3 SEM TDC CHM M 3 (N/O)

2019

(November)

CHEMISTRY

(Major)

Course: 303

(Organic Chemistry—I)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks: 48

Pass Marks: 14

Time: 2 hours

- 1. Select the correct answers from the following: 1×5=5
 - (a) Which compound does not give haloform reaction?

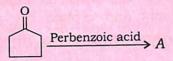
- (ii) C₂H₅OH
- (iii) CH₃COOH
- (iv) R CH3

- (b) Which of the following intermediates involves in the Reimer-Tiemann reaction?
 - (i) Carbocation
 - (ii) Carbanion
 - (iii) Carbene
 - (iv) Nitrene
- (c) Pick out the correct answer for the following reduction:

$$\stackrel{R}{>} = 0 \xrightarrow{\text{Clemmensen reduction}} \stackrel{R}{>} CH_2$$

- (i) $NH_2 NH_2$, NaOH
- (ii) LiAlH₄
- (iii) Zn/Hg and HCl
- (iv) Sn and conc. HCl
- (d) Which of the following phenols is most acidic?
 - (i) o-nitrophenol
 - (ii) p-nitrophenol
 - (iii) 2, 4-dinitrophenol
 - (iv) 2, 4, 6-trinitrophenol

(e) In the reaction



the product A is



2. Answer any four of the following questions: $1\frac{1}{4} \times 4 = 6$

- (a) Giving a suitable example, explain the $S_N 1$ reaction.
- (b) What happens when Grignard reagent reacts with CO₂?
- (c) Aromatic alcohols are acidic in nature but aliphatic alcohols are not. Explain.

(d) Arrange the following carbonyl compounds in the order of increasing dipole moment and explain:

CH3COCH3, HCHO, CH3CHO

(e) How will you convert benzoyl chloride to benzaldehyde and then acetophenone?

UNIT-I

Answer	any <i>two</i> of the following questions: $4\times$	2=8
3. (a)	Benzyl chloride can undergo both $S_N 1$ and $S_N 2$ reactions with high rate. Explain.	2
(b)	Using organometallic compound, how you would prepare the following (any one):	2
	(i) A 3° alcohol from an ethyl ester by using Grignard reagent(ii) Methylcyclohexyl ketone by using methyl lithium	
	metryr ntrium	
4. (a)	The rate of $S_N 2$ reactions does not depend on the polarity of the solvents used in the reaction. Explain.	2
(b)	What is diazotization reaction? How would you prepare chloro- and bromo-	

benzene by using Sandmeyer's reaction?

(Continued)

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- 5. (a) How is benzyne intermediate generated?

 Why is it so reactive?
 - (b) Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides?

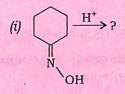
UNIT-II

Answer any two of the following questions: $5\times2=10$

6. (a) Complete the following reaction and suggest the mechanism: 3

$$\begin{array}{c|cccc} Ph & CH_3 \\ & & | & | \\ Ph - C - C - CH_3 & \xrightarrow{H^+} ? \\ & | & | \\ OH & OH \end{array}$$

- (b) How is glycerol obtained from oils and fats? What happens when nitric acid is allowed to react with glycerol? 1+1=2
- 7. (a) Complete the following reactions: 1+1=2



(ii)
$$\begin{bmatrix} OH & PI_3 \\ OH & OH \end{bmatrix}$$
?

- (b) Distinguish between 1°, 2° and 3° alcohols by using Victor Meyer test. 3
- 8. (a) Complete the following reaction: 2

$$\frac{\text{① OSO}_4}{\text{② aq. NaHSO}_3} ?$$

(b) Complete the following reactions and write their mechanisms (any two):

11/2×2=3

(i)
$$OH + CCl_4 \xrightarrow{NaOH} ?$$

(ii)
$$OCOCH_3$$

$$AlCl_3 (anhy.) ?$$

(iii)
$$\sim$$
 O $\xrightarrow{\text{Al(OCHMe}_2)_3}$?

