4/CHE–251 (Th) (Syllabus–2023)

2025

(May–June)

FYUP : 4th Semester Examination

CHEMISTRY

(Organic Chemistry—I)

(CHE–251)

(Theory)

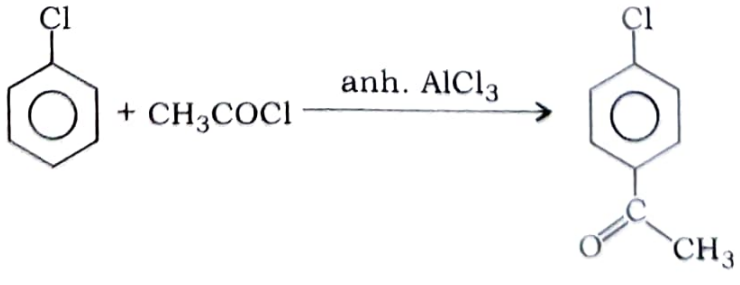
Marks : 75

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. *(a)* Why are nucleophilic substitution reactions of aryl halides difficult? How can the rate of nucleophilic substitution be made easier? 2+1=3

(b) Write the mechanism of the following reaction : 2



(c) How can you distinguish among primary, secondary and tertiary alcohols by Victor-Meyers method? 3

(d) Complete the following reactions : 1×3=3

(i) $CH_3—CH_2—OH + SOCl_2 \longrightarrow$?

(ii) Glycerol + HNO_3 (excess) $\xrightarrow{\text{conc. } H_2SO_4}$?

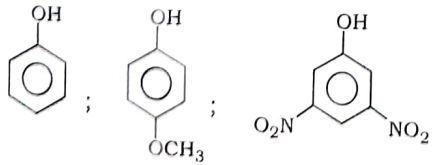
(iii) $\begin{matrix} CH_2—OH \\ | \\ CH_2—OH \end{matrix}$ + HCl $\xrightarrow{200\ ^\circ C}$?

(e) How does ethylene epoxide react with (i) C_2H_5OH and (ii) $LiAlH_4$? 1+1=2

(f) With the help of relevant equations show how phenol is obtained from cumene. 2

(g) With proper mechanism write the products obtained when phenol undergoes Reimer-Tiemann reaction. 2½

(h) Arrange the following molecules in order of increasing acid strength and explain giving proper reasons : 1½

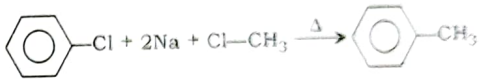


(Continued)

OR

2. (a) Why does ethylbromide undergo nucleophilic substitution reaction more easily compared to bromobenzene? 2½

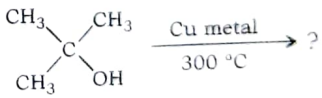
(b) Write the mechanism of the following reaction : 2½



(c) What do you mean by oxymercuration-demercuration of alkenes? What happens when propene undergoes this reaction? 1+2=3

(d) Write the correct products of the following reactions : 1×3=3

(i) $R—\overset{\overset{O}{\|}}{C}—Cl + C_2H_5—OH \longrightarrow$?

(ii)  ?

(iii) $\begin{matrix} CH_2—OH \\ | \\ CH_2—OH \end{matrix} \xrightarrow{HIO_4}$?

(Turn Over)

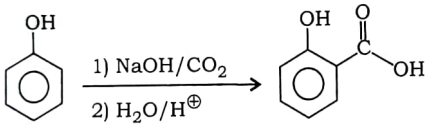
(e) Give the reaction of ethylene epoxide with the following : 1×2=2

(i) HCN

(ii) NH_3

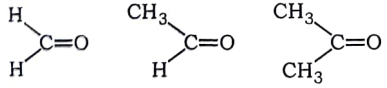
(f) How can you obtain phenol from a mixture of benzene and conc. H_2SO_4? 2

