

Entrance Examinations – 2018
Ph.D. Chemistry

TIME: 2 HOURS

MAXIMUM MARKS: 80

HALL TICKET NUMBER:

INSTRUCTIONS

1. Write your **HALL TICKET NUMBER** in the space provided above and also on the **OMR ANSWER SHEET** given to you.
2. Make sure that pages numbered from **1 - 20** are present (excluding 4 pages assigned for rough work).
3. There are eighty (80) multiple choice questions in this paper (**20 in Part-A** and **60 in Part-B**). You are required to answer all **questions of Part-A** and a **maximum of 20 questions of Part-B**. If more than the required number of questions are answered in Part-B, **only the first 20 questions attempted** will be evaluated.
4. Each question in Part-A and Part-B carries **two marks**.
5. **There is negative marking** for both Part-A and Part-B. **Each wrong answer carries - 0.66 mark.**
6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7. Hand over the OMR answer sheet to the invigilator at the end of the examination.
8. In case of a tie, the marks obtained in the first 20 questions (**Part-A**) will be used to determine the order of merit.
8. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
9. Calculators are allowed. Cell phones are not allowed.
10. Useful constants are provided just above the Part-A in the question paper.
11. OMR without hall ticket number will not be evaluated and University shall not be held responsible.

Useful Constants:

Rydberg constant = 109737 cm^{-1} ; Faraday constant = 96500 C ; Planck constant = $6.625 \times 10^{-34} \text{ J s}$;
 Speed of light = $2.998 \times 10^8 \text{ m s}^{-1}$; Boltzmann constant = $1.380 \times 10^{-23} \text{ J K}^{-1}$; Gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ = $0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ = $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$; Mass of electron = $9.109 \times 10^{-31} \text{ kg}$; Mass of proton = $1.672 \times 10^{-27} \text{ kg}$; Charge of electron = $1.6 \times 10^{-19} \text{ C}$; 1 bar = 10^5 N m^{-2} ; RT/F (at 298.15 K) = 0.0257 V ; Avogadro number = 6.022×10^{23} ; Speed of light = $3.0 \times 10^8 \text{ m s}^{-1}$

Part-A

- Choose the correct statement from the following for the titration of a solution containing magnesium and calcium ions with EDTA in the presence of solochrome black (eriochrome black T)
 - EDTA reacts first with free calcium ions, then with free magnesium ions and finally with magnesium-indicator complex
 - EDTA reacts first with free calcium ions, then with magnesium-indicator complex and finally with free magnesium ions
 - EDTA reacts first with free magnesium ions, then with magnesium-indicator complex and finally with free calcium ion
 - EDTA reacts first with magnesium-indicator complex, then with free magnesium ions and finally with free calcium ions

- The first element of the g-block would have the atomic number

[A] 120	[B] 121	[C] 122	[D] 123
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- The unit cell parameters $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$ and $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ correspond, respectively, to the crystal systems:
 - tetragonal and hexagonal
 - monoclinic and orthorhombic
 - trigonal and triclinic
 - hexagonal and tetragonal

4. The increasing order of strength of the supramolecular interactions ion-dipole, cation- π and van der Waals forces is:
- [A] ion-dipole < cation- π < van der Waals forces
[B] van der Waals forces < cation- π < ion-dipole
[C] cation- π < ion-dipole < van der Waals forces
[D] van der Waals forces < ion-dipole < cation- π
5. The principal axis of rotation (C_n) in a regular icosahedron is:
- [A] C_4 [B] C_5 [C] C_6 [D] C_7
6. Acid strength of group 15-17 hydroacids (EH_n), where E is element and n is 3, 2 or 1
- [A] increases down a group and increases horizontally from left to right
[B] decreases down a group and increases horizontally from left to right
[C] decreases down a group and decreases horizontally from left to right
[D] increases down a group and decrease horizontally from left to right
7. The compound generally used for vulcanization of rubber is:
- [A] 2-mercaptobenzothiazole [B] isooctane
[C] methyl *t*-butyl ether [D] tetraethyl lead
8. The biosynthetic precursor for steroids is:
- [A] secologanin [B] shikimic acid
[C] mevalonic acid [D] α -ketoglutaric acid
9. The byproduct formed in the Hock phenol manufacturing process is:
- [A] acetic acid [B] acetone
[C] ethanol [D] propionic acid

