

CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

- Note : 1) Attempt question one and fourteen other questions.
2) Log table is enclosed.

1. Attempt any three of the following :

A) Assign structure to the molecule having given data : 6

Mol-formula $C_9H_{10}O$

IR : No bands above 3100 and no band in 2000-1650 cm^{-1} region.

PMR : δ 1.15 (3H, t, J = 7.5 Hz), 3.5 (2H, q, J = 7.5 Hz) 4.4 (2H, s), 7.2 (5H, s)

Mass : m/z 91 (base peak)

B) Deduce the structure of the molecule having mol. formula $C_{10}H_{11}O_2Cl$ 6

UV : λ max 245, (ϵ , 18,000)

IR : 3000-2920, 1745, 1600 1580, 820 cm^{-1} .

PMR : δ 2.0 (3H, s), 2.8 (2H, t, J = 6 Hz)
4.1 (2H, t, J = 6 Hz), 7.1 (2H, d, J = 8 Hz),
7.3 (2H, d, J = 8 Hz)

C) The Mossbauer spectrum of $Na_2Fe(CN)_6$ consists of a singlet, while that of $Na_2Fe(CN)_5NO$ shows a quadrupole doublet. Explain the above behaviour. 6

D) The EPR spectrum of the methyl radical shows four lines. Explain this behaviour. 6

E) Draw rotational energy level diagram for a heteronuclear diatomic molecule behaving as non-rigid rotator. Draw the resulting microwave spectrum showing intensities and separations qualitatively. 6

F) Explain the concept of group frequencies of the vibrations of a molecule. State the factors causing shift in group frequencies. 6

2. A) Draw qualitative MO energy diagrams for C_2 , N_2 and O_2 molecules. 6

B) On the basis of above, how will you account for the following force constants (values in Nm^{-1}) ?
 C_2 (930); N_2 (2260); O_2 (1140). 7

3. Treat the problem of an oscillator described by the potential 13
 $V(x) = \frac{1}{2}kx^2 + \beta x^3 + \gamma x^4$ by first-order perturbation theory. Obtain the energy expression. Use the unperturbed wavefunction.

$$\psi_0(x) = (\alpha/\pi)^{1/4} \exp(-\alpha x^2/2)$$

Where $\alpha = (\mu k)^{1/2} / h$.

[Hint : Use $\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$ along with integration by parts]

4. Denoting the three spin orbitals of the Li atoms as $1s\alpha$, $1s\beta$, and $2s\alpha$, write down the corresponding Slater determinantal wave function. Normalize the wave function. 13
5. The equilibrium bond length (R_e) and dipole moment (μ) for HBr molecule are 141 pm and 2.6×10^{-30} Cm respectively. Determine the values of charges on H and Br. Repeat the exercise for HCl molecule with $R_e = 127$ pm and $\mu = 3.4 \times 10^{-30}$ Cm. Comment upon the relative values of charges in HCl and HBr. 13

[Given : $e = 1.6 \times 10^{-19}$ C]

6. A) For an ideal gas, if $\left(\frac{\partial E}{\partial V}\right)_T = 0$ 6

show that $\left(\frac{\partial E}{\partial P}\right)_T$ is also zero

- B) Show that, in general 7

$$C_p - C_v = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

7. A) Using the relation $S = k \ln W$, show that the change in entropy for isothermal expansion of one mole of an ideal gas from volume V_1 to V_2 is given by. 8

$$\Delta S = R \ln (V_2/V_1)$$

- B) Calculate the vibrational partition function for NO at 25°C and 1 atm. pressure. 5
 (Given : Vibrational frequency of $\text{NO}^- : \bar{\omega} = 1907 \text{ cm}^{-1}$)

8. A) The infrared absorption spectrum of gaseous NO exhibit the fundamental and the first overtone transitions centered around 1876.06 and 3724.20 cm^{-1} respectively. Estimate the vibrational frequency and anharmonicity of NO. 7

