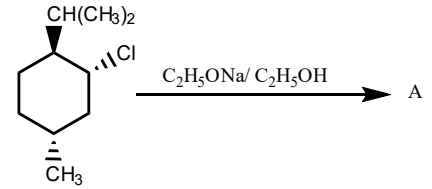
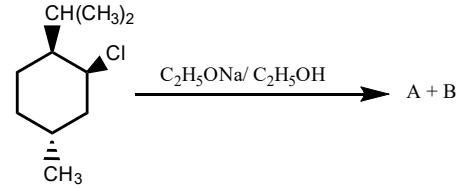
(b) E2 –elimination of 2- Bromobutane with NaOEt in EtOH yields 19% of 1- butane whereas same NaOEt in ^{t}BuOH increases the yields of 1- butene to 38 % . Explain 2

(c) Menthyl chloride reacts with sodium ethoxide in ethanol to give a single product. By contrast, neomenthyl chloride treated in the same fashion gives an additional product which is the major product. Moreover, menthyl chloride reacts much more slowly than neomenthyl chloride. Predict the product (s) and analyse the reaction mechanistically to explain these observations. 3

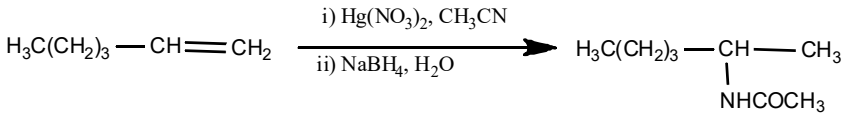


Menthyl chloride



Neomenthyl chloride

(d) Provide plausible mechanism for the following transformation. 2



★★★

PG ODD SEMESTER EXAMINATION, 2022

CHEMISTRY

1st Semester

Course No. : CHMCC - 502

(Organic Chemistry- I)

Full Marks : 70

Pass Marks : 28

Time : 3 hours

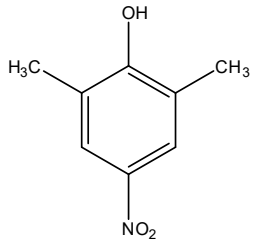
The figures in the margin indicate full marks for the questions

(Answer any five questions, taking one from each unit)

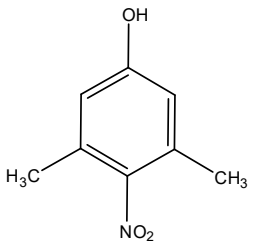
UNIT - I

1. (a) Assign π –MO energy levels of Cyclooctatetraene and Cyclobutadiene with the help of Frost's cycle and estimate delocalization energy in unit of β 3

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



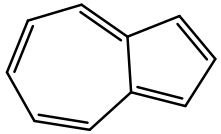
A



B

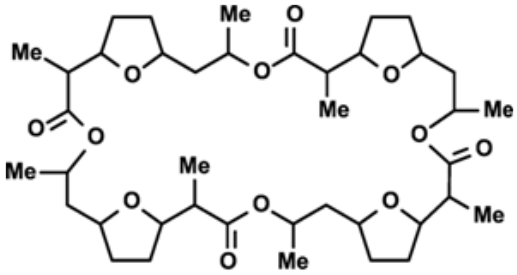
(c) Explain why cyclopentadiene is much more acidic than 1,3 cyclohexadiene. 2

(d) Azulene ($C_{10}H_8$) is a deep-blue compound with the structure shown below: Account for its aromaticity and its dipole moment (μ = 1.0 D). 2



Azulene

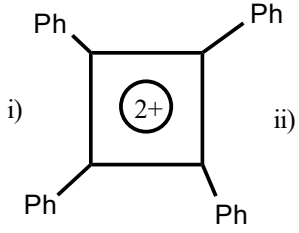
(e) Correlate between the activity of antibiotic Nonactin and crown ether. 2



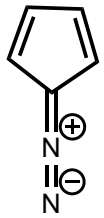
nonactin

(f) The given species are aromatic, nonaromatic or antiaromatic and why? 3

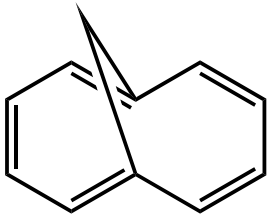
i)