UNIT-III

Answer any one of the following questions:

8

9. (a) Complete the following reactions and write the mechanisms: 3×2=6

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(Continued)

(ii)
$$C_6H_5CHO + CH_3COCH_3 \xrightarrow{NaOH} ?$$
(Cross aldol condensation)

- (b) Trichloroacetaldehyde is more reactive towards the nucleophilic addition reaction than acetaldehyde. Explain.
- 10. (a) Complete the following reactions and write down the probable mechanisms (any two): 3×2=6

(i)
$$+ AC_2O \xrightarrow{ACONa}$$
 ? (Perkin reaction)

(ii)
$$R-C-R' \xrightarrow{PCl_5}$$
 ? (Beckmann rearrangement)

- (b) Synthesize the following (any two): 1×2=2
 - (i) MVK from acetone
 - (ii) Cinnamaldehyde by using Claisen-Schmidt condensation
 - (iii) Coumarin from o-hydroxybenzaldehyde

2

UNIT-IV

Ansv	ver a	ny one of the following questions:
11.	(a)	Synthesize tartaric acid from acetylene. What happens when fumaric acid is treated with alk. KMnO ₄ ? 1+1=2
	(b)	Complete the following reaction and discuss the mechanism involved:
EtC	OC(C	$CH_2)_5COOEt \xrightarrow{EtONa}$? (Dieckmann condensation)
	(c)	How would you prepare the following? 2+2=4
		(i) Phenylacetic acid using an organometallic compound
		(ii) Butanoic acid from propanoic acid using Arndt-Eistert synthesis
12.	(a)	Explain with a suitable example that optically active acyl azides undergo Curtius rearrangement with complete retention of configuration.
44	(b)	Complete the following reaction and suggest the mechanism:
	Вє	enzophenone + BrCH ₂ COOC ₂ H ₅ $\xrightarrow{\text{(1) Zn/ether}}$?
	(c)	Explain why pK_a value of chloroacetic acid is lower than pK_a value of acetic acid.

(d) Complete the following reactions: 1+1=2

(i)
$$2H_2N-C-NH_2 \xrightarrow{\Delta}$$
?

(ii)
$$CH_3 - S - CH_3 \xrightarrow{H_2O_2}$$
?

UNIT-V

Answer any one of the following questions:

2

- 13. How would you prepare a thiol from an alkyl halide by using Grignard reaction? What happens when a thiol reacts with an aldehyde in presence of HCl? 1+1=2
- 14. What are thioethers? How do you obtain diethyl thioether from ethyl marcaptan? 1+1=2

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(Old Course)

Full Marks: 48

Pass Marks: 19

Time: 3 hours

- 1. Select the correct answer from the following: 1×5=5
 - (a) Phenol is treated with chloroform in the presence of aqueous sodium hydroxide at 340 K temperature. The product is
 - (i) salicylaldehyde
 - (ii) salicylic acid
 - (iii) aspirin
 - (iv) phenolphthalein
 - (b) The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is
 - (i) acidified K2Cr2O7
 - (ii) alkaline KMnO4
 - (iii) chromic anhydride in glacial acetic acid
 - (iv) pyridinium chlorochromate

- (c) HO-CH₂-CH(OH)-CH₂-OH on heating with KHSO₄ gives
 - (i) $CH_2 = CH CHO$
 - (ii) CHO-CHO
 - (iii) CH₃ CH₂ CHO
 - (iv) 2HCOOH
- (d) Among the following compounds which is most acidic?
 - (i) p-nitrophenol
 - (ii) p-hydroxy benzoic acid
 - (iii) o-hydroxy benzoic acid
 - (iv) p-toluic acid
- (e) Arrange the following acids with increasing acid strength:
 - (i) C₆H₅OH
- (ii) HCOOH
 - (iii) CH3COOH
 - (iv) CICH2COOH
- 2. Answer any four of the following questions:

11/2×4=6

(a) Why are aryl and vinyl halides less reactive towards nucleophilic substitution?

- (b) Convert phenol to salicylaldehyde.
- (c) Identify A and B in the following reaction:

$$CH_3CHO \xrightarrow{NaOH} A \xrightarrow{Heat} B$$

- (d) How is diethyl malonate prepared from acetic acid?
- (e) Is fumaric acid soluble in water? Synthesize fumaric acid from glyoxalic acid.