14. Increase in pressure decreases the melting point of ice; this is because the enthalpy and volume change of melting, ΔH and ΔV respectively are such that:
- [A] $\Delta H > 0, \Delta V > 0$
[B] $\Delta H > 0, \Delta V < 0$
[C] $\Delta H < 0, \Delta V > 0$
[D] $\Delta H < 0, \Delta V < 0$
15. The second order rate constant for the, $O + O_2 \rightarrow O_2 + O$, exchange reaction is $1.26 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The value of this rate constant in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is:
- [A] 7.59×10^5 [B] 5.79×10^5
[C] 7.95×10^5 [D] 9.75×10^5
16. If q is the single particle partition function, then the partition function for N independent and indistinguishable particles is, approximately,
- [A] q^N [B] $\frac{q^N}{N!}$
[C] Nq [D] $N \ln q$
17. A crystal has a cubic unit cell with A atoms at the corners and B atoms at the face centers. If one of the A atoms is missing in each unit cell then the formula of the compound is:
- [A] A_7B_{18} [B] A_7B_{24}
[C] A_7B_3 [D] A_3B_2
18. Variance is an important parameter in the description of error in measurements on a system. It is defined as:
- [A] square of the mean of the deviations from the mean [B] mean of the deviations from the square of the mean
[C] mean of the square of the deviations from the mean [D] square of the mean of the square of the deviations from the mean

19. Among the following electrochemical cells, the electrolyte concentration cell is:

- [A] $\text{Pt (s)} | \text{H}_2(\text{g}) | \text{HCl (aq., } a_1) | \text{AgCl} | \text{Ag (s)}$
 [B] $\text{Pt (s)} | \text{H}_2(\text{g}) | \text{HCl (aq., } a_1) || \text{NaOH (aq., } a_2) | \text{O}_2(\text{g}) | \text{Pt (s)}$
 [C] $\text{Pt (s)} | \text{H}_2(\text{g}) | \text{HCl (aq., } a_1) || \text{HCl (aq., } a_2) | \text{H}_2(\text{g}) | \text{Pt (s)}$
 [D] $\text{Pt (s)} | \text{H}_2(\text{g, } p_1) | \text{HCl (aq., } a_1) | \text{H}_2(\text{g, } p_2) | \text{Pt (s)}$

20. For a molecule, all the Raman inactive vibrations are infrared active. The symmetry point group of the molecule can be:

- [A] C_{3h} [B] D_{3h}
 [C] D_{3d} [D] C_{2v}

Part-B

21. Choose the correct statement with respect to the following two electron transfer reactions:

- (i) $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-} + [*\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-} \rightarrow [\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-} + [*\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$
 (ii) $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} + 5\text{H}_3\text{O}^+ \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{2+} + [\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+} + 5\text{NH}_4^+$

- [A] both involve outer sphere mechanism
 [B] both involve inner sphere mechanism
 [C] reactions (i) and (ii) follow inner and outer sphere mechanisms respectively
 [D] reactions (i) and (ii) follow outer and inner sphere mechanisms respectively

22. The spectroscopic ground state and the total number of electronic transitions for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ are, respectively,

- [A] ${}^3\text{A}_{2g}$ and 2 [B] ${}^3\text{T}_{1g}$ and 3
 [C] ${}^3\text{A}_{2g}$ and 3 [D] ${}^3\text{T}_{1g}$ and 2

23. Choose the correct statement with respect to the compounds Mn_3O_4 , Fe_3O_4 , and $\text{Co}^{\text{II}}(\text{Fe}^{\text{III}})_2\text{O}_4$
- [A] Fe_3O_4 and $\text{Co}^{\text{II}}(\text{Fe}^{\text{III}})_2\text{O}_4$ are inverse spinels
 [B] Mn_3O_4 and $\text{Co}^{\text{II}}(\text{Fe}^{\text{III}})_2\text{O}_4$ are inverse spinels
 [C] Mn_3O_4 and $\text{Co}^{\text{II}}(\text{Fe}^{\text{III}})_2\text{O}_4$ are normal spinels
 [D] all of these are inverse spinels
24. The complex ion $[\text{TiL}_6]^{3+}$ (L = monodentate neutral ligand) has an absorption maximum at 510 nm. The CFSE for this complex is close to:
- [A] 19608 cm^{-1} [B] 11765 cm^{-1}
 [C] 7843 cm^{-1} [D] 23530 cm^{-1}
25. The standard reduction potential (E°) of $\text{MnO}_4^{2-} + 4\text{H}^+ + 2\text{e} \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$ is 2.26 V. If the concentration of manganate is 1 M, the formal potential (E) of the above reduction at pH = 4 is:
- [A] 0.57 [B] 1.79 [C] 2.26 [D] 2.73
26. Which of the following configurations in an octahedral crystal field will have the spin magnetic moment of 2.84 B.M.?
- [A] d^4 (in strong ligand field) [B] d^3 (in weak as well as in strong ligand fields)
 [C] d^4 (in weak ligand field) [D] d^5 (in strong ligand field)
27. The cluster valence electron count and the structure of the metal framework in $[\text{Os}_6(\text{CO})_{18}]^{2-}$ are:
- [A] 82 and capped trigonal bipyramid [B] 84 and capped square-pyramid
 [C] 86 and octahedron [D] 88 and trigonal prism
28. The enzyme nitrogenase fixes N_2 in plants by evolving H_2 . The number of electrons and protons associated with the enzyme, respectively, are:
- [A] 8 and 6 [B] 3 and 4
 [C] 4 and 3 [D] 6 and 6

