#### 2022

# 3rd Semester Examination CHEMISTRY (Honours)

Paper: C 7-T

[Organic Chemistry - III]

(CBCS)

Full Marks: 40

Time: Two Hours

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

### Group - A

Answer any five questions.

 $2 \times 5 = 10$ 

 (a) Explain the following observation for the hydration equilibrium constants.

$$+ H_2O$$
 $+ H_2O$ 
 $+$ 

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(b) Account for the product of the following reaction and suggest a suitable mechanism for it.

- (c) Considering all possible isomers, predict how many products are formed when 1-hexene is treated with NBS in presence of peroxide in  $CCl_4$ .
- (d) Predict the product and suggest a suitable mechanism for the following reaction.

- (e) How will you prepare (E)-2-butene from 2-butyne?
- (f) Identify the product of the following reaction.

$$\frac{(i) Hg(OAc)_{2}}{(ii) NaBH_{4}/H_{2}O, Et_{2}O}$$

- (g) Optically active 2, 3-butanediol reacts with  $HIO_4$  at a faster rate than does the meso isomer-explain.
- (h) Identify the product and show the mechanism involved in the following reaction.

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Answer any four questions.

 $5 \times 4 = 20$ 

(a) Aldehydes reduce Tollen's reagent but ketones do not — Explain.

(b) 
$$\underbrace{ Ph_3P - CH_2CH_2CH_3}_{PaNH_2/HF}$$

Explain the difference in the product stereoselectivity for the above reactions with suitable mechanism.

3. (a) There are three possible sites for enolate formation from the compound (**K**), but only one enolate is capable of forming stable product. Account for the observation.

(b) Two isomeric alkenes (A) and (B) give same

product (C) upon acid catalyzed hydration. Ozonolysis of (A) gives one mole of each butan-2-one and formaldehyde, while ozonolysis of (B) gives one mole of acetone and acetaldehyde. Identify (A), (B), (C) and outline the reaction for the formation of (C) from (A) and (B).

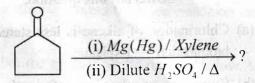
- (a) Hydroboration of 2-methyl-2-pentene at 25°C followed by oxidation with alkaline H<sub>2</sub>O<sub>2</sub> yields 2-methyl-3-pentanol but hydroboration at 160°C followed by oxidation yields 4-methyl-1-pentanol-Explain.
  - (b) What are the products if the following hydrolysis reactions are carried out in  $H_2O^{18}$  medium? Elaborate the mechanism of the reaction in each case.

$$\begin{array}{c|c}
 & H^{+}/H_{2}O^{18} \\
 & & ?
\end{array}$$

$$\begin{array}{c}
 & \circ \\
 & OH/H_{2}O^{18}
\end{array}$$
?

5. (a) Organolithiums add to  $\alpha, \beta$ -unsaturated ketones by 1, 4-addition reaction in presence of small amount of polar aprotic solvent, HMPA — Explain. 2

(b) Identify the products of the following reaction with mechanism.



- 6. (a) Show with mechanism that iodine can be used as a catalyst for aromatic bromination.
  - (b) Compounds (P) and (Q) both are treated with NaOH producing a single compound (R). Identify
    (R) and suggest a plausible mechanism for its formation starting from either of the substrate.

- 7. (a) Write any four principles of green chemistry. Give an example of Michael addition reaction under solvent free condition.
  - (b) How would you carry out the synthesis of (A) and (B) from acetone utilizing  $\alpha$ -bromoester in each of the following transformations?

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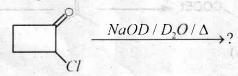
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Answer any one question.

 $10 \times 1 = 10$ 

- 8. (a) Chlorination of alkene is less stereospecific than bromination Explain.
  - (b) Suggest mechanism for the following transformations: 2×2

- (c) Nitration of dimethyl aniline gives mainly *m*-nitro derivative when concentrated nitric and sulfuric acids are used but mainly *o*-and *p*-nitro derivatives in less acidic conditions Explain.
- (d) Carry out the following transformation. 2  $Br CH_2CH_2CHO \rightarrow EtC \equiv C CH_2CH_2CHO$
- 9. (a) Predict the product with plausible mechanism. 2



- (b) Preparation of a ketone by addition of one equivalent of an ester to Grignard reagent is usually not a suitable process but reverse addition improves the yield of the ketone Explain.
- (c) Predict the product of the reaction below. Include a rationalization based on detailed analysis of competing transition state geometries.

(d) Show each of the following transformations could be accomplished by listing the required reagents and their sequences. 2×2