

TDP (Honours) 4th Semester Exam., 2019

CHEMISTRY

(Honours)

FOURTH PAPER

(Group-A)

Full Marks : 48

Time : 2 hours

*The figures in the margin indicate full marks
for the questions*

Write the answers of each Unit in a separate book

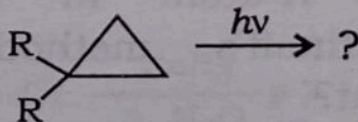
UNIT—I

(Organic Chemistry)

(Marks : 24)

Answer *any two* questions

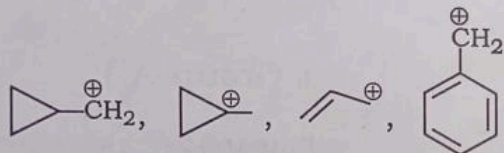
1. (a) State the hybridization state of carbon in both singlet and triplet carbene. Write the structure of the product in the following reaction :



(2)

(b) Addition of singlet carbene to *cis*- or *trans*-2-butene is stereospecific but that of triplet carbene is non-stereospecific. Explain with mechanism.

(c) Arrange the following in ascending order of stability. Justify by giving reasons :



(d) What are nitrenes? How can nitrenes be generated from methyl azide?

(e) Give two examples of reactions where benzyne forms as intermediate. Write the reactions involved. $(1+1)+3+3+(1+1)+2=12$

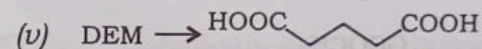
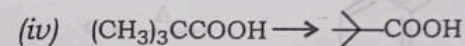
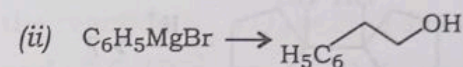
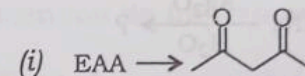
2. (a) What is abnormal Grignard reaction? Explain by taking a suitable example.

(b) Ethylacetoacetate (EAA) shows reactions for both ketone and unsaturated alcohol. Explain. Give reactions for both.

(c) How one can determine the number of active H-atom in a molecule by Zerewitinoff's method using Grignard reagent?

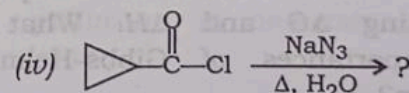
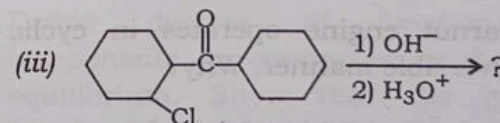
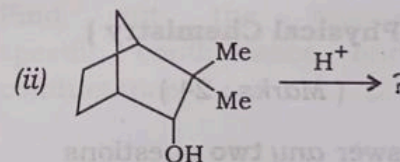
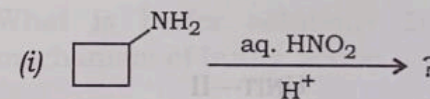
(3)

(d) Convert the following (any three) :

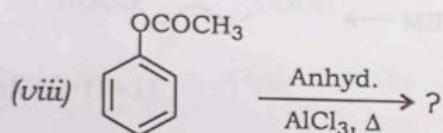
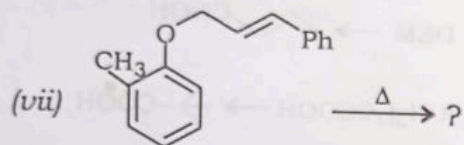
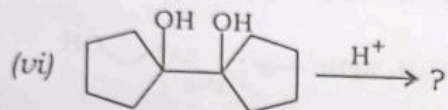
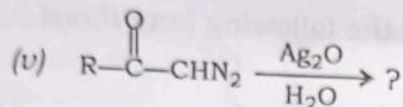


$$(1+1)+2+2+(2 \times 3)=12$$

3. (a) Write the product(s) and the mechanisms of the following reactions (any five) :



(4)



- (b) What happens when *n*-BuLi reacts with acetone? Write the reaction. $(2 \times 5) + 2 = 12$

UNIT—II

(Physical Chemistry)

(Marks : 24)

Answer any two questions

4. (a) Carnot engine operates in cyclic and reversible manner. Why?
- (b) Derive Gibbs-Helmholtz equation connecting ΔG and ΔH . What are the importances of Gibbs-Helmholtz equation?

(5)

- (c) State third-law of thermodynamics and mention its importance.