- B) The frequencies of the $J = 0 \rightarrow J = 1$ rotational transitions in the microwave absorption spectra of $^{12}\text{C} - ^{16}\text{O}$ and $^{13}\text{C} - ^{16}\text{O}$ molecules are observed to be 3.84235 and 3.67337 cm^{-1} respectively. Assuming atomic weights of $^{12}\text{C} = 12.00$ and $^{16}\text{O} = 16.00$, estimate the atomic weight of ^{13}C . 6
9. A) Write down the Gibbs-Helmholtz equation. Use this equation to obtain the van-Hoff's equation for the temperature dependence of the equilibrium constant K_p . What useful information is obtained by plotting $\ln K_p$ vs $\frac{1}{T}$? 8
- B) The equilibrium constant for the reaction

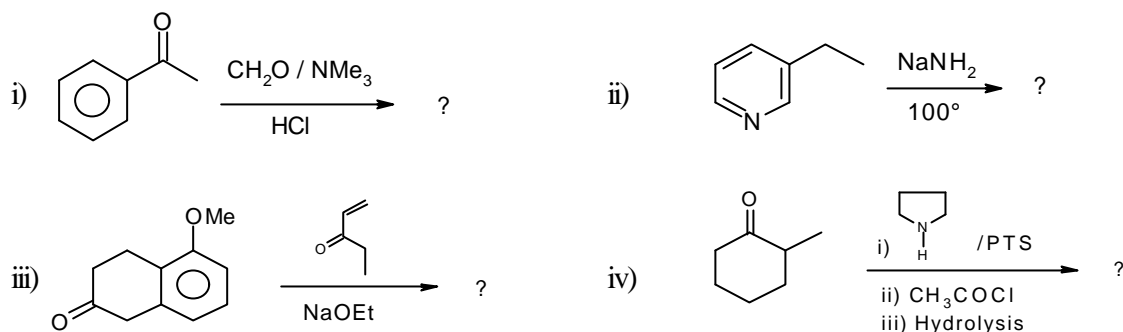
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
at 298 K is 16.35 . What would be the equilibrium constant at 273 K if heat of the reaction in this temperature range is $-25.4 \text{ kJ mol}^{-1}$? 5
10. A) Write down the relation between cell potential and free energy change for the cell chemical reaction. How is it possible to evaluate the enthalpy and entropy of the cell reactions.? 8
- B) What is the information gained by employing the techniques of Auger spectroscopy and ESCA regarding the nature of adsorbed molecules on to the solid surface. 5
11. A) Draw the phase diagrams for 9
i) $\text{KI} + \text{Water}$ – a cooling mixture forming an eutectic at -23°C and $52\% \text{ KI}$.
ii) $\text{Zinc} + \text{Magnesium}$ which shows a compound formation : $\text{Mg}(\text{Zn})_2$
Define clearly the various regions / sections of the phase diagrams.
- B) State how many phases are present in the following systems : 4
i) $\text{Ice} \rightleftharpoons \text{Water} \rightleftharpoons \text{Water vapour}$
ii) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{g})$
12. A) A reaction is second order in one of the reactants with a rate constant $k_r = 0.5 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$. Calculate the half life period ($t_{1/2}$) when the initial concentration is : 7
i) 0.2 mol dm^{-3}
and ii) 0.1 mol dm^{-3}
- B) Explain the terms : 6
i) Micelles
ii) Number average molar mass \overline{M}_n
iii) Mass-average molar mass \overline{M}_m

13. A) Explain the double-sphere model for the reaction between ions in solution. 7
- B) Write the differentiate rate equations for the following reactions : 6
- i) $2A + B \rightarrow$
- ii) $A + 2B + 2C \rightarrow$
- iii) $3A + B \rightarrow 2C + D + 2E$
14. A) Iron metal is heated in oxygen atmosphere so that FeO, Fe₂O₃ and Fe₃O₄ phases are formed. Draw a schematic diagram to show the positions of the various phases formed at the metal-oxygen interface. 7
- B) State the limitations of the free electron theory of metals. 6
15. A) KCl is doped with CdCl₂. Draw a schematic curve of log σ vs 1/T. (σ = electrical conductivity). Comment on the trends shown by the curve. 6
- B) Explain the types of point defects present in nickel oxide and zinc oxide. 7
16. A) Draw a block diagram of a flame spectrometer and label various components of the instrument. 7
- B) Distinguish between any two of the following : 6
- i) Voltametry and Polarography
- ii) Limiting current and residual current
- iii) Linear-scan polarography and pulse polarography
17. A) Sketch a cell having a silver indicator electrode as the cathode and a saturated calomel electrode as an anode, that could be used for determination of S²⁻. 7
- B) Define any three of the following : 6
- i) Coulometric titration
- ii) Working electrode
- iii) Concentration polarisation
- iv) Faraday
- v) Controlled-cathode potential eletrolysis
18. A) Why turbidimetry is compared with colorimetry, while nephelometry is compared with fluorimetry ? 6
- B) Calcium oxalate dihydrate was heated from room temperature to 900°C. Draw a schematic DTA curve and label various steps involved in it. 7

