RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [2017-20]

B.A./B.Sc. THIRD SEMESTER (July – December) 2018

Mid-Semester Examination, September 2018

Date : 24/09/2018

Time : 11 am – 1pm

CHEMISTRY (Honours)

Paper: III

Full Marks : 50

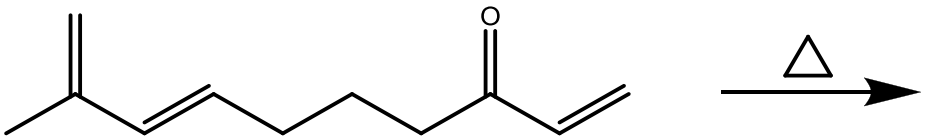
[Use a separate Answer Book for each group]

Group – A

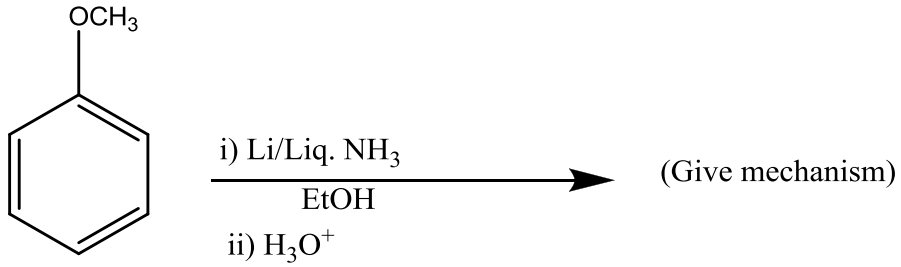
Answer **any two** questions of the following**:** (2 × 8)

1. a) Show the product(s) of the following reactions with proper explaination: 2 × 2

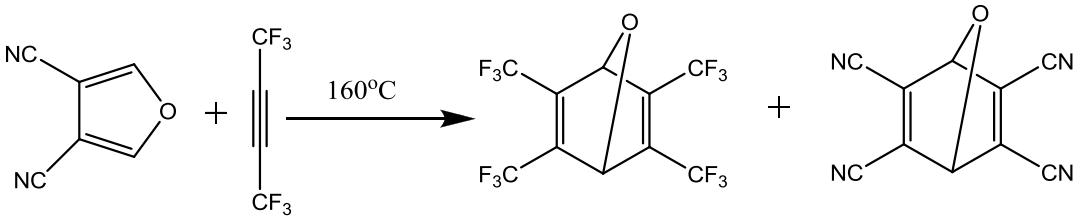
(i)



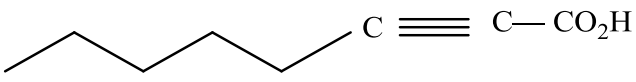
(ii)



b) Explain the following observation with proper mechanism: 2

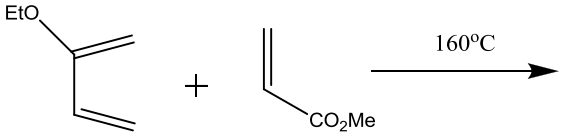


c) Prepare the following compound starting from C_2H_2 (no mechanism required) 2

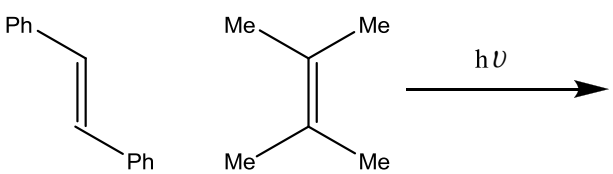


2. a) Write down the structure of the product(s) in the following reaction with explanations : 2 × 2

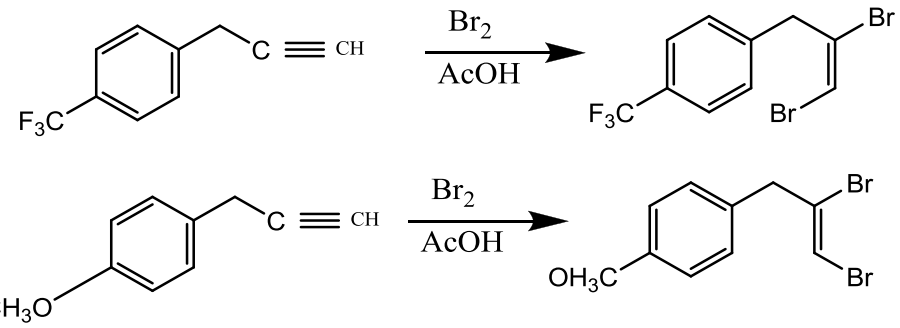
(i)



