CHEMISTRY
Paper – III

Time Allowed : Three Hours

Maximum Marks : 200

Question Paper Specific Instructions

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

*There are **TEN** questions divided under **TWO** sections.*

*Candidate has to attempt **SIX** questions in all.*

*Question no. **1** in Section A and Question no. **6** in Section B are **compulsory**. Of the remaining questions in each section candidates have to answer **FOUR** questions choosing **TWO** from each section.*

The number of marks carried by a question / part is indicated against it.

All parts and sub-parts of a question are to be attempted together in the Question-cum-Answer Booklet.

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 the Question-cum-Answer Booklet must be clearly struck off.

*Answers must be written in **ENGLISH** only.*

Neat sketches are to be drawn to illustrate answers, wherever required.

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

Assume suitable data, if necessary, and indicate the same clearly.

SECTION A

Attempt any *three* questions including question no. 1 which is compulsory. ●

Q1. **Answer all of the questions given below. Give reasons for the following observation :**   *5×8=40*

- (a) Phenolphthalein indicator cannot be used in the titration of sodium carbonate with hydrochloric acid solution.   *5*

- (b) Iodimetric titrations are usually carried out in neutral solutions.   *5*

- (c) A small amount of magnesium salt is added to the EDTA solution used for the titration of calcium by using Eriochrome Black T indicator.   *5*

- (d) Source modulation is used in atomic absorption spectroscopy.   *5*

- (e) Zone broadening is inevitable in column chromatographic analysis.   *5*

- (f) ICP method is better suited for multielemental analysis than flame atomic absorption method.   *5*

- (g) Glass pH electrode tends to indicate a pH lower than the actual pH in strongly basic solutions.   *5*

- (h) Electron capture detector is a selective detector.   *5*
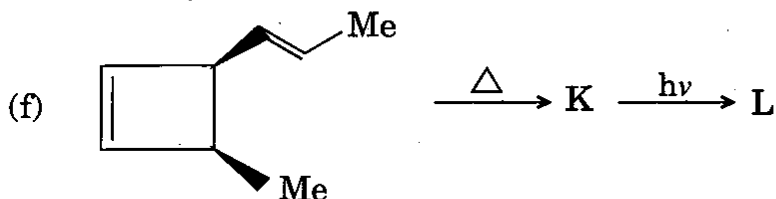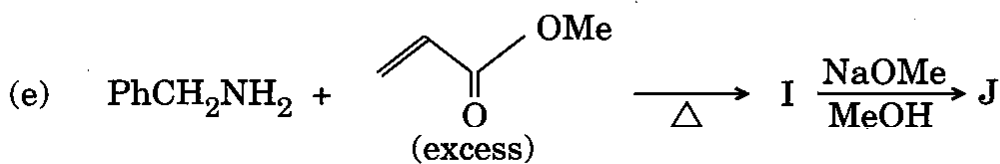
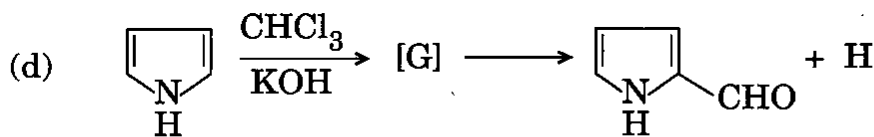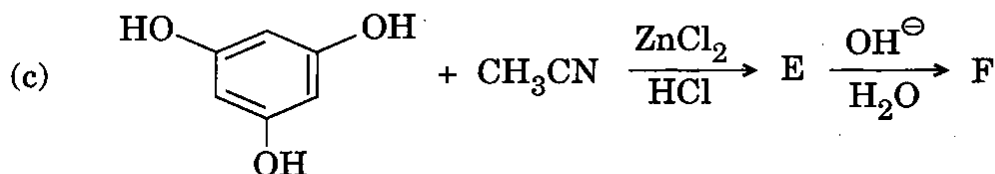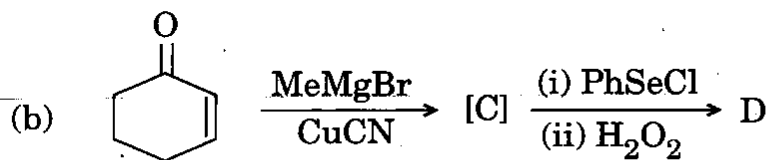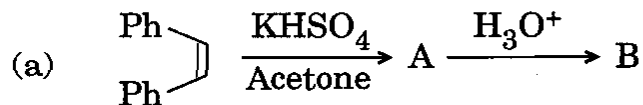**Q2.** Distinguish between the following :

