

This question paper contains 31 printed pages]

HPAS (Main)—2012

CHEMISTRY

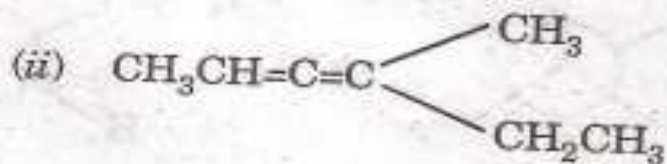
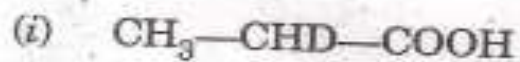
Paper II

Time : 3 Hours

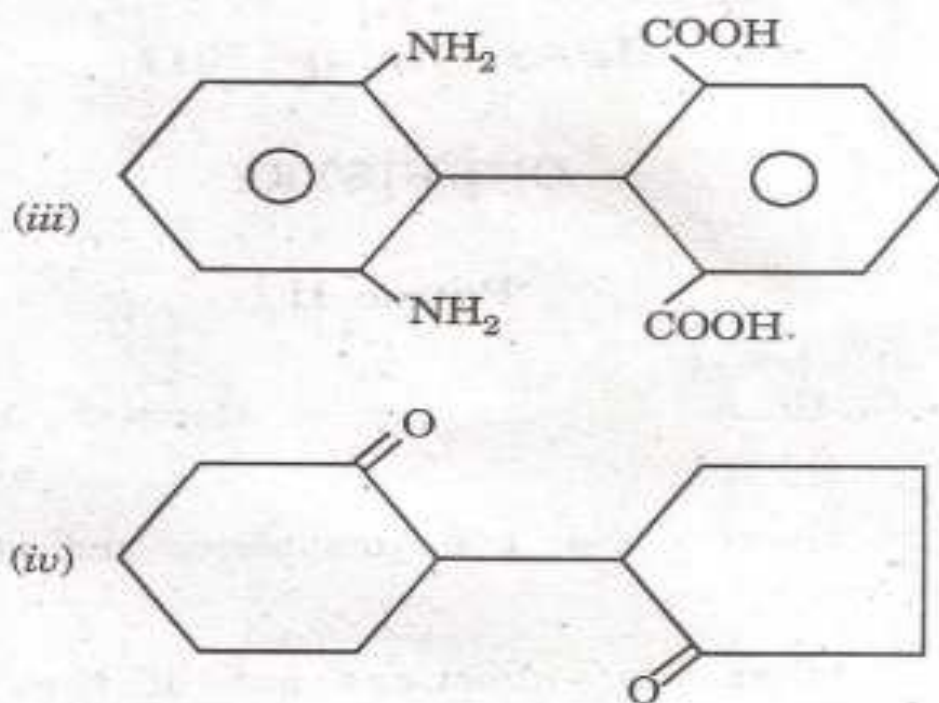
Maximum Marks : 150

Note :— Question No. 1 is compulsory and attempt any other *four* questions out of the remaining seven questions i.e. attempt *five* questions in all. *All* parts of a question must be attempted in continuation at one place.

1. (a) Which of the following is achiral ?

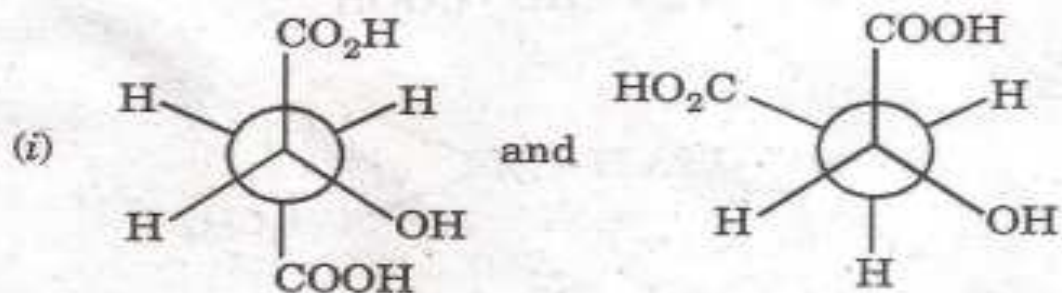


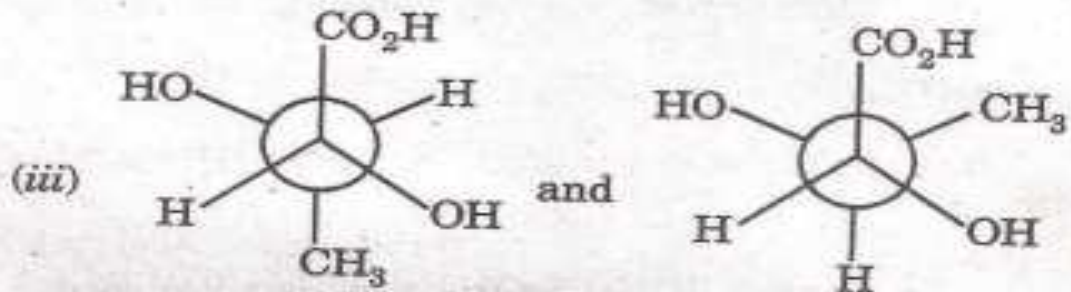
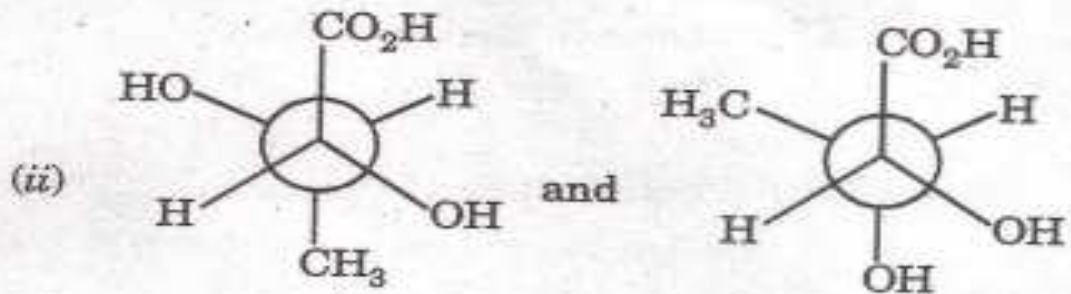
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(b) Give the Fischer projection for (R) and (S)-2-bromopentane and convert them into "Wedge and dotted line representation".

