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

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)* Discuss the isolation of fullerenes from soot.

(ii) Show that the fullerene architecture follows Euler's polyhedron formula :

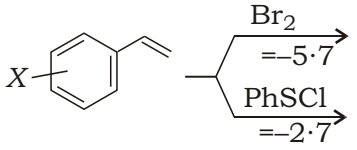
V (vertices) + F (faces) – E (edges) = 2

(iii) How does fullerene act as HIV drug? 1½+2+1½=5

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

(c) *(i)* Prove that *p*-nitrophenyl acetic acid is 2·4 times more acidic than phenylacetic acid using Hammett values. 3

(ii) Write the products and depict the mechanism of the following reactions with appropriate explanation : 3



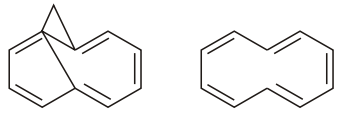
2. *(a)* What are annulenes? Comment on the aromaticity of annulenes. 1+2=3

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

(c) Justify the following :

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

(ii) Aromatic properties are exhibited by *A* but not by *B*. 2

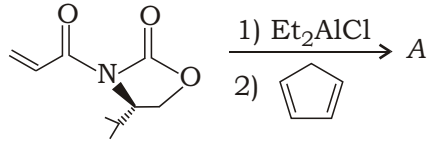


A *B*

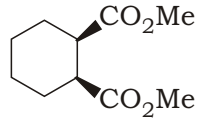
(d) Explain the high dipole moment of azulene (1·08D). What is the direction of the dipole? 3

UNIT—II

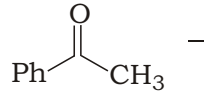
3. *(a)* Suggest the stereochemistry of the products for the following reactions : 2×4=8

(i) 

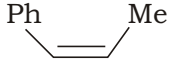
A

(ii) 

Pigliver esterase → *B*

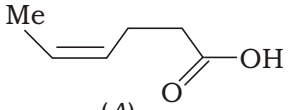
(iii) 

10% CBS, BH_3 → C (97% e.e.)

(iv) 

aq. NaOCl, DCM, Mn-salen cat.

(b) What is expected when compound (*A*) is treated with I_2? Show a detailed conversion to the final product. 3



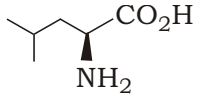
(*A*)

(c) Provide the Newman projection and Fischer projection for the *erythro*- and *threo*- forms of

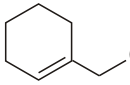
$H_3C — CH(OH) — CH(Cl)CH_3$ 2

(d) Comment on the optical properties of *cis*- and *trans*-decalin by representing their conformations to support the answer. 2

4. *(a)* Identify the following reactions as enantioselective/enentiospecific or diastereoselective/diastereospecific after providing the major products for each of the following reactions : 2+2=4

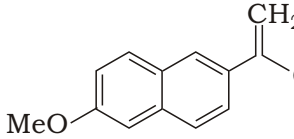
(i) 

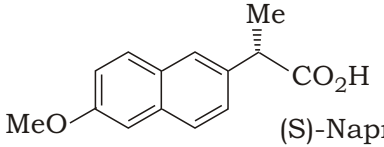
HNO_2, H_2O

(ii) 

(+) DET, OOH, $Ti(^iOpr)_4$, 4 Å Ms

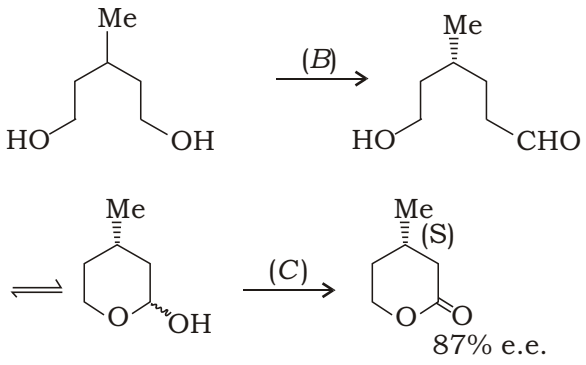
(b) Suggest the best suited catalysts/ enzymes/reagents to carry out the following transformations. Provide the exact stereochemistry of the reagent/ catalysts, wherever applicable. 2×3=6

(i) 

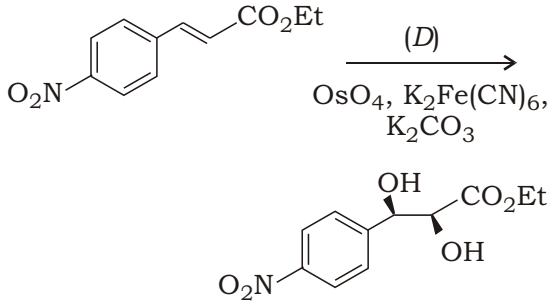
H_2, (*A*) → 

(S)-Naproxen
97% e.e.