- (a) Co-precipitation and Post-precipitation   *5*

- (b) Iodimetry and Iodometry   *5*

- (c) Gas liquid chromatography and High performance liquid chromatography   *5*

- (d) Proximate analysis and Ultimate analysis   *5*

- (e) Aniline point and Cloud point   *5*

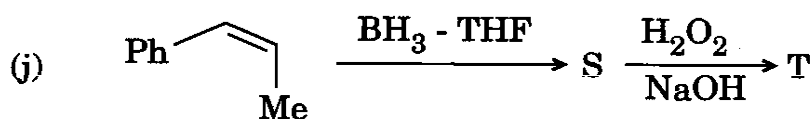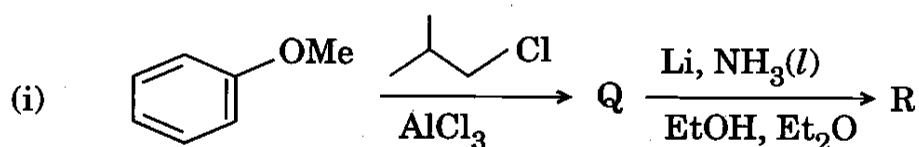- (f) Primary standard and Secondary standard in volumetric analysis   *5*
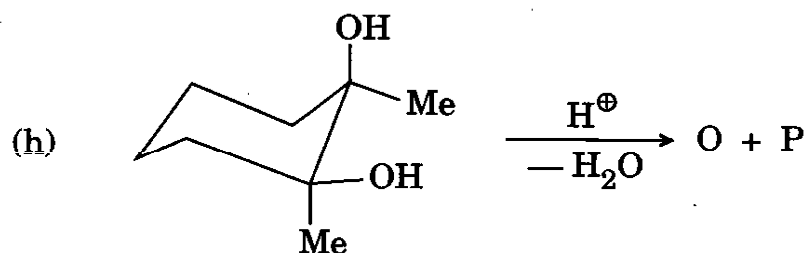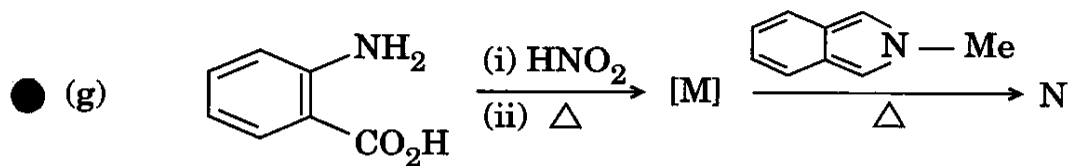
Q3. (a) A mixture of HCl and H_3PO_4 is titrated with 0·1000 M NaOH. The first end point (methyl red) occurs at 35·00 mL, and the second end point (bromothymol blue) occurs at a total of 50·00 mL. Calculate the millimoles of HCl and H_3PO_4 present in the solution. **10**

(b) What weight of pyrite ore must be taken for analysis so that the $BaSO_4$ precipitate weight obtained will be equal to one-half that of the percent S in the sample ? **10**

(c) (i) Explain why a wash liquid is an electrolyte in gravimetric analysis. **5**

(ii) Calculate the solubility of silver chloride in 0·1 M $NaNO_3$. **5**

Given : $K^0_{sp} = 1·0 \times 10^{-10}$

$f_{Ag^+} = 0·75$ and $f_{Cl^-} = 0·76$

Q4. (a) Explain the principles of chelation titration indicators. **10**

(b) Calculate the height equivalent to a theoretical plate, in cm, of a gas chromatographic column of 3 ft length in a chromatographic analysis. **10**

Given $t_R = 52·3$ mm and $W_B = 9·0$ mm

(c) (i) Calculate the absorbance of a $3·49 \times 10^{-5}$ M solution of Fe $(SCN)^{2+}$ complex with maximum absorption at 580 nm. **5**
Given : Molar absorptivity of the complex is
$$7·00 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$$

(ii) A sample in a 1·0 cm cell is determined with a spectrometer to transmit 80% light at a certain wavelength. If the absorptivity of this substance at this wavelength is 2·0, what is the concentration of the substance ? **5**

Q5. (a) Describe the role of indicator electrode in potentiometry. **10**

(b) An ore was analyzed for manganese content by converting the manganese to Mn_3O_4 and weighed. If a 1·52 g sample yields Mn_3O_4 weighing 0·126 g, what is the percent Mn_2O_3 in the sample ? **10**