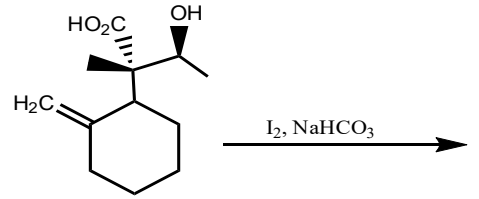
ii)



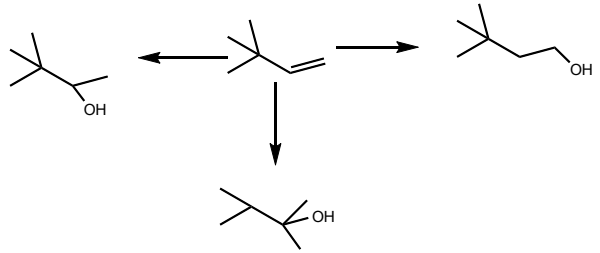
iii)



ii)



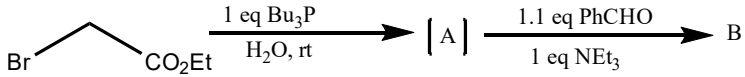
(c) Carry out the following transformation with suitable reagent (s) and reaction condition also provide the mechanism and explain it. 2x3 = 6



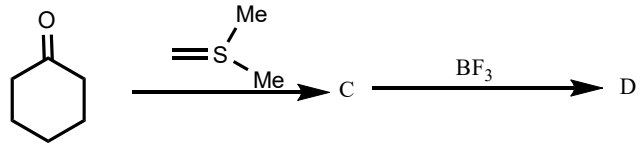
(d) Predict the product when 3- buten-2-ol is allowed to react with aqueous HBr. $1\frac{1}{2}$

10. (a) Complete the following reaction (s) and provide the mechanism. $2^1/_2+2^1/_2+2 = 7$

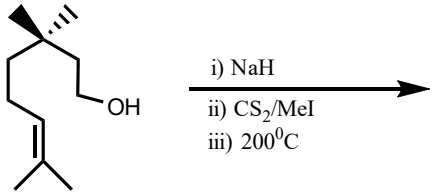
(i)

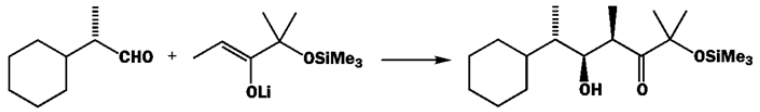


(ii)

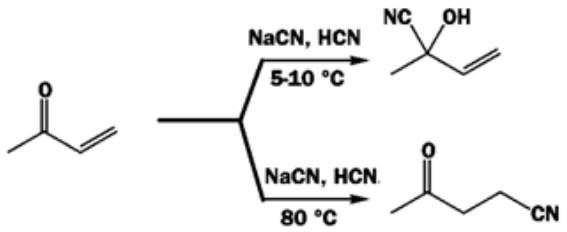


(iii)



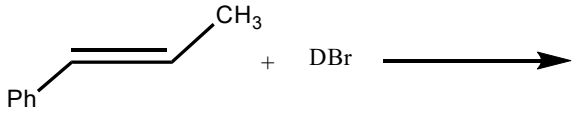
(ii) 

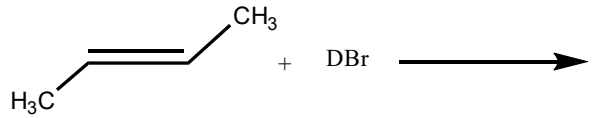
(d) Suggest reasons for the different outcomes of the following reactions (with mechanism). 2



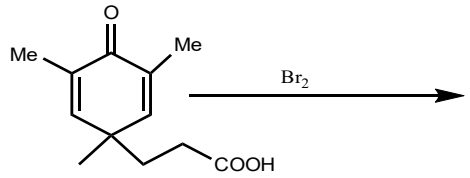
UNIT - V

9. (a) Provide the major product (with stereochemistry) of the following reaction(s) and explain the difference in mechanism. 3

