

Ph.D ENTRANCE EXAMINATION, APRIL 2022

CHEMISTRY

Time : Two Hours

Maximum : 100 Marks

Answer all questions.

Section A

Answer the questions in a separate sheet (provided) ; no negative mark for wrong answers.

1. The term 'umpolung' in organic reaction mechanism refers to :

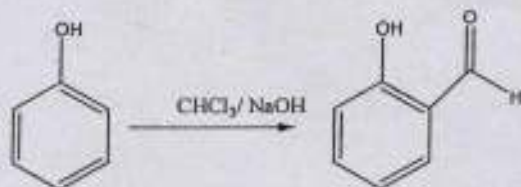
- (A) Reversal of solvent polarity.
- (B) Reversal of polarity at reaction centre.
- (C) Increase of solvent polarity.
- (D) Increase of polarity at reaction centre.

2. The following transformation denotes :



- (A) Steven's rearrangement.
- (B) Dieckmann rearrangement.
- (C) Favorskii rearrangement.
- (D) Wagner-Meerwein rearrangement.

3. The intermediate in the following reaction is :



- | | |
|----------------|------------------------|
| (A) Carbene. | (B) Free radical. |
| (C) Carbanion. | (D) Dichlororocarbene. |

Turn over

4. In which one of the following general reaction types would diethyl ether be a common choice for a solvent ?

- (A) Diels-Alder cycloadditions.
- (B) Nucleophilic substitution reactions.
- (C) Electrophilic addition reactions.
- (D) Reactions involving Grignard reagents.

5. For the following compounds I, II and III the aromatic compounds are :



I



II



III

- (A) I, II and III.
- (B) I and II only.
- (C) II and III only.
- (D) I and III only.

6. The reaction shown below proceeds through

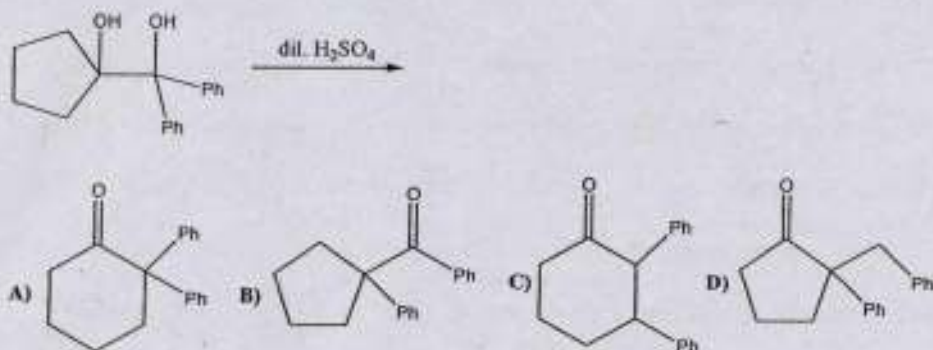


- (A) Michael addition followed by aldol condensation.
- (B) Aldol condensation followed by Michael addition.
- (C) Mannich reaction followed by aldol condensation.
- (D) McMurry coupling followed by aldol reaction

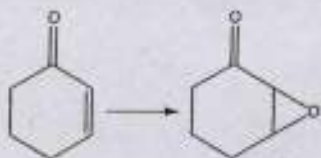
7. Claisen rearrangement is :

- (A) [2, 3] sigmatropic rearrangement.
- (B) [1, 3] sigmatropic rearrangement.
- (C) [3, 3] sigmatropic rearrangement.
- (D) [1, 5] sigmatropic rearrangement.

8. The major product of the following reaction is :



9. The most suitable reagent for achieving the following conversion is :



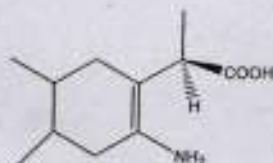
(A) m-CPBA.

(B) $\text{H}_2\text{O}_2/\text{OH}^-$.

(C) OsO_4 .

(D) SeO_2/AcOH .

10. The stereochemical notations of the given compound are :



(A) (1Z, 3S).

