Course Code : SHCHE/303C-7(T)

### SH-III/Chemistry-303C-7(T)/19

# B. Sc. Semester III (Honours) Examination, 2018-19 CHEMISTRY

**Course ID : 31413** 

Course Title: Organic Chemistry III

## Time: 1 Hour 15 Minutes

The figures in the margin indicate full marks. Candidates are required to give their answers in their own words as far as practicable.

- **1.** Answer *any five* questions:
  - (a) Give the product of the following reaction:

PhCH=CHCOPh  $\xrightarrow{\text{CH}_3\text{Li}}$ ?

(b) Give the product of the following reaction:

+ CHCl<sub>3</sub> 
$$\xrightarrow{K^+ \overline{O} Bu^t}$$
?

- (c) What are Ylides?
- (d) Write the first listed of twelve principles of Green Chemistry.
- (e) Indicate which benzene ring of PhNHCOPh you would expect to be attacked in nitration.
- (f) Which solvent acetone, benzene, water or ethanol is the greenest solvent?
- (g) Write the  $B_{AC^2}$  mechanism for the hydrolysis of methyl benzoate.
- (h) What is the reagent used in Meerwin-Pondorf-Verley reduction?
- 2. Answer *any two* questions:

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- (a) (i) Treatment of  $(CH_3)_3 CCH = CH_2$  with conc. HCl gives a mixture of two isomeric chlorides. Suggest reasonable structures for these two compounds and offer a mechanistic explanation for their formation.
  - (ii) How can be the conversion of PhCHO to PhCDO be done?
  - (iii) Among toluene and t-butylbenzene, which one is more reactive in electrophilic substitution and why?  $2+1\frac{1}{2}=5$

# Full Marks: 25

 $1 \times 5 = 5$ 

5×2=10

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(b) (i) Predict the product(s) of the following reaction with mechanism. Show how deuterium labelling experiment may be used to establish this mechanism.



(ii) Write down the products:



- (c) (i) Discuss the stereochemical outcome of the addition of bromine to *cis*-2-butene.
  - (ii) What happens when acetaldehyde is treated with  $H_2^{18}O$  in presence of a little mineral acid?



(d) (i) Provide the missing reagents and intermediates in the following synthesis:



- (ii) For the preparation of alkylbenzene it is advisable to carry out acylation followed by Clemensen reduction or other reduction over direct alkylation of benzene.— Justify.
- (iii) Arrange the following compounds in order of increasing rate of nitration PhCl, PhNO<sub>2</sub>, PhNHCOCH<sub>3</sub>. 2+2+1=5
- 3. Answer *any one* question:

 $10 \times 1 = 10$ 

- (a) (i) Give the general mechanism of electrophilic aromatic substitution and draw the energy profile diagram. How the kinetic isotope effect throws light on this mechanism regarding the stage of loss of proton from the  $\sigma$ -complex intermediate?
  - (ii) Predict the product(s) of the following reaction and give mechanism:



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(iii) Compound A  $(C_5H_8O_2)$  liberated CO<sub>2</sub> from NaHCO<sub>3</sub>. It existed in two forms neither of which is optically active. On hydrogenation, it yielded B $(C_5H_{10}O_2)$  which would be resolved in two enantiomorphs. Suggest the structures for A and B.

(3)

(iv) Offer reasonable mechanism for the following product formation: 4+2+2+2=10



(b) (i) Identify the compounds A–D in the following reaction sequence and show mechanism for formation of D from C.

$$CH_3 COCH_3 \xrightarrow{NaNH_2} A \xrightarrow{C_2H_2} B \xrightarrow{H^+} C \xrightarrow{HOAc} D$$

- (ii) What factor accounts for the fact that two nitrogen atoms of semicarbazide are relatively non nucleophilic when reacts with a ketone (or an aldehyde)?
- (iii) Carry out the following conversion:

 $Ph CH_2 CH_3 \longrightarrow Ph CH_2 CH_2 OH$ 

(iv) Predict the major product with plausible mechanism.



31/2+1+2+11/2+2=10

(v) Write product with mechanism:

