

This question paper contains 16+4 printed pages]

HPAS (M)—2014

CHEMISTRY

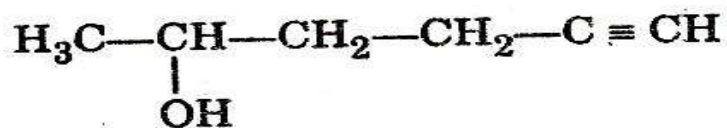
Paper II

Time : 3 Hours

Maximum Marks : 150

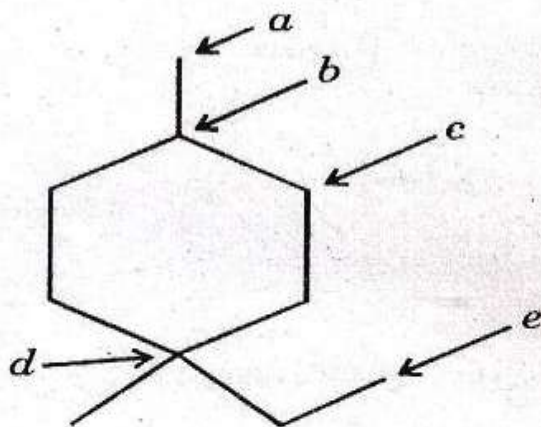
Note :— Attempt five questions in all. Question No. 1 is compulsory. All parts of a question must be attempted in continuation at one place.

1. (a) Give the IUPAC name of the following compound :

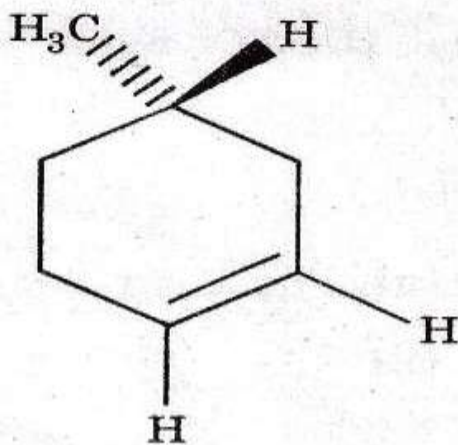


P.T.O.

- (b) Designate primary, secondary, tertiary and quaternary carbon atoms in the following compound :



- (c) Assign absolute configuration as "R" or "S" to the following compound :

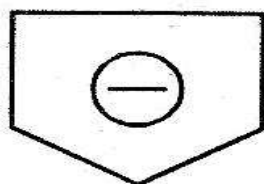


(d) Ortho-xylene boils at a higher temperature than the para-xylene. Explain.

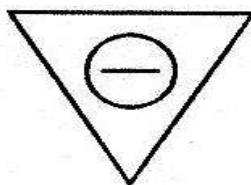
(e) The picric acid possesses appreciable acidic property. How would you account for the fact ?

(f) Explain why the pyrrole is less basic than pyridine ?

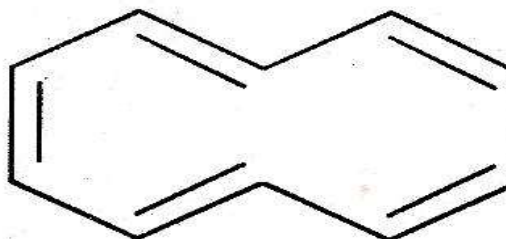
(g) Designate aromatic, antiaromatic and non-aromatic in the following species :



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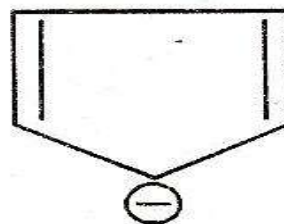
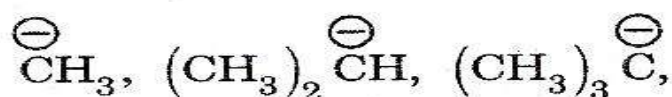


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(h) What are ambident nucleophiles ? Explain with suitable examples.