- (d) The value of equilibrium constant K_p for the reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ are 4.08×10^{-4} and 3.6×10^{-3} at 2000 K and 2500 K respectively. Calculate the enthalpy change in this temperature change.

$$2 + (3 + 1) + (1 + 2) + 3 = 12$$

5. (a) State Debye-Hückel equation and mention the significance of the symbols used in.

- (b) Derive thermodynamically Clausius-Clapeyron equation.

- (c) What is buffer solution? Discuss the mechanism of buffer action.

- (d) Find out the relation between specific conductance and equivalent conductance. $(2 + 2) + 3 + (1 + 2) + 2 = 12$

6. (a) Define degrees of freedom and components in connection with phase equilibrium. Show that the greatest number of phases that can be co-exist in equilibrium in one-component system is three.

(b) Explain the following terms :

(i) Eutectic point

(ii) Critical solution temperature

(c) pH of water at 70 °C is less than 7. Does it mean that water becomes acidic at 70 °C?

(d) In a moving boundary experiment with 0.02 (N) NaCl, a current of 0.0016 ampere moved the boundary through a distance of 6 cm in 2070 sec. Cross-section of the tube is 0.1115 cm^2 . Calculate the transport number of ions.

$$(2+2)+(1\frac{1}{2}+1\frac{1}{2})+2+3=12$$

★★★

TDP (Honours) 4th Semester Exam., 2018

CHEMISTRY

(Honours)

FOURTH PAPER

(Group-A)

Full Marks : 48

Time : 2 hours

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for the questions*

Write the answers of each Unit in a separate book

UNIT—I

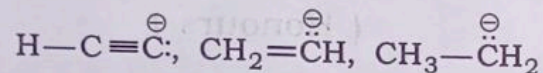
(Organic Chemistry)

(Marks : 24)

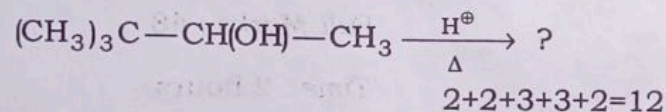
Answer any two questions

1. (a) Write the structure of carbenes.
- (b) Give two examples of reactions where carbene forms as intermediate. Write the reaction.
- (c) Explain the structure of benzyne. Why is it more reactive?

- (d) Arrange the following carbanion in increasing order of their stability. Justify by giving reasons :

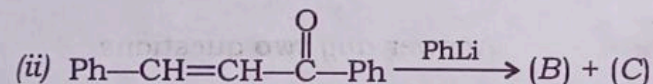
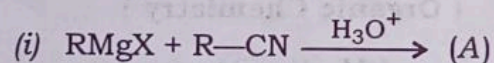


- (e) Write the product(s) and give the mechanism of the following transformation :



2. (a) Write the structure of Grignard reagent in ether.

- (b) Identify the products A, B and C in the following reactions :



- (c) Li-isopropyl when reacts with diisopropyl ketone gives 3° alcohol but (iPr)MgBr with (iPr)₂CO does not give 3° alcohol. Explain why.

- (d) Write the preparation of Dimedone from DEM and mesityl oxide.

- (e) Write the mechanism of formation of crotonic acid from EAA.

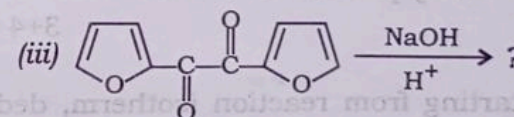
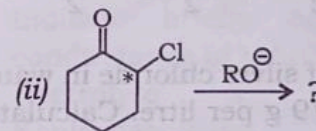
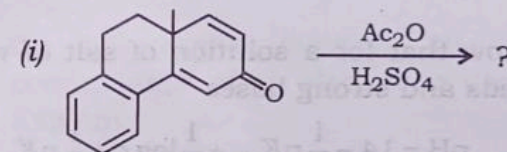
- (f) Why is EAA acidic in nature?

$$2+3+2+2+2+1=12$$

3. (a) Explain the Claisen rearrangement with suitable example.

- (b) Explain the mechanism of formation of caprolactum from cyclohexanone oxime.

- (c) Write the product(s) and the mechanisms of the following reactions :



$$3+3+(2\times 3)=12$$

(4)

UNIT—II

(Physical Chemistry)

(Marks : 24)

Answer any **two** questions

4. (a) Explain the following statements :

(i) CdI_2 shows abnormal transport number.

(ii) Hydrolysis of salts of strong acids and strong bases is not possible.

(b) What is transport number? Describe the Hittorf's method for the determination of transport number.