(c) 0·40 g of an alloy was analyzed for nickel by gravimetric method using dimethyl glyoxime reagent. The weight of the nickel as glyoximate after washing and drying comes to a constant weight of 0·285 g. Calculate the percentage of nickel in the alloy. (M.Wt. of nickel dimethyl glyoximate = 290·93) **10**

SECTION B

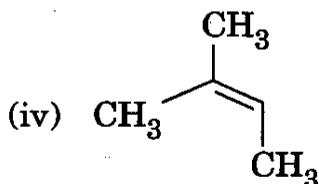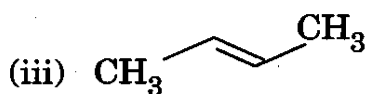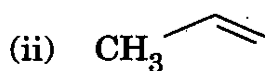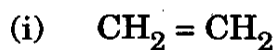**Attempt any *three* questions including question no. 6 which is compulsory.**

Q6. Identify compound/intermediate 'A' to 'T' with appropriate stereochemistry (if any) in the following transformations : 4×10=40

(a) $\xrightarrow[\text{Acetone}]{\text{KHSO}_4}$ A $\xrightarrow{\text{H}_3\text{O}^+}$ B

(b) $\xrightarrow[\text{CuCN}]{\text{MeMgBr}}$ [C] $\xrightarrow[\text{(ii) H}_2\text{O}_2]{\text{(i) PhSeCl}}$ D

(c) + CH_3CN $\xrightarrow[\text{HCl}]{\text{ZnCl}_2}$ E $\xrightarrow[\text{H}_2\text{O}]{\text{OH}^\ominus}$ F

(d) $\xrightarrow[\text{KOH}]{\text{CHCl}_3}$ [G] $\longrightarrow$ + H

(e) $PhCH_2NH_2$ + (excess) $\xrightarrow{\triangle}$ I $\xrightarrow[\text{MeOH}]{\text{NaOMe}}$ J

(f) $\xrightarrow{\triangle}$ K $\xrightarrow{h\nu}$ L

(g)

$$\underset{CO_2H}{\overset{NH_2}{\text{(anthranilic acid)}}} \xrightarrow[\text{(ii) } \triangle]{\text{(i) HNO}_2} \text{[M]} \xrightarrow[\triangle]{\text{N—Me}} \text{N}$$

(h)

$$\xrightarrow[-H_2O]{H^{\oplus}} O + P$$

(i)

$$\xrightarrow[\text{AlCl}_3]{} Q \xrightarrow[\text{EtOH, Et}_2\text{O}]{\text{Li, NH}_3(l)} R$$

(j)

$$\text{Ph} \diagup \underset{Me}{} \xrightarrow[]{\text{BH}_3\text{ - THF}} S \xrightarrow[\text{NaOH}]{\text{H}_2\text{O}_2} T$$

Q7. **(a)** Identify the most reactive alkene of the following when reacted with meta-chloroperbenzoic acid. Justify your answer. *5*

(i) $CH_2 = CH_2$
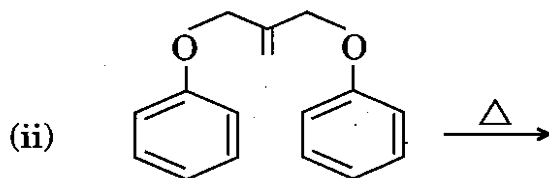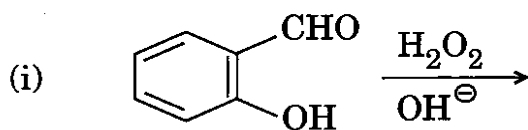
(ii) $CH_3 \diagup\!\!\!\!\diagdown$

(iii) $CH_3 \diagup\!\!\diagdown\!\!\diagup CH_3$

(iv) $\underset{CH_3}{\overset{CH_3}{CH_3}}\diagdown\!\!\diagup\!\!\diagdown CH_3$

(b) Arrange the following amines in decreasing order of their basicity. Rationalize your answer. 5
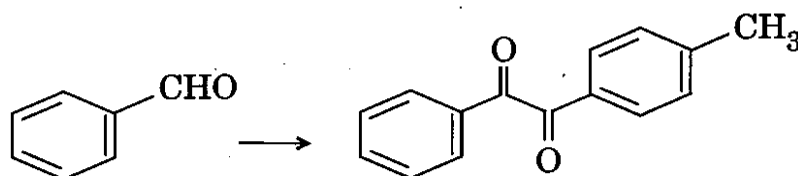
(i)

(ii)

(iii)