(i) Arrange the following carbanions in order of their decreasing stability :



(j) The sulfur content of an organic compound is 26.7%. If the organic compound contains two sulfur atoms, what is the molecular weight of the compound ?

$$10 \times 3 = 30$$

2. (a) A nucleophile reacts with an aldehyde to form addition product whereas it produced substitution product in the case of acyl chlorides.

Explain.

- (b) What carboxylic acid would be formed if the malonic ester synthesis was carried out with one equivalent of malonic ester, one equivalent of 1, 5-dibromopentane and two equivalents of base ?
- (c) Describe the ring-opening polymerization of propylene oxide.
- (d) Will an acyl chloride afford an amide on treatment with an aqueous solution of pyridine ? Explain.
- (e) How would you prepare D-arabinose from D-glucose ?

5×6=30

P.T.O.

3. (a) Write short notes on the following reaction

intermediates :

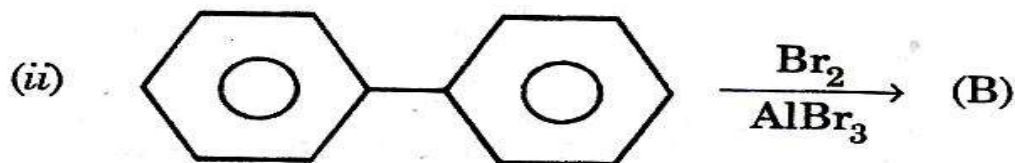
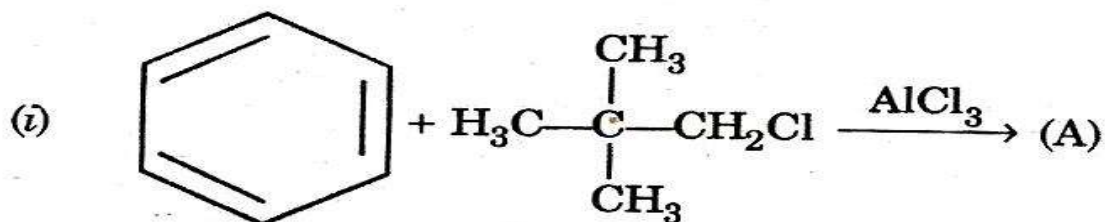
(i) Carbocation

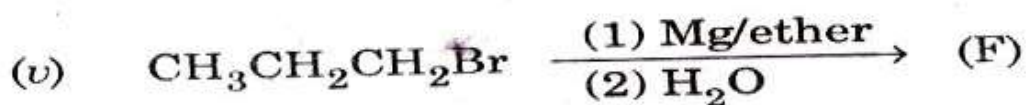
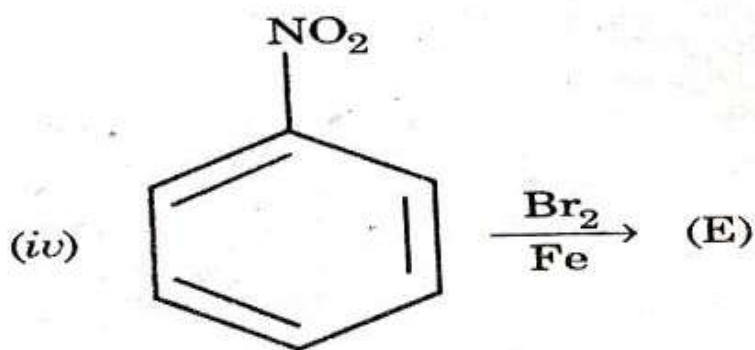
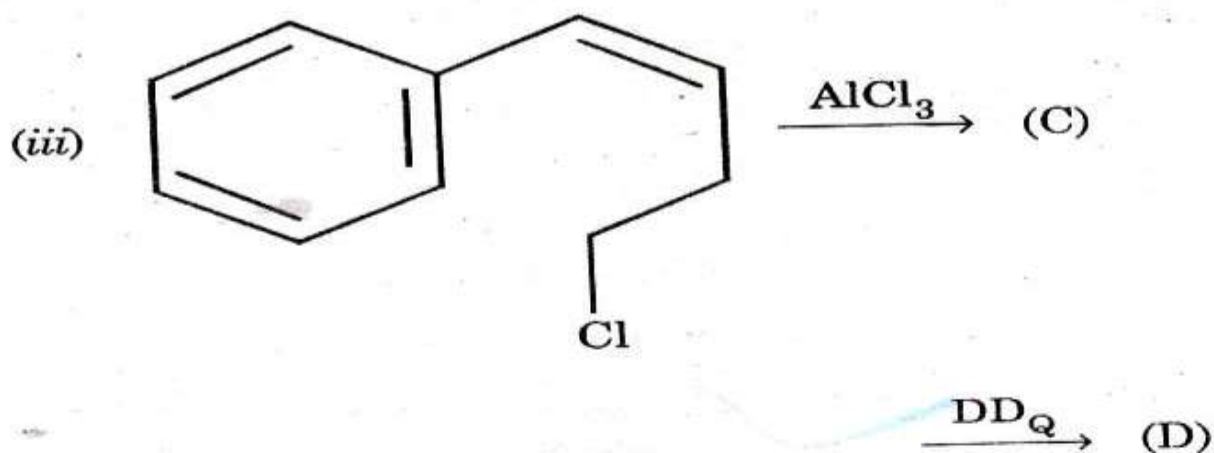
(ii) Nitrene

