PG Odd Semester (CBCS) Exam., December—2017

CHEMISTRY

(1st Semester)

Course No. : CH–102 (C)

(Organic Chemistry—I)

Full Marks : 75
Pass Marks : 30

Time : 3 hours

The figures in the margin indicate full marks for the questions

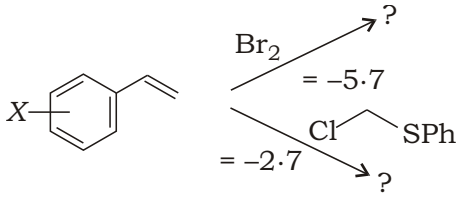
Answer **five** questions, selecting **one** from each Unit

UNIT—I

1. *(a)* *(i)* 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 with suitable explanation in each case : 1½+1½=3



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

(b) Explain the antiaromaticity of cyclobutane and homoaromaticity of cyclooctatrienyl cation. 2+1=3

(c) Describe the chemical consequence of aromaticity. 2

(d) What are cryptands? Write the structure of [2.2.1] cryptand. Why are cryptands considered to be more selective than crown ethers? 1+1+2=4

2. *(a)* What are rotaxanes? How do they differ from catenanes? 3

(b) What are crown ethers? Give the synthesis of 15-crown-6. 2

(c) Explain the effect of inductive and mesomeric effect on the acidity and basicity of the compounds with two examples. 2

(d) Explain phase-transfer catalysis with suitable examples. 3

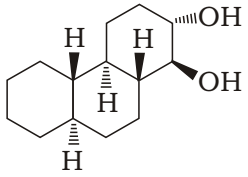
(e) Write brief notes on the following : 2½+2½=5

(i) Charge-transfer complexes and their functions

(ii) Cyclodextrins and their utilities

UNIT—II

3. (a) (i) Draw the most stable conformation for the compound *A* :

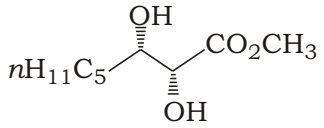


(A)

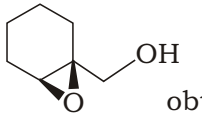
(ii) What is the stereochemical outcome of conformers of *cis*-decalin? 1½+½=2

(b) What is chiral auxiliary? Mention the strategies and give an example. ½+1+1½=3

(c) How can the following compounds be obtained through enantioselective reagent controlled procedures? Suggest the substrate and reagents to synthesize them : 2½+2½=5

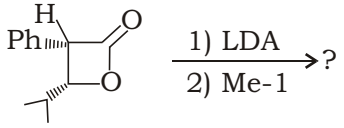
(i) 

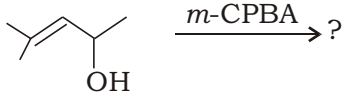
(2*R*, 3*S*) obtained at about 96% ee

(ii) 

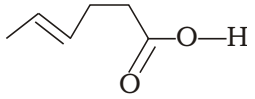
obtained at about 93% ee

(d) Suggest the products (most stable) for the following stereoselective reactions : 2

(i) 

(ii) 

(e) Explain the stereospecificity by demonstrating the iodolactonization of species (*D*) by treating it with I_2 :



(D)

Show the stereochemical outcome. 3

4. *(a)* Explain the concepts of homotopic and enantiotopic ligands and faces. 4

(b) Give a brief account of the stereochemistry of spirans and allenes. 4

(c) Out of *cis*- decalin and *trans*-decalin, which is optically active and why? Explain which conformation of 9-methyldecalin is stable. 4

(d) Write brief notes on : 3

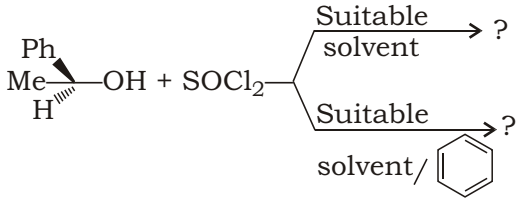
(i) Asymmetric transformation using chiral catalyst

(ii) Absolute and relative configurations

UNIT—III

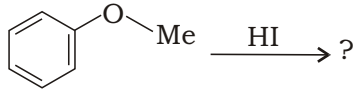
5. *(a)* Write the mechanism of S_N1 reaction with the support of orbital description. What is the role of 'intimate ion pair' in the stereochemistry of the products. 3+2=5

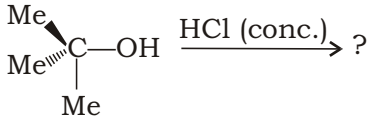
(b) Explain the products of the following reactions : 2+2=4



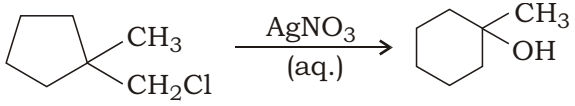
(c) Write the products of the following reactions : 1×3=3

(i) $H_2C{=}CCl_2 \xrightarrow[\text{(excess)}]{\text{ArSH}}$?

