CSM – 17/19

Chemistry

Paper – II

Time : 3 hours

Full Marks : 300

The figures in the right-hand margin indicate marks.

Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and any ***three*** *of the remaining questions, selecting at least* ***one*** *from each Section.*

SECTION – A

1. Answer any **three** questions of the following : $20 \times 3 = 60$

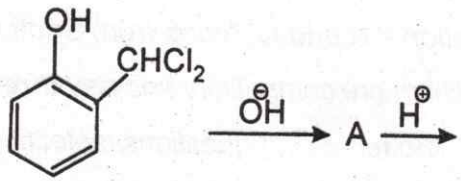
   (a) (i) Discuss the energy profile diagram of an exothermic reaction.

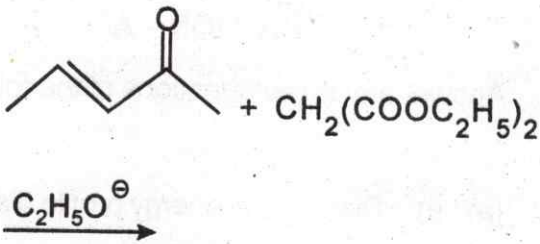
   (ii) Explain the aromatic character of benzene. Why all bonds in benzene are equal length ?

(iii) How will you differentiate between inductive effect and resonance effect ?

(iv) Discuss the various methods used to determine reaction mechanism.

(b) (i) Predict the product of the following reactions :

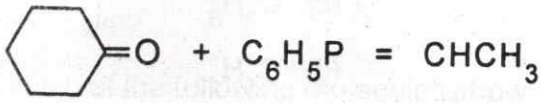




(ii) Discuss the structure and stability of carbene.

(iii) Write a short note on Wagner-Meerwin rearrangement.

(iv) Predict the product of following reactions with mechanism.



$\longrightarrow$?

(c) (i) The absorbance of 5.4×10^{-4} M solution of Fe^{3+} at 530 nm was 0.54, when measure in a cell with 1 cm path length. Calculate the molar absorption coefficient.

Acrolein (CH_2 = CHCHO) absorbs at 217 nm(ϵ_{max} = 16000). What is the concentration (g/ml) required to observed absorbance at 0.8 when the cell length is 1 cm ?

(ii) Write the structural formula for the compounds with the following molecular formula that show only one signal in their PMR spectra :

(a) C_3H_4

(b) C_8H_{18}

(c) C_3H_6

(d) C_5H_{12}

(e) C_2H_6O

(iii) How can you distinguish between inter and intra molecular hydrogen bonding by PMR spectroscopy ?

(iv) How can you distinguish among hexane, 1-hexene and hexyne on the basis of IR spectroscopy ?

(d) (i) What is the difference between photochemical and thermal reaction ? Discuss with suitable example.

(ii) Discuss the use of NBS (N-bromosuccinamide) as a reagent ?

(iii) What is Fischer-indole synthesis ? Write the mechanism.

(iv) What do you understand by sigmatropic rearrangements ? Give examples of [1, 3], [1, 5] sigmatropic rearrangements.

2. Answer the following questions as directed :

(a) Explain the following sentences : 10

(i) (A) Cyclopentadienyl anion shows aromatic character.

(B) Aryl halides are far less reactive than alkyl halides.

(C) Lower alcohols are soluble in water.

(D) When allyl chloride reacts with sodium phenoxide, we get a mixture of phenol allyl ether and 0-allylohenol.