(iii) Benzyne.

(b) Give the main organic products A to F in the

following reactions :





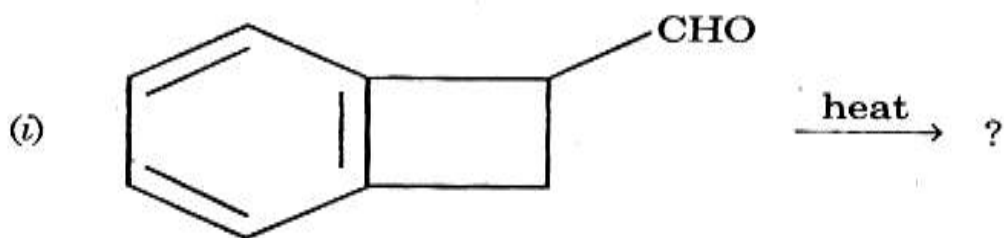
(c) Explain why :

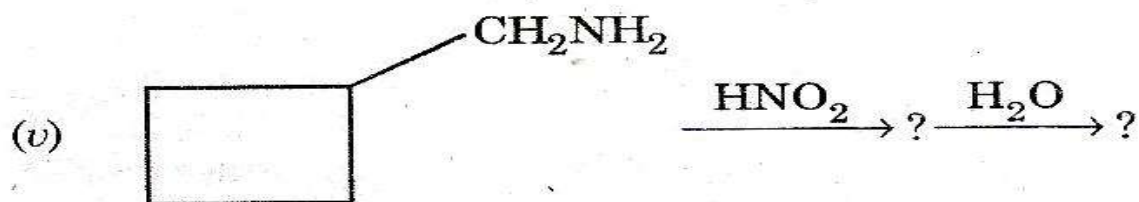
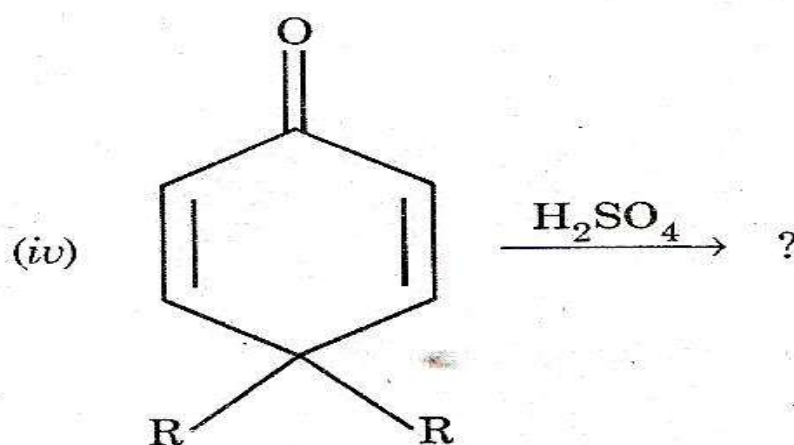
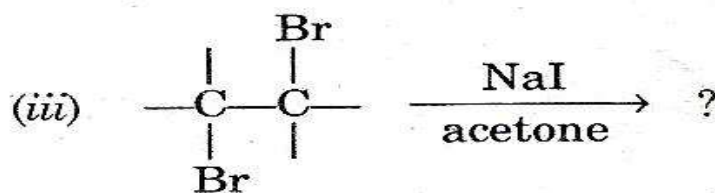
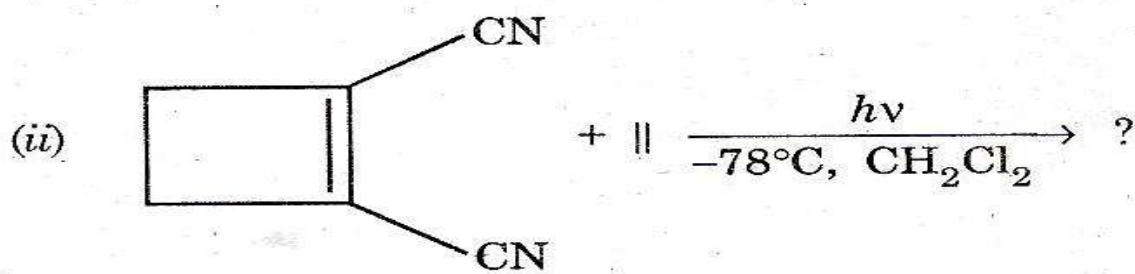
- (i) Neo-menthyl chloride when treated with NaOEt/EtOH undergoes dehydrochlorination at a faster rate than menthyl chloride.