29. Photosystem II of photosynthesis contains:

- [A] tetranuclear magnesium cluster as the catalytic site responsible for the reduction of water
- [B] tetranuclear manganese cluster as the catalytic site responsible for the oxidation of water
- [C] tetranuclear iron cluster as the catalytic site responsible for the reduction of CO_2
- [D] tetranuclear cobalt cluster as the catalytic site responsible for the oxidation of glucose.

30. Photochemical reaction of $\text{Fe}(\text{CO})_5$ under ambient condition produces:

- [A] $\text{Fe}_2(\text{CO})_{10}$
- [B] $\text{Fe}_2(\text{CO})_9$
- [C] $\text{Fe}_3(\text{CO})_{12}$
- [D] $\text{Fe}_4(\text{CO})_{12}$

31. Among the following, the correct statement(s) for an ionophore is/are:

- (i) It is a biological species devoid of ions.
- (ii) It reversibly binds ions.
- (iii) It is a lipid soluble entity which transports ions across a cell membrane.

- [A] only (i)
- [B] only (ii)
- [C] only (iii)
- [D] (ii) and (iii)

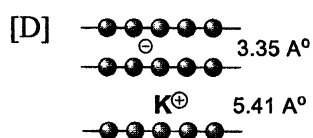
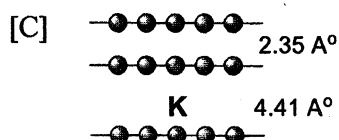
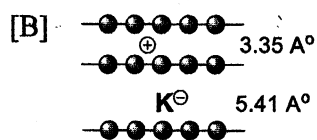
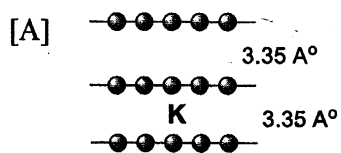
32. Given that $2(\eta^5\text{-C}_5\text{H}_5)_2\text{Co} + \text{I}_2 \rightarrow \text{Product A}$; $\text{Product A} + \text{H}^- \rightarrow \text{Product B}$, the hapticities (*i.e.*, 'n' value in η^n) of the two cyclopentadienyl rings in products A and B (both follow 18-e rule) are:

- [A] A: η^5, η^5 and B: η^5, η^4
- [B] A: η^5, η^4 and B: η^5, η^3
- [C] A: η^5, η^4 and B: η^5, η^1
- [D] A: η^5, η^3 and B: η^5, η^3

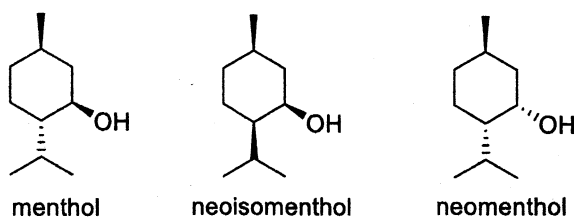
33. The number of lines expected for the X-band ESR spectrum of Cu^{2+} ion in solution state is:

- [A] 2
- [B] 3
- [C] 4
- [D] 5

40. Which of the following best represents the structure of graphite potassium intercalation compound?

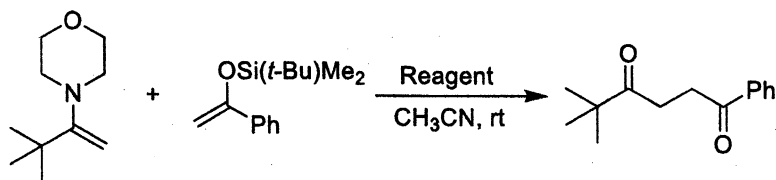


41. The increasing order of rate of esterification of the following isomeric menthols with benzoyl chloride is:



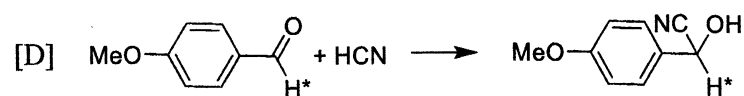
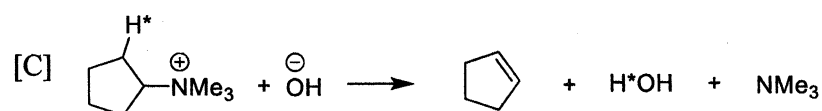
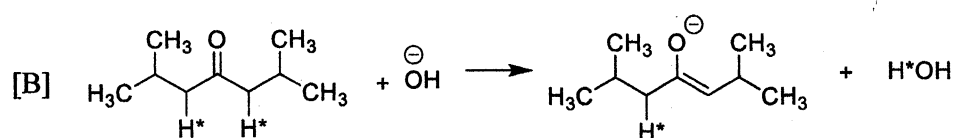
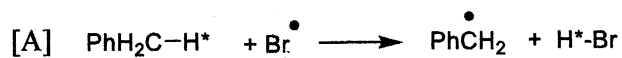
- [A] menthol < neoisomenthol < neomenthol
 [B] neomenthol < neoisomenthol < menthol
 [C] neoisomenthol < neomenthol < menthol
 [D] neomenthol < menthol < neoisomenthol

42. The suitable reagent for the following reaction is:

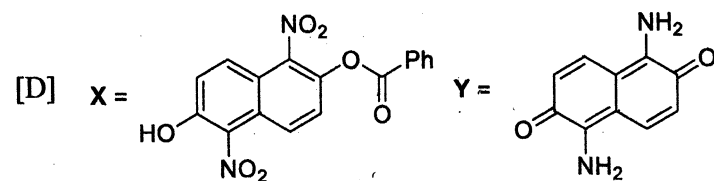
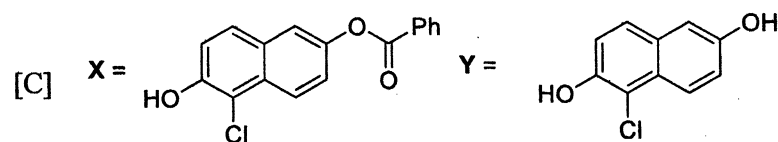
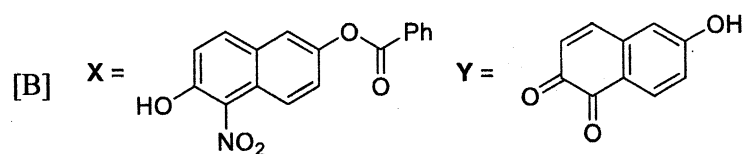
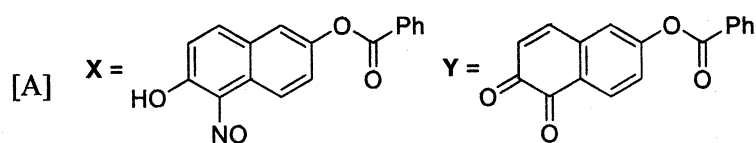
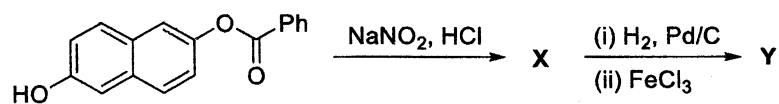


- [A] ceric ammonium nitrate (CAN) [B] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)
 [C] OsO₄ [D] RuO₄

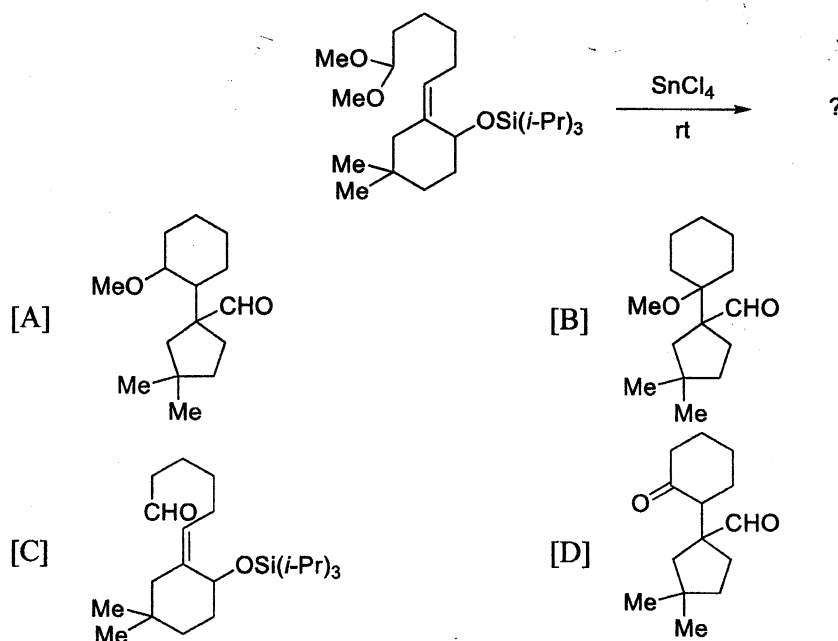
43. Which one of the following reactions does not exhibit the primary kinetic isotopic effect?