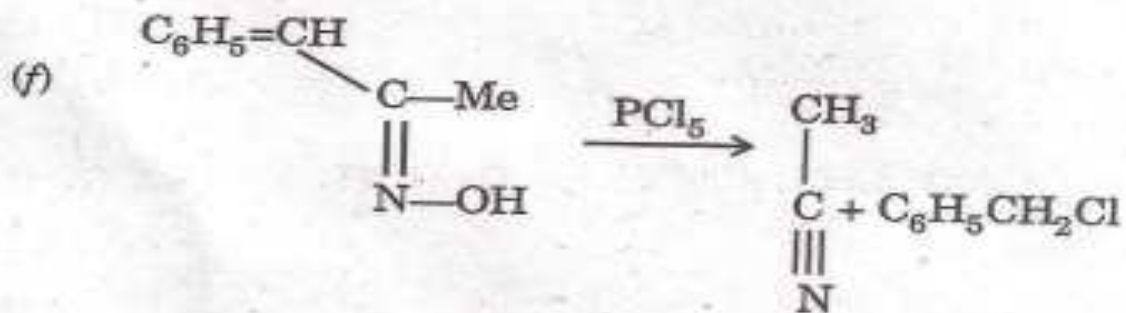
(c) Classify as enantiomeric pair or diastereomeric pair or identical pair :





(d) Define Prelog's rule citing at least two examples.

(e) What is Walden inversion ? Explain citing an example.



is an example of :

(i) Beckmann rearrangement

(ii) Thermal decomposition

(iii) Fragmentation reaction

(iv) Fries rearrangement

(g) The acid strength of HCN, HCOOH, CH<sub>3</sub>COOH and ClCH<sub>2</sub>COOH are in the order :

(i) HCN > HCOOH > CH<sub>3</sub>COOH > ClCH<sub>2</sub>COOH

(ii) HCN > HCOOH > ClCH<sub>2</sub>COOH >

CH<sub>3</sub>COOH

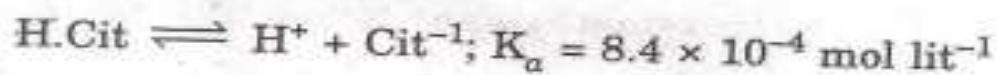
(iii) ClCH<sub>2</sub>COOH > HCOOH > CH<sub>3</sub>COOH >

HCN

(iv) HCOOH > ClCH<sub>2</sub>COOH > CH<sub>3</sub>COOH >

HCN

(h) Lemon juice normally has a pH of 2. If all the acid in the juice is citric acid and there are no citrate salts present, what will be the citric acid concentration, [H.Cit], in the lemon juice ? Assume only the first dissociation constant of the acid to be important.



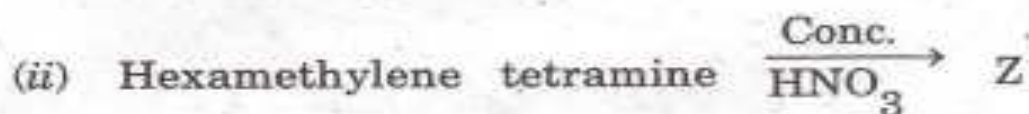
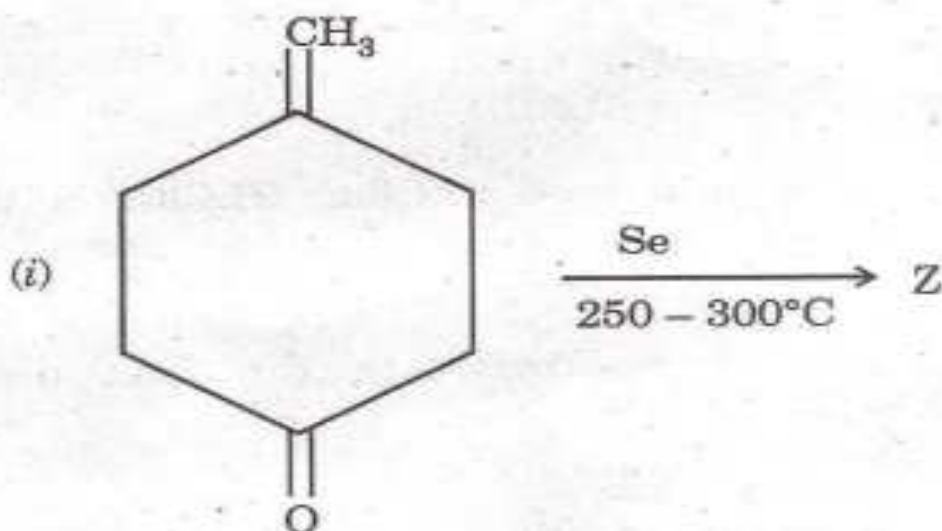
(i)  $8.4 \times 10^{-4} \text{ M}$

(ii)  $4.2 \times 10^{-4} \text{ M}$

(iii)  $16.8 \times 10^{-4} \text{ M}$

(iv)  $12 \times 10^{-1} \text{ M}$

(i) Complete the following reactions :



(j) Give structure and chemical names (IUPAC) of the following :

(i) Tamoxifen (antiestrogen)

(ii) Streptomycin (antibiotic).

10×3=30

2. (a) Explain the following terms citing examples :

(i) Hyperconjugative effect

(ii) Hydrogen bond.