(B) (1E, 3R).

(C) (1Z, 3R).

(D) (1E, 3R).

11. Natural product limonene is a :
- (A) Monocyclic monoterpene. (B) Monocyclic sesquiterpene.
(C) Bicyclic sesqui terpene. (D) Acyclic monoterpone.
12. ΔH of a reaction is equal to the slope in a plot of :
- (A) ΔG versus reciprocal of Temperature.
(B) ΔG versus Temperature.
(C) $[\Delta G/T]$ versus Temperature.
(D) $[\Delta G/T]$ versus reciprocal of Temperature
13. Quantum wires represent which type of nanomaterials ?
- (A) 0-D nanomaterials. (B) 1-D nanomaterials.
(C) 2-D nanomaterials. (D) 3-D nanomaterials.
14. The phenomenon of size-tunable light emission is exhibited by :
- (A) Silica nano-particles. (B) Iron oxide nano-particles.
(C) Quantum dots. (D) Metal nano-particles.
15. In AFM, the interaction of electron beam with sample may lead to production of electrons, which undergo a single or multiple scattering events. Such electrons are termed as :
- (A) Back scattered electrons.
(B) Secondary electrons.
(C) Auger electrons.
(D) None of these.
16. The fullerene (C_{60}) consists of :
- (A) 12 hexagonal faces and 20 pentagonal faces.
(B) 20 hexagonal faces and 12 pentagonal faces.
(C) 12 hexagonal faces and 12 pentagonal faces.
(D) 20 hexagonal faces and 20 pentagonal faces.

17. For a polymer sample, the number average and weight average molar mass can be respectively obtained by

- (A) Osmometry and viscometry.
- (B) Viscometry and light scattering method.
- (C) Light scattering and sedimentation method.
- (D) Osmometry and light scattering method.

18. The grand canonical ensembles are ensembles with constant values for :

- (A) E, V and N .
- (B) E, V and μ .
- (C) T, V and N .
- (D) T, V and μ .

19. The Langmuir adsorption isotherm for a gas A_2 , undergoing dissociative adsorption is (P-the pressure).

- (A) $\theta = \frac{KP}{1 + KP}$.
- (B) $\theta = \frac{2KP}{1 + 2KP}$.
- (C) $\theta = \frac{\sqrt{KP}}{1 + \sqrt{(KP)}}$.
- (D) $\theta = (KP)^2 / 1 + (KP)^2$.

20. The value of rotational quantum number (J) corresponding to the maximum population is :

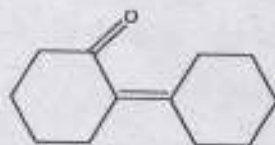
- (A) $J_{\max} = \left[\frac{kT}{2hcB} \right]^{1/2} - 1/2$.
- (B) $J_{\max} = \left[\frac{kT}{hB} \right]^{1/2} - 1/2$.
- (C) $J_{\max} = \left[\frac{hT}{cB} \right]^{1/2} - 1/2$.
- (D) $J_{\max} = \left[\frac{hcB}{kT} \right]^{1/2} - 1/2$.

21. The selection rule for the hyperfine transition in the ESR spectrum is :

- (A) $\Delta m_s = +1$ and $\Delta m_l = \pm 1$.
- (B) $\Delta m_s = \pm 1$ and $\Delta m_l = 0$.
- (C) $\Delta m_s = +1$ and $\Delta m_l = 0$.
- (D) $\Delta m_s = 0$ and $\Delta m_l = \pm 1$.

