

Hall Ticket Number

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Q.B.No.

100249

Booklet Code :

A

Marks : 100

**JL-417-CHEM**

Time : 120 Minutes

**Paper-III**

Signature of the Candidate

Signature of the Invigilator

**INSTRUCTIONS TO THE CANDIDATE**

**(Read the Instructions carefully before Answering)**

1. Separate Optical Mark Reader (OMR) Answer Sheet is supplied to you along with Question Paper Booklet. Please read and follow the instructions on the OMR Answer Sheet for marking the responses and the required data.
2. The candidate should ensure that the **Booklet Code printed on OMR Answer Sheet and Booklet Code supplied are same.**
3. **Immediately on opening the Question Paper Booklet by tearing off the paper seal, please check for (i) The same booklet code (A/B/C/D) on each page. (ii) Serial Number of the questions (1-100), (iii) The number of pages and (iv) Correct Printing.** In case of any defect, please report to the invigilator and ask for replacement of booklet with same code within five minutes from the commencement of the test.
4. Electronic gadgets like Cell Phone, Calculator, Watches and Mathematical/Log Tables are not permitted into the examination hall.
5. **There will be 1/4 negative mark for every wrong answer.** However, if the response to the question is left blank without answering, there will be no penalty of negative mark for that question.
6. Record your answer on the OMR answer sheet by using Blue/Black ball point pen to darken the appropriate circles of (1), (2), (3) or (4) corresponding to the concerned question number in the OMR answer sheet. Darkening of more than one circle against any question automatically gets invalidated and will be treated as wrong answer.
7. Change of an answer is **NOT** allowed.
8. Rough work should be done only in the space provided in the Question Paper Booklet.
9. **Return the OMR Answer Sheet and Question Paper Booklet to the invigilator before leaving the examination hall.** Failure to return the OMR sheet and Question Paper Booklet is liable for criminal action.

This Booklet consists of 33 Pages for 100 Questions +2 pages of Rough Work  
+1 Title Page i.e. Total 36 pages

- Which one of the following molecules is *not* having lone pair of electrons on central atom ?
 

(1) $\text{SnCl}_2$	(2) $\text{XeF}_2$
(3) $\text{SCl}_2$	(4) $\text{CdBr}_2$
- Which of the following order is *correct* with respect to polars character ?
 

(1) $\text{NH}_3 < \text{H}_2\text{O} < \text{HF} < \text{H}_2\text{S}$	(2) $\text{H}_2\text{S} < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$
(3) $\text{H}_2\text{O} < \text{NH}_3 < \text{H}_2\text{S} < \text{HF}$	(4) $\text{HF} < \text{H}_2\text{O} < \text{NH}_3 < \text{H}_2\text{S}$
- In which of the following compounds formation, *d* orbitals are not involved in hybridization ?
 

(1) $\text{XeF}_2$	(2) $\text{XeO}_2\text{F}_2$
(3) $\text{XeF}_4$	(4) $\text{XeO}_4$
- The hybridization of central atom in  $\text{ClF}_5$ ,  $[\text{SbF}_5]^{2-}$ ,  $\text{ICl}_4$  respectively is :
 

(1) $sp^3d$ , $sp^3d^2$ , $sp^3d$	(2) $sp^3d^2$ , $sp^3d$ , $sp^3$
(3) $sp^3d$ , $sp^3d$ , $sp^2d$	(4) $sp^3d^2$ , $sp^3d^2$ , $sp^3d^2$
- Among the following reactions, which one differs from other reactions ?
 

(1) $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$	(2) $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$
(3) $\text{P}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3$	(4) $\text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{HClO}_4$
- Oxygen is *not* evolved when ozone reacts with :
 

(1) $\text{KI}$	(2) $\text{Hg}$
(3) $\text{H}_2\text{O}_2$	(4) $\text{SO}_2$
- Which pair of ions has same colour ?
 

(1) $\text{Cr}^{3+}$ , $\text{Mn}^{3+}$	(2) $\text{Ti}^{3+}$ , $\text{Fe}^{3+}$
(3) $\text{V}^{3+}$ , $\text{Co}^{3+}$	(4) $\text{Fe}^{3+}$ , $\text{Co}^{3+}$

8. Which of the following statements are *correct* ?

- (i) The +IV state is the predominant oxidation state for Ce.
- (ii)  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  can be easily reduced by  $\text{CaCl}_2$ .
- (iii)  $\text{Gd}^{3+}$  is intensely coloured.
- (iv)  $\text{La}^{3+}$  is paramagnetic.

- (1) (i), (ii), (iii), (iv)                      (2) (i) and (ii) only  
(3) (iii) and (iv) only                      (4) (i) and (iii) only

9. Which one of the following represents calcination process ?

- (1)  $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
- (2)  $\text{Ag}_2\text{S} + 2\text{NaCl} \xrightarrow{\Delta} 2\text{AgCl} + \text{Na}_2\text{S}$
- (3)  $2\text{Cu}_2\text{S} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{Cu}_2\text{O} + 2\text{SO}_2$
- (4)  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}\uparrow$

10. Observe the following :

Mineral	Type of Mineral
(A) Covellite	Sulphide
(B) Hydroxy apatite	Phosphate
(C) Anglesite	Sulphate
(D) Corundum	Oxide

Which of the pairs are *correctly* matched ?

- (1) A, B and C only                      (2) B and D only  
(3) A, B, C and D                      (4) C and D only

11. Which of the following statements are *correct* ?
- (i) Zinc spelter contains some impurities such as Cd and Pb.
- (ii) Cupellation is a method used to refine metals having oxidisable impurities.
- (iii) Barite is beryllium ore.
- (1) (i), (ii) and (iii)                      (2) (i) and (ii) only
- (3) (ii) and (iii) only                      (4) (i) and (iii) only
12. The following reactions represent concentration of ore by leaching :
- $$\text{Ag}_2\text{S} + \text{NaCN} \rightarrow \text{A}$$
- $$\text{A} + \text{Zn} \rightarrow \text{B} + \text{Ag}$$
- A and B are respectively :
- (1)  $\text{Na}_3[\text{Ag}(\text{CN})_3]$ ,  $\text{Na}_2[\text{Zn}(\text{CN})_4]$       (2)  $\text{Na}[\text{Ag}(\text{CN})_2]$ ,  $\text{Na}[\text{Zn}(\text{CN})_3]$
- (3)  $\text{Na}_2[\text{Zn}(\text{CN})_4]$ ,  $\text{Na}_2[\text{Ag}(\text{CN})_4]$       (4)  $\text{Na}[\text{Ag}(\text{CN})_2]$ ,  $\text{Na}_2[\text{Zn}(\text{CN})_4]$
13. Which of the following metals can be refined by cupellation ?
- (1) Ag    (2) Ti
- (3) Al    (4) Mn
14. Which of the following statements is *true* about the magnetic behaviour of the complexes,  $\text{Ni}(\text{CO})_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{NiCl}_4^{2-}$  ?
- (1)  $\text{Ni}(\text{CO})_4$  and  $\text{NiCl}_4^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic
- (2)  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $\text{Ni}(\text{CO})_4$  is paramagnetic
- (3)  $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{NiCl}_4]^{2-}$  is paramagnetic
- (4)  $\text{Ni}(\text{CO})_4$  is diamagnetic and  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic

15. Which of the following configurations, for an octahedral first row  $d$ -block metal ions is expected to show orbital contribution to magnetic moment ?

- (1)  $t_{2g}^2$  (2)  $t_{2g}^3$   
(3)  $t_{2g}^6 e_g^1$  (4)  $t_{2g}^6 e_g^2$

16. Choose the *correct* order of energies of  $d$  orbitals in linear geometry :

- (1)  $d_{xy} \approx d_{xz} \approx d_{yz} < d_{x^2-y^2} < d_{z^2}$   
(2)  $d_{xy} \approx d_{x^2-y^2} < d_{xz} \approx d_{yz} < d_{z^2}$   
(3)  $d_{xy} < d_{x^2-y^2} < d_{xz} \approx d_{yz} < d_{z^2}$   
(4)  $d_{z^2} < d_{xz} \approx d_{yz} = d_{xy} \approx d_{x^2-y^2}$

17. The octahedral complex/complex ion which exists as facial and meridional isomers is :

- (1) Tris (ethylenediamine) cobalt (III)  
(2) Dichlorodiglycinato cobalt (III)  
(3) Triglycinato cobalt (III)  
(4) Trioxalato cobaltate (III)

18. Term symbol for an empty or completely filled subshell is :

- (1)  $^1S_0$  (2)  $^1D_2$   
(3)  $^3P_0$  (4)  $^1P_0$

19. Which of the following trends has a negative correlation with hardness ?

- (1) Oxidation state (2) Polarizability  
(3) Electronegativity (4) Charge density

20. According to Irving-William series of stability, for a given ligand, the order of stability of complexes formed from depositive metal ions,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Fe^{2+}$  and  $Cu^{2+}$  is :

- (1)  $Ba^{2+} < Fe^{2+} < Cu^{2+} < Sr^{2+}$  (2)  $Sr^{2+} < Ba^{2+} < Fe^{2+} < Cu^{2+}$   
(3)  $Ba^{2+} < Sr^{2+} < Fe^{2+} < Cu^{2+}$  (4)  $Ba^{2+} < Fe^{2+} < Cu^{2+} < Sr^{2+}$

21. Match the following :

Complex	log K value
(A) $[\text{Fe}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	(I) 7.7
(B) $[\text{Fe}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$	(II) 3.7
(C) $[\text{Fe}(\text{trien})(\text{H}_2\text{O})_2]^{2+}$	(III) 8.8

	(A)	(B)	(C)
(1)	(I)	(II)	(III)
(2)	(II)	(I)	(III)
(3)	(III)	(II)	(I)
(4)	(II)	(III)	(I)

22. Identify the *correct* sequence of trans-effect in the substitution reactions involving Pt(II) and the ligands  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{NO}_2^-$ .