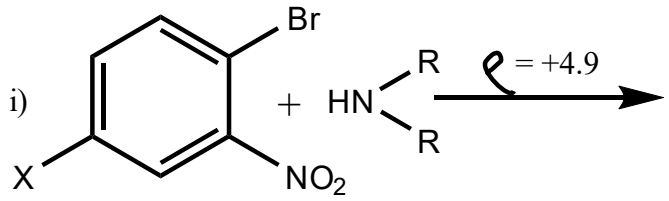


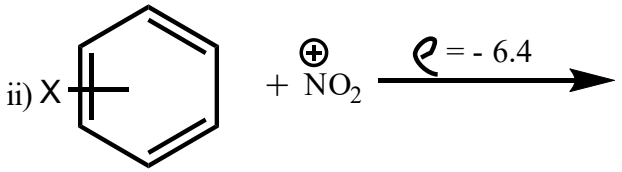


(b) Provide the major product(s) of the following reaction and suggest plausible mechanism. $1\frac{1}{2}+2=3\frac{1}{2}$

i) 

2. (a) Write the products and depict the mechanism of the following reactions with appropriate explanation in light of Hammett reaction constant (ρ). 2+2 = 4

i) 

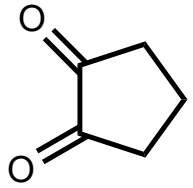
ii) 

(b) Discuss the structure and bonding of Cyclodextrin. 2

(c) Cyclooctatetraene (COT) adds one proton when treated with concentrated sulfuric acid and forms a cation. Comment on the stability and chemical shift values in ^1H –NMR of this cation. 2

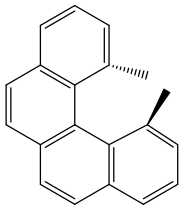
(d) What is Rotaxanes and Catenanes? Discuss the statistical synthetic approach of Rotaxanes. 2+2 = 4

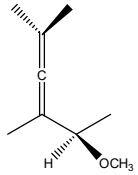
(e) Arrange the following in the increasing order of enol content. Give reasons: 2

(ii)$CH_3COCOCH_3$ *v/s* 

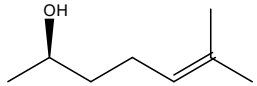
UNIT - II

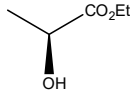
3. (a) From the given options, identity the compounds that are optically active, Provide R/S or P/M configuration. 2

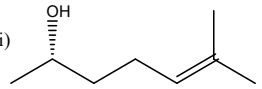


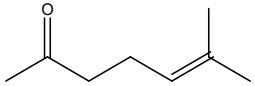


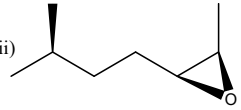
(b) Carry out the following conversions by suggesting the reagents/substrates/products along with the correct stereochemistry (where applicable). Also, identify each of these reactions as enantiospecific/diastereospecific or enantioselective/diastereoselective. 3×3 = 9

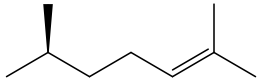
(i) 

From 

(ii) 

From 

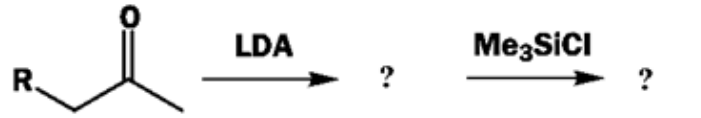
(iii) 

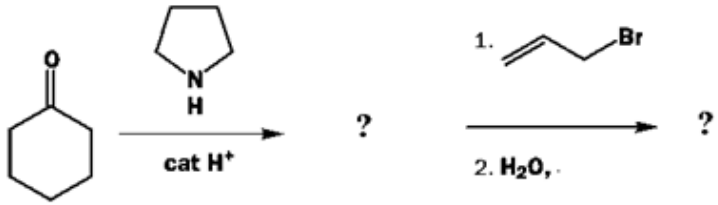
From 

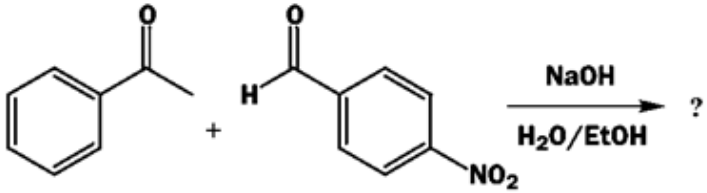
(c) Provide the structures of (i) S-BINAP and (ii) AD-mix-??(include the oxidants/promoters/others) 1+2 = 3

4. (a) Provide the staggered and eclipsed erythro and threo representations in Newman's projection. Also provide their Fischer and sawhorse representation. Assign absolute configuration for them. 2

