PAPER : IIT-JAM 2011

CHEMISTRY-CY

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

1. The pair of semimetals in the following is:
(a) Al, Si (b) Ge, As (c) Sb, Te (d) Ca, B

2. The most probable oxidation states for both Cr and Mo are
(a) +2, +3, +4 (b) +2, +3, +5 (c) +2, +3, +6 (d) +3, +4, +5

3. The correct order of acidic character is:
(a) $Al_2O_3 > MgO > SiO_2 > P_4O_{10}$ (b) $P_4O_{10} > Al_2O_3 > MgO > SiO_2$
(c) $P_4O_{10} > SiO_2 > Al_2O_3 > MgO$ (d) $SiO_2 > P_4O_{10} > Al_2O_3 > MgO$

4. The pair of amphoteric oxides is:
(a) VO, Cr_2O_3 (b) V_2O_3, Cr_2O_3 (c) VO_2, Cr_2O_3 (d) V_2O_5, CrO_3

5. In the structure of $B_4O_5(OH)_4^{2-}$
(a) All four B atoms are trigonal planar
(b) One B atom is tetrahedral and the other three are trigonal planar.
(c) Three B atoms are tetrahedral and one is trigonal planar.
(d) Two B atoms are tetrahedral and the other two are trigonal planar.

6. The pH of an aqueous solution of Al^{3+} is likely to be
(a) Neutral (b) Acidic (c) Slightly basic (d) Highly basic.

7. Hydrolysis of $(CH_3)_2SiCl_2$ and CH_3SiCl_3 leads to
(a) Linear chain and cross-linked silicones, respectively
(b) Cross-linked and linear chain silicones, respectively.
(c) Linear chain silicones only
(d) Cross-linked silicones only.

8. The oxide that has the inverse spinel strucrure is:
(a) $FeCr_2O_4$ (b) $MnCr_2O_4$ (c) $CoAl_2O_4$ (d) Fe_2CoO_4

9. The transition metal monoxide that shows metallic conductivity is:
(a) NiO (b) MnO (c) TiO (d) CoO

10. The metal that is extracted by the reduction method is:
(a) Al (b) Au (c) Hg (d) Mg

11. The most viscous liquid is:
(a) Water (b) Methanol (c) Ethylene glycol (d) Glycerol

12. In ammonical buffer, oxine (8-hydroxyquinoline) forms yellow precipitate with
(a) Mg(II) (b) Ca (II) (c) Ba (II) (d) Sr (II)

13. Addition of an aqueous solution of Fe(II) to potassium hexacyanochromate (III) produces a brick-red coloured complex, which turns dark green at 100 ºC. The dark green complex is:
(a) $Fe_4[Cr(CN)_6]_3$ (b) $KFe[Cr(CN)_6]$ (c) $KCr[Fe(CN)_6]$ (d) $Fe[Cr(CN)_6]$

14. In the following equation X is:

$$^{241}_{95}\text{Am} + \alpha \longrightarrow {}^{243}_{97}\text{Bk} + \text{X}$$

(a) $2\,{}^{1}_{0}\text{n}$ (b) ${}^{1}_{0}\text{n}$ (c) $2\,{}^{1}_{1}\text{H}$ (d) ${}^{4}_{2}\text{He}$

15. Based on the principle of equipartition of energy, the molar heat capacity of CO_2 at constant volume $C_{v,m}$ is:
(a) 3.5 R (b) 6R (c) 6.5R (d) 9R

16. One mole of a van der waals gas undergoes reversible isothermal transformation from an initial volume V_1 to a final volume V_2. The expression for the work done is:

(a) $RT\ln\dfrac{V_2}{V_1} + a\left(V_2 - V_1\right)$ (b) $-RT\ln\dfrac{V_2 - b}{V_1 - b} + a\left(\dfrac{1}{V_1} - \dfrac{1}{V_2}\right)$

(c) $RT\ln\dfrac{P_2}{P_1}$ (d) $RT\ln\dfrac{V_2 - b}{V_1 - b} - a\left(\dfrac{1}{V_1} - \dfrac{1}{V_2}\right)$

17. The scalar product of two vectors u and v, where $u = 2\hat{i} + 3\hat{j} - 5\hat{k}$ and $v = \hat{i} + \hat{j} + 3\hat{k}$, is:

(a) –10 (b) $2\hat{i} + 3\hat{j} - 15\hat{k}$ (c) $3\hat{i} + 4\hat{j} - 2\hat{k}$ (d) 10

