

This question paper contains 8 printed pages]

Roll No.

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S. No. of Question Paper : 6492

Unique Paper Code : 32171401

Name of the Paper : Inorganic Chemistry-III : Coordination
Chemistry

Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt five questions in all.

Question No. 1 is compulsory.

1. (a) What is the number of 3d electrons associated with the transition metal in the following compounds/ions ?
- (i) K_2MnO_4 (ii) $[V(NO_2)_6]^{3-}$
- (iii) FeO_4^{2-} (iv) $K_2[Co(N_3)_4]$
- (b) Transition metals usually show variable oxidation states differing in unit of one. Explain.
- (c) Predict on the basis of trans-effect, the geometry of products [X] and [Y] which result from the following

P.T.O.

reactions :



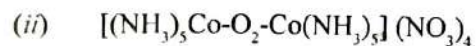
- (d) Assuming that the following ions are present in high-spin octahedral complexes, which of these ions will have a radius equal to that as expected for an ion in a spherical environment? Justify your answer.



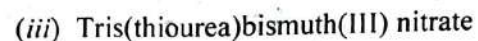
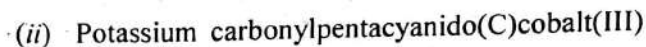
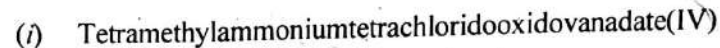
- (e) Transition metals are suitable as catalysts. Explain.

- (f) In general, UV-Visible absorption bands of transition metal ions are broad, whereas those of *f*-block metal ions are sharp. Explain. 2,2,2,3,3,3

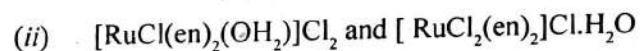
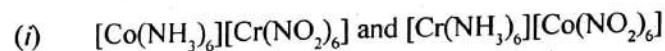
2. (a) Give the IUPAC names of the following :



- (b) Write the formulae of the following :



- (c) Name the type of isomerism in the following pairs of isomers and discuss a method to distinguish them :



- (d) Will the value of Δ_o in $[\text{CoI}_6]^{3-}$ increase or decrease if :



Give reasons in support of the choice. 6,3,3,3

3. (a) Give all possible geometrical isomers of (i) $[\text{Co}(\text{gly})_2(\text{H}_2\text{O})_2]^+$ (ii) $[\text{Cr}(\text{H}_2\text{O})_3(\text{py})_3]^{3+}$ and indicate which one of these will show optical activity.

- (b) Give the stepwise formation of $[\text{Cu}(\text{en})_3]^{2+}$ from $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Compare the stability of Cu(II) com-

plexes : $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_4(\text{en})]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$, $[\text{Cu}(\text{en})_3]^{2+}$ and explain why $k_1 < k_2 > k_3$?

- (c) Explain how Werner experimentally verified the fact that hexa-coordinated complexes are octahedral and not planar hexagonal or trigonal prismatic ? 6,5,4

4. (a) Compare the property/behaviour indicated for the following compounds. Also explain the reason for your choice.

(i) Strongly Oxidizing : CrO_3 or WO_3

(ii) Basic Oxide : CrO or CrO_3

(iii) Anomalous electronic Configuration : Nickel or Copper

- (b) (i) For a metal ion having d^6 configuration in an octahedral complex, the magnitude of crystal field splitting is $32,200 \text{ cm}^{-1}$, and the electron-pairing energy is $17,600 \text{ cm}^{-1}$. Predict whether the complex will be high spin or low spin. Calculate the crystal field stabilization energy for the predictable spin state.

- (ii) Give name of the ligand 'dmg', classify it on the basis of its denticity and show its mode of attachment to the central metal ion.