(b) (i) Give a brief account of the modern methods of detecting free radicals.

(ii) Illustrate 'cross-over' experiments in reaction mechanism in organic chemistry.

(c) Justify :

(i) For the  $S_N2$  reaction,  $Cl^- + RI \xrightarrow[25^\circ C]{\text{acetone}}$

$RCl + I^-$ , the relative rates, when R = methyl

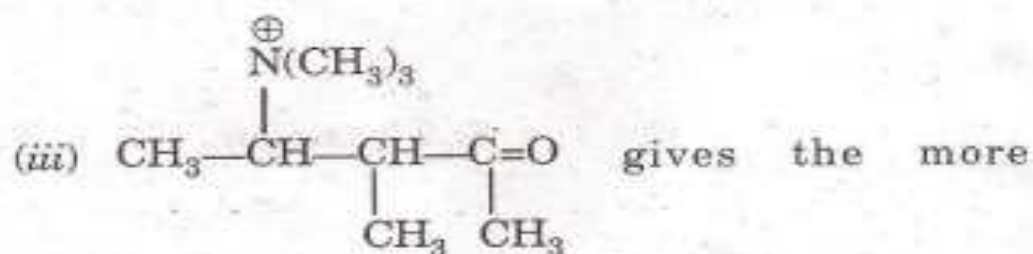
and neopentyl are roughly  $1 : 10^{-6}$ .

(ii) Compared to ethoxide ion, phenoxide ion is a better leaving group.

(d) Explain the following, citing examples in each cases :

(i) Elimination *versus* substitution

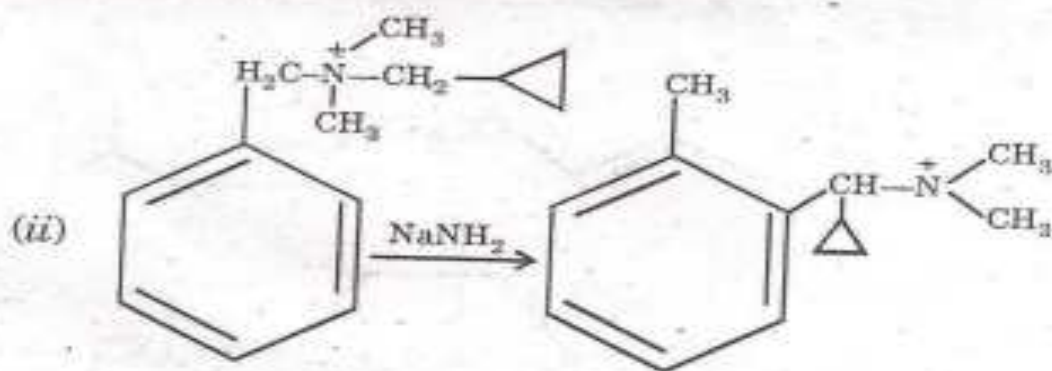
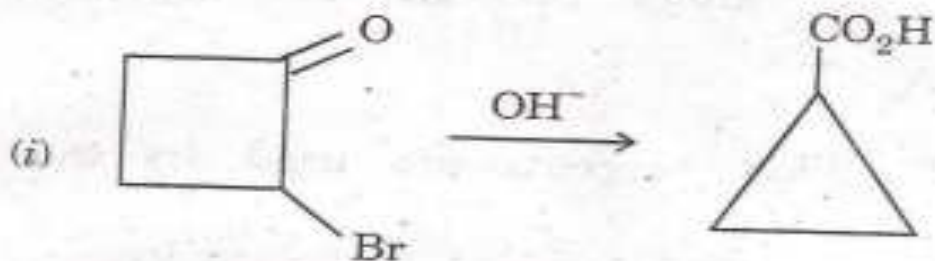
(ii) Basicity *versus* Nucleophilicity



substituted alkene on treatment with base.



- (e) Explain the mechanism involved in the following rearrangements :



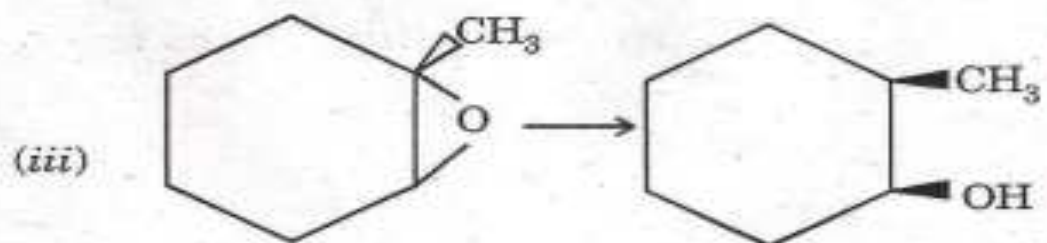
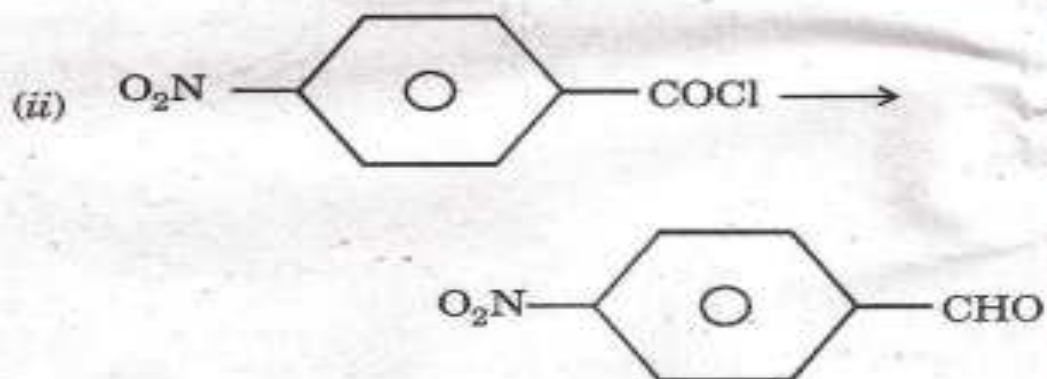
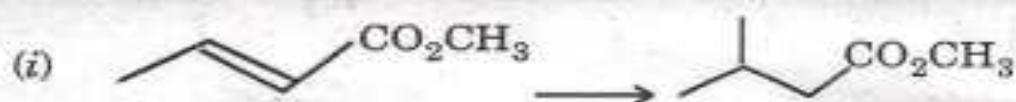
5×6=30

