# 3 SEM TDC CHM M 3 (N/O)

2018

( November )

**CHEMISTRY** 

(Major)

Course: 303

## ( Organic Chemistry—I )

The figures in the margin indicate full marks for the questions

(New Course)

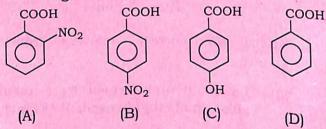
Full Marks: 48

Pass Marks: 14

Time: 2 hours

- 1. Select the correct answers from the following: 1×5=5
  - (a) The compound formed as a result of oxidation of ethyl benzene by KMnO<sub>4</sub> is
    - (i) benzyl alcohol
    - (ii) benzophenone
    - (iii) acetophenone
    - (iv) benzoic acid

- (b) The intermediate involved in the Reimer-Tiemann reaction is
  - (i) CHCl<sub>2</sub>
  - (ii) :CCl2
  - (iii) ⊖ CCl<sub>3</sub>
  - (iv) CHO
- (c) Which of the following is a Michael acceptor?
  - (i) Acrolein
  - (ii) Acetone
  - (iii) Cyclohexene
  - (iv) Formaldehyde
- (d) The correct order of acid strength of the following acids



is

- (i) A < B < C < D
- (ii) B < C < A < D
- (iii) C < B < D < A
- (iv) C < D < B < A

- (e) An organic compound with MF C<sub>8</sub>H<sub>8</sub>O forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid. The compound is
  - (i) 2-ethyl benzaldehyde
  - (ii) 2-methyl benzaldehyde
  - (iii) 3-methyl benzaldehyde
  - (iv) acetophenone
- 2. Answer any four of the following questions:  $1\frac{1}{2} \times 4 = 6$ 
  - (a) A haloalkane reacts with KCN to form alkyl nitrile while with AgCN forms alkyl isonitrile as major product. Explain.
  - (b) How will you prepare MVK from vinyl acetylene?
  - (c) Define S<sub>N</sub>1 reaction. Explain with the help of an example.
  - (d) How does Lucas reagent help in the distinction of primary, secondary and tertiary alcohols? Discuss the reactions involved.

(e) Arrange the following acids in increasing order of their acid strengths with appropriate reasoning:

> CH<sub>3</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH, CICH<sub>2</sub>COOH, BrCH<sub>2</sub>COOH

#### UNIT-I

Answer any two of the following questions:

 $4 \times 2 = 8$ 

3. (a) Discuss how the nature of the solvent influences the relative reactivity in nucleophilic substitution reactions.

2

(b) Write the mechanism of the following reaction showing the participation of a neighbouring group:

2

4. (a) The rate of S<sub>N</sub>1 reactions increases with increasing polarity of the solvents. Explain.

2

(b) Using organometallic compound, how would you prepare 3° alcohol from ethyl acetate?

5. (a) Synthesize the following: 1+1=2

- (i) Ethyl bromide by Hundsiecker reaction
- (ii) Fluorobenzene through diazonium salt
- (b) Complete the following reaction and predict the mechanism: 1/2+11/2=2

$$RCOCH_3 + X_2 \xrightarrow{OH^-} ?$$

$$(X = halogen)$$

### UNIT-II

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

6. (a) Synthesize the following:

1+1=2

- (i) Picric acid from phenol
- (ii) m-nitrophenol from m-dinitrobenzene
- (b) Complete the following reaction and write the mechanism:

$$C(CH_3)_3 \xrightarrow{F_3CCOOOH} ?$$

- 7. (a) Discuss the solubility in water and b.pt. of 1°, 2° and 3° alcohols.
  - (b) Hydroxylation by OSO<sub>4</sub> of an alkene gives a *cis*-diol whereas hydroxylation via epoxidation of the same alkene gives a *trans*-diol. Explain.
- 8. (a) Complete the following reactions: 1+1=2

(i) 
$$C(OH)Ph_2 \xrightarrow{H^{\Theta}}$$
?

- (ii)  $HOCH_2CH(OH)CH_2OH \xrightarrow{HI (excess)}$ ?
- (b) Predict the product and write the mechanism of the following reaction:

Ph Ph 
$$\frac{1) \text{ RCO}_3\text{H}}{2) \text{ OH}^-/\text{H}_2\text{O}}$$
?

2

3 .