- |   |   |
|---|---|
| (1) $\text{OH}^- > \text{Cl}^- > \text{NO}_2^- > \text{CN}^-$ | (2) $\text{NO}_2^- > \text{Cl}^- > \text{OH}^- > \text{CN}^-$ |
| (3) $\text{CN}^- > \text{NO}_2^- > \text{Cl}^- > \text{OH}^-$ | (4) $\text{Cl}^- > \text{OH}^- > \text{NO}_2^- > \text{CN}^-$ |

23. Which of the following statements is/are *correct* about electron transfer reactions through inner sphere mechanism ?

- (a) The rate of electron transfer increases if the bridging ligand has unsaturation in the structure.
- (b) The rate of electron transfer decreases with increase in the nucleophilic character of the bridging ligand.
- (c) Inner sphere electron transfer reactions are faster than similar reactions occurring through outer-sphere mechanism.

- |                 |                 |
|-----------------|-----------------|
| (1) (a) and (b) | (2) (b) and (c) |
| (3) (a) and (c) | (4) (a) only    |

24. Conjugate acid of  $[\text{Ti}(\text{OH}_2)_5(\text{OH})]^{2+}$  is :

- (1)  $[\text{Ti}(\text{OH}_2)_6]^{3+}$
- (2)  $[\text{Ti}(\text{OH}_2)_4(\text{OH})_2]^+$
- (3)  $[\text{Ti}(\text{OH}_2)_5\text{O}]^+$
- (4)  $[(\text{H}_2\text{O})_4\text{Ti}(\mu\text{-OH})_2\text{Ti}(\text{OH}_2)_4]^{4+}$

25. Which of the following complexes have/has thermodynamic stability but is/are kinetically inert ?
- (A)  $[\text{Ni}(\text{CN})_4]^{2-}$   
(B)  $[\text{Cr}(\text{CN})_6]^{3-}$   
(C)  $[\text{Mn}(\text{CN})_6]^{3-}$
- (1) (A) and (B) (2) (B) only  
(3) (B) and (C) (4) (A) only
26. Which is isolobal with  $-\text{CH}_3$  ?
- (1)  $\text{Fe}(\text{CO})_5$  (2)  $\text{Cr}(\text{CO})_5$   
(3)  $\text{Ni}(\text{CO})_3$  (4)  $\text{Mn}(\text{CO})_5$
27. The total number of metal-metal bonds in  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  respectively is :
- (1) 3 and 6 (2) 4 and 5  
(3) Zero and 4 (4) 3 and 4
28. In oxyhemoglobin, the coordinated dioxygen is best described by which of the following ?
- (1) Molecular  $\text{O}_2$  with linear  $\text{Fe}-\text{O}-\text{O}$   
(2) Molecular  $\text{O}_2$  with bent  $\text{Fe}-\text{O}-\text{O}$   
(3)  $[\text{O}_2]^-$   
(4)  $[\text{O}_2]^{2-}$
29. In the binding of oxygen to myoglobin, the relationship between the concentration of oxygen and the fraction of binding sites occupied, can be described as :
- (1) Sigmoidal (2) Linear with -ve slope  
(3) Linear with +ve slope (4) Hyperbolic
30. The oxidation states of the copper ions and of the  $\text{O}_2$  ligand in oxyhemocyanin are :
- (1) One  $\text{Cu}(\text{I})$ , one  $\text{Cu}(\text{II})$  and one  $\text{O}^{2-}$   
(2) Two  $\text{Cu}(\text{II})$  ions and one  $\text{O}_2^{2-}$   
(3) Two  $\text{Cu}(\text{II})$  ions and one  $\text{O}^{2-}$   
(4) One  $\text{Cu}(\text{I})$ , one  $\text{Cu}(\text{II})$  and one  $\text{O}_2^{2-}$

31. Which of the following statements are *correct* ?
- (i) HPLC is a liquid-liquid chromatography technique.
  - (ii) GC technique can be used for volatile compounds only.
  - (iii) Silica gel-G is the stationary phase of column chromatography technique.
- (1) (i) and (ii) only                      (2) (i), (ii) and (iii)
- (3) (ii) and (iii) only                      (4) (i) and (iii) only
32. Which of the following is *not* the term related to chromatography ?
- (1) Adsorption                                  (2) Retention
- (3) Absorption                                  (4) Partition
33. Which one of the following Gas-chromatography detectors uses  $N_2$  as the carrier gas ?
- (1) Electron capture detector              (2) Flame ionization detector
- (3) Thermal conductivity detector      (4) Fluorescence detector
34. One of the statements about Henry's law  $P = K_H X$  is correct ( $P =$  Pressure,  $K_H =$  Henry's constant,  $X =$  mole fraction) :
- (1) Intercept gives Henry's constant  $K_H$
- (2)  $K_H$  values of all gases are same
- (3)  $K_H$  is inversely related to solubility of gas
- (4)  $K_H$  is independent of nature of gas



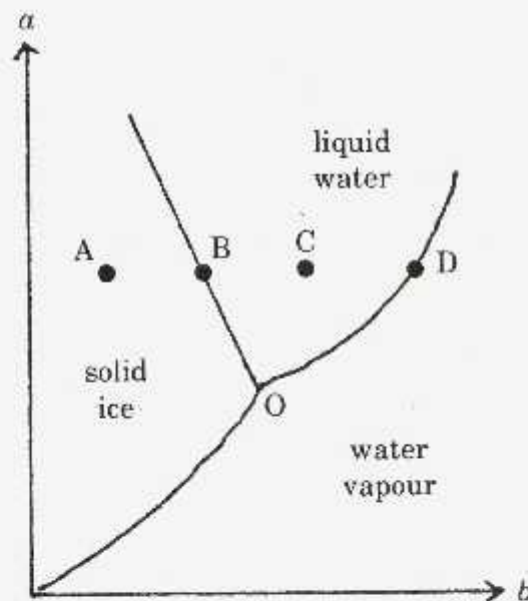
35. 3% (W/W) aqueous solution of a solute (molar mass  $60 \text{ g mol}^{-1}$ ) is with same boiling point as the 9% aqueous solution of  $x$ . Calculate the molecular mass of  $x$  in  $\text{gms mol}^{-1}$  :

- (1) 19.186 (2) 191.86  
 (3) 60 (4) 180

36. At 300 K, 25 g of a non-volatile solute dissolved in 1000 mL of water gave an osmotic pressure of 3 atm. What is the concentration (in  $\text{mol L}^{-1}$ ) of the solution ?

- (1)  $\frac{1}{8.2}$  (2)  $\frac{1}{82}$   
 (3)  $\frac{25}{8.2}$  (4)  $\frac{1}{8.2 \times 25}$

37. The phase diagram of water is shown below ( $a = \text{pressure}$ ;  $b = \text{temperature}$ ) :

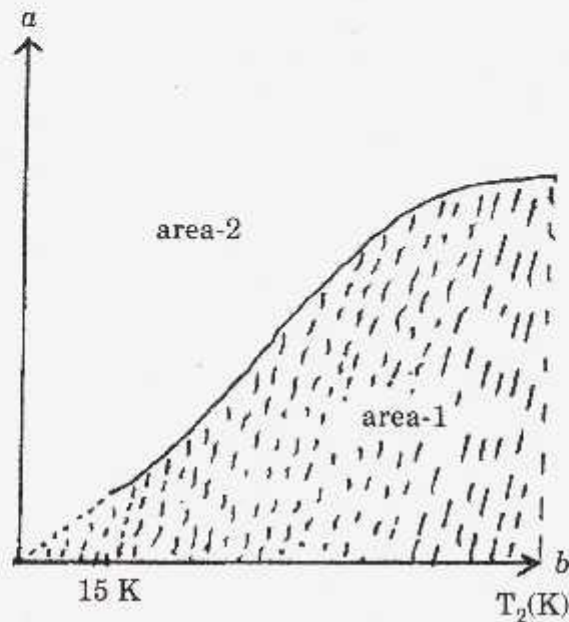


The number of degrees of freedom at points A, B, C, D is respectively :

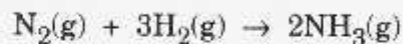
- (1) 2, 1, 2, 1 (2) 1, 2, 1, 2  
 (3) 2, 2, 1, 1 (4) 1, 2, 2, 1



42. The variation of  $C_p$  with temperature (from 15K to  $T_2(K)$ ) is shown below. The dotted line represents the extrapolation to  $T(K) = 0$ . Which one of the following is correct ? ( $a = C_p$ ;  $b = T(K)$ )



- (1) The area under the curve (area-1) gives an estimation of free energy
  - (2) The area above the curve (area-2) gives an estimation of absolute entropy
  - (3) The area under the curve (area-1) gives an estimation of absolute entropy
  - (4) The area under the curve (area-1) gives an estimation of enthalpy
43. Consider the reaction :



carried out at the constant temperature and pressure. If  $\Delta H$  and  $\Delta U$  are the enthalpy and internal energy changes for the reaction, which of the following expressions is correct ?

