(Pages : 4) **K – 3308**

Reg. No. : ……………………

Name : ……………………

Fifth Semester B.Sc. Degree Examination, February 2021

First Degree Programme under CBCSS

Chemistry

Core Course VII

CH 1543 – ORGANIC CHEMISTRY – II

(2018 Admission – Regular)

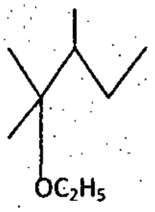
Time : 3 Hours Max. Marks : 80

SECTION – A

Very short answer type question.

Answer **all** questions. **Each** question carries **1** mark.

1. Give the IUPAC name of the given compound.



2. What is Bayer -Villiger oxidation?

3. $A + C_2H_5MgBr \longrightarrow B \xrightarrow{H_2O/H^+}$ 2-Methylbutan-2-ol. Identify A.

4. What happens when formaldehyde is treated with ammonia?

5. Name the strongest halogenated acetic acid.

P.T.O.

6. Give the name of the product formed when ethanamine is heated with chloroform and alcoholic potash.

7. In what type of reactions the percentage atom economy is 100?

8. Mention any two advantages of a microwave assisted reaction when compared to its thermal reaction with same concentrations.

9. Mention the general nature of electronic spectrum of a species in solution.

10. How many signals will be obtained for the protons of TMS in its NMR spectrum?

(10 × 1 = 10 Marks)

SECTION – B

Answer any **eight** questions. **Each** question carries **2** marks.

11. How is benzamide converted into aniline?

12. Arrange ortho, para and meta chloro anilines in the increasing order of basicities

13. Define bathochromic effect.

14. Mention the conditions for a molecule to be IR active.

15. Sketch the schematic PMR spectrum of toluene.

16. How many PMR peaks will be obtained for C_2H_5Br?

17. Explain green synthesis. Illustrate with one example.

18. What kind of feed stock should be used for green synthesis?

19. How is phenol converted into benzene?

20. How is coumarine prepared from salicylaldehyde?

21. With the help of equations, explain haloform test.

22. How does ethanal react with $NaHSO_3$? Give the equation.

23. Distinguish acetophenone and benzophenone chemically.

24. What happens when cinnamic acid is treated with dry soda lime?

25. How is tosyl chloride prepared?

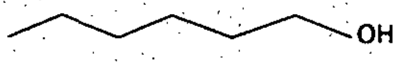
26. What is Nef's reaction?

(8 × 2 = 16 Marks)

SECTION – C

Answer any **six** questions. **Each** question carries **4** marks.

27. How do the following reagents react with alcohols given against them?

(a) Jone's reagent 

(b) Collins reagent 

28. Explain what happens when primary and secondary alcohols react with alkaline $KMNO_4$.

29. Explain Lucas test to distinguish primary secondary and tertiary alcohols.

30. Explain Knoevenagel reaction with mechanism.

31. Explain the reactions of methyl magnesium bromide with the following compounds. What happens when the product is subsequently hydrolysed in acid medium?

(a) Propanal (b) Benzaldehyde

32. Explain how oxalic acid is commercially prepared. Explain the action of the following on oxalic acid.

(a) Con. Sulphuric acid (b) Heat

33. How is saccharin synthesized? Give equations.

34. Explain Hoffmann's bromamide reaction.

35. Draw the schematic PMR spectrum of ultrapure ethanol and explain.

36. Explain microwave synthesis. Give two examples one in aqueous medium and one in organic solvent.

37. How *will* you convert (a) butanoic acid into butane (b) aniline to para bromoaniline?

38. How can the isomers of C_2H_6O be differentiated using NMR spectroscopy?

(6 × 4 = 24 Marks)

SECTION – D

Answer any **two** questions. **Each** question carries **15** marks.

39. Discuss the mechanisms of the following reactions.

(a) Perkin (b) Beckmann rearrangement (c) Claisen rearrangement.

40. (a) Explain the splitting of PMR signals into multiplets due to the spin-spin coupling, taking chloroethane as an example.

(b) Explain crown ethers and its importance.

(c) Explain how is a $-O-CH_3$ group estimated? **5+5+5**

41. *What is green chemistry? Explain the need for green chemistry.* Mention the goals of it. Discuss the limitations of green chemistry.

42. (a) How does phenol react with (i) CO_2 (ii) $CHCl_3$ and NaOH (iii) Br_2 in CC_{14} (iv) $NaNO_2$ and H_2SO_4

