U.G. 3rd Semester Examination-2022 CHEMISTRY [HONOURS]

Course Code: CHEM-H-CC-T-7

Full Marks: 40

Time: $2\frac{1}{2}$ Hours

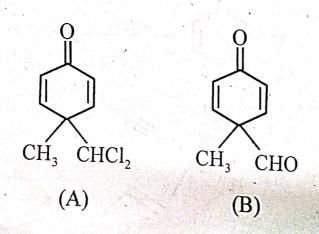
The figures in the right-hand margin indicate marks.

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

1. Answer any five from the following questions:

 $2\times5=10$

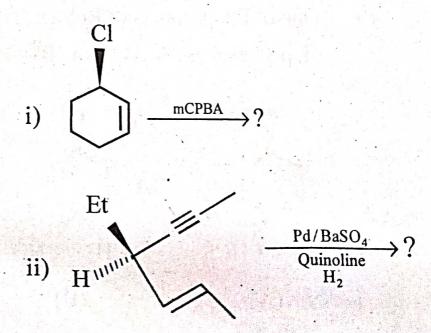
- a) Bromination of acetophenone in presence of (i) AlCl₃ (catalytic) and (ii) AlCl₃ (excess) gives different product-Explain.
- b) Hydrogenation of alkene is an exothernic process, still it requires a catalyst— explain.
- c) One of the products of Reimer-Tieman reaction of p-Cresol is 'A' but not 'B'—explain.



- d) Dimedone in acid medium can be used for the separation of acetaldehyde and formaldehyde from their mixture. Explain the fact.
- e) Compare the stabilities of the following molecules with proper reason.

I-Butene, Cis-2-Butene and trans-2-Butene

- Explain 'umpolung' with suitable example.
- g) Washing of crude m-dinitrobenzene with aqueous Na₂SO₃ removes the contaminated ortho- and para- isomers. Give reason.
- h) How will you convert benzil to diphenylacetylene via hydrazone formation?
- 2. Answer any **two** from the following: $5 \times 2 = 10$
 - a) I) Predict the product(s) with proper stereochemistry.



II) Indicate the structure of A, B and C in the following reaction sequences:

 $(1\frac{1}{2}+1\frac{1}{2})+2=5$

- b) i) Give one evidence for the formation of σ -complex and π -complex in electrophilic substitution reaction.
 - ii) Write down the mechanism of the following conversions:

I)
$$\stackrel{O}{\longleftarrow} \stackrel{Cl}{\longleftarrow} \stackrel{NaOEt}{\longleftarrow} \stackrel{COOEt}{\longleftarrow} \stackrel{O}{\longleftarrow} \stackrel{O}{\longrightarrow} \stackrel{O}{\longleftarrow} \stackrel{O}{\longrightarrow} \stackrel{O}{\longleftarrow} \stackrel{O}{\longleftarrow} \stackrel{O}{\longrightarrow} \stackrel{O}{\longrightarrow}$$

[Turn over]

c) i) Compare the reactivity of the following pair towards HCN.

- ii) What happens when Iso-propyl magnesium bromide is added to Diisopropyl ketone? Explain your answer with mechanism.
- d) i) Identify [A] and [B]

$$\begin{array}{c|c}
O & & \Delta \\
\hline
 & & \\
H_2/Ni & [B]
\end{array}$$

- ii) How Catechol can be synthesized from phenol? Give equations. 2+3=5
- 3. Answer any two from the following: $10 \times 2 = 20$
 - a) i) What is benzyne? Why it is so reactive?
 - ii) Predict the structure of 'A', 'B' and 'C' in the following reaction sequences.

 Explain their formation with mechanism.

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(4)

$$>= O + CH_2 - COOCMe_3 \xrightarrow{\text{NAOB}} \Lambda \xrightarrow{\text{CO}_2} B + C$$

CI

- iii) DBU/MeI can be used for methylation of RCOOH in stead of CH₂N₂. Justify.
- iv) What is Girard reagent-T? Give its one use. 3+3+2+2
- b) Give the products with plausible mechanism: $2 \times 5 = 10$

$$\begin{array}{c} \text{OCH}_3\\ \text{Cl} \\ \hline \\ \text{NaNH}_2 \\ \hline \\ \text{Liq. NH}_3 \end{array}$$

$$HO$$
 HO $+ CH_3CN$ $ZnCl_2$ HCl HO

iv) PhCOCOPh $\xrightarrow{\text{8H}}$ $\xrightarrow{\text{H}_{3}O^{\oplus}}$

$$(V) \qquad (CH_2O + (CH_3)_2 NH \xrightarrow{HCI}$$

- c) i) Sulphonation of benzene shows primary kinetic isotope effect —explain.
 - ii) How will you convert erytho-1, 2-diphenyl-1,2-ethenediol to z-stilbene?
 - iii) Predict the product with mechanism:

$$O_{2}N \xrightarrow{OH} OH \xrightarrow{PPh_{3} \atop DEAD \atop THF}?$$

iv) Write down the structure of B with proper stereochemistry:

v) Give the streostructure of the product with proper reason:

$$\frac{\text{(i)Me}_{2}\text{Culi/THF-78}^{\circ}\text{C}}{\text{(ii)H}_{3}\text{O}^{\oplus}}$$

2+2+2+2+2=10

d) i) Indicate the major product of the following reaction:

$$CO_2Me$$
 \longrightarrow ?

ii) Convert:

iii) Give explanation of the following observation:

$$\begin{array}{c}
 & \xrightarrow{\text{MeMgBr}} & \xrightarrow{\text{MeMgBr}} & \xrightarrow{\text{H}_3\text{O}^+} & \xrightarrow{\text{H}_3\text{O}^+} & \xrightarrow{\text{R}} & \xrightarrow{\text{R}}
\end{array}$$

$$\begin{array}{c}
 & \xrightarrow{\text{MeMgBr}} & \xrightarrow{\text{H}_3\text{O}^+} & \xrightarrow{\text{R}_3\text{O}^+} & \xrightarrow{\text{R}_3\text{O}^+$$

iv) Suggest two sets of reactants to prepare the following alkane using Corey-House strategy and choose the better set with proper reason.

$$CH_3 - CH - CH_2 - CH_3$$
 CH_3

2+3+2+3=10