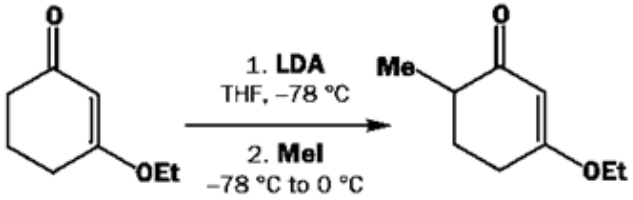
8. (a) Predict the product (mechanism not required). 1+1+1=3

(i) 

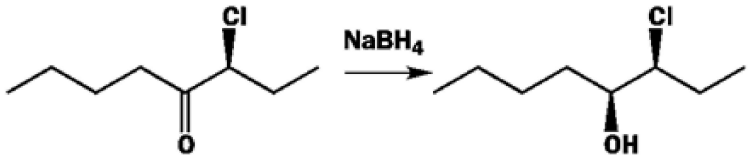
(ii) 

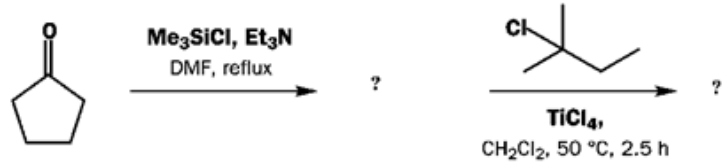
(iii) 

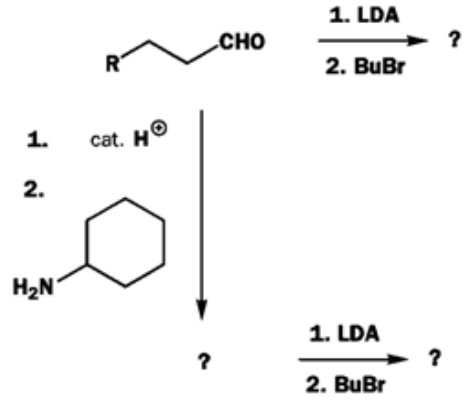
(b) Provide Mechanism of the following reaction 2



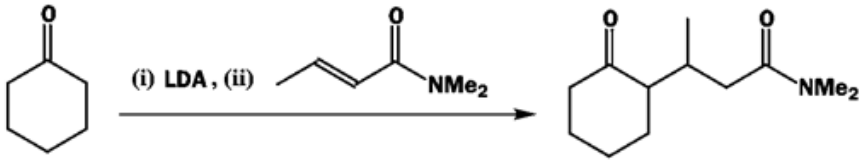
(c) Explain the stereoselectivity in this reaction 3+3 = 6

(i) 

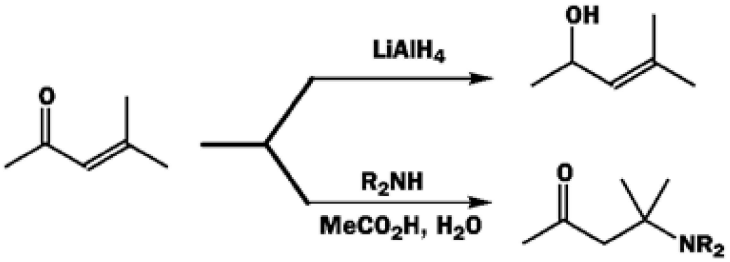
(ii) 

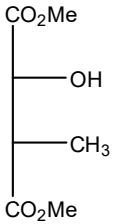
(iii) 

(b) Provide Mechanism of the following reaction 2



(c) Suggest reasons for the different outcomes of the following reactions (with mechanism), 3

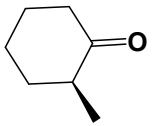


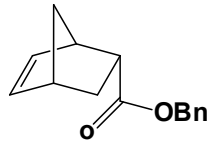


(b) Provide the reagents/catalysts/conditions/catalytic cycles (where applicable) and all relevant information along with supportive mechanism in support of the following:
2.5 + 2+2 +2.5 = 9

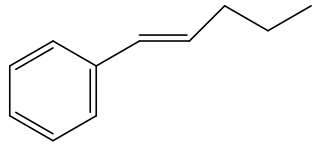
i. How can BH_3 be employed to achieve an asymmetric reduction of 2-phenyl cyclopentanone?

ii. From cyclohexanone and cyclopentadiene, how can the following enantiomers be obtained, separately?