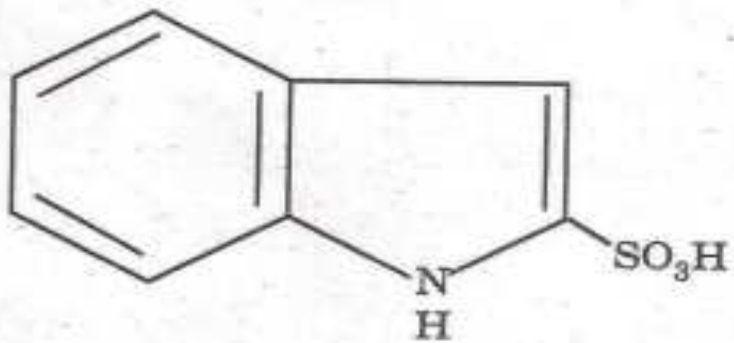
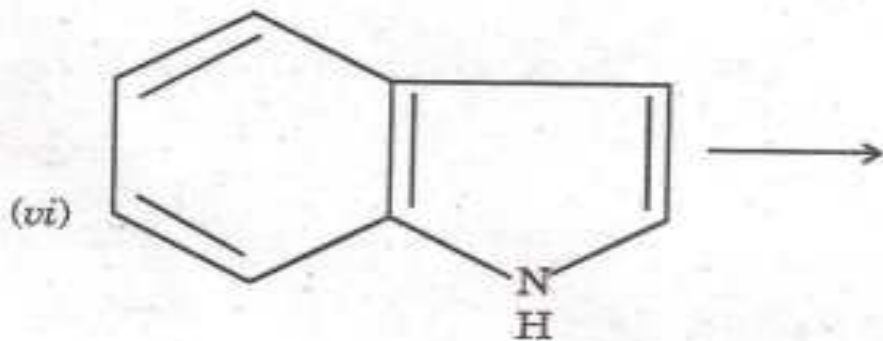
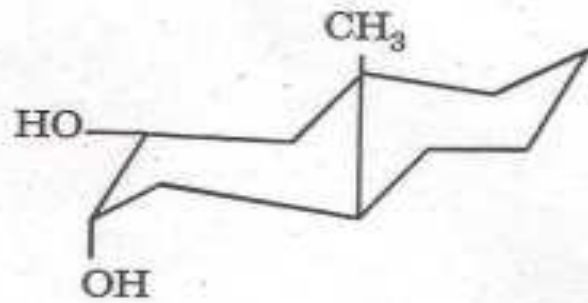
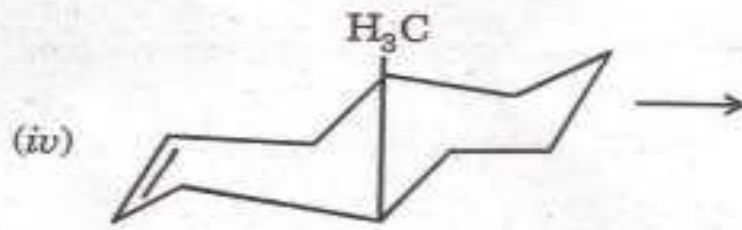
3. (a) (i) Differentiate between 'resonance' and 'hyperconjugation' with *two* examples each.

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(ii) Write and explain the mechanism of uncatalyzed nucleophilic addition to carbonyl group. Also cite an example.

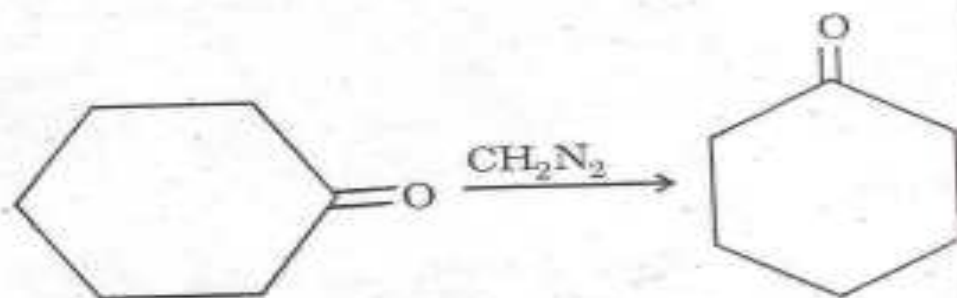
(b) What reagents are used for the following conversions ?



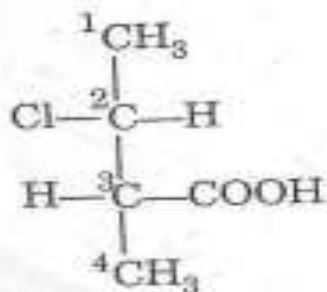


(c) (i) How many stereoisomers are possible for 1,3-dichloro-3-bromo butane ? Explain.