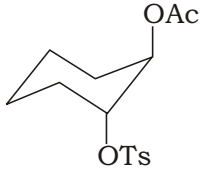
(ii) 

(iii) 

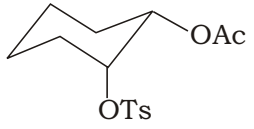
(d) Outline the mechanism for the following transformation : 3



6. *(a)* Explain why the trans-isomer *(I)* undergoes acetolysis 670 times faster than the *cis*-isomer *(II)* and the product has the same stereochemistry : 2+2=4

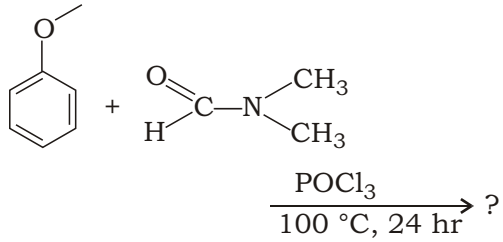


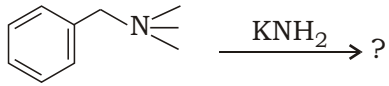
(I)

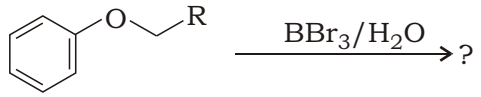


(II)

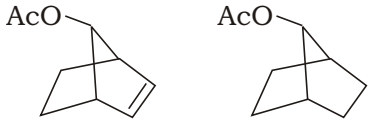
(b) Write the products and mechanisms for the following reactions : 3+2+2=7

(i) 

(ii) 

(iii) 

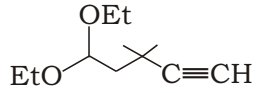
(c) Explain why isomer *(I)* undergoes acetolysis 10^{11} times faster than isomer *(II)*. Isomer *(I)* gives the product with retention of configuration while isomer *(II)* gives the product with inversion : 4

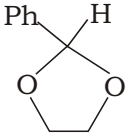


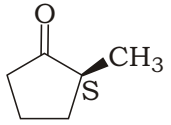
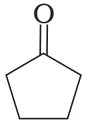
(I) *(II)*

UNIT—IV

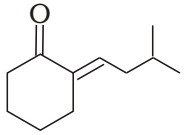
7. *(a)* Suggest the starting materials and reagents to obtain the following (give stepwise mechanism) : 2½×4=10

(i)  from an aldehyde

(ii)  from an aldehyde

(iii)  from 

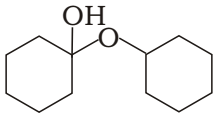
(80% ee)

(iv)  from cyclohexanone

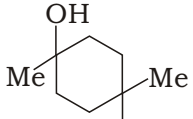
(b) Düsopropyl ketone reacts with MeMgBr affording the expected alcohol, but $Me_2CHMgBr$ fails to react with the said ketone. Give reasons. 3

(c) Explain in aqueous medium, hexafluoro acetone is completely hydrated but with acetone hydration is negligible. 2

8. *(a)* Each of the compounds *(A)* and *(B)* is a hemiacetal and, therefore, formed from an alcohol and a carbonyl compound. In each case, give the structures of the original materials : 2+2=4

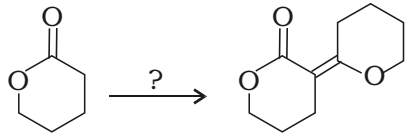
(i) 

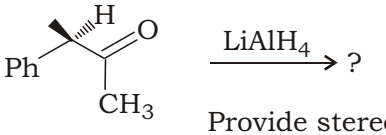
(A)

(ii) 

(B)

