PG Odd Semester (CBCS) Exam., December—2018

CHEMISTRY

(1st Semester)

Course No. : CHMCC–102

(Organic Chemistry—I)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

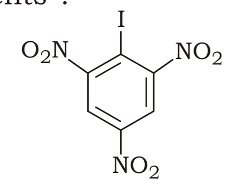
The figures in the margin indicate full marks for the questions

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

UNIT—I

1. *(a)* ^{1}H-NMR study of [18] annulene shows two types of proton, 12 protons at 9·00 ppm, 6 protons at 3·00 ppm. On the other hand, when treated with potassium in THF at –20 °C, the chemical shift is found to be reversed; 6 protons at 29·5 28·1 ppm and 12 protons at 1·13 ppm. Identify the protons and provide explanation. 2½

(b) Picryl iodide (*I*) exhibits two types of C—N bond distances (C—N distances to be 1·45 Å and 1·35 Å). Identify and give the comments : 1½



(*I*)

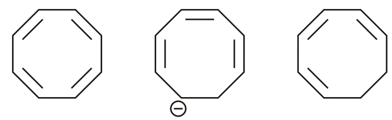
(c) What are crown ethers? Write the synthesis of 18-crown-6. State the role of crown ether in the increase of rate of a nucleophilic substitution reaction in presence of $CN^{\ominus}$ nucleophile. 4

(d) Explain why, 1-chloro-1-methyl cyclopentane undergoes solvolysis 43·7 times faster than ^{t}BuCl in 80% ethanol at 25 °C. 2

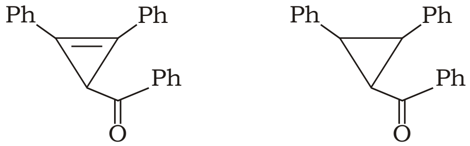
(e) How are catenanes different from rotaxanes? 1½

(f) Provide reactions which exhibit smaller (+ve or –ve) reaction constant ( ). 2½

2. *(a)* Arrange the following compounds in order of increasing stability with explanation : 2



(b) Which of the following compounds is more acidic and why? 2



(c) Acetoacetic ester exists in the enolic form 0·4% in water and 19·8% in toluene. Why? 2

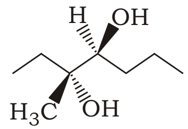
(d) What is inclusion compound? Depict the role of cyclodextrins as a host in the formation of inclusion compound. 3

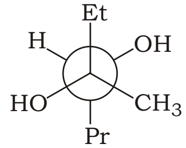
(e) Write a short note on electron doner-acceptor complex. 2½

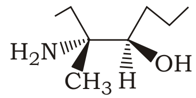
(f) Base-catalyzed hydrolysis of ethyl-*m*-nitrobenzoate is 63·5 times faster than that of unsubstituted ester under parallel condition. Predict the rate of the base-catalyzed hydrolysis of ethyl-*p*-methoxy benzoate under same reaction conditions. (Given, $_{m}\ NO_2$ 0·71 and $_{p}\ MeO$ 0·27) 2½

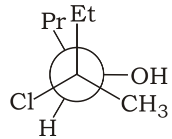
UNIT—II

3. (a) Provide sawhorse projection of the given wedge formula and Newman projections by retaining their configurations. Assign *R* and *S* configurations of the asymmetric centres : 1×4=4

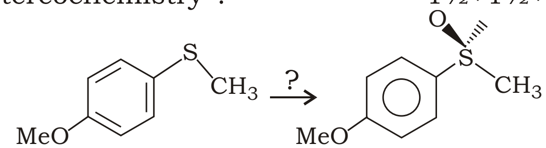
(i) 

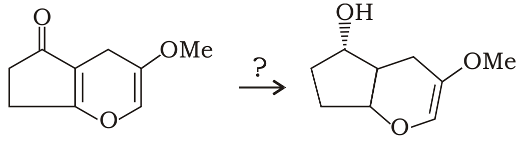
(ii) 

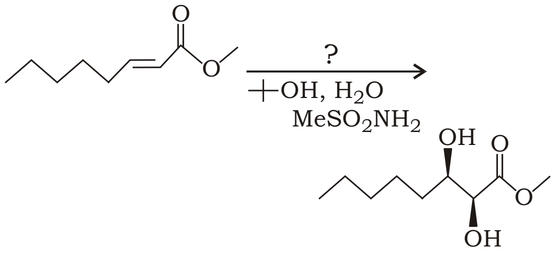
(iii) 

(iv) 

(b) Achieve the following stereochemical asymmetric synthesis by providing appropriate reagents along with other promoters. Provide the structures of these reagents to depict their stereochemistry : 1½+1½+2=5

(i) 

(ii) 

(iii) 

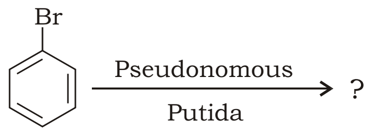
(c) *(i)* Provide the names of three incompatible functional groups for sharpless asymmetric epoxidation reaction.

