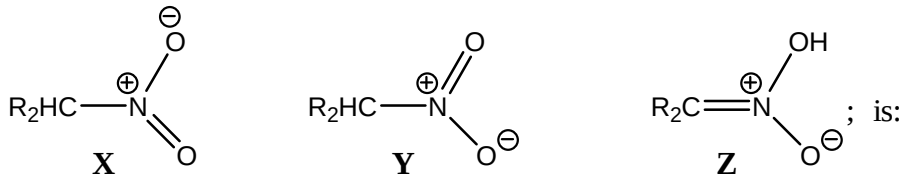
PAPER : IIT-JAM 2008

CHEMISTRY-CY

NOTE: Attempt ALL the **44 questions.** Questions 1-30 **(Objective questions)** carry ***three*** marks each and questions 31-44 **(Subjective questions)** carry ***fifteen*** marks each.

1. The correct statement describing the relationship between

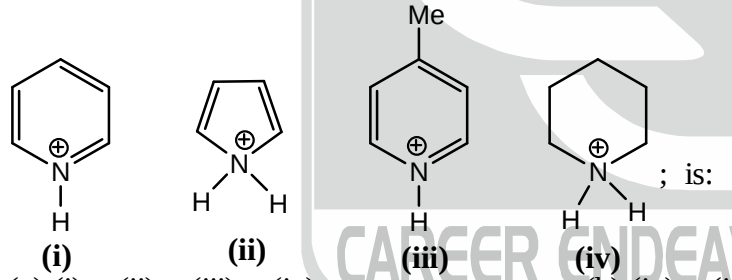


; is:

(a) X and Y are resonance structures and Z is a tautomer
(b) X and Y are tautomers and Z is a resonance structure.
(c) X, Y and Z are all resonance structures.
(d) X, Y and Z are all tautomers.

2. Among the following, the correct statement concerning the optical activity is:
(a) A molecule containing two or more chiral centres is always optically active.
(b) A molecule containing just one chiral centre is always optically active
(c) A molecule possessing alternating axis of symmetry is optically active.
(d) An optically active molecule should have at least one chiral centre.

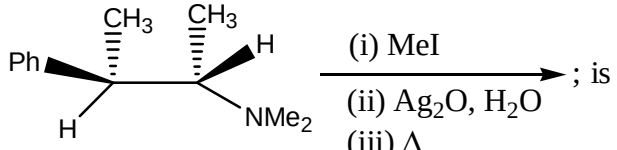
3. The correct order of acidity among.



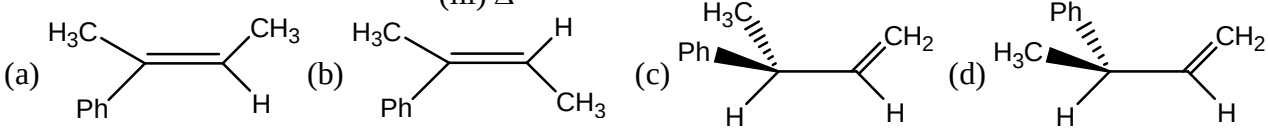
; is:

(a) (i) < (ii) < (iii) < (iv)
(b) (iv) < (iii) < (i) < (ii)
(c) (ii) < (i) < (iii) < (iv)
(d) (ii) < (iv) < (i) < (iii)

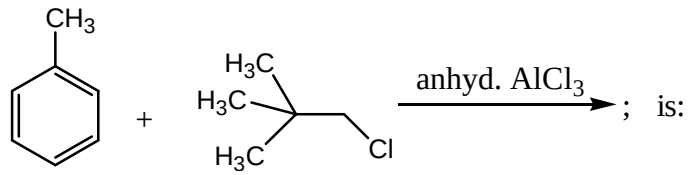
4. The major product obtained in the following reaction.