(ii) Explain the mechanism of the following ring expansion :



(d) (i) The stereochemical designation for 2 and 3 carbon atoms in the following structure are ....?..... Also explain :



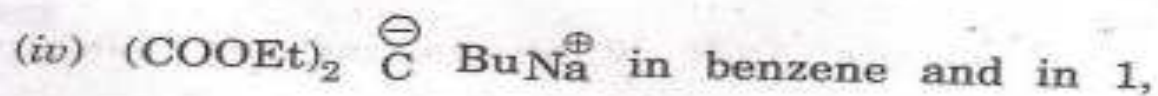
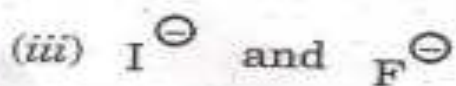
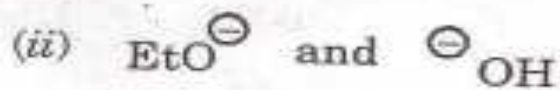
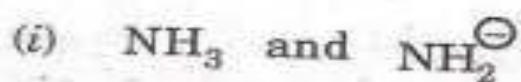
(ii) What are benzyne intermediates ? Discuss

its role in aromatic nucleophilic substitution

(S<sub>N</sub>-Ar) reactions.

(e) Which reagent in each of the following pairs

is more nucleophilic and why ?

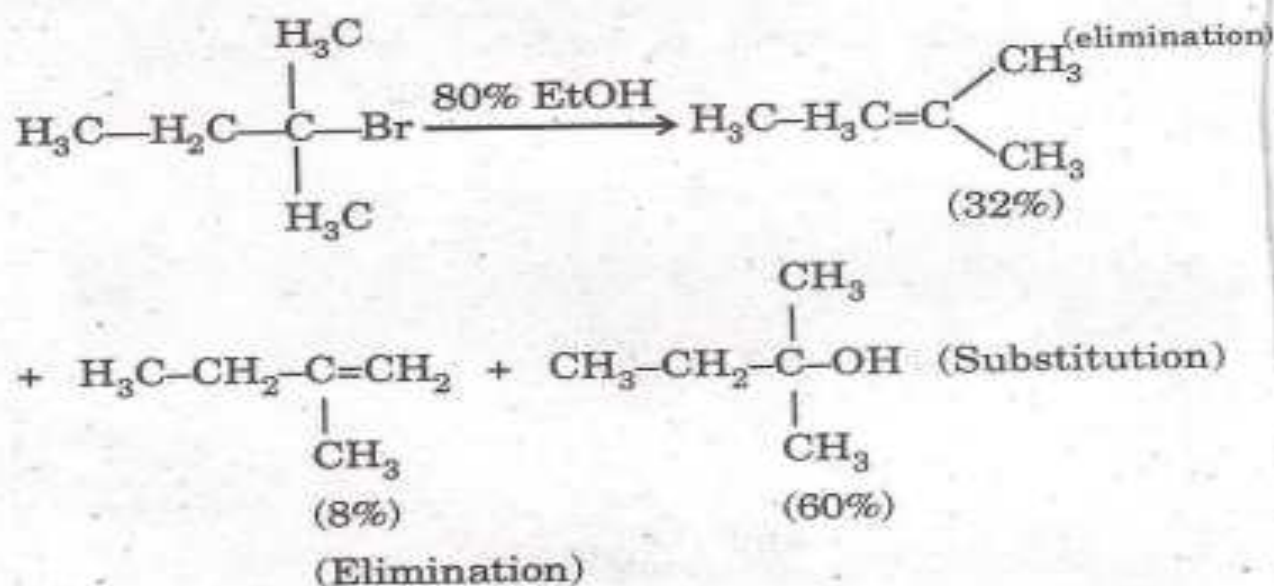


2 dimethoxyethane.

5×6=30

P.T.O.

4. (a) (i) Explain the formation of the products in the following reaction. Account for the %age yield.



- (ii) A compound with the molecular formula

$\text{C}_8\text{H}_{11}\text{N}$  shows infrared absorption near

2.9 microns ( $3448 \text{ cm}^{-1}$ ); UV absorption

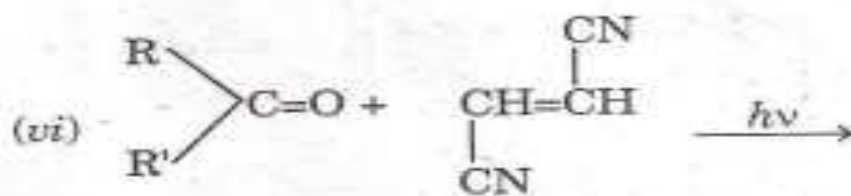
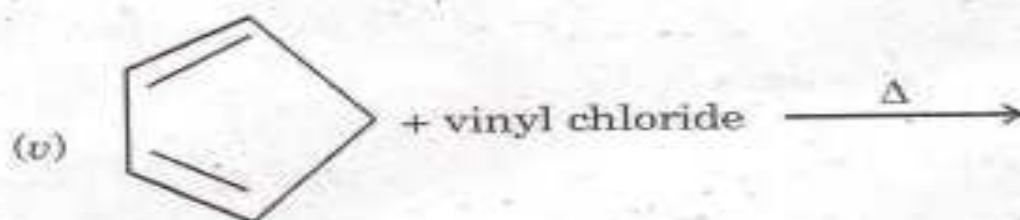
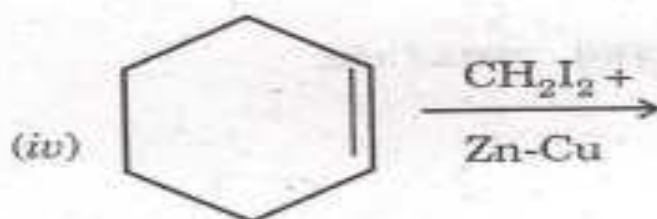
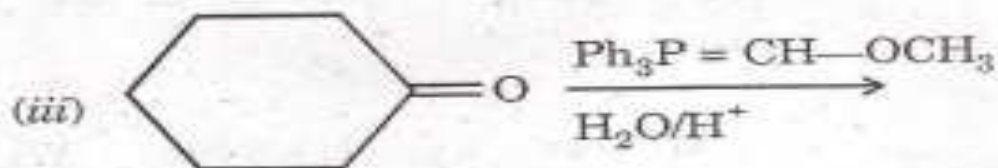
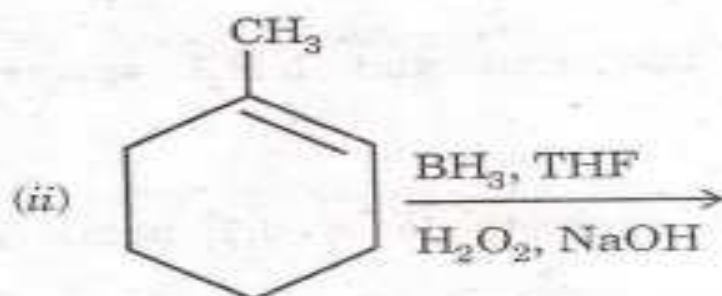
at 235 nm; and NMR spectrum with two doublets ( $\delta = 6.7$  ppm); a singlet at 3.2 ppm; a quartet at 2.5 ppm and a triplet at 1.1 ppm. Write the compound structure.