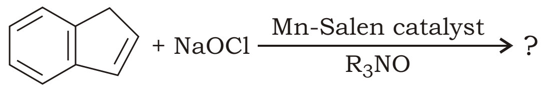
(ii) Portray the catalytic cycle of the oxidation of  with Mn-Salen catalyst in presence of aqueous NaOCl.

(iii) What is the role of an additive in a Jacobsen-Katsuki epoxidation? With examples, provide the most probable pathway for the asymmetric oxidation of olefins.

1+2+2=5

4. *(a)* How to achieve the following asymmetric synthesis? Provide the products along with their absolute configuration. Identify each reaction as stereospecific or stereoselective : 1½+1½=3

(i) 

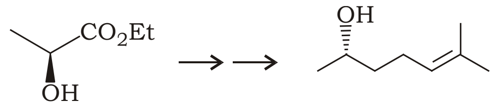
(ii) 

(b) Schematically depict the catalytic cycle of the sharpless epoxidation. 3

(c) *(i)* BH_3 cannot reduce ketones to generate asymmetric alcohols in *ee*. Provide a stepwise mechanism for the generation of a chiral catalyst which can achieve the asymmetric synthesis through a chiral pool strategy. 2½

(ii) Provide a methodology for converting OsO_4 into a chiral reagent capable of asymmetric synthesis. 2½

(d) How can (S)-sulcatol be obtained from (S)-ethyl lactate? Discuss briefly :

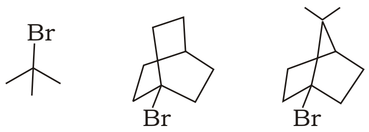


(S)-Ethyl lactate (S)-Sulcatol

Identify this stereochemical conversion as streospecific or stereoselective. 2½+½=3

UNIT—III

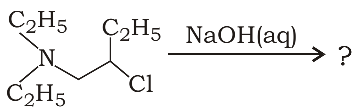
5. *(a)* Explain the rate of the nucleophilic substitution reaction of the following compounds : 3



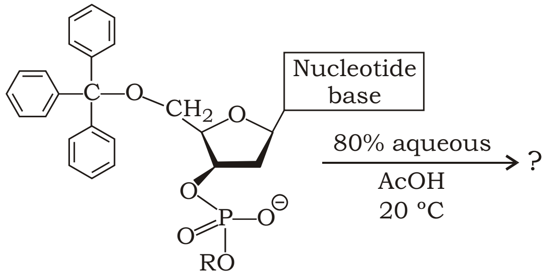
rate 1 10^{-6} 10^{-14}

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

(i)



(ii)



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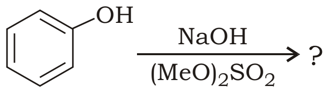

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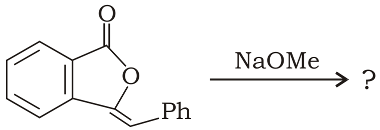
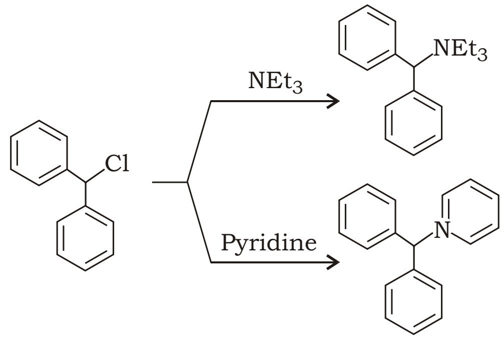
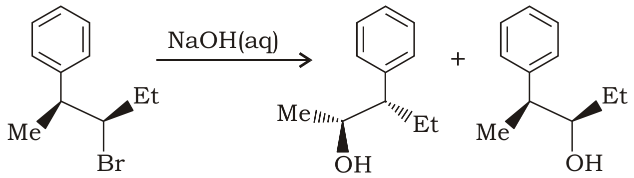


(c) How do you ascertain the higher nucleophilicity of pyridine in comparison to triethyl amine in the following reaction? 2

