D.K.M. COLLEGE FOR WOMEN (AUTONOMOUS), VELLORE-1

II SEMESTER

ORGANIC CHEMISTRY-II

UNIT-I

ADDITION TO CARBON – CARBON AND CARBON – HETERO MULTIPLE BONDS

Section-A (6 Marks)

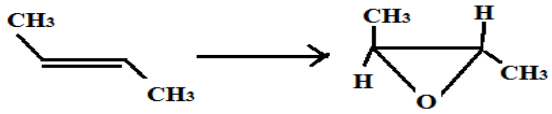
1. Illustrate the regioselectivity of hydroboration reaction with an example
2. Predict the major product and give the mechanism of following reactions

   (i) Trans-2-butene $\xrightarrow{Cl_2,\ CH_3COOH}$?

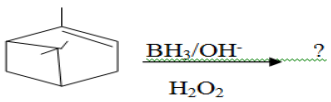
   (ii) CH_3-CH=CH_2 $\xrightarrow{NOCl}$?
3. Mention the four important method of generation of carbenes. Comment on their structure.
4. (a) Account for the following

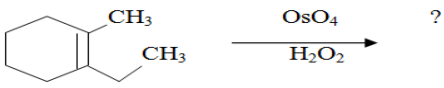
   Addition of triplet carbine to trans-2-butene gives a non streospecific product wheras the ci-2- butene gives a stereospecific product (4)

   (b)How do you bring about the following transformation? (2)



5. Give an example of Simmon Smith reaction (6)
6. Predict the products in the following reactions with stereochemistry

(i)


(ii)


(iii) $C_6H_5COCH_3$ $\xrightarrow[B^-]{CH_2O/HNMe_2}$?

7. Define a 1,3 dipole. Give two examples. How do you compare 1,3 dipolar cycloadditon reaction with Diels Alder reaction? (6)

8. What is Woodward Prevost reaction? Explain(6)

9. Write briefly the stereochemistry of carbene addition to olefinic bond.

10. (a) Erythro-3-bromo-2-butanol on reaction with HBr gives meso2,3 dibromobutane while the threo isomer gives active 2,3 dibromo butane. Rationalize (2)

(b) With mechanism explain the benzoin condensation (4)

Section-B (15 Marks)

11. (a) Give a brief account on the addition of halogen and nitrosyl chloride to olefins (5)

(b) Describe in detail about the electrophilic, nucleophilic and neighbouring group participation mechanisms (10)

12. (a) Write short note on hydration of olefins and acetylenes (5)

(b) Explain in detail about the hydroboration and hydroxylation reactions (10)

13. Enumerate the product formation and its mechanism of the following naming reactions

(a) Stobbe condensation

(b) Wittig and Wittig Horner reaction

(c) Mannich reaction

14. Predict the product and mechanism of the following reaction (3x5=15)

(a) R_2NH + HCHO+ CH_3-CH$(CN)_2$ $\xrightarrow{OH^-}$?

(b)Benzaldehyde+ Diethyl Succinate $\xrightarrow{\text{sodium ethoxide}}$?

(c) Acetone+ ethyl acetate $\xrightarrow{\text{strong base}}$?

15. Predict the product and mechanism of the following reactions (3x5=15)

(a) Succinaldehyde + Methyl amine + Acetone $\xrightarrow{\text{strong base}}$?

(b) CH_3-CH=CH COOEt + CH_2 $(COOEt)_2$ $\xrightarrow{\text{sodium ethoxide}}$?

(c) $CH_3COCH_3 + ClCH_2COOEt \xrightarrow{\text{sodium ethoxide}}$?

16. (a) Explain in detail about the electrophilic addition to conjugated dienes (7)

(b) Account for the following with detailed explanation

Addition of bromine to maleic acid gives dl 2,3 dibromobutane while the addition of bromine to fumaric acid fives the meso form. (8)

UNIT – II ELIMINATION REACTIONS

Section-A (6 Marks)

1. Write a short note on oxidation of cyclohexanone.
2. Give an account on conformation of ethane and 2-bromo 1-chloro ethane.
3. Explain the conformation of cyclohexanone and its esterfication process.
4. Briefly explain the difference between the conformation and configuration.
5. Write a note on 9-methyl decalin with comparison on decalin.
6. Explain the reduction of cyclohexane carboxylic acid.

Section-B (15 Marks)

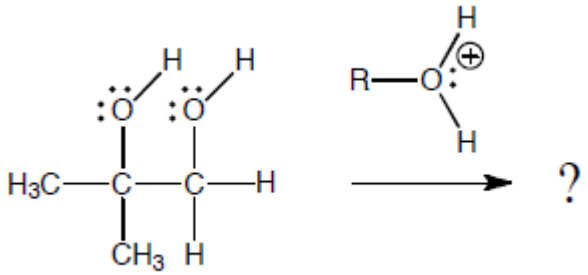
7. Describe in detail about conformation of cyclohexane and di substituted cyclohexane.
8. i. Explain the conformation of decalin and 9-methyl decalin.(7)
   ii. Explain the esterfication process of carboxylic acid and which stable form Cis or Trans conformation(8)