#### UNIT-III

Answer any one of the following questions:

8

2

- 9. (a) Complete the following reactions and write down the mechanisms: 3×2=6
  - (i)  $CH_3CHO \xrightarrow{NaOH} (Aldol condensation)$

(ii) 
$$Ph$$
  $c=0 + CH_2-COOEt$   $Me_3COK/Me_3COH$   $CH_2-COOEt$  (Stobbe condensation)

- (b) How would you distinguish between 2-pentanone and 3-pentanone?
- 10. (a) Complete the following reactions and write down the probable mechanisms

  (any two):

  3×2=6

(Turn Over)

- (b) Synthesize the following (any two): 1×2=2
  - (i) MVK from 2-butanone
  - (ii) Cinnamaldehyde from benzaldehyde
  - (iii) Acrolein from glycerol

#### UNIT-IV

Answer any one of the following questions:

- 9
- 11. (a) Why do carboxylic acids not give the characteristic reactions of carbonyl group?
- 2
- (b) Identify A, B and C in the following reactions:

3

$$\begin{array}{c|c}
\text{COOH} \\
\hline
& \text{conc. HNO}_3 \\
\hline
& \text{conc. H}_2\text{SO}_4
\end{array}
\xrightarrow{A} \xrightarrow{\text{SOCl}_2} B \xrightarrow{\text{NaBH}_4} C$$

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(Continued)

- (c) Synthesize the following: 2+2=4
  - (i) Succinic acid from ethylene bromide
  - (ii) Propanoic acid to ethanoic acid by Hoffmann degradation
- 12. (a) Complete the following reactions:  $1\times3=3$

(i) 
$$CH_2$$
— $COOH$   
 $C(OH)COOH$   $\xrightarrow{H^+}$  ?  
 $CH_2COOH$ 

(iii) 
$$OOOH \xrightarrow{PCl_5}$$
?

- (b) Convert benzoic acid to phenyl acetic acid by using Arndt-Eistert reaction. 2
- (c) Prepare propanoic acid from butanoyl chloride by using Curtius rearrangement.
- (d) Complete the following reaction and discuss the mechanism of the reaction: 2

$$\begin{array}{ccc} & & & & & & & \\ & & & & & \\ & & & & \\ Ph & & & & \\ & & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

## UNIT-V

	wer any one of the following questions:	2
13.	Give one method of preparation of thioether. What happens when a thiol reacts with an aldehyde in the presence of hydrochloric acid?	

2

14. What are thioethers? How would you prepare a thioether from alkyl halide by  $S_N 2$  reaction?  $\frac{1}{2} + \frac{1}{2} = 2$ 

# (Old Course)

Full Marks: 48

Pass Marks: 19

Time: 3 hours

1. Answer/Select the correct answers from the following: 1×5=5

(a) The appropriate reagent for the transformation

$$O_2N$$
— $CH_3$   $\longrightarrow$   $O_2N$ — $CHO$ 

is

- (i) SeO<sub>2</sub>
- (ii) alk. KMnO<sub>4</sub>
- (iii) CrO3/Ac2O
- (iv) Na2Cr2O7/H2SO4
- (b) HO—(CH<sub>2</sub>)<sub>2</sub>OH on heating with periodic acid gives
  - (i) 2HCOOH
  - (ii) 2HCHO
  - (iii) CHO—CHO
  - (iv) 2CO2

- (c) The best reagent to convert pent-3en-2-ol into pent-3-en-2-one is
  - (i) acidified K2Cr2O7
  - (ii) alk. KMnO<sub>4</sub>
  - (iii) PCC
  - (iv) chromic anhydride
- (d) Which of the following compounds will give yellow ppt. with I<sub>2</sub> and alkali?
  - (i) 2-hydroxypropane
  - (ii) Methyl acetate
  - (iii) Acetophenone
  - (iv) Acetamide
- (e) Arrange the following acids with increasing acid strength:
  - (i)  $C_6H_5OH$
  - (ii) HCOOH
  - (iii) CH3COOH
  - (iv) CICH2COOH

2. Answer any four of the following questions:

11/2×4=6

- (a) A haloalkane reacts with HNO<sub>2</sub> to form alkyl nitrite while AgNO<sub>2</sub> forms nitroalkane as the major product. Explain.
- (b) How will you convert a carboxylic acid to an acid chloride using S<sub>N</sub>1 reaction and then to a corresponding aldehyde?
- (c) Synthesize cinnamaldehyde by using Claisen-Schmidt reaction.
- (d) How will you convert benzoyl chloride to benzaldehyde and then acetophenone?
- (e) Write the steps to carry out the conversion of phenol to salicylic acid.

### UNIT-I

Answer any two of the following questions:

 $4 \times 2 = 8$ 

3. (a) What products do you expect when neopentyl iodide undergoes slow  $S_N 1$  and  $S_N 2$  reactions respectively?

$$(CH3)3C-CH2-I \xrightarrow{H2O/OH' SN2} ?$$

$$H2O SN1 ?$$

(b) Complete the following reactions:

(i) + Me<sub>2</sub>CHMgBr 
$$\longrightarrow$$
 ?  $\xrightarrow{\text{H}_3\text{O}^+}$  ?

