(3 Hours)

N.B.: 1. All questions are compulsory   **Total Marks: 80**
2. Answer all sub questions together
3. Figures to right indicate full marks

Q.1 A) Assign R/ S, E/Z or D/L notations and nomenclate the following as per IUPAC rule.   [4M]

(R)-2-hydroxypropanal

(i)
(1R)-2-nitrocyclopentanol

(ii)

(iii)
(R)-4-bromopentan-2-one

(Z)-4-amino-3-chloropent-3-enoic acid

(iv)
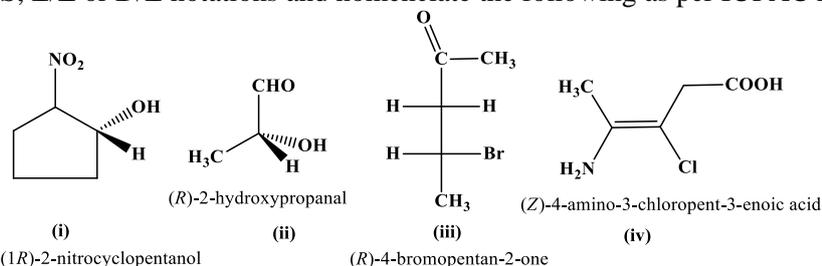
B) Give suitable structures for the following compounds.   [4M]

    i.   (Z)-3-Chlorohex-3-en-1-yne
    ii.   (S)-Ethyl 4-cyano-3-oxopentanoate
    iii.   3-Bromocyclohex-2,5-dienoic acid
   iv.   4-Cyclopropyl-1-butene

(Z)-3-Chlorohex-3-en-1-yne
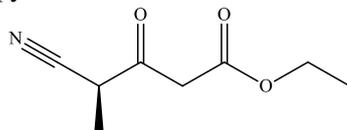
(S)-Ethyl 4-cyano-3-oxopentanoate
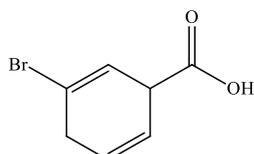
3-Bromocyclohex-2,5-dienoic acid
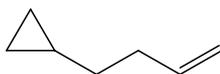
4-Cyclopropyl-1-butene

C) Answer the following questions **(ANY SIX)**   [12M]
i. Draw and identify the HOMO and LUMO of **Formaldehyde**.
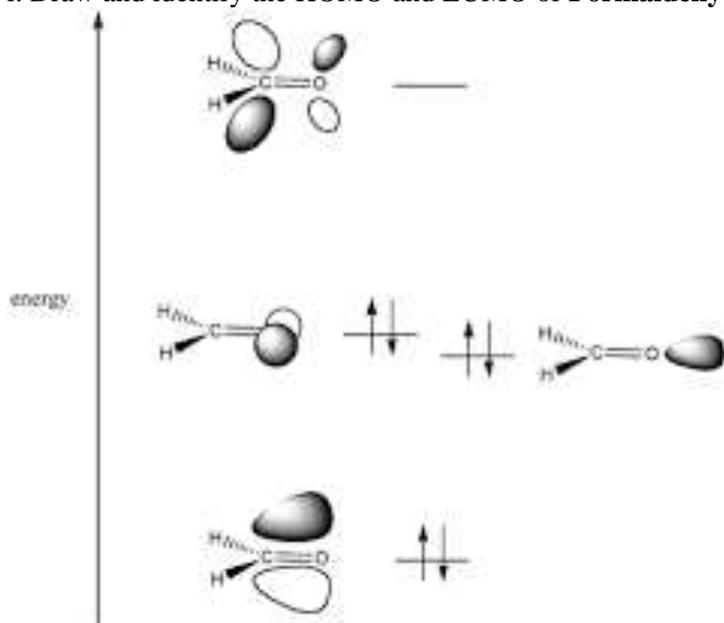
ii. Draw resonating structure of the following molecules

(i)

(i)

(ii)

(ii)
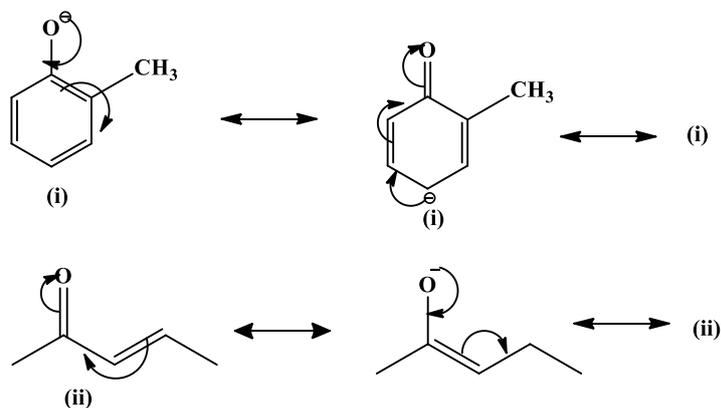
iii. Represent 2(S)-2-Hydroxybutanoic acid using Fischer and Newmann projection formulae.