- (ii) 3-Bromopropanal undergoes base-catalyzed dehydrobromination at a faster rate than does the 2-bromopropanal.

- (d) Discuss the mechanism for an aromatic nucleophilic substitution (S_NAr) involving Meisenheimer complex.

- (e) Complete the following chemical equations :





5×6=30

P.T.O.

4. (a) Explain why :

(i) Alkaline hydrolysis of alkyl halides to alcohols

is generally slow, but the reaction becomes

rapid if catalytic amounts of KI are added

to the reaction mixture.

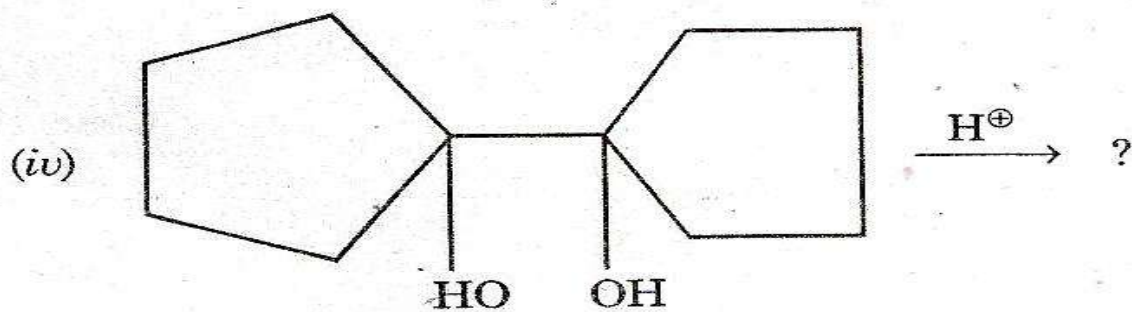
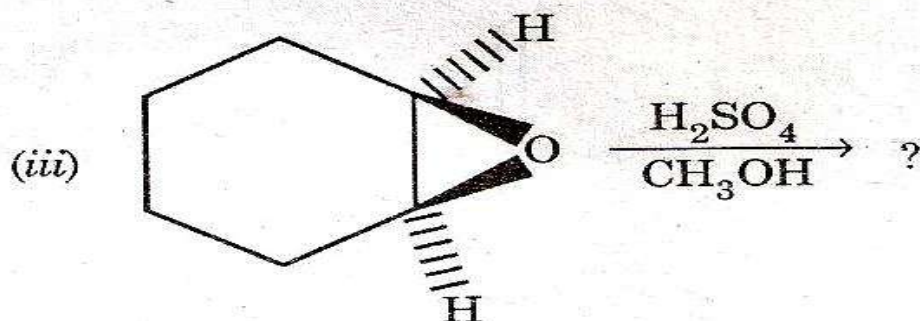
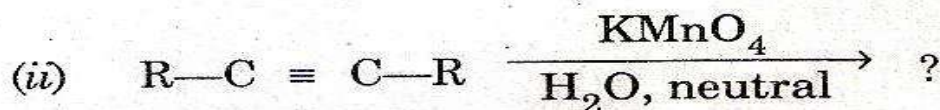
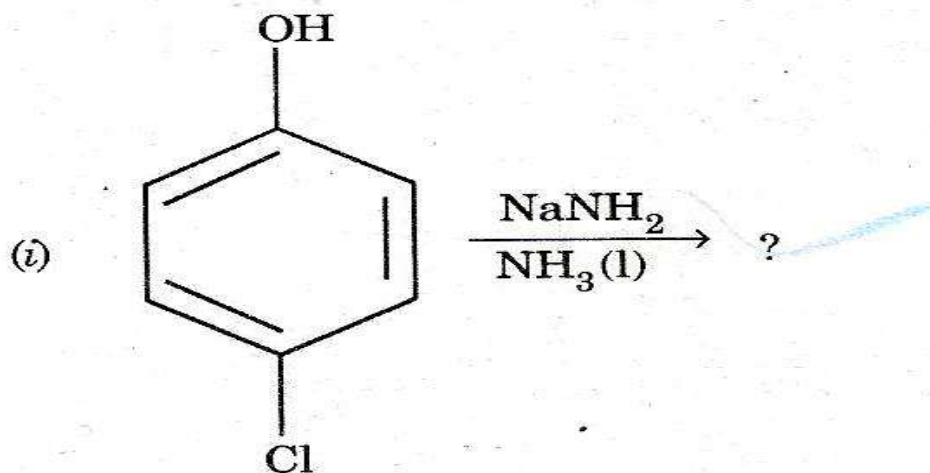
(ii) Vinyl halides are usually reluctant to

undergo S_N1 reaction.

(b) Discuss the role of crown ethers in phase-transfer

catalysis.

(c) Predict the major products in the following reactions :

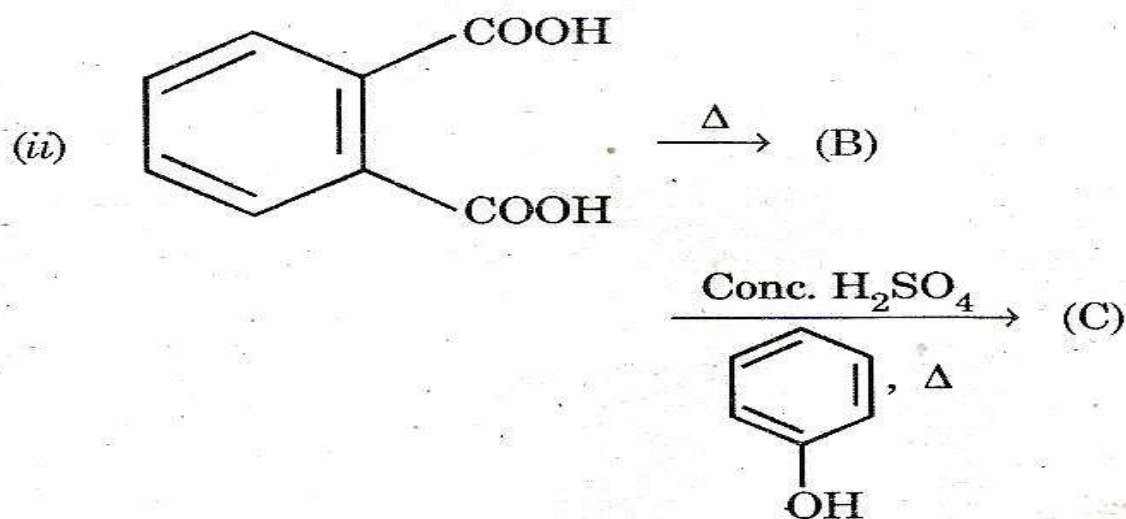
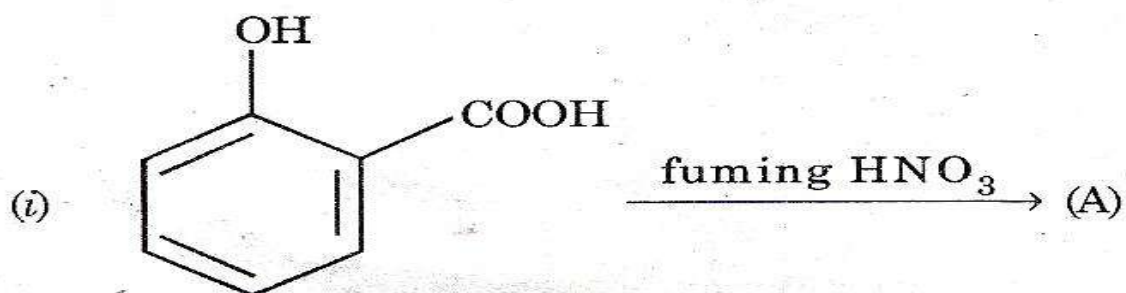