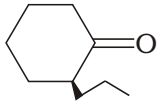
(ii)



(iii)

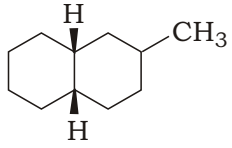


(c) Highlight the strategy used for obtaining e.e. through chiral auxiliary. Explain the production of



from cyclohexanone. 3

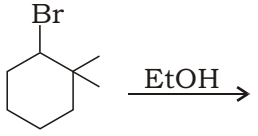
(d) Draw the most stable conformer of the decalin derivative : 2



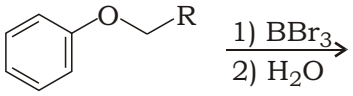
UNIT—III

5. *(a)* Predict the product(s) and suggest plausible mechanism : 2×5=10

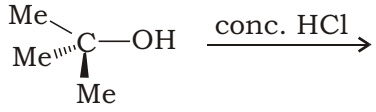
(i)



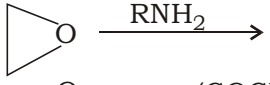
(ii)



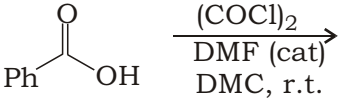
(iii)



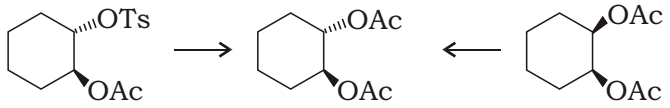
(iv)



(v)



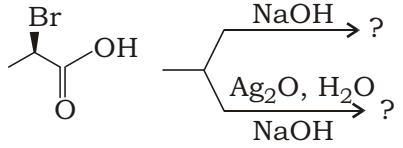
(b) Suggest plausible mechanism for the acetolysis of isomer (I) and isomer (II). Explain the role of stereochemistry. 3+2=5



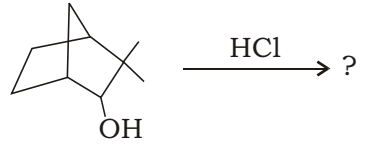
6. *(a)* Provide the mechanism of S_N2 reactions with the support of frontier orbital description. Comment on the stereochemistry of the product. 3+1=4

(b) Write the product(s) and suggest plausible mechanism for the following : 4+2+3=9

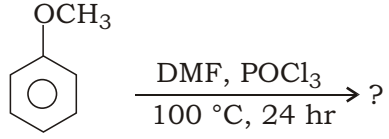
(i)



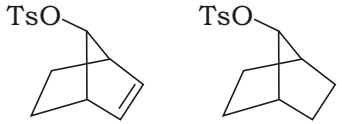
(ii)



(iii)



(c) Explain why isomer (*I*) undergoes acetolysis 10^{11} times faster than isomer (*II*). 2

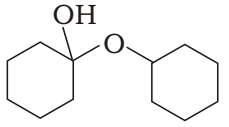


(*I*) (*II*)

UNIT—IV

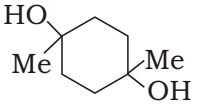
7. *(a)* Each of the compounds (*A*) and (*B*) is a hemiacetal and therefore, formed from an alcohol and a carbonyl compound. In each case, give the structures of the original materials : 2+2=4

(i)



(*A*)

(ii)

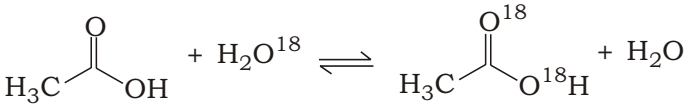


(*B*)

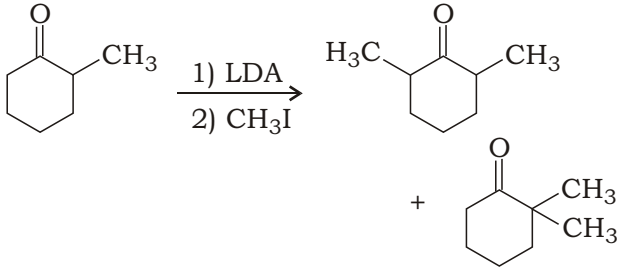
(b) Explain the following observation : 2+2=4

(i) Ketones do not hydrate considerably but in cyclopropanones, the three-membered ring ketones undergo hydration to a significant extent.

(ii) When a carboxylic acid is dissolved in isotopically labelled water, the label is incorporated into both oxygens of the acid :



(c) In the following reaction, two products are possible. Examine the reaction and explain which one is thermodynamic and which one is kinetic product : 3

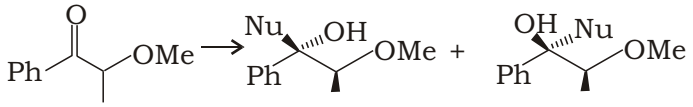


(d) How is Stork enamine reaction related to Michael addition? 2

(e) Taking suitable example, explain 'aldol reaction has a chair-like transition state'. 2