UNIT-I

Answer any *two* of the following questions: $4 \times 2 = 8$

- 3. (a) Why is aryl halide less reactive towards nucleophilic substitution?
 - (b) How does aryl halide react with sodium metal?
- 4. (a) Complete the following reaction: 1

 S-Butanol-2 $\xrightarrow{\text{SOCl}_2 \text{ in ether}}$ (A) $\xrightarrow{\text{aq. KOH}}$ (B)
 - (b) Comment on the following statement: In all $S_N 2$ reactions, the rate increases with increasing polarity of the solvent.
 - (c) How will you convert aniline to bromobenzene using Sandmeyer reaction?

2

1

5. (a) Complete the following:

(i)
$$CN$$
 $LiAlH_4 \rightarrow ?$

(ii) ROH + NH₃
$$\frac{\text{ZnCl}_2}{300 \,^{\circ}\text{C}} \Rightarrow ?$$

(b) A haloalkane reacts with KCN to form alkyl nitrile while AgCN forms alkyl isonitrile as major product. Explain.

UNIT-II

Answer any two of the following questions: $5\times2=10$

6. (a) Complete the following reaction and discuss the mechanism:

- (b) How would you prepare p-cresol from p-toluidine?
- 7. (a) What is diazotization reaction of amine?
 Why is diazotization reaction carried out
 at low temperature? 2+1=3
 - (b) Formylation of phenol with CHCl₃ and conc. NaOH gives salicylaldehyde as the major product. What is the reaction? Discuss the mechanism of the reaction.

2

2

- 8. (a) How can you distinguish 1°, 2° and 3° alcohol with the help of Lucas' reagent? Discuss the reaction involved.
 - (b) Complete the following reactions (any two):

(i) Me
$$\stackrel{\text{Me}}{-}$$
 Ph $\stackrel{\text{H}^+}{|}$? OH OH

(ii)
$$CH_2OH \xrightarrow{H_3PO_4}$$
 ?

(iii)
$$C_6H_5CHO + CH_3 - C - CH_3 \xrightarrow{10\% \text{ NaOH}}$$
?

UNIT-III

Answer any one of the following questions:

8

3

2

- **9.** Complete the following reactions with mechanisms (any *four*): 2×4=8
 - (i) CH₃CHO OH⁻ ? (Aldol condensation)

(ii)
$$R - C - R' \xrightarrow{\text{Aluminum isopropoxide}}$$
 ? (MPV)

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(Continued)

(iii)
$$\langle \bigcirc \rangle$$
 $C - C - \langle \bigcirc \rangle$ $KOH \rightarrow ?$

(Benzil-benzilic acid rearrangement)

(v)
$$\sim$$
 CHO $\xrightarrow{\text{KCN/DMF}}$? (Benzoin condensation)

10. (a) Convert the following:

2+2=4

- (i) Acetylene to acetaldehyde
- (ii) Toluene to benzaldehyde
- (b) Prepare cyclohexanal from cyclohexanone by using Darzens glycidic ester condensation.
- (c) How would you prepare acrolein from glycerol? 2

UNIT-IV

Answer any one of the following questions:

9

2

11. (a) Why is acetic acid weaker than fumaric acid but benzoic acid is stronger than p-methoxy benzoic acid?

2

(Turn Over)

	(b)	(i) Complete the following conversion: Benzoic acid to Phenylacetic acid by Arndt-Eistert synthesis	2
		(ii) Discuss and compare the acidity of p-nitrobenzoic acid and p-toluic acid.	2
	(c)	Synthesize cyclobutylamine from cyclobutane carboxylic acid by using Schmidt reaction.	3
12.	(a)	Explain with a suitable example that optically active acyl azides undergo Curtius rearrangement with complete retention of configuration.	3
	(b)	Synthesize the following: 2+2	2=4
		(i) Pyruvic acid from tartaric acid (ii) Tartaric acid from acetylene	
	(c)	Discuss the mechanism of acid-catalyzed hydrolysis of ester.	2
		Unit—V	
Ansv	ver a	ny one of the following questions :	2
13.	Whi	ch is more acidic—thiol or alcohol? How	
		ald you prepare diethyl thioether from	
			1=2
14.		thiols be oxidized? What happens when nioether is hydrolyzed with NaOH? 1+1	1=2
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