

Test Booklet Code & No.

प्रश्नपत्रिका कोड व क्र.

D

## Paper-III CHEMICAL SCIENCE

### Signature and Name of Invigilator

1. (Signature) .....

(Name) .....

2. (Signature) .....

(Name) .....

**MAY - 33316**

**Time Allowed : 2½ Hours]**

Number of Pages in this Booklet : 32

Seat No.

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(In figures as in Admit Card)

Seat No. .....

(In words)

OMR Sheet No.

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(To be filled by the Candidate)

**[Maximum Marks : 150**

Number of Questions in this Booklet : 75

### Instructions for the Candidates

1. Write your Seat No. and OMR Sheet No. in the space provided on the top of this page.
2. This paper consists of **75** objective type questions. Each question will carry **two** marks. All questions of Paper-III will be compulsory, covering entire syllabus (including all electives, without options).
3. At the commencement of examination, the question booklet will be given to the student. In the first 5 minutes, you are requested to open the booklet and compulsorily examine it as follows :
  - (i) To have access to the Question Booklet, tear off the paper seal on the edge of this cover page. Do not accept a booklet without sticker-seal or open booklet.
  - (ii) **Tally the number of pages and number of questions in the booklet with the information printed on the cover page.** Faulty booklets due to missing pages/questions or questions repeated or not in serial order or any other discrepancy should not be accepted and correct booklet should be obtained from the invigilator within the period of 5 minutes. Afterwards, neither the Question Booklet will be replaced nor any extra time will be given. The same may please be noted.
  - (iii) After this verification is over, the OMR Sheet Number should be entered on this Test Booklet.
4. Each question has four alternative responses marked (A), (B), (C) and (D). You have to darken the circle as indicated below on the correct response against each item.  
**Example :** where (C) is the correct response.  


5. Your responses to the items are to be indicated in the **OMR Sheet given inside the Booklet only**. If you mark at any place other than in the circle in the OMR Sheet, it will not be evaluated.
6. Read instructions given inside carefully.
7. Rough Work is to be done at the end of this booklet.
8. If you write your Name, Seat Number, Phone Number or put any mark on any part of the OMR Sheet, except for the space allotted for the relevant entries, which may disclose your identity, or use abusive language or employ any other unfair means, you will render yourself liable to disqualification.
9. You have to return original OMR Sheet to the invigilator at the end of the examination compulsorily and must not carry it with you outside the Examination Hall. You are, however, allowed to carry the Test Booklet and duplicate copy of OMR Sheet on conclusion of examination.
10. **Use only Blue/Black Ball point pen.**
11. **Use of any calculator or log table, etc., is prohibited.**
12. **There is no negative marking for incorrect answers.**

1. प्रश्नार्थीनी अपाला आसन क्रमांक या पृष्ठावराल वरच्या कोफऱ्यात लिहावा. तसेच आपणांस दिलेल्या उत्तरपत्रिकेचा क्रमांक त्याखाली लिहावा.
2. सदर प्रश्नपत्रिकेते 75 बहुप्रयायी प्रश्न आहेत. प्रत्येक प्रश्नास दोन गुण आहेत. या प्रश्नपत्रिकेतील सर्व प्रश्न सोडविणे अनिवार्य आहे. सदरचे प्रश्न हे या विषयाच्या संपूर्ण अभ्यासक्रमावर आधारित आहेत.
3. परीक्षा सुरु झाल्यावर विद्यार्थ्याला प्रश्नपत्रिका दिली जाईल. सुरुवातीच्या 5 मिनिटांमध्ये आपण सदर प्रश्नपत्रिका उघडून खालील बाबी अवश्य तपासून पहाव्यात.
  - (i) प्रश्नपत्रिका उघडण्यासाठी प्रश्नपत्रिकवर लावलेले सील उघडावे. सील नसलेली किंवा सील उघडलेली प्रश्नपत्रिका स्विकारू नवे.
  - (ii) पहिल्या पृष्ठावर नमूद केल्याप्रमाणे प्रश्नपत्रिकेची एकूण पृष्ठे तसेच प्रश्नपत्रिकेतील एकूण प्रश्नांची संख्या पडताळून पहाव्यात. पृष्ठे कमी असलेली/कमी प्रश्न असलेली/प्रश्नांचा चूकीचा क्रम असलेली किंवा इतर त्रुटी असलेली सदोष प्रश्नपत्रिका सुरुवातीच्या 5 मिनिटातच पर्यवेक्षकाला परत देऊन दुसरी प्रश्नपत्रिका मागावन घावावी. त्यानंतर प्रश्नपत्रिका बदलून मिळणार नाही तसेच वेळीची वाढवून मिळणार नाही याची कृपया विद्यार्थ्यांनी नोंद घावावी.
  - (iii) वरीलप्रमाणे सर्व पडताळून पहिल्यानंतरच प्रश्नपत्रिकेवर ओ.एम.आर. उत्तरपत्रिकेचा नंबर लिहावा.
4. प्रत्येक प्रश्नासाठी (A), (B), (C) आणि (D) अर्थी चार विकल्प उत्तरे दिली आहेत. त्यातील योग्य उत्तराचा रकाना खाली दर्शविल्याप्रमाणे ठळकपणे काळ्या/निव्वा करावा.  
**उदा. :** जर (C) हे योग्य उत्तर असेल तर.  

5. या प्रश्नपत्रिकेतील प्रश्नांची उत्तरे ओ.एम.आर. उत्तरपत्रिकेतच दर्शवावीत. इतर टिकापी लिहिलेली उत्तरे तपासली जागार नाहीत.
6. आत दिलेल्या सुचना काळजीपूर्वक वाचाव्यात.
7. प्रश्नपत्रिकच्या शेवटी जोडलेल्या को-या पानावरच कन्वे काम करावे.
8. जर आपण ओ.एम.आर. वर नमूद केलेल्या टिकाणा व्यातिरीक इतर कोठेही नाव, आसन क्रमांक, फोन नंबर किंवा ओळख पेटेल अशी कोणतीही खणिकोलेली आढळून आल्यास अथवा असभ्य भाषेचा वापर किंवा इतर गैरमार्गाचा अवलंब केल्यास विद्यार्थ्याला परीक्षेस अपात्र उत्तिष्ठात येईल.
9. परीक्षा संपल्यानंतर विद्यार्थ्यांनी मूळ ओ.एम.आर. उत्तरपत्रिका पर्यवेक्षकांकडे परत करणे आवश्यक आहे. तथापी, प्रश्नपत्रिका व ओ.एम.आर. उत्तरपत्रिकेची द्वितीय प्रत आपल्याबरोबर नेण्यास विद्यार्थ्यांना परवानगी आहे.
10. फक्त निव्वा किंवा काळ्या बॉल पेनचाच वापर करावा.
11. कॅलक्युलेटर किंवा लॉग टेबल वापरण्यास परवानगी नाही.
12. चुकीच्या उत्तरासाठी गुण कपात केली जाणार नाही.

