii) Corresponding Newman projection for



(iv)



D(–) DET, Ti (O^{i}pr)$_4$ → [*J*]

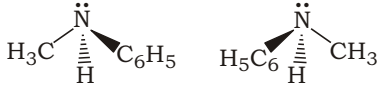
OOH, DCM, 4 Å MS

Comment if the reaction is regio-selective or chemoselective.

(e) Identify the following pair as either identical enantiomers/diastereomers after assign (*R*) or (*S*) configuration : ½+½=1

(i)

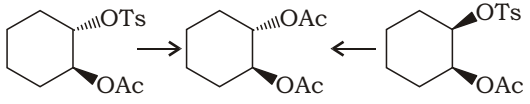
(ii)



UNIT—III

5. *(a)* Provide the mechanism of S_N2 reactions with the support of frontier orbital description. Comment on the stereochemistry of the product. 3+1=4

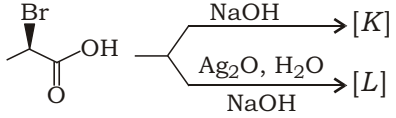
(b) Suggest probable mechanism for the acetolysis of the isomer (*I*) and isomer (*II*). Explain the role of stereochemistry :



(*I*) (*II*)

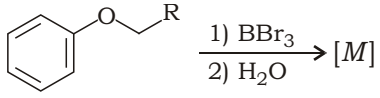
Explain why isomer (*I*) undergoes acetolysis 670 times faster than the isomer (*II*). 3+1½+1½=6

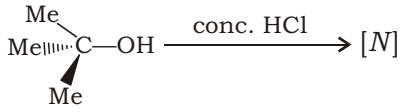
(c) Write the product(s) and suggest plausible mechanism for the following : 4

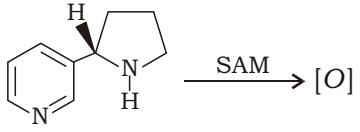


6. *(a)* Explain how sulfur master stops replication of DNA and leads to cell death. 3

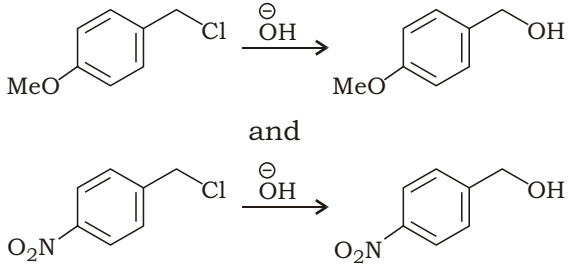
(b) Predict the product(s) and suggest the mechanism for the following reactions : 2×3=6

(i) 

(ii) 

(iii) 

(c) Predict the mechanism for the following conversion : 3

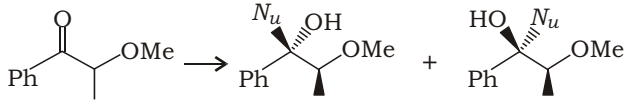


(d) Explain why, isomer (1) undergoes acetolysis 10^{11} times faster than isomer (2). Isomer (1) gives the product with the retention of the configuration, while isomer (2) gives the product with inversion : 2

(1) (2)

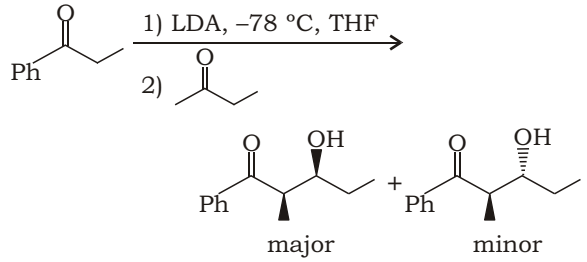
UNIT—IV

7. *(a)* Provide the mechanism and justify stereochemical outcome of the products : 2+3=5

(i) 

$NaBH_4$(N_u = H)	73%	27%
Me_2Hg(N_u = Me)	1%	99%

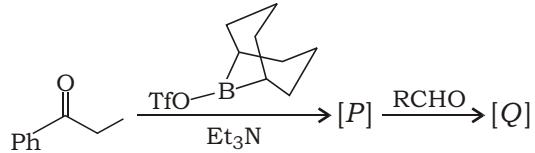
(ii)



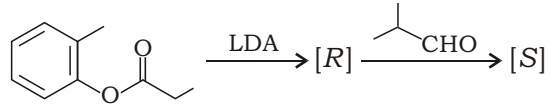
(b) Taking suitable example, explain, "aldol reaction has a chair-like transition state". 3

(c) Complete the reaction and visualize the mechanism : (½+½+2)×2=6

(i)



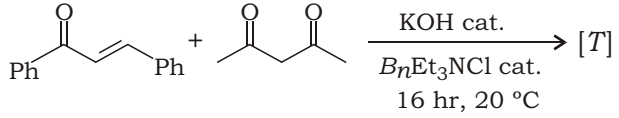
(ii)