18. The minimum concentration of silver ions that is required that is required to start the precipitation of Ag_2S ($K_{sp} = 1\times10^{-51}$) in a 0.1 M solution of S^{2-} is:
(a) 1×10^{-49} M (b) 1×10^{-50} M (c) 1×10^{-26} M (d) 1×10^{-25} M

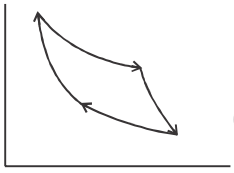
19. Identify the correct statement regarding Einsteins's photoelectric effect
(a) The number of electrons ejected depends on the wavelength of incident radiation.
(b) Electron ejection can occur at any wavelength of incident radiation.
(c) The number of electrons ejected at a given incident wavelength depends on the intensity of the radition.
(d) The kinetic energy of the ejected electrons is independent of the wavelength of incident radiation.

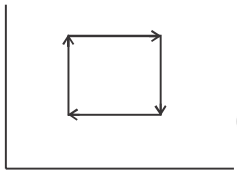
20. The hydrolysis constant (K_h) of NH_4Cl is 5.6×10^{-10}. The concentration of H_3O^+ in a 0.1 M solution of NH_4Cl at equilibrium is:

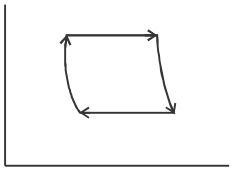
(a) $\sqrt{5.6\times10^{-11}}$ (b) $\sqrt{5.6\times10^{-10}}$ (c) 5.6×10^{-10} (d) 2.8×10^{-5}

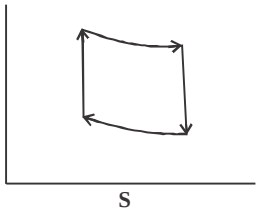
21. The acid dissociation constant (K_a) for HCOOH, CH_3COOH, $CH_2ClCOOH$ and HCN at 25°C are $1.8\times10^{-4}, 1.8\times10^{-5}, 1.4\times10^{-3}$ and 4.8×10^{-10}, respectively. The acid that gives highest pH at the equivalence point when 0.2 M solution of each acid is titrated with a 0.2 M solution of sodium hydroxide is:
(a) HCOOH (b) CH_3COOH (c) $CH_2ClCOOH$ (d) HCN.

22. For an ideal gas undergoing reversible Carnot Cycle, the plot of enthalpy (H) versus entropy (S) is:

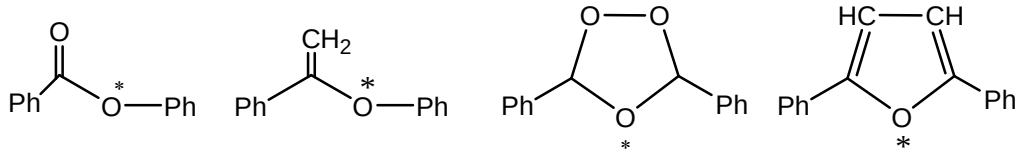
(a) 

(b) 

(c) 

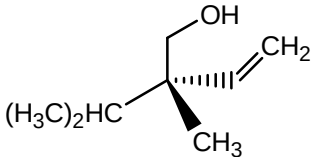
(d) 

23. Hybridizations of the atoms indicated with the asterisk (*) in the following compounds sequentially are



(a) sp^2, sp^2, sp^3, sp^2 (b) sp^2, sp^3, sp^3, sp^2 (c) sp^3, sp^3, sp^3, sp^2 (d) sp^2, sp^2, sp^3, sp^3

24. The Cahn-Ingold-Prelog (CIP) priorities of the groups and the absolute configuration (R/S) of the following compounds are



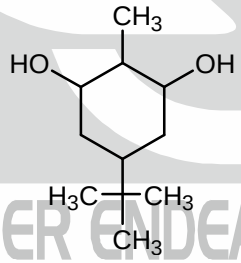
(a) $CH_2OH > CH(CH_3)_2 > CH = CH_2 > CH_3$ and S

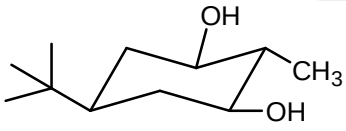
(b) $CH_2OH > CH = CH_2 > CH(CH_3)_2 > CH_3$ and S

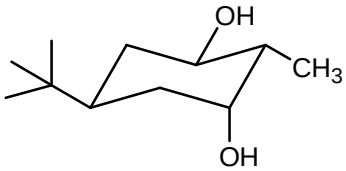
(c) $CH_2OH > CH = CH_2 > CH(CH_3)_2 > CH_3$ and R

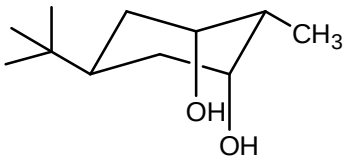
(d) $CH_2OH > CH(CH_3)_2 > CH = CH_2 > CH_3$ and R

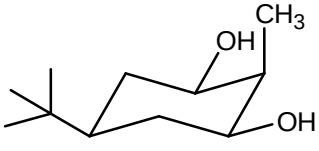
25. The optically active stereoisomer of the following compound is:



(a) 

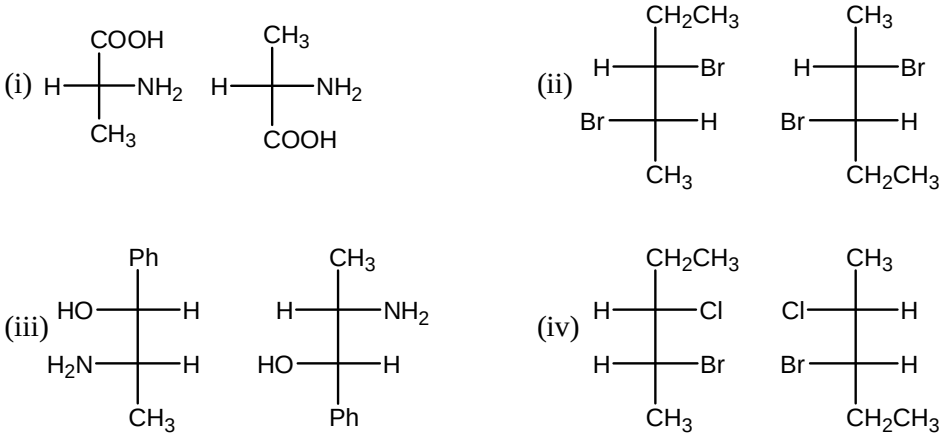
(b) 

(c) 

(d) 

26. The correct relationship within each pair of the natural products is:
(a) Camphor – terpene; insulin – protein; nicotine – alkaloids; streptomycin – carbohydrate
(b) Camphor – terpene; insulin – carbohydrate; nicotine – alkaloid; streptomycin – lipid
(c) Camphor – alkaloid; insulin – protein; nicotine – terpene; streptomycin – carbohydrate.
(d) Camphor – carbohydrate; insulin – protein; nicotine – alkaloid; streptomycin –terpene.

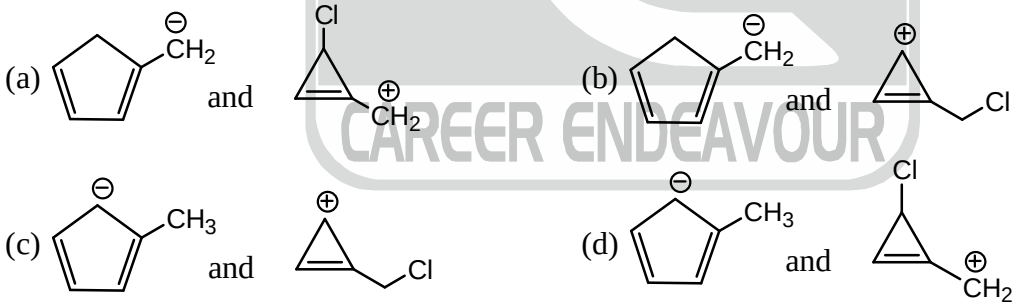
27. The correct sequence of relationships between the compounds of the following pairs i-iv is:



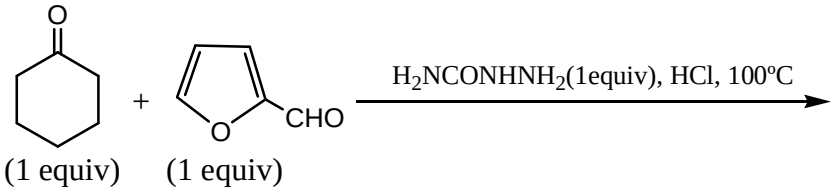
(a) Identical, enantiomers, diastereomers and structural isomers.
(b) Enantiomers, identical, structural isomers and diastereomers.
(c) Enantiomers, identical, diasteromers and structural isomers.
(d) Identical, identical, diastereomers and structural isomers.

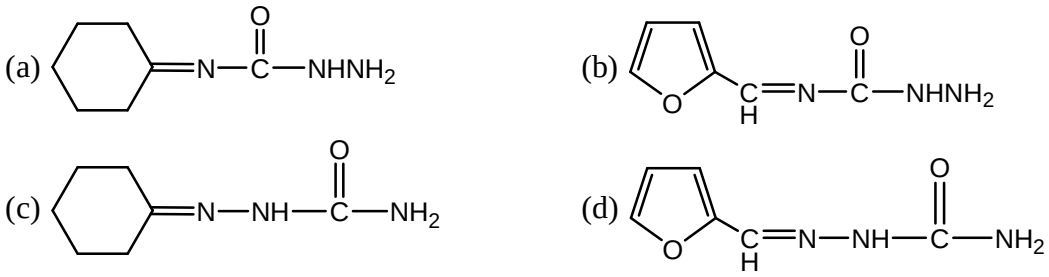
28. The INCORRECT statement in the following is:
(a) The nucleobase pairs are aligned perpendicular to the helical axis in DNA.
(b) RNA contains uracil and thymine, but DNA contains only thymine.
(c) All naturally occuring amino acids with the exception of glycine are chiral
(d) All enzymes are proteins, but all proteins are not necessarily enzymes.

29. The product P and Q in the following reactions, respectively, are



30. The major product in the following reaction is:





31. (a) In the following reactions, identify X, Y and Z. **[9]**

$$Na_2SO_3 + S \xrightarrow{\text{boiling water}} X(\text{colorless solid})$$

$$AgBr \xrightarrow{\text{excess X}} Y(\text{soluble complex})$$

$$X + Cl_2 + H_2O \xrightarrow{\text{boiling water}} Z + HCl$$

(b) Draw the structures of $S_4N_4H_4$ and $N_4S_4F_4$. **[6]**

32. (a) The magnetic moment of $\left[Fe(phen)_2(NCS)_2\right]$ varies with temperature. The magnetic moments at 200 K and 50 K are 4.9 B.M. and 0 B.M., respectively. Write the d-electron configurations of Fe at both temperatures and give reason for the observed change in the magnetic moment. (phen = 1, 10-phenanthroline) **[6]**

(b) PCl_5 exists as a discrete covalent molecule in the gaseous state, but is ionic in the solid state. Draw the structures of PCl_5 in gaseous and solid states. **[9]**

33. In the following equilibrium and reactions, identify species B to E. **[15]**
Write the balanced chemical equation for the conversion of C to E.

$$A \xrightarrow{pH > 6} B \underset{}{\overset{\text{dil. HCl}}{\rightleftharpoons}} C$$

- oxide of Cr
- solid
- no d-electrons

- yellow color
- tetrahedral

- strong oxidizing agent

$$B + \text{diphenylcarbazide} \longrightarrow D(\text{violet color})$$

$$C + HCl \longrightarrow E(\text{greenish yellow gas})$$

34. (a) Identify species A and C in the following. **[9]**
Write the balanced chemical equation for the conversion of A to A^{3+}.

$$A + \text{aqua regia} \longrightarrow A^{3+} + NO$$

$$A^{3+} + I^- \longrightarrow B(\text{black precipitate})$$

$$B + I^-(\text{excess}) \rightleftharpoons C(\text{orange color})$$

Hint: C on the dilution with water gives B

(b) Draw the structures of X and Y in the following reactions. **[6]**

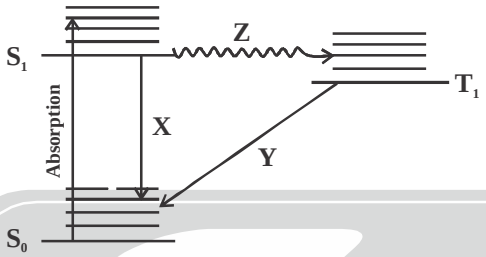
(i) Borazine + HCl $\longrightarrow$ X

(ii) Borazine + Br_2 $\longrightarrow$ Y

35. (a) The molar conductances at infinite dilution for $BaCl_2$, KCl, K_2SO_4 and Cl^- are 280, 150, 300 and $76\ \Omega^{-1}m^2mol^{-1}$, respectively. Calculate the transport number of Ba^{2+} in $BaSO_4$ solution at infinite dilution. **[9]**

(b) If 4 moles of a MX_2 salt in 1 kg of water raises the boiling point of water by 3.2 K. Calculate the degree of dissociation of MX_2 in the solution. **[6]**
[For water, $k_b = 0.5$ K kg mol^{-1}]

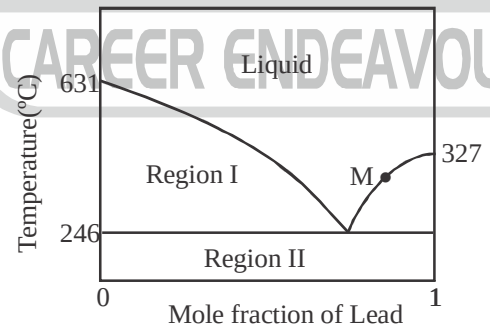
36. (a) For the reaction $R \rightarrow P$, the plot of ln[R] versus time (t) gives a straight line with a negative slope. The half life for the reaction is 3 minutes.
(ln 2 = 0.693, ln 0.1 = – 2.303)
(i) Derivative the expression for $t_{1/2}$.
(ii) Calculate the slope of the straight line **[9]**
(iii) Calculate the time required for the concentration of R to decrease to 10% of its initial value.
(b) Shown below is the Jablonski diagram that describes various photophysical processes. The solid arrows $(\rightarrow)$ represent radiative transitions and the wave arrow ($\rightsquigarrow$) represents a non-radiative transition. **[6]**



(i) Name the photophysical pathways X, Y and Z.
(ii) Which of the radiative decays is faster?

37. (a) (i) Given that $\Delta G = -nFE$, derive the expression for the temperature dependence of the cell potential (E) in terms of the change in entropy (ΔS). **[9]**

(ii) For a cell reaction, E(at 25ºC) = 1.26 V, n =2 and $\Delta S = -96.5 \text{ J K}^{-1}\text{mol}^{-1}$. Calculate E at 85º C by assuming ΔS to be independent of temperature. (F = 96500 C mol^{-1}).
(b) The phase diagram for the lead-antimony system at a certain pressure is given below.



(i) Identify the phases and components in region I and region II.
(ii) Calculate the number of degrees of freedom (Variance) at point M. **[6]**

38. (a) One mole of an ideal gas initially at 300 K and at a pressure of 10 atm undergoes adiabatic expansion.
(i) Reversibly and
(ii) Irreversibly against a constant external pressure of 2 atm until the final pressure becomes equal to the external pressure.

Calculate ΔS_{system} for (i) and (ii). For (ii), express the final answer in terms of R. Given: Molar heat capacity at constant volume $C_{v,m}$ = 3R/2. **[9]**

(b) For the following equilibrium at 300 ºC.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate K_p when N_2O_4 is 30% dissociated and the total pressure is 2 bar. **[6]**

39. (a) The Maxwell probability distribution of molecular speeds for a gas is:

$$F(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)dv$$

where 'v' is the speed, 'm' the mass of a gas molecule and k the Boltzmann constant.
(i) Use F(v) to show that the most probable speed v_{mp} is given by the expression.

$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2}$$

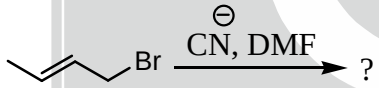
(ii) Use R = 8 J K^{-1} mol^{-1} in the above expression to calculate the v_{mp} for $CH_4(g)$ at 127 ºC. **[9]**

(b) The wavefunction of a quantum state of hydrogen atom with principal quantum number n = 2 is:

$$\psi_{2\ell m}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$$

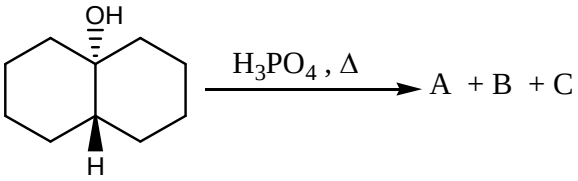
(i) Identify the values of quantum numbers *l* and m and hence the atomic orbital.
(ii) Find where the radial node of the wavefunction occurs. **[6]**

40. (a) Write the possible substitution products in the following reactions. Indicate the types of mechanisms ($S_N1/S_N2/S_N2'$) that is/are operative in each reaction. **[9]**

(i) 

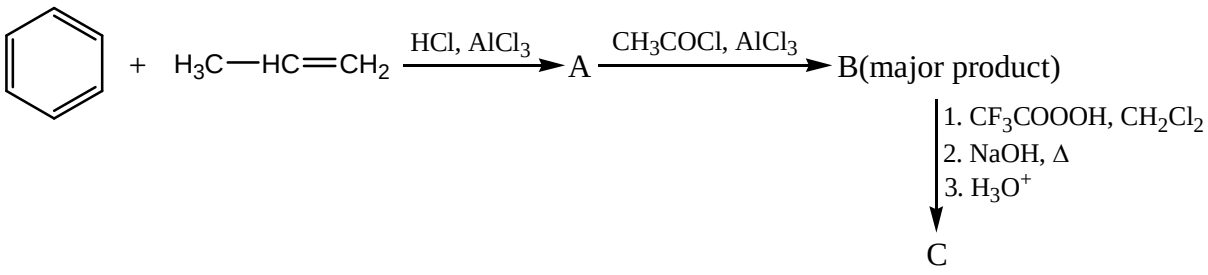
(ii) 

(b) Write the elimination products A to C in the following reaction. Identify the major product

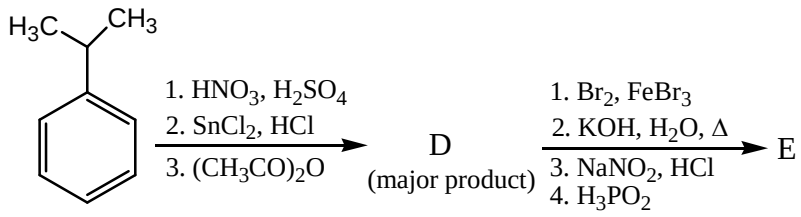


[6]

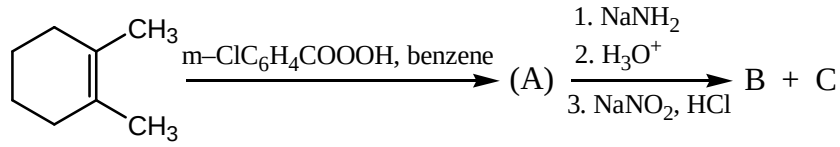
41. (a) Write the structures of A to C in the following reaction sequence. **[9]**



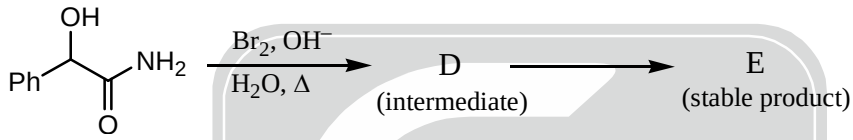
(b) Write the structures of D and E in the reactions given below. **[6]**



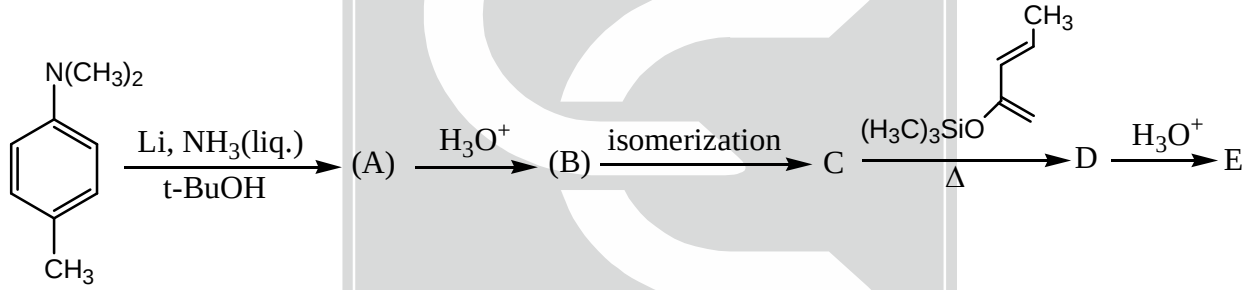
42. (a) Write the structures of A to C in the following reaction sequence. **[9]**



(b) Write the structures of D and E in the following reaction. **[6]**



43. Write the structures of products A to E in the following reaction sequence. **[15]**



44. Oxanamide O, a tranquilizer, is synthesized according to the following reaction scheme. Write the missing structures and reagents K to O. **[15]**