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## Chemical Science

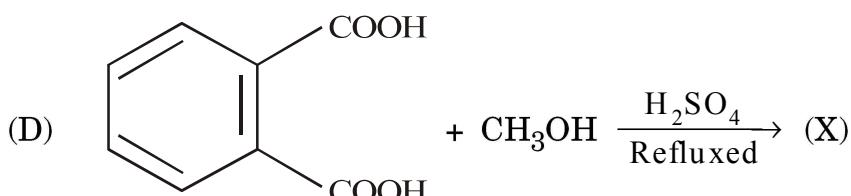
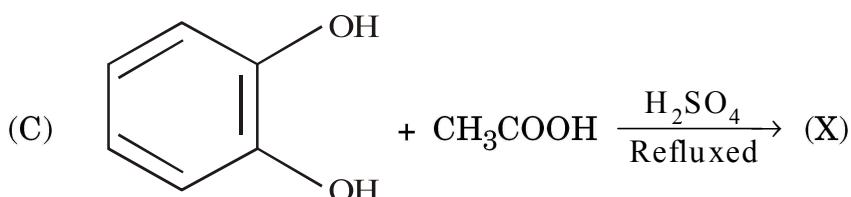
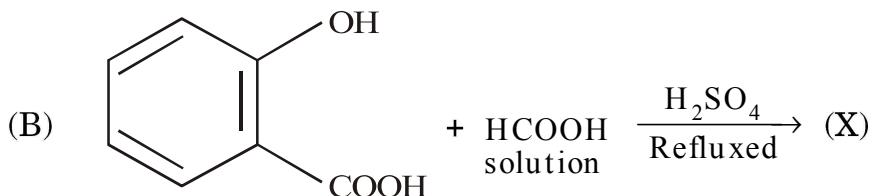
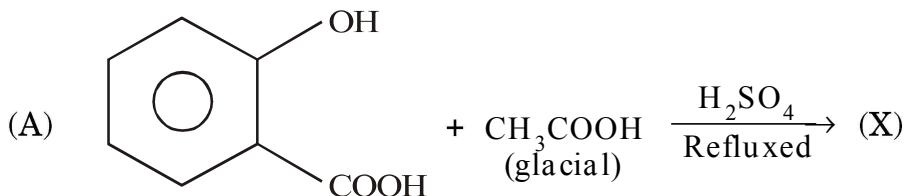
### Paper III

Time Allowed : 2½ Hours]

[Maximum Marks : 150]

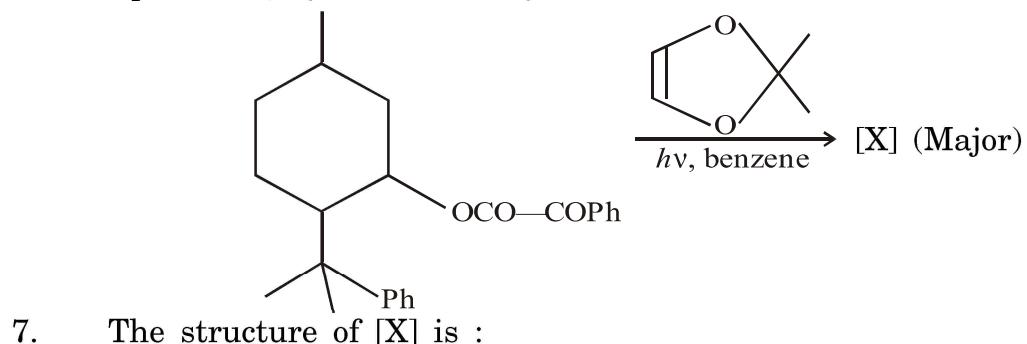
**Note :** This paper contains **Seventy Five (75)** multiple choice questions, each question carrying **Two (2)** marks. Attempt *All* questions.

1. One of the statement is *true* in case of Nucleotides :
  - (A) They are phosphoric acid esters of Pyrimidines
  - (B) They are phosphoric acid esters of Sugars
  - (C) They are phosphoric acid esters of Purines
  - (D) They are phosphoric acid esters of Nucleosides
2. The oil of winter green (X) is formed in one of the following reactions :



3. The carbonyl compounds exhibits electrophilic functionality because they have :
- A Low Energy LUMO  $\sigma^*$  orbital
  - A Low Energy HOMO  $\pi^*$  orbital
  - A Low Energy LUMO  $\pi^*$  orbital
  - A Low Energy HOMO  $\sigma^*$  orbital
4. In emulsion polymerization method, the initiator used is :
- Soluble in monomer
  - Soluble in water
  - Soluble in both water and monomer
  - Insoluble in both water and monomer
5. Simple following alkene is a weak nucleophile and reacts with X = electrophile given below, identify the best suitable electrophile and Y = product :
- Alkene                              Product
- X = Br<sub>2</sub> and Y = Dibromoalkane
  - X = NO and Y = Nitrosoalkane
  - X = NO<sub>2</sub> and Y = Nitroalkane
  - X = CO and Y = Carboxylalkane
6.  ${}^\Theta\text{BH}_4$  can have electrons from B-H bond available for donation, although  ${}^\Theta\text{BH}_4$  devoid lone pair of electrons of  $\pi$  orbital electron it act as :
- |                       |                      |
|-----------------------|----------------------|
| (A) poor nucleophile  | (B) good nucleophile |
| (C) good electrophile | (D) neutral species  |

Linked problems, Q. No. 7 and Q. No. 8 :



7. The structure of [X] is :

- (A)
- (B)
- (C)
- (D)

8. The name of the above reaction is :

- (A) Paterno-Buchi reaction      (B) Barton reaction  
(C) Michael addition      (D) Ene reaction

9. When gamma-ray photon with sufficiently high energy interacts with matter, pair production can occur. In this process, the photon is totally absorbed in creating :

- (A) a positron      (B) an electron  
(C) a positron and an electron      (D) a neutron

10. Two 10.0 ml aliquots of sea water were taken for neutron activation analysis. Exactly 1.0 ml of a standard solution containing  $1.0 \mu\text{g Al}^{3+}$  was added to one aliquot and 1.0 ml of distilled water was added to other aliquot. The two samples were then irradiated simultaneously in a homogeneous neutron flux. After a brief cooling period, the gamma radiation from the decay of  $^{28}\text{Al}$  was counted for each sample. The solution diluted with distilled water gave a counting rate of 2200 cpm whereas the solution containing the added  $\text{Al}^{3+}$  gave 4200 cpm. What is the mass of Al in the 10 ml aliquot ?

- (A) 2.2  $\mu\text{g}$       (B) 1.1  $\mu\text{g}$   
(C) 2.4  $\mu\text{g}$       (D) 1.2  $\mu\text{g}$

11. Which one of the following is an example of  $\beta$ -decay ?
- (A)  $^{48}_{24}\text{Cr} + ^0_1\text{e} \rightarrow ^{48}_{23}\text{V} + \text{X-rays}$   
(B)  $^{238}_{92}\text{U} \rightarrow ^{234}_{90}\text{Th} + ^4_2\text{He}$   
(C)  $^9_4\text{Be} + ^4_2\text{He} \rightarrow ^{12}_6\text{C} + ^1_0\text{n} + 5.7\text{MeV}$   
(D)  $^{23}_{11}\text{Na} + ^1_0\text{n} \rightarrow ^{24}_{11}\text{Na} + \text{gamma rays}$
12. Edge dislocations result when :
- (A) atoms in one layer do not match up precisely with those of the next  
(B) atoms in one layer do match up with those of the next  
(C) cations migrate to the surface  
(D) anions migrate to the surface
13. Frenkel defect is caused when :
- (A) Anions are missing from its lattice sites  
(B) Cations are migrated to nearby interstitial sites  
(C) Cations and equal number of anions migrate from its lattice sites to the surface of crystal  
(D) Cations are migrating from its lattice sites to the surface of crystal
14. For transition metal (M) spinels, M(II) [M'III]<sub>2</sub>O<sub>4</sub> is considered a normal spinel, while M'(III) [M(II) M'(III)]O<sub>4</sub> is considered an inverse spinel. Based on these consideration which one of the following is *true* ?
- (A) Fe<sub>3</sub>O<sub>4</sub> is a normal spinel  
(B) Ni(II)Fe<sub>2</sub>O<sub>4</sub> is a normal spinel  
(C) Co<sub>3</sub>O<sub>4</sub> is an inverse spinel  
(D) Mn<sub>3</sub>O<sub>4</sub> is a normal spinel