19. A) Give IUPAC nomenclature for the following : 8
- $[\text{CoSO}_4(\text{NH}_3)_4]\text{NO}_3$
 - $[\text{Zn}(\text{NCS})_4]^{2+}$
 - $[\text{Cr}(\text{en})_3]\text{Cl}_3$
 - $\text{Fe}(\text{C}_5\text{H}_5)_2$
- B) Account for any one of the following : 5
- $\text{Ni}(\text{CO})_4$ is tetrahedral
 - $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar.
20. A) Draw the crystal structures of NaCl and CsCl. What is the coordination number of the metal ion in each case ? Explain why these two salts adopt different structures ? 7
- B) i) What are the main ores of lead ? 6
 ii) What is red lead ? Mention its use.
21. A) Suggest reasons why PF_5 exists while NF_5 does not 5
- B) What are phosphazenes ? How are they prepared ? Write their structures ? 8
22. A) How is $\text{Na}_2\text{S}_2\text{O}_3$ prepared ? Explain its use in photography and in volumetric analysis ? 9
- B) Write balanced chemical equations for the reaction of H_2O_2 with an 4
- acidified solution of KMnO_4
 - acidic solution of potassiumhexa-cyanoferrate (II)
23. A) Explain the absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ 7
- B) Explain diamagnetic nature of $[\text{Co}(\text{en})_3]^{3+}$ and paramagnetic nature of $[\text{CoF}_6]^{3-}$. 6
24. A) Give the structure of haemoglobin (Schematic presentation). 6
- B) The half life of ${}_{83}\text{Bi}^{210}$ is 5 days. What fraction of the radioactive bismuth will be left after 30 days ? 7
25. A) Draw molecular orbital diagram of $[\text{Co}(\text{NH}_3)_6]^{3+}$. 6
- B) Explain Jahn-Teller effect in Mn^{3+} ion. 7

26. Predict the product and name the reaction involved.

13



27. A) Explain in brief the following observations.

6

- Sigma ortho constants of general applicability are not available
- The ρ value for ionization of benzoic acids is higher in ethanol ($\rho = 2.27$) than in water ($\rho = 1$)
- The sign of ρ value for basic hydrolysis of benzamides is +ve but in case of hydrolysis it is -ve.

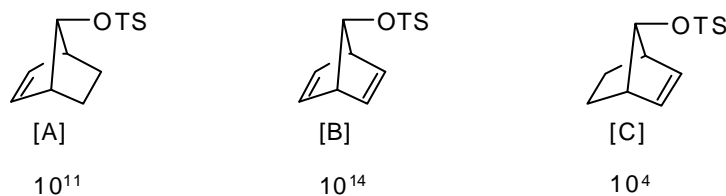
B) Match the Hammett sigma values with appropriate substituent.

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Groups	σ values
H	-0.27
m-OMe	0
m-NO ₂	0.11
p-OMe	0.71

C) Explain the difference in the reactivity towards acetolysis of A, B and C.