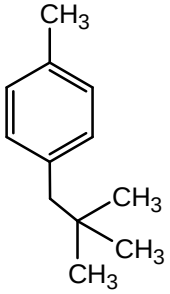
; is

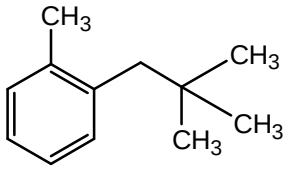


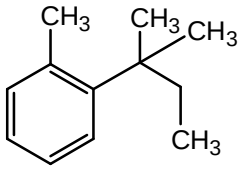
5. The major product of the following reaction

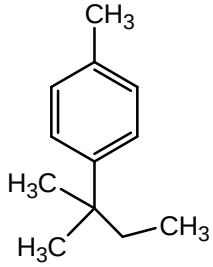


; is:

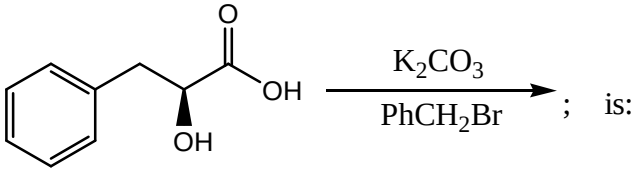
(a) 

(b) 

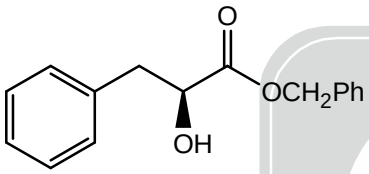
(c) 

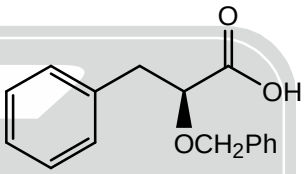
(d) 

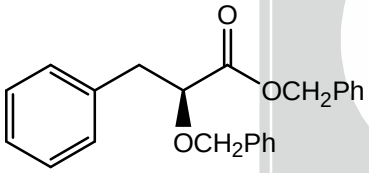
6. The major product obtained in the following reaction

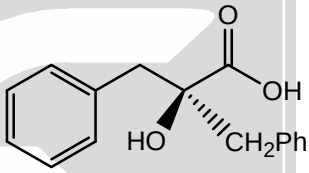


; is:

(a) 

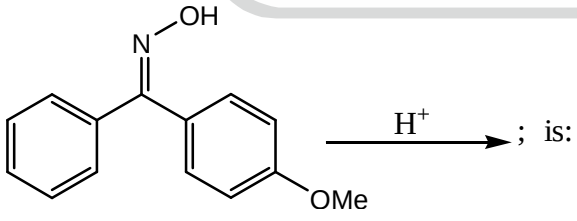
(b) 

(c) 

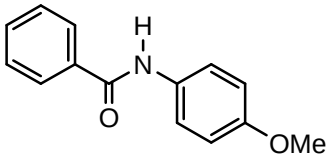
(d) 

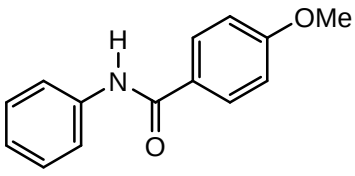
7. R(–)2–Bromooctane on treatment with aqueous KOH mainly gives 2-octanol that is:
(a) Optically active with 'R' configuration (b) Optically active with 'S' configuration
(c) A racemic mixture (d) A meso compound

8. The major product obtained in the following reaction

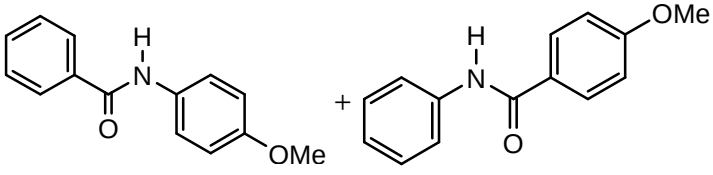


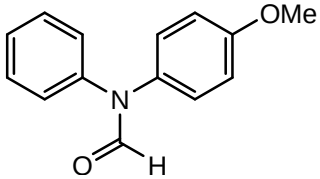
; is:

(a) 

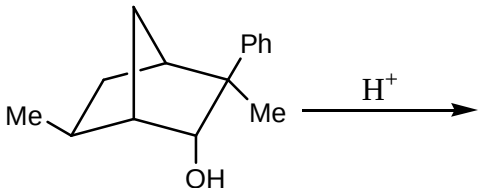
(b) 

