## 3 SEM TDC CHM M 3

2015

(November)

CHEMISTRY

(Major)

Course: 303

### ( Organic Chemistry—I )

Full Marks: 48

Pass Marks: 19 (Backlog) /14 (2014 onwards)

Time: 3 hours/2 hours

The figures in the margin indicate full marks for the questions

1. Select the correct choice :

 $1 \times 5 = 5$ 

- (a) Which one is more reactive towards S<sub>N</sub>1 reaction?
  - (i) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>—Br
  - (ii)  $C_6H_5$ — $CH(C_6H_5)Br$
  - (iii) C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)Br
  - (iv) C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) Br

ONa
$$(b) \qquad \bigcirc \text{OH} + \text{CHCl}_3 + \text{NaOH} \rightarrow \bigcirc \text{ONa}$$

$$\text{CHO}$$

The electrophile involved in the above reaction is

- (i) dichloromethyl cation (CHCl<sub>2</sub>)
- (ii) dichlorocarbene (:CCl2)
- (iii) trichloromethyl anion (CCl3)
- (iv) formyl cation (CHO)

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(Turn Over)

(c) Among the given compounds, the most succeptible to nucleophilic attack at the carbonyl group is

- (d) Which of the following compound will give yellow ppt with I<sub>2</sub> and alkali?
  - (i) 2-Hydroxy propane
  - (ii) Acetophenone
  - (iii) Methyl acetate
  - (iv) Acetamide
- (e) Which of the following carboxylic acids undergoes decarboxylation easily?

(i) 
$$C_6H_5$$
— $C$ — $CH_2$ — $C$ — $OH$ 

(ii)  $C_6H_5$ — $C$ — $COOH$ 

(iii)  $C_6H_5$ — $CH$ — $C$ — $OH$ 

OH

OH

OH

NH<sub>2</sub>

**2.** Answer any four of the following:  $2 \times 4 = 8$ 

(a) Arrange the following compounds in order of reactivity towards  $S_N 2$  displacement with proper reasons:

2-Bromo-2-methyl butane, 1-bromopentane, 2-bromopentane

(b) Complete the following reactions:

$$CH_2 \xrightarrow{1) B_2H_6/THF} (A) \xrightarrow{C_5H_5NHCrO_3Cl} (B)$$

- (c) Why is the reactivity of all three classes of alcohols with conc. HCl and ZnCl<sub>2</sub> (Lucas' reagent) different?
- (d) Convert benzoic acid to benzaldehyde and then benzophenone.
- (e) Acetaldehyde undergoes aldol condensation but trimethyl acetaldehyde does not. Explain.

#### UNIT-I

### Answer any two questions

3. (a) Give the configuration(s) of the following substitution product(s) that will be obtained in the following reactions:

obtained in the following reactions:
$$(i) \qquad \begin{array}{c} C_2H_5 \\ CH_3 \\ Br \end{array} \qquad \begin{array}{c} (High \ concentration) \\ C_2H_5 \\ CH_3 \\ Br \end{array} \qquad \begin{array}{c} (High \ concentration) \\ C_2H_5 \\ CH_3 \\ Br \end{array}$$

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(Turn Over)

(b) Using organometallic compound, how would you prepare the following (any one)?

2

- (i) A 3° alcohol from an ethyl ester (by using RMgX)
- (ii) Methyl cyclohexyl ketone (by using methyl lithium)
- **4.** (a) Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides?

2

(b) Complete the following reactions (any one):

2

(i) 
$$RMgC1 + ? \rightarrow ? \xrightarrow{H_3O^+} R - NH_2$$

(ii) Me—CH—CH<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>MgBr 
$$\xrightarrow{1)$$
 Et<sub>2</sub>O  $\xrightarrow{2)}$  H<sub>3</sub>O<sup>+</sup> ?

5. (a) When the reaction of an alcohol and thionyl chloride is carried out in the presence of pyridine, alkyl halide forms with inversion of configuration. What is the mechanism of the reaction?

2

(b) A haloalkane reacts with KCN to form alkylcyanide while AgCN forms isocyanide as the major product. Explain.