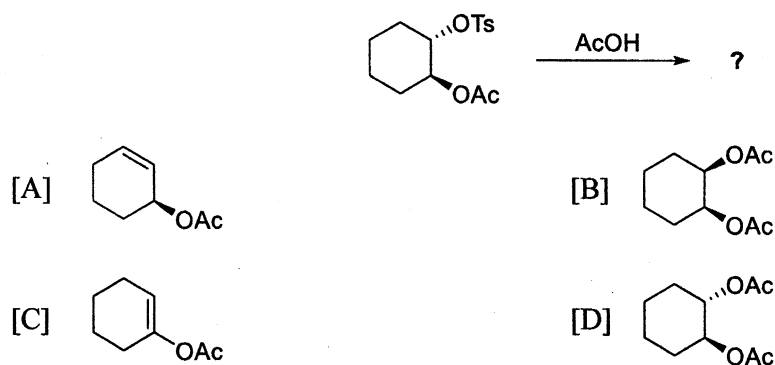
44. Identify the products X and Y of the following reaction sequence:



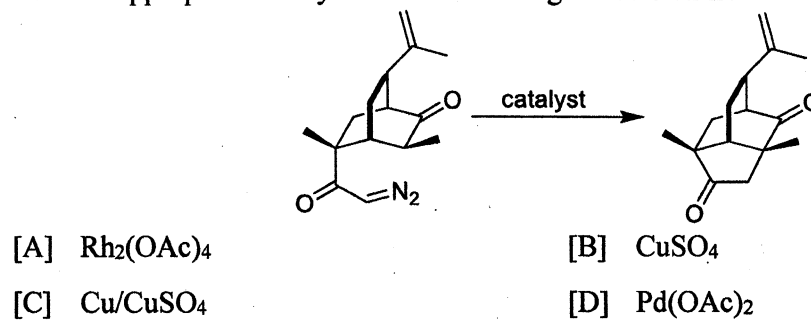
45. The major product formed in the following transformation is:



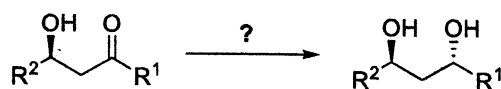
46. The major product formed in the following reaction is:



47. The most appropriate catalyst for the following conversion is:



48. The most appropriate reagent for the following stereoselective reduction is:



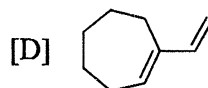
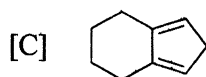
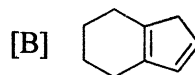
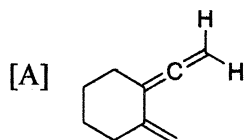
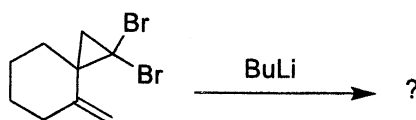
[A] NaBH_4

[B] $\text{Et}_2\text{BOMe}, \text{NaBH}_4, \text{H}_2\text{O}_2$

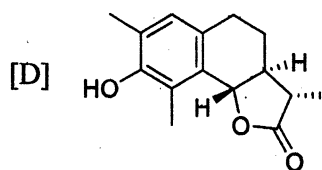
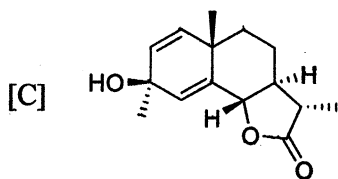
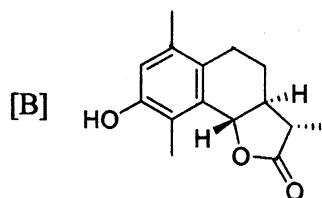
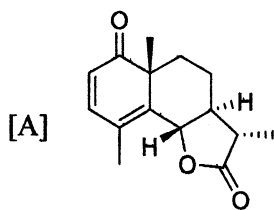
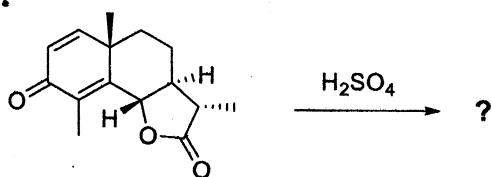
[C] LiAlH_4

[D] $\text{Me}_4\text{NBH}(\text{OAc})_3$

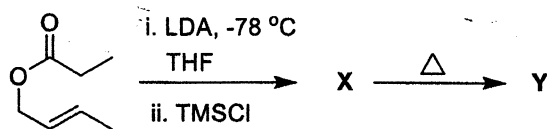
49. The major product formed in the following reaction is:

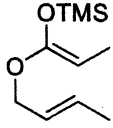
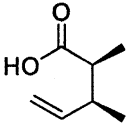
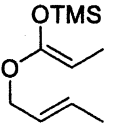
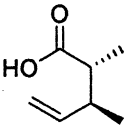
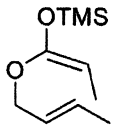
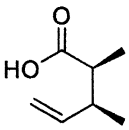
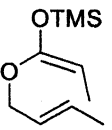
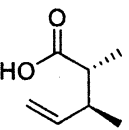


50. The major product formed in the sulfuric acid mediated rearrangement of the sesquiterpene, santonin, is:



51. The products X and Y in the following reaction are, respectively,

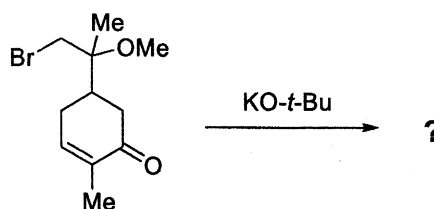


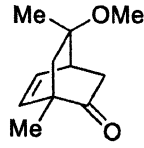
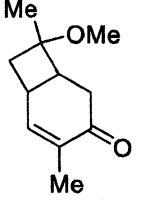
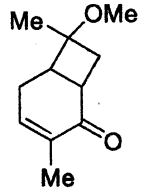
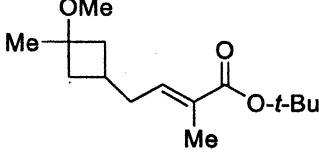
- [A]  and  [B]  and 
- [C]  and  [D]  and 

52. In the mass spectra of 4-methyl-2-pentanone and 3-methyl-2-pentanone, McLafferty rearrangement leads to peaks at m/z values of:

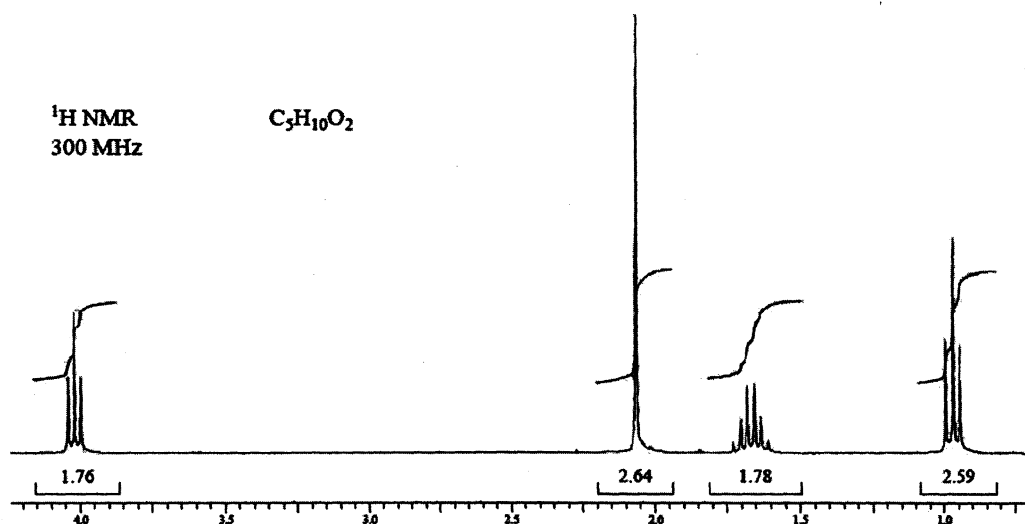
- [A] 30 and 44 respectively [B] 58 and 72 respectively
[C] 44 and 58 respectively [D] 72 and 84 respectively