(b) Explain (i) MPV reduction. (ii) Wolf Kishner reduction. **8+7**

43. Write notes on

(a) Ascent and descent series in aliphatic carboxylic acid

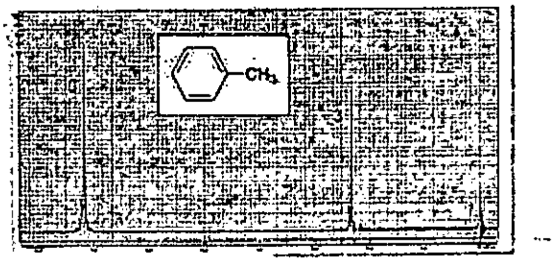
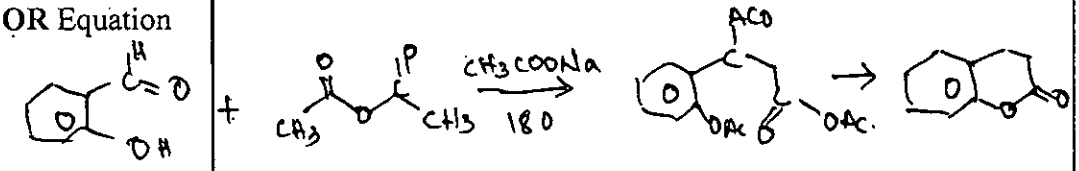
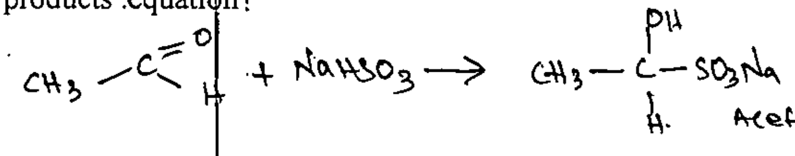
(b) Auxochrome chromophore concept.

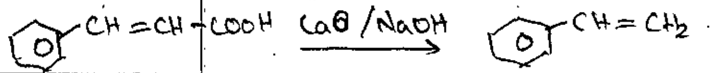
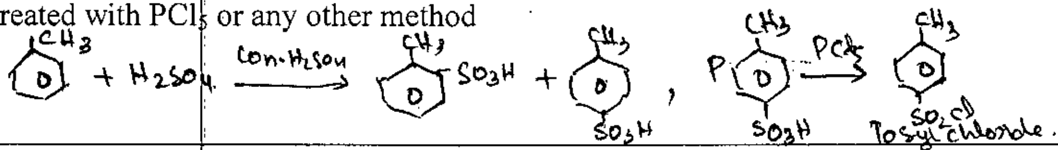
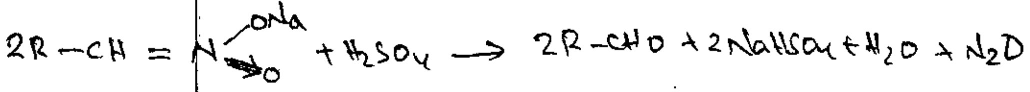
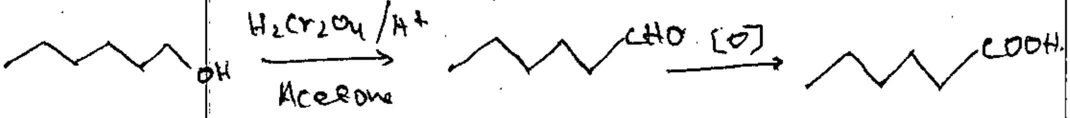
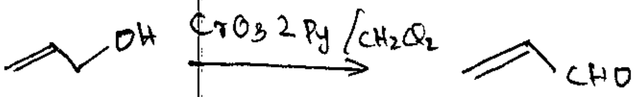
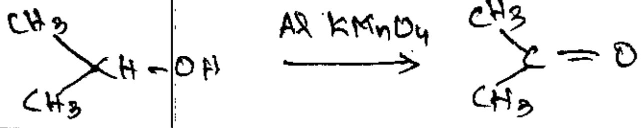
44. Discuss various aspects related to the basic strengths of three kinds of aliphatic amines and ammonia.