- |                           |                           |
|---------------------------|---------------------------|
| (1) $\Delta H = 0$        | (2) $\Delta H > \Delta U$ |
| (3) $\Delta H < \Delta U$ | (4) $\Delta H = \Delta U$ |

44. Among the following, the state functions are :
- (a) Internal energy
  - (b) The work in irreversible expansion of an ideal gas
  - (c) The work in reversible expansion of an ideal gas at constant temperature
  - (d) Molar enthalpy

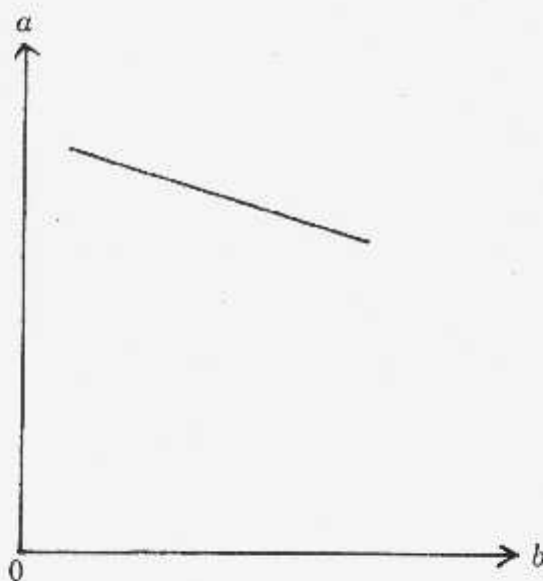
- (1) (a), (c), (d)                                       (2) (c), (d)
- (3) (b), (c)   (4) (a), (d)

45. At 25°C, calculate log  $K_{eq}$  for the reaction :



given that  $E_{cell}^0 = 1.36$  V :

- (1) 460   (2) 4.602
  - (3) 0.4602   (4) 46.02
46. At 25°C, the following graph is obtained for KCl which obeys Debye-Huckel-Onsager equation :



$a$  and  $b$  are respectively :

- (1) Molar conductance and concentration of KCl
- (2) Conductance and square root of concentration of KCl
- (3) Molar conductance and square root of concentration of KCl
- (4) Conductance and concentration of KCl

47. Match the following :

**List 1**

- (I) Hydrogen electrode
- (II) Specific conductance
- (III) Kohlrausch's law
- (IV) Nernst equation

**List 2**

- (a) Electrode potential
- (b) Pt, H<sub>2</sub> (2 bar)/H<sup>+</sup> (0.1) M
- (c) Oxidation electrode
- (d)  $\lambda^0 = \lambda_+^0 + \lambda_-^0$
- (e)  $\lambda_m = \lambda_m^0 - A\sqrt{C}$
- (f) s cm<sup>-1</sup>

- |     | (I) | (II) | (III) | (IV) |
|-----|-----|------|-------|------|
| (1) | (a) | (b)  | (e)   | (c)  |
| (2) | (c) | (f)  | (d)   | (a)  |
| (3) | (b) | (c)  | (d)   | (a)  |
| (4) | (b) | (f)  | (d)   | (a)  |

48. The standard emf of a cell having one electron exchange is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is :

- |                      |                     |
|----------------------|---------------------|
| (1) 10 <sup>30</sup> | (2) 10 <sup>5</sup> |
| (3) 10 <sup>10</sup> | (4) 10 <sup>8</sup> |

49. Which of the following statements are correct if  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$  and  $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.136 \text{ V}$  ?

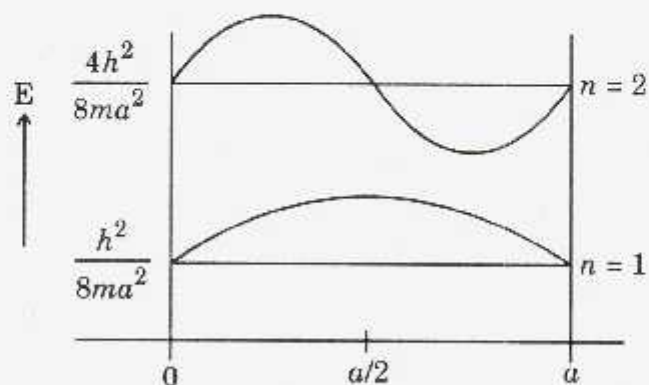
- (a) Cu can be oxidised by H<sup>+</sup> ions
- (b) Sn<sup>2+</sup> can be reduced by H<sub>2</sub>(g)
- (c) Cu<sup>2+</sup> ions can be reduced by H<sub>2</sub>(g)
- (d) Sn can be oxidised by Cu<sup>2+</sup>

The correct answer is :

- |                   |                   |
|-------------------|-------------------|
| (1) (a), (b), (c) | (2) (b), (c), (d) |
| (3) (a), (b)      | (4) (c), (d)      |

50. The plots of energy levels and wave functions of a particle in 1-dimensional box with length 'a' and wave function  $\psi_n$  are given below.

The wave function for  $n = 2$  vanishes at :



- (1) 0 and  $a$  only  
 (2)  $0, \frac{a}{2}, a$   
 (3) 0 only  
 (4)  $a$  only
51. The operator  $\hat{A} = \frac{\partial}{\partial x}$  and  $\hat{B} = x$ , then the commutator  $[A, B]$  turns out to be :

- (1) 0  
 (2) -1  
 (3) 1  
 (4)  $h/2\pi$

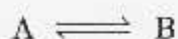
52. The operator  $\hat{H}$  of a particle in  $\hat{H}\psi = E\psi$  is referred to as :

- (1) Hermitian  
 (2) Hamiltonian  
 (3) Linear  
 (4) Non-linear

53. The time dependent Schrödinger wave equation is :

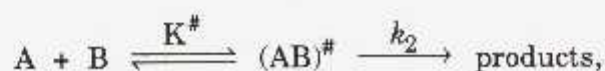
- (1)  $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi$   
 (2)  $-\frac{2m}{\hbar^2} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x)$   
 (3)  $i\hbar \frac{\partial \psi(x, t)}{\partial t} = E\psi(x, t)$   
 (4)  $-i\hbar \frac{\partial \psi(x, t)}{\partial t} = E\psi(x, t)$

54. Calculate  $k_f$  for the given reaction :



The initial concentration of A is 0.15 M, concentration of B at time 't' equal to 10 seconds is 0.056 M, and equilibrium concentration of B is 0.064 M :

- (1)  $0.88 \text{ s}^{-1}$  (2)  $0.088 \text{ s}^{-1}$   
 (3)  $0.1182 \text{ s}^{-1}$  (4)  $0.01182 \text{ s}^{-1}$
55. According to collision theory of bimolecular gaseous reactions, the pre-exponential factor (A) is proportional to :
- (assume, steric factor ( $p$ ) = 1;  $d_{av}$  = collision diameter; T = temperature)
- (1)  $A \propto d_{av} \sqrt{T}$  (2)  $A \propto d_{av}^2 T$   
 (3)  $A \propto d_{av}^2 \sqrt{T}$  (4)  $A \propto \sqrt{d_{av} T}$
56. According to thermodynamic formulation of activated complex theory, for the reaction :



$k_2$  is given by :

(constant =  $\frac{k_B T}{h}$ ;  $\Delta S^\#$  = standard entropy of activation;  $(\Delta H^\#)$  = standard enthalpy of activation)

- (1)  $k_2 = \text{constant} \cdot \exp\left(\frac{\Delta S^\#}{RT}\right) \cdot \exp\left(-\frac{(\Delta H^\#)}{R}\right)$   
 (2)  $k_2 = \text{constant} \cdot \exp\left(\frac{\Delta S^\#}{R}\right) \cdot \exp\left(\frac{(\Delta H^\#)}{RT}\right)$   
 (3)  $k_2 = \text{constant} \cdot \exp\left(-\frac{\Delta S^\#}{R}\right) \cdot \exp\left(-\frac{(\Delta H^\#)}{RT}\right)$   
 (4)  $k_2 = \text{constant} \cdot \exp\left(\frac{\Delta S^\#}{R}\right) \cdot \exp\left(-\frac{(\Delta H^\#)}{RT}\right)$

57. The intensity of phosphorescence in the absence ( $I_P^0$ ) and presence ( $I_P$ ) of a quencher (Q) is measured. A plot of  $\frac{I_P^0}{I_P}$  (on y-axis) as a function of concentration of Q (on x-axis) gave straight line with intercept. The intercept is equal to :

( $k_Q$  = rate constant of phosphorescence;  $\tau_{T_1}$  = life time of triplet excited state)

- |                      |                                |
|----------------------|--------------------------------|
| (1) $k_Q \tau_{T_1}$ | (2) $\frac{1}{k_Q \tau_{T_1}}$ |
| (3) 1.0              | (4) Zero                       |

58. In a flash photolysis experiment, the spectrometer is set up such that the light is passing through illuminated reaction cell with  $\lambda_{\max}$  of free radical only. A flash of energy ( $10^5$  J) is given for 10  $\mu$ s. Which one of the following statements is correct ?

- (1) The rate of disappearance of radicals is equal to the rate of increase of transmitted light.
- (2) The rate of disappearance of radicals is equal to the rate of decrease of transmitted light.
- (3) The rate of formation of radicals is equal to the rate of decrease of scattered light.
- (4) The rate of formation of radicals is equal to unity.



59. Match the following :

- |  |  |
|--|--|
| (I) $A^* + A \rightarrow 2A + \text{heat}$ | (A) $\frac{1}{k_{IC} + k_{ISC} + k_f}$   |
| (II) Fluorescence quantum yield $\phi_f$   | (B) $\frac{1}{k}$                        |
| (III) Natural radiative life time $\tau^0$ | (C) Self-quenching                       |
| (IV) $A^* \rightarrow A + \text{heat}$     | (D) $\frac{k_f}{k_{IC} + k_{ISC} + k_f}$ |
|  | (E) Internal conversion                  |

- |     |     |      |       |      |
|-----|-----|------|-------|------|
|     | (I) | (II) | (III) | (IV) |
| (1) | (C) | (A)  | (B)   | (E)  |
| (2) | (E) | (A)  | (B)   | (C)  |
| (3) | (C) | (D)  | (B)   | (E)  |
| (4) | (C) | (A)  | (B)   | (E)  |

60. Fluorescence efficiency decreases due to one of the following factors in polynuclear aromatic hydrocarbons :

- (1) Increase with increasing number of condensed rings
- (2) Planarity of the ring
- (3) Steric hinderance due to substituents
- (4) Large energy separation between excited singlet  $S_1$  and triplet  $T_1$

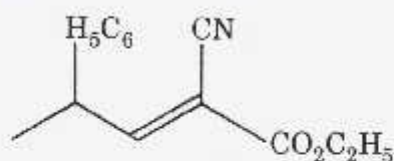
61. Calculate the triplet life time  $\Gamma_p$  of phosphorescence decay of 1-Iodonaphthalene in seconds :

$$(K_p = 350 \text{ s}^{-1}; \phi_p = 0.70 \text{ at } 77 \text{ K}; \phi_f = 10^{-4} \text{ at } 77 \text{ K})$$

- |           |          |
|-----------|----------|
| (1) 0.002 | (2) 0.02 |
| (3) 500   | (4) 5    |