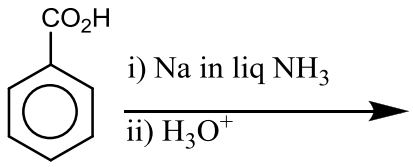
(ii)



b) Explain the following product formation with proper mechanism: 2



c) Write down the structure of the product with mechanism: 2



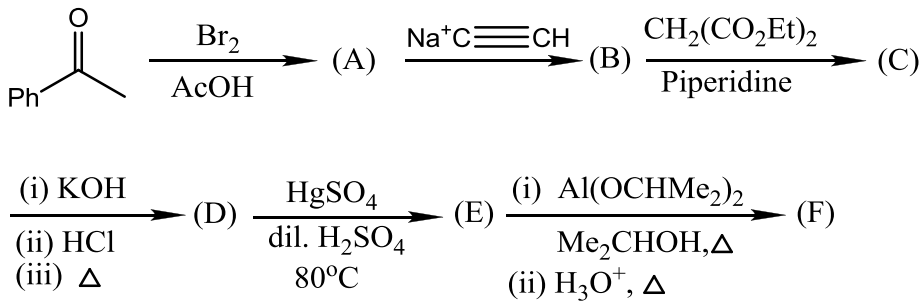
3. a) Justify the following statements: 3

(i) Cyclopropanone forms stable hydrate.

(ii) Paranitrobenzaldehyde does not give self benzoin type condensation.

(iii) Acetophenone gives phenacyl bromide when brominated in glacial ACOH.

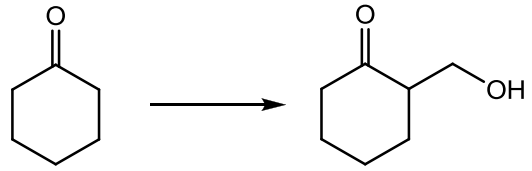
b) Identify (A) to (F) in the following reaction sequence: 5



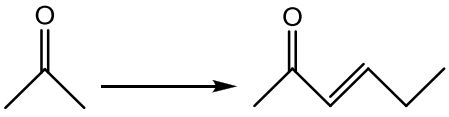
OR

Carryout the following conversions. (mechanism is not necessary). 4 × 2

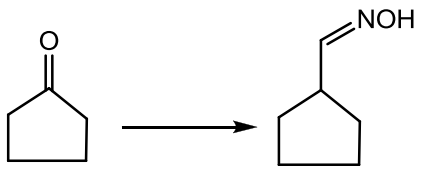
(i)



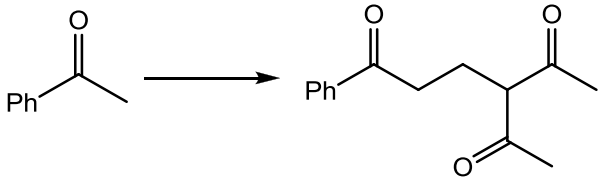
(ii)



(iii)



(iv)



(2)

Group – B

Answer **any one** from question no. 5 to 5 : (2 × 8)

5. a) How do you get Rayleigh-Jeans formula from Planck's radiation formula for Black-body radiation ? Define Ultraviolet Catastrophe, with plot. 2+1

   b) de Broglie equation satisfactorily explains the energy splitting for a conjugated diene system. Justify or criticise. 3

   c) Get the explicit form of $\left(\frac{d}{dx}+1\right)^2$ 2

OR

6. a) (i) For the linear operators $\hat{\alpha}, \hat{\beta}, \hat{\gamma}$ prove that $\left[\alpha,\left[\beta,\gamma\right]\right]+\left[\beta,\left[\gamma,\alpha\right]\right]+\left[\gamma,\left[\alpha,\beta\right]=0\right]$.

   (ii) Is 'Square root' (operator) a linear operator? Explain. 3+1

   b) The maximum Compton shift is independent to any wavelength used. Justify or criticize. 2

   c) Use the property of operators to evaluate $\left[\hat{x}^2, \hat{p}_x\right]$ where $\hat{p}_x$ is the momentum operator along *x* axis. 2

Attempt any **one** from question no. 7 to 8 :

7. Consider a reaction represented as $A \rightarrow B + C$

   (i) Write down the expression for the reaction quotient at any arbitrary instant in terms of partial pressure and also the expression for free energy change (ΔG) in terms of standard free energy change (ΔG^o) and reaction quotient (Q_p). (1+1)+(1×3)+1+(1+1)

8. Consider a reaction represented as $A \rightarrow B$

   (i) Express the net free energy change of the reaction in terms of free energy of mixing and standard free energy change.