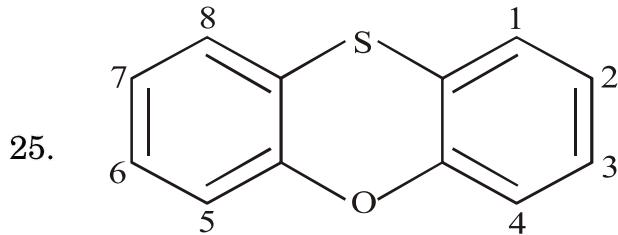


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19. Which of the following complexes has zero orbital moment ?
- (A)  $[\text{Mn}(\text{CN})_6]^{4-}$       (B)  $[\text{Mn}(\text{CN})_6]^{3-}$   
(C)  $[\text{Mn}(\text{H}_2\text{O})_6]^{5+}$       (D)  $[\text{FeF}_6]^{3-}$
20. The number of valence electrons in  $\text{Ni}(\eta^3\text{-allyl})_2$  and  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$  is, respectively :
- (A) 18 and 17      (B) 16 and 18  
(C) 14 and 19      (D) 16 and 17
21. How many M-M bonds should form in complex  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$  in order to obey 18 electron rule ? [Given : At. no. of Mo = 42]
- (A) 1      (B) 2  
(C) 3      (D) 4
22. Which of the following is a stable 18 electron species ?
- (A)  $\text{Ni}(\eta^3\text{-allyl})_2$   
(B)  $\text{Ru}(\eta^5\text{-C}_7\text{H}_7)(\eta^1\text{-C}_6\text{H}_5)\text{CO}$   
(C)  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_2$   
(D)  $\text{Rh}(\text{PPh}_3)_2\text{COCl}$
23. The  $\pi$ -acidic ligands stabilize the metal ions in lower oxidation states because of :
- (A)  $\text{L} \rightarrow \text{M}$   $\pi$ -interaction  
(B) Stronger  $\text{L} \rightarrow \text{M}$   $\sigma$ -interaction  
(C) Synergic effect  
(D) Neutralization of the positive charge over the metal ion.

24. Which of the following will undergo the easiest hydrogenation ?

- |  |  |
|--|--|
| (A) $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ | (B) $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ |
| (C) $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2$ | (D) $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ |



Yields a monolithiated product on lithiation with Li(s) in an inert solvent.

Which C atom is expected to exchange H with Li ?

- |       |       |
|-------|-------|
| (A) 1 | (B) 2 |
| (C) 3 | (D) 4 |

26. During a ligand substitution reaction, if an intermediate with higher coordination is formed, the possible mechanism of the reaction is :

- |       |                  |
|-------|------------------|
| (A) A | (B) $\text{I}_a$ |
| (C) D | (D) $\text{I}_d$ |

27. Which of the following is expected to undergo the fastest inner sphere reduction by  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ?

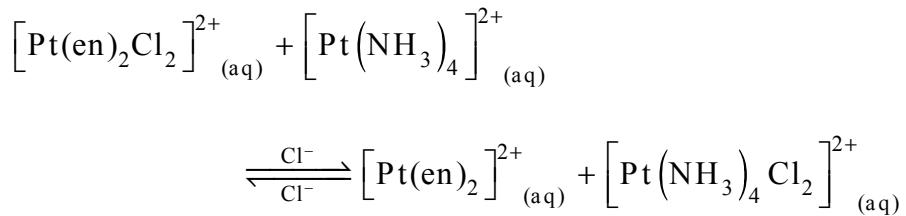
- |   |   |
|---|---|
| (A) $[\text{Co}(\text{PY})_6]^{3+}$                 | (B) $[\text{Co}(\text{PY})_5 \text{ (ampy)}]^{3+}$  |
| (C) $[\text{Fe}(\text{PY})_5 \text{ (dampy)}]^{3+}$ | (D) $[\text{Co}(\text{PY})_5 \text{ (dampy)}]^{3+}$ |

[PY = pyridine]

ampy = 4-aminopyridine

dampy = 3, 5-diaminopyridine]

28. The reaction :



is an example of :

- (A) Isomerization reaction      (B) Ligand substitution reaction  
 (C) Electron transfer process      (D) Reproportionation reaction

29. A 4Fe-3S protein has :

- (A) 4 sulphides and 3Fe bound to cysteine residues  
 (B) 3 sulphides and 4Fe bound to cysteine residues  
 (C) 4 Fe and 3 cysteine residues  
 (D) 4 sulphides out of which 3 are bridging between the Fe ions

30. The MET-APO form of the active site in hemocyanin has :

- (A) One  $\text{Cu}^+$       (B) One  $\text{Cu}^{2+}$   
 (C) One  $\text{Cu}^{1+}$  and one  $\text{Cu}^{2+}$       (D) Two  $\text{Cu}^{2+}$

31. Which of the following has the lowest nephelauxetic ratio ?

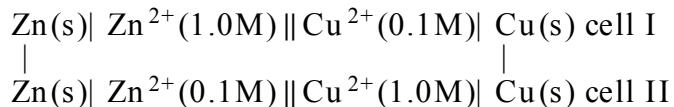
- (A)  $[\text{RuCl}_6]^{3-}$       (B)  $[\text{Fe}(\text{PY})_4\text{Cl}_2]$   
 (C)  $[\text{Ru}(\text{NH}_3)_6]^{2+}$       (D)  $[\text{Ru}(\text{bipy})_3]^{2+}$

[bipy = 2, 2'-bipyridine]

[PY = pyridine]