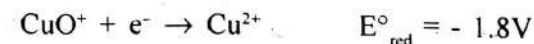
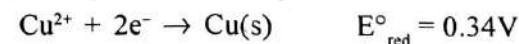
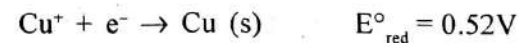
- (c) Predict and explain the following complexes would be labile or inert according to VBT ?

(i) $[\text{V}(\text{NH}_3)_6]^{3+}$ (ii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ 6,5,4

5. (a) (i) Define Jahn-Teller theorem. (ii) Hexa-coordinated structures are found to possess distorted octahedral structures due to Jahn-Teller Distortions. Rank the following compounds in terms of their degree of deviation from regular octahedral structure. (iii) Explain your reasoning with the help of crystal field splitting diagram.

$[\text{Cr}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{OH}_2)_6]^{2+}$, and $[\text{Cr}(\text{OH}_2)_6]^{3+}$

- (b) Draw the Latimer diagram for Copper in acidic medium. Given the standard reduction potentials in volts at 25°C as follows :



Based on the Latimer diagram :

- (i) Which is the most stable species?
- (ii) Which is the most oxidizing species and why?
- (iii) Calculate $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+}$ in acidic medium.
- (iv) Justify disproportionation of Cu^+ in aqueous solution.
- (c) How do the VB resonance structures $\text{M}^- \leftarrow : \text{C} \equiv \text{O} :^+$
 $\leftrightarrow \text{M}=\text{C}=\text{O}$: explain the electroneutrality principle ? 6,5,4
6. (a) Using the valence bond method, assign (i) hybridization
 (ii) Geometry and (iii) predict the magnetic moment (in Bohr magnetons) for the following two complexes :
 $[\text{Cr}(\text{en})_3]^{2+}$ and $[\text{Ni}(\text{CO})_4]$.
- (b) Draw the labelled molecular orbital energy level diagram for the complex $[\text{MnF}_6]^{4-}$ ion and give the distribution of electrons in the molecular orbitals as per the molecular orbital theory.
- (i) On adding 5 drops of 0.1 M of a solution of potassium ferricyanide (A) to 20 mL of 0.02 M ferrous sulphate solution, a blue coloured com-

pound B is obtained as major product. (i) Identify B, (ii) Predict the spin only magnetic moment of Compound A using CFT, (iii) Explain the possibility of quenching of magnetic moment of compound A and (iv) Predict and explain whether A would have spin forbidden or spin allowed d-d transition.

6,5,4

7. Attempt any *five* of the following :

- (a) What is lanthanide contraction ? What is its effect on the chemistry of 5d series of transition elements ?
- (b) Though +3 oxidation state is the most stable oxidation state for lanthanides, some lanthanides can also have an oxidation state of +2 or +4. Explain giving examples.
- (c) The CFSE is highly useful to determine whether a spinel structure would be normal or inverse. When do some AB_2O_4 compounds having transition elements as A and/or B prefer the inverse Spinel structure ?
- (d) On addition of an acidified hydrogen peroxide solution to potassium dichromate solution, a deep blue solution

- of compound A is obtained. On standing for a few seconds, the compound A decomposes and the blue colour fades away. However, if a layer of water immiscible solvent like diethyl ether is added to potassium dichromate solution before adding acidified hydrogen peroxide solution, the deep blue colour gets extracted in the ethereal layer due to the formation of B. (i) Identify the compounds A and B. (ii) Give the chemical equation involved in the formation of compound A. (iii) Give the structure of compound A.
- (e) How would you explain the high trans directing ability of pi-acceptor ligands in square planar nucleophilic substitution reactions?
- (f) It is commonly observed that d^3 and d^8 ions prefer octahedral geometry. Comment.
- (g) All tetrahedral complexes are high spin. Explain. 5×3

(5)

This question paper contains 7 printed pages]

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S. No. of Question Paper : 6493

Unique Paper Code : 32171402

Name of the Paper : Organic Chemistry-III, Heterocyclic

Chemistry

Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt six questions in all.

