

This question paper contains 16 printed pages]

**HPAS (M)—2015**

**CHEMISTRY**

**Paper II**

*Time : 3 Hours*

*Maximum Marks : 150*

*Note :— Attempt five questions in all. Question No. 1 is compulsory. All parts of a question must be attempted in continuation at one place.*

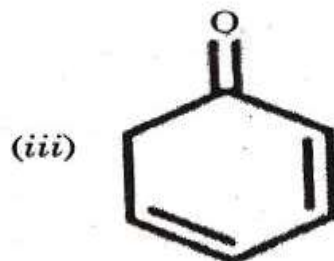
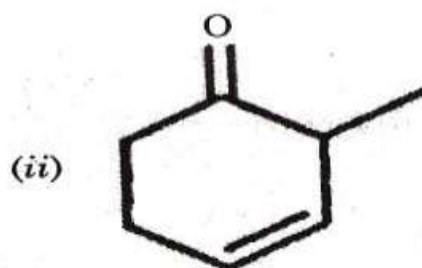
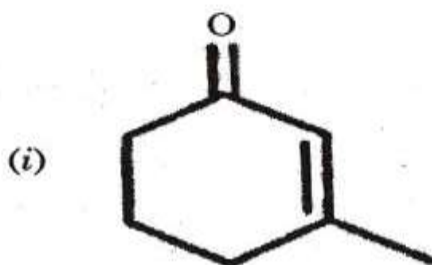
1. Attempt any *ten* of the following : 3×10=30

- (a) Explain why  $\alpha$ -glucopyranose is oxidized by  $\text{HIO}_4$  more rapidly than the  $\beta$ -anomer at the 1, 2-bond.

P.T.O.

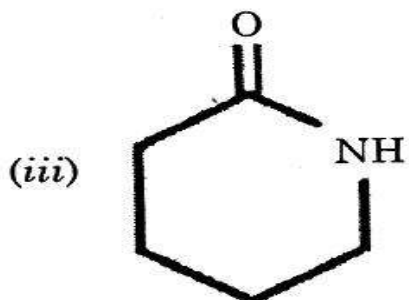
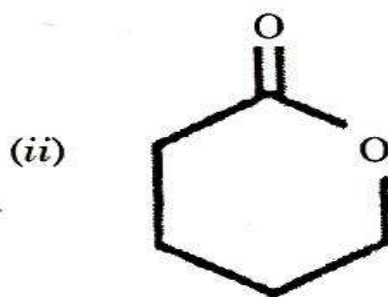
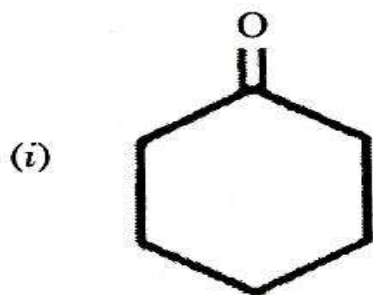
(b) Mustard gas  $(\text{ClCH}_2\text{CH}_2)_2\text{S}$  is hydrolyzed by  $\text{H}_2\text{O}$  much faster than expected for primary alkyl halides. Offer an explanation for this observation ?

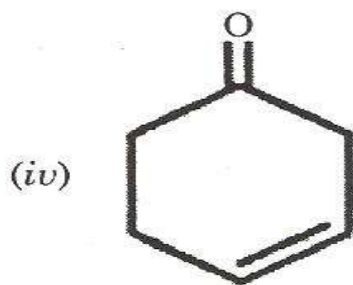
(c) Arrange the following in order of decreasing  $\lambda_{\text{max}}$  ?



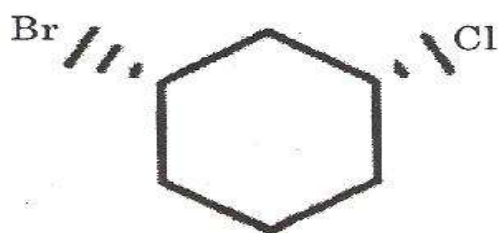
(d) What will be the correct order of basicity of benzene, toluene, (o, m, p) xylene, and mesitylene salts dissolved in  $\text{HBF}_4$  ?