(c) An equimolar mixture of

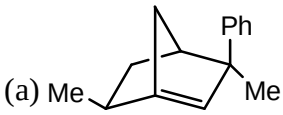


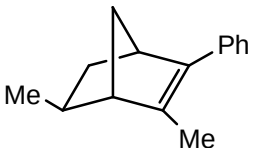
(d) 

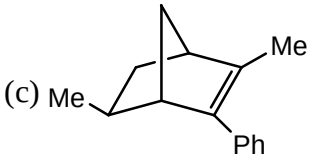
9. The major product obtained in the following reaction

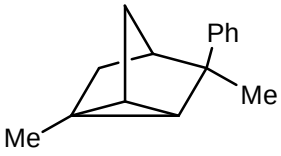


; is:

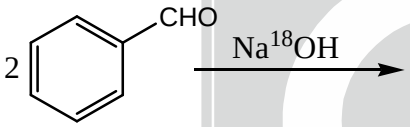
(a) 

(b) 

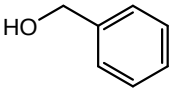
(c) 

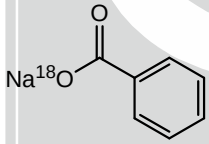
(d) 

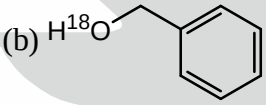
10. The products of the following reaction

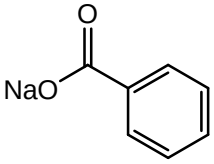


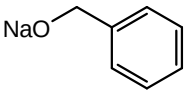
are

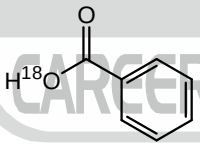
(a) 

and 

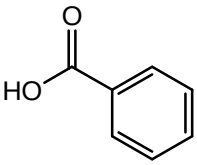
(b) 

and 

(c) 

and 

(d) 

and 

11. When one mole of of ice is converted to water at 0ºC and 1 atm, the work done (L atm) is:
(a) 1.1×10^{-4} (b) 2.0×10^{-3} (c) 2.0×10^{-4} (d) 1.1×10^{-5}.

12. When 100 g of water is reversibly heated from 50ºC to 75ºC at 1 atm, the change in entropy (JK^{-1}) of the universe is:
(a) –0.31 (b) 0.31 (c) 0 (d) 3.1

13. For a zero order reaction, units of the rate constant is expressed as
(a) M^1s^{-1} (b) M^0s^{-1} (c) $M^{-1}s^{-1}$ (d) M^0s^0

14. 1×10^{-6} moles of the enzyme carbonic anhydrase dehydrates H_2CO_3 to produce 0.6 mol of CO_2 per second. The turnover number of the enzyme is:
(a) $N_A\times6\times10^{-5}$ (b) $(1/6)\times10^{-5}$ (c) $\left(6\times10^5\right)/N_A$ (d) 6×10^5

15. Given that the most probable speed of oxygen gas is 1000 ms^{-1}, the mean/average speed (ms^{-1}) under the same conditions is:
(a) 1224 (b) 1128 (c) 886 (d) 816

16. If the electron were spin 3/2 particles, instead of spin 1/2, then the number of electrons that can be accomodated in a level are
(a) 2 (b) 3 (c) 4 (d) 5

17. For a particle in a cubic box, the total number of quantum numbers needed to specify its state are
(a) 1 (b) 2 (c) 3 (d) 9

18. The maximum number of phases that can co-exist in equilibrium for a one component system is:
(a) 1 (b) 2 (c) 3 (d) 4

19. With increasing pressure, the temperature range over which the liquid state is stable.
(a) Decreases (b) Increases
(c) Remains constant (d) Decreases till the critical pressure and then increases.

20. The conductance at infinite dilution follows the order
(a) $Li^+ > Na^+ > K^+$ (b) $Na^+ > Li^+ > K^+$ (c) $K^+ > Li^+ > Na^+$ (d) $K^+ > Na^+ > Li^+$

21. The V-shape of SO_2 is due to the presence of
(a) Two $\sigma-$ and one $\pi-$bonds.
(b) Two $\sigma-$ and two $\pi-$bonds.
(c) Two $\sigma-$bonds and one lone pair of electrons
(d) Two $\sigma-$ and two $\pi-$bonds, and one lone pair of electrons.

