



Register Number:

Date:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27

B.Sc. CHEMISTRY – V SEMESTER

SEMESTER EXAMINATION: OCTOBER 2021

(Examination conducted in January-March 2022)

CH 5118 – ORGANIC CHEMISTRY

Time: 2 ½ hours

Max. marks: 70

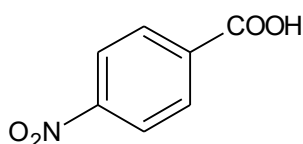
Note: This question paper has four printed pages and three parts.

PART A

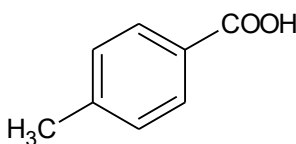
Answer any **SIX** questions from the following.

(6 x 2 = 12 marks)

1. Write the reaction of Grignard reagent with a ketone.
2. Give a general reaction for the preparation of organolithium compounds.
3. Write the structure of a molecule that is i) aromatic ii) antiaromatic.
4. A 300-MHz NMR spectrometer records a proton that absorbs at a frequency 2130 Hz downfield (deshielded) from TMS. What is the chemical shift of this proton?
5. Write the mechanism of acyl substitution (nucleophilic addition-elimination) reaction.
6. Which carboxylic acid would you expect to be stronger? Justify your choice



or



7. Why is an alkylamine more basic than ammonia?
8. In a ¹H NMR experiment, why do the protons of the benzene ring experience greater deshielding?

PART B

Answer any **EIGHT** questions from the following.

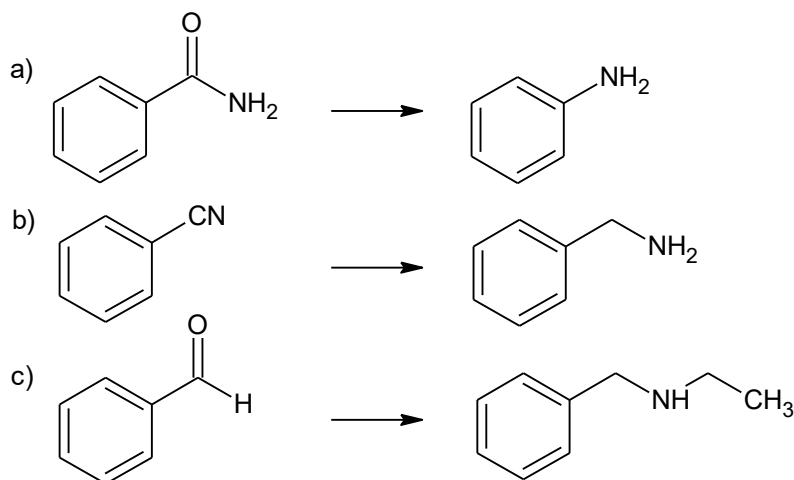
(8 x 6 = 48 marks)

9. Give two general methods of synthesising i) an aldehyde ii) a ketone.
10. Write the mechanism of aldol condensation reaction.
11. How does the –NO₂ group in nitrobenzene influence the reactivity of the aromatic ring towards electrophilic substitution? On the basis of the stability of arenium ions, explain how this group in nitrobenzene influences the orientation of the incoming electrophile.
12. a) Based on heat of hydrogenation, show that benzene is more stable than hypothetical "cyclohexatriene."
b) What is keto-enol tautomerism? Give an example.

13. a) The UV spectrum of acetone (CH_3COCH_3) shows two absorption bands at $\lambda_{\text{max}} = 195 \text{ nm}$ and $\lambda_{\text{max}} = 274 \text{ nm}$. Which electronic transition is responsible for each of these bands? Explain your answer.

b) The ^1H NMR spectrum of undecadeuteriocyclohexane ($\text{C}_6\text{D}_{11}\text{H}$) obtained at room temperature is different from that obtained at -100°C . Explain.

14. How would you bring about the following conversions?



15. a) Write chemical equations to show the action of nitrous acid on 1° , 2° and 3° aromatic amines?