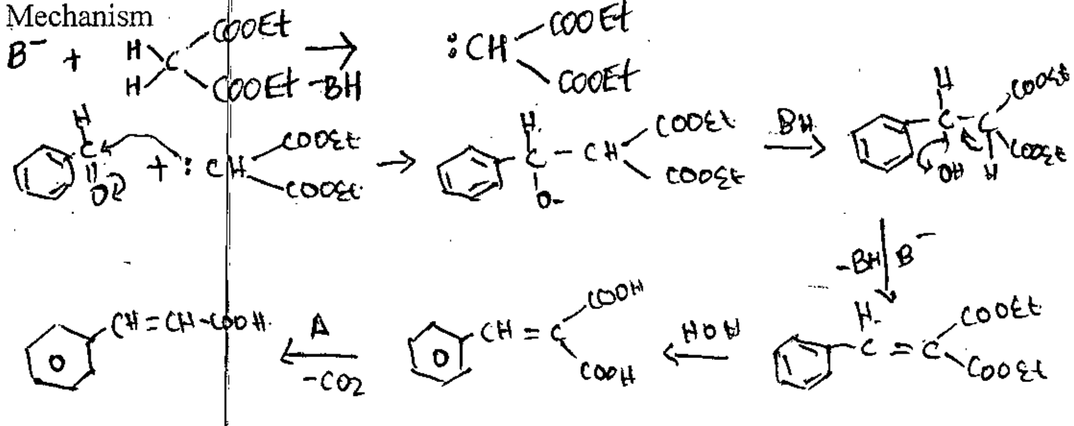
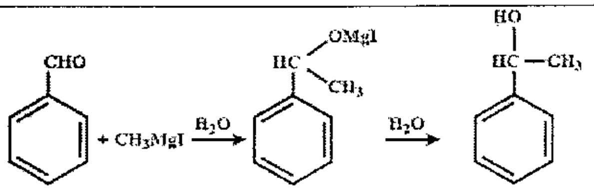
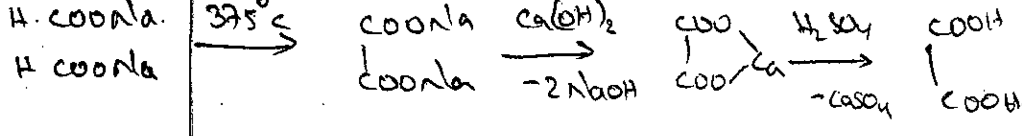
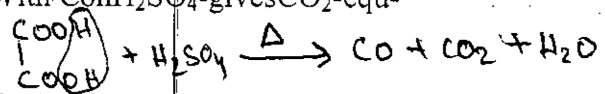
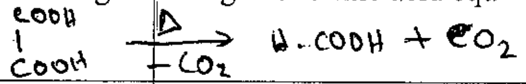
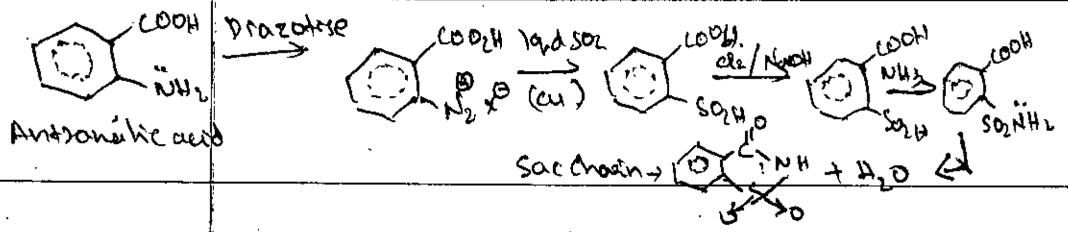
(2 × 15 = 30 Marks)

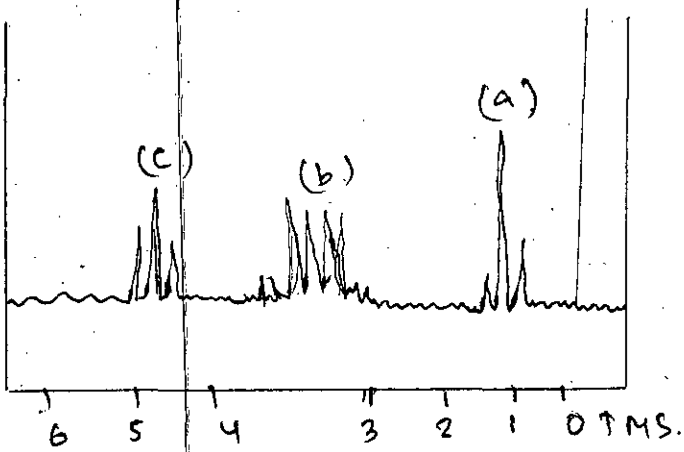
Fifth Semester B.Sc Degree Examination, February 2021
First Degree Programme under CBCSS
Core CourseVII .CH 1543 QP code-K-3308
ORGANIC CHEMISTRY-II
(2018 Admissions Regular)