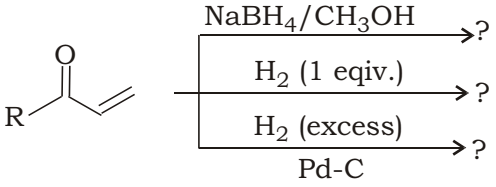
(b) Propose the mechanism for each of the following transformation : 3+3=6

(i) 

(ii) 

Provide stereochemical outcome

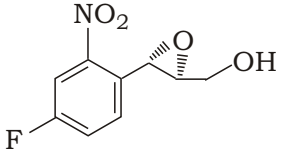
(c) Suggest the products of the following reactions : 1×3=3



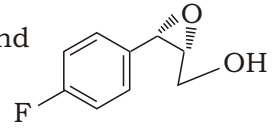
(d) How is stork enamine reaction related to Michael addition? 2

UNIT—V

9. *(a)* What is regioselectivity? How does regioselectivity determine the reaction of H_3CMgI with species *(A)* and *(B)*? ½+1½=2

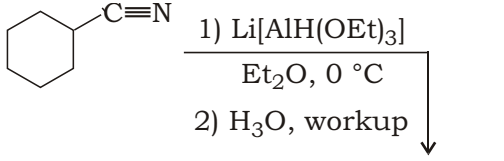


(A)

and 

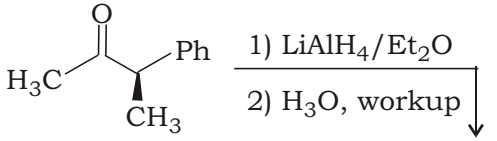
(B)

(b) Suggest the products for the following reactions by emphasizing upon the instruction given for each example :

(i) 

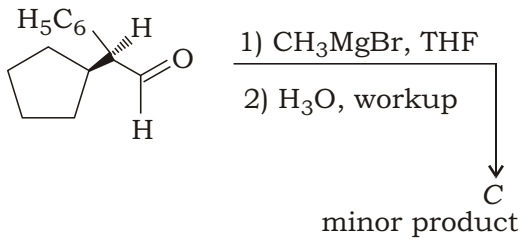
A
major product

Give a stepwise mechanism to derive the desired product.

(ii) 

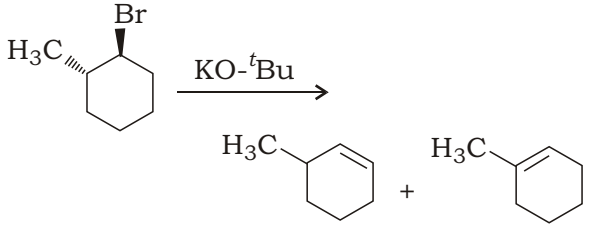
B
major product

Show the stereochemistry, depict the product formation through Newman projection formula.

(iii) 

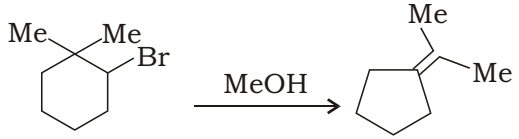
Trace the stereochemical pathway and explain why the desired product is not a major product. 2+2½+2½=7

(c) Suggest the mechanism of the following reaction : 3



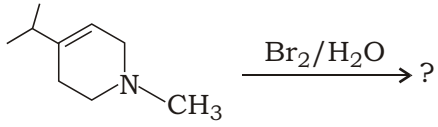
(d) Osmylation and hydroboration via cyclic intermediates give *cis*-product. Give reasons. 3

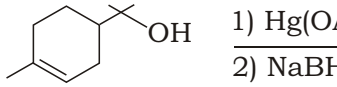
10. *(a)* Suggest the mechanism of the following rearrangement : 2

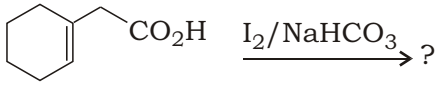


(b) Describe regioselectivity and stereo-selectivity of *E*2 elimination. 4

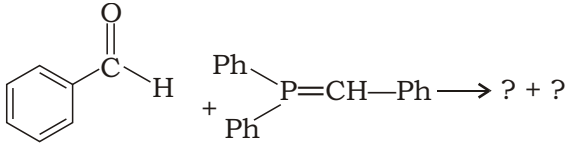
(c) Provide the major products for the following reactions. Mention the stereochemistry : 2×3=6

(i) 

(ii) 

(iii) 

(d) Provide both the thermodynamically and kinetically controlled products for the following reaction with supportive mechanism. Comment which are the major products. 1½+1½=3



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