2(S)-2-Hydroxybutanoic acid

COOH

HO———H

H———H

CH₃

COOH

HO H

H₃C H

HOOC

COOH

H———OH

CH₃
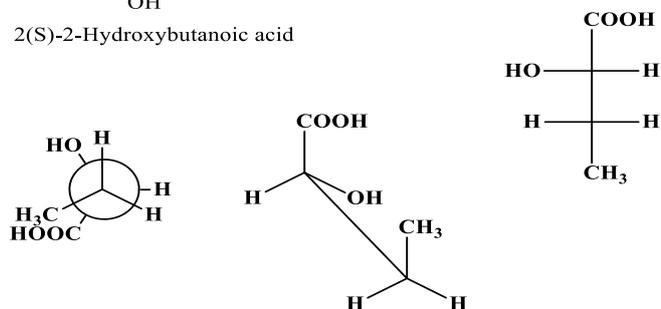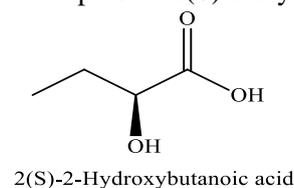
iv. Identify the relationship between following chiral structures

COOH
H   Br
H   Br
CH₃

(A)

HOOC   H
Br
H₃C
H
Br

(B)
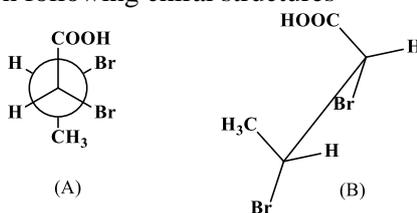
diastereomers

v. Write conjugate acid/base of the **N,N,N-trimethylamine** and **chloroacetic acid**

CH₃
|
NH⁺
H₃C   CH₃

ClCH_2COO⁻
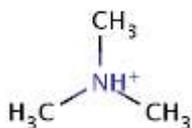
vi. Identify the electrophiles and nucleophiles in the given reaction.

$$CH_3COOH + CH_3OH \xrightarrow{H_2SO_4} CH_3COOCH_3 + H_2O$$
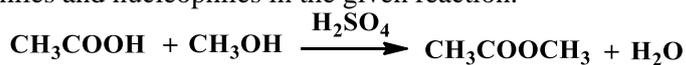
Electrophile: H2SO4 and acetic acid
Nucleophile : Methanol

vii. Arrange the following carbocations in increasing order of stability & justify the same.

(i)   (ii)   (iii)
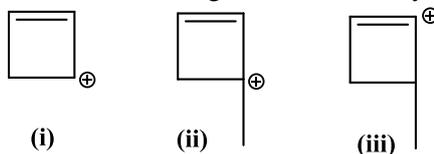
III more unstable than II and I. Most stable carbocation is II as it's a 3° carbocation

Q.2. i. Draw the molecular orbital energy diagram for acetone & Label the orbitals.   [2M]
ii. Identify the hybridization state of the underlined atom from the given molecule.   [2M]
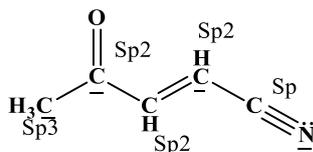
iii. List the following alkyl halides in decreasing order of S_N1 reactivity. Justify your answer.
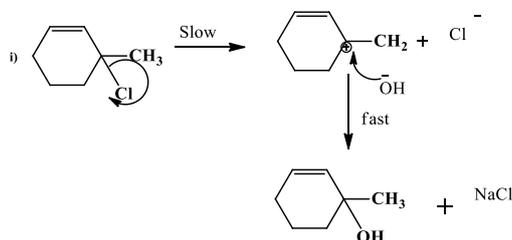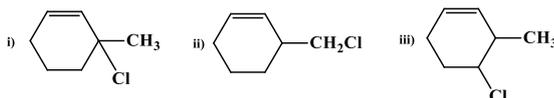
Order of reactivity tertiary>secondary> primary alkyl halide
i)>iii)>ii)

Propose the mechanism of the most active compound with alcoholic NaOH.   [4M]

iv. Draw the energy profile diagram to depict the following reactions and identify the transition states, identify whether the reaction is endothermic or exothermic.   [4M]
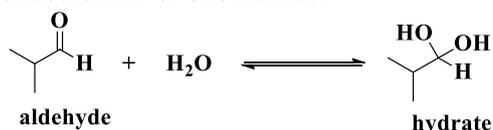
Clayden 243

Q.3 i. Discuss Bayer strain in cycloalkane   [2M]
Transannular strain exists when there is steric repulsion between atoms. Eclipsing (torsional) strain exists when a cycloalkane is unable to adopt a staggered conformation around a C-C bond, and bond angle strain is the energy needed to distort the tetrahedral carbons enough to close the ring.