(iv)
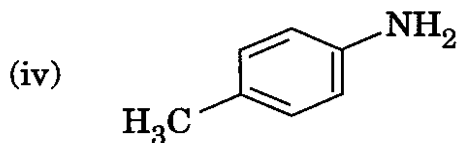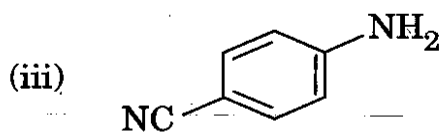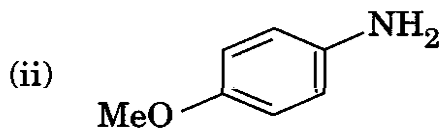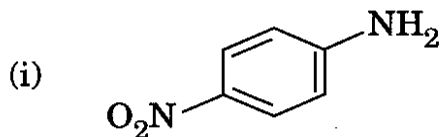
(c) Identify the product of the following transformations. Give the possible mechanism. $5 \times 2 = 10$
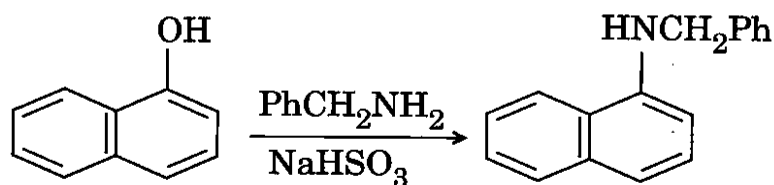
(i)

(ii)

(d) Give a synthetic sequence for the following transformation with appropriate reagents and conditions. 5
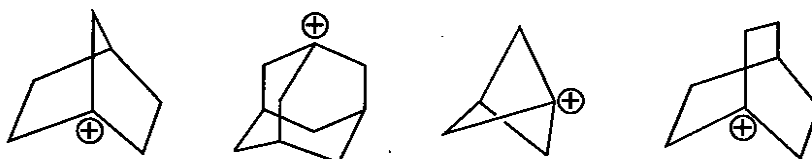
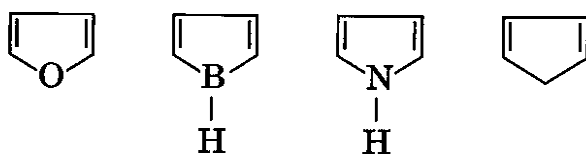(e) Suggest a suitable mechanism for the following transformation. 5

Q8. (a) Arrange the following carbocations in order of increasing stability. Justify your answer. 5
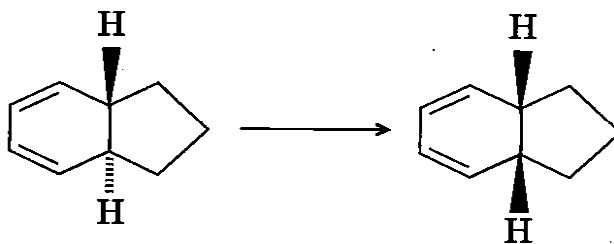

(b) Identify an anti-aromatic compound from the following. Rationalise your answer. 5

(c) Illustrate the following transformation with appropriate reagents and conditions. 5

(d) Arrange the following carbonyl compounds in order of increasing pKa. Rationalize the assigned order. 5

$(CH_3CO)_2CH_2$, CH_3CHO, CH_3COCH_3, $(CH_3CO)_3CH$

(e) The unknown compound 'A' with molecular formula $C_{10}H_{16}O$ adds 2 moles of bromine to give a tetrabromo derivative. It also forms hydrazone, reduces Fehling's solution and absorbs at 200 nm in UV. Compound 'A' undergoes retro-aldol reaction with boiling aqueous K_2CO_3 solution to give acetaldehyde and compound 'B'. The compound 'B' gives positive haloform test and yields acetone and 4-oxopentanoic acid on oxidative ozonolysis. Identify A and B and rationalize your answer.
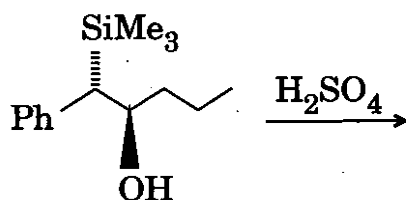
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Q9. (a) Write the structure of the product formed when chlorotriphenylmethane is reacted with metallic silver. Justify your answer.
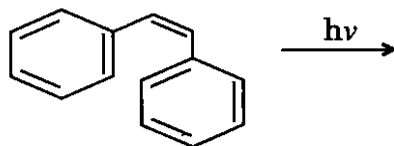
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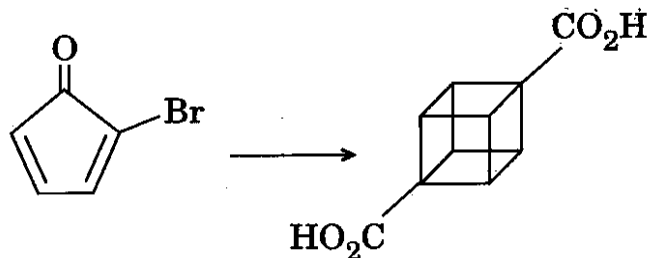(b) Identify the product and comment on the stereochemical outcome of the reaction.