(e) List the following compounds in order of decreasing frequency of  $\text{C}=\text{O}$  absorption :



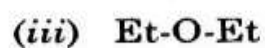
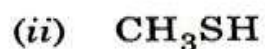
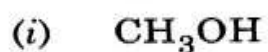


- (f) Assign R and S configuration for the following compound :



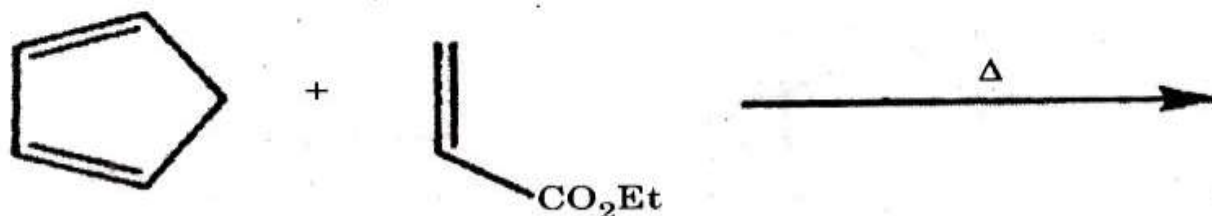
- (g) How many non-equivalent protons are present in L-valine.
- (h) How will you differentiate a double doublet (non-first order spectra) having intensity ratio of 1 : 3 : 3 : 1 with a quartet ?

(i) Arrange the following compounds in order to their correct boiling point (highest to lowest) :



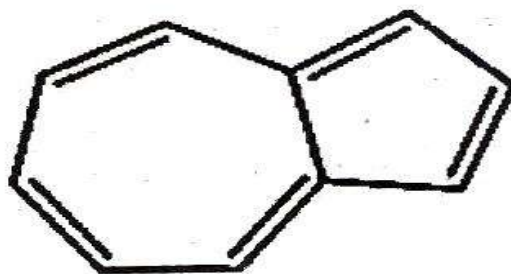
(j) What is Molish test ? What will happen when D-glucose is treated with Molish reagent ?

(k) What will be the major product in the following reaction ?



P.T.O.

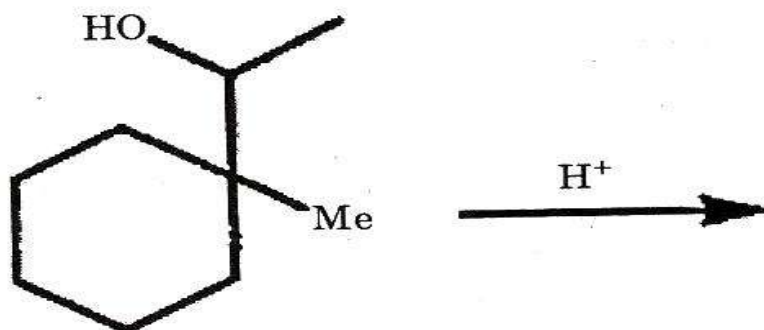
- (l) Why does the azulene compound have a large molecular dipole ?



**Azulene**

2. Attempt any *five* of the following : 6×5=30

- (a) Identify the product in the following reaction and propose suitable mechanism :



- (b) Sodium salt of sulphanilic acid can readily be acetylated with  $\text{Ac}_2\text{O}$ , but not the free acid, why ?
- (c) *meta*-*tert*-butylphenol reacts with chlorine to give tri-chloro-derivative; with bromine it gives dibromo derivative and with iodine it gives moniodo derivative, identify these products and give suitable explanation for their formation ?
- (d) How would you differentiate  $\alpha$ -D-glucose and  $\beta$ -D-glucose by  $^1\text{H}$  NMR based on chemical shift and coupling constant ?
- (e) Which of the following compounds will undergo faster hydrolysis via  $\text{S}_{\text{N}}1$  process ? Give proper explanation to support your answer :

**A****B**

P.T.O.