   (ii) Draw a schematic diagram which shows how standard free energy, free energy of mixing and the total free energy changes during the reaction.

   (iii) Show the location of the equilibrium and explain its origin from the graph.
   (Given that the standard free energy of B is greater than that of A) 2+3+(1+2)

Group – C

9. Answer **any two** questions of the following**:** (2 × 9)

   a) 'Cu^{+2} ion acts as a cosolvating agent for aqueous solution of glycine' – explain. 2

   b) What will be the pH of the solution obtained by mixing 10 ml of 0.2 (N) KOH with 30 ml of 0.1 (N) CH_3COOH? (K_a of $CH_3COOH = 2 \times 10^{-5}$). 2

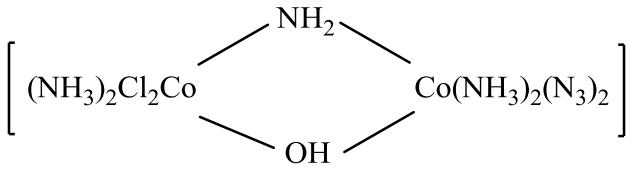
   c) Why ethylenediamine tetraacelate forms 1:1 complex with metal ions? Draw the structure of an octahedral complex of such a ligand and state the number of chelate rings formed. 2

   d) Arrange the complexes in order of their molar conductivities: 1

$Pt(NH_3)_6Cl_4$, $Pt(NH_3)_3Cl_4$, K_2PtCl_6

e) Give IUPAC names of the following complexes: 2

(i) $NH_4[Cr(NCS)_4(NH_3)_2]$

(ii) 

OR

10. a) $(CH_3)_2S$ functions as a stronger base to B_2H_6 than $(CH_3)_2O$ though BF_3 forms stronger adduct with $(CH_3)_2O$ than with $(CH_3)_2S$ – explain on the basis of hyperconjugation effect on acidity and basicity. 2

b) Select the following ions which will interact favourably: 2

Ag^+, Ni^{+4}, I^-, IO_6^{5-}

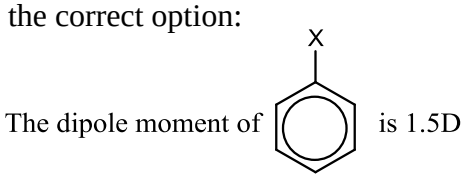
c) Successive pK_a values of H_3PO_4 are 2.1, 7.4 and 12.7 respectively. Explain the data using Pauling's rules. 2

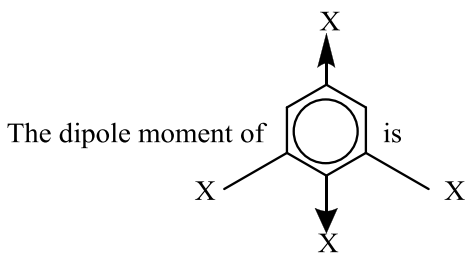
d) A solution of 0.1332 g of $CrCl_3.6H_2O$ was passed through a cation enchange resin in the acid form. 98.0 ml of a standard caustic soda solution (containing 5.0 g NaOH/litre) was required for the titration of the liberated acid. Determine the correct formulation of the complex and give its IUPAC name. Given atomic weight of Cr is 52. 3

11. a) Sketch the MO energy level diagram for NO and account for the differences in bond energy and bond lengths tabulated below: 2+1+1+1

Species	D_{N-O} (kJ/mol)	d_{N-O} (pm)
NO	626.86	115.1
NO^+	1046.9	106.3
NO^-	487.8	125.8

b) Choose the correct option: 1+1+1+1

(i) 



1. 2.25D 2. 1.55D 3. 1.50D 4. 3.0D

(ii) Find the pair that has the same bond order with diamagnetic and paramagnetic properties respectively.

1. F_2 and O_2 2. Li_2 and B_2 3. N_2 and O_2^{2-} 4. None of these

(iii) A neutral molecule XF_3 has zero dipole moment. The element X is most likely to be

1. Boron 2. Carbon 3. Chlorine 4. More than 1 option is correct

(iv) Type of hybridization possessed by carbanions and carbocations, respectively are

1. sp and sp^3d 2. sp^3d^2 and sp 3. sp^3 and sp^2
4. It depends on the carbocation and carbanion

OR

12. a) State and explain the Walsh diagram with orbital overlapping picture. Give the molecular orbital configuration of water molecule. 3+2

b) Discuss the 3c-4e bonding, taking a suitable example, in the light of MO concept. 4

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