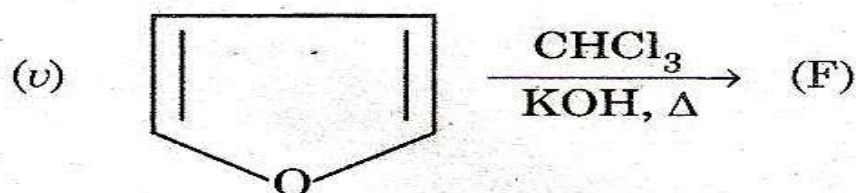
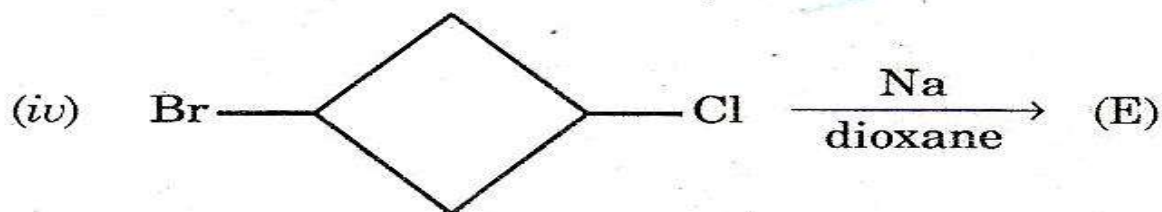
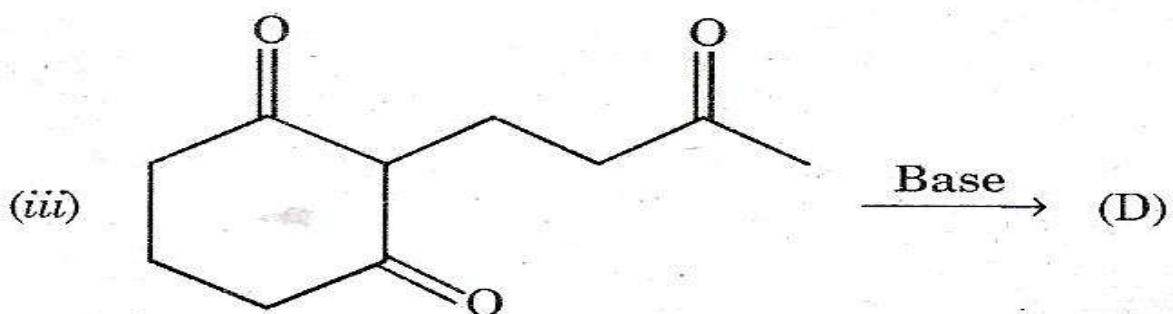
P.T.O.

