Himachal Pradesh Administrative Service Combined Competitive (Main / Written) Examination, 2020

# CHEMISTRY (PAPER-II)

Time allowed: 3 Hours                                                                 Maximum Marks: 100

## QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions.

1. There are EIGHT questions printed in English.

2. Candidate has to attempt FIVE questions in all.

3. Question No.1 is compulsory. Out of the remaining SEVEN questions, FOUR are to be attempted.

4. All questions carry equal marks. The number of marks carried by a question / part is indicated against it.

5. Write answers in legible handwriting. Each part of the question must be answered in sequence and in the same continuation.

6. Unless otherwise mentioned, symbols and notations carry their usual standard meanings.

7. Assume suitable data, if considered necessary, and indicated the same clearly.

8. Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in answer book must be clearly struck off.

9. Re-evaluation / Re-checking of answer book of the candidate is not allowed.

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1. (a) Indicate the relative epoxidation behavior of the following compounds giving reasons: (5)
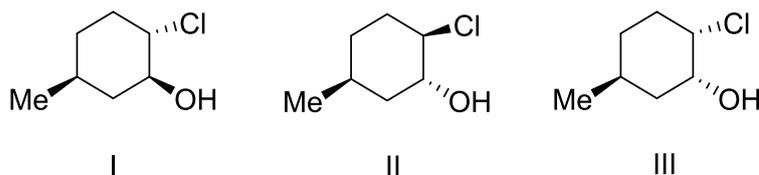


(b) Account for the scrambling of deuterium in 3-deuterioindene on heating. (5)

(c) Arrange the following compounds in terms of decreasing reactivity toward Norrish type I process giving the reasons: (5)
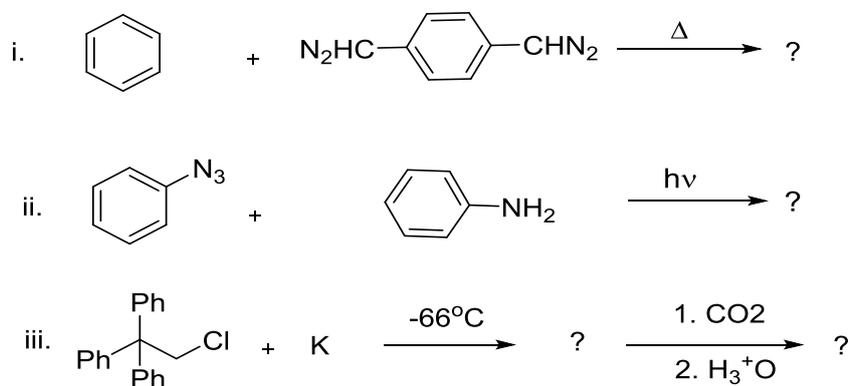
I      II      III      IV
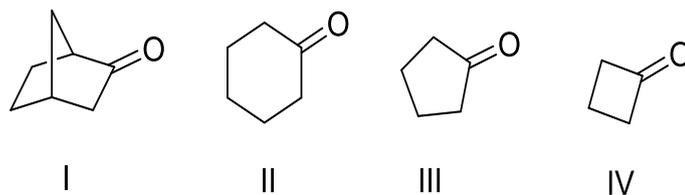
(d) Comment upon the $v_{C=O}$ (cm$^{-1}$) stretch in the following model compounds:     (5)
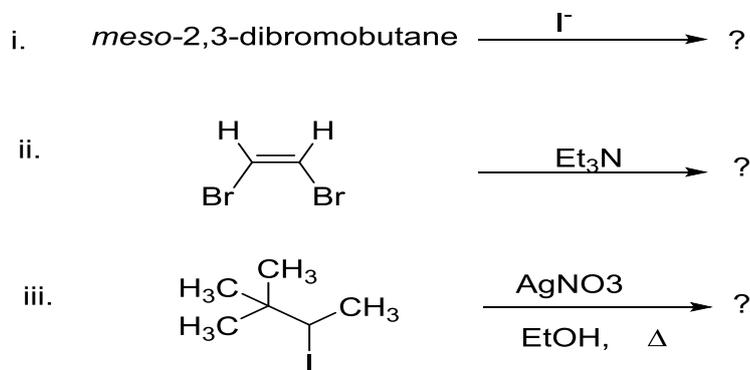