(b) Identify the product in each of the following

reactions :



P.T.O.





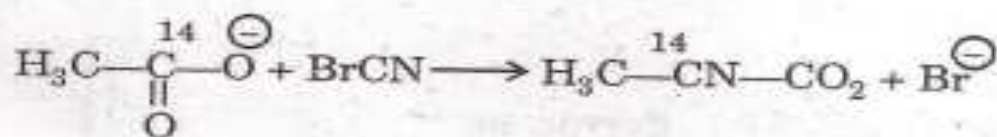
(c) (i) Write the functions of inorganic catalysts

in the preparation of stereoregular

polymers.

(ii) Explain the mechanism of the reaction in

which :



the carbon is isotopically labelled.

(d) (i) Write the classification of carbohydrates

with examples.

(ii) What are general characteristics of free radicals, cite few examples also.

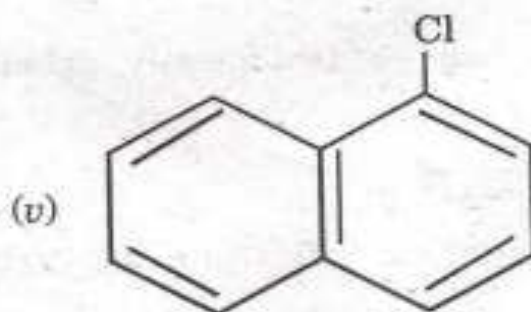
(e) Write the point group notation for the following molecules :

(i) Allene

(ii)  $\text{H}_2\text{O}_2$

(iii)  $\text{CHClBrF}$

(iv) Ferrocene

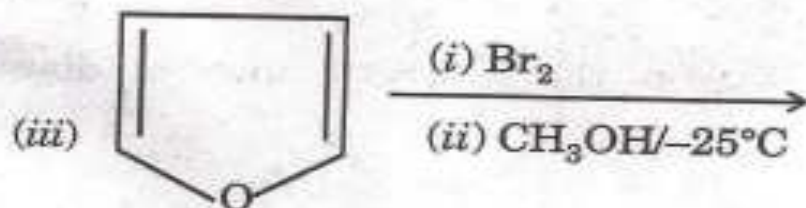
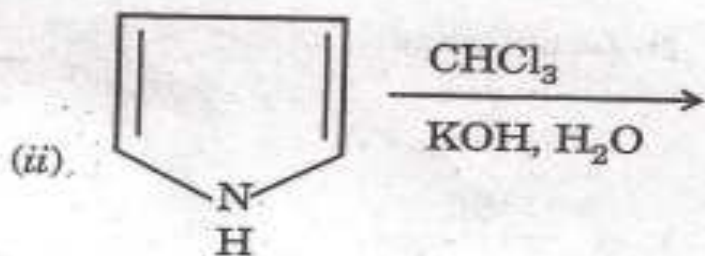
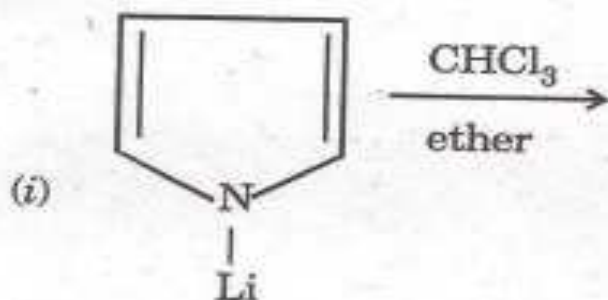


(vi)  $\text{H}_2\text{O}$ .

(5×6=30)

5. (a) Give the structures of the products, suggesting suitable reaction mechanisms for the following

reactions :



(b) What is hydroformylation ? Discuss the mechanism of hydroformylation brought out by the use of cobalt compound as catalyst.

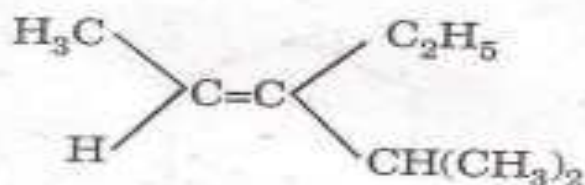
(c) Write in brief about—(citing at least two examples each)

(i) E-Z notations

(ii) R-S notations.

(d) Explain the synthetic uses of diazonium salts with examples and reactions.

