Answer the following questions (any *five*):

1.



UNIVERSITY OF NORTH BENGAL

B.Sc. Honours Part-II Examination, 2020

CHEMISTRY

PAPER-III

Time Allotted: 2 Hours Full Marks: 30

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

All symbols are of usual significance.

 $2 \times 5 = 10$

Answer Question No. 1 and any two from the rest

	(a)	Write two uses of Grignard reagent.	
	(b)	Alcohols are weaker acids than phenol but stronger nucleophiles. — Explain.	
	(c)	Allyl chloride is more reactive than vinyl chloride. — Explain why.	
	(d)	Draw two conformations of <i>meso</i> -2,3-dibromobutane in sawhorse. One with σ plane and the another with inversion point.	
	(e)	Why should a Grignard reagent be prepared in an anhydrous conditions?	
	(f)	Why HI is used as better reagent to cleave an ether rather than HBr?	
2.	(a)	How will you prepare 3-ethylpentane-3-ol using Grignard reagent?	3
	(b)	Explain the mechanism involved in Meerwein-Ponndorf-Verley reduction of a typical ketone. Mention one synthetic advantage of carring out MPV reduction.	2+1 = 3
	(c)	2,4,6-trimethyl benzoic acid is very difficult to esterify. — Explain.	2
	(d)	Mention three conditions which control S_N1 and S_N2 reaction and how?	2
3.	(a)	Which of the following would be most and least readily hydrolysed with NaOH and why?	$1\frac{1}{2}$
		MeCO ₂ Me ; Me ₃ CCO ₂ Me ; MeCOOBu ^t	
	(b)	Between ΘNH_2 and $NH_2 - NH_2$ which serve as better nucleophile and why?	$1\frac{1}{2}$
	(c)	Can you synthesis Me ₃ C-O-CMe ₃ by using Williamson's method? Give reason.	2
	(d)	What do you mean by ylide? How does an ylide acquire stabilization?	1+2=3
	(e)	How can you convert benzaldehyde to acetophenone by means of Umpolung reaction?	2

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- 4. (a) Explain how compounds with two chiral centres are classified as "erythro" and "threo" forms.
 - (b) Compound containing no chiral centre but show specific rotation.
 - (c) Compound containing more than one chiral centre but does not show specific rotation.
 - (d) Distinguish between the following:
 - (i) Acetonitrile and Methyl isocyanide 2
 - (ii) *o*-phenylenediamine and *m*-phenylenediamine.
- 5. Write short notes (any *five*):

 $2 \times 5 = 10$

2

(i) NBS

(ii) B_2H_6

(iii) HIO₄

(i)

- (iv) Gabriel-Phthalimide Synthesis
- (v) Arndt-Eistert Synthesis
- (vi) Lossen reaction
- (vii) Zeisel's method.
- 6. (a) Give R/S designation for the following molecules.
 - Me C = C = C COOH COOH
 - (b) Explain the following terms giving suitable example (any *two*):

 $2 \times 2 = 4$

2

- (i) Pseudo asymmetric centre
- (ii) Centre of symmetry
- (iii) Resolution.
- (c) Write short notes (any *two*):

 $2 \times 2 = 4$

- (i) Knoevenagel condensation
- (ii) Reimer-Tiemann reaction
- (iii) Wittig reaction.
- 7. (a) Predict the product(s) with mechanism (any *three*):

 $2 \times 3 = 6$

(i)
$$\langle | | \rangle = O \xrightarrow{(i) Ph_3P = CHOMe} ?$$

(iii)
$$O_2Me$$
 CO_2Me $LiAlH_4$

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(iv) OHC – CH = CH – CHO + 2CH₃OH
$$\stackrel{\text{H}^{\oplus}}{\longrightarrow}$$
?

(v)
$$COOH$$

$$CH_3Li \rightarrow ?$$

(b) Arrange the following in increasing order of nucleophilicity:

1+1=2

- (i) PhO^{\ominus} , EtO^{\ominus} , AcO^{\ominus}
- (ii) $PhNH_2$, $NH_2 NH_2$, NH_3 , NH_3
- (c) Arrange the following in the increasing order of nucleophilicity in (i) ethanol and 1+1 = 2 (ii) DMSO:

$$F^{\ominus}$$
, Cl^{\ominus} and I^{\ominus}

8. (a) Carry out the following conversations (any *two*):

 $2 \times 2 = 4$

(i)
$$H_2C = \bigcirc \longrightarrow H_3C - \bigcirc \longrightarrow C$$

$$(ii) \bigcirc = 0 \longrightarrow \bigcirc = 0$$

$$(iii) \longrightarrow \bigvee_{N}$$

- (b) Complete the following reactions and comment.
 - $-CH_3 \xrightarrow{KMnO_4} ? \xrightarrow{SOCl_2} ? \xrightarrow{NH_3} ? \xrightarrow{Br_2/NaOH} ?$
- (c) Identify the following products:

1+1=2

4

$$Ph - CH = CH - \stackrel{O}{C} - Ph \xrightarrow{(i) PhLi, Et_2O} (A)$$

$$(ii) H_3O^{\oplus}$$

$$(ii) PhMgBr$$

$$(ii) H_3O^{\oplus}$$

$$(iii) H_3O^{\oplus}$$

9. (a) What is Robinson annelation reaction? Discuss its mechanism.

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- (b) Arrange the following compounds in order to their increasing stability towards dehydration reaction and give reason.

$$OH$$
 OH OH OH

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(c) Which mechanism, $S_N 1$ or $S_N 2$ is favourable for reaction of each of the following $1 \frac{1}{2} \times 2 = 3$ substrate (any *two*):

(i) MeO
$$\longrightarrow$$
 CH₂Cl

(ii)
$$O_2N$$
 — CH₂Cl

- (iii) MeO CH₂Cl
- (d) Give an example of alternative axis of symmetry.

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10.(a) What is Beckmann rearrangement? Discuss its mechanism.

1+2 = 3

(b) Give the products with mechanism (any *two*):

 $2 \times 2 = 4$

(i)
$$O_2N$$
 \longrightarrow $CO - CO$ \longrightarrow $\stackrel{\Theta}{\longrightarrow}$ $\stackrel{\Omega}{\longrightarrow}$

(ii)
$$Ph - C - CHO \xrightarrow{\ThetaOH} ?$$

(iii)
$$Me_2C(OH)C(NH_2) Ph_2 \xrightarrow{NaNO_2/HCl}$$
?

(c) How a mixture of 1°, 2° and 3° amines are separated by Hinsberg's method?

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