2017

(5th Semester)

CHEMISTRY

FIFTH PAPER (CHEM–351)

(Organic Chemistry—II)

Full Marks : 55

Time : 2½ hours

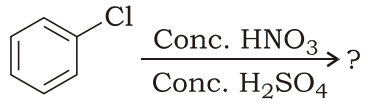
(PART : B—DESCRIPTIVE)

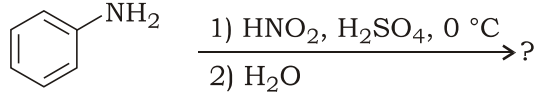
(*Marks* : 35)

The figures in the margin indicate full marks for the questions

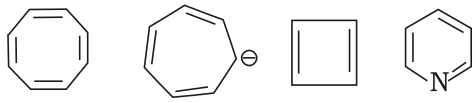
1. *(a)* Draw the resonance molecular orbital picture of benzene. 2

(b) Complete the following transformations with suitable mechanism : 2+2=4

(i) 

(ii) 

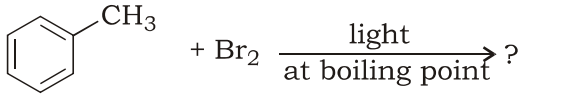
(c) Which of the following species satisfy Hückel's rule? Explain. 1



OR

2. *(a)* Explain why the acidity of *m*-nitrophenol is much lower than its *o*- and *p*-isomers. 2

(b) Complete the following reaction (mechanism not required) : 1×3=3

(i) 

(ii) 

(iii) 

(c) What do you mean by nuclear and side chain halogenations? Give examples. 2

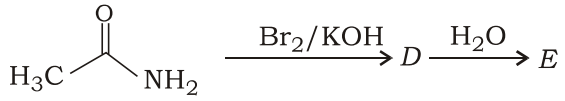
3. *(a)* Arrange the following in their increasing order of acidity. Explain. 2

$CH_3CH_2CH_2COOH$, $CH_3CH_2CH(Cl)COOH$, $CH_3CH(Cl)CH_2COOH$, $ClCH_2CH_2CH_2COOH$

(b) Write one chemical test to confirm the presence of carbonyl group. 1

(c) Write the product(s) of the following reactions with suitable mechanism : 2×2=4

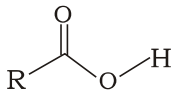
(i) $2HCHO \xrightleftharpoons{50\%\ NaOH} ?$

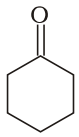
(ii)  $\xrightarrow{Br_2/KOH} D \xrightarrow{H_2O} E$

OR

4. (a) Compound *(A)* C_4H_8O forms phenyl-hydrazone. It fails to react with Tollen's reagent but gives iodoform test. On reduction with Zn-Hg/HCl, *(A)* yields *n*-butane. Assign structure *(A)*. 2

(b) Complete the following reactions : 3+2=5

(i)  $\xrightarrow{SOCl_2} A \xrightarrow{2CH_2N_2} B \xrightarrow[2)\ H_2O]{1)\ Ag} C$

(ii)  $\xrightarrow[2)\ H_2O/H^+]{1)\ CH_3MgBr} ?$

5. (a) Write the Hinsberg's test to distinguish between 1°, 2° and 3° amines. 2

(b) Explain active methylene compounds with suitable examples. 1½

(c) What will happen when methyl amine reacts with acetyl chloride? Write the mechanism of the reaction. 1½

(d) Differentiate between tautomerism and resonance. 2

OR

6. (a) Complete the following chemical transformations : 2½×2=5

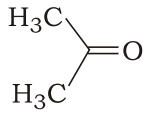
(i) $CH_3COCH_2CO_2C_2H_5 \longrightarrow CH_3CH_2CH_2CH_2CO_2H$

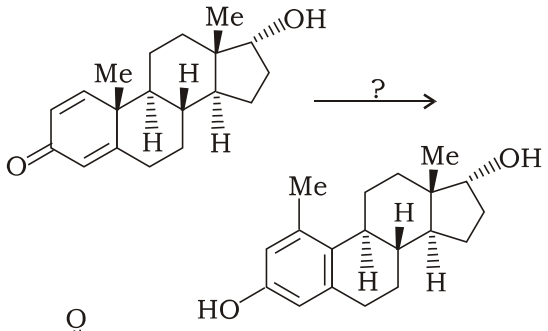
(ii) $CH_2(CO_2C_2H_5)_2 \longrightarrow CH_3CH_2CH_2CO_2H$

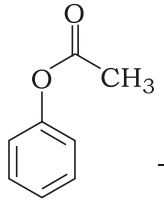
(b) "Aryl amines are weaker bases than alkyl amines." Explain. 2

7. (a) Explain $B_{AC}2$ mechanism for the hydrolysis of easter. 2

(b) Complete the following reactions with suitable mechanism (any *two*) : 2½×2=5

(i)  $+ BrCH_2COOEt \xrightarrow[2)\ H_2O]{1)\ Zn/ether} ?$

(ii) 

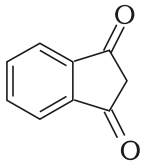
(iii) 

$\xrightarrow[H_2O]{\text{Anhy. } AlCl_3}$?

OR

8. *(a)* Write a brief note on the formation of carbon-carbon double bond. 2

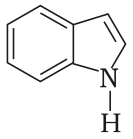
(b) Complete the following transformations with suitable mechanism (any *two*) : 2½×2=5

(i) 

+ 

$\xrightarrow[THF]{t\text{-BuOK}}$?

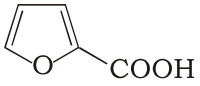
(ii)  $\xrightarrow[AlCl_3]{CH_3CH_2Cl}$?