X            Y
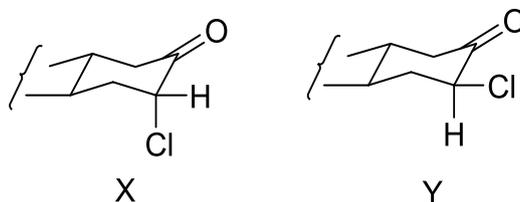
2. (a) Define and explain homoaromaticity choosing suitable examples.     (5)
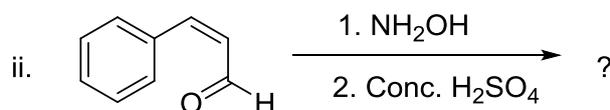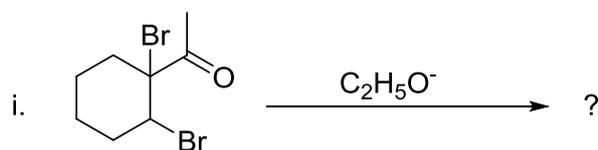
(b) Complete the following reactions:     (6)

i. 

ii. 

iii. 

(c) Complete the following reactions with mechanisms:     (9)

i.    *meso*-2,3-dibromobutane $\xrightarrow{\text{I}^-}$ ?
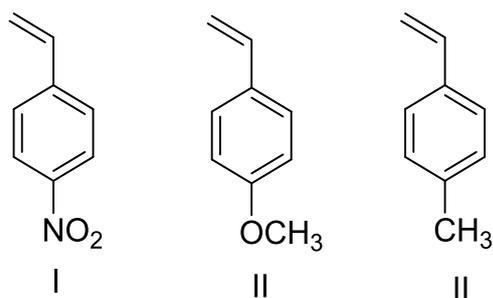
ii. 

iii. 

3. (a) Explain, how the following factors enhance the rate of the enzyme catalyzed reactions:     (8)

(i) Proximity and orientation

2

(ii)   Acid-base catalysis

(b)   Write down the structures of:                                         (5)

   (i)   Nylon 6

   (ii)   Nylon 66

   (iii)  Kevlar

   (iv)  Poly(ethylene terephthalate)

   (v)   Neoprene

(c)   Give the products distribution (major and minor products) obtained in Birch reduction of anisole and benzoic acid separately.                         (3)

(d)   Giving the suitable examples comment upon the oxidation of *cis*- and *trans*-cyclohexanediols with $Pb(OAc)_4$                                           (4)

4. (a)   Giving their mechanisms complete the following reactions:            (10)



i.   [structure: cyclohexane with Br and acetyl group, Br substituent] $\xrightarrow{C_2H_5O^-}$ ?

ii.   [structure: cinnamaldehyde (Z)] $\xrightarrow[\text{2. Conc. } H_2SO_4]{\text{1. } NH_2OH}$ ?

(b)   What is green chemistry? Write a short note it.                         (5)

(c)   Arrange the following monomers in order of decreasing ability to undergo (i) anionic polymerization and cationic polymerization respectively:             (5)
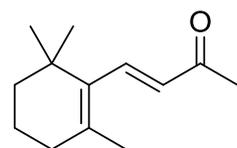


   $NO_2$ — I        $OCH_3$ — II        $CH_3$ — II

5. (a)   Complete the following reactions along with their mechanisms:        (10)
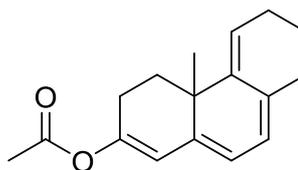
i.



EtONA (1 equivalent) → ?

ii.



+ (excess) HO⁻ → ?
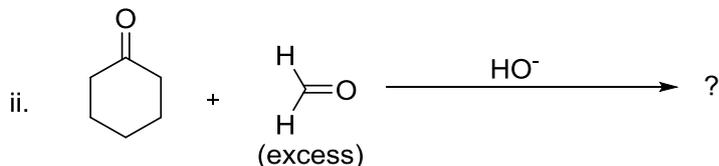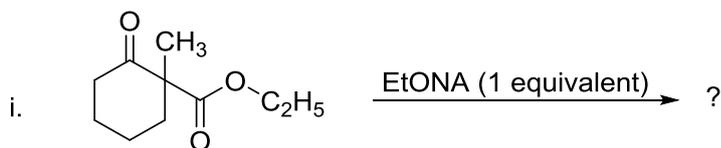
(b) Calculate the $\lambda_{max}$ for each of the following compounds: (6)
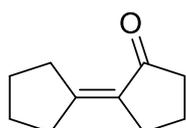