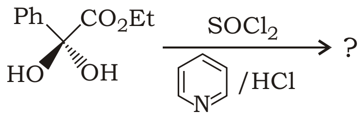


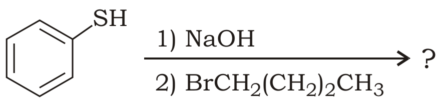
6. *(a)* Suggest the mechanism supporting the formation of *A* and *B* in the following reaction : 3

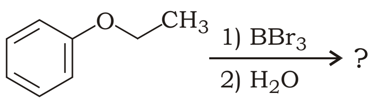


(*A*) (*B*)

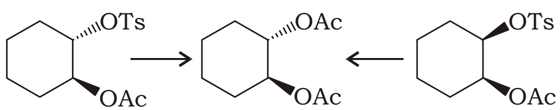
(b) Predict the product(s) of the following reaction with suggestive mechanism : 3+2+2=7

(i) 

(ii) 

(iii) 

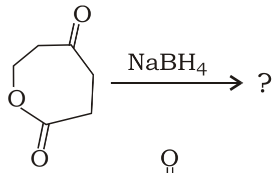
(c) Suggest plausible mechanism for the acetolysis of isomer (*I*) and isomer (*II*). Explain why, isomer (*I*) undergoes acetolysis 670 times faster than the isomer (*II*) : 4

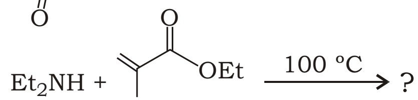


(*I*) (*II*)

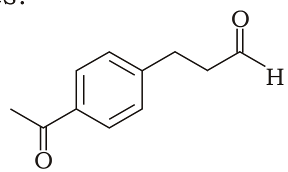
UNIT—IV

7. *(a)* Complete the following reactions and suggest mechanism : 2×2=4

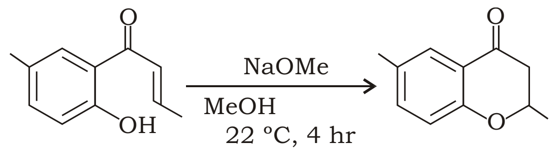
(i) 

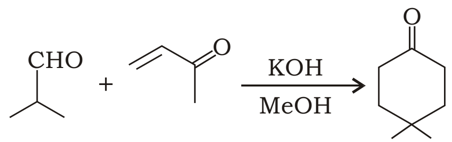
(ii) 

(b) There are three possible products from the reduction of this compound with sodium borohydride. What are their structures? 3

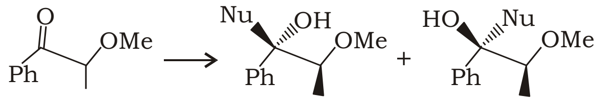


(c) Provide the mechanism for the following reactions : 2×2=4

(i) 

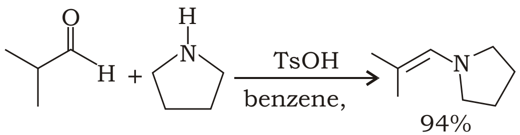
(ii) 

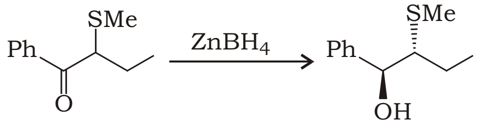
(d) Explain the difference of yield in the following reaction in the two given conditions : 3

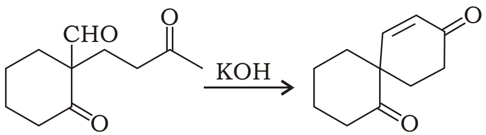


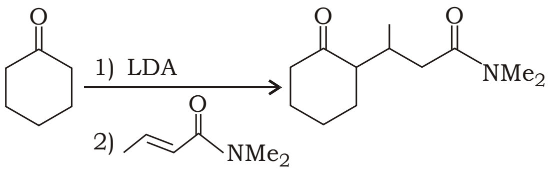
$NaBH_4$ (Nu=H)	73%	27%
Me_2Mg (Nu=Me)	1%	99%

8. (a) Provide plausible mechanism for the following reactions : 2×4=8

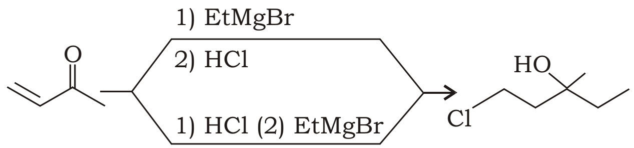
(i) 