(ii) How you will perform the following conversion ? 10

(A) Benzaldehyde to styrene

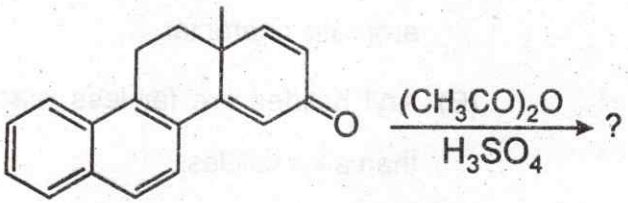
(B) Phenol to coumarin

(C) Acetyl chloride to acetophenone

(D) Acetone to 4-phenylbutanone

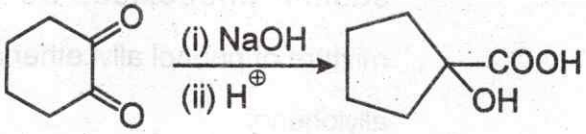
(b) Answer **all** questions as directed : 5×4 = 20

(i) Predict the product of Following reaction with mechanism :

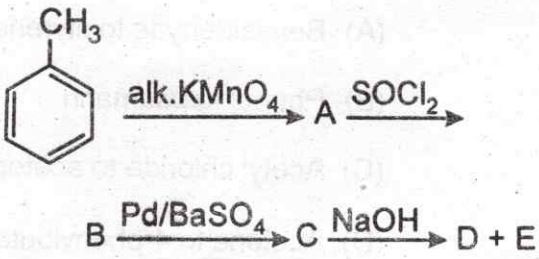


(ii) Discuss about benzoin condensation.

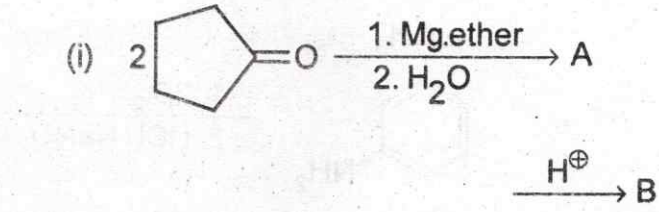
(iii) Give the mechanism of the following reaction :



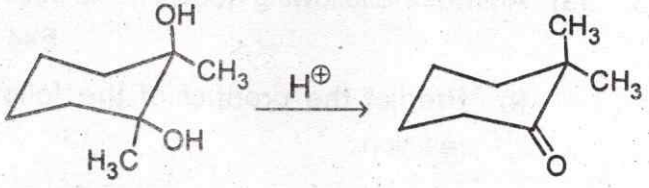
(iv) Write the structure of A, B, C, D and E in the following reaction :



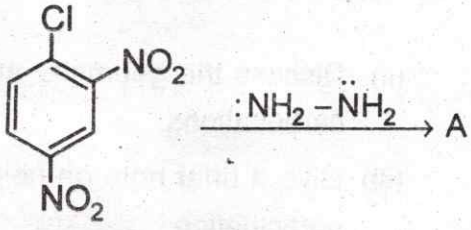
(c) Predict the product of the following reaction : $5 \times 4 = 20$

(i) 

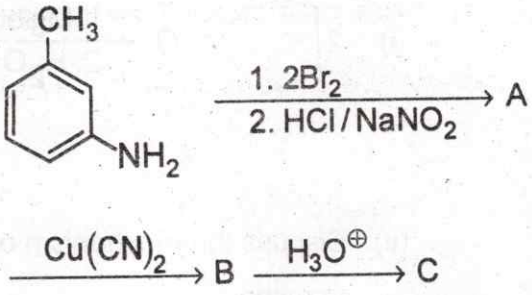
(ii) Discuss the mechanism of the following reaction :



(iii) Predict the product of the following reaction :

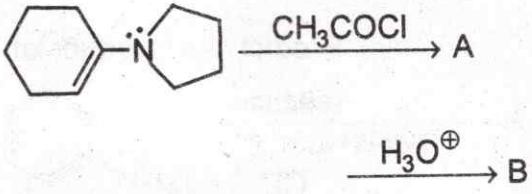


(iv) Predict the product of the following reaction :



3. (a) Answer the following questions as directed : 5×4 = 20

(i) Predict the product of the following reaction :



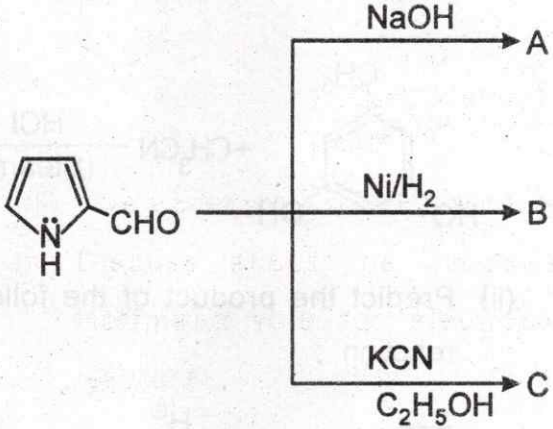
(ii) Discuss the geometry and stability of carbocations.