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(c) Identify the product of the following transformation. Use Woodward – Hoffmann rule to explain the outcome of the reaction.
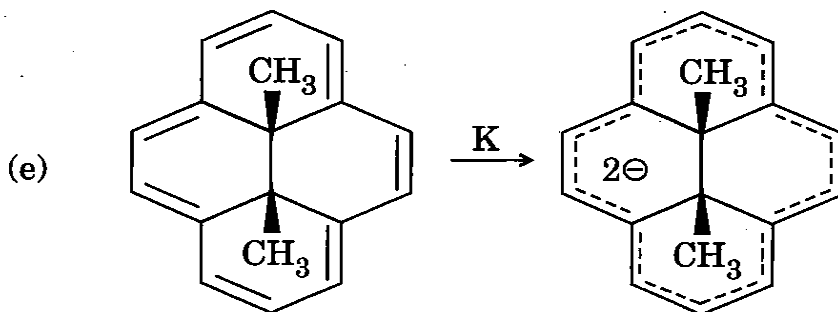
5

(d) Give a synthetic sequence for the following transformation with appropriate reagents and conditions.

5

YLO-T-CHEM   8

(e)

(i) Identify the reactant and the product as aromatic, anti-aromatic and non-aromatic.

(ii) Assign the reason for appearance of methyl proton of reactant and product at − 4·25 ppm and 21 ppm, respectively.   *10*

Q10. (a) O − H stretching frequency of BHT (2,6-di(tert-butyl)-4-methyl phenol) is observed at 3600 cm^{-1} as a sharp band, while in paracetamol (p-hydroxy phenylacetamide), it appears as a broad band between 3300 − 3000 cm^{-1}. Why ?   *5*
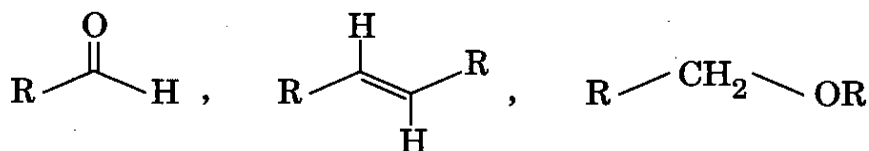
(b) The unknown compound having molecular formula C_4H_8O has absorption band at 1070 cm^{-1} in IR spectrum. In its ^1H NMR spectrum, two multiples are observed with 1 : 1 ratio. Identify the compound and explain your answer.   *5*
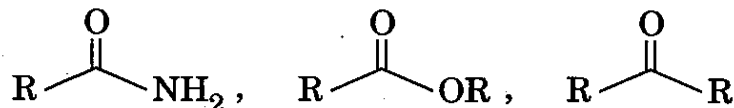
(c) Identify the following as per given direction :   *2 × 5 = 10*

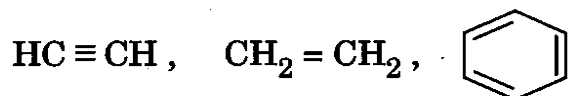(i) The most down-field proton in ^1H NMR is in

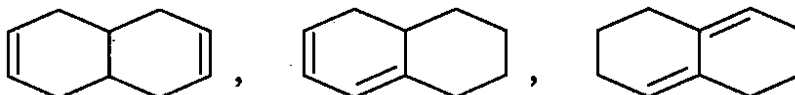(ii) The highest carbonyl stretching frequency is observed in

(iii) The compound exhibiting odd molecular ion peak in mass spectrum is

BHT, DDQ, DMF

(iv) The most up-field carbon in ^{13}C NMR is in

$$HC \equiv CH, \quad CH_2 = CH_2,$$

(v) The highest λ_{max} in UV is observed in

(d) Identify the organic compound which showed the following spectroscopic data :   **10**

UV : λ_{max} 262 nm

IR :   Significant absorption bands at 3340, 3000, 1040 cm^{-1}

^1H NMR : δ 1·9 (1H, S : exchangeable with D_2O)

        2·9 (2H, t), 3·8 (2H, t), 7·2 – 7·4 (4H, m)

^{13}C NMR : δ 39, 62, 126, 128, 129, 139

Mass :   m/z 122, 92, 91