- (f) What will be the major products in the photochemical decomposition of methyl neopentyl ketone ? Propose suitable mechanism for this conversion.

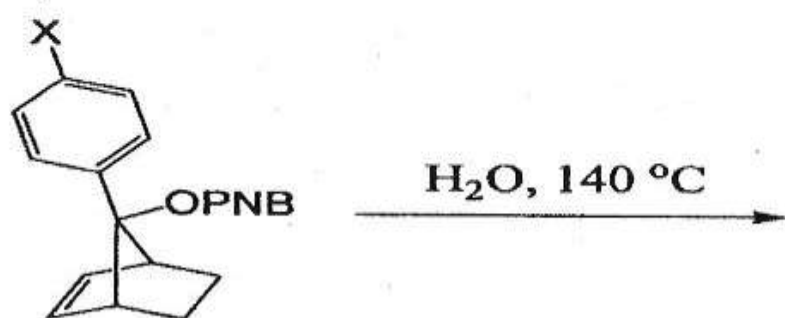
3. Attempt *all* of the following :

6×5=30

- (a) On the basis of the fact that the  $\pi$  bond of an alkyne is weaker than the  $\pi$  bond of an alkene, it is expected that an alkyne might be more reactive than an alkene. However, electrophilic addition to an alkyne occurs more slowly than an alkene ? Explain.
- (b) Propose a mechanism for the conversion of ethylene glycol into dioxane by conc  $\text{H}_2\text{SO}_4$ .
- (c) Compound A on solvolysis gives one product with retention of configuration while compound B under

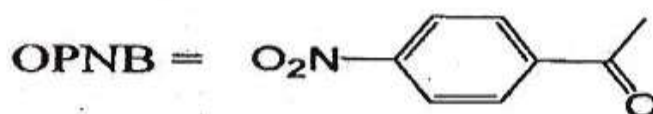


identical conditions gives mixture of *anti* and *syn* product. Identify the products and propose suitable mechanism.