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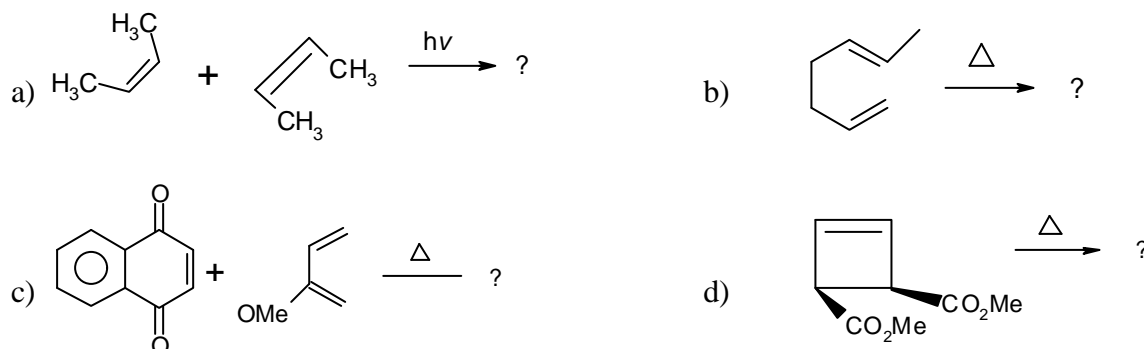


28. Predict the product and its stereochemistry (if any) for the following reactions. Indicate for each reaction.

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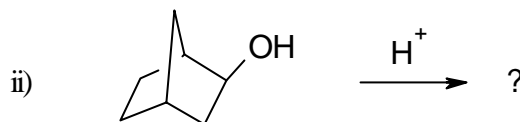
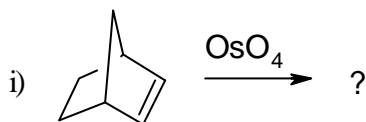
i) type of pericyclic reaction

ii) necessary selection rule



29. A) Predict and explain the formation of product in the following reactions.

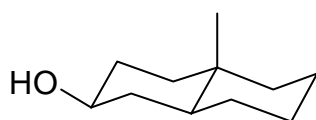
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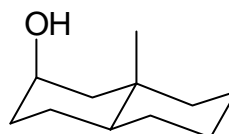
B) Arrange the following alcohols in decreasing order of reactivity towards chromic acid oxidation.

Explain the order.

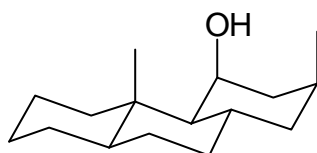
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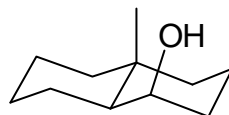
(1)



(2)



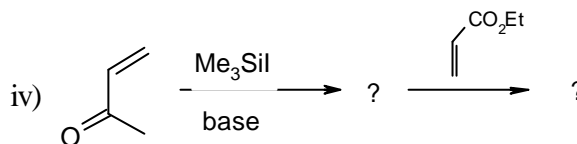
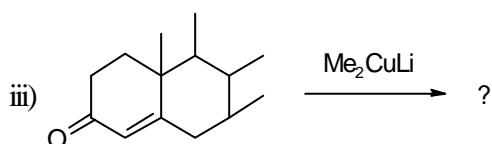
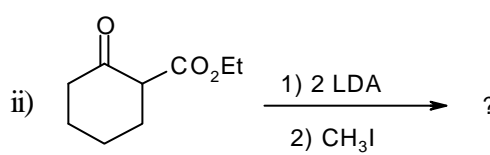
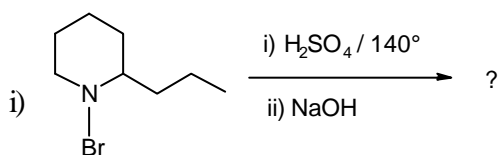
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(4)

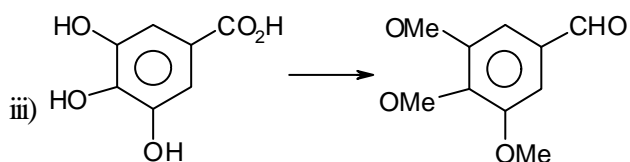
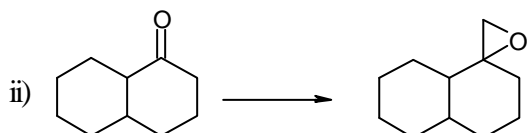
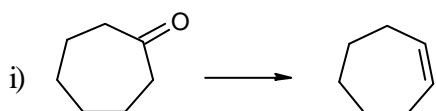
30. Predict and explain the formation of product in the following reactions.