(g) Write the mechanism of the following reaction : 2½



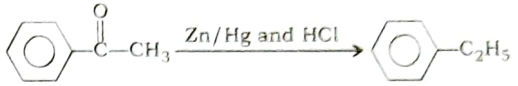
(h) Why is phenol practically insoluble in water but alcohols of comparable molecular mass are highly soluble in water? 1½

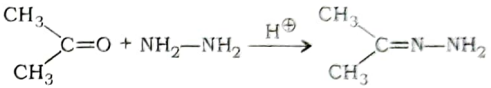
3. (a) Arrange the following molecules in order of increasing reactivity towards HCN with proper justification : 2



(b) What type of molecules respond to haloform reaction? What happens when pentan-2-one undergoes haloform reaction? 1+2=3

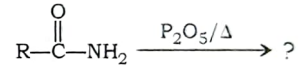
(c) Write the mechanism of the following reactions : 2×2=4

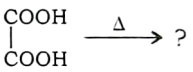
(i) 

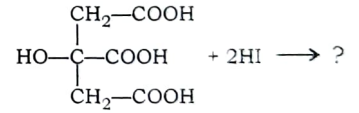
(ii) 

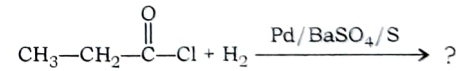
(d) Why is α-chloroacetic acid a stronger acid than acetic acid? 2

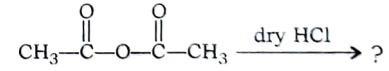
(e) Complete the following reactions : 1×5=5

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(f) Give a method for the preparation of succinic acid with proper reactions. 2

OR

4. *(a)* Write the mechanism of the following reactions : 3×2=6

(i) Benzoin condensation

(ii) Perkin's reaction

(b) Why are α-hydrogen atoms of aldehydes and ketones acidic in nature? How does carbanion stabilize itself when the α-H atom is abstracted by a base? 1+1=2

(c) Write a simple chemical test to distinguish between benzaldehyde and acetaldehyde. 1

(d) During the preparation of an ester by the reaction between carboxylic acids and alcohols in the presence of conc. H_2SO_4, why should the ester be removed from the reaction medium at regular intervals of time? 2

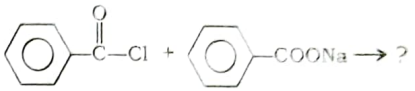
(e) Write the correct products of the following reactions : 1×5=5

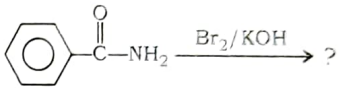
(i) $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} ?$

(ii) $\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{SOCl_2} ?$

(Continued)

(iii) $HO-\overset{\overset{CH_2-COOH}{|}}{\underset{\underset{CH_2-COOH}{|}}{C}}-COOH \xrightarrow{\text{fuming } H_2SO_4} ?$

(iv)  $\longrightarrow ?$

(v)  $\xrightarrow{Br_2/KOH} ?$

(f) Write a method of preparation of tartaric acid. 2

5. *(a)* Write the mechanism of nitration of benzene to nitrobenzene. 2

(b) What happens when—

(i) nitrobenzene is treated with $LiAlH_4$;

(ii) nitrobenzene is reduced in neutral medium in the presence of zinc dust and aqueous NH_4Cl;

(iii) nitrobenzene is reduced with zinc and NaOH? 1+1+1=3

(c) Why is Gabriel-phthalimide synthesis not used for the preparation of primary aromatic amines? 2

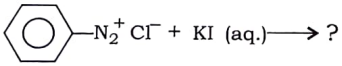
(Turn Over)

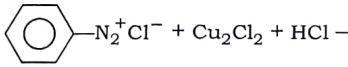
(d) Explain why a substantial amount of *m*-nitroaniline is formed during nitration though the $-NH_2$ group is *ortho-* and *para*-directing towards electrophilic substitution reactions. 2

(e) Why is aniline less basic than cyclohexylamine? 1

(f) Why are aromatic diazonium chlorides more stable than their aliphatic counterparts? 2

(g) Complete the following reactions : 1×3=3

(i)  ?