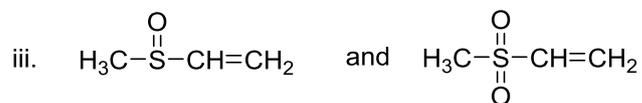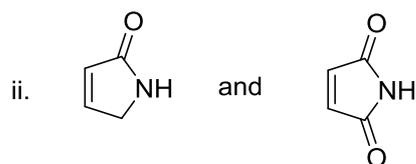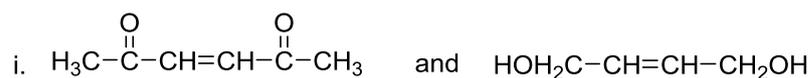I                    II                    II
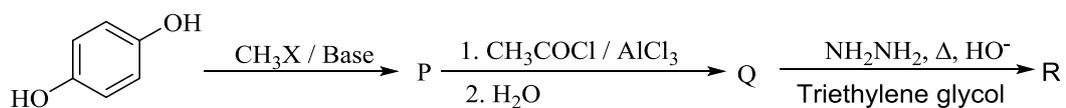
(c) In each pair below, indicate the dienophile that you would expect to be more reactive in Diel-Alder reaction. (4)

i. $H_3C-\overset{O}{\underset{\|}{C}}-CH=CH-\overset{O}{\underset{\|}{C}}-CH_3$  and  $HOH_2C-CH=CH-CH_2OH$

ii.   and  

iii. $H_3C-\overset{O}{\underset{\|}{S}}-CH=CH_2$  and  $H_3C-\overset{O}{\underset{\underset{O}{\|}}{\overset{\|}{S}}}-CH=CH_2$
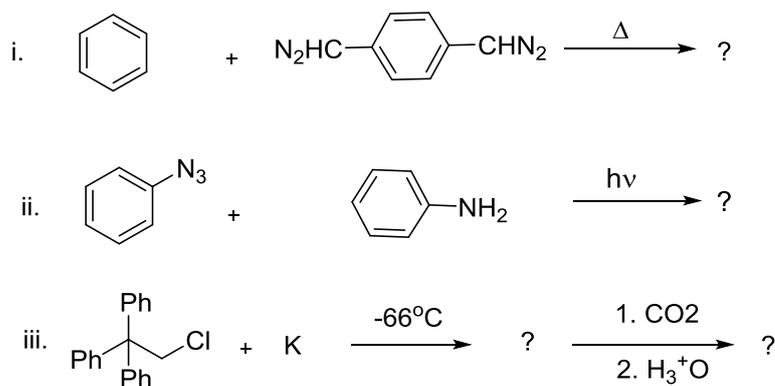
6. (a) Write the structures of species **P, Q** and **R** in the following reaction sequence. Also give the mechanism of formation of **R** from **Q** : (5)



$\xrightarrow{CH_3X \, / \, Base}$ P $\xrightarrow[\text{2. } H_2O]{\text{1. } CH_3COCl \, / \, AlCl_3}$ Q $\xrightarrow[\text{Triethylene glycol}]{NH_2NH_2, \, \Delta, \, HO^-}$ R

(b) What are the main significant peaks in the mass spectrum of n-butylbenzene? Elaborate by giving the fragmentation pattern? (5)

(c) Complete the following reactions' sequences; (6)

4

i. [benzene ring] + $N_2HC$—[benzene ring]—$CHN_2$ $\xrightarrow{\Delta}$ ?

ii. [benzene ring]—$N_3$ + [benzene ring]—$NH_2$ $\xrightarrow{h\nu}$ ?

iii. $Ph$—$C(Ph)(Ph)$—$CH_2$—$Cl$ + K $\xrightarrow{-66°C}$ ? $\xrightarrow[\text{2. } H_3^+O]{\text{1. } CO_2}$ ?

(d) The identification of products has been the main tool in the determination of reaction mechanism of Von-Richter reaction. Explain. (4)

7. (a) A compound **X**, in its elemental analysis is found to contain C, H and O, rapidly gets hydrolyzed in slightly acidic solution to give compound **Y** and a volatile alcohol. Identify the compounds **X** and **Y** using the following $^1H$ NMR data: (6)
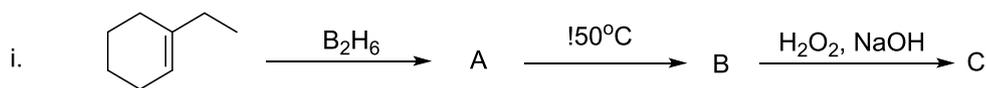
Compound **X** ($^1H$ NMR data) = δ 2.80 (2H, d, $J = 6.0$Hz); δ 3.21 (6H, s);
δ 4.41 (1H, t, $J = 6.0$Hz); δ 7.13 (5H, m unsymm. pattern)