Question No. 1 carries 15 marks.

All other questions are of 12 marks each.

1. (a) A resolvable amine (A) is subjected to exhaustive methylation with MeI to give (B). (B), when subjected to Hofmann elimination gives (C), an alkene. On reductive ozonolysis the isolated alkene, (C), yields an equimolar mixture of methanal and pentanal. Deduce the structure of A, B and C. Write all the involved reactions and products and also justify your choice of A.

P.T.O.

- (b) Write the mechanism for acid catalyzed hydrolysis of alkyl nitriles to amides.
- (c) Indole shows electrophilic substitution at position-3 whereas pyrrole undergoes electrophilic substitution reaction at 2-position. Explain with the help of suitable structures.
- (d) Explain the order of reactivity of furan, thiophene and pyrrole towards Friedel-Crafts acylation reaction.

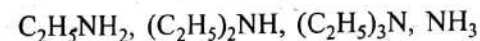
6,3,3,3

2. (a) How will you synthesize naphthalene by Howarth synthesis ?
- (b) Phenanthrene shows addition reactions at 9, 10 position. Explain.
- (c) C_1-C_2 bond in anthracene is shorter than C_2-C_3 bond. Explain with the help of appropriate structures.
- (d) Anthracene undergoes Diels-Alder reaction. Explain. Write the involved reaction.

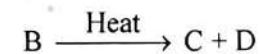
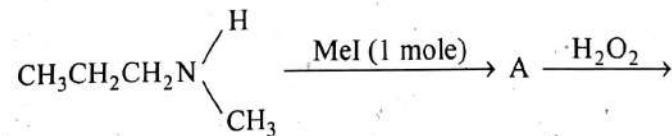
3,3,3,3

3. (a) Give the mechanism of Gabriel phthalamide synthesis and explain why neopentylamine and aniline cannot be prepared by Gabriel phthalamide synthesis.

- (b) Arrange the following in the increasing order of basicity in both the gaseous phase as well as aqueous phase, giving reasons for your answer.



- (c) Coupling reactions of diazonium salts do not take place in strongly acidic or strongly alkaline conditions. Explain using suitable structures. 4,4,4
4. (a) How will you distinguish between aniline, N-ethylaniline and N,N-diethylaniline using Hinsberg's method ?
- (b) How will primary, secondary and tertiary nitroalkanes react with nitrous acid ? Give the involved reactions.
- (c) N-ethyl-N-methylamine is chiral but non-resolvable however 2-aminobutane is resolvable. Explain, giving all the structures involved.
- (d) Complete the following reaction and also name the reaction involved in conversion of B to C & D :



3,3,3,3

P.T.O.

5. (a) How will you carry out the following conversions (any three) :

(i) Naphthalene to 1-Naphthoic acid

(ii) Benzene to 1, 3, 5-tribromobenzene

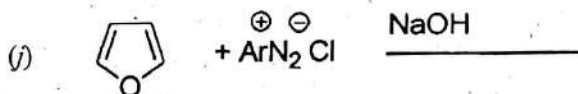
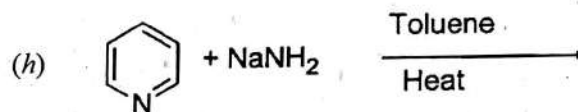
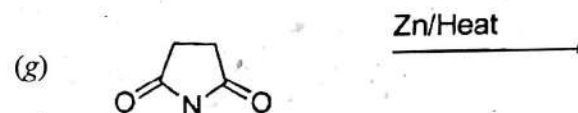
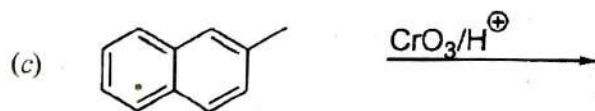
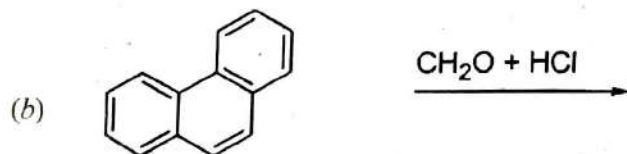
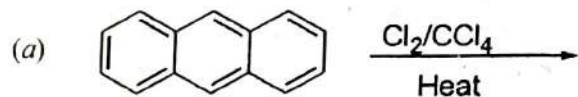
(iii) Furan to 1-acetylpyrrole