2

### UNIT-II

# Answer any two questions

6. (a) Complete the following reaction:

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

- (b) Outline all the steps involved in the synthesis of the following compounds (any one):
  - (i) m-Nitrophenol from benzene
  - (ii) Benzyl chloride from benzene by chloromethylation

2

2

2

4

- 7. (a) p-Cresol reacts with CHCl<sub>3</sub> in alkaline medium to give a compound (A), which on treatment with HCN followed by acidic hydrolysis gives chiral carboxylic acid. Assign the structure.
  - (b) How would you synthesize αβ unsaturated alcohol and aldehyde from glycerol?
- 8. Complete the following reaction and discuss its mechanism:

$$\begin{array}{c|c}
Me \\
C - Me \\
OH OH
\end{array}$$
?

P16—3500/118 (Turn Over)

## UNIT-III

# Answer any one question

- 9. (a) How will you convert—
  - (i) ethanal to but-2-en-oic acid;
  - (ii)  $\bigcirc$  =0  $\rightarrow$   $\bigcirc$  -CHO (via Darzen glycidic ester condensation)? 2+2=4
  - (b) Complete the following reactions and write the probable mechanisms (any two): 2×2=4
    - (Stobbe condensation)

(ii) MeO—C—C—C—
$$\frac{0}{1}$$
 KOH  $\frac{1}{2}$  H<sub>3</sub>O<sup>+</sup> ?

(Benzil benzilic acid rearrangement)

- (iii) Benzaldehyde +  $Ac_2O \xrightarrow{AcONa}$ ? (Perkin reaction)
- 10. (a) How would you prepare the following (any two)? 2×2=4
  - (i) MVK from acetone
  - (ii) Cinnamaldehyde by using Claisen-Schmidt condensation
  - (iii) Coumarin from o-hydroxy benzaldehyde

(b)	Discuss the mechanism of the reaction						ion
	with	the	given	evidences	(any	two)	
							2×2=

(i) Antimigration in the Beckmann rearrangement

- (ii) Reduction of acetophenone with amalgamated zinc in presence of conc. HCl
- (iii) Hydride transfer in the MPV reduction

#### UNIT-IV

### Answer any one question

**11.** (a) Arrange the following acids in increasing order of their relative acid strength with proper explanation:

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$$\begin{array}{c} \mathrm{CH_3-\!CH_2-\!CH(Br)COOH,} \\ \mathrm{CH_3-\!CH(Br)-\!CH_2-\!COOH,} \\ \mathrm{(CH_3)_2CHCOOH,} \\ \mathrm{CH_3-\!CH_2-\!COOH} \end{array}$$

(b) Show the mechanistic steps of the following reaction:

R—C≡N  $\rightarrow$  a β-keto ester (Reformatsky reaction)

- (c) Synthesize the following (any two): 2×2=4
  - (i) Propanoic acid from butanoyl chloride by using Curtius rearrangement

- (ii) Citric acid from glycerol
- (iii) Cinnamic acid from benzaldehyde by using Knoevenagel reaction
- 12. (a) How will you convert acetic acid to
  (i) malonic acid and (ii) t-butyl alcohol?

  1+1=2
  - (b) Complete the following reaction and discuss the mechanism involved in the reaction:

$$\begin{array}{c} \text{H} & \text{O} \\ \text{H} & \text{O} \\ \text{CH}_{3} & \text{C-C-NH}_{2} & \xrightarrow{\text{Br}_{2}/\text{NaOH}} \end{array} ?$$

(S-2-Phenylpropanamide)

- (c) How would you synthesize the following? 2×2=4
  - (i) Cinnamic acid by Reformatsky reaction
  - (ii) Cyclopentanone from esters of adipic acid by Dieckmann reaction

#### UNIT-V

# Answer any one question

- Which is the stronger acid, ROH or RSH?
  What happens when ethanethiol reacts with acetone in presence of HCl?

  1+1=2
- 14. How would you prepare a sulphonic acid by the Strecker reaction? What happens when a thioether is oxidized with H<sub>2</sub>O<sub>2</sub>?

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