(e) (i) The following geometrical isomer has 'Z' designation. Explain :

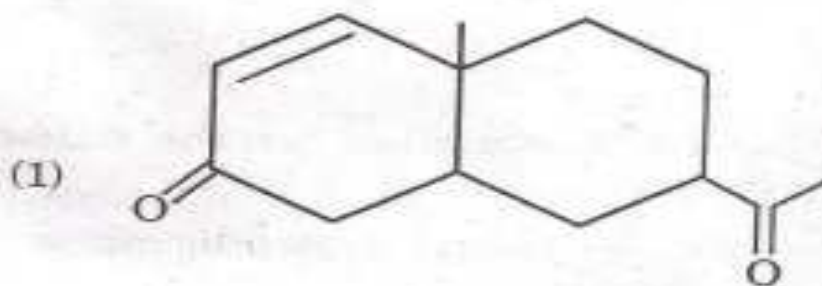


(ii) The chemical shift  $\delta = 7.08$  (5, r);  $2.46$  (2, q);

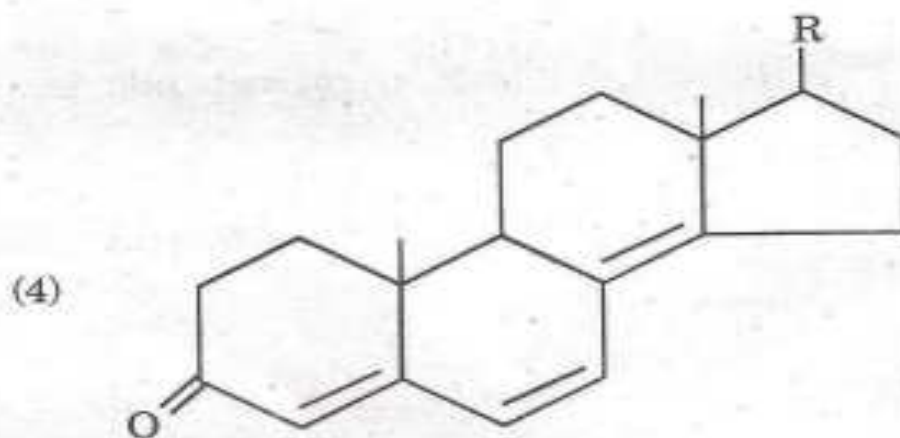
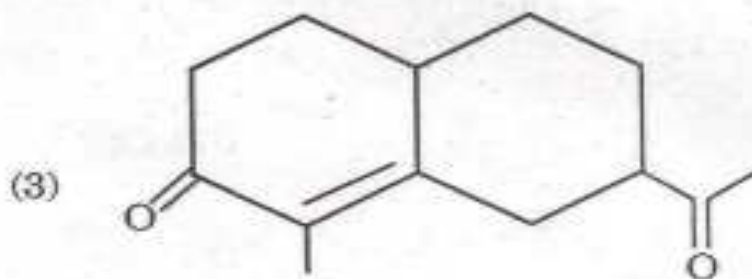
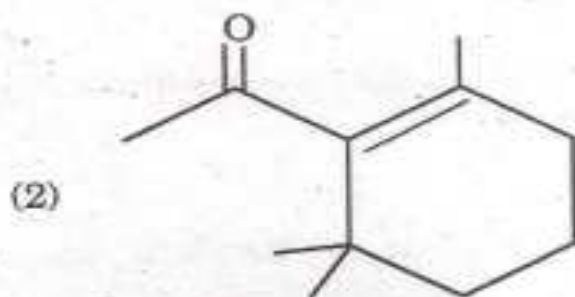
$1.08$  (3, t) corresponds to.....

(iii) Which of the following natural product will

show  $\lambda_{\max} = 254$  nm ? Explain why ?



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5×6=30

6. (a) Give explanation for the following statements :

- (i) Triphenyl cyclopropene is less acidic than triphenyl methane.

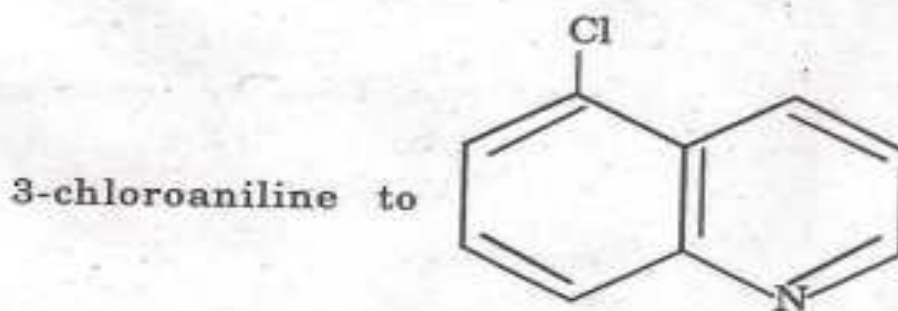
(ii) Tropilium bromide gives precipitate with



(iii)  is less acidic

than .

(b) (i) Describe the sequence of steps and mechanism involved in the conversion of



P.T.O.

by Skraup's synthesis by the use of glycerol,  $H_2SO_4$  and other reagents needed.

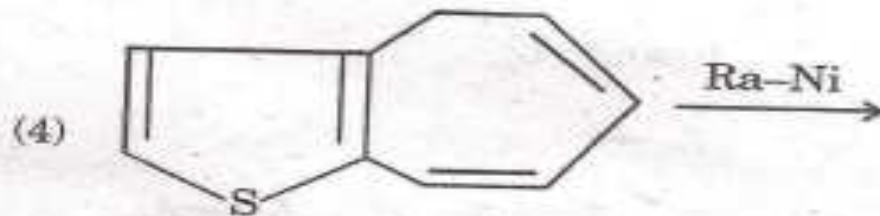
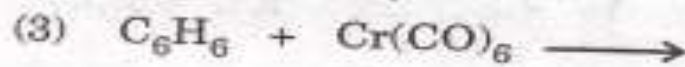
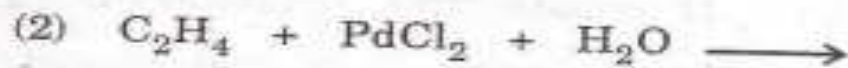
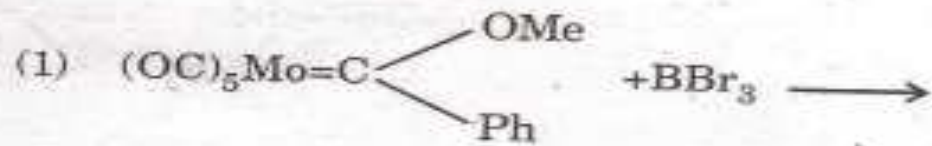
(ii) Explain the principle of mutarotation, citing examples.

