Total No. of Printed Pages-7 Roll No. _____

1(CCE-M)6

CHEMISTRY-II

[05]

Time Allowed -3 Hours *Maximum Marks-300*

INSTRUCTIONS

i) Answers must be written in English.

ii) The number of marks carried by each question is indicated at the end of the question.

iii) The answer to each question or part there of should begin on a fresh page.

iv) Your answer should be precise and coherent.

v) The part/parts of the same question must be answered together and should not be interposed between answers to other questions.

vi) **Candidates should attempt any FIVE questions**

vii) If you encounter any typographical error, please read it as it appears in the text book.

viii) Candidates are in their own interest advised to go through the General instructions on the back side of the title page of the answer script for strict adherence

ix) No continuation sheets shall be provided to any candidate under any circumstances.

x) Candidates shall put a cross (X) on blank pages of answer script

xi) No blank page be left in between answer to various questions.

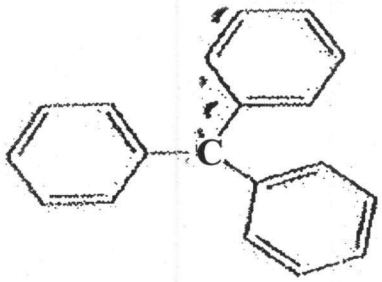
xii) No programmable Calculator is allowed.

xiii) No stencil (with different markings) is allowed.

xiv) In no circumstances help of scribe will be allowed.

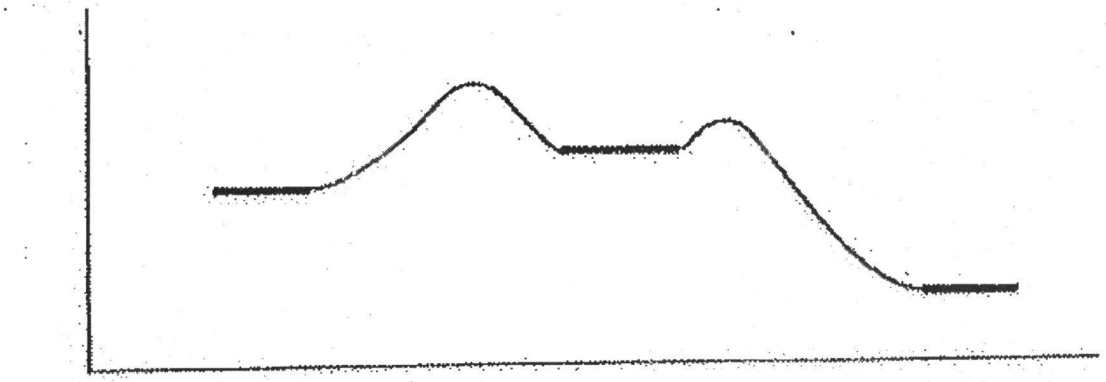
Note: Attempt any **FIVE** questions.

1. a) The triphenylmethyl cation is so stable that some of its salts can be stored for months. Explain why this cation is so stable ? **(15)**



triphenylmethyl cation

b) Consider the following reaction - energy diagram.



(i) Label the reactants and the products. Label the activation energy for the first step and the second step.

(ii) Is the overall reaction endothermic or exothermic? What is the sign of ΔH^0?

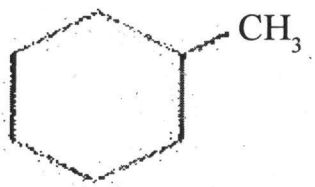
(iii) Which points in the curve correspond to intermediates? Which correspond to transition states?

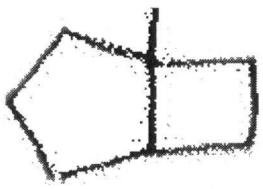
(iv) Label the transition state of the rate - limiting step. **(15)**

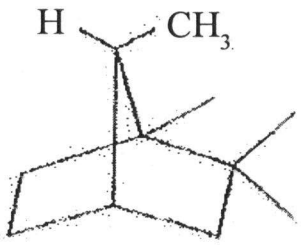
C. Label each hydrogen atom in the following compounds as primary (1^0), secondary (2^0), and tertiary (3^0) **(15)**

(i) $CH_3CH_2CH(CH_3)_2$.

(ii) $(CH_3)_3CCH_2C(CH_3)_3$.

(iii) 

(iv) 

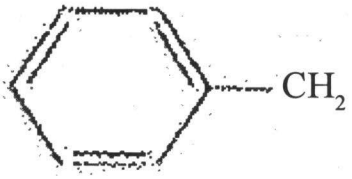
(v) 

(d) When dichloromethane is treated with strong NAOH, an intermediate is generated that reacts like a carbine. Draw the structure of this reactive intermediate and propose a mechanism for its formation. **(15)**

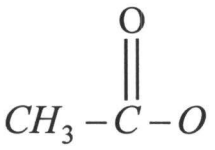
2. (a) Draw the important resonance structures of the following radicals **(15)**

i) $CH_2 = CH - CH_2$

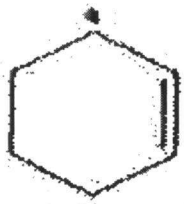
ii)



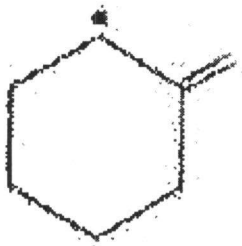
iii)



iv)



v)



(b) Rank the following in decreasing order of their reactivity toward the SN^2 reaction with sodium ethoxide ($Na^{+-}OCH_2CH_3$) in ethanol **(15)**

i) Methyl chloride.