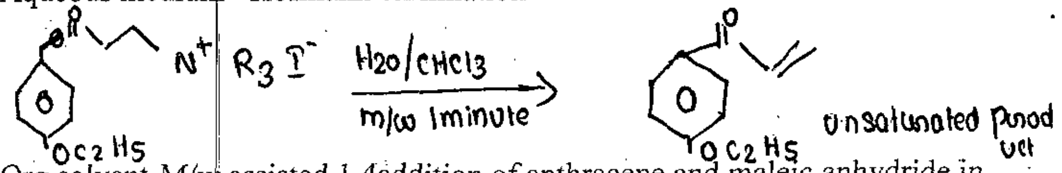
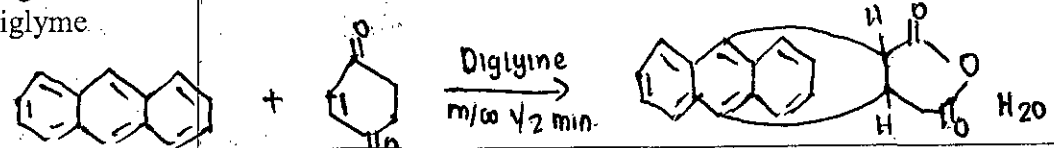
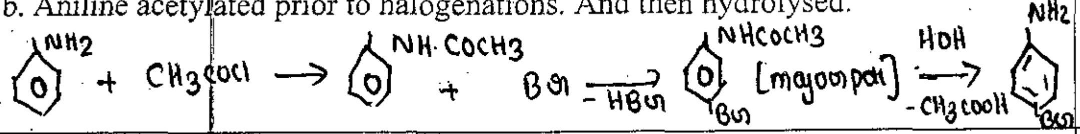
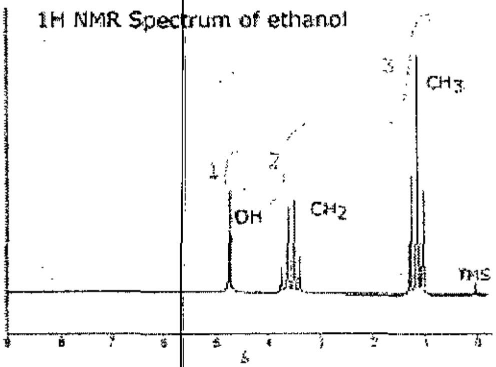
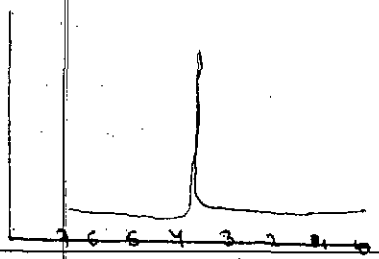
	Section A	
1	*Give the IUPAC name of the given compound*	
	2-Ethoxy-2,3-dimethyl pentane	1
2	*What is Bayer-Villiger oxidation?*	
	An organic reaction that forms an ester from a ketone or a lactone using peroxoacids or peroxide as oxidant	1
3	$A+C_2H_5MgBr \longrightarrow B \xrightarrow{H_2O/H^+}$ *2-Methylbutan-2-ol.Identify A*	1
	CH_3-CO-CH_3	
4.	*What happens when formaldehyde is treated with ammonia*	
	$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$ Or Urotropin is formed	1
5.	*Name the strongest halogenated acetic acid*	1
	trifluoro acetic acid	
6.	*Give the name of the product formed when ethanamine is heated with chloroform and alcoholic potash*	
	Ethyl isocyanide	1
7.	*In what type of reaction the percentage atom economy is 100*	
	Addition reaction	1
8.	*Mention any two advantages of a microwave assisted reaction when compared to thermal reaction with same concentration*	
	Greater yield, faster rate, energy efficiency	1
9.	*Mention the general nature of electronic spectrum of a species in solution*	
	Electronic spectrum give broad bands when in solution	1
10.	*How many signals will be obtained for the protons of TMS in its NMR spectrum*	
	One signal	1
	Section B	
11.	*How is benzamide converted to aniline?*	
	By Hofmann''s bromamide reaction (Either equation or statement) $R-CO-NH_2 + Br_2 + 4KOH \rightarrow R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$ R is C_6H_5.	2
12.	*Arrange ortho,para and meta chloroanilines in the increasing order of basicities*	
	p-chloro aniline> m-chloro aniline> o-chloro aniline	2
13.	*Define bathochromic effect*	
	Shift in absorption max towards longer wavelength region	2
14.	*Mention the conditions for a molecule to be IR active.*	

	It should have permanent dipole moment:or any other relevant point $\Delta V = \pm 1$	2
15.	*Sketch the schematic PMR spectrum of toluene*	
	NMR Spectrum of Toluene 	2
16.	*How many PMR peaks will be obtained for C_2H_5Br*	
	2 peaks Triplet of 3 protons and quartet of 2 protons	2
17.	*Explain green synthesis.Illustrate with example.*	
	Microwave assisted or ultrawave assisted synthesis with any one eg	2
18.	*What kind of feed stock should be used for green synthesis?*	2
	Renewable	
19.	*How is phenol converted to benzene?*	
	Phenol on distillation with Zn dust or equ of the reaction 	2
20.	*How is coumarine prepared from salicylaldehyde?*	2
	Salicylaldehyde treated with acetic anhydride and sodium acetate **OR** Equation 	
21.	*With the help of equations explain haloform test*	
	Aldehydes and ketones having at least one (CH_3CO) group **react** with halogens in presence of NaOH or sodium hypohalite to form **haloform** (CHX_3) and salt of carboxylic acids having one carbon atom less than salt of carbonyl compound. Eq: $CH_3CHO + 3Cl_2 + 4NaOH \longrightarrow CHCl_3 + 3NaCl + HCOONa + 3H_2O$	1 1
22.	*How does ethanal react with NaHSO3? Give the equation.*	1
	Ethanal react with sodium bisulphite (sodium hydrogen sulphite) to give addition products .Equation: $CH_3-C(=O)H + NaHSO_3 \longrightarrow CH_3-C(OH)(H)-SO_3Na$ Acetaldehyde sodium bisulphite.	1
23.	*Distinguish acetophenone and benzophenone chemically.*	2
	Acetophenone being a methyl ketone gives iodoform test-Yellow ppt	