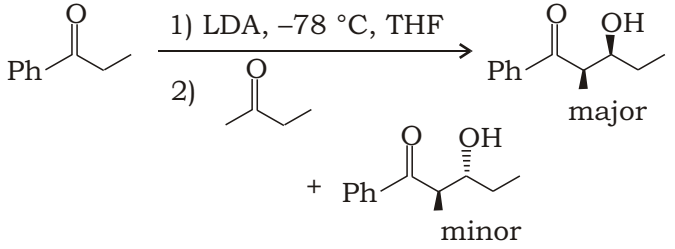
8. *(a)* Provide the mechanism and justify stereochemical outcome of the products : 2+3=5

(i)



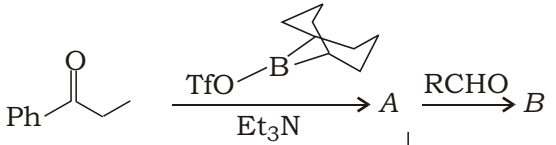
$NaBH_4$ (Nu=H)	73%	27%
Me_2Hg (Nu=Me)	1%	99%

(ii)

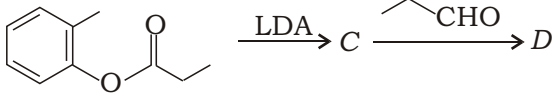


(b) Complete the reaction and depict the mechanism : (½+½+2)×2=6

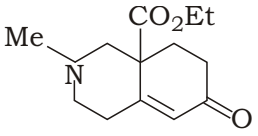
(i)



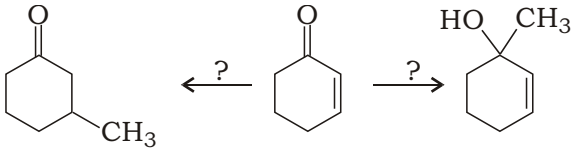
(ii)



(c) How could you use Robinson annulation to make the following compound? 3



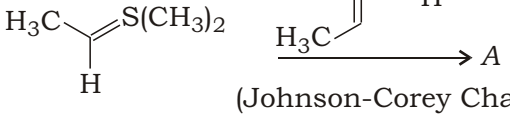
(d) Provide suitable reagents : ½+½=1



UNIT—V

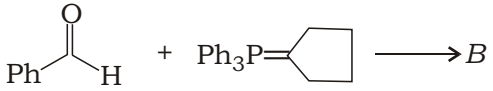
9. (a) Delineate the formation of products for the following reactions (provide stereochemical outcomes through mechanism) : 3×4=12

(i)



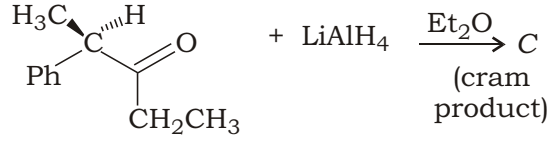
(Johnson-Corey Chaykovsky product)

(ii)

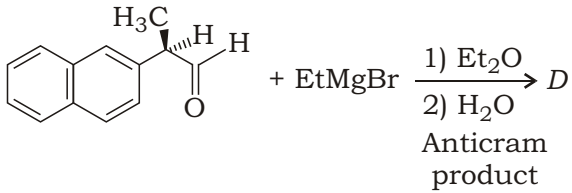


(Kinetically controlled product)

(iii)



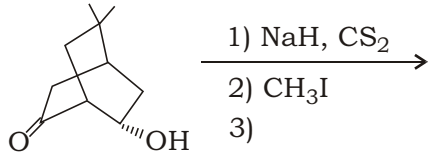
(iv)



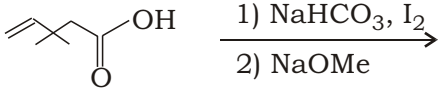
(b) Design an alkene synthesis from a secondary alcohol and $POCl_3$ using pyridine as a base. State the advantage of using pyridine. 3

10. (a) Provide the product(s) and suggest plausible mechanism : 2×4=8

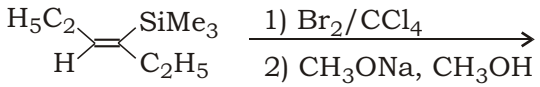
(i)



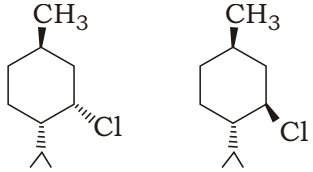
(ii)



(iii) $CH_3CH{=}CH_2 \xrightarrow[2)\ CO,\ HO\text{-}(CH_2)_3\text{-}OH \\ 3)\ H_2O,\ \overset{\ominus}{O}H]{1)\ B_2H_6}$

(iv) 

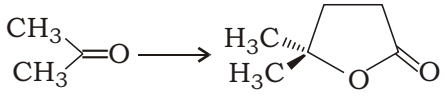
(b) Predict the product(s) with mechanism of *E*2 elimination reaction of isomer (*A*) and (*B*) in the presence of NaOEt. Which isomer will react faster and why? Explain. 4



(*A*)

(*B*)

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



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