UNIT-III MOLECULAR REARRANGEMENTS

Section-A (6 Marks)

1. Give the mechanism of Wagner-Meervin reaction.
2. In the pinacol-pinacolone rearrangement of Ph-Me-C(OH)-C(OH)-Ph-Me and $Ph_2C(OH)$-C(OH)-Me_2 a phenyl group migrates in the former but a methyl group migrates in the latter-Account.
3. Give a brief account on Von ritcher rearrangement

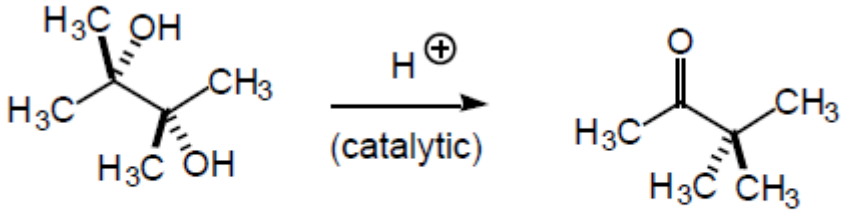
4. The following 1,2 diol undergoes the pinacol rearrangement. Predict the structure of the product.



5. The rearrangement of pinacol (**1**) to pinacolone (**2**) in acid solution was first reported in 1860.

Write a mechanism for this process. Related rearrangements of compounds bearing hydroxyl

groups on adjacent carbons (1,2-diols) are now generally known as *pinacol rearrangements*.



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Section-B (15 Marks)

4. a) Outline the mechanism of Dienone-Phenol rearrangement.

b) Explain Stevens rearrangement.

c) Discuss the mechanism of Baeyer- Villiger rearrangement.

5. Explain in detail about the Wolf rearrangement and Demjanov rearrangement.

6. Ouline the mechanism of the following rearrangements

(a) Dienone – phenol rearrangement

(b) Favorski rearrangement

UNIT-IV OXIDATION

Section-A (6 Marks)

1. Discuss the role of SeO_2 in the oxidation of methylene to carbonyl group.

2. Explain the mechanism of two different methods of oxidation of CH_2 adjacent to C=O.

3. Discuss in detail about the use of DMSO in combination with DCC and acetic anhydride in oxidizing alcohols.

4. Discuss in detail about the oxidation of aryl methanes

5. Give a brief account on allylic oxidation of olefins

6. Write short note on dehydrogenation by quinones and lead tetraactate

Section-B (15 Marks)

7. Describe in detail about the dehydrogenation by SeO_2 and $Hg(OAc)_2$

8. Explain in detail about the following reactions

(i) Formation of C-C bond in phenol coupling –

(ii) acetylene coupling

(iii) allylic oxidation of glycols

9. Discuss in detail about the following

(i) Ozonolysis

(ii) oxidation of olefinic double bonds and unsaturated carbonyl compounds

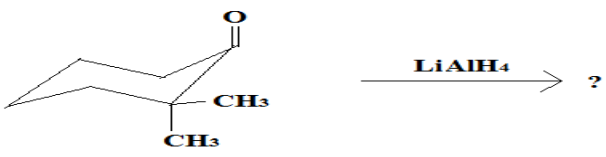
UNIT-V REDUCTION

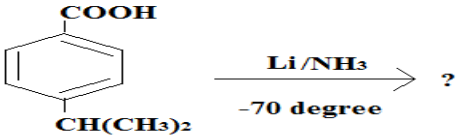
Section-A (6 Marks)

1. Predict the product and mechanism for the following reaction

(i) Acetopheneone $\xrightarrow{ZnHg/HCl}$?

(ii)



(iii) 

2. Discuss the mode of reduction of an aromatic compound containing either nitro group or methoxy group under birch reduction condition

3. Write the product and mechanism of the following

(i) CH_2=CH-CHO $\xrightarrow[\text{Isopropyl alcohol}]{Al[OHC(CH_3)_2]}$?

(ii) $C_6H_5COC_6H_5$ $\xrightarrow[KOH]{N_2H_4}$?

4. Give a brief account on selectrides.

5. Explain in detail about the method of generation of carbenes and nitrenes.

6. Discuss in detail about the reduction reaction carried out using sodium cyanoborohydride

7. Ennumerate in detail about the modification of Wolf Kishner reduction reaction.

Section-B (15 marks)

8. Write short note on

(i) Catalytic hydrogenation (10)

(ii) Sommelet reaction (5)

9. Describe in detail about carbenes and nitrenes (15).

10. Explain in detail about the following reducing agents

(i) Lithium Aluminium hydride

(ii) Sodium borohydride

(iii) tritertiarybutoxyaluminium hydride

(iv) trialkyltin hydride

(v) hydrazines

11. Discuss in detail about the following reactions

(i) Clemmenson reduction

(ii) Wolf Kishner reduction

(iii) MPV reduction

12. (a) Describe in detail about the selectivity in reduction of 4-t-butylcyclohexanone using selected hydride reductions (7)

(b) Explain in detail about the catalytic hydrogenation reaction (8)