22. The correct order of the mean bond energies in the binary hydrides is:
(a) $CH_4 > NH_3 > H_2O > HF$ (b) $NH_3 > CH_4 > H_2O > HF$
(c) $HF > H_2O > CH_4 > NH_3$ (d) $HF > H_2O > NH_3 > CH_4$

23. In CsCl structure, the number of Cs^+ ions that occupy second nearest neighbour locations of a Cs^+ ion is:
(a) 6 (b) 8 (c) 10 (d) 12

24. In the process

$$^{234}_{92}U \longrightarrow ^{230}_{90}Th + X$$

X is:

(a) α particle (b) $\beta-$particle (c) β^+-emission (d) $\gamma-$emission

25. For tetrahedral complexes, which always exhibit high spin states, the maximum CFSE (crystal field stablization energy) is:
(a) -8 Dq (b) –12 Dq (c) –16 Dq (d) –20 Dq

26. The most abundant element in earth's crust is:
(a) Aluminium (b) Iron (c) Silicon (d) Oxygen

27. Metal-carbon multiple bonds in metal carbonyl are preferably identified from the stretching frequency of
(a) Carbon-oxygen bond (b) Metal-carbon bond
(c) Metal-oxygen bond (d) Carbon-carbon bond

28. In general, magnetic moment of paramagnetic complexes varies with temperature as
(a) T^2 (b) T (c) T^{2-} (d) T^{-1}.

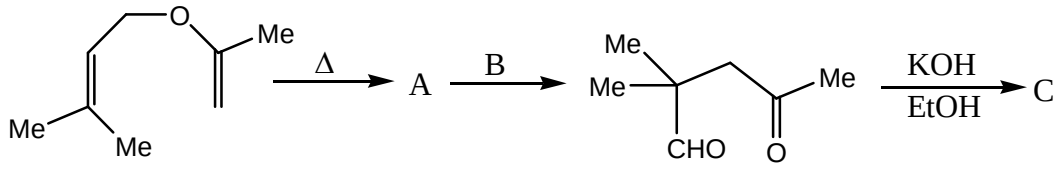
29. The compound having an S-S single bond is:

(a) $H_2S_2O_3$ (b) $H_2S_2O_4$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

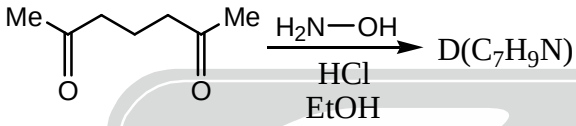
30. In a reaction, $Na_2S_2O_3$ is converted to $Na_2S_4O_6$. The equivalent weight of $Na_2S_2O_3$ for this reaction is (mol. wt. of $Na_2S_2O_3$ = M)

(a) M (b) M/4 (c) M/2 (d) M/3

31. (a) Identify A, B and C in the following reaction sequence. **[9]**

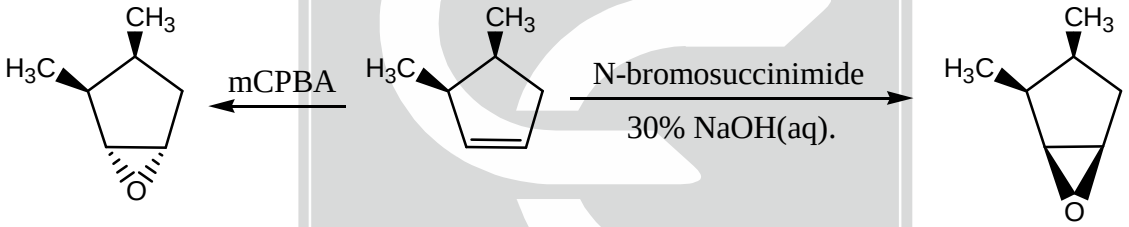


(b) Identify D in the following reaction and suggest a suitable mechanism for its formation.