(iii) Give a brief note on neighbour group participation.

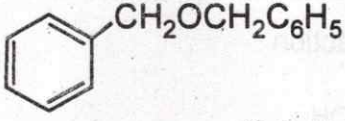
(iv) Discuss about the substitution reaction in pyrrole.

(b) Answer the following questions as directed : 5×4 = 20

(i) Predict the product from the given reactions :



(ii) Predict the product of the following reaction :



$$\xrightarrow[(ii)\ H^{\oplus}]{(i)\ C_6H_5Li(ether)} ?$$

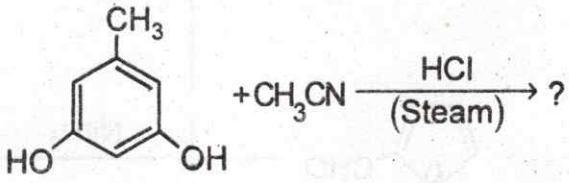
(iii) Give a brief note on ElcB mechanism.

(iv) Discuss about the Woodward-Hoffmann rule for electrocyclic reactions.

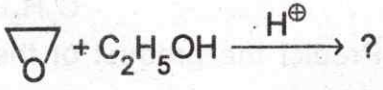
(c) Answer the following questions as directed :

5×4 = 20

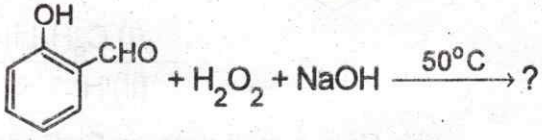
(i) Predict the product of the follwoing reaction :



(ii) Predict the product of the following reaction :



(iii) Predict the product of the following reaction :



(iv) Discuss about Bischler-Napieralski reactions.

4. Answer any **ten** questions as directed :

$6 \times 10 = 60$

(a) Arrange the following compounds in the decreasing order of reactivity in Perkin reaction and explain :

$p\text{-}CH_3C_6H_4CHO$; $p\text{-}Me_2NC_6H_4CHO$; $p\text{-}O_2NC_6H_4CHO$.

(b) Discuss Wittig reaction with one example.

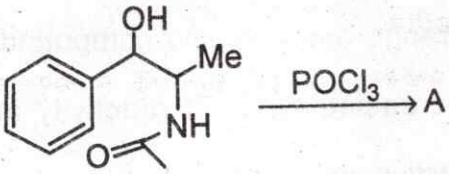
(c) How will you differentiate between ordinary ketone and methyl ketone ?

(d) Explain the base catalyzed mechanism of hydrolysis of ester.

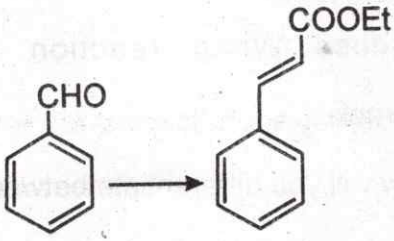
(e) Discuss about singlet and triplet states in photochemistry.

(f) Write the mechanism of Von-Richter rearrangement.

(g) Write the product of the given reaction with mechanism :



(h) How to convert the given reaction ? Write its mechanism.



(i) Write one method for preparation of indole.

(j) How chlorobenzene is prepared from aniline ? Explain its mechanism.

(k) How to convert benzaldehyde to toluene ? Explain with mechanism.

(l) Write short note on Skraup synthesis and explain its mechanism.