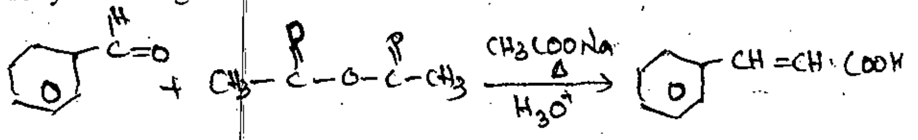
	obtained.Benzophenone does not answer iodoform test OR equation $CH_3-CO-C_6H_5 \xrightarrow[test]{Iodoform} CHI_3 + 3NaI + C_6H_5COONa + 3H_2O$	
24.	*What happens when cinnamic acid is treated with dry sodalime?*	2
	.Styrene is obtained or equation for the same 	
25	How is tosyl chloride prepared?	
	Toluene with chloro sulfonic acid or Toluene with sulphuric acid and sodiumsalt treated with PCl_5 or any other method 	2
26	What is Nef''s reaction?	
	Primary and secondary nitroalkanes may be hydrolysed by first converting them to their salt of aciform by NaOH which on boiling with H_2SO_4 produces aldehydes and ketones respectively OR Equ  $2R-CH=N(ONa)\rightarrow O + H_2SO_4 \rightarrow 2R-CHO + 2NaHSO_4 + H_2O + N_2O$	2
	Section C	
27.	*How do the following reagents react with alcohols given against them?*	
	a.Oxidation to Hexanoic acid with equ; 	2
	b. Selective oxidation to aldehyde,Propenal-with equ 	2
28	*Explain what happens when primary and secondary alcohols react with alkaline KMnO4?*	
	Primary alcohols oxidsed to aldehydes $CH_3-CH_2-CH_2-OH \xrightarrow{Al.\ KMnO_4} CH_3-CH_2-CHO$ Secondary alcohols to ketones 	2 2
29.	*Explain Lucas test to distinguish primary, secondary and tertiary alcholos.*	
	Alcohols on treatment with Lucas reagent give cloudiness due to formation of alkyl chloride.Tertiary reacts immediatetly, Secondary within 5 mts and primary does not react at room temperature	4

30..	*Explain Knoevenagel reaction with mechanism* When Malonic ester is treated with aldehydes or ketones,in the presence of base such as pyridine α,β-unsaturated esters are formed. This on hydrolysis and decarboxylation yield α,β-unsaturated acids. 2marks Mechanism 	2marks 2
31.	*Explain the reactions of methyl magnesium bromide with the following compounds.What happens when the product is subsequently hydrolysed in acid medium?a.Propanal b.benzaldehyde*	
	a.2-butanol is obtained	2
	b.  1-Phenylethanol	2
32.	*Explain how oxalic acid is commercially prepared. Explain the action of the following on oxalic acid. a).Con.Sulphuric acid b).Heat*	2+1+1
	Oxalic acid is prepared by heating sodium formate at 375°C,when sodium oxalate is formed. This is converted to calcium oxalate by treatment with lime. This when acidified with dil H_2SO_4 gives oxalic acid equ  $\begin{matrix}H.COONa\\H\ COONa\end{matrix} \xrightarrow{375^\circ C} \begin{matrix}COONa\\COONa\end{matrix} \xrightarrow[-2NaOH]{Ca(OH)_2} \begin{matrix}COO\\COO\end{matrix}Ca \xrightarrow[-CaSO_4]{H_2SO_4} \begin{matrix}COOH\\COOH\end{matrix}$ a)With ConH_2SO_4-givesCO_2-equ-  $\begin{matrix}COOH\\COOH\end{matrix} + H_2SO_4 \xrightarrow{\Delta} CO + CO_2 + H_2O$ b)On heating at 190c gives formic acid equ  $\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[-CO_2]{\Delta} H.COOH + CO_2$	2 1 1
33.	*How is Saccharin synthesized?Give equations.*	
	From anthranilic aid & from Toluene.	2 2
		

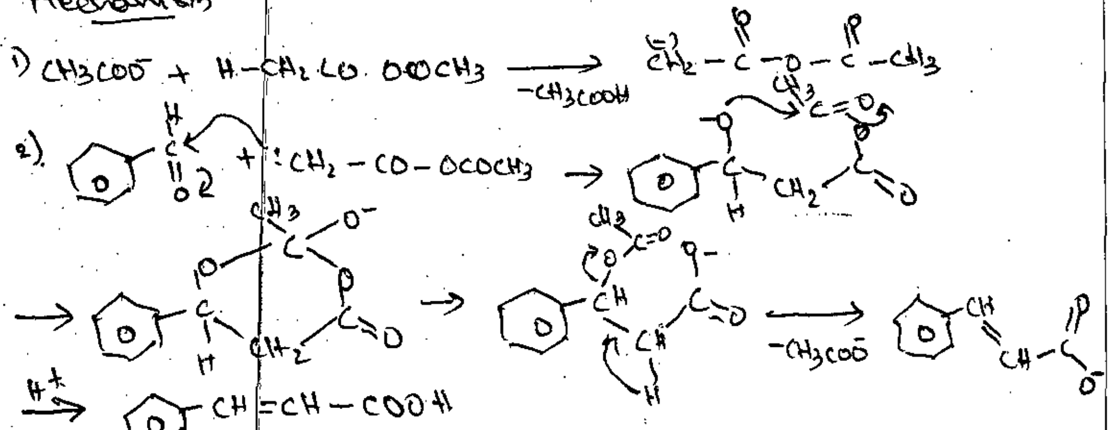
34	*Explain Hofmanns bromamide reaction.*	
	Hofmann''s bromamide reaction-Amides when heated with Br_2 and alkali yield amine having one carbon atom less than the amide- .Equ: $R-CO-NH_2 + Br_2 + 4KOH \xrightarrow{70^\circ C} R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$ $C_6H_5CONH_2 + Br_2 + 4KOH \xrightarrow{10^\circ C} C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$	2 2
35.	*Draw the schematic PMR spectrum of ultrapure ethanol and explain*	
	NMR SPECTRUM OF PURE ETHANOL (i) Triplet at δ1.2 ppm for CH_3 protons due to coupling with CH_2 proton (ii) multiplet consisting of eight lines for CH_2 protons atδ3.62ppm-CH_2 is under the influence of two kind of proton hence coupling given by $(n_a+1)(n_b+1)=(3+1)(1+1)=8$ lines Triplet for OH proton at δ5.28ppm.This is because of coupling to CH_2 proton $\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{c}{OH}$  	2 X 2(sketch)
36	*Explain microwave synthesis. Give two examples one in aqueous medium and one in organic solvent.*	
	Works on the basis of aligning dipoles of the material in an external field via excitation produced by microwave e/m radiation.	1