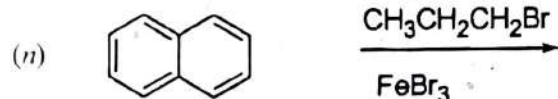
(iv) Quinoline to 8-hydroxyquinoline $3 \times 3 = 9$

(b) Pyridine is deactivated towards electrophilic substitution reaction and shows nucleophilic substitution reactions at positions-2 and 6. Explain, giving suitable structures.

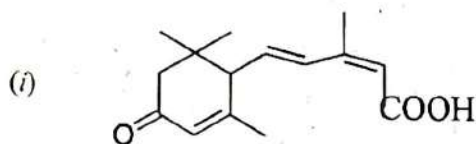
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6. Complete the following reactions (any twelve) : $12 \times 1 = 12$





7. (a) Mark out isoprene units in the following with dotted lines and name the class of terpenes to which each one of the following belongs :



- (b) Citral contains an α , β -unsaturated carbonyl group. Justify giving all the involved reactions.
- (c) How will you show the presence of the following in an alkaloid ? Explain giving suitable reactions :
- (i) N-methyl group
- (ii) Carboxylic group
- (d) Discuss the reactions which indicate the position of linkage between pyridine and N-methyl pyrrolidene in Nicotine.

8. (a) Write short notes on (any two) : 2×4=8
- (i) Friedlander synthesis of quinoline
- (ii) Knorr pyrrole synthesis
- (iii) Hantzsch synthesis for substituted pyridine
- (b) Give reasons : 2×2=4
- (i) Quinoline is less reactive than benzene for electrophilic substitution reaction in acidic medium.
- (ii) Furan gets polymerized in the acidic medium. Explain with the help of the reaction equation.



6

This question paper contains 7 printed pages.

21/5/18

Your Roll No.

Sl. No. of Ques. Paper: 6494

HC

Unique Paper Code : 32171403

Name of Paper : C X : Physical Chemistry IV

Name of Course : B.Sc. (Hons.) Chemistry

Semester : IV

Duration : 3 hours

Maximum Marks : 75

*(Write your Roll No. on the top immediately
on receipt of this question paper.)*

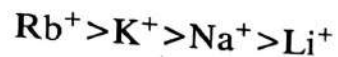
*Attempt six questions in all.
Question No. 1 is compulsory.
Attempt at least one question
from each Section.*

*Use of scientific calculator and
graph is permitted.*

1. Explain any *five* of the following:

- (a) Reactions of third and higher orders are usually not very common.
- (b) Difference between order and molecularity of a reaction.
- (c) Role of Uranyl ion in the photochemical decomposition of oxalic acid.
- (d) Equivalent conductance values for alkali metals are in the order:

P. T. O.

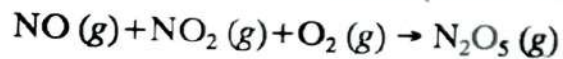


- (e) Specific conductance decreases while molar conductance increases with dilution.
- (f) The amide ion in liquid ammonia has abnormally high transference number.