(ii) 

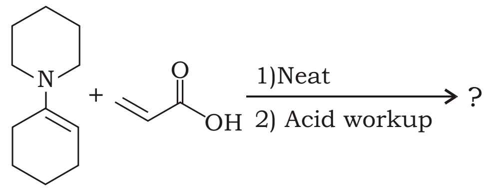
(iii) 

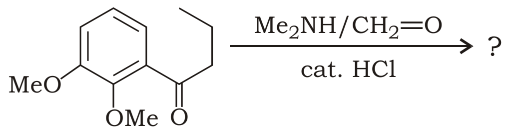
(iv) 

(b) Which of the two routes shown here would actually lead to the product? Why? 1+2=3



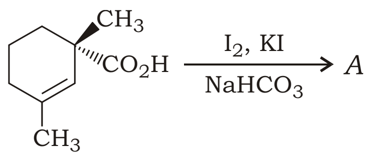
(c) Complete the following reactions and visualize the mechanism : 1½×2=3

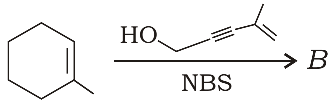
(i) 

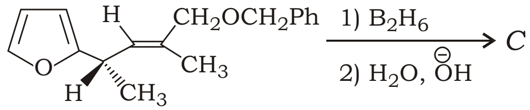
(ii) 

UNIT—V

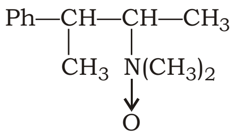
9. (a) Predict the major product of the following reactions. Suggest mechanism : 2×3=6

(i) 

(ii) 

(iii) 

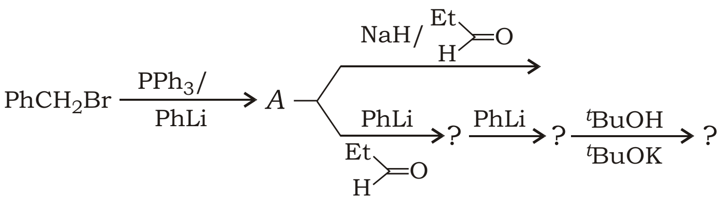
(b) Predict the product with suggestive mechanism when *threo*- and *erythro*-isomers of the following compound is heated at 150 °C : 3



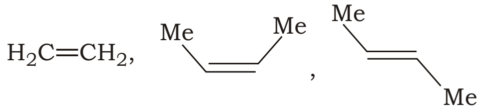
Threo ⟶ ?

Erythro ⟶ ?

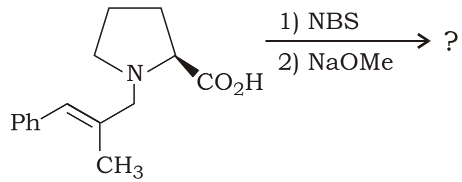
(c) Which of the following reactions will give major product? Provide mechanism in support of the major product : 4

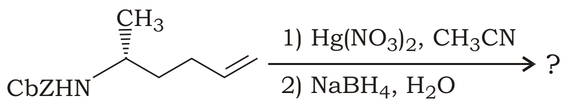


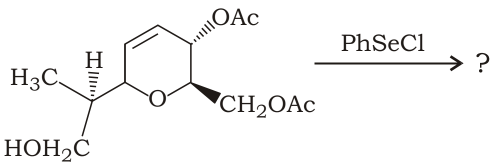
(d) Arrange the following compound in increasing order of reactivity with Br_2 in methanol : 1

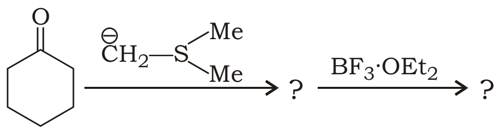


10. *(a)* Predict the major product with plausible mechanism : 2×4=8

(i) 

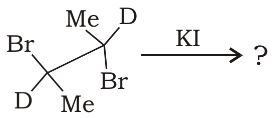
(ii) 

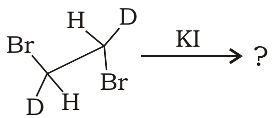
(iii) 

(iv) 

(b) What are stereospecific and stereo-selective reactions? "Addition of Br_2 in CCl_4 with *E*- and *Z*-2-butene is stereospecific but with *E*- and *Z*-1-phenyl propene is not stereospecific." Explain with mechanism with proper reasons. 4

(c) Provide the mechanism of the following reactions : 2

(i) 

(ii) 

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