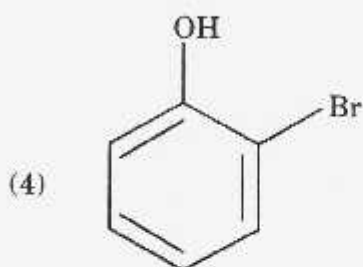
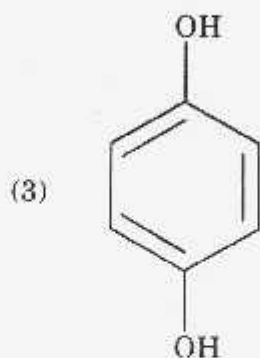
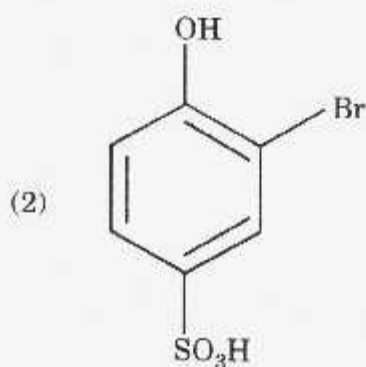
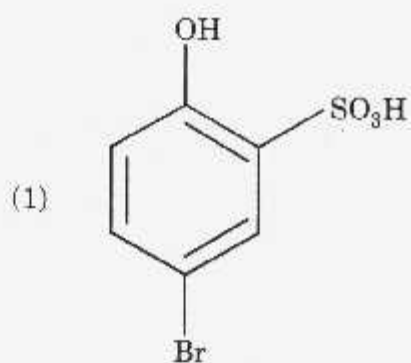
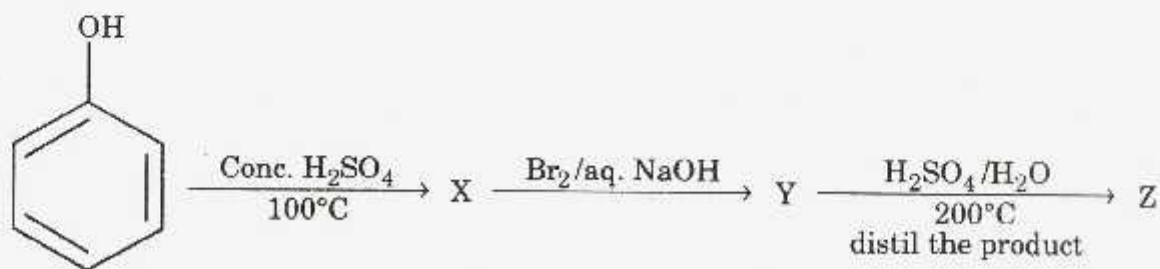
62. The magnetic susceptibility of a material is found to be  $-1.4 \times 10^{-6}$  emu. The material is :
- (1) Paramagnetic (2) Ferromagnetic  
 (3) Antiferromagnetic (4) Diamagnetic
63. The number of Bravais Lattices present in cubic and orthorhombic lattices is respectively :
- (1) 3, 3 (2) 4, 4  
 (3) 3, 4 (4) 4, 3
64. Which one of the following is an intrinsic semiconductor ?
- (1) Diamond (2) Arsenic doped silicon  
 (3) Indium doped silicon (4) Germanium
65. A solid crystallizes in primitive cubic lattice. It has cubic close packing. The total number of octahedral and tetrahedral voids present per unit cell is respectively :
- (1) 2, 2 (2) 1, 2  
 (3) 2, 1 (4) 1, 1
66. According to Langevin's theory of diamagnetism, the correct relationship between atomic radius (R) and atomic susceptibility ( $\chi_A$ ) is :
- (z = atomic number)
- (1)  $R^2 = 0.35 \times 10^{-10} \frac{\chi_A}{Z}$  (2)  $R^2 = -0.35 \times 10^{-10} \frac{\chi_A}{Z}$   
 (3)  $R^2 = -0.35 \times 10^{-10} \frac{Z}{\chi_A}$  (4)  $R^2 = 0.35 \times 10^{-10} \frac{Z}{\chi_A}$

67. The IUPAC name of the following compound is :

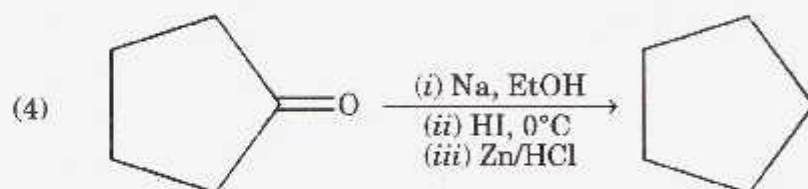
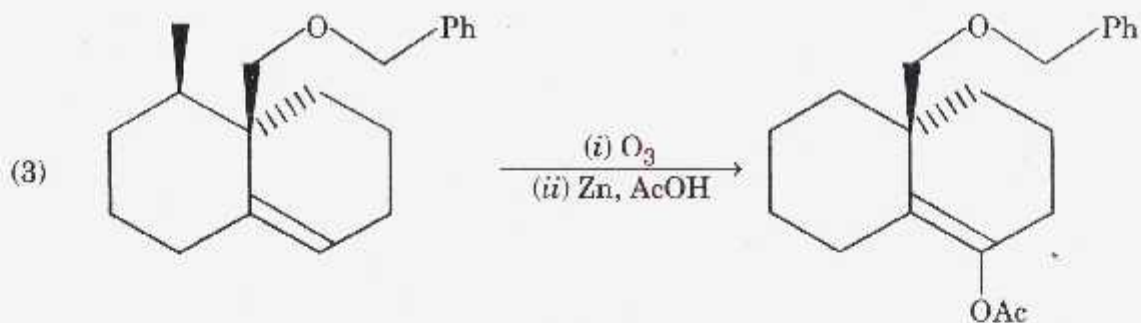
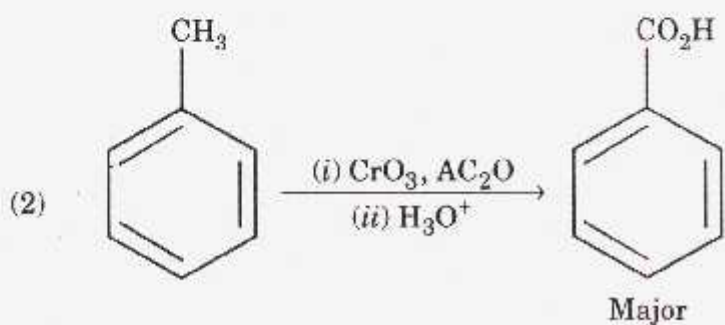
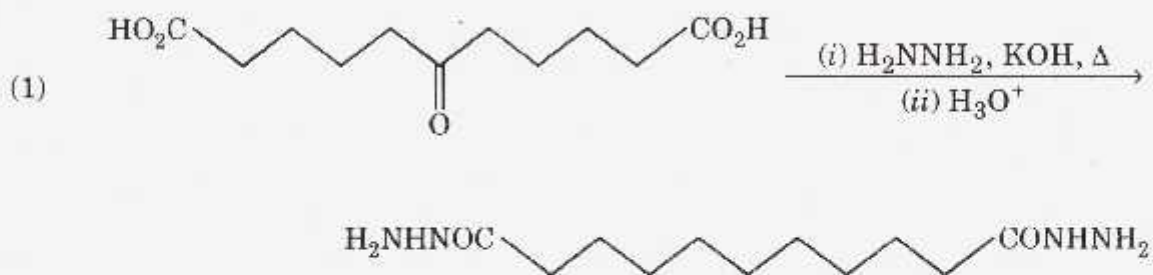


- (1) (Z)-2-ethoxycarbonyl-4-phenylpent-2-enitrile
- (2) (E)-ethyl-2-cyano-4-phenylpent-2-enoate
- (3) (E)-2-ethoxycarbonyl-4-phenylpent-2-enitrile
- (4) (Z)-ethyl-2-cyano-4-phenylpent-2-enoate

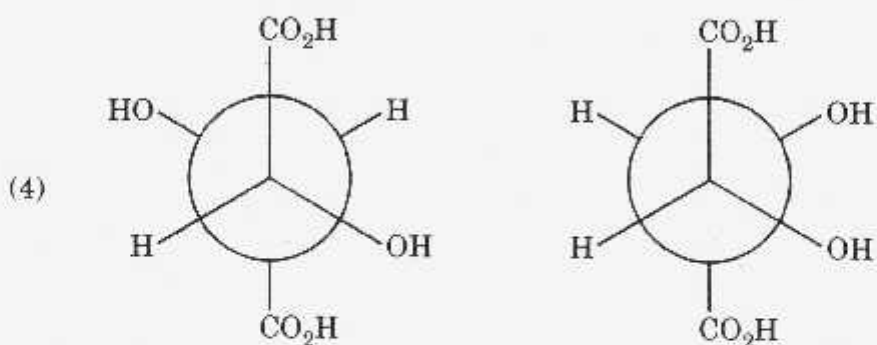
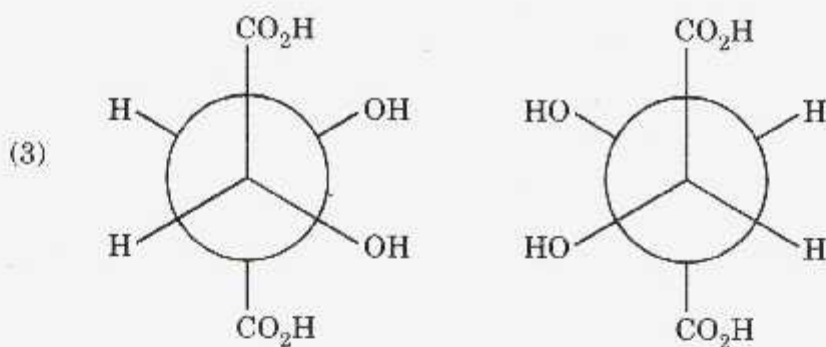
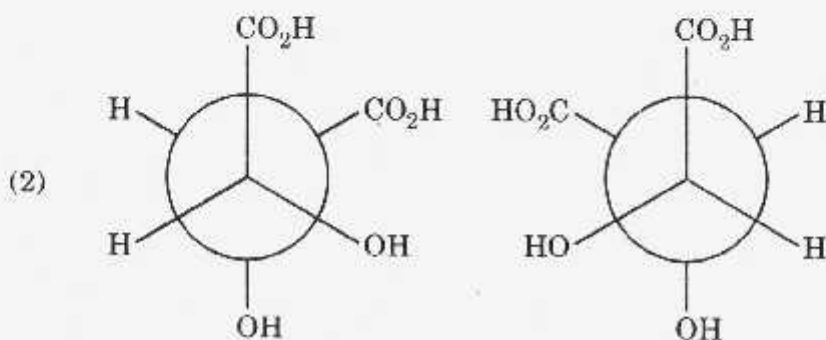
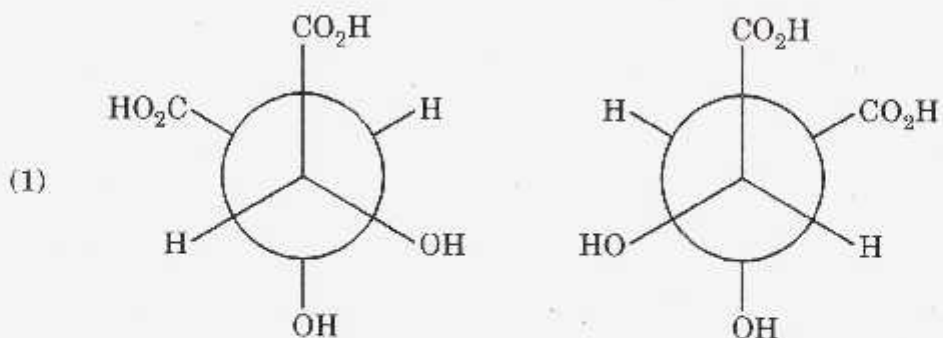
68. In the following reaction sequence the 'Z' is :



