

chemistry III (Rev)

Q.P. Code : 35912

[Time: 2½ Hours]

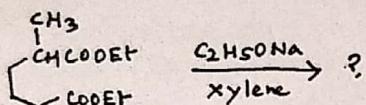
[Marks: 60]

Please check whether you have got the right question paper.

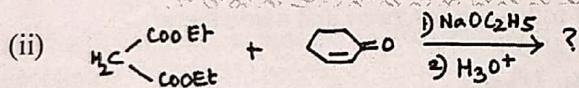
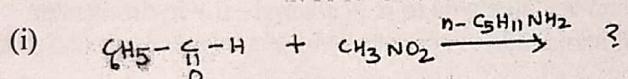
- N.B: 1. All questions are compulsory.
 2. Figures to the right indicate full marks.

1. (A) Answer any two of the following:

(a) Complete the following reaction and give the mechanism: 04



(b) Predict the products and name the following reactions: 04

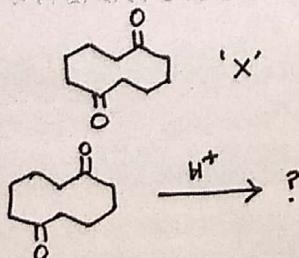


(c) What is Robinson's annulation? Explain its mechanism. 04

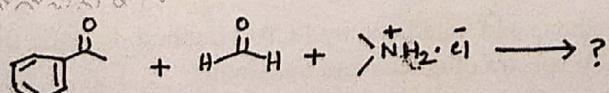
(d) Explain thermodynamic and kinetic control of enolate formation with a suitable example. 04

(B) Answer any one of the following:-

(a) Identify the position(s) of enolisation in the molecule 'X' and give the mechanism for the formation of the major product when 'X' is treated with an acid. 04



(b) Complete the following reaction, name it and give the mechanism: 04



Turn Over

2. (A) Answer any two of the following:

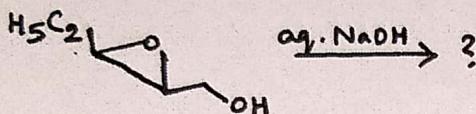
(a) Explain the following rearrangement reactions with one example each:

(i) Wolff

(ii) Nef

(b) What is Brook rearrangement? Explain its mechanism.

(c) Complete the following reaction and give its mechanism:

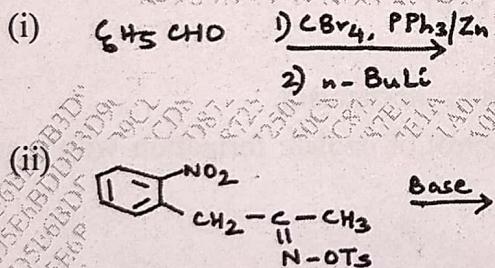


(d) Give the mechanism for the following conversions:

(i) Ethyl acrylate and acetaldehyde to α -alkenyl- β -hydroxyester
 (ii) 3,3-Dimethylbutanamide to neopentylamine

(B) Answer **any one** of the following:

(a) Predict the products of the following reactions and name them:



(b) What is Wittig rearrangement? Give its mechanism.

3. (A) Answer any one of the following:

(a) Draw the π – MO diagrams with distribution of electrons for the reactants of Diels-Alder reaction. Explain the interaction of FMOs.

(b) How are the following compounds distinguished using IR spectroscopy?

(i) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$, $\text{CH}_3\text{C}\equiv\text{C-CH}_3$ and $\text{CH}_3\text{C}\equiv\text{N}$

(ii) o-and p-hydroxybenzaldehydes.

(c) Draw the π -MOs of ethene and butadiene by LCAO method. Explain the effect of conjugation on the UV spectra of ethene and butadiene.

- (d) Draw the MOs diagram for the allyl anion and allyl cation. Show the interaction of their FMOs . Predict the product of the reaction between the two ions. 04

(B) Answer any one of the following:

- (a) The $n \rightarrow \pi$ transition of acetone appears at 279 nm in hexane, 272 nm in ethanol and 264.5 nm in water. Explain. 04

- (b) Explain the following in IR spectroscopy with suitable examples: 04

- (i) Vibrational coupling
- (ii) Nature of hydrogen bonding

4. (A) Answer any two of the following:

- (a) 'Acetylenic protons appear at around 2.8 ppm in NMR spectra'. Explain. 04

- (b) Explain the following in NMR spectroscopy: 04

- (i) spin –spin coupling constant
- (ii) Karplus curve and its significance

- (c) How will you differentiate between o-, m- and p-xylenes on the basis of their proton decoupled ^{13}C NMR spectra. 04

- (d) An organic compound 'A' (molecular formula ($\text{C}_6\text{H}_{12}\text{O}_2$) showed the following IR and ^1H NMR spectral data. Assign the structure to the compound. 04

IR (neat) ν_{max} 2950, 2850, 1730, 1480, 1460, 1400 cm^{-1}

^1H NMR: δ ppm 1.20 (9H,s); 3.70 (3H,s)

(B) Answer any one of the following:

- (a) Give the fragmentation pattern of the following molecules in mass spectrometry: 04

- (i) 2, 2 – Dimethylbutane
- (ii) Pentanal

- (b) Deduce the structure of the compound having the following spectral data: 04

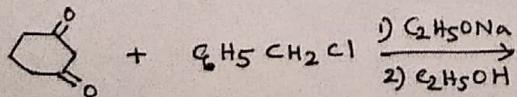
UV = No absorption above 210 nm

IR (CCl_4) = 2940 (m); 1265 (w); 690 (s) cm^{-1}

^1H NMR: (CCl_4) = δ 3.5 (2H,d); 3.3 (1H, m); 1.25 (2H, d)

5. Answer any four of the following: 12

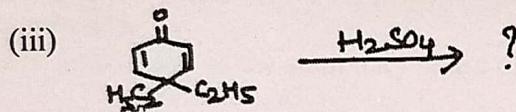
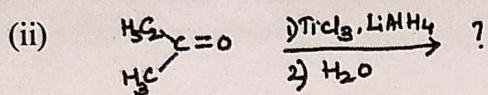
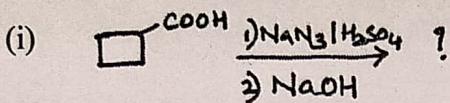
- (A) Complete the following reaction and give the mechanism:



Turn Over

(B) What is Claisen ester condensation? Give an example.

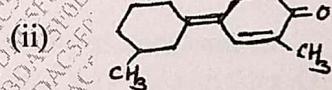
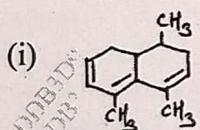
(C) Complete the following reactions:



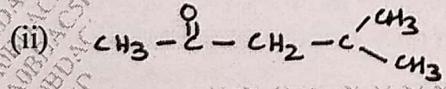
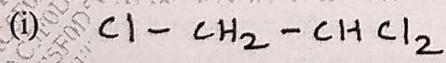
(D) Explain the mechanism of Rupe rearrangement with a suitable example.

(E) What are soft nucleophiles and soft electrophiles? Give one example of each.

(F) Calculate the λ_{max} of the following compounds:



(G) Give the number of signals and splitting pattern observed in the PMR spectra of the following molecules:



(H) Explain the following terms in mass spectrometry:

(i) Retro Diels Alder Reaction

(ii) Nitrogen Rule