5×3

SECTION A

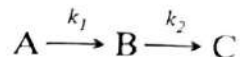
2. (a) Derive the integrated rate law equation for a second order reaction for equal concentrations of both reactants. 4
- (b) The rate constant for the decomposition of nitrogen peroxide is $0.516 \text{ L mol}^{-1} \text{ s}^{-1}$ at 592 K and $1.70 \text{ L mol}^{-1} \text{ s}^{-1}$ at 627 K. Calculate the activation energy for the reaction. 4
- (c) Given the following experimental data, find the rate law and the rate constant for the reaction:



Run	[NO] ₀ /M	[NO ₂] ₀ /M	[O ₂] ₀ /M	Initial Rate/Ms ⁻¹
1.	0.10	0.10	0.10	2.1×10^{-2}
2.	0.20	0.10	0.10	4.2×10^{-2}
3.	0.20	0.30	0.20	1.26×10^{-1}
4.	0.10	0.10	0.20	2.1×10^{-2}

4

3. (a) Consider two consecutive first order reactions:

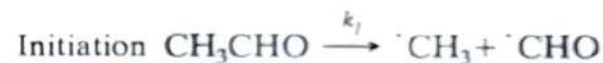


where $k_1 \neq k_2$ and at time $t=0$ only A is present. Derive expressions for [A], [B] and [C] at time t in terms of the rate constants k_1 and k_2 . Show graphically the concentrations of A, B and C as function of time for the condition $k_2 \gg k_1$. 6

- (b) The proposed mechanism for the thermal decomposition of acetaldehyde:



is as follows:



Propagation



Derive the differential rate law for the formation of CH₄ using steady state approximation:

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Also determine the chain length for this reaction. 6

4. (a) Describe the collision theory of bimolecular gaseous reactions and derive the expression for the rate constant on its basis:

P. T. O.

$$k_2 = p N_A \left\{ \pi \sigma_{AB}^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} \right\} \exp(-E_0/RT)$$

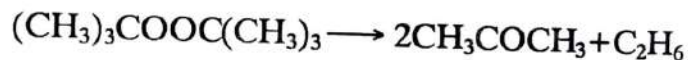
Explain the significance of the term p in the above expression.

6

- (b) The following data were obtained at a constant volume for the decomposition of di-tertiarybutyl peroxide in the gas phase at 427.7 K.

t/min	0	3	6	9	12	15	18	21
p/torr	169.3	189.2	207.1	224.4	240.2	255.0	269.7	282.6

The reaction is:



Show that the reaction is of first order and calculate its rate constant.

6

SECTION B

5. (a) Describe the moving boundary method for determining the transport number of ions. 4
- (b) A dilute solution of potassium chloride was placed between two Pt electrodes 10.0 cm apart, across which a potential of 6.0 volts was applied. How far would the K^+ ion move in 2 hours at 25°C?
- Given: Molar ionic conductance of K^+ ion at infinite dilution at 25°C is known to be $73.52 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$. 4
- (c) State the Kohlraush's law of independent migration of ions.

The molar conductance of CH_3COONa , HCl and NaCl at infinite dilution are 91.0×10^{-4} , 426.16×10^{-4} and $126.45 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ respectively at 25°C. Calculate molar conductance at infinite dilution (λ_m^0) for acetic acid. 6

6. (a) Discuss qualitatively the Debye-Hückel-Onsager theory as applied to the variation with dilution of molar conductivity of a dilute solution of a strong electrolyte. 6
- (b) Conductivity of a saturated solution of CaF_2 at 290 K was found to be $4.2 \times 10^{-5} \text{ S cm}^{-1}$. The conductivity of water used for making the solution was $2.0 \times 10^{-6} \text{ S cm}^{-1}$. The molar ionic conductivities at infinite dilution of Ca^{2+} and F^- are 104.0 and 48.0 $\text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the solubility and solubility product of calcium fluoride. 6

7. Write short notes on any *three* of the following:

- (a) Conductometric titrations
- (b) Wien effect and Debye-Falkenhagen effect
- (c) Abnormal Transference Number
- (d) Determination of hydrolysis constant of salts from conductometric measurements. 3×4

SECTION C

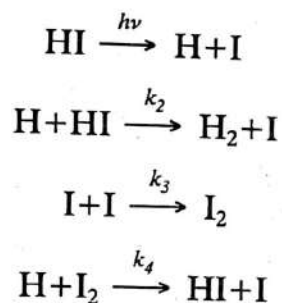
8. (a) Absorption of UV radiation decomposes acetone according to the reaction:



The quantum yield of the reaction at 280 nm is 0.2. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of $7.50 \times 10^{-3} \text{ J s}^{-1}$. Calculate the rate of formation of CO.

