2018

**CBCS** 

3rd Semester

**CHEMISTRY** 

PAPER-C7T

(Honours)

Full Marks: 40

Time: 2 Hours

The figures in the right-hand margin indicate full marks.

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

Illustrate the answers wherever necessary.

## Organic Chemistry-III

## Group-A

1. Answer any five questions:

 $2 \times 5$ 

(a) The addition of bromine to ethylene  $(H_2C = CH_2)$  in presence of excess chloride anion produces Br-CH<sub>2</sub>- $CH_2$ -Cl as one of the products. Explain mechanistically.

- (b) Explain why is phenyl group in biphenyl an activating, and ortho and para orienting?
- (c) Provide suitable reagent and conditions for the following conversions

$$\stackrel{\text{OH}}{\longleftarrow} \stackrel{\text{OH}}{\longleftarrow} \stackrel{\text{OH}}{\longrightarrow} \stackrel{\text{$$

- (d) A careful study of the reaction of 2,4,6-trinitroanisole with sodium methoxide revealed that two different Meisenheimer complexes were present. Suggest reasonable structures for these two complexes.
- (e) The nitrile (A) can be hydrolyzed very readily to the variety corresponding amide, B, which is extremely difficult to hydrolyze further. Explain

(f) Aldehydes (MeCHO) are generally more reactive than ketones (MeCOMe) toward nucleophilic attach. Justify the statement mentioning the general effects.

(g) Explain the role of Na+ in NaBH<sub>4</sub> reduction of a ketone (i) in aqueous medium and (ii) in dry THF medium.

(h) Convert : 
$$\bigcap_{NO_2}^{COCH_3}$$
 (using organo

metallic compound).

## Group-B

Answer any four questions.

4×5

- (a) Two ozonides are formed when Me<sub>2</sub>C = CMe<sub>2</sub> is treated with ozone in presence of HCHO. Give mechanism of the formation of two products.
  - (b) What product can you expect from the following reaction? Depict the stereochemical outcome at every step.

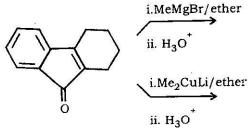
$$Br_2/NaOH$$
 $CO_2H$ 

- 3. What is meant by  $\sigma$ -complex and  $\pi$ -complex? Draw the energy profile diagram of an aromatic electrophilic substitution reaction which passes through  $\sigma$ -complex and  $\pi$ -complex and formation of  $\sigma$ -complex is ratelimiting. Give experimental evidence for the formation of  $\sigma$ -complex and  $\pi$ -complex. 2+2+1
- 4. (a) Why Friedel-Craft alkylation of benzene with 1-chloropropane gives isopropyl benzene? How would you prepare n-propylbenzene from benzene? 2
  - (b) Write the twelve principles of Green chemistry. 3
- 5. (a) Under comparable conditions, the general base catalyzed elimination of bisulphite ion from A is about 10 times greater than from B. Give reason.

(b) Explain why ethyl formate condenses with 2-methyl cyclohexanone in the presence of a base to yield (A) and not (B):

H<sub>3</sub>C 
$$\parallel$$
 C—H  $\parallel$  CHO  $\parallel$  CHO  $\parallel$  CH<sub>3</sub>

- 6 (a) How would you introduce aldehyde group in the aromatic nucleus by a reaction involving carbene intermediate. Give mechanism.
  - (b) Predict the product(s) in the following reaction with plausible mechanism.



7. (a) Discuss the sterospecificity of reduction of the following alkyne to alkene when reacted with sodium in liquid ammonia.



(b) Complete the following reaction sequence and give mechanism for formation of [B] from [A].

$$H_3C-CHO \xrightarrow{SeO_2} [A] \xrightarrow{1. Conc.NaOH/\Delta} [B]$$

$$2. H_1O^{\dagger}$$

## Group-C

Answer any one question.

1×10

8. (a) Write the product of the reaction. What is the relationship between P and Q?

Trans-2-butene 
$$\xrightarrow{\operatorname{Br}_2/\operatorname{CCl}_4}$$
 [A]  $\stackrel{[P]}{\swarrow}$  [Q]

(b) Write mechanisms to show the products in the following reaction when:

(i) 
$$X = -NO2$$
 (ii)  $X = -OMe$ 

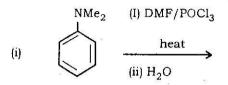
$$X \longrightarrow C1 \xrightarrow{NaNH_2} Liq. NH_3$$

Given Evidences in favour of the mechanisms proposed.

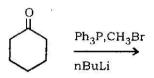
(c) Given the product of the following reaction and explain the advantages of the given reagent over the conventional basic reagent used to carry out the reaction.

$$\begin{array}{c|c} & CHO \\ \hline \\ COCH_3 \\ \end{array} \begin{array}{c} + & OH \\ \hline \\ & \\ R \end{array} \begin{array}{c} & \text{hydrotalcite} \\ \hline \\ & \\ \end{array} \end{array}$$

9. (a) Indicate the product(s) and explain the mechanism involved.



(b) Predict the product(s) and give plausible mechanism their formation:



(c) Write down the product of the following reactions showing the plausible mechanism in each case.

 $3 \times 2$ 

Ph

C/18/BSc/3nd Sem/CEMH/C7T