22. The residual entropy of CO molecule will be theoretically equal to :
- (A) 11.52 J/K/mol. (B) 5.76 J/K/mol.
(C) 2.88 J/K/mol. (D) Zero.
23. According to Michaelis-Menten theory of enzyme catalyst, the Michaelis constant K_m is the substrate concentration at which ?
- (A) Rate, $r = V_{\max}$. (B) Rate, $r = \frac{V_{\max}}{2}$.
(C) Rate, $r = \frac{V_{\max}}{4}$. (D) Rate, $r = V_{\max}^2$.
24. The term symbol of gaseous oxygen molecule in the ground state is :
- (A) $^1\Sigma_g^+$. (B) $^3\Sigma_g^-$.
(C) $^3\Sigma_g^+$. (D) $^2\Sigma_u^+$.
25. The commutators $[\hat{L}_x, \hat{L}_y]$ and $[\hat{L}^2, \hat{L}_y]$ will be :
- (A) Zero and zero. (B) $\hat{L}_z$ and zero.
(C) $\hat{L}_z$ and $i\hbar/2\pi \hat{L}_y$. (D) $i\hbar/2\pi \hat{L}_z$ and zero.
26. The value of the normalization constant for the solution of Φ equation in the hydrogen atom problem is :
- (A) $1/\pi$. (B) $1/2\pi$.
(C) $[1/2\pi]^{1/2}$. (D) $[1/\pi]^{1/2}$.
27. In the X-ray diffraction pattern for a BCC lattice, hkl can have :
- (A) Any value. (B) Odd values.
(C) Even values. (D) $h + k + l$ even.
28. According to Hückel Molecular Orbital (HMO) treatment, the resonance energy of 1,3-butadiene is
- (A) Zero. (B) 4.472β .
(C) 0.472β . (D) $4\alpha + 4.472 \beta$.

29. The internal energy (U) is related to the partition function (q) as :
- (A) $U = nRT^2 \left[\frac{\partial \ln q}{\partial T} \right]_v$ (B) $U = nRT^2 \left[\frac{\partial \ln q}{\partial T} \right]_p$
- (C) $U = nRT \left[\frac{\partial \ln q}{\partial T} \right]_v$ (D) $U = nRT \left[\frac{\partial \ln q}{\partial T} \right]_p$
30. How many signals do you expect to see in the ^1H NMR spectra of 2-bromopropane ($\text{CH}_3)_2\text{CHBr}$ and 1-bromopropane $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$?
- (A) 1-Bromopropane : 3 ; 2-bromopropane : 3.
 (B) 1-Bromopropane : 2 ; 2-bromopropane : 2.
 (C) 1-Bromopropane : 2 ; 2-bromopropane : 3.
 (D) 1-Bromopropane : 3 ; 2-bromopropane : 2.
31. The ^{13}C NMR spectrum of a compound A contains two signals and in the ^1H NMR spectrum there is a singlet. Which compound is consistent with these data ?
- (A) Bromoethane. (B) Acetone.
 (C) Dichloromethane. (D) Ethanol.
32. The PMR spectrum of $[\text{}^{11}\text{BH}_4^-]$ has (I of $^{11}\text{B} = 3/2$).
- (A) Quintet of equal intensity.
 (B) Quintet with intensity (1 : 4 : 6 : 4 : 1).
 (C) Quartet of equal intensity.
 (D) Quartet with intensity (1 : 3 : 3 : 1).
33. According to Woodward -Fieser rules, the theoretical value of λ_{max} for the given molecule will be



- (A) 264 nm. (B) 254 nm.
 (C) 269 nm. (D) 259 nm.

34. The $fac-[M(CO)_3L_3]$ complexes shows two C-O stretching bands in their IR spectrum. Which of the following molybdenum complexes have lowest energy stretching bands ?
- (A) $fac-[Mo(CO)_3(PF_3)_3]$. (B) $fac-[Mo(CO)_3(PCl_3)_3]$.
(C) $fac-[Mo(CO)_3(PClPh_2)_3]$. (D) $fac-[Mo(CO)_3(PMe_3)_3]$.
35. Resonance line source in AAS is :
- (A) Mg K α radiation source. (B) Hollow cathode lamp.
(C) Klyston lamp. (D) Interferometer.
36. $Fe_2(CO)_9$ cluster contains :
- (A) All terminals CO groups.
(B) Terminal CO groups and two bridging CO groups.
(C) Terminal CO groups and one bridging CO groups.
(D) Terminal CO groups and three bridging CO groups.
37. Ethane molecule in its staggered conformation belongs to the point group :
- (A) C_{2v} . (B) D_{3h} .
(C) D_{3d} . (D) C_{2h} .
38. Which is correct about DEPT 90 ^{13}C NMR spectrum :
- (A) Produce signals for all protonated carbon atoms.
(B) CH and CH_3 peaks are positive and CH_2 peaks are negative.
(C) CH and CH_3 peaks are negative and CH_2 peaks are positive.
(D) Only CH peaks are visible.
39. The sulphur-nitrogen compound that exhibits metallic type conductivity is :
- (A) $S_4N_4H_4$. (B) S_2N_2 .
(C) S_4N_4 . (D) $(SN)_x$.
40. In *phyllo* silicates, number of oxygen shared between silicon atoms will be :
- (A) 1. (B) 2.
(C) 3. (D) 4.