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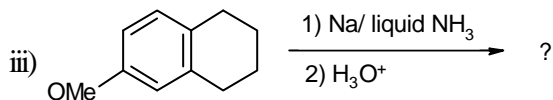
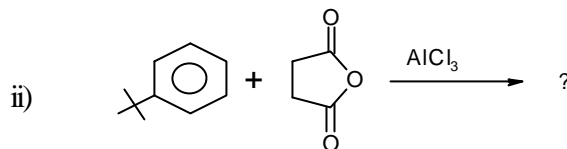
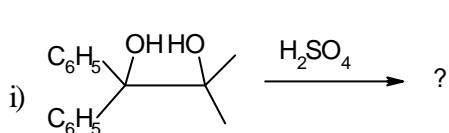
31. A) Indicate the reagents for the following conversions which may involve more than one step.

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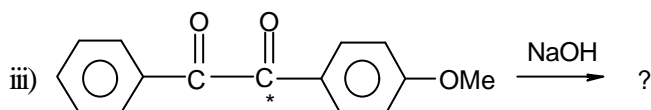
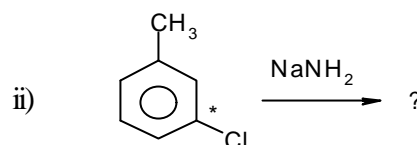
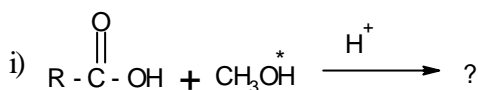
B) Predict the product in the following reactions.

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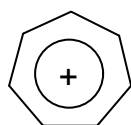
32. A) Trace the position of label in the product. Explain your answer.

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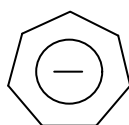


B) Classify following systems into aromatic, nonaromatic, antiaromatic giving reasons.

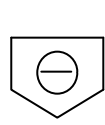
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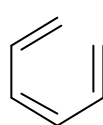
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(2)



(3)



(4)

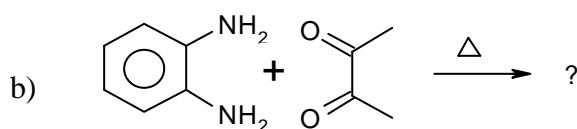
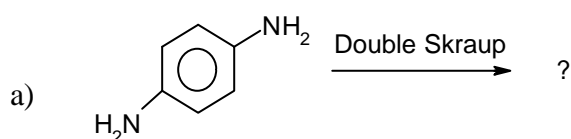
[16]-Annulene

(5)

33. Predict the product in the following.

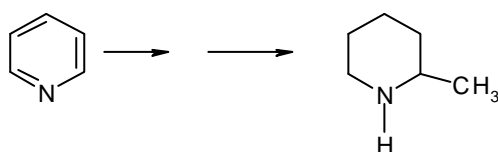
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A)



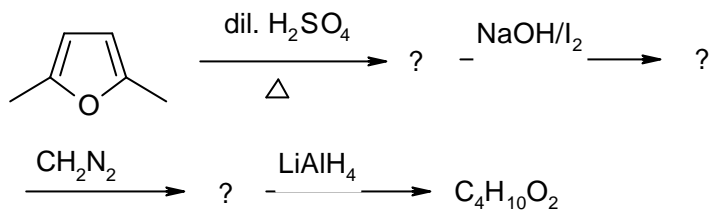
B) How will you carry out the following conversions.

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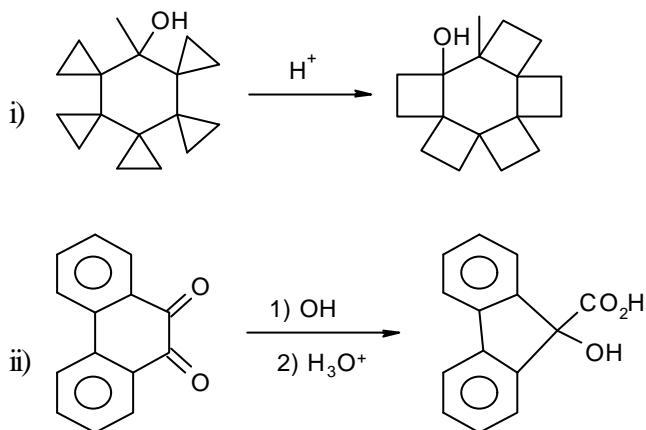
C) Identify the products of each step.