(d) How would you convert glucose into fructose and vice-versa ?

(e) Give a short account of S_N1 , S_N2 and S_Ni reactions. 5×6=30

5. (a) Give the main organic products A to F in the following reactions :





(b) Justify the following facts :

- (i) Triphenyl methyl cation is more stable than methyl cation.

(ii) A solution of triphenylacetic acid in conc.

H_2SO_4 affords CH_3OCPh_3 when poured into

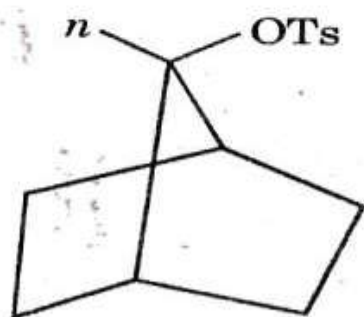
methanol.

(iii) Acidity of methanol is greater than *t*-butanol

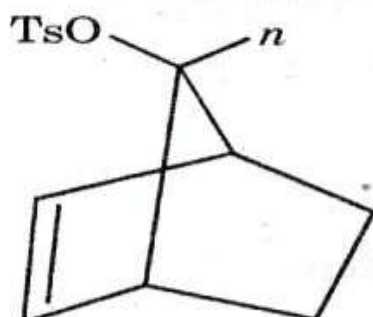
in aqueous solution.

(c) Justify the relative rates of acetolysis of the

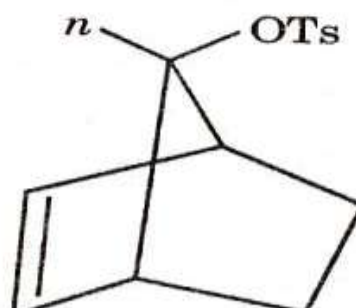
following compounds :



A



B



C

$$K_{\text{rel}} : 1 : 10^4 : 10^{11}$$

(d) How would you carry out the following transformations ?

- (i) Benzil \rightarrow Benzilic acid
- (ii) Phenol \rightarrow Salicylaldehyde
- (iii) Aniline \rightarrow *p*-Bromoaniline
- (iv) Toluene \rightarrow *p*-Aminobenzoic acid
- (v) $\text{C}_6\text{H}_5\text{CHO} \rightarrow$ Benzil
- (vi) *m*-dinitrobenzene \rightarrow *m*-Nitroaniline.

(e) Write short notes on any *three* of the following :

- (i) Fischer indole synthesis
- (ii) Aldol condensation
- (iii) Wolf rearrangement
- (iv) Baeyer-Villiger oxidation.

5×6=30

P.T.O.

6. (a) What is invert sugar ? Explain with a suitable example.
- (b) The mass spectra of two different cycloalkanes show a molecular ion peak at $m/z = 98$. One spectrum shows a base peak at $m/z = 69$, and the other shows a base peak at $m/z = 83$. Identify the cycloalkanes.
- (c) A solution of an organic compound in ethanol shows an absorbance of 0.52 at 236 nm in a cell with a 1 cm light path. Its molar absorptivity in ethanol at that wavelength is 12,600. What is the concentration of the compound ?

(d) Describe *one* synthetic use of the following

reagents :

(i) SeO_2

(ii) LiAlH_4

(iii) $n\text{-BuLi}$

(iv) NaBH_4

(v) NBS

(vi) HIO_4

(e) How would you distinguish 1, 2-, 1, 3- and

1, 4-dinitrobenzene by using ^1H -NMR and

^{13}C -NMR spectroscopy ?

5×6=30

P.T.O.