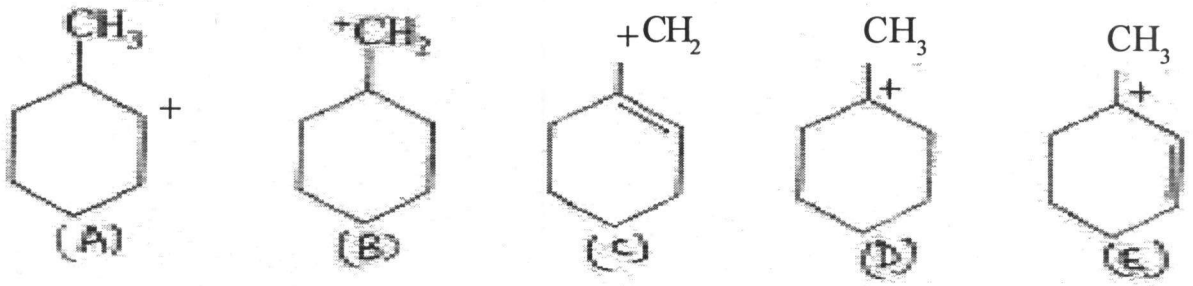
ii) isopropyl bromide.

ii) t- butyl iodide.

iv) methyl iodide.

v) neopentyl bromide

(c) List the following carbocations in decreasing order of their stability.**(15)**



(d) For each pair, predict the stronger nucleophile in the SN^2 reaction (using an alchol as the solvent). Explain your prediction. **(5×3=15)**

i) $(CH_3CH_2)_3 N \, or \, (CH_3CH_2)_2 NH$

ii) $(CH_3)_2 O \, or \, (CH_3)_2 S$

iii) $NH_3 \, or \, PH_3$

iv) $CH_3S^- or CH_3OH$

v) $(CH_3)_3N \ or (CH_3)_2O$

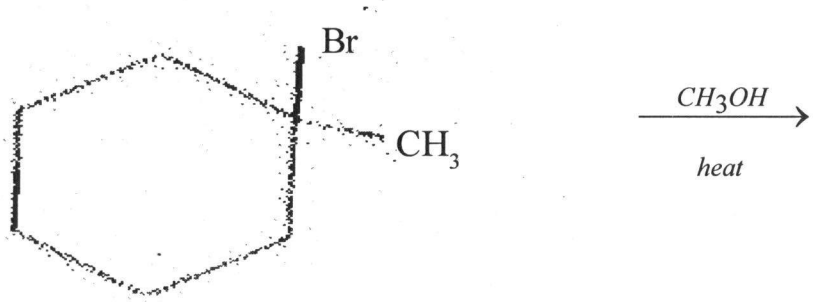
3. a) Predict the elimination products of the following reactions. When two alkenes are possible, predict which one will be the major product. Explain your answers, showing the degree of substitution of each double bond in the products. **(20)**

i) 2- bromopentane + $NaOCH_3$.

ii) 3- bromo -3- methylpentane + NaOMe (Me = methyl, CH_3)

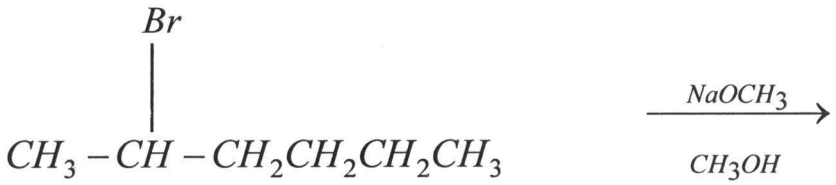
b) Predict the mechanisms and products of the following reactions **(20)**

i)



1 - bromo - 1 - methylcyclohexane

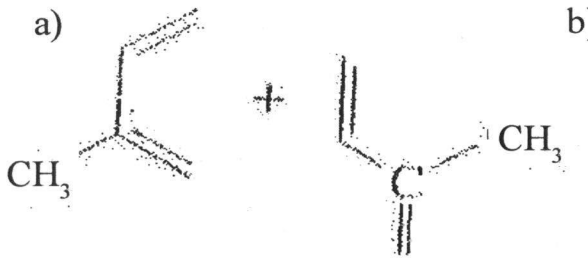
ii)