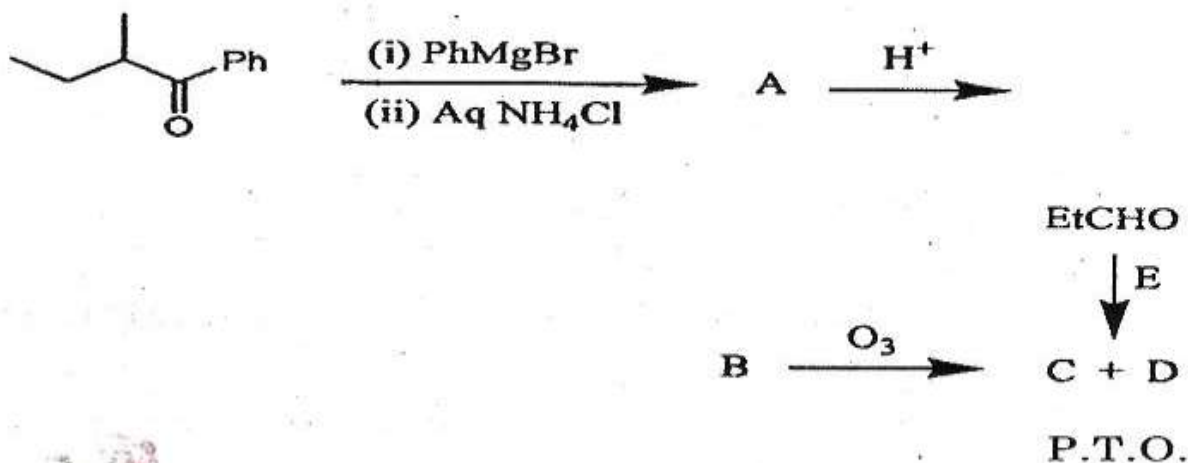


**A; X = H**

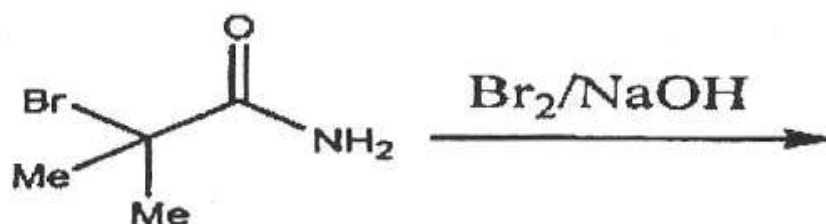
**B; X = NMe<sub>2</sub>**



(d) Give structure of A-E in the following reaction :



- (e) Identify the product in the following reaction and give suitable explanation to justify your answer.



4. Attempt *all* of the following :

6×5=30

- (a) A compound of with molecular formula  $\text{C}_7\text{H}_7\text{NO}$  shows the following spectral data :

$^1\text{H}$  NMR : 2.83 (m, 2H), 3.82 (m, 1H), 7.52 (d,

$J = 8 \text{ Hz}$ , 2H), 8.66 (d,  $J = 8 \text{ Hz}$ , 2H);

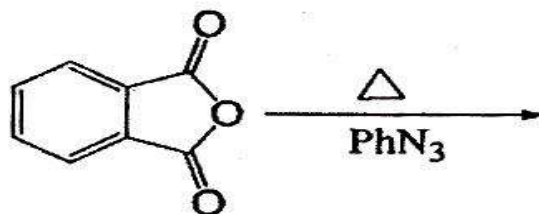
$^{13}\text{C}$  NMR : 48.8 (–) 57.3 (+), 123.2 (+), 149.7 (+),

152.7 (quart); MS (m/z) : 121 ( $\text{M}^+$ ). Find out

structure of the compound, and assign all the peaks.

- (b) *Cis*-2-butene on reaction with diazomethane under thermal condition yields *cis*-1, 2-dimethylcyclopropane, while under photochemical conditions it yields mixture of *cis* and *trans*-1, 2-dimethylcyclopropane. Name the intermediate involved in both the reactions and propose mechanism of their formation.
- (c) Both *cis* and *trans*-2-acetoxy cyclohexyl tosylate on acetolysis affords same product. Identify the product and justify your answer with the help of suitable mechanism.
- (d) How would you differentiate *cis* and *trans* stilbene with the help of  $^1\text{H}$  NMR ?

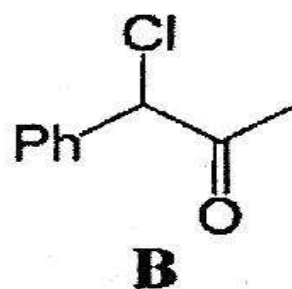
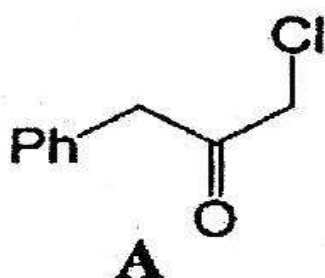
- (e) Identify the product in the following conversion, name the intermediate involved in this transformation and propose suitable mechanism :



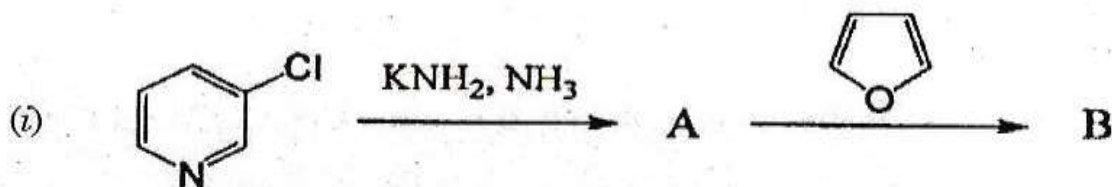
5. Attempt any *five* of the following : 6×5=30

- (a) Phthalic acid diethyl ester shows a base peak at  $m/z$  149 in the MS, propose the fragmentation pattern that accounts the base peak at  $m/z$  149.
- (b) The  $^1\text{H}$  NMR spectrum of a mixture of acetone and  $\text{CH}_2\text{Cl}_2$  shows two singlets at 2.30 and 5.24 ppm with the integration ratio of 2.3 to 1. Calculate the percentage of acetone and  $\text{CH}_2\text{Cl}_2$  ?