	Aqueous medium –Hofmann elimination in water and chloroform  Org.solvent-M/w assisted 1;4addition of anthracene and maleic anhydride in diglyme  	1.5 1.5
37.	*How will you convert(a) butanoic acid into butane (b)aniline to para bromo aniline*	
	a..Reduction with $LiAlH_4$ .Equ $CH_3-CH_2-CH_2-COOH \xrightarrow{LiAlH_4} CH_3-CH_2-CH_2-CH_3$ OR $CH_3-CH_2-CH_2-COOH \xrightarrow{NaOH/CaO} CH_3-CH_2-CH_3 + Cl_2$ $CH_3-CH_2-CH_2Cl + 2Na \xrightarrow{ether} CH_3-CH_2-CH_2-CH_3$ b. Aniline acetylated prior to halogenations. And then hydrolysed.  	2 2
38.	*How can the isomers of C_2H_6O be differentiated using NMR spectroscopy?*	
	Ethanol- answer given above for question no 35 or the spectrum of impure ethanol.	2
	 	
	Dimethyl ether-gives a singlet of 6H-(either explanation or sketch of spectrum) 	2
39 .	*Discuss the mechanism of the following reactions.* *a. Perkin reaction b. Beckmann rearrangement c.Claisen rearrangement*	
	(Give 5 marks each for a,b and c with mechanism and discussion and if only discussion without equ give two marks each) a.Perkin reaction Addition of acid anhydrides containing alpha hydrogen atom to aromatic aldehydes in presence of base to form α-β-unsaturated acids.it is initiated	

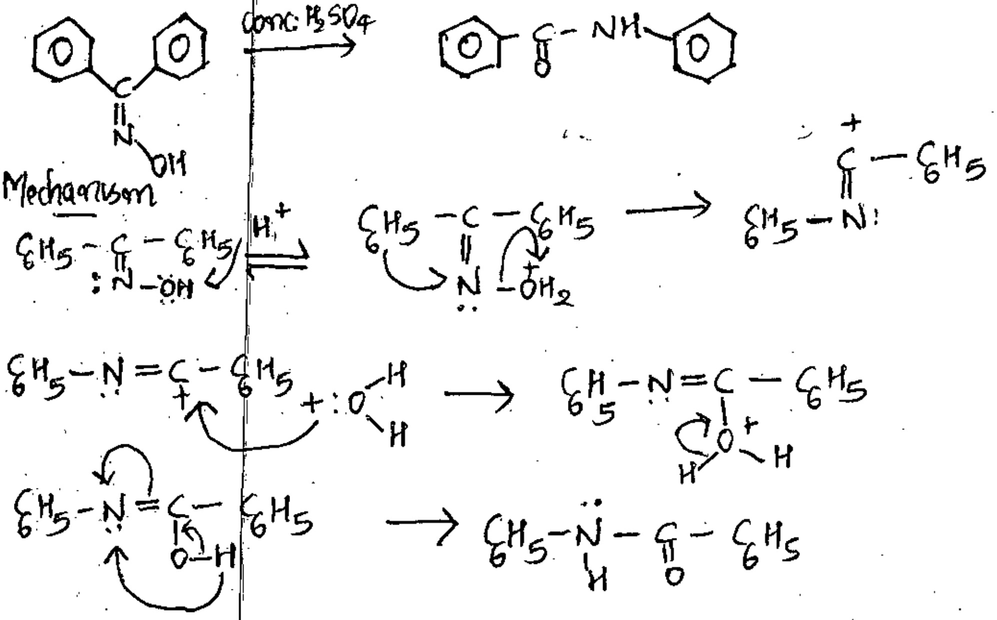
by formation of carbanion from anion followed by nucleophilic to aromatic aldehyde having no α H atom