(c) Show that for a solution of salt of weak acids and strong bases

$$\text{pH} = 14 - \frac{1}{2} \text{p}K_w + \frac{1}{2} \log c + \frac{1}{2} \text{p}K_a$$

(d) The solubility of silver chloride in water at 25°C is 0.00179 g per litre. Calculate its solubility product at 25°C .

3+4+3+2=12

5. (a) Starting from reaction isotherm, deduce van't Hoff equation at constant pressure.

(b) Derive thermodynamically

$$F = C - P + 2$$

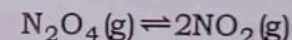
(5)

(c) Calculate the entropy change involved in the isothermal reversible expansion of 10 moles of an ideal gas from a volume of 20 litres to a volume of 40 litres at 27°C .

5+4+3=12

6. (a) An invariant point has no degree of freedom. Explain.

(b) Calculate the number of phases, components and degree of freedom in the system



(c) State Nernst heat theorem and mention its consequences.

(d) On progressive dilution, the specific conductance of an electrolyte decreases. Explain.

(e) Indicate briefly how the equivalent conductance at infinite dilution of a weak electrolyte is calculated, using Kohlrausch's law.

2½+2½+3+2+2=12

(a) Calculate the entropy change involved in the isothermal reversible expansion of 10 moles of an ideal gas from a volume of 20 litres to a volume of 40 litres at 27°C .

$$2+4+3=12$$

(b) An invariant point has no degree of freedom. Explain.

(c) Calculate the number of phases, components and degree of freedom in the system.



(d) State the Heterogeneous theorem and mention its consequences.

(e) On progressive dilution, the specific conductance of an electrolyte decreases. Explain.

(f) Indicate briefly how the equivalent conductance at infinite dilution of a weak electrolyte is calculated, using Kohlrausch's law.

TDP (Honours) 4th Semester Exam., 2017

CHEMISTRY

(Honours)

FOURTH PAPER (Group—A)

Full Marks : 48

Time : 2 hours

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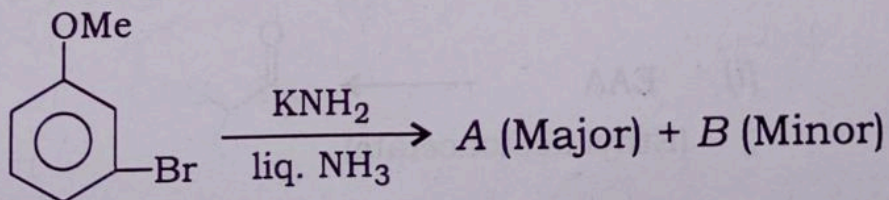
UNIT—I

(Marks : 24)

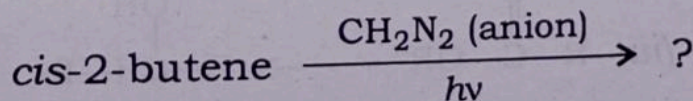
Answer any **two** questions

1. (a) Why is aryne called 1,2-dehydrobenzene rather than benzyne?

- (b) Identify A and B with proper justification :

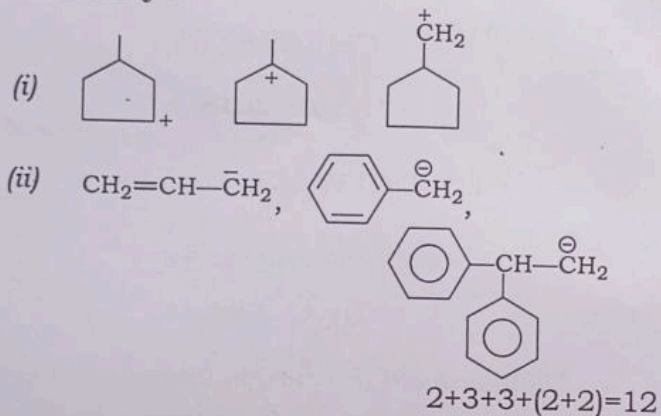


- (c) Write the mechanism of the following reaction :



(2)

- (d) Arrange the following in descending order of stability :

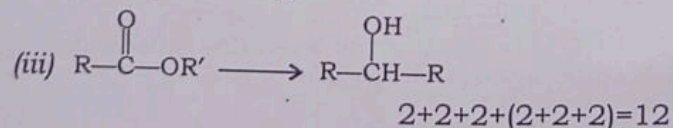
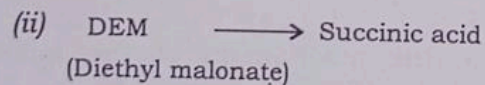
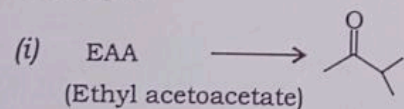


2. (a) What happens when isopropyl bromide reacts with diisopropyl ketone?