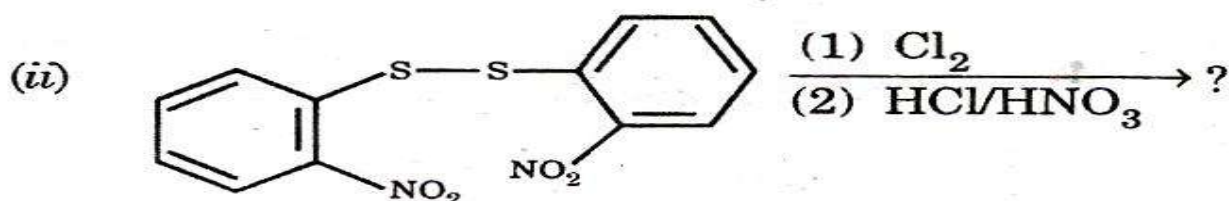
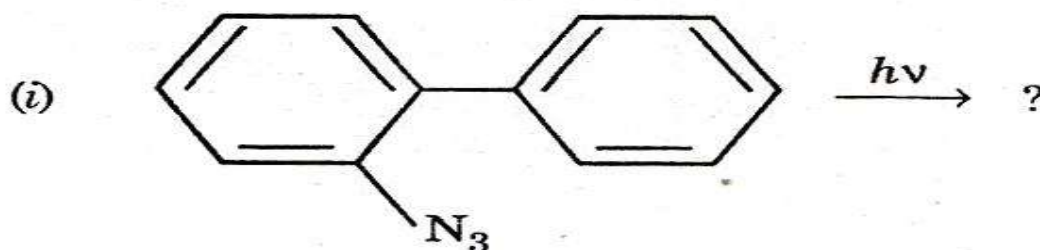
7. (a) Treatment of $\text{Me}_3\text{CCH}=\text{CH}_2$ and $\text{Me}_3\text{CCHOHMe}$ with conc. HCl gives the two isomeric alkyl chlorides. What are these products ? Explain.
- (b) A compound $\text{C}_4\text{H}_6\text{O}_2$ shows a very strong IR band at 1721 cm^{-1} and its NMR spectrum shows only one singlet signal. Give the structure of compound with suitable explanation.
- (c) The acid-catalysed hydrolysis of ethylbenzoate has a " ρ " value of $+0.144$. What will be the effect of $-\text{I}$ groups on the rate ? Explain.

(d) Explain, why ?

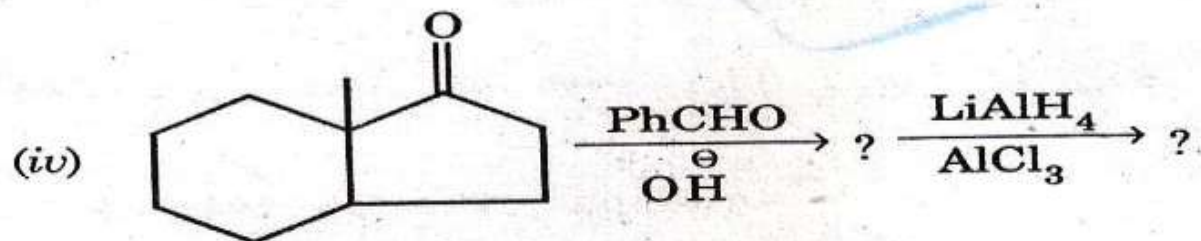
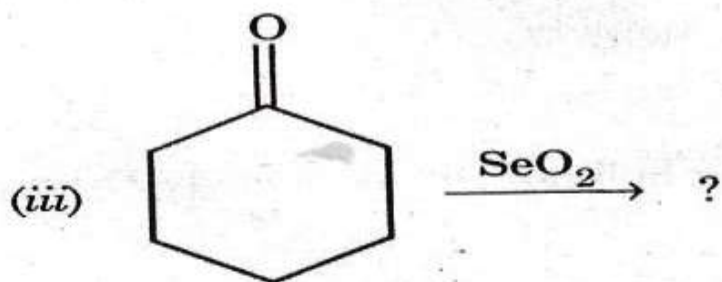
(i) Alcohols are weaker acids than phenols but are stronger nucleophiles.

(ii) The rate of reaction of Ph_2CHCl in aqueous ethanol with KF to afford benzhydryl fluoride is retarded by the addition of NaCl .

(e) Complete the following equations :



P.T.O.



5×6=30