(c) (i) What is Ziegler-Natta catalyst ? Explain its role in the polymerization of alkenes.

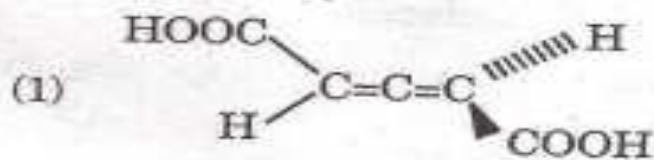
(ii) Define fluxionality in organometallic complexes. Give *two* examples of fluxional complexes.



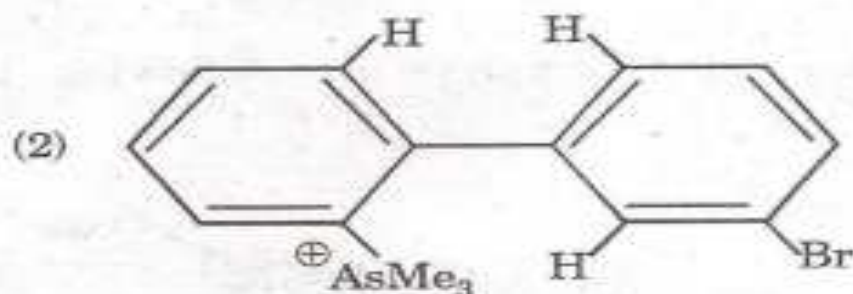
(d) (i) Complete the following equations :



(ii) Assign (R) and (S) for the following :



P.T.O.



- (e) Illustrate the principle of enantioselectivity citing the specific reaction of acetophenone with an organometallic hydride which has a chiral ligand L. 5×6=30

7. (a) (i) Explain the following statements ;

- (1) Cyclooctatetraene is a tub-shaped molecule
- (2) Dianion of cyclobutatetraene is planar.

- (ii) How is tropine prepared starting from acetone, methylamine and succindialdehyde?
- (b) How does fluxconality differ from isomerisation and tautomerisation ? Why is NMR preferred for revealing the occurrence of stereochemical non-rigidity ?
- (c) Write a short note on photochemistry of simple organic molecules with examples.
- (d) What are polyoxyphenylenes, polyphenylene oxides, and polyphenylene ethers ? Explain their synthesis mechanism also.

- (e) (i) Explain the mechanism of formation of the  
ozonides



- (ii) Comment on catalytic hydrogenation of  
alkenes. 5×6=30

8. (a) (i) Define amalgam and alloy. Citing *two*  
examples each.
- (ii) Give at least *four* examples of alloys  
having non-metals as additional elements.
- (iii) Write *four* well known alloys of iron and  
also cite at least *one* application of each.

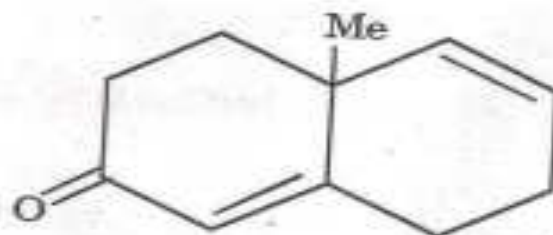
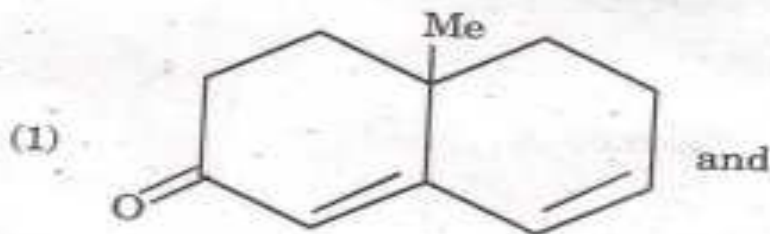
(b) Illustrate with a specific example, the synthetic application of the following reagents :

(i) DDQ

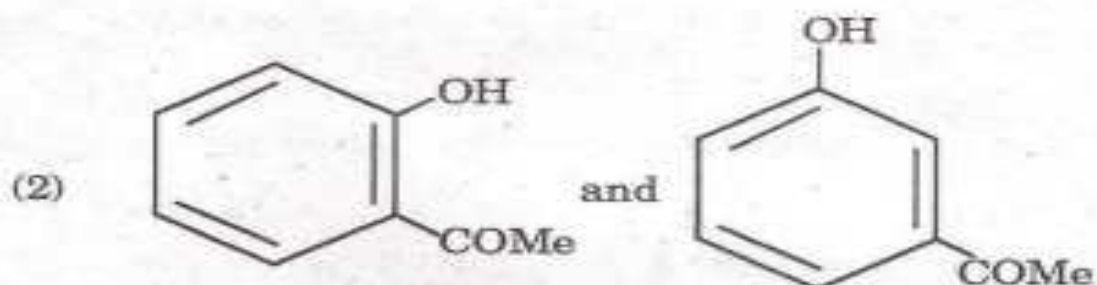
(ii) Wilkinson's catalyst

(iii) 1, 3-dithione.

(c) Indicate how the following pairs of compounds can be differentiated spectroscopically :



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(d) Bring out the important structural features of the active sites or metal centres of :

(1) deoxyhaemoglobin

(2) Vitamin  $\text{B}_{12}$  and

(3) Cytochrome C.

(e) (i) Indicate by a cycle the four steps involved in the oxidation of water to release  $\text{O}_2$  in photosystem-II.

- (ii) Name a few metalloproteins (enzymes) in which porphyrin ligands are involved. What structural features of the ligand systems are responsible for the enzyme activity ?

5×6=30