53. The major product formed in the following reaction is:



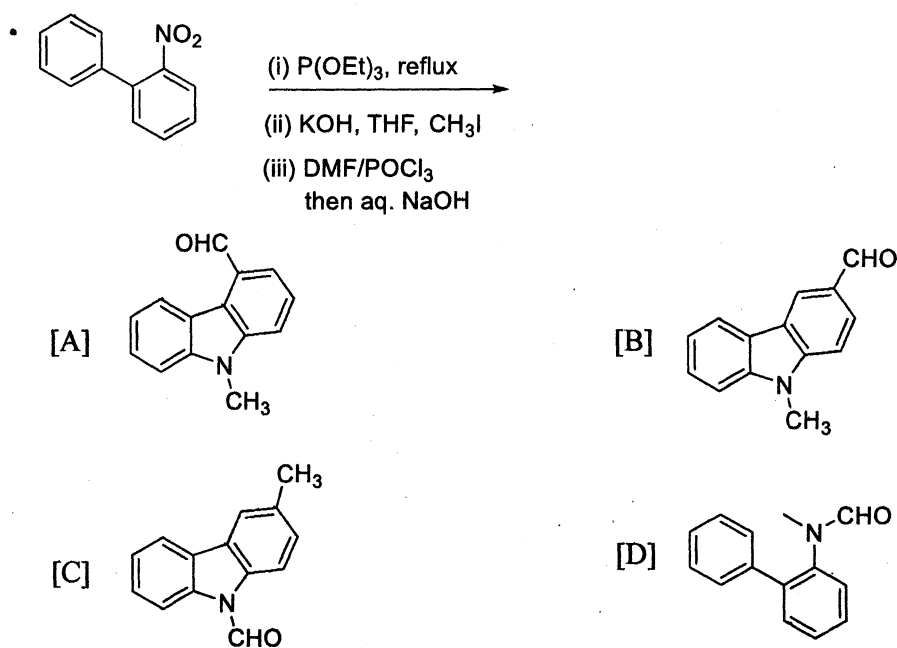
- [A]  [B] 
- [C]  [D] 

54. Compound A (C₅H₁₀O₂) gives the following ¹H-NMR spectrum. The resonances at δ = 0.95, 1.65, 2.05 and 4.00 ppm are with an intensity ratio of 3:2:3:2. Assign the most likely structure to the compound A from the options given.

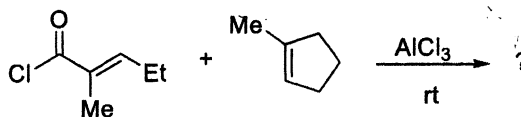


- [A] propyl acetate
[B] isopropyl acetate
[C] methyl butyrate
[D] ethyl propionate

55. Identify the product of the following reaction:

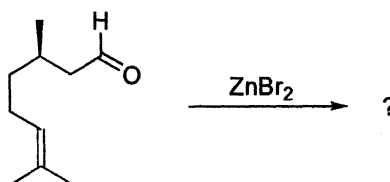


56. The major product formed in the following transformation is:



- [A]
- [B]
- [C]
- [D]

57. The major product formed in the following reaction is:



- [A]
- [B]
- [C]
- [D]

58. Acid catalyzed conversion of *p*-tosylhydrazone of 2,3-epoxy-3-methylcyclopentanone into hex-5-yn-2-one is an example of:

- [A] Eschenmoscher fragmentation [B] Grob fragmentation
 [C] Smiles rearrangement [D] Ferrier rearrangement

63. If s_a and s_b represent $1s$ orbitals of atoms H_a and H_b , respectively, in H_2 , then the valence bond wave function of ground state H_2 molecule is:

- [A] $s_a(1)s_a(2) + s_b(1)s_b(2)$ [B] $s_a(1)s_b(2) + s_a(2)s_b(1)$
 [C] $s_a(1)s_a(2) - s_b(1)s_b(2)$ [D] $s_a(1)s_b(2) - s_a(2)s_b(1)$

64. For which of the following wave functions, does the Heisenberg uncertainty relation read $\Delta x \Delta p_x = \hbar/2$.

- [A] harmonic oscillator ground state [B] hydrogen atom ground state
 [C] particle in a box ground state [D] free particle

65. A system possesses only two energy levels at 0 and $k_B T$. The energy level at $k_B T$ is doubly degenerate. The probability that the system will be in the energy state at $k_B T$ is approximately:

- [A] 0.73 [B] 0.27
 [C] 0.43 [D] 0.54

66. The number of ways that two electrons can be assigned to the spin orbitals of $3d$ subshell of an atom is:

- [A] 10 [B] 15
 [C] 30 [D] 45

67. A first order reaction, $A \rightarrow B + C$, is 35% complete in 325 s. The time required for the 90% completion of the reaction is approximately:

- [A] 836 s [B] 20 min
 [C] 30 min [D] 90 min

68. Isothermal compressibility is defined as, $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$. For a perfect gas (volume = V , temperature = T , pressure = p), κ_T is equal to:

- [A] pV [B] $p^{-1}V$
 [C] $V^{-1}T$ [D] p^{-1}

69. The temperature coefficient of the standard cell potential $\left(\frac{dE^0}{dT}\right)$ is related to the standard reaction enthalpy ($\Delta_r H^0$) as:

$$[A] \quad \Delta_r H^0 = -nF \left[TE^0 + \frac{dE^0}{dT} \right]$$

$$[B] \quad \Delta_r H^0 = -nF \left[E^0 - \frac{dE^0}{dT} \right]$$

$$[C] \quad \Delta_r H^0 = nF \left[E^0 + T \frac{dE^0}{dT} \right]$$

$$[D] \quad \Delta_r H^0 = -nF \left[E^0 - T \frac{dE^0}{dT} \right]$$

70. 1 mol of a substance A, with heat capacity $C_{p,m} = 100 \text{ J K}^{-1} \text{ mol}^{-1}$ at 270 K is heated to 300 K by placing it in contact with a very large metal block, B (with infinite heat capacity) at 300 K. The entropy change, ΔS ($\text{J K}^{-1} \text{ mol}^{-1}$) of A and B respectively are:

$$[A] \quad -10.0 \text{ and } +9.5$$

$$[B] \quad +10.0 \text{ and } -9.5$$

$$[C] \quad -10.0 \text{ and } +10.5$$

$$[D] \quad +10.5 \text{ and } -10.0$$

71. The equilibrium constant of a reaction is 10.0 and 1.0 at $T = 100 \text{ K}$ and 200 K , respectively. The enthalpy of the reaction (in cal mol^{-1}) is approximately:

$$\bullet [A] \quad 460$$

$$[B] \quad 920$$

$$[C] \quad -920$$

$$[D] \quad -460$$

72. The standard cell potential for the cell $\text{Pt (s)} | \text{H}_2(\text{g}, 1 \text{ atm.}) | \text{HCl (aq.)} | \text{AgCl (s)} | \text{Ag (s)}$ is 0.222 V. At 25°C , the measured cell potential is found to be 0.385 V. The pH of the HCl solution is:

$$[A] \quad 1.76$$

$$[B] \quad 1.38$$

$$[C] \quad 2.38$$

$$[D] \quad 2.76$$

73. Solution of a polymer with concentration of $2 \times 10^{-3} \text{ g/mL}$ at 30°C has an osmotic pressure of 0.004 atm. The average molecular weight of the polymer is:

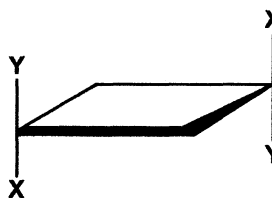
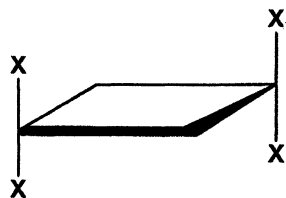
$$[A] \quad 2.48 \times 10^4 \text{ g/mol}$$

$$[B] \quad 1.24 \times 10^4 \text{ g/mol}$$

$$[C] \quad 2.60 \times 10^3 \text{ g/mol}$$

$$[D] \quad 6.20 \times 10^3 \text{ g/mol}$$

74. The point groups of the following structures are, respectively,:



[A] C_{2h} and C_{2v}

[B] C_{2v} and D_{2v}

[C] D_{2h} and C_{2h}

[D] D_{2d} and C_{2v}

75. The saturated vapor pressures of toluene and *o*-xylene are, respectively, 53 kPa and 20 kPa at 90 °C. A mixture of these two liquids boils at 90 °C when the pressure is 50 kPa. Assuming it to be an ideal mixture, the mole fraction of toluene is:

[A] 0.50

[B] 0.73

[C] 0.91

[D] 0.98

76. In a diffraction experiment using X-ray of wavelength 1.54 Å on a crystal with a cubic unit cell with lattice constant 2.96 Å, the scattering from (*hkl*) plane is observed as 31.4°. Which of the following is this Miller plane?

[A] (1 1 1)

[B] (0 0 2)

[C] (0 1 1)

[D] (0 2 1)

77. The molecule AB has reduced mass of 1.072×10^{-26} kg. The force constant of the AB bond is 1622 Nm^{-1} . The fundamental vibrational wave number of the molecule in cm^{-1} is:

[A] 690

[B] 1035

[C] 2070

[D] 4140

78. The ratio of the rotational constants, B_1/B_2 , of the isotopomers (1) $^{13}\text{C}^{15}\text{N}$ and (2) $^{12}\text{C}^{14}\text{N}$ having the same bond length of 117 pm is:

[A] 0.47

[B] 0.93

[C] 1.00

[D] 1.0

79. The rotor classification, benzene, methane and hydrogen sulphide are, respectively,:

- [A] symmetric top, spherical top and asymmetric top
- [B] symmetric top, asymmetric top and spherical top
- [C] spherical top, asymmetric top and symmetric top
- [D] asymmetric top, symmetric top and spherical top

80. The Maxwell relation that can be derived directly from the equation, $dG = Vdp - SdT$ is:

[A] $\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$

[B] $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

[C] $\left(\frac{\partial V}{\partial S}\right)_p = +\left(\frac{\partial p}{\partial T}\right)_S$

[D] $\left(\frac{\partial T}{\partial V}\right)_S = +\left(\frac{\partial p}{\partial S}\right)_V$