69. Which one of the following reactions is correct ?

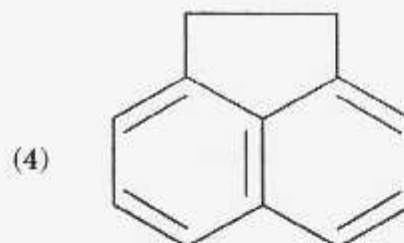
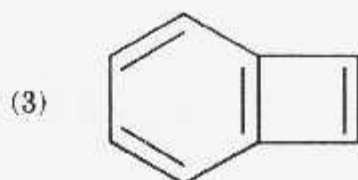
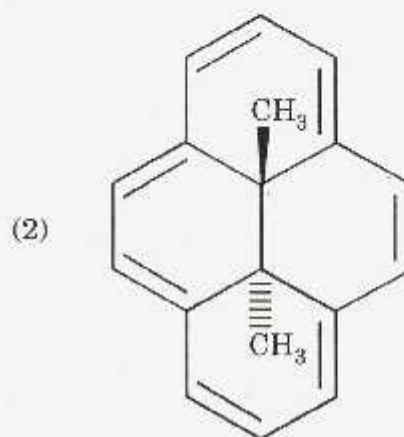
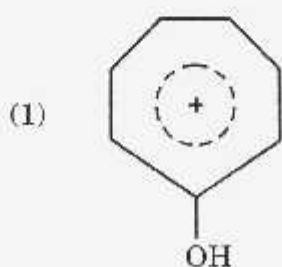


70. Which of the following pairs is the *correct* projections of meso-tartaric acid ?

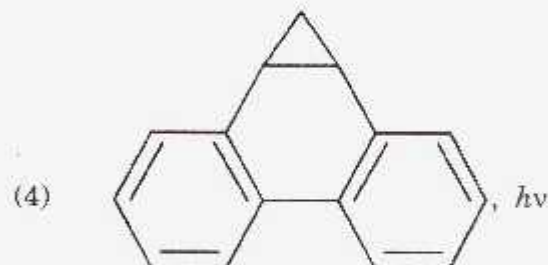
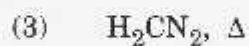
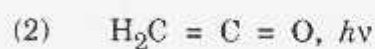


71. An optically active oxime on treatment with Lewis acid followed by complete hydrolysis gave (R)-3-phenylbutanoic acid and methyl amine. The configuration of optically active oxime is :
- |            |            |
|------------|------------|
| (1) (S), E | (2) (S), Z |
| (3) (R), E | (4) (R), Z |
72. When the polymethylene bridge having  $-(CH_2)_8-$  is incorporated into 2-bromohydroquinone, the resulting derivative is :
- (1) Optically active due to planar chirality
  - (2) Always optically inactive due to racemic form
  - (3) Optically active due to axial chirality
  - (4) Optically active due to helicity
73. Which one of the following statements is *correct* ?
- (1) Homomeric conformations always give structural isomeric products with different rates of reactivity.
  - (2) Enantiomeric conformers under achiral medium give enantiomeric products and diastereomeric products with different rates of reactivity.
  - (3) Diastereomeric conformers under achiral medium give identical products and diastereomeric products with same rates of reactivity.
  - (4) Enantiomeric conformers under chiral medium give enantiomeric products with different rates of reactivity.
74. The stereochemical relationship between pairs of (+)AC, (-)AP and (-)SC and (+)SC of *n*-butane are respectively :
- (1) Conformational diastereomers and conformational enantiomers
  - (2) Configurational diastereomers and configurational enantiomers
  - (3) Configurational enantiomers and configurational diastereomers
  - (4) Conformational enantiomers and conformational diastereomers

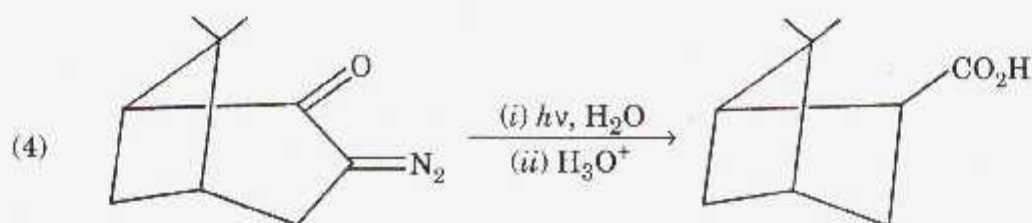
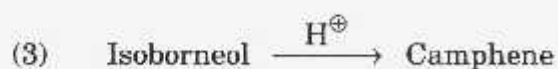
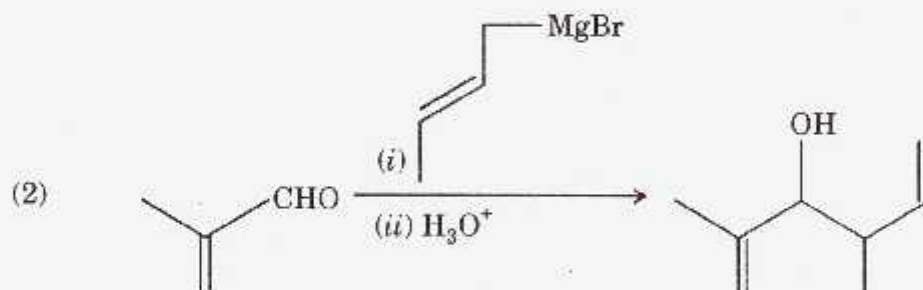
75. Which one of the following statements is *not correct* ?
- (1) Hydroxytropylium chloride is an antiaromatic molecule.
  - (2) Increase of hyperconjugation in olefins lowers the heat of hydrogenation.
  - (3) Resonance stabilization occurs more in carboxylate ion than in the parent acid.
  - (4) 3-methylene-1, 4-pentadiene is a cross conjugated molecule.
76. Which one of the following is *not aromatic* ?



77. Which of the following is *not* the source of carbene ?



78. Which of the following reactions involves Wagner-Meerwein rearrangement ?



79. Match the following :

**List-I**

**(Characteristics of Mechanism)**

- (I) 2, 3-sigmatropic rearrangement
- (II) Heisenheimer complex is intermediate
- (III) Cyclopropanone intermediate
- (IV) Nucleophilic intramolecular 1, 2-shift

**List-II**

**(Name reaction)**

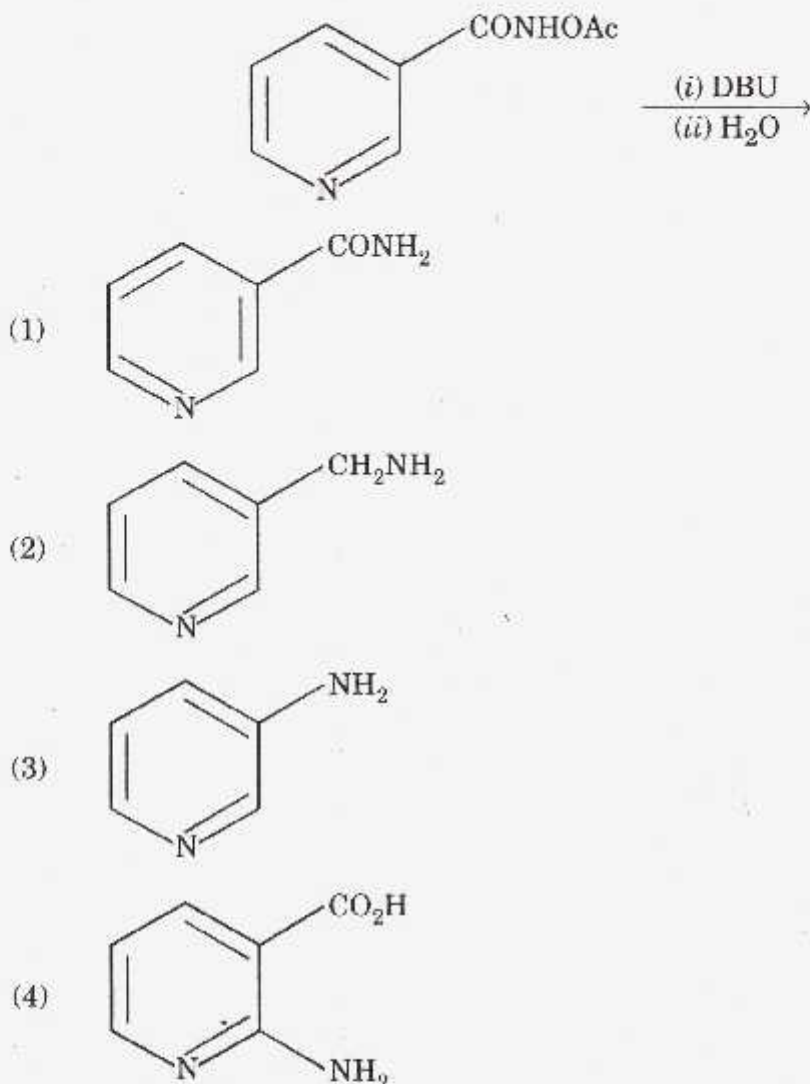
- (A) Smiles
- (B) Beckmann
- (C) Sommet-Hauser
- (D) Favorski