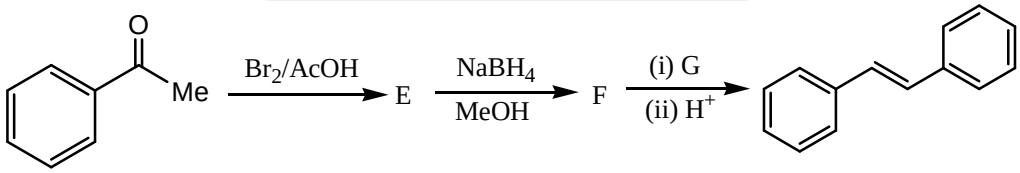
[6]

32. (a) Explain with the help of mechanisms, the observed stereoselectivity in the following epoxide formation reactions. **[9]**



(b) Explain on the basis of conformational analysis why (1R, 2S)–1, 2-dimethyl-cyclohexane is optically inactive at room temperature. **[6]**

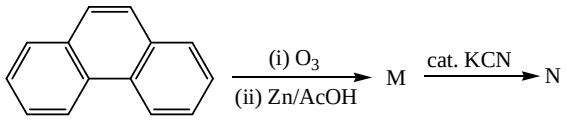
33. (a) Identify E, F and G in the following synthetic transformation: **[9]**



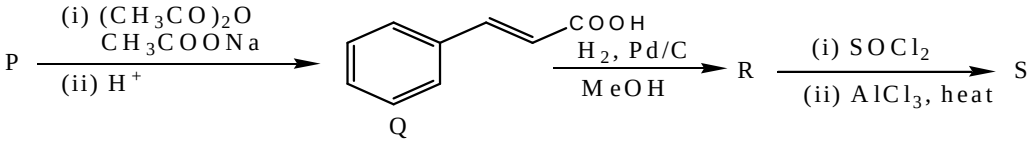
(b) An optically active compound H (C_5H_6O) on treatment with H_2 in the presence of Lindlar's catayst gave a compound I (C_5H_8O). Upon hydrogenation with H_2 and Pd/C, compound H gave J($C_5H_{12}O$). Both I and J were found to be optically inactive. Identify H, I and J. **[6]**

34. (a) A disaccharide K gives a silver mirror with Tollen's reagent. Treatment of K with MeOH/HCl gives a monomethyl derivative L, which does not react with Tollen's reagent. Methylation of K with Me_2SO_4 and NaOH affords an octamethyl derivative of K, which upon acidic hydrolysis gives a 1:1 mixture of 2, 3, 4, 6-tetra-O-methyl-D-glucose and 2, 3, 4-tri-O-methyl-D-glucose. Disaccharide K is also hydrolysed by the enzyme maltase. Identify K and L with proper stereochemistry. **[9]**

(b) Identify M and N in the following reaction sequence. **[6]**



35. In the following reaction sequence, identify P, R and S. Suggest suitable mechanism for the conversion of $P \rightarrow Q$ and $R \rightarrow S$. **[15]**



36. (a) Consider the reactions. **[9]**

(I) $Cr_2O_7^{2-} + H_2O_2 \xrightarrow{A} CrO(O_2)_2 \xrightarrow{\text{room temperature}} Cr^{3+}$

Unstable

(II) $Cr^{3+} + H_2O_2 \xrightarrow{B} CrO_4^{2-}$

(i) Identify A and B.

(ii) What is the role of H_2O_2 in (I) and how does A favour the formation of Cr^{3+}?

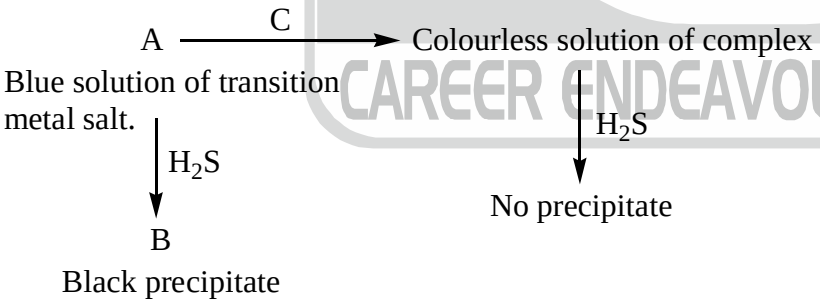
(iii) What is the role of H_2O_2 in (II) and how does B favour the formation CrO_4^{2-}?