SECTION – B

5. Answer any **three** questions of the following :

$20 \times 3 = 60$

(a) Write synthesis of the following polymers with chemical equations :

Polystyrene, Terylene, Nylon, Styrene-Butadiene rubber (SBR)

(b) Write two most important synthetic uses of the following all compounds :

B_2H_6, $Pb(OAC)_4$, n-Buli, OsO_4.

(c) Explain number average and mass average molecular mass of polymer ?

Equal number of molecules with $M_1 = 10^4$ and $M_2 = 10^5$ are mixed. Calculate the number average and mass average molecular mass of polymer and also calculate polydispersity of the polymer sample.

(d) (i) The molecular formula of a compound $C_5H_8O_3$ gives the following NMR data :

Singlet δ(2.12)3H

Triplet δ(2.25)2H

Triplet δ(2.5)2H

Singlet δ(11.1)1H

Predict the structure of the compound.

(ii) How molecular mass of a polymer is determined by light scattering method ?

6. Answer any **five** questions of the following :

12×5 = 60

(a) (i) An unknown substance has molecular ion peak at m/z = 107 with a relative intensity 100. The relative intensity of M + 1 peak is 8.0 and M + 2 peak is 0.30. What is the molecular formula of the compound ?

(ii) Determine the structure of the compound whose m/z values are 74, 56, 43, 31 (base peak).

(b) (i) Calculate the magnetic field needed to satisfy the resonance condition of a proton at 150MHz (g_N = 5.85, β_N = 5.05×10^{-27})

(ii) Predict the ^{1}HNMR spectra of 1-Phenyl ethylamine.

(c) (i) How will you distinguish three isomeric butanols on the basis of mass spectrometry ?

(ii) Explain why aromatic protons are more deshielded than ethylenic protons although both the types of protons are attached to sp^2 hybridized carbon ?

(d) (i) The infrared spectrum of an organic C_7H_5N shows prominent bands at 3060 cm, 2250 cm^{-1}, 1600 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1}, 1450 cm^{-1}, 750 cm^{-1}, 700 cm^{-1}. Predict the structure of the compound.

(ii) What is the difference in C = 0 stretching frequency of O-hydroxy benzoic acid and p-hydroxy benzoic acid ?

(e) (i) How many normal modes of vibrations are possible in the following molecules ?

OCS, SO_2, BCl_3, $CH \equiv CH$, C_6H_6

(ii) Using harmonic oscillator concept, calculate zero-point vibrational energy of HCl given that the force constant of HCl is 516 Nm^{-1}.

(f) (i) Assume that a molecule undergoes spectroscopic transition from ground state to an excited state where it's lifetime is 10^{-4}s. Calculate approximate uncertainty in excited state energy level and width of the spectral line in Hz.

(ii) What is the vibrational frequency corresponding to a thermal energy of kT at 298K ? What is the wavelength of this radiation ?

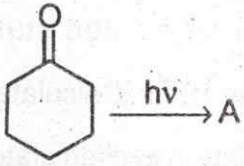
7. Answer any **ten** questions from the following : 6×10 = 60

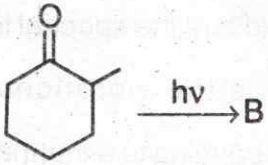
(a) Explain di-π methane rearrangement with example.

(b) Explain Norrish type-I cleavage with mechanism.

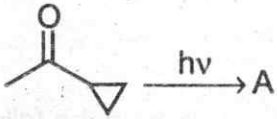
(c) Write short note on Photo Fries arrangement with example.