The correct answer is :

- |     |     |      |       |      |
|-----|-----|------|-------|------|
|     | (I) | (II) | (III) | (IV) |
| (1) | (C) | (A)  | (D)   | (B)  |
| (2) | (A) | (C)  | (D)   | (B)  |
| (3) | (C) | (B)  | (D)   | (A)  |
| (4) | (C) | (D)  | (A)   | (B)  |



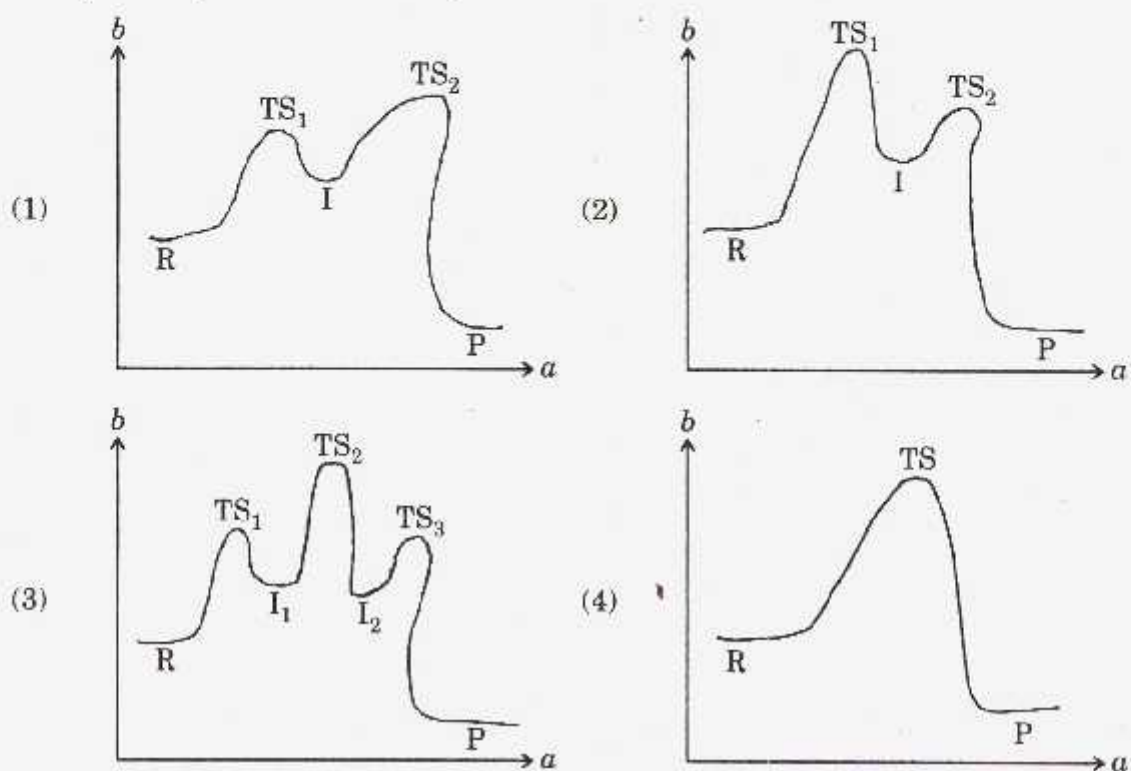
80. The product obtained in the following reaction is :



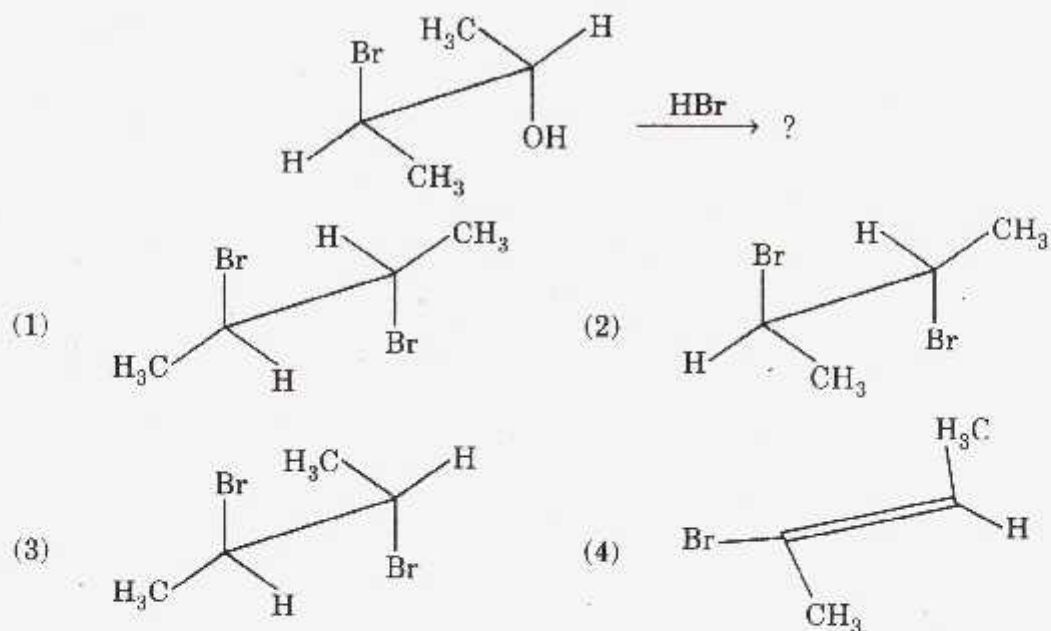
81. Which of the following statements is *not correct* ?

- (1) Dehydrobromination of meso-stilbene dibromide yields the cis olefin.
- (2) Trans 4-ter-Butylcyclohexyl-1-p-toluene sulfonate will not undergo  $E_2$  elimination reaction.
- (3) In the presence of  $KOBu^t$ , 2-bromo-2-methyl-butane gives 2-methylbut-1-ene as major product.
- (4)  $E_2$  elimination reaction of trans 2, 3-dichloro-norborane is slower than that of cis isomer.

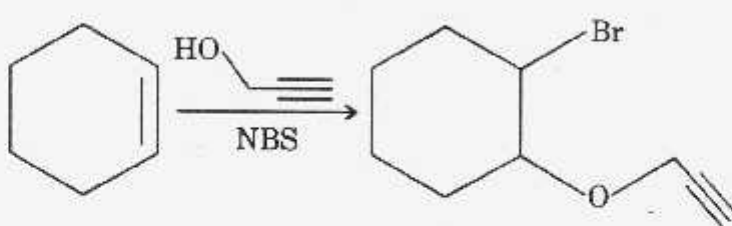
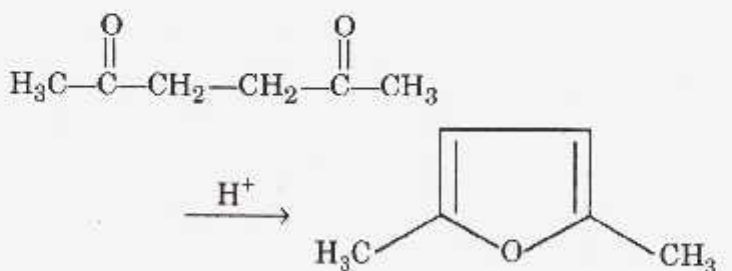
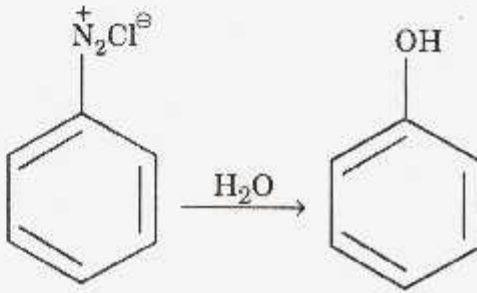
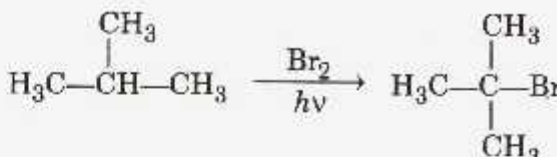
82. The energy profile diagram which represents the nitration of benzene is :  
 ( $b$  = potential energy;  $a$  = reaction coordinate; TS = transition state; R = reactant;  
 P = product; I = intermediate)