(ii)  ?

(iii) $R-COOH + CH_2N_2 \longrightarrow$?

(h) How will you confirm the presence of urea by the Biuret test? 2

(i) How does urea react with—

(i) acetyl chloride;

(ii) hydrazine? 1+1=2

OR

6. (a) Why are aromatic nitro-compounds exclusively meta-directing towards electrophilic substitution reactions? 2

(b) Why are α-H atoms of primary and secondary nitroalkanes reactive towards alkalis? 1

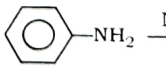
(c) Write the mechanism of the following reaction : 2

$$CH_3-CH_2-NO_2 + H_2O \xrightarrow[RCOOH + NH_2OH]{\text{Conc. } H_2SO_4} ?$$

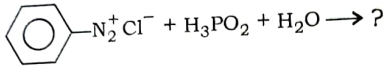
(d) How can you distinguish among primary, secondary and tertiary amines by Hinsberg's method? 3

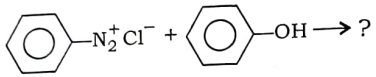
(e) Write the correct products of the following reactions : 1×2=2

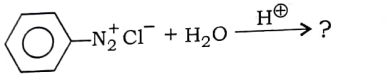
(i) $C_2H_5-N(H)-H + CHCl_3 + KOH\ (alc.) \xrightarrow{\Delta} ?$

(ii)  $\xrightarrow[(0-5)\ ^\circ C]{NaNO_2 + HCl}$?

(f) Write the products obtained during the following reactions : 1×5=5

(i)  $+ H_3PO_2 + H_2O \longrightarrow ?$

(ii)  $+$ $\longrightarrow ?$

(iii)  $+ H_2O \xrightarrow{H^{\oplus}} ?$

(iv) $R-\overset{O}{\overset{\|}{C}}-R + CH_2N_2 \longrightarrow ?$

(v) $CH_2N_2 + 4[H] \xrightarrow{Na/Hg} ?$

(g) Why does urea behave as a weak base in spite of having two $-NH_2$ groups? 2

(h) Write the reaction of urea with—

(i) HNO_3;

(ii) water in the presence of an acid. 1+1=2

7. (a) Why should Grignard reagents be prepared under anhydrous conditions? Write the reaction of phenyl magnesium bromide with water. 1+1=2

(b) Write a method of preparation of an organolithium compound with proper equation. 2

(c) How can you prepare—

(i) butanoic acid;

(ii) crotonic acid ($CH_3-CH=CH-COOH$) from ethylacetoacetate? 3+3=6

(d) How will you carry out the following conversions? 2×3=6

(i) Benzene to benzaldehyde

(ii) Chlorobenzene to *p*-nitrophenol

(iii) Ethyl magnesium chloride to propan-1-ol

(e) What happens when—

(i) methyl lithium reacts with CO_2 followed by hydrolysis;

(ii) ethyl magnesium bromide reacts with HCN and the addition product obtained is hydrolyzed? 1½+1½=3

OR

8. (a) How can you differentiate between tautomerism and resonance? 2

(b) How can you obtain—

(i) isopropyl alcohol;

(ii) *t*-butyl alcohol using a suitable Grignard reagent? 1½+1½=3

(c) How can you carry out the following conversions? 2×3=6

(i) Ethanol to 3-hydroxybutanal

(ii) Benzoic acid to benzaldehyde

(iii) Aniline to benzyl alcohol

(d) How can you convert diethyl malonate to—

(i) succinic acid;

(ii) ethyl methyl ketone? 3+3=6

(e) Write the reaction of methyl lithium with ethylene epoxide. 2

★ ★ ★