- 4. (a) Comment on the following statement:

  In all  $S_N 2$  reactions, the rate increases with increasing polarity of the solvent.
  - (b) Synthesize the following: 1+1=2
    - (i) 1-bromobutane from pentanoic acid by Hundsiecker's reaction
    - (ii) Chloro- or bromobenzene from aniline by using Sandmeyer reaction
- 5. (a) Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides?
  - (b) Complete any one of the following reactions:
    - (i) RMgBr +?  $\longrightarrow$ ?  $\xrightarrow{\text{H}_3\text{O}^+}$  R—NH<sub>2</sub>
    - (ii) Me—CH—CH<sub>2</sub> + EtMgBr  $\xrightarrow{1)$  Et<sub>2</sub>O  $\xrightarrow{2)$  H<sub>3</sub>O<sup>+</sup> ?

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(Continued)

2

2

## UNIT-II

Answer any two of the following questions:  $5 \times 2 = 10$ 

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

 $\begin{array}{c}
O \\
\hline
CF_3CO_3H
\end{array}$ ? (B-V oxidation)

- (b) Synthesize m-cresol from p-toluidine. 2
- 7. (a) What is diazotization? How would you prepare bromobenzene by using Sandmeyer reaction?

(b) Discuss the benzyne mechanism for aromatic nucleophilic substitution reaction. Give evidence in support of the proposed mechanism.

- 8. (a) How does Victor Mayer test help in the distinction of 1°, 2° and 3° alcohols?

  Discuss the reactions involved.
  - (b) Complete the following reactions (any two):

(i)  $\xrightarrow{\text{OH OH}} \xrightarrow{\text{HIO}_4/\text{oxidation}}$ ?

3

2

3

3

(ii) Ph 
$$\xrightarrow{\text{Ph Me}}$$
 Me  $\xrightarrow{\text{H}^+}$  ?

#### UNIT-III

Answer any one of the following questions:

8

9. Complete the following reactions with mechanisms (any four): 2×4=8

(i) 
$$CHO + CH_3COCH_3 \xrightarrow{OH'}$$
? (cross-Aldol reaction)

(ii) 
$$R = C = R' \xrightarrow{Al(OCHMe_2)_3} ? (MPV)$$

(iv) MeO 
$$\longrightarrow$$
 C  $\longrightarrow$  ?

(Benzil-Benzilic â rearrangement)

(v) 
$$R-C-R' \xrightarrow{NH_2-NH_2}$$
?

(Wolff-Kishner reduction)

- 10. (a) Prepare 2-methyl propanal from acetone by using Darzens' glycidic ester condensation.
  - (b) How would you prepare the following (any two)? 2×2=4
    - (i) MVK from acetone
    - (ii) Cinnamaldehyde by using Claisen-Schmidt condensation
    - (iii) Acrolein from glycerol
  - (c) What do you expect, benzaldehyde to be more reactive or less reactive in nucleophilic addition reaction than propanal? Explain.

2

## UNIT-IV

Answ	ver a	ny one of the following questions:	9
11.	(a)	Discuss the mechanism of acid-catalyzed hydrolysis of ester.	3
	(b)	Why is acetic acid weaker than fumaric acid but benzoic acid is stronger than p-methoxy benzoic acid?	2
	(c)	How would you prepare the following? 2×2	=4
		(i) Phenylacetic acid using an organo- metallic compound	
		(ii) Butanoic acid from propanoic acid using Arndt-Eistert synthesis	
12.	(a)	Synthesize citric acid by using the following route:	3
	Diet	hyloxalate + Ethyl acetate EtONa	
		oxalacetic ester $\xrightarrow{Zn + BrCH_2COOEt}$ citric â	
	(b)	Synthesize the following: 2×2	=4
		(i) Pyruvic acid from tartaric acid	
		(ii) Cyclobutyl amine from cyclobutane carboxylic acid by using Schmidt reaction	
	(c)	What happens when fumaric acid is subjected to hydroxylation with alk. KMnO <sub>4</sub> ?	2

#### UNIT-V

# Answer any one of the following questions:

2

- 13. How would you prepare n-propyl mercaptan from a suitable alkyl halide by using Grignard reaction? What happens when a thiol is treated with  $H_2O_2$ ? 1+1=2
- 14. How would you prepare diethyl thioether from ethyl mercaptan? What happens when a thioether is hydrolyzed with NaOH? 1+1=2

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