83. The product obtained in the following reaction is :



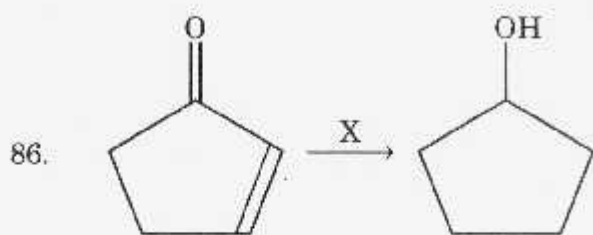
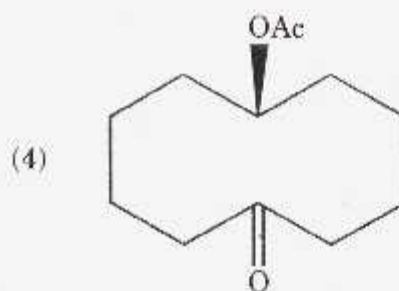
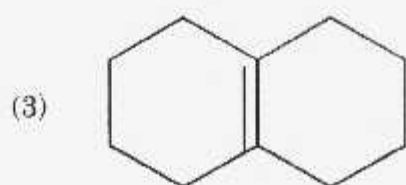
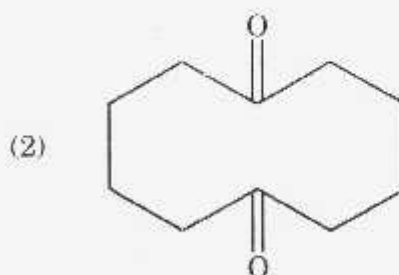
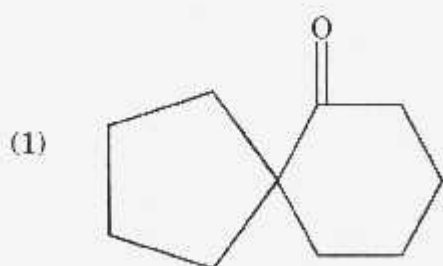
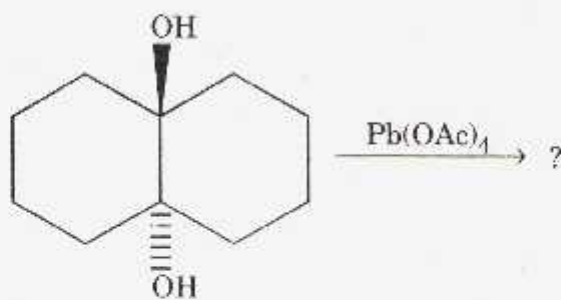
84. Match the following :

	List-I	List-II
(A)		(I) Nucleophilic addition
(B)		(II) Electrophilic addition
(C)		(III) Nucleophilic substitution
(D)		(IV) Free radical substitution

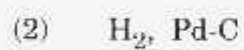
The correct answer is :

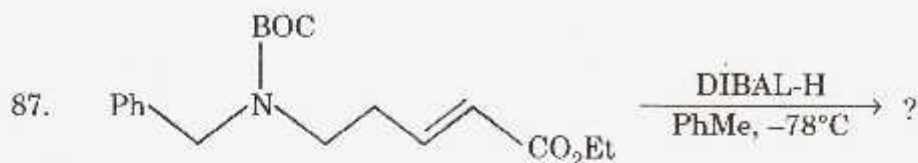
	(A)	(B)	(C)	(D)
(1)	(IV)	(I)	(II)	(III)
(2)	(I)	(II)	(III)	(IV)
(3)	(II)	(I)	(III)	(IV)
(4)	(I)	(III)	(IV)	(II)

85. What is the product obtained in the following reaction ?

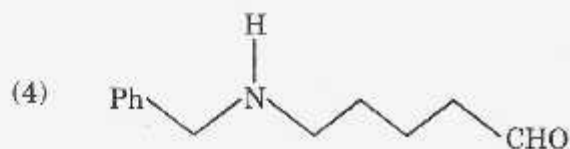
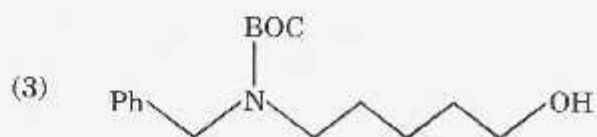
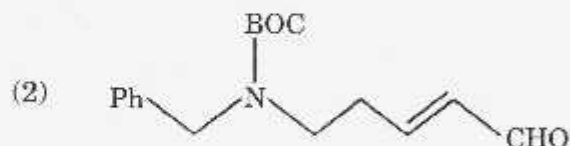
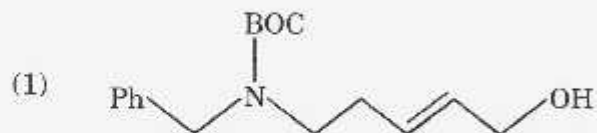


The reagent 'X' is :





The product in the above reaction is :



88. The reagents which are used in a sequence to convert furan to a mixture of salt of furoic acid and furfuryl alcohol, are :

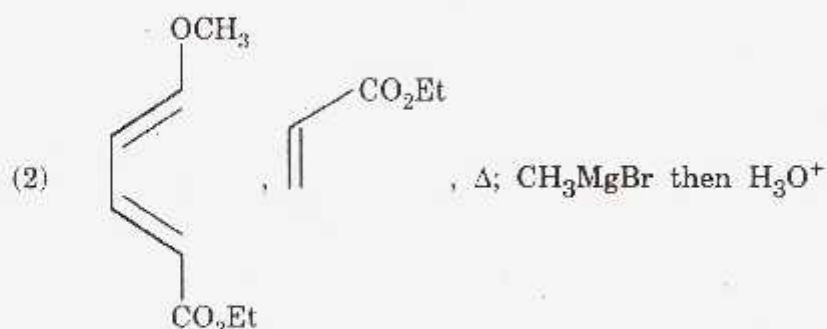
- (1) DMF,  $\text{POCl}_3$  then  $\text{H}_3\text{O}^+$ ;  $\text{NaOAc}/\text{Ac}_2\text{O}$
- (2)  $\text{Ac}_2\text{O}$ ,  $\text{BF}_3$  then  $\text{H}_3\text{O}^+$ ; Con.  $\text{KOH}_{(\text{aq})}$
- (3)  $\text{HCN}$ ,  $\text{HCl}$  then  $\text{H}_3\text{O}^+$ ; Con.  $\text{KOH}_{(\text{aq})}$
- (4)  $n\text{-C}_4\text{HgLi}$ ,  $\text{CO}_2$  then  $\text{H}_3\text{O}^+$ ; Con.  $\text{KOH}_{(\text{aq})}$

89. Which one of the following statements is *not correct* ?

- (1) Isoquinoline is a stronger base than quinoline.
- (2) When benzaldehyde is heated with an aminoacetal and further cyclized in presence of acid, quinoline is obtained.
- (3) Quinoline treated with  $\text{NaNH}_2$  forms 2-aminoquinoline.
- (4) Pyridine N-oxide reacted with nitrating mixture (Con.  $\text{HNO}_3$  and Con.  $\text{H}_2\text{SO}_4$ ) and then with  $\text{PCl}_3$  in chloroform forms 4-nitropyridine.

90. The reactants and reagents which are used in the synthesis of  $\alpha$ -terpineol by making use of Diels-Alder reaction are :

(1) isoprene, methyl vinyl ether,  $\Delta$ ;  $H_3O^+$



(3) isoprene, methyl acrylate,  $\Delta$ ;  $H_3CMgBr$  then  $H_3O^+$

(4) isoprene, methyl vinyl ketone,  $\Delta$ ;  $H_3CMgBr$  then  $H_3O^+$

91. Quininic acid on oxidation with chromic acid gives :

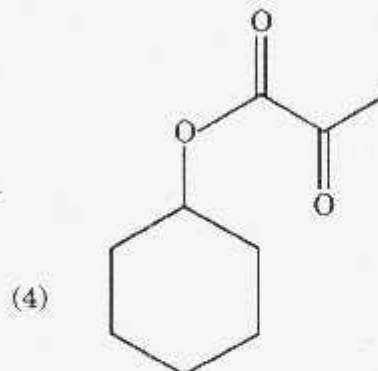
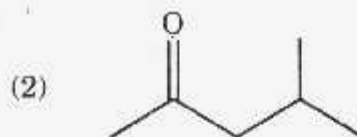
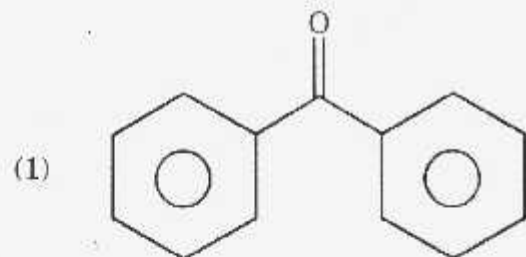
(1) Pyridine-2, 3-dicarboxylic acid

(2) Quinoline-4-carboxylic acid

(3) 6-hydroxyquinoline

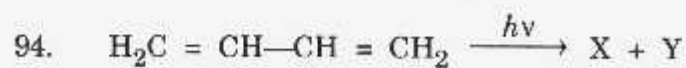
(4) pyridine-2, 3, 4-tricarboxylic acid

92. Which of the following compounds *does not* undergo Norrish type II cleavage ?

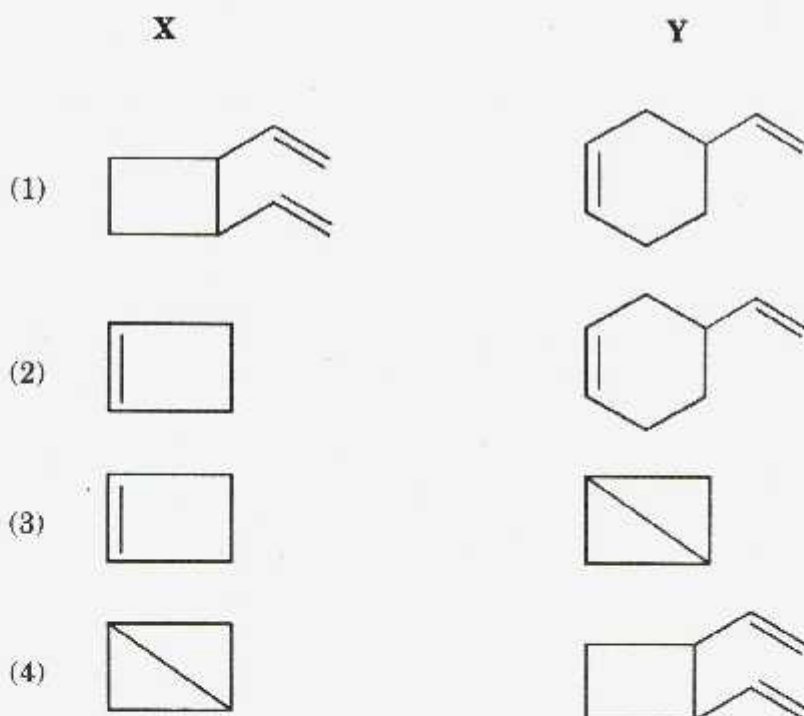


93. Photochemical irradiation of cis, trans-hexa-2, 4-diene forms a mixture of cis, trans-hexa-2, 4-diene, cis, cis-hexa-2, 4-diene and trans-trans-hexa-2, 4-diene. This reaction involves :

