[4923]-40

M.Sc. - II
ORGANIC CHEMISTRY
CH - 350 : Organic Reaction Mechanism
(2008 Pattern) (Semester - III)

Time : 3 Hours]   *[Max. Marks : 80*
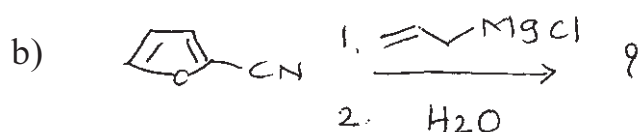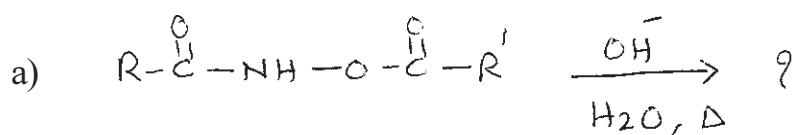
Instructions to the candidates:
  1) *All questions are compulsory.*
  2) *Figures to the right indicate full marks.*
  3) *Answers to the two sections should be written in separate answer books.*

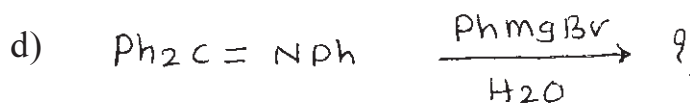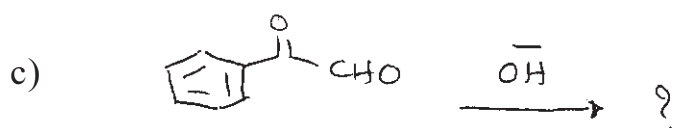## SECTION - I

Q1) Attempt <u>any four</u> of the following: **[12]**

  a) Halogenation of unsymmetrical dialkyl ketone in acid and base catalysed conditions give different products. Explain.

  b) Explain the neighbouring group participation by heteroatoms.

  c) Discuss the generation and stability of carbenes with suitable examples.

  d) Give the synthetic applications of Henry reaction.

  e) Explain the significance of σ and ρ.

Q2) Predict the products with mechanism in <u>any four</u> of the following: **[16]**

  a) $R-\overset{O}{\overset{\|}{C}}-NH-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[\text{H}_2\text{O}, \Delta]{\overline{\text{OH}}}$?

  b) $\xrightarrow[\text{2. } \text{H}_2\text{O}]{\text{1. } \diagup\diagdown\text{MgCl}}$?

c)

$\xrightarrow{\overline{O}H}$?

d) $Ph_2C = NPh$ $\xrightarrow[H_2O]{PhMgBr}$?

e)

$\xrightarrow{H_2O}$?

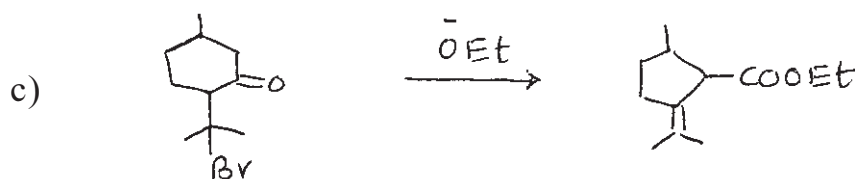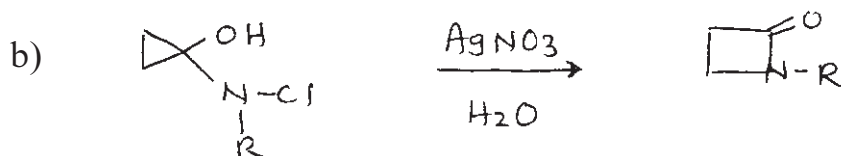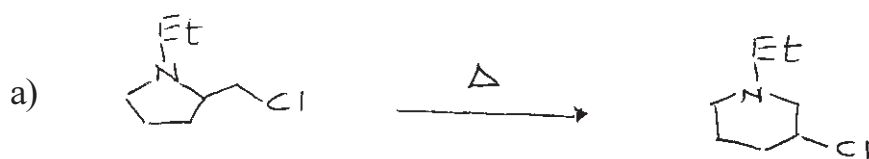**Q3)** Write notes on <u>any three</u> of the following: **[12]**

a) Kinetic isotope effect to determine reaction Mechanism.

b) Use of pyridoxal in reductive amination.

c) Crossover experiments.

d) Dieckmann cyclisation.

SECTION - II

Q4) Suggest the mechanism in <u>any four</u> of the following: **[16]**

a)

$\xrightarrow{\Delta}$

b)

$\xrightarrow[H_2O]{AgNO_3}$

c)

$\xrightarrow{\overline{O}Et}$

d)

e)

Q5) Answer <u>any four</u> of the following: [12]

a) Explain linear and non-linear Hammett plots.

b) Discuss Newmann rule of six with an example.

c) Explain the sandmeyer reaction with a suitable example.

d) Explain the reduction of pyruvic acid by NADH.

e) Substitution at β-position reduces the rate of hydrolysis in $A_{AC}{}^2$ mechanism. Explain.
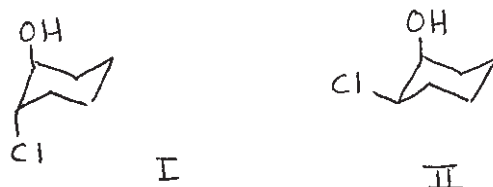
Q6) Answer <u>any four</u> of the following: [12]

a) The pka of a p-chlorobenzoic acid is 3.98, pka of benzoic acid is 4.19. Calculate σ for P-Cl group.

b) Which of the following is more acidic? Justify.

 and

c) Predict, which of the following will undergo epoxide formation readily. Explain.

d) How will you prove the formation of cyclopropanone as an intermediate in Favorskii rearrangement. Explain.

e) Thioester hydrolysis occurs more rapidly than ordinary ester hydrolysis. Explain.