(b) With the help of equations, illustrate the role of a cis-1, 2-diol in the titration of boric acid with sodium hydroxide. **[6]**

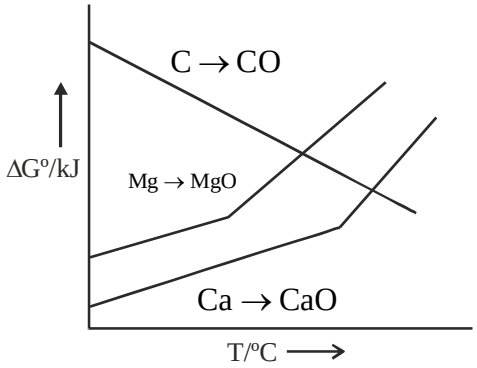
37. (a) Draw the structure of anionic Ca(II)-EDTA chelate. How many rings are formed in the chelate and specify the number of atoms in each ring? **[9]**

(b) Based on VSEPR theory draw the most stable structure of ClF_3 and XeF_4. **[6]**

38. (a) Identify A, B and C in the following reaction scheme **[9]**



(b) From the Ellingham diagram given below, identify the metal oxide that can be reduced at a lower temperature by carbon. Justify. **[6]**



39. (a) For th e complexes $\left[FeF_6\right]^{3-}$ and $\left[Fe(CN)_6\right]^{3-}$. **[9]**

(i) Show the hybridization using VB(valence bond) theory
(ii) Calculate the CFSE (crystal field stabilization energy)

(b) Identify the dark blue complex formed when $\left[Fe(CN)_6\right]^{3-}$ is treated with $FeSO_4$ and account for the origin of its colour. **[6]**

40. (a) Consider the equilibrium, $A(g) \rightleftharpoons B(g) + C(g)$ **[9]**

At a constant pressure of 1 atm, A dissociates to the extent to the extent of 50% at 500 K. Calculate ΔG^0 (kJ mol^{-1}) for the reaction.

(b) Consider the following redox system. **[6]**

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2 \qquad E^0 = 0.699 \text{ V}$$

Calculate the pH of the solution at 298 K, if the redox potential of the system is 0.817 V.

41. (a) A stream of oxygen molecules at 500 K exits from a pin-hole in an oven and strikes a slit that selects the molecules travelling in a specific direction. Given that the pressure outside the oven 2.5×10^{-7} atm, estimate the maximum distance at which the slit must be placed from the pin-hole, in order to produce a collimated beam of oxygen. (Radius of O_2 = 1.8×10^{-10} m) **[9]**

(b) Liquid water is to be circulated to transfer heat from a source to a sink at 1 atm. Considering this arrangement as a Carnot engine, calculate the maximum theoretical efficiency that can be expected from the system. **[6]**

42. (a) Using Heisenberg's uncertainty principle, derive an expression for the approximate ground state energy of a particle of mass m in a one dimensional box of length L. **[9]**

(b) The rate of a chemical reaction doubles when the temperature is changed from 300 K to 310 K. Calculate the activation energy (kJ mol^{-1}) for the reaction. **[6]**

43. (a) Consider the reaction.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) \qquad \Delta H^0 = -606.9 \text{ kJ mol}^{-1}$$ **[9]**

Assuming ideal behaviour, calculate ΔU^0 when 1 mol of CH_4 is completely oxidized at STP.

(b) A photochemical reaction was carried out using monochromatic radiation (490 nm) of intensity 100 W. When the sample was irradiated for 30 min, 0.3 mol of the reactant was decomposed. Estimate the quantum efficiency assuming 50% absorption. **[6]**

44. (a) Given that, $C_P - C_V = \dfrac{\alpha^2 TV}{\kappa_T}$ where $\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ and $\kappa_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ **[9]**

for a pure substance, show that $C_P - C_V = R$ for 1 mol of an ideal gas.

(b) Find the eigenvalues of the following 3×3 matrix given that 2 is one of the eigen values. Compute the determinant of matrix **using the eigen values.** **[6]**

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -2 \\ 1 & -1 & 1 \end{pmatrix}$$