Ring Strain in Cycloalkanes

If a cycloalkane requires bond angles **different to 109.5°** then the sp3 orbitals cannot overlap as efficiently as possible.
This gives rise to **angle strain (Bayer strain).**
Consider planar cyclobutane:

109.5°
tetrahedral angle

19.5°
angle compression

90°

eclipsed   eclipsed

H H   H H

H H   H H

Newman projection of planar cyclobutane
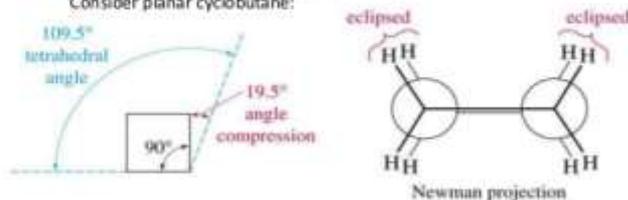
Along with the angle strain, there is also eclipsing of the hydrogens – torsional strain.
The combination of angle and torsional strains is called **Ring Strain.**
Calculation of Ring Strain
This is calculated through heats of combustion.
Already seen that alkanes can be combusted – so can cycloalkanes.

ii. Arrange the order of reactivity of following nucleophiles   [2M]
Sodium t-butoxide, Sodium methoxide, Sodium acetate
Sodium t-butoxide>Sodium methoxide>Sodium acetate

iii. What is Hoffmann rule? Complete the following reaction and suggest the mechanism (E1/ E2) [4M]

Zaitsev product   Non-Zaitsev product
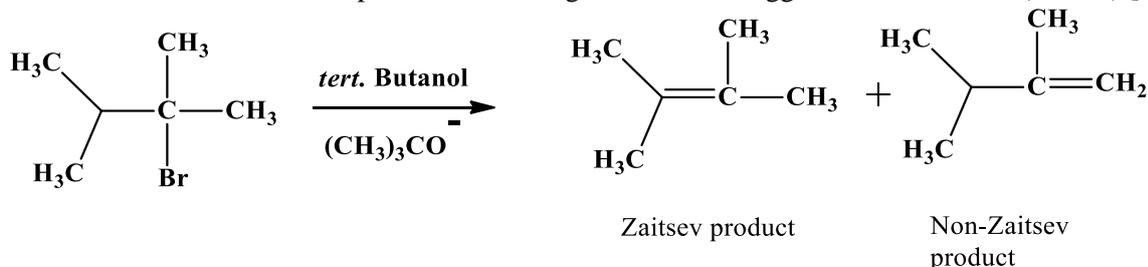
The Hofmann Elimination is an elimination reaction of alkylammonium salts that forms C-C double bonds [pi bonds]. [note] It proceeds through a concerted E2 mechanism. In contrast with most elimination reactions that yield alkenes, which follow the Zaitsev (Saytzeff) rule, the Hofmann elimination tends to provide the less substituted alkene. In this post we go through the difference between Hofmann elimination and Zaitsev elimination and explain the key features in the Hofmann degradation mechanism that result in its preference for the "less substituted" alkene.

iv. Write a note on epoxidation of **trans 2-butene** and comment on the stereochemistry of the product. [4M]

trans   trans
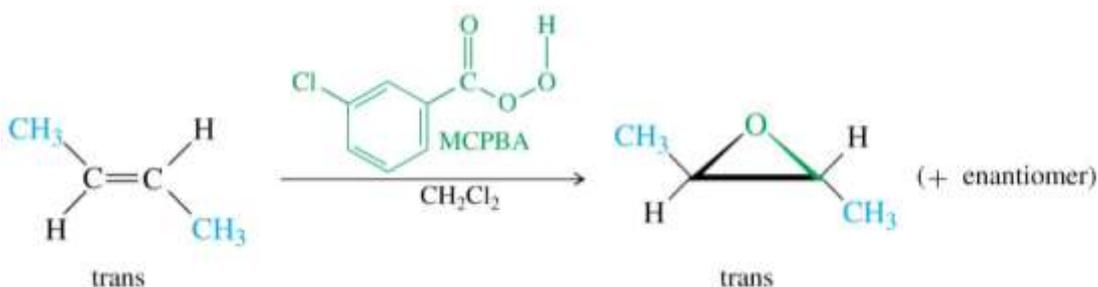
Alkene molecule cannot rotate and change its cis or trans geometry during the reaction. So the epoxide retains whatever stereochemistry is present in the alkene.
The ring opens by treating it with NaOH and can yield racemic mixtures, however the epoxide ring won't have .