41. Which among the following metallocenes is having highest reducing strength ?
(A) $[(\eta^5 - \text{Cp})_2\text{Fe}]$. (B) $[(\eta^5 - \text{Cp})_2\text{Co}]$.
(C) $[(\eta^5 - \text{Cp})_2\text{Mn}]$. (D) $[(\eta^5 - \text{Cp})_2\text{Ni}]$.
42. According to Wades rule the structures of molecules $\text{C}_2\text{B}_{10}\text{H}_{12}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ are :
(A) *closo* and *nido*. (B) *arachno* and *nido*.
(C) *nido* and *arachno*. (D) *closo* and *closo*.
43. The Total Electron Count (TEC) and structure of the carbonyl cluster $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ is :
(A) 86 and *closo*. (B) 86 and *nido*.
(C) 81 and *closo*. (D) 81 and *arachno*.
44. The Re-Re bond order in $[\text{Re}_2\text{Cl}_8]^{2-}$ is :
(A) 1. (B) 2.
(C) 3. (D) 4.
45. In the molecule Cp_4Ti :
(A) All Cp rings are penta hapto.
(B) Two Cp rings are penta hapto and two Cp rings are dihapto.
(C) Two Cp rings are penta hapto and two Cp rings are monohapto.
(D) All Cp rings are monohapto.
46. Which is *incorrect* about oxy'hemocyanin ?
(A) Both Cu are in +II state.
(B) Paramagnetic in nature.
(C) Diamagnetic due to antiferromagnetic coupling.
(D) It is intensively blue coloured due to LMCT.

47. The co-ordination number and geometry of $[\text{Ce}(\text{NO}_3)_6]^{3-}$ are respectively :
- (A) 6 and octahedral. (B) 12 and icosahedral.
(C) 6 and trigonal prismatic. (D) 12 and dodecahedral.
48. The least basic hydroxide among the following is :
- (A) $\text{Dy}(\text{OH})_3$. (B) $\text{Ce}(\text{OH})_3$.
(C) $\text{Lu}(\text{OH})_3$. (D) $\text{La}(\text{OH})_3$.
49. The oxidation state of the central metal iron in *met*-hemoglobin is :
- (A) +2. (B) +3.
(C) 0. (D) +4.
50. Which of the following statement is correct about the structure of PCl_3F_2 .
- (A) The fluorine atoms prefers to occupy the planar position.
(B) The fluorine atoms prefers to occupy the axial position.
(C) One fluorine is axial and the other is planar.
(D) None of these.

(50 × 1 = 50 marks)

Section B

Each question carries 5 marks.

Answer in the space provided.

1. Briefly explain spin state crossover with suitable example.
2. Discuss the preparation and structures of fluorides of noble gas xenon.
3. State and explain the Jahn-Teller theorem.
4. Write a short note on carbon nanotubes, their synthesis and uses.
5. Outline $\text{S}_\text{N}2$ Mechanism. What is Walden inversion ?

6. Briefly Explain the Cram's rule.
7. Describe the formation, structure and chemical reactions of carbenes.
8. Briefly state the postulates of quantum mechanics.
9. Obtain the Maxwell thermodynamic relations.
10. Explain the band theory of solids.

(10 × 5 = 50 marks)