- (c) Using Boord synthesis how would you prepare hex-3-ene ?
- (d) 3-Methyl-indole on reaction with  $\text{CH}_2\text{Cl}_2/\text{MeLi}$  leads to the formation of rearranged product. Propose structure of the rearranged product, name of the intermediate involved in this conversion and mechanism of this transformation ?
- (e) Both compounds A and B on treatment with sodium methoxide lead to the formation of same product. Identify the product and propose the mechanism :



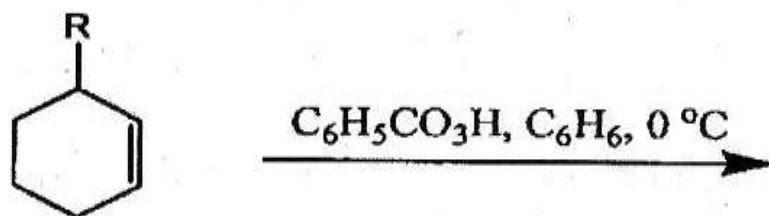
(f) Complete the following reaction :



6. Attempt *all* of the following :

6×5=30

(a) Find out the products in the following reaction (compounds A and B) with correct stereochemistry ?

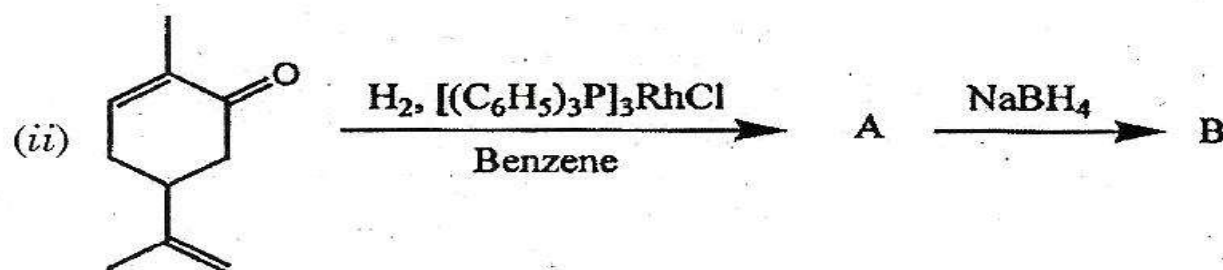
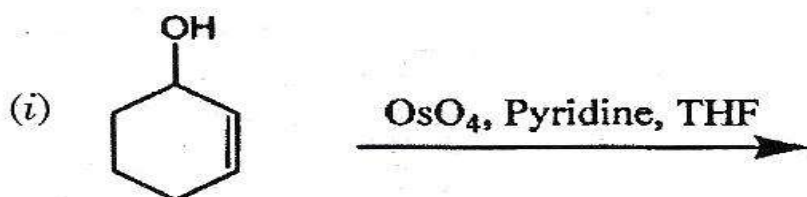


A, R = OCOMe

B, R = OH



- (b) What will be the major product in the following reactions, and give correct stereochemistry in case of reaction (i) ?



- (c) 2-Methyl-butanal shows base peak at  $m/z$  58, while 3-methyl-butanal shows base peak at  $m/z$  44. Explain with the help of fragmentation pattern.
- (d) Name the amino acids which do not give positive ninhydrin test. Give structure of ninhydrin, and the complex that is formed by the reaction of ninhydrin with amino acid.

- (e) *Cis*-1, 2-dimethyl-cyclohexane-1, 2-diol and its *trans* isomer on treatment with acid gives different products. Identify the products and propose suitable mechanism for both the reactions.