6

- (b) Mechanism for photochemical decomposition of HI is as follows:

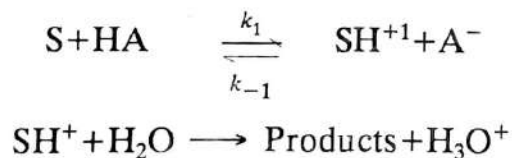


Show that quantum efficiency for this reaction is:

$$\phi = \frac{2}{1 + \frac{k_4 [\text{I}_2]}{k_2 [\text{HI}]}}$$

6

9. (a) An acid HA catalyses the substrate S to products as follows:



Derive the rate law for the reaction. State when it becomes an example of 'general acid catalysis' and when it is an example of 'specific hydrogen ion catalysis'.

6

- (b) Using the Michaelis-Menten equation for an enzyme catalysed reaction, determine the value of Michaelis constant from the following data:

6

[S] Substrate Concentration mol/dm ³	r ₀ (Initial Rate) mol dm ⁻³ s ⁻¹
0.4	2.40
1.0	4.80
2.0	7.40
3.0	8.70
4.0	9.50
5.0	10.50

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14/5

Sl - No. 7 Q.P. : 6218

Unique Paper Code : 2172401
 Name of the Paper : Conceptual Organic Chemistry
 Name of the Course : ~~B.Sc~~ Chemistry (Allied Courses)
 Semester : IV
 Duration : 3 hrs
 Maximum Marks : 75

F-10



Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt Six questions in all
3. Question 1 is Compulsory

1. Explain the following (*Any five*)

5x3=15

- a) In monosubstituted cyclohexanes, why does a substituent prefer to occupy an equatorial position?
- b) Why nitration of toluene is much faster compared to nitration of nitrobenzene? What is/are the product(s) formed in each case.
- c) Alkynes are less reactive than alkenes towards electrophilic addition reaction. Why?
- d) The addition of HCN to carbonyl compounds occurs in the presence of a catalyst, whereas addition of NaHSO₃ (sodium bisulphite) does not require any catalyst.
- e) Addition of one mole of HBr to PhCH=CHCH₃ gives different products in the presence and in the absence of peroxides.
- f) Although halogens are deactivating in aromatic electrophilic substitution but are *ortho* and *para* directors.

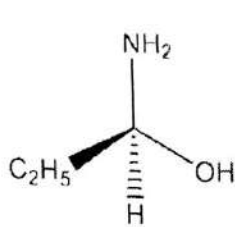
2.

- a) Define 'Conformation' and 'Configuration'. 2
- b) Draw the Newman projection for different conformations possible for butane. Discuss their stability. 3
- c) Give an account for S_N1 and S_N2 reactions mechanism. 4
- d) Aldehydes are more reactive than ketones towards nucleophilic addition reactions. Why? 3

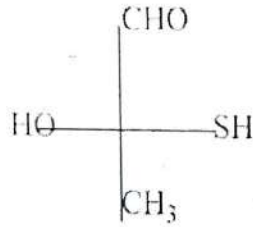
3.

a) Assign R and S configuration of the following

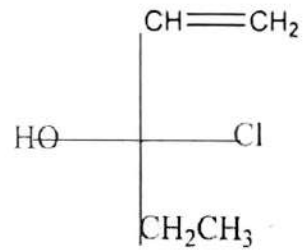
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(a)