(iii) 

+ HCHO + $(C_2H_5)_2NH$

$\xrightarrow[H_2O]{\text{AcOH, 100 °C}}$?

9. *(a)* Complete the following transformations (any *three*, mechanism not required) : 1×3=3

(i) 

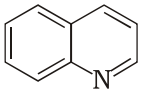
$\xrightarrow[2)\ \Delta,\ -CO_2]{1)\ H_2SO_4}$?

(ii) 

+ CH_3COONO_2 ⟶ ?

(iii) 

$\xrightarrow[2)\ H_2O]{1)\ NaNH_2,\ heat}$?

(iv) 

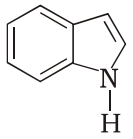
$\xrightarrow[\text{Below 500 °C}]{Br_2,\ \text{vapour phase}}$?

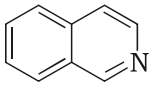
(b) How will you synthesise isoquinoline by Bischler-Napieralski method? Give chemical equations. 4

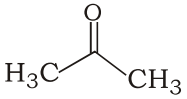
OR

10. *(a)* Mention one method of preparation for pyridine. Give the chemical equation. 2

(b) Complete the following reactions with suitable mechanism (any *two*) : 2½×2=5

(i)  + $(CH_3CO)_2$ $\xrightarrow{AlCl_3}$?

(ii)  $\xrightarrow[2)\ H_2O]{1)\ EtMgBr/150\ °C}$? $\xrightarrow[2)\ PhCOEt]{1)\ KNH_2}$?

(iii)  + $PhNHNH_2$ $\xrightarrow[\Delta]{Phosphoric\ acid}$?

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2017

(5th Semester)

CHEMISTRY

FIFTH PAPER (Chem–351)

(Organic Chemistry—II)

(PART : A—OBJECTIVE)

(*Marks* : 20)

The figures in the margin indicate full marks for the questions

SECTION—I

(*Marks* : 5)

Put a Tick (✓) mark against the correct answer in the brackets provided : 1×5=5

1. Which of the following statements with respect to phenol is true?

(a) Phenol reacts with ammonia in the presence of $ZnCl_2$ to give 2-hydroxy aniline ( )

(b) Phenol undergoes nitration with dilute nitric acid to form *m*-nitrophenol ( )

(c) Phenol can be prepared by hydrolysis of aryl halides with aqueous NaOH ( )

(d) The boiling point of *o*-nitrophenol is higher than its *meta*- and *para*-isomers ( )

2. Ketones are the first oxidation product of

(a) 1°-alcohols ( )

(b) 2°-alcohols ( )

(c) 1°-amines ( )

(d) carboxylic acids ( )

3. Aniline on treatment with bromine water gives

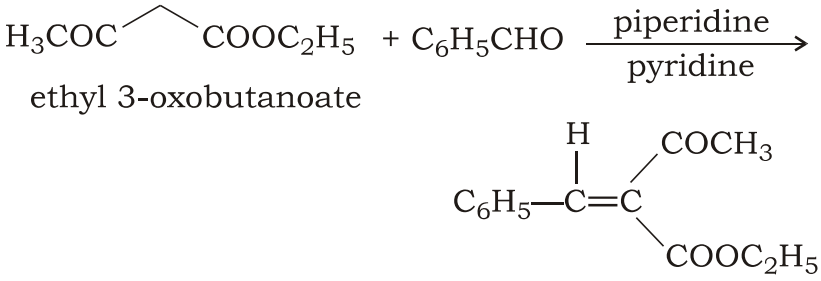
(a) 2-bromoaniline ( )

(b) 3-bromoaniline ( )

(c) 4-bromoaniline ( )

(d) 2,4,6-tribromoaniline ( )

4. In the following transformation, ethyl 3-oxobutanoate reacts with benzaldehyde in the presence of piperidine-pyridine mixture as a catalyst to give ethyl 2-benzylidene-3-oxobutanoate.



ethyl 3-oxobutanoate

ethyl 2-benzylidene-3-oxobutanoate

This type of reaction is known as

(a) Claisen-Schmidt reaction ( )

(b) Mannich reaction ( )

(c) Knoevenagel reaction ( )

(d) Michael addition reaction ( )

5. The order of aromaticity in pyrrole, furan and thiophene is

(a) thiophene > pyrrole > furan ( )

(b) thiophene > furan > pyrrole ( )

(c) furan > pyrrole > thiophene ( )

(d) furan > thiophene > pyrrole ( )

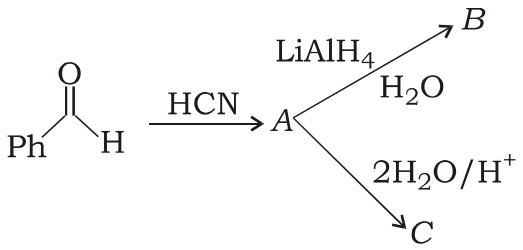
SECTION—II

(*Marks* : 15)

Answer the following questions in not more than *6* sentences each : 3×5=15

1. Unlike alkyl halides, aryl halides do not react with nucleophiles under normal laboratory conditions. Explain.

2. Complete the following reactions :

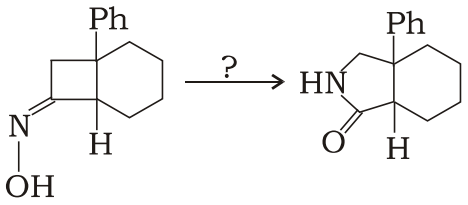


3. Write the chemical reaction of ethyl amine with—

(a) $NaNO_2/HCl$

(b) $CHCl_3/KOH$

4. Which reagent is used for the following alteration? Complete the reaction using proper reaction mechanism.



5. Explain why nitration of pyrrole predominantly take place at C-2- position.

★ ★ ★