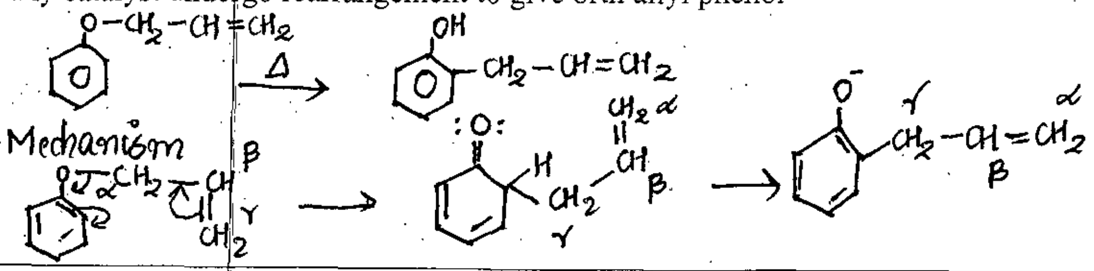
Mechanism

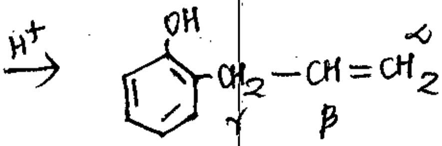


b. Beckmann rearrangement Ketoximes and aldoximes when treated with acidic reagents rearrange to N-substituted amides



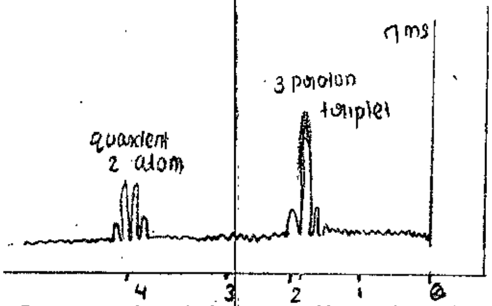
Claisen rearrangement-Allylphenylether when heated to 200°C in the absence of any catalyst undergo rearrangement to give orth allyl phenol





40 *a.Explain the splitting of PMR signals into multiplets due to spin-spin coupling, taking chloroethane as example. b.Explain crown ethers and its importance. c.Explain how is a-OCH₃ group estimated.*

Chloroethane has two sets of peaks in PMR-Has 2 kinds of protons-Triplet of methyl proton-due to coupling with CH_2 proton (n+1 rule).^{δ} value around 2 due to deshielding effect of chlorine on adjacent carbon.Spin spin coupling give rise to1:2:1 triplet,because CH_2 proton can adopt three different orientation with respect to external field.Quaret of CH_2 proton due to coupling with CH_3 .CH_3 can adopt 4 different orientation w.r.to external magnetic field in the ratio 1:3:3:1.Deshielded due to effect of chlorine (^{δ} around 4).



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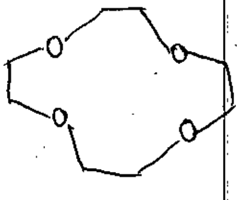
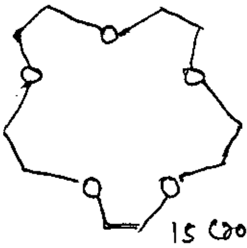
b. Crown ether-Macrocyclic poly ethers-ring with more than 12 c atom-resembles crown-importance-form complex with meal ions-inclusion compound –used to separate cations –as phase transfer catalyst-for resolution of racemic mixture.



12 crown-4



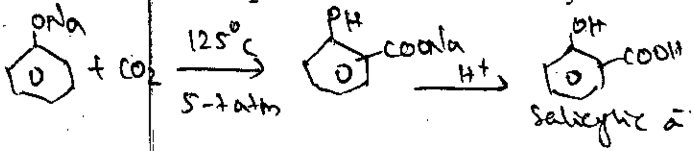
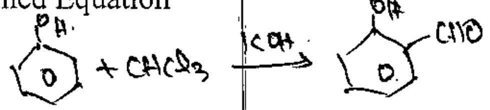
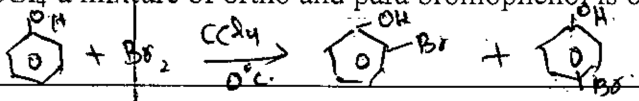
15 crown-5

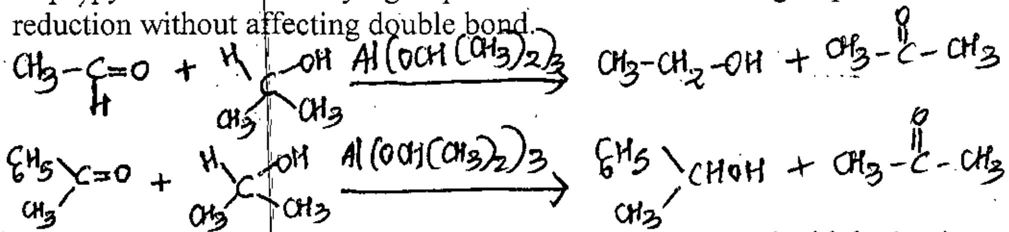
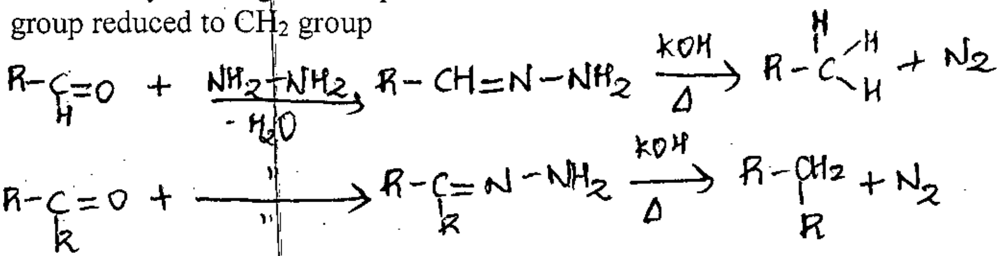
5