- (b) RLi with CO_2 gives $\text{R}-\text{C}(=\text{O})-\text{R}$ but RMgX gives RCOOH only. Why?

- (c) Write the preparation of diethyl malonate from ethanol.

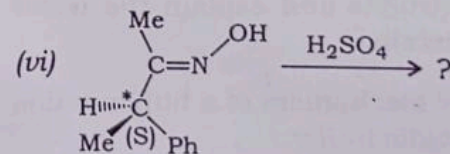
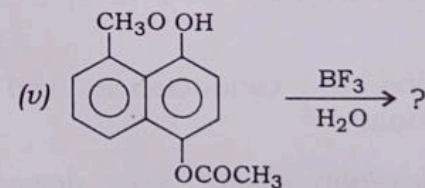
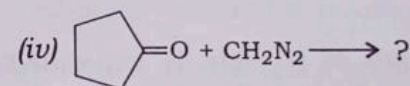
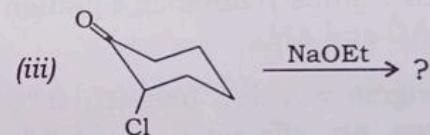
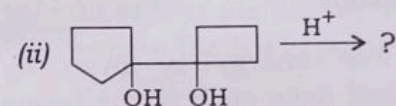
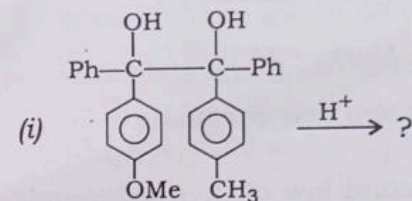
- (d) How do you perform the following reactions?



(Continued)

(3)

3. Predict the products and give probable mechanisms of the following reactions : $2 \times 6 = 12$



(4)

UNIT—II

(Physical Chemistry)

(Marks : 24)

Answer any **two** questions

4. (a) State the second law of thermodynamics in terms of entropy.
- (b) The Gibbs' free energy is given by $G = H - TS$. What does each of the terms signify? Derive Gibbs-Helmholtz equation connecting ΔG and ΔH .
- (c) A Carnot engine working between 0°C and $t^\circ\text{C}$ has an efficiency of 26.8%. Calculate t .
- (d) At 25°C 28 gm of N_2 gas is expanded isothermally and reversibly from 10 atm to 1 atm. Calculate ΔS . $2+(2+3)+3+2=12$
5. (a) Define equivalent conductance and mention its unit.
- (b) What is relaxation effect? Write down Debye-Hückel-Onsager equation for strong electrolyte and explain the terms involved therein.
- (c) Explain the mechanism of a buffer action using an acidic buffer.

(5)

- (d) What is common-ion effect? Give an example of application of solubility product principle in analytical chemistry.
- (e) Calculate the mean activity coefficient of 0.01 (M) KCl solution at 25°C .
[$A_{\text{H}_2\text{O}} = 0.509$ at 25°C] $1+3\frac{1}{2}+2\frac{1}{2}+3+2=12$
6. (a) What is triple point? "For one component system the triple point is invariant point." Explain.
- (b) Derive thermodynamically Clausius-Clapeyron equation stating all the assumptions and approximations.
- (c) Discuss the principle of steam distillation of an immiscible liquid pair.
- (d) Draw a solubility curve of phenol-water system. From the curve, explain the CST.
 $2+4+3+3=12$

For a reaction on the surface of a solid, the rate of reaction is proportional to the surface area of the solid.

(c) Calculate the rate of reaction for the reaction of 0.01 mol of A with 0.01 mol of B in a solution of 25.0 cm³ of water.

(d) What is the rate of reaction for the reaction of 0.01 mol of A with 0.01 mol of B in a solution of 25.0 cm³ of water?

(e) Explain the difference between the rate of reaction and the rate of change of concentration.

(f) Explain the difference between the rate of reaction and the rate of change of concentration.

(g) Explain the difference between the rate of reaction and the rate of change of concentration.

(h) Explain the difference between the rate of reaction and the rate of change of concentration.

(i) Explain the difference between the rate of reaction and the rate of change of concentration.

(j) Explain the difference between the rate of reaction and the rate of change of concentration.