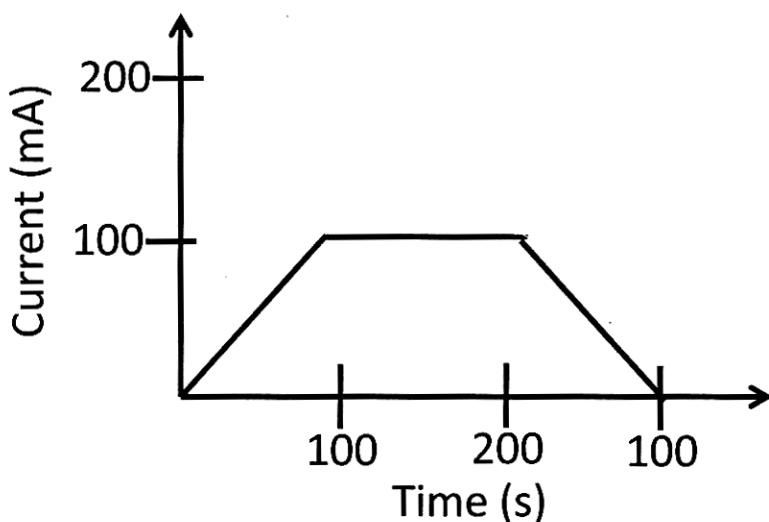
32. On the basis of cluster valence electron count, the structure of the metallic framework in  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Ru}_4(\text{CO})_{16}$  can be predicted to be respectively :
- (A) Tetrahedral and square planar  
(B) Square planar and butterfly  
(C) Butterfly and tetrahedral  
(D) Square planar and tetrahedral
33. A solution containing 10.0 ppm  $\text{KMnO}_4$  had a transmittance of 0.1 in a 2.0 cm cell at 520 nm. The absorptivity of  $\text{KMnO}_4$  solution is :
- (A)  $5.0 \times 10^2 \text{ Lg}^{-1} \text{ cm}^{-1}$       (B)  $5.0 \times 10^3 \text{ Lg}^{-1} \text{ cm}^{-1}$   
(C)  $2.5 \times 10^2 \text{ Lg}^{-1} \text{ cm}^{-1}$       (D)  $2.5 \times 10^3 \text{ Lg}^{-1} \text{ cm}^{-1}$
34. An acid HB has a distribution coefficient of 8.8 between an organic solvent and water. At pH 6.0, exactly half of the material is extracted into the organic solvent from an equal volume of the aqueous phase. The dissociation constant of acid HB is :
- (A)  $8.8 \times 10^{-6}$       (B)  $7.8 \times 10^{-6}$   
(C)  $9.8 \times 10^{-6}$       (D)  $6.8 \times 10^{-6}$
35. Which of the following is used as sources of radiation in uv-visible spectrophotometer ?
- (A) Tungsten lamp  
(B) Deuterium lamp  
(C) Tungsten and deuterium lamp  
(D) Xenon arc lamp

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Which statement is *correct* ?

39. The following graph represents current-time curve for the deposition of Cu. Based on this graph, the amount of Cu deposited would be (Given : Atomic weight of Cu = 63) :



- (A) 6.3 g (B) 63 g  
(C)  $6.3 \times 10^{-3}$  g (D)  $6.3 \times 10^{-4}$  g

40. Which of the following shows maximum osmotic pressure in water ?  
(A) 1 M NaCl (B) 1 M MgCl<sub>2</sub>  
(C) 1 M (NH<sub>3</sub>)<sub>3</sub> PO<sub>4</sub> (D) 1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>

41. Which of the following reactions is involved in the fuel cell ?  
(A) Cd + 2Ni(OH)<sub>3</sub> → CdO + 2Ni(OH)<sub>2</sub> + H<sub>2</sub>O  
(B) Pb + PbO<sub>2</sub> + 2H<sub>2</sub>SO<sub>4</sub> → 2PbSO<sub>4</sub> + 2H<sub>2</sub>O  
(C) 2H<sub>2</sub> + O<sub>2</sub> → 2H<sub>2</sub>O  
(D) 2Fe + O<sub>2</sub> + 4H<sup>+</sup> → 2Fe<sup>2+</sup> + 2H<sub>2</sub>O

42. The trial function for the particle in 1D box (with  $0 \leq x \leq a$ ) leading to the best possible ground state energy employing the variational method should be :

- (A)  $x^\alpha (a - x)^\beta$       (B)  $\sin\left(\frac{\pi x}{a}\right)$   
(C)  $x(a - x)$       (D)  $x^2 (a - x)^2$

43. 24 J is consumed to blow a soap bubble of the radius 1 cm. The surface tension at air-water interface would be around :

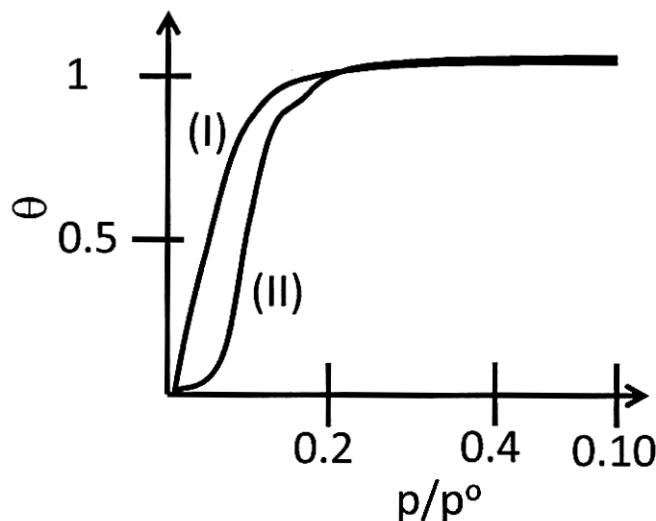
(Hint :  $W = \gamma \times A$ )

- (A)  $100 \text{ Jm}^{-2}$       (B)  $10 \text{ Jm}^{-2}$   
(C)  $1 \text{ Jm}^{-2}$       (D)  $1000 \text{ Jm}^{-2}$

44. Out of the following which of the point group can a molecule have a dipole moment ?

- (A)  $C_{2v}$       (B)  $D_{2d}$   
(C)  $D_{2h}$       (D)  $C_{\infty h}$

45. Which statement is appropriate for the following two adsorption isotherms ?



- (A) Plot (I) is a classic case of lateral interaction i.e. Frumkin-Fowler-Guggenheim (FFG) adsorption isotherm
- (B) Plot (II) is classic case of Langmuir adsorption isotherm
- (C) Plot (II) is a case of FFG adsorption isotherm
- (D) Practically there is no difference between (I) and (II)
46. Which of the following relations is *not correct* for an ideal gas ?

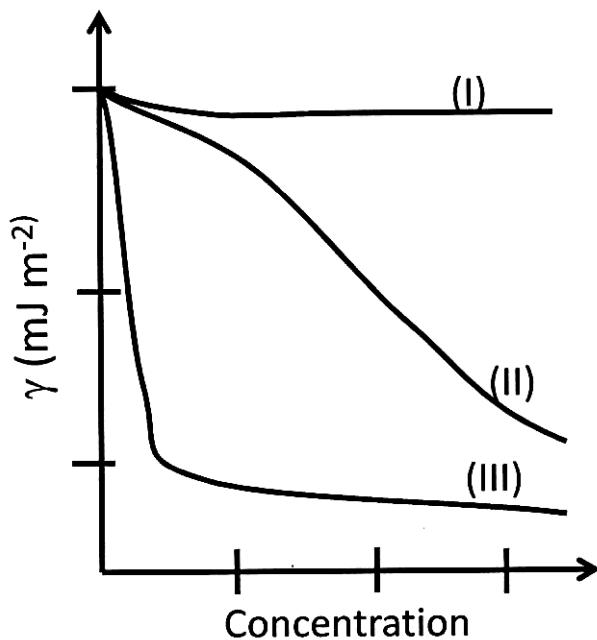
$$(A) \left( \frac{\partial H}{\partial T} \right)_p - R = \left( \frac{\partial H}{\partial T} \right)_v$$

$$(B) \left( \frac{\partial H}{\partial T} \right)_p > \left( \frac{\partial H}{\partial T} \right)_v$$

$$(C) \left( \frac{\partial U}{\partial V} \right)_T = 0$$

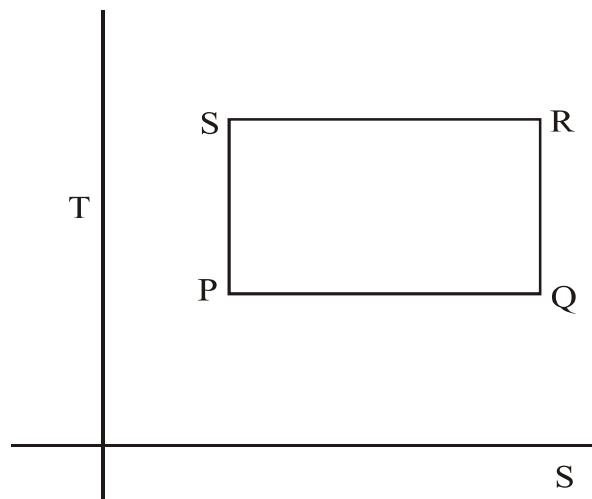
$$(D) \left( \frac{\partial H}{\partial T} \right)_p + R = \left( \frac{\partial H}{\partial T} \right)_v$$

47. Consider the following three plots for the surface tensions noted for three different solutes. Based on this which statement is most appropriate ?



- (A) All three plots are for surface active agents.
- (B) From these plots, the critical micelles concentrations can be estimated.
- (C) Among these, plot (III) is for a surfactant and plot (I) is possibly for an electrolyte.
- (D) Among (II) and (III), plot II is for more active surface active agent.

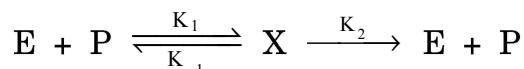
48. If the Carnot cycle in enthalpy-temperature diagram shows :



then the system rejects heat to the surroundings in going from :

- |   |   |
|---|---|
| <p>(A) <math>R \rightarrow S</math></p> <p>(C) <math>Q \rightarrow P</math></p> | <p>(B) <math>P \rightarrow Q</math></p> <p>(D) <math>S \rightarrow R</math></p> |
|---|---|

49. In the Michaelis-Menten mechanism for the enzymolysis :



The steady-state approximation leads to a concentration of an intermediate :

$$[X] = \frac{K_1 E_0 S_0}{K_1 S_0 + K_{-1} + K_2}$$

Then the initial rate of reaction is given as :

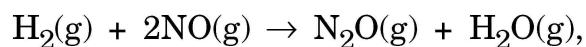
$$(A) \quad v_0 = \frac{K_2 S_0}{1 + \left( \frac{K_{-1} + K_2}{K_1} \right) \frac{1}{E_0}} \quad (B) \quad v_0 = \frac{V_m}{1 + \frac{K_m}{E_0 S_0}}$$

$$(C) \quad v_0 = \frac{K_2 E_0}{1 + \left( \frac{K_{-1} + K_2}{K_1} \right) S_0} \quad (D) \quad v_0 = \frac{V_m}{1 + \frac{K_m}{E_0}}$$

50. What is the de Broglie wavelength associated with a particle in 1D box ( $0 \leq x \leq a$ ) with the width of 5 Å in its first excited state (the PE inside the box is zero and that outside being infinity) :

- |           |         |
|-----------|---------|
| (A) 10 Å  | (B) 5 Å |
| (C) 2.5 Å | (D) 1 Å |

51. Laughing gas N<sub>2</sub>O, can be prepared from H<sub>2</sub> and NO :



A study of initial concentration verses initial rates at certain tempeature yield the following data :

Set	[H <sub>2</sub> ], M	[NO], M	R <sub>0</sub> Ms <sup>-1</sup>
1	0.1	0.5	$2.560 \times 10^{-6}$
2	0.2	0.3	$1.843 \times 10^{-6}$
3	0.1	0.3	$9.216 \times 10^{-7}$
4	0.2	0.6	$7.373 \times 10^{-6}$

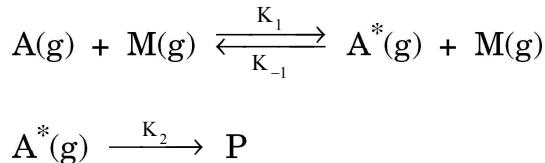
Which of the following is the *correct* rate law ?

- |  |   |
|--|---|
| (A) R = K[H <sub>2</sub> ] [NO] <sup>2</sup> | (B) R = K[NO] <sup>2</sup>              |
| (C) R = K[H <sub>2</sub> ] [NO]              | (D) R = K[H <sub>2</sub> ] <sup>2</sup> |

52. The commutator  $[\hat{x}, \hat{p}_x]$  is equal to :

- |                 |       |
|-----------------|-------|
| (A) $-i\hbar$   | (B) 0 |
| (C) $\hat{p}_z$ | (D) 1 |

53. In the Lindemann mechanism for the unimolecular reaction :



The apparent rate constant is given by :

$$K_{\text{obs}} = \frac{K_1 K_2 [M]}{K_2 + K_{-1} [M]}$$

- (A) At high pressure the reaction becomes zeroth order w.r.t. A
  - (B) At high pressure the reaction becomes first order w.r.t. M
  - (C) At high pressure the reaction becomes first order w.r.t. A
  - (D) Pressure has no effect on the order of reaction
54. The average separation of  $2p_z$  electron of the H atom from the nucleus will be ( $a_0$  Bohr radius) :
- (A)  $3a_0/2$
  - (B)  $5a_0$
  - (C)  $4a_0$
  - (D)  $a_0$
55. Upon increasing temperature of the solution, Debye-Huckel reciprocal length ( $x^{-1}$ ) will :
- (A) Increase
  - (B) Decrease
  - (C) No change
  - (D) Initially increase, passes through maxima and then decrease

56. Which of the following statements is *not correct* about the quantum mechanical harmonic oscillator ?

- (A) The amplitude of a quantum mechanical harmonic oscillator in its ground state will not exceed its classical value in lower energy states.
- (B) The average values of  $\langle x \rangle$  and  $\langle p \rangle$  are zero.
- (C) In highly excited states the quantum mechanical oscillator behaves as a classical oscillator
- (D) The wave function for quantum mechanical harmonic oscillator is always either odd or even.

57. The free energy of mixing for the ideal solution is given by :

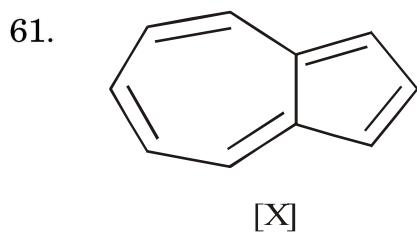
$$\Delta G_{\text{mix}} = RT(x_A \ln x_A + x_B \ln x_B)$$

$\therefore x_A$  and  $x_B$  are respective mole fractions from the expression one can deduce that :

- (A) The mixing is not spontaneous and  $\Delta G = +ve$
- (B) The mixing is spontaneous and  $\Delta G$  is negative and maximum at  $X = 1/2$
- (C) The mixing is exothermic
- (D) The mixing is endothermic

Among the ions [A], [B] and [C], given :

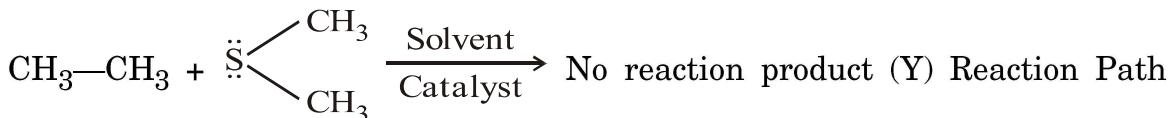
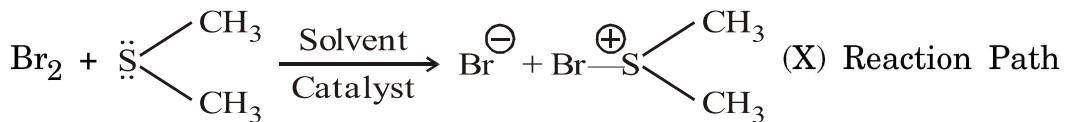
- (A) A is aromatic, B is homoaromatic and C is antiaromatic
  - (B) A is homoaromatic, B is aromatic and C is antiaromatic
  - (C) A is aromatic, B is antiaromatic and C is homoaromatic
  - (D) A is homoaromatic, B is antiaromatic and C is aromatic



The most *correct* statement about compound [X] is :

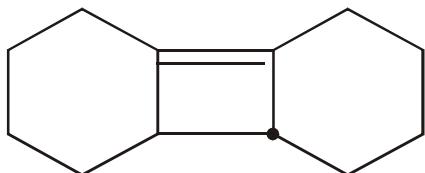
- (A) It is aromatic
  - (B) It is aromatic and has high dipole moment than expected
  - (C) It is aromatic but has no dipole moment
  - (D) It is antiaromatic

62. Justify the answer given in the statement below for reaction (X) and reaction (Y) pathways :

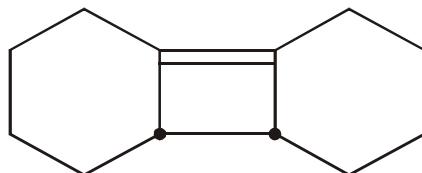


- (A) Lone pair of electrons are donated from S-atom to Br—Br to form new S-Br band, in (X) path but not possible to break C—C bond in (Y) path
- (B) Lone pair of electrons are donated from Br—Br to S-atom in path (X), but not possible to donate  $\text{CH}_3-\text{CH}_3$   $\sigma$ -bond to S-atom in path (Y)
- (C) Lone pair of electrons are restricted by S-atom to donate in both (X) path and (Y) path, but catalytic reagent may do this in path (X) only
- (D) Lone pair of electrons are blocked by S-atom in path (Y) but bromine procure electron pair from solvent in path (X)

63.



X

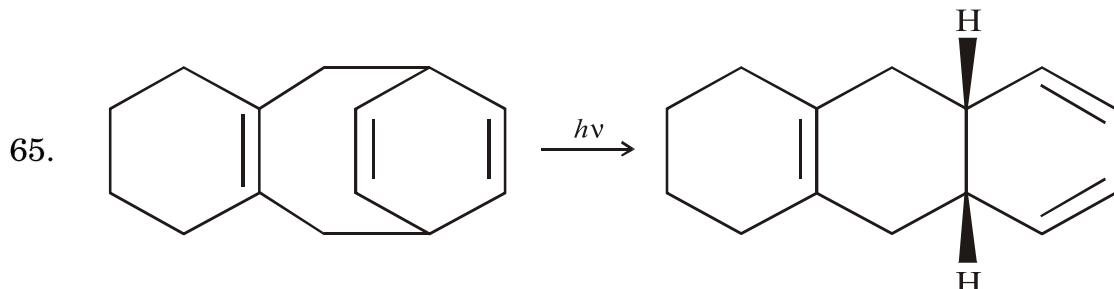
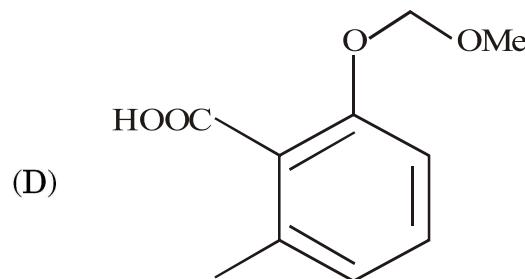
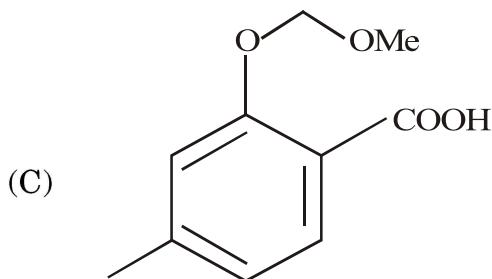
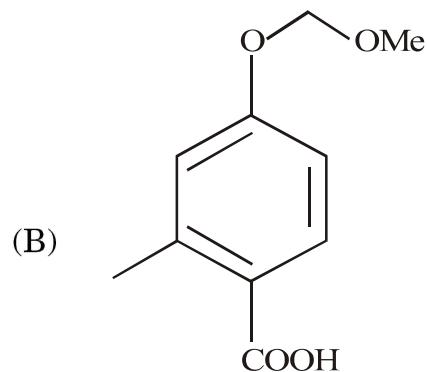
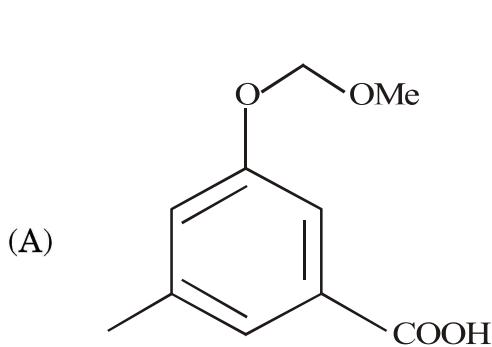


Y

Both X and Y are subjected to thermal ring opening. It will be observed that :

- (A) X undergoes ring opening, more readily compared to Y
- (B) Y undergoes ring opening, more readily compared to X
- (C) The rate of ring opening reaction is same for both molecules X and Y
- (D) Y does not undergo ring opening even at high temperature

64. Methoxymethyl ether of *m*-cresol is reacted with *t*-BuLi in dry ether and the product is reacted with dry ice followed by acidic work-up. The major product (X) formed has structure :



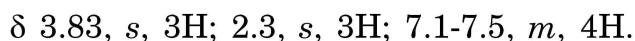
The above reaction involves :

- (A) [1, 3] sigmatropic carbon migration with inversion at migrating center
- (B) [1, 3] sigmatropic carbon migration with retention at migrating center
- (C) [1, 3] sigmatropic hydrogen migration
- (D) [1, 5] sigmatropic carbon migration with retention at migrating center

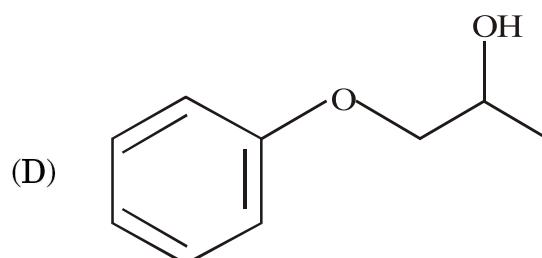
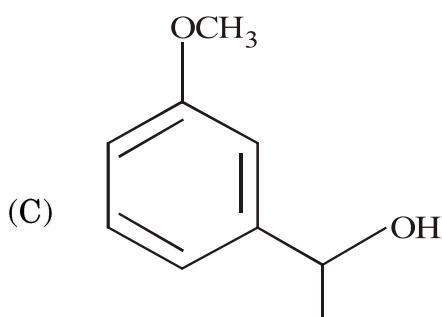
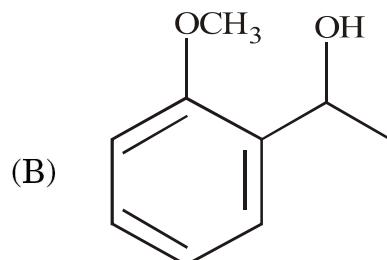
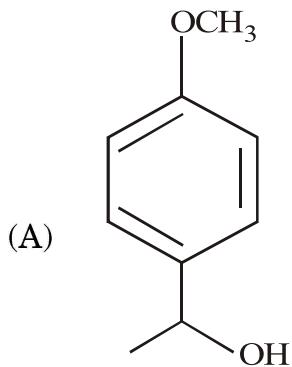
66. Pericyclic disrotatory ring opening of 1, 3-cyclo hexadiene to 1, 3, 5- hexatriene could be considered as :

- (A)  $[\pi^2s + \sigma^2a]$  cycloaddition      (B)  $[\pi^2a + \sigma^2a]$  cycloaddition  
 (C)  $[\pi^4s + \sigma^2s]$  cycloaddition      (D)  $[\pi^4a + \sigma^2a]$  cycloaddition

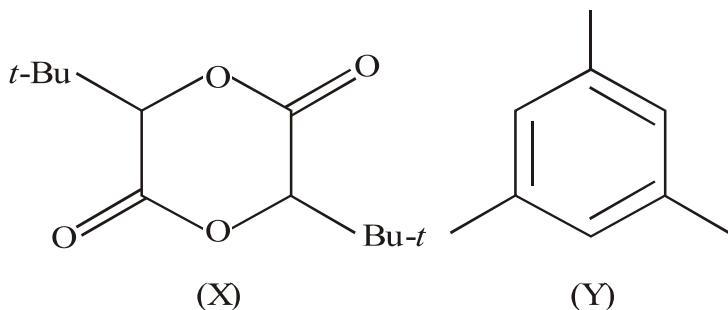
67. An aromatic ether ( $C_7H_8O$ ) is reacted with *n*-butyl lithium and the ether derivative obtained is reacted with an aliphatic aldehyde to form Y( $C_9H_{12}O_2$ ). Y on oxidation forms compound Z( $C_9H_{10}O_2$ ). Compound Z has the following PMR data :



The structure of compound [Y] is :



68

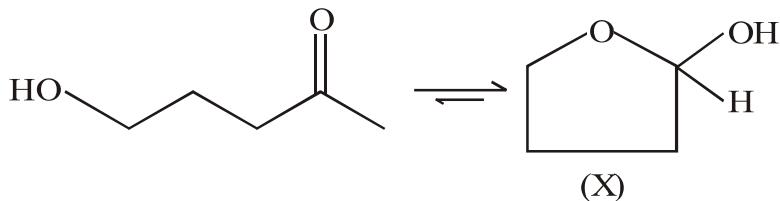


Compounds (X) and (Y) exhibit two singlets each in their  $^1\text{H}$  NMR spectrum.

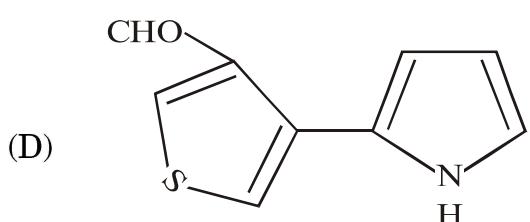
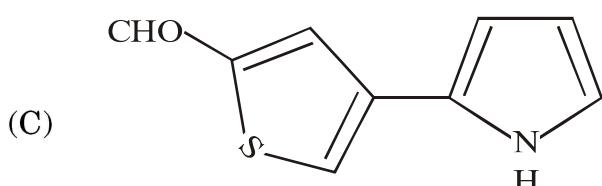
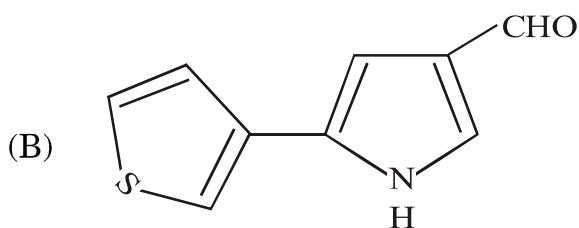
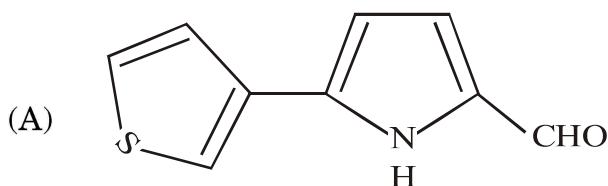
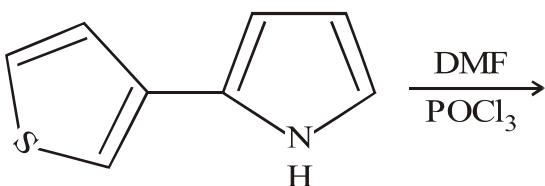
The expected chemical shifts in  $\delta$  units are :

- (A) 2.3 and 7.2 for X; 0.95 and 4.8 for Y
  - (B) 0.95 and 4.8 for X; 2.3 and 7.2 for Y
  - (C) 0.95 and 7.2 for X; 2.3 and 4.8 for Y
  - (D) 2.3 and 4.8 for X; 0.95 and 7.2 for Y

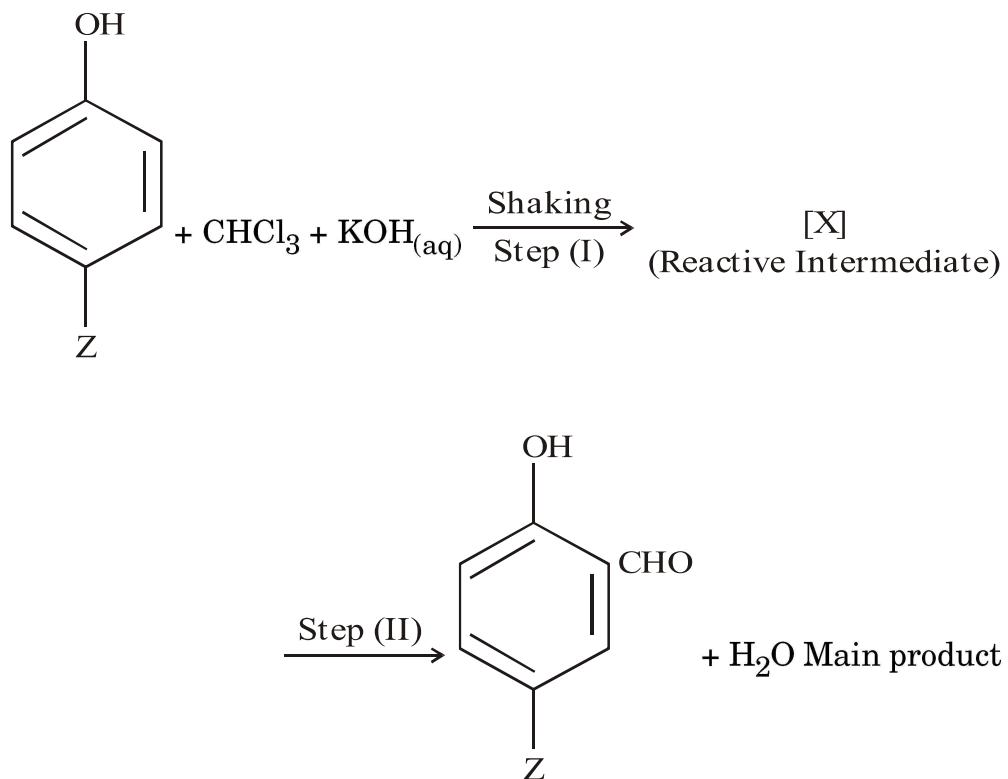
69. Identify the name of product (X) in the following transformation :