(i) 

(ii) 

iii. How can OsO_4 be utilized for asymmetric synthesis during oxidation of the given olefinic compound?

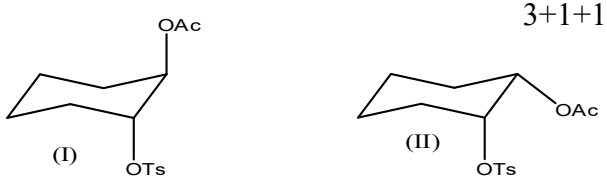


(c) Provide the structures of: (i) the catalytic reagent used for generating asymmetric sulphoxides and (ii) (S,S)-Mn-Salen complex. 1.5× 2 = 3

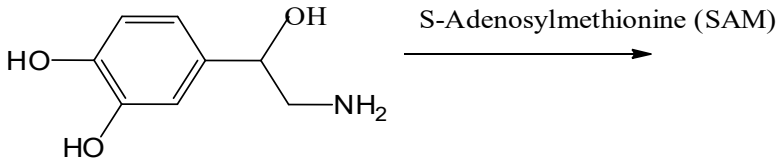
UNIT - III

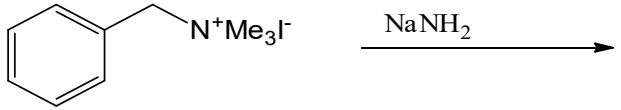
5. (a) Suggest plausible mechanism in the acetolysis of isomer

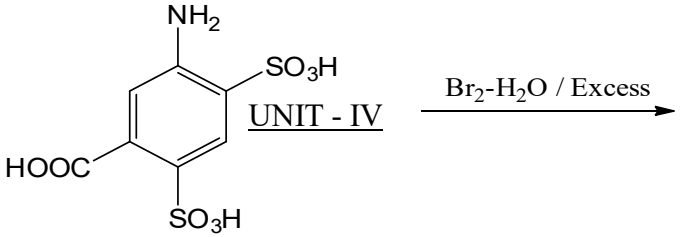
(I) and Isomer (II). Show that stereochemistry plays a significant role in this reaction. Explain why isomer (I) undergoes acetolysis 670 times faster than the isomer (II). 3+1+1 = 5



(b) Predict the product(s) for the following reaction with supporting mechanism. 2+2+2 = 6

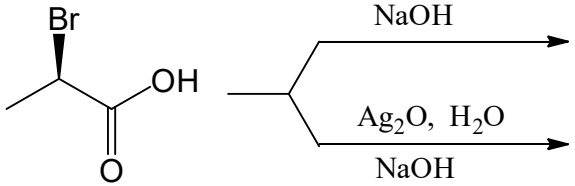
i) 

ii) 

iii) 

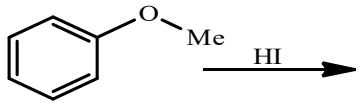
UNIT - IV

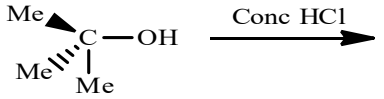
(c) Write the product(s) and suggest olausible mechanism for the following: 3



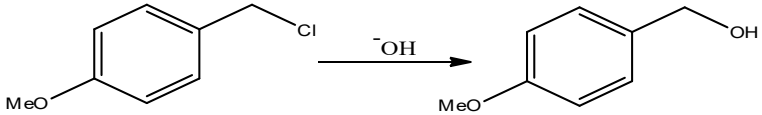
6. (a) Provide plausible mechanism of S_N1 reaction taking appropriate reagents. (b) Comment on the stereochemistry of the products. (c) Sometimes extra inverted product is form in S_N1 reaction: Justify (d) Explain why concentration of nucleophile has no effect on the rate of an S_N1 reaction. 3+2+1+1 = 7

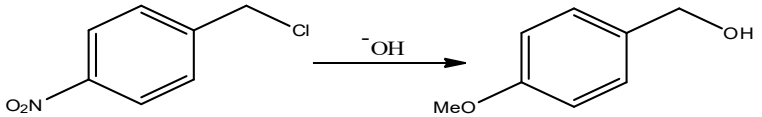
(b) Predict the product(s) and suggest appropriate mechanism in support of the products. 2+2 = 4

(i) 

(ii) 

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





UNIT - IV

7. (a) Predict the product and provide the mechanism. 3x3=9

(i)