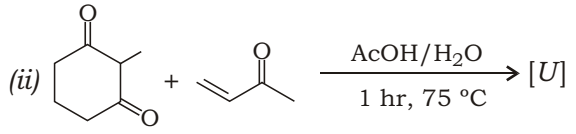
8. *(a)* Wittig reaction is generally observed to produce syn-alkene. Justify or criticize. 2

(b) Complete the following reaction and provide mechanism : (½+1½)×3=6

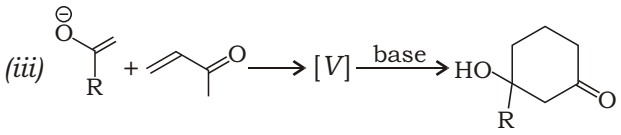
(i)



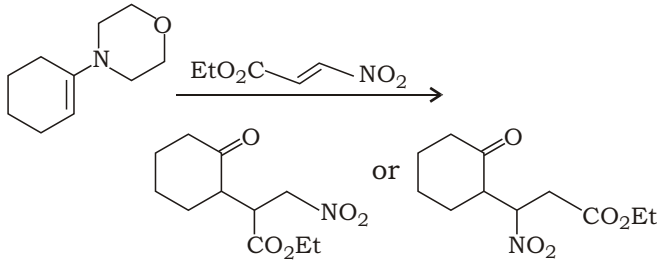
(ii)



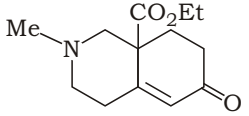
(iii)



(c) For the following reaction, predict the major product. Justify with reasoning and mechanism : ½+1+1½=3

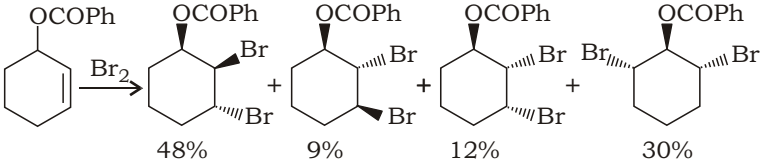


(d) How would you use the Robinson annulation to make the following compound? 3



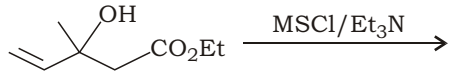
UNIT—V

9. *(a)* The bromination of 3-aryloxy-cyclohexene gives rise to a mixture of stereoisomeric and positionally isomeric addition products. The product composition for the following reaction is shown below. Give the plausible mechanism for formation of each product and also describe the factors which will affect the product ratio : 4

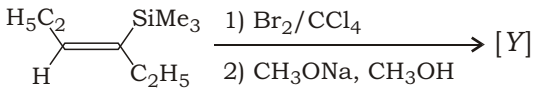


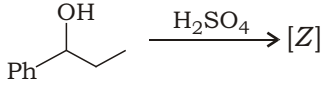
(b) Predict the major product of the following reaction with plausible mechanism :

2+2+2+1=7

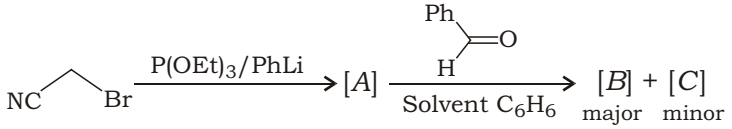
(i) 

(ii) $H_3C(CH_2)_4—CH=CH_2 \xrightarrow[2)\ NaBH_4,\ H_2O]{1)\ Hg(NO_3)_2,\ CH_3CN} [X]$

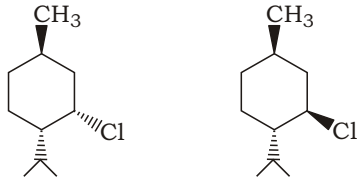
(iii) 

(iv) 

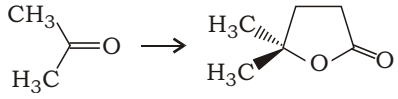
(c) Complete the following reaction with suggestive mechanism. Comment on the stereochemical outcome of the final products : 3



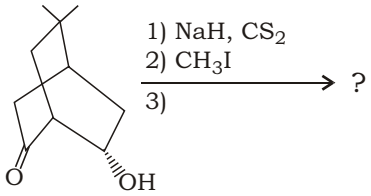
10. *(a)* Predict the product(s) with mechanism of *E*2 elimination reaction of isomer (*A*) and (*B*) in the presence of NaOEt. Which isomer will react faster and why? Explain. 4

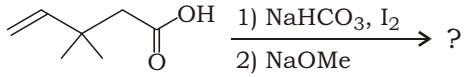


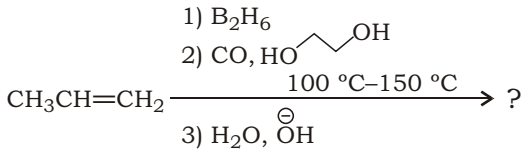
(b) Carry out the following conversion using a sulphur containing reagent : 3



(c) Provide the product(s) and suggest plausible mechanism : 2+2+3=7

(i) 

(ii) 

(iii) 

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