## CHEMISTRY-CY

Q.1 – Q.25 : Carry ONE mark each.

1. Consider N particles at temperature T, pressure P, volume V and chemical potential μ having energy E. The parameters that are kept constant for a canonical ensemble are
   (a) N, V, T   (b) N, V, E   (c) N, P, T   (d) μ, V, T

2. For *ortho*-hydrogen, the nuclear wavefunction and the rotational quantum number, respectively, are
   (a) antisymmetric and even   (b) symmetric and odd
   (c) symmetric and even   (d) antisymmetric and odd

3. m_1 and m_2 are the slopes (dP/dT) of the solid-liquid equilibrium lines in the P-T phase diagrams of H_2O and CO_2, respectively. For $P < 10$ atm