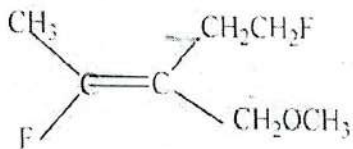
(b)



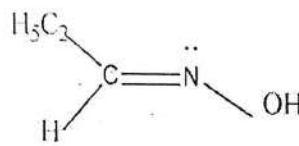
(c)

b) Assign E/Z configuration of the following

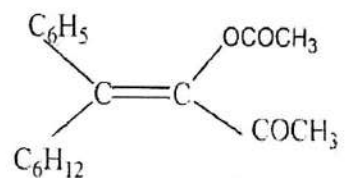
3



(a)



(b)



(c)

c) Giving mechanism involved write the structure of alcohol formed from CH₃CH=CH₂, under following conditions:

6

- i. Hydroboration- Oxidation
- ii. Oxymercuration- demercuration
- iii. Acid catalysed hydration

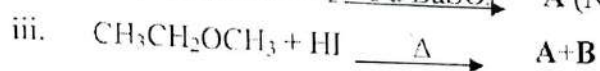
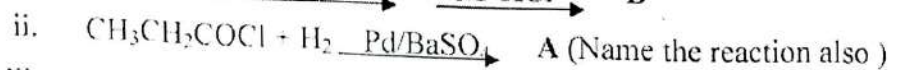
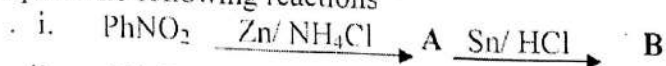
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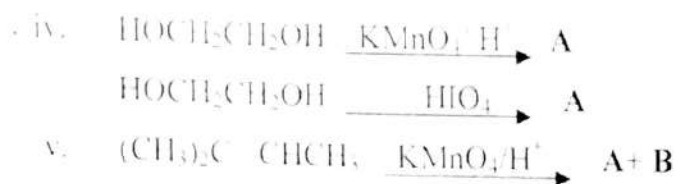
- a) Write all the stereoisomers of 2,3- Dibromobutane and give the relationship among them. 2
- b) What is Tollen's reagent. Give its reaction with propanal 2
- c) Give an account for the Hell-Volhard- Zelinsky reaction with mechanism. 3
- d) Give the mechanism for the alkaline hydrolysis of an ester. 3
- e) What is the difference between enantiomers and diastereomers? Explain with the help of suitable example. 2

5.

a) Complete the following reactions

5×1=5





- b) Why sulfonation is known as reversible electrophilic substitution reaction? 2
- c) Why phenol is more acidic than ethyl alcohol 2
- d) Draw all possible conformations of cyclohexane. Which amongst these is most stable? Give reason for your answer 3

6.

- a) Complete the following reaction and give the name and the mechanism involved 3



- b) Why chloroacetic acid is a stronger acid than acetic acid? 2
- c) Arrange the haloalkanes in the following series in the increasing order of reactivity towards $\text{S}_{\text{N}}1$ reactions 4
- i. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$; $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$; $(\text{CH}_3)_3\text{Br}$
- ii. $(\text{CH}_3)_2\text{CHBr}$; $(\text{CH}_3)_2\text{CHCl}$; $(\text{CH}_3)_2\text{CHI}$
- d) Explain Claisen condensation reaction with the help of mechanism 3

7. How will you convert 6x2=12

- a) But-1-ene to but-2-ene
- b) Propyne to cis but-2-ene
- c) Benzene to toluene via Grignard reagent
- d) Benzene to *meta*-nitrobenzoic acid
- e) Propan-1-ol to propan-2-ol
- f) Benzene diazonium chloride to phenol

8. Write short note on (Any four) 4x3=12

- a) Racemic mixture
- b) Hoffmann's elimination
- c) Friedal Craft's acylation
- d) Cross Aldol Condensation
- e) Oppenauer oxidation
- f) Iodoform reaction