TDP (Honours) 4th Semester Exam., 2016

CHEMISTRY
(Honours)

FOURTH PAPER (Group-A)

Full Marks : 48

Time : 2 hours

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for the questions*

Write the answers of each Unit in a separate book

UNIT—I

(Marks : 24)

Answer **any two** questions

1. (a) What are carbenes? Draw orbital diagram of both singlet and triplet carbenes.
- (b) What is trapping experiment? Write the structure of product formed when benzyne is trapped by anthracene.

(2)

- (c) Compare the stability of the following carbocations :



(A)



(B)



(C)

- (d) What are nitrenes? How can nitrenes be generated from organic azide?

$$(2+2)+(2+1)+3+2=12$$

2. (a) What are active methylene compounds? How can you synthesize the following compounds using active methylene compounds as starting materials (any two)?

(i) Butanone

(ii) Cyclobutane carboxylic acid

(iii) 5-oxo-hexanoic acid

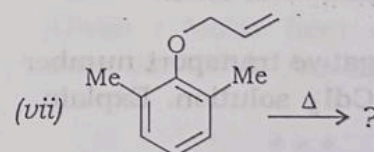
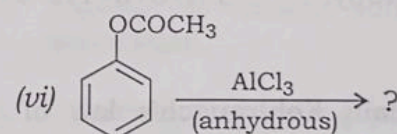
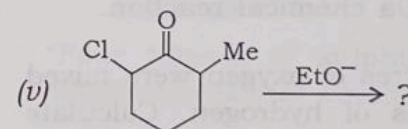
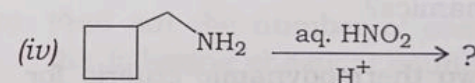
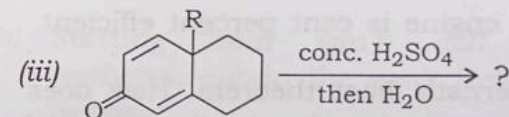
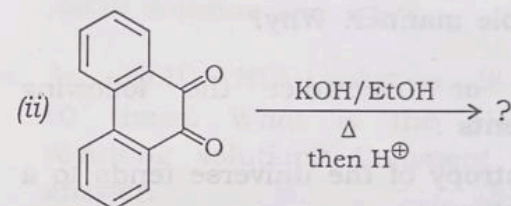
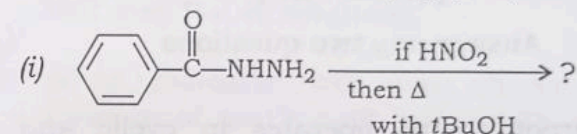
- (b) What are organolithium reagents? How are they prepared in the laboratory?

- (c) Give an example of a reaction where a Grignard reagent acts as reducing agent, not a nucleophile. What is the reason behind this behaviour?

$$(2+2+2)+(2+2)+2=12$$

(3)

3. Predict the product(s) with suitable mechanism in each case (any four) : $3 \times 4 = 12$



UNIT—II

(Marks : 24)

Answer any **two** questions

4. (a) Carnot engine operates in cyclic and reversible manner. Why?
- (b) Justify or contradict the following statements :
- (i) Entropy of the universe tends to a maximum.
- (ii) No engine is cent percent efficient.
- (c) State Nernst's heat theorem. How does this theorem give rise to third law of thermodynamics?
- (d) Indicate two thermodynamic criteria for spontaneity of a chemical reaction.
- (e) At NTP, 2.8 litres of oxygen were mixed with 19.6 litres of hydrogen. Calculate increase in entropy. $1\frac{1}{2}+3+3+1\frac{1}{2}+3=12$
5. (a) State and explain Kohlrausch's law of independent migration of ions.
- (b) Cd^{2+} has got negative transport number in concentrated CdI_2 solution. Explain.

- (c) Draw and explain the nature of conductometric titration curve between HCl and NaOH solutions.
- (d) What indicator will you choose for titration of acetic acid ($\text{p}K_a = 4.75$) with NaOH solution and why?
- (e) An $N/10$ HCl solution is diluted 10^7 times. What is the pH of the resulting solution? Comment on your answer. $3+2+3+2+2=12$
6. (a) Starting from van't Hoff reaction isotherm, obtain the van't Hoff reaction isobar.
- (b) Find out the number of components in the following chemical equilibrium :
- $$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$
- "Four phases of sulphur cannot exist simultaneously at equilibrium." Justify.
- (c) Explain the eutectic points with suitable illustration.
- (d) Calculate the boiling point of H_2O at a place where the pressure is 0.5 atm. [Given : Molar heat of vaporization of water is 40.7 kJ/mole] $4+3+2+3=12$