Q. 4 i.   Define Enthalpy. Comment on the ΔG, ΔH, ΔS of the given reaction.   [4M]
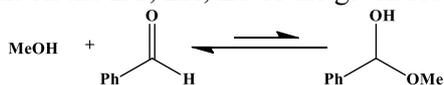
ii. Which one of the following pair is expected to exhibit H-bonding and why. Justify your answer
Phenylethylamine and Anisole [2M]

R=H
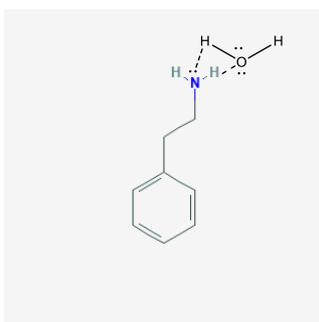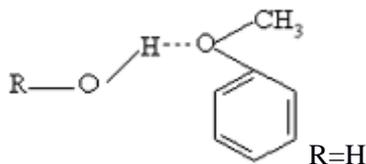
iii. On the basis of solubility, justify the increasing order of logP for the following compounds [2M]
Benzene (logP= 2.13), **Bromobenzene** (logP= 2.99), **Chlorobenzene** (logP= 2.84), **Fluorobenzene** (logP= 2.27)
Bromobenzene is more hydrophobic and can cross the lipoidal barrier easily than chlorobenzene. Fluorobenzene is moe hydrophobic than benzene.

iv. Identify the best leaving group MeO^-, ^-OH, NH_2^- and justify. [2M]
Read clayden Chapter of equilibria

v. Identify whether the given molecules are chiral or achiral and Justify. [2M]

Achiral   Achiral
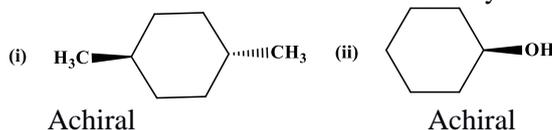
Q.5 i. Arrange the following compounds in increasing order of acidity & Justify. [2M]
o-Nitrobenzoic, p-Nitrobenzoic acid and m-Nitrobenzoic acid
The acidity of ortho-nitrobenzoic acid more as compared with para-nitrobenzoic acid is believed to be a result of the so called "ortho effect". The explanation is relying on the steric inhibition of the resonance of the COOH group. The ortho substituent may force the carboxyl group out of the plane of the benzene ring, thus decreasing the resonance of the molecule. At the same time carboxylate anion COO- is believed to be less sterically hindered and more apt to be in the energetically favorable planar configuration. This makes an additional reason to the ortho substituted acid to pass to the anion form thereby increasing its acidity as compared with the meta and para substituted acids.
O nitro benzoic acid=pka value =2.17

M nitro benzoic acid=pka value=3.43

P nitro benzoic acid=pka value=3.45

ii. Arrange the following compounds in increasing order of basicity & Justify. [2M]
Aniline, Cyclohexylamine, Hexanamine
Hexaneamine is stronger than Cyclohexylamine and cyclohexanamine is a stronger base than aniline. This is because lone pair of electrons on the N- atom of aniline is declocalized over the benzene ring. ... Further N- atom inaniline is sp2 hybridized and in cyclohexylamine it is sp3 hybridized.

iii. With the help of energy profile diagram draw various conformers of **n-butane**. Comment on their relative stability. [4M]
read std book, Kalsi or Nasipuri or Eliel

iv. Give the scheme for acid degradation/ base degradation of Paracetamol. [4M]
read notes (Patric

Q.6 i. Distinguish between the terms - intermediates and transition states giving suitable examples and support your answer by drawing energy profile diagram. [4M]

ii. Identify whether the given molecules are aromatic, nonaromatic or antiaromatic. [4M]

(i) (ii) (iii) (iv)
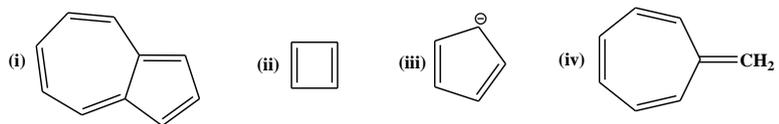
i)   nonaromatic   ii) Antiaromatic, iii) aromatic, iv) non aromatic

iii. Give the product   [4M]

A   B   C   D

$\xrightarrow{K_2Cr_2O_7}$ A $\xrightarrow{Ag(NH_3)_2^+}$ B $\xrightarrow{SOCl_2}$ C $\xrightarrow{NH_3}$ D