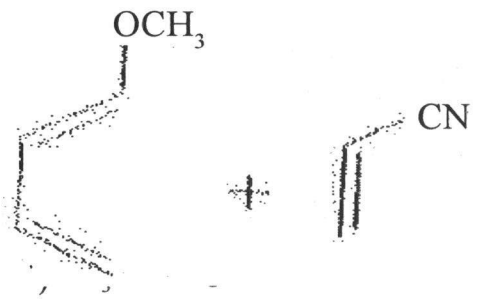
2 - bromohexane

c) Predict the products of the following Diels-Alder reactions. **(20)**

a)



b)



4. a) Why are the cyanoanili ions, C_6H_4 ,

ions $C_6H_5\overset{+}{N}H_3$? **(15)**

b) Explain the mechanism of the following

i) Claisen condensation

ii) Dieckmann condensation

iii) Michael addition **(15)**

c) Propose a mechanism for the base-catalyzed aldol condensation of acetone. **(15)**

d) In Friedel- Crafts reactions, nitrobenzene is often used as a solvent. Why does it not compete with aromatic substrate for this reaction? **(15)**

5. (a) What is nitrogen rule as applied in mass spectrometry ? can you predict from the molecular ion peak.

i) About the presence or absence of nitrogen atom.

ii) About the number of nitrogen atoms in molecules using this formula ?

b) Rubber is a polymer of isoprene. It is sometime called polyisoprene. There are two forms of polyisoprene: cis-polyisoprene is soft, flexible material and generally associated with the term "rubber" : gutta- percha, or trans-polyisoprene, is a much harder material.

i) Draw the monomeric units of cis - and trans - polyisoprene.

ii) Consider the structures of the polymers and comment on why one from is rubbery and the other is hard. **(15)**

c) Draw the structures of isotactic poly (acrylonitrile) and syndiotactic polystyrene. **(15)**

d) Isobutylene and isoprene copolymerize to give "butyl rubber ". Draw the structure of the repeating unit in butyl rubber, assuming that two monomers alternate. **(15)**

6. a) Write short notes on . **(20)**

i) Reformstsky reaction

ii) Pinacol - Pinacolone rearrangement

iii) Wangner - Meerwein' and Beckmann rearrangements

iv) Reimer - Tieman reactions

b) One milligram of a compound of molecular wright 160 is dissolved in 10 mL of ethanol, and the solution is poured into a 1- cm cell. The UV spectrum is taken, and there is an absorption at λ_{max}. The maximum absorbance at 247 nm is 0.50. Calculate the value of ε for this absorption. **(20)**

c) Explain the following terms **(4 × 5 = 20)**

i) IR - active and IR - inactive vibrations

ii) M + 1 and M + 2 peaks.

iii) TMS

iv) Spin - spin coupling

7. a) In a 300 - MHz spectrometer, the protons in iodomethane absorb at a position 650 Hz down - field from TMS.

i) What is the chemical shift of these protons?

ii) Determine the difference in the magnetic field required for resonance of the iodomethane protons compared with TMS protons.

iii) What will be the chemical shift of the iodomethane protons in a 60 MHz spectrometer?

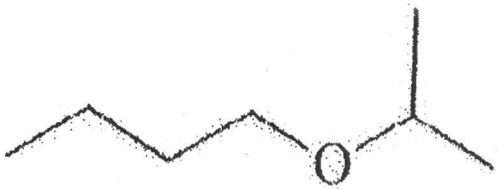
iv) How many hertz downfield from TMS would they absorb at 60 MHz?**(20)**

b) An unknown compound (C_3H_2NCl) shows moderately strong IR absorptions around 1650 cm^{-1} and 2200 cm^{-1}. Its NMR spectrum consist of two doublets (J = 14 Hz) at δ 5.9 and δ 7.1. Propose a structure consistent with these data. **(20)**

c) The IR spectrum of gaseous HCI shows a series of peaks centred at about 2900 cm^{-1} corresponding to rotational transitions of the HCI molecules. Closer examination of each adsorption peaks shows it to consist of two peaks with a size ratio of approximately 3:1. Explain this behavior. **(20)**

8. a) Ethers are not easily differentiated by their infrared spectra, but they tend to form predictable fragments in the mass spectrum. The following compounds give similar but distinctive mass spectra

butyl propyl ether



butyl isopropyl ether

Both compounds give prominent peaks at m/z 116,73,57 and 43. But one compound gives a distinctive strong peak at 87, and other compound gives a strong peak at 101. Determine which compound gives the peak at 87 and which one gives the peak at 101. Propose fragmentations to account for the ions at m/z 116, 101, 87, and 73. **(20)**

b) The central carbon atom of an allene is a member of two double bonds, and it has an interesting orbital arrangement that holds the two ends of the molecule at right angles to each other.

i) Draw an orbital diagram of allene, showing why the two ends are perpendicular.

ii) Draw the two enantiomers of 1,3 - dichloroallene. A model maybe helpful. **(20)**

c) Predict the number of components and their intensities in the ESR spectrum of the benzene radical anion, $C_6H_6^-$. **(20)**