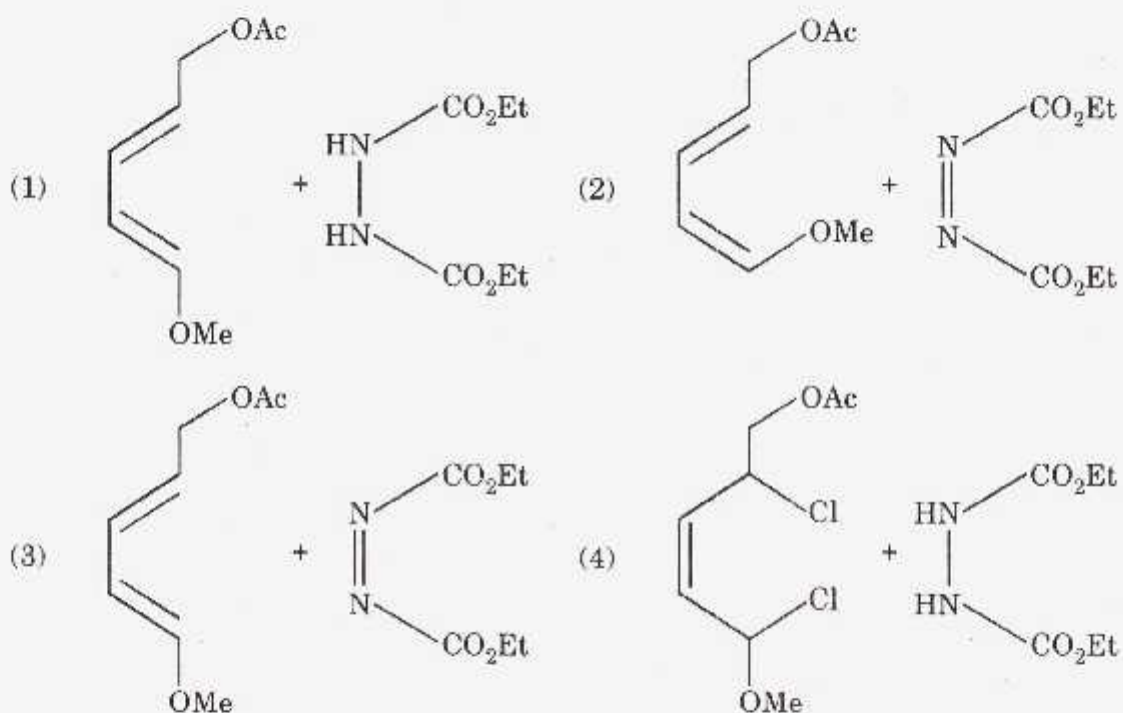
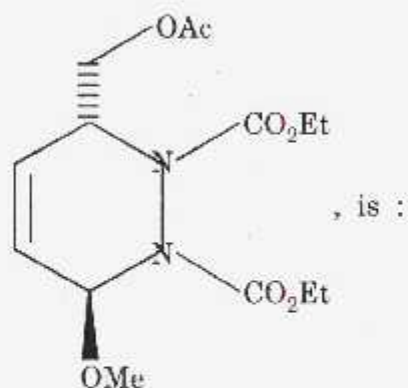
- (1) Di- $\pi$  methane rearrangement
- (2) Photoisomerisation
- (3) Paterno-Buchi reaction
- (4) Photo reduction



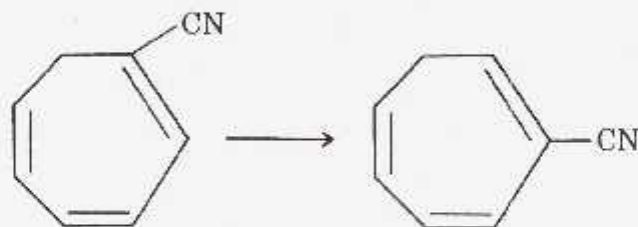
the products 'X' and 'Y' are :



95. Reactants used for the formation of



96. The reaction condition required and the type of shift involved in the following reaction respectively are :



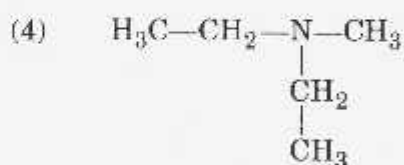
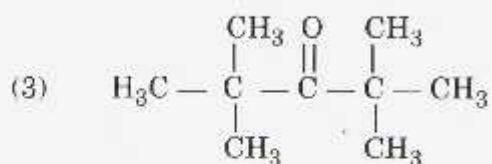
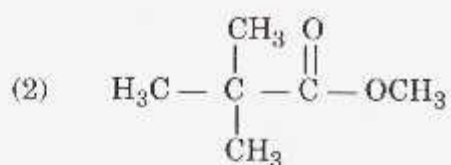
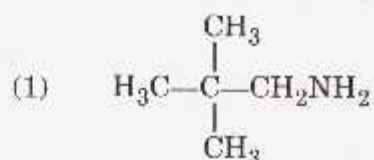
- (1)  $\Delta$ , [1, 5] suprafacial  
 (2)  $h\nu$ , [1, 3] suprafacial  
 (3)  $\Delta$ , [1, 7] antarafacial  
 (4)  $h\nu$ , [1, 7] suprafacial



97. Which of the following statements is *not correct* ?

- (1) The vibrational frequency of a bond decreases as the bond strength decreases.
- (2)  $C \equiv C$  stretching frequency is higher than  $C = C$  stretching frequency.
- (3) O—H stretching frequency is higher than O—D stretching frequency.
- (4) The vibrational frequency of a bond increases as the reduced mass of the molecule increases.

98. Which one the following compounds will *not* show three signals in their corresponding  $^{13}\text{C}$ -NMR spectra ?



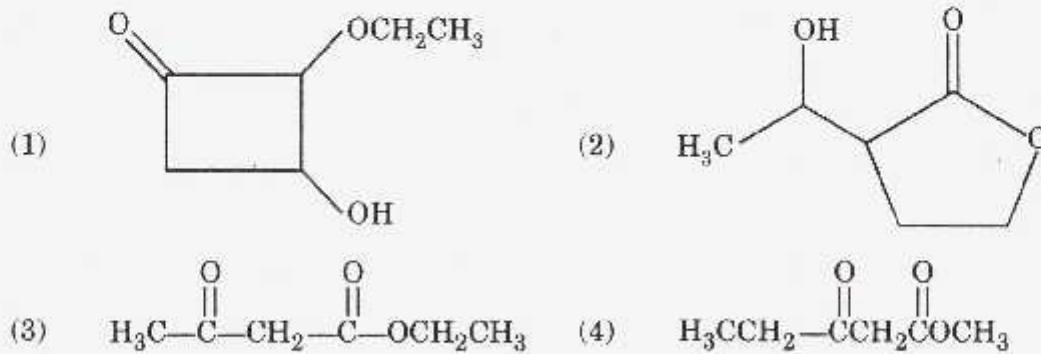
99. An organic compound 'A' with molecular formula  $C_6H_{10}O_3$  exhibits the following spectral data :

IR( $\bar{\nu}$ ,  $cm^{-1}$ ) : 2950, 1725, 1705  $cm^{-1}$

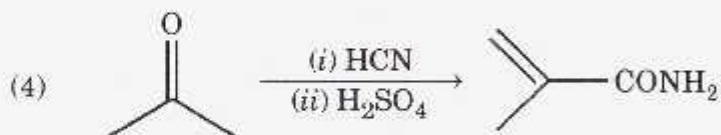
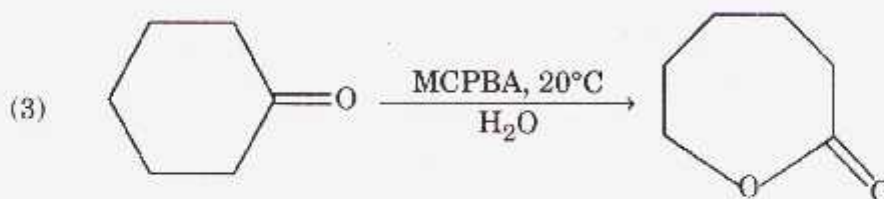
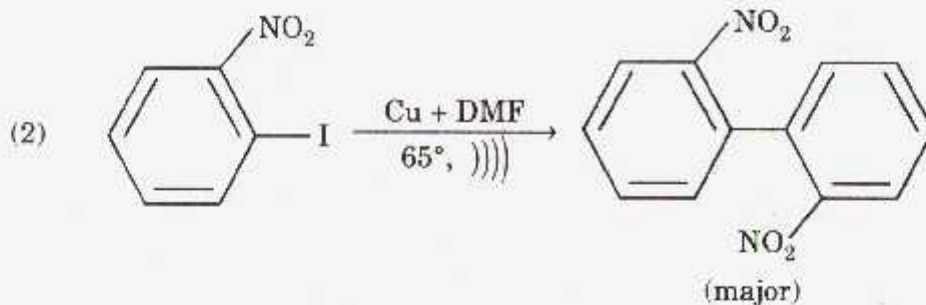
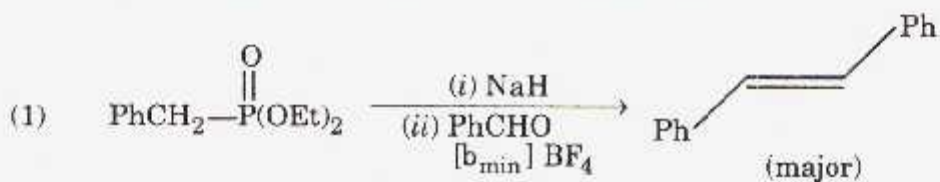
Mass ( $m/z$ ) : 130, 87, 43, 29

$^1H-NMR$  ( $\delta ppm$ ) : 4.20(s), 3.5(q), 2.3(s), 1.3(t)

The structure of the compound 'A' is :



100. Which one of the following is *not* a green reaction ?



Space for Rough Work

## Space for Rough Work