Compound **Y** ($^1H$ NMR data) = δ 3.68 (2H, d, $J = 3.0$Hz); δ 7.3 (5H, m unsymm. pattern); δ 9.70 (1H, t, $J = 3.0$Hz)
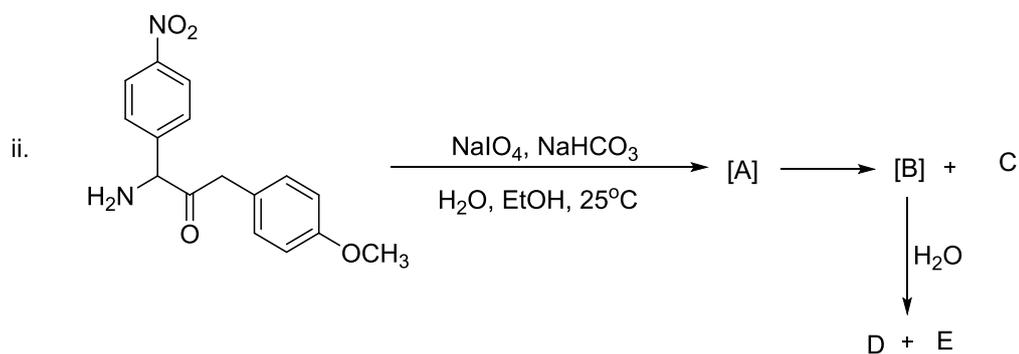
(b) Complete the following reactions giving their mechanisms: (6)

i. [methyl cyclopropyl ketone] $\xrightarrow{h\nu}$ ?

ii. $Ph$—$C(=O)$—$Ph$ + R—≡—R $\xrightarrow{h\nu}$ ?
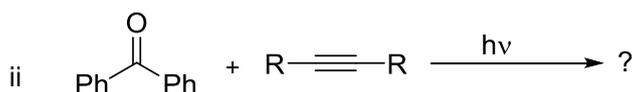
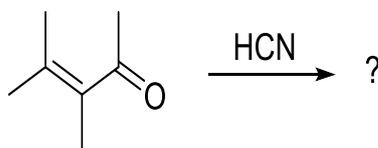(c) Complete the following sequences of the reactions by writing the structures of the compounds formed: (3+5)

5

i.



$$\text{(1-ethylcyclohexene)} \xrightarrow{B_2H_6} A \xrightarrow{150^\circ C} B \xrightarrow{H_2O_2,\ NaOH} C$$

3

ii.



$$\xrightarrow[\text{H}_2\text{O, EtOH, 25}^\circ\text{C}]{\text{NaIO}_4,\ \text{NaHCO}_3} [A] \longrightarrow [B] \ + \ C$$
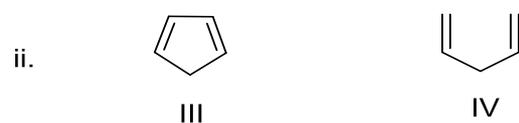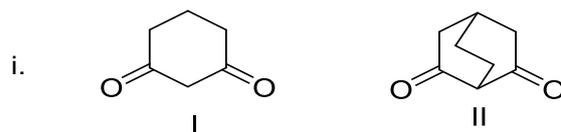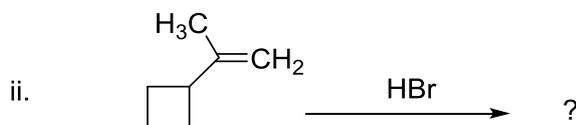
$$[B] \xrightarrow{H_2O} D + E$$

5
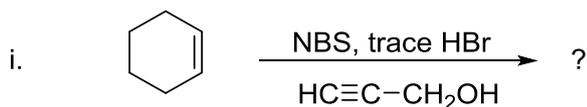
8. (a) Invoking the idea of kinetic and thermodynamic control, give the products' spread in the following reaction: (5)



$$\xrightarrow{HCN} \ ?$$
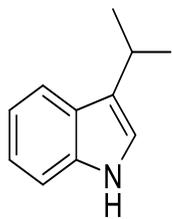
(b) In each of the following pairs which one more acidic and why? (4)

i.



I



II

ii.



III



IV

(c) Give the product(s) in the following reactions along with their mechanisms: (5)

i.



$$\xrightarrow[\text{HC}\equiv\text{C}-\text{CH}_2\text{OH}]{\text{NBS, trace HBr}} \ ?$$
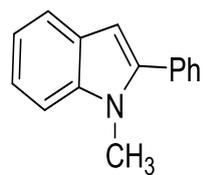
ii.



$$\xrightarrow{HBr} \ ?$$

(d) Predict the starting substrates for the synthesis of following compounds by Fischer Indole synthesis: (6)

A



B



C

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