(d) Write the major product of the given reactions and explain its mechanism :

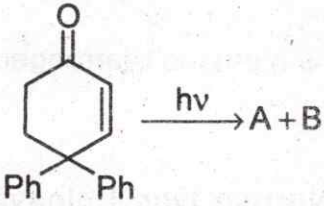
(i) 

(ii) 

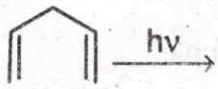
(e) Write the product of the given reaction :



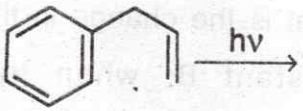
(f) Write the product of the given reaction :



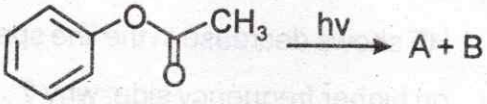
(g) Write the product and mechanism of the given reaction :



(h) Write the product and mechanism of the given reaction :

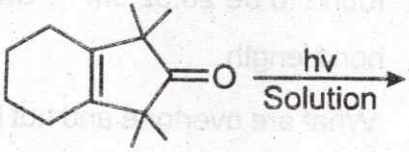


(i) Write the products and mechanism of the given reaction :

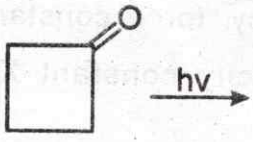


(j) Write short note on intersystem crossing.

(k) Write the major product of the given reaction :



(l) Write the product and mechanism of the given reaction :



8. Answer any **six** questions of the following :

$10 \times 6 = 60$

(a) (i) What is the change in the rotational constant B, when hydrogen is replaced by deuterium in hydrogen molecule ?

(ii) The observed rotational spectrum of HF shows decrease in the line spectrum on higher frequency side, why ?

(iii) The separation between lines in the rotational spectrum of HCl molecule was found to be 20.92 cm^{-1}. Calculate the bond length.

(b) (i) What are overtone and hot bands ?

(ii) CO shows an intense band at 2142 cm^{-1} and a weak absorption band at 4260 cm^{-1}. Calculate the fundamental frequency, force constant and an harmonicity constant X_e for CO molecule.

(c) (i) Why the rotational spectroscopy studied only in gaseous state of atoms or molecule ?

Which of the following molecules show pure rotational spectra in microwave region ?

CH_3F, BF_3, C_6H_6, CH_2F_2, XeF_4, C_2H_6 staggered form

(ii) Calculate the rotational constant of HCl where H-Cl bond length is 136pm.

(d) (i) A compound has the molecular formula $C_7H_6O_2$. It gives an IR absorption band at 1771 cm^{-1}. On treatment with $LiAlH_4$ it is converted into a compound B which shows characteristic IR absorption bands at 3330 cm^{-1} and 1050 cm^{-1}. Assign structures of compounds A and B.

(ii) Arrange the following in-order of decreasing carbonyl frequency with explanation.

Ester, Aldehyde, Carboxylic acid, Ketone, Amide, Acid chloride.

(e) (i) What is coupling constant ? Discuss the factors affecting coupling constant.

(ii) A compund with molecular formula C_8H_8O gives the following ^{1}HNMR data :

Multiplet δ(7.25)5H

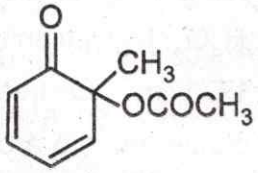
Doublet δ(2.8)2H

Triplet δ(9.78)1H

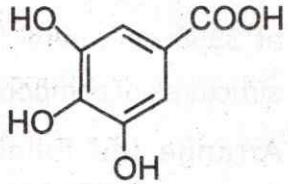
Predict the structure of the compound.

(f) (i) Predict λ_{max} of the following compounds using Woodward-Fieser rule :

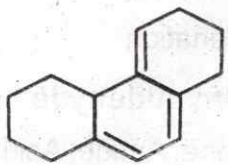
(A)



(B)



(C)



(ii) A basic solution containing 5.4×10^{-4} M solution of $K_2Cr_2O_7$ transmit 60% of the incident radiation when placed in a 1.0 cm cell. Find the absorbance of the solution.

(g) (i) What is the basic principle of ESR ? Calculate g value of Fe^{3+}. Predict the ESR of Cu(biguanide)$_2^{2+}$ and $C_{10}H_8^-$.

(ii) What is McLafferty rearrangement ? Explain with the help of propanoic acid. Predict the structure of the compound which shows m/z peak at 88,70, 55, 42,31(B) 29.