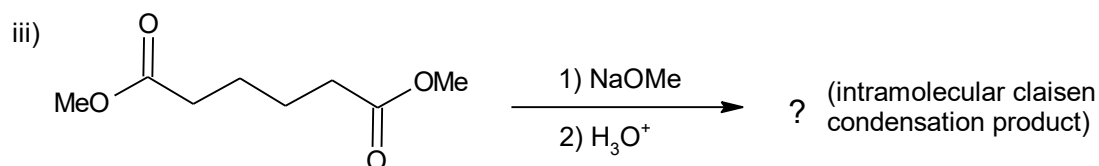
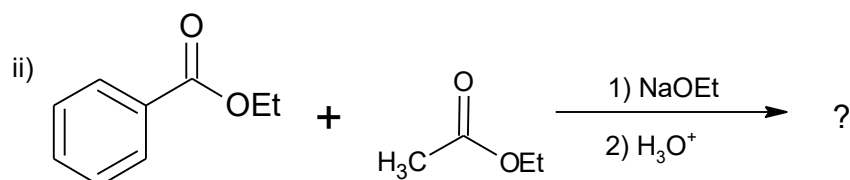
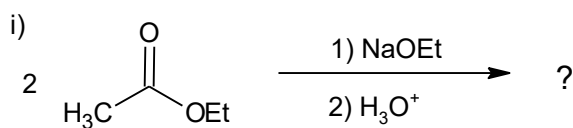
b) What is diazo coupling reaction? Give an example.

16. a) What happens when citral is subjected to ozonolysis reaction? What information do these reaction products give regarding the structure of citral?

b) How was the point of linkage in nicotine between pyridine and pyrrolidine rings established?

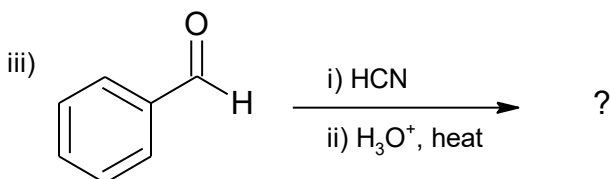
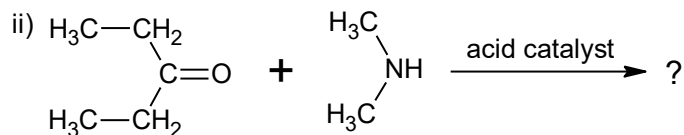
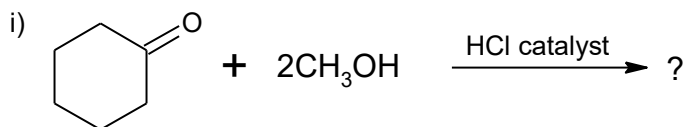
17. a) Give any two general methods of preparing carboxylic acids.

b) Write the Claisen condensation product of the following reactions:



18. a) What is Wittig reaction? Give an example.

b) Complete the following reactions:



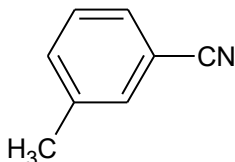
PART C

Answer any **TWO** questions from the following.

(2 x 5 = 10 marks)

19. Outline all steps in the malonic ester synthesis of 2-methylpentanoic acid.


20. Write the reaction sequence with appropriate reagent(s) to obtain the following compound from benzene.



21. Given here is the ^1H NMR spectra and IR absorption peak of compounds A. With proper reasoning, propose a structure for this compound

Compound A	Molecular formula:	$\text{C}_6\text{H}_{14}\text{O}$
	IR absorptions at	$3200\text{-}3600\text{ cm}^{-1}$
	^1H NMR data:	triplet δ 0.8 (6H); singlet δ 1.0 (3H); quartet δ 1.5 (4H); singlet δ 1.6 (1H)

Important IR Stretching Frequencies

Type of bond	Wavenumber (cm ⁻¹)	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

APPROXIMATE PROTON CHEMICAL SHIFTS

Type of Proton	Chemical Shift (δ, ppm)	Type of Proton	Chemical Shift (δ, ppm)
1° Alkyl, RCH ₃	0.8–1.2	Alkyl bromide, RCH ₂ Br	3.4–3.6
2° Alkyl, RCH ₂ R	1.2–1.5	Alkyl chloride, RCH ₂ Cl	3.6–3.8
3° Alkyl, R ₃ CH	1.4–1.8	Vinylic, R ₂ C=CH ₂	4.6–5.0
Allylic, R ₂ C=C—CH ₃ R	1.6–1.9	Vinylic, R ₂ C=CH R	5.2–5.7
Ketone, RC(=O)CH ₃	2.1–2.6	Aromatic, ArH	6.0–8.5
Benzylic, ArCH ₃	2.2–2.5	Aldehyde, RCH=O	9.5–10.5
Acetylenic, RC≡CH	2.5–3.1	Alcohol hydroxyl, ROH	0.5–6.0 ^a
Alkyl iodide, RCH ₂ I	3.1–3.3	Amino, R—NH ₂	1.0–5.0 ^a
Ether, ROCH ₂ R	3.3–3.9	Phenolic, ArOH	4.5–7.7 ^a
Alcohol, HOCH ₂ R	3.3–4.0	Carboxylic, RCOOH	10–13 ^a