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34. A) Propose the mechanism for the following :

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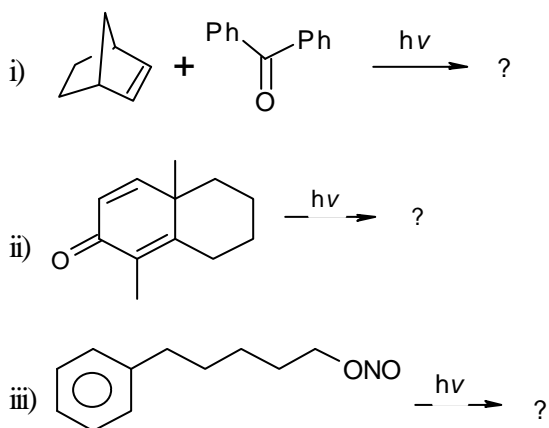
B) Match the following

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- | | |
|---|-------------------|
| i) Digestive enzyme for hydrolysis of peptide links | a) Rhodopsin |
| ii) Protein in retina | b) Chymotrypsin |
| iii) Always bonded to thymine in DNA | c) DNA polymerase |
| iv) Replication | d) Adenine |

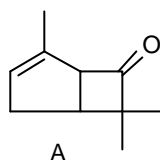
i) ii) iii) iv)

35. Predict the product of the following photochemical reactions. Explain the process involved. 13



36. Structure A has been assigned to a naturally occurring monoterpene, $C_{10}H_{14}O$

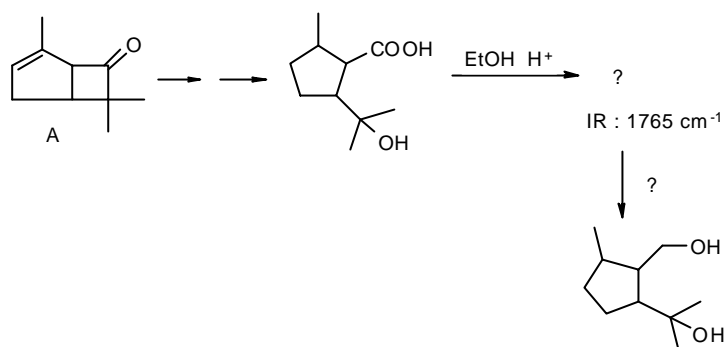
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A) What data (spectroscopic and / or chemical) will you collect to prove

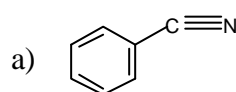
- i) presence of cyclobutanone
- ii) methyl attached to the olefinic linkage
- iii) presence of a gem-dimethyl group

B) Complete the following reaction sequence by inserting structures of reagents.

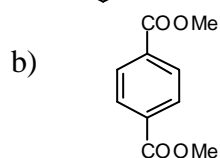


37. A) Match the following

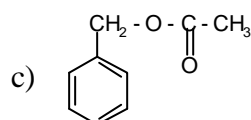
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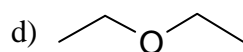
i) Two singlets in PMR



ii) transparent in UV



iii) IR absorption band at 2250 cm^{-1}



iv) m/z 91 (100%)

B) Deduce the structure of a compound C_7H_8O having following spectral data.

3

Justify your answer.

IR : 3350 (broad), 1600, 1100, 760 cm^{-1} .

PMR : δ 3.8 (1H), 4.3 (2H), 7.2 (5H)

C) Assign structure to a compound which shows following spectral properties.

4

MS : m/z 134 (M^+)

IR : 1685, 1600, 820 cm^{-1} .

PMR : 2.2 (3H, s), 2.3 (3H, s), 7.2 (2H, d, $J = 8.0\text{ Hz}$), 7.8 (2H, d, $J = 8.0\text{ Hz}$)

Assign signals.

What base peak would you expect in the mass spectrum ?