(8 pages)

Reg. No. : .....

Code No. : 7770 **Sub. Code : WCHM 11**

M.Sc. (CBCS) DEGREE EXAMINATION, NOVEMBER 2023.

First Semester

Chemistry – Core

ORGANIC REACTION MECHANISM – I

(For those who joined in July 2023 onwards)

Time : Three hours Maximum : 75 marks

PART A — (15 × 1 = 15 marks)

Answer ALL questions.

Choose the correct answer :

1. The value of K_H/K_D, is less than one in the case of

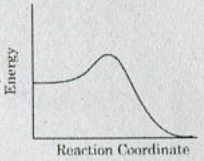
   (a) primary isotope effect

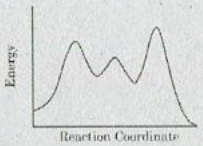
   (b) secondary isotope effect

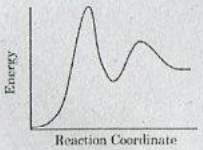
   (c) inverse isotope effect

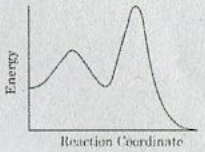
   (d) hyperconjugative effect

2. Which reaction coordinate diagram represents a mechanism where the second step is the rate determining step?

   (a) 

   (b) 

   (c) 

   (d) 

3. Carbene gives _____ when trapped with alkene.

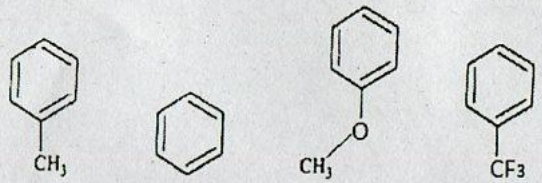
   (a) dienes

   (b) azo compounds

   (c) cyclopropane

   (d) bicyclobutane

4. What is the decreasing order of reactivity of following compounds in electrophilic substitution?



I II III IV

(a) III > I > II > IV (b) IV > I > II > III

(c) II > III > II > IV (d) I > III > II > IV

5. Nitro group is meta-directing in electrophilic aromatic substitution reactions because it

(a) increases electron density at meta-position

(b) increases electrons density at ortho and para-positions

(c) decreases electron density at meta-position

(d) decreases electron density at ortho and para-positions

6. Tropolone is

(a) non-aromatic (b) antiaromatic

(c) aromatic (d) homoaromatic

7. I^- is a better leaving group than other halides because I^- is a _____.

(a) Weak base (b) Strong base

(c) Weak acid (d) Strong acid

8. Which among the following is an ambident nucleophile?

(a) OH^- (b) CN^-

(c) Cl^- (d) NH_2^-

9. The rate of S_N2 reactions are higher in allyl chloride due to _____.

(i) stabilization of transition state by resonance

(ii) stabilization of carbocation by electron releasing group

(iii) overlapping of the nucleophile

(iv) steric effect

(a) Both (i) and (ii) (b) Both (i) and (iii)

(c) Both (ii) and (iv) (d) All the above

10. Which of the following is optically active due to presence of chiral plane?

(a) Allene (b) Spiranes

(c) Biphenyls (d) ANSA compounds

11. Which of the following has chiral axis

(a) Binaphthyl (b) Biphenyl

(c) ANSA compounds (d) Annulene

12. When HCHO reacts with CH_3MgI it gives same ethanol as it has

(a) homotopic faces (b) diastereotopic faces

(c) enantiotopic faces (d) inactive faces

13. In cyclohexane, the dihedral angle between the C-C bonds are _____.

(a) 56° (b) 60°

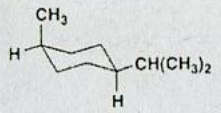
(c) 180° (d) 120°

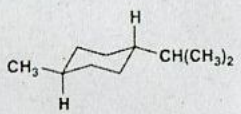
14. Anti-conformation of 1, 2-diol is less stable than _____ conformation.

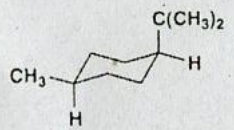
(a) eclipsed (b) gauche

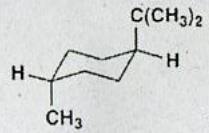
(c) both (a) and (b) (d) none of the above

15. Which is the most stable structure of 1-isopropyl-4-methylcyclohexane?

(a) 

(b) 

(c) 

(d) 

PART B — (5 × 4 = 20 marks)

Answer ALL questions, choosing either (a) or (b).

16. (a) State and explain Hammonds Postulate with an example.

Or

(b) Comment on the types, structure and stability of carbenes.

17. (a) Write a short note on aromaticity in annulenes.

Or

(b) What are the factors that influence the orientation of disubstitution in phenol and nitrobenzene?

18. (a) Discuss the mechanism of Von Richter rearrangement.

Or

(b) Write a short note on Benzyne mechanism.

19. (a) Differentiate stereoselective and stereospecific reactions with examples.

Or

(b) Explain Cram's rule with an example.

20. (a) List and discuss the conformations and relative energies of disubstituted cyclohexane.

Or

(b) Describe the conformations and properties of decalin.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

21. (a) Derive Hammett equation. How does the value of σ and ρ help in determining mechanism of a reaction?

Or

(b) Describe how the rate of a reaction helps in determining the mechanism.

22. (a) Discuss the mechanism of Friedel Crafts alkylation and acylation. Explain the reaction with nitrobenzene and aniline.

Or

(b) Discuss the mechanism of (i) S_E2 (ii) S_Ei. Give evidences.

23. (a) Give the mechanism for (i) Smiles rearrangement (ii) Bucherer reaction.

Or

(b) Explain the use of Grunwald-Winstein equation.

24. (a) Using Cahn – Ingold – Prelog's rules How can we assign RJS configuration for allenes and biphenyls.

Or

(b) Illustrate with examples (i) asymmetric synthesis (ii) asymmetric transformation.

25. (a) Discuss the conformations of cyclohexane and ring inversion.

Or

(b) State octant rule. With examples show how to predict the sign of cotton effect in decalones and steroids.

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