c.R-O-CH_3+HI→R-OH+CH_3I, CH_3I+$AgNO_3$→AgI+CH_3NO_3,1mole of AgI=One methoxy group-Let mass of sample be M_1g,Mass of AgI=m_2g,Molar mass of sample=Mg/mol,m_1/M moles of comp=m_2/234 moles of AgI=m_2/234 mol of OCH_3. 1 mole of compound contains m_2/234xM/m1 moles of OCH3

5

41 *What is green chemistry? Explain the need for green chemistry. Mention the goals of it. Discuss the limitations of green chemistry.*

	Green chemistry def- Green chemistry is the utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products **Need:** present practice leads to pollution and negative impact on environments-produce hazardous chemicals-only solution in the adaptation of the concept of green chemistry.Thus green chemistry becomes sustainable. Goals-Safe environment –minimize the use and generation of hazardous chemicals-minimise pollution at its source-minimize the efficiency of any chemical choice-minimise the consumption of energy-limiting the use of non-renewable stock materials-minimize the production of non bio degradable materials-maximize the use of renewable resources-Extend the durability and recyclability of products(12 principles) Limitation: high implementing costs, lack of information, no known alternative **chemical** or raw material inputs, no known alternative process technology, uncertainty about performance	3 2 8 2
42.	*a. How does phenol react with (i)CO_2 (ii) $CHCl_3$ and NaOH (iii) Br_2 in CCl_4 (iv) $NaNO_2$ and H_2SO_4* *b.Explain (i) MPV reduction (ii) Wolf Kiishner Reduction*	
a.	I. Phenol on reaction with CO_2 – Kolbe reaction- Salicylic acid is formed Equation  II. phenol with $CHCl_3$ and NaOH -Reimer-Tiemann reaction-Salicylaldehyde is formed Equation  III. Br_2 in CCl_4-a mixture of ortho and para bromophenol is obtained Equation 	1 1 1 1 1

	IV.$NaNO_2$ and H_2SO_4-Libermann reaction—a deep blue or green colour due to formation of indophenols hydrogen sulphate-turns red on dilution due to conversion to indophenols-on addition of NaOH it again turns green due to formation of sodium salt of indophenols	1 2
b.	i) MPV reduction—Reaction of aldehyde or ketone with aluminium isopropoxide in isopropyl alcohol-carbonyl group reduced to alcoholic group.Used in selective reduction without affecting double bond.  ii)Wolf Kishner reduction—reaction of carbonyl compound with hydrazine followed by a strong base in presence of solvents like DEG or DMSO-carbonyl group reduced to CH_2 group 	3.5 3.5
43.	*Write notes on (a) Ascent and descent series in carboxylic Acids* *b.Auxochrome chromophore concept*	
a	Ascent in acid $R\text{-}COOH \xrightarrow{Ca(OH)_2} (R\text{-}COO)_2Ca \xrightarrow[\text{disti}]{(HCOO)_2Ca} R\text{-}CHO \xrightarrow[CH_3OH,\,H^+]{NaBH_4} R\text{-}CH_2\text{-}OH \xrightarrow{\text{red } P/Br_2}$ $R\text{-}CH_2\text{-}Br \xrightarrow{KCN} R\text{-}CH_2\text{-}CN \xrightarrow{HOH} R\text{-}CH_2\text{-}COOH.$ Descent $R\text{-}CH_2\text{-}COOH \xrightarrow{NH_3} R\text{-}CH_2\text{-}COONH_4 \xrightarrow{\Delta} R\text{-}CH_2\text{-}CONH_2 \xrightarrow{Br_2/KOH}$ $R\text{-}CH_2\text{-}NH_2 \xrightarrow{NaNO_2/HCl} R\text{-}CH_2\text{-}OH \xrightarrow{KMnO_4/H^+} R\text{-}COOH.$	8
b	chromophore-isolated covalently bonded group that shows characteristic absorption in uv or visible region.give egs-2types-1.which undergo ∏-∏ transition give eg-2. which undergo n-∏ transition eg. Auxochrome-Group which does not itself act as chromophore but whose presence	7

	shifts absorption to longer wavelength.give eg.The effect of auxochrome is because of its ability to extend conjugation of chromophore.	
44	*Discuss various aspects related to the basic strengths of three kinds of aliphatic amines and ammonia.*	
	Ammonia is basic in nature due to unshared electron pair on nitrogen. Generally amines are basic.-due to availability of lone pair of electrons on nitrogen atom. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups.Greater the number of alkyl group ,stronger the base. Expected order $3^0>2^0>1^0$ But the actual order is $2^0>1^0>3^0$ Bulkier the alkyl group, lower the basic strength of tertiary amines (steric effect).(Explanation with example)	15

Approved

Dr. DHANYA VISWAM