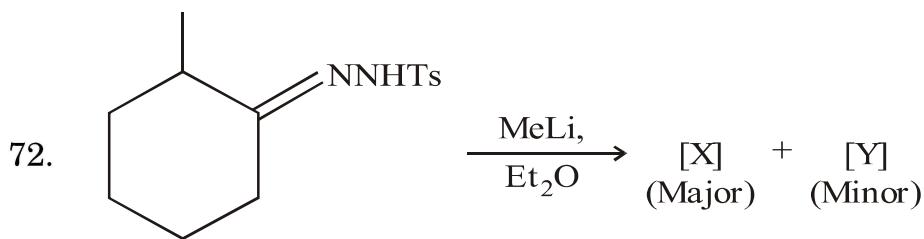
70. The major product (X) in the following reaction is :



71. In the following reaction, first step involved deprotonation of chloroform by strong base (usually KOH) to form the reactive intermediate (X) as :

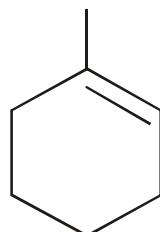


- (A) X = Dichlorocarbanion ion
- (B) X = Trichlorocarbanion ion
- (C) X = Dichlorocarbene species
- (D) X = Chlorohydrin species

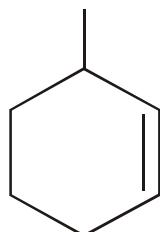


The above reaction is an example of ..... reaction and structure of [X] is :

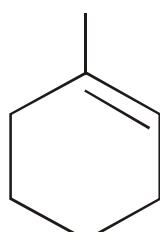
- (A) Stevens rearrangement, X =



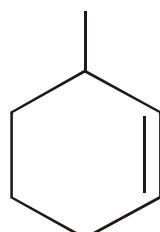
- (B) Shapiro reaction, X =



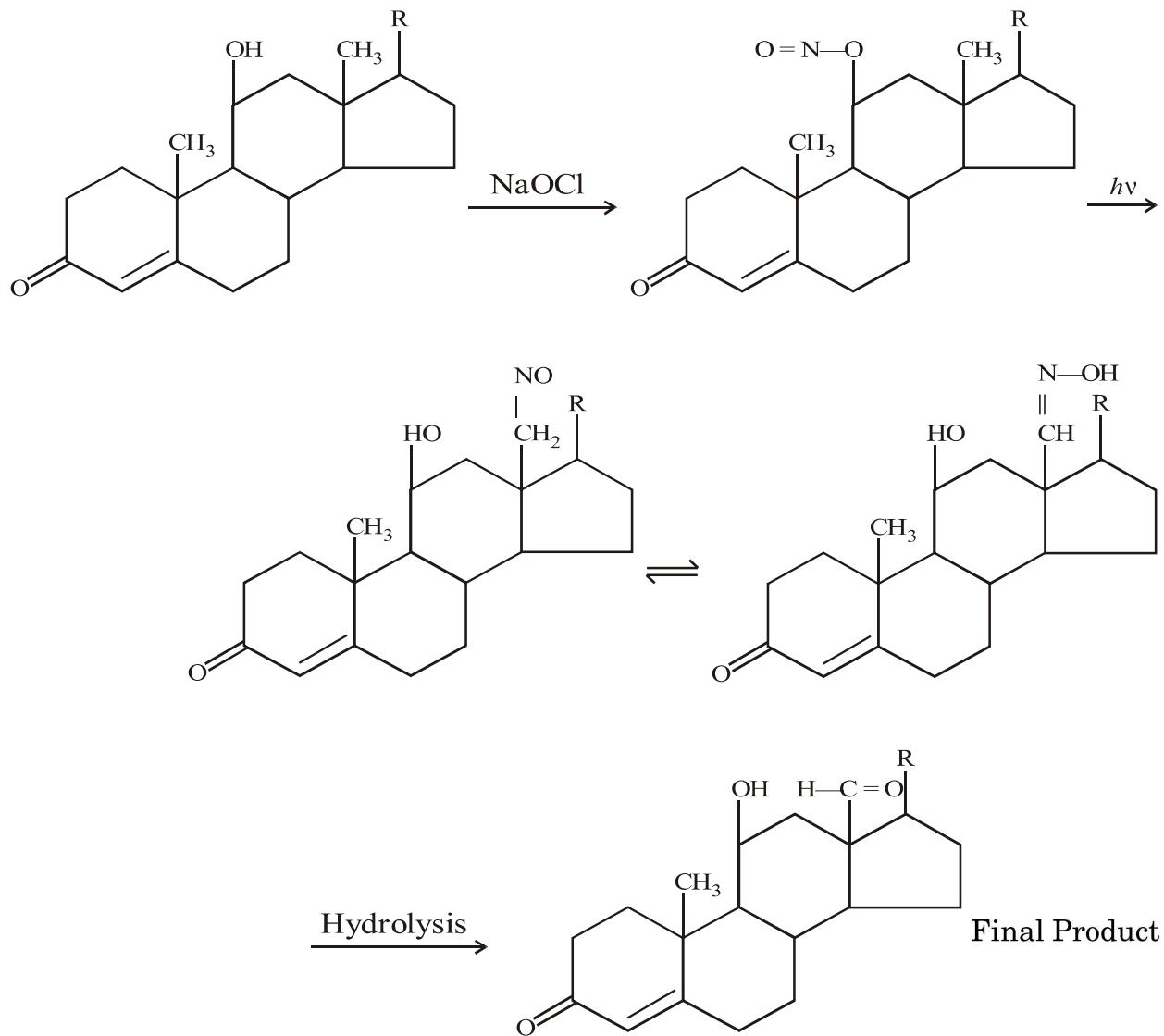
- (C) Shapiro reaction, X =



- (D) Stevens rearrangement, X =



73. Identify the following conversion :



- (A) Ene Reaction
- (B) Hofmann Löffler Reaction
- (C) Barton Reaction
- (D) Shapiro Reaction

74. Thymine is a pyrimidine base present in DNA, its carbohydrate substitution in 2-deoxyribofuranose is attached to :

- (A) N-3 of Thymine
- (B) N-1 of Thymine
- (C) Both N-1 and N-3 of Thymine
- (D) Neither N-1 nor N-3 of Thymine

75. Match the following combinations and choose suitable pairs :

- |                       |              |
|-----------------------|--------------|
| (L) $\beta$ -Carotene | (1) Protein  |
| (M) Morphine          | (2) Alkaloid |
| (N) Alanin            | (3) Steroid  |
| (O) Estrogen          | (4) Terpene  |
- (A) (L)—(3)      (M)—(1)      (N)—(4)      (O)—(2)
- (B) (L)—(1)      (M)—(3)      (N)—(2)      (O)—(4)
- (C) (L)—(4)      (M)—(2)      (N)—(1)      (O)—(3)
- (D) (L)—(2)      (M)—(4)      (N)—(3)      (O)—(1)

**MAY - 33316/III—D**

**ROUGH WORK**