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

B.Sc. CHEMISTRY-V SEMESTER

SEMESTER EXAMINATION - OCTOBER 2019

CH 5115-ORGANIC CHEMISTRY

Time: 2.5 hrs. **Max.marks:70**

This question paper has three pages and contains three parts (21 questions). NMR and IR spectral data are given at the end of the question paper.

PART A

Answer any six questions. **(2 x 6 = 12)**

1. How can you cleave ethers?
2. How is benzoyl chloride converted to benzaldehyde?
3. How can you convert propanol to propanal.
4. Calculate the chemical shift value of a proton appearing at 2000 Hz measured using a 400 MHz instrument and give the unit.
5. How do you prepare a carboxylic acid using Grignard reagent?
6. How is a primary amine prepared by Gabriel synthesis?
7. What is isoprene rule? What do you mean by a monoterpene.
8. How does glucose react with bromine water?

PART B

Answer any eight questions. **(6 x 8 = 48)**

9. (a) Give a reaction each for acid and base catalysed ring opening of unsymmetrical epoxides. Comment on the regioselectivity of these reactions.
   (b) How do you convert α-D-glucose to α-D-methylglucoside? How can you distinguish between them using Tollen's reagent?

10. (a) Between aldehydes and ketones, which is more reactive towards nucleophilic addition? Explain.
    (b) Draw the enol form of pentane-2,4-dione. Which of these two forms, keto or enol form of this compound, is more stable? Why?

11. Write chemical equations for the following reactions:
    (i) Michael addition
    (ii) Claisen–Schmidt reaction
    (iii) Wittig reaction

12. a) With suitable examples explain the effect of conjugation on UV absorption maximum.
    (b) Explain the NMR spectrum of pure ethanol.

13. (a) How does the magnetic field due to circulation of π electrons affect the location of NMR signal of protons in case of acetylene and benzene?
    (b) What are the two factors that frequency of IR stretching vibration related to? Give an example each to support the two factors.

14. (a) How can you convert (i) an aldehyde (ii) a nitilre to a carboxylic acid?
(b) Give the mechanism of Claisen condensation of ethyl acetate in the presence of a base.

15. (a) How does a ketone react with 1 mol of alcohol in the presence of an acid? What happens when two moles of alcohol is reacted?
(b) How do you synthesise (i) an aldehyde form an ester (ii) ketone by Friedel Craft's reaction?

16. (a) Give an example of diazotization of an aromatic primary amine followed by coupling reaction.
(b) Compare the basicity of 1°, 2° and 3° amines in vapour phase.

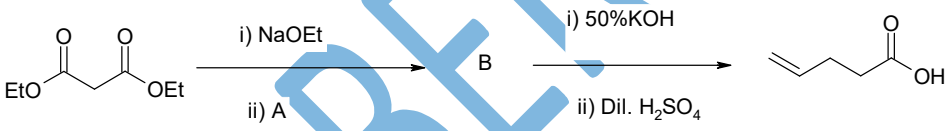
17. (a) Write chemical equations for Kiliani-Fischer synthesis of an aldotetrose from gyceraldehyde.
(b) Explain mutarotation of glucose.

18. (a) Give reaction to prove the position of double bonds in citral.
(b) How is the structure of the side chain confirmed in nicotine?

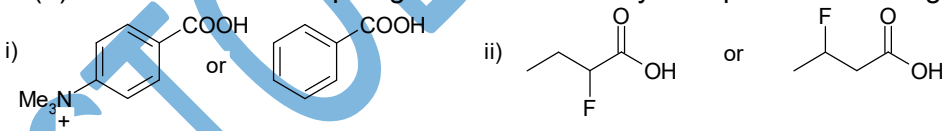
PART-C

Answer any four questions. **(5x2=10)**

19. (a) Identify **A**and **B** in the following synthesis.



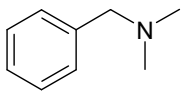
(b) Which acid of each pair given below would you expect to be stronger?



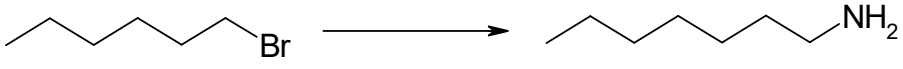
(3+2)

20. Two isomeric compounds **A** and **B** with molecular formula $C_5H_{10}O$, show a significant IR absorption at 1710-1740 cm^{-1}, and UV absorption around 290 nm. The ^1H NMR signals for these two compounds are as given below. Interpret the spectra and suggest the structures of **A** and **B**.
A: δ 2.55 (septet, 1H), 2.10 (singlet, 3H), 1.05 (doublet, 6H)
B: δ 2.38 (triplet, 2H), 2.10 (singlet, 3H), 1.57 (multiplet, 2H), 0.88 (triplet, 3H)

21. (a) How can you prepare the following amine by reductive amination?



(b) Show how you would use a nitrile to carry out the following reaction.



(3+2)

TABLE 9.1 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_2Br	3.4–3.6
2° Alkyl, RCH_2R	1.2–1.5	Alkyl chloride, RCH_2Cl	3.6–3.8
3° Alkyl, R_3CH	1.4–1.8	Vinylic, $R_2C=CH_2$	4.6–5.0
Allylic, $R_2C=C(R)-CH_3$	1.6–1.9	Vinylic, $R_2C=CH(R)$	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, $RC(=O)H$	9.5–10.5
Acetylenic, RC≡CH	2.5–3.1	Alcohol hydroxyl, ROH	0.5–6.0[a]
Alkyl iodide, RCH_2I	3.1–3.3	Amino, RNH_2	1.0–5.0[a]
Ether, $ROCH_2R$	3.3–3.9	Phenolic, ArOH	4.5–7.7[a]
Alcohol, $HOCH_2R$	3.3–4.0	Carboxylic, $RC(=O)OH$	10–13[a]

TABLE 2.7 Characteristic Infrared Absorptions of Groups

Group		Frequency Range (cm^{-1})	Intensity[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $-CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $-C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C—C (stretching)		1620–1680	(v)
R—CH=CH_2	(out-of-plane C—H bendings)	985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$		880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
C=C (stretching)		1450–1600	(m)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o-Disubstituted		735–770	(s)
m-Disubstituted		680–725	(s)
	and	750–810	(very s)
p-Disubstituted		800–860	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
O—H (stretching)			
Alcohols, phenols (dilute solutions)		3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)		3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)		2500–3000	(broad, v)
F. Ethers and Alcohols			
C—O—C (stretching)		1020–1275	(s)
G. Aldehydes, Ketones, Ethers, Carboxylic Acids, and Amides			
C=O (stretching)		1630–1780	(s)
Aldehydes		1690–1740	(s)
Ketones		1680–1750	(s)
Esters		1735–1750	(s)
Carboxylic acids		1710–1780	(s)
Amides		1630–1690	(s)
H. Amines			
N—H		3300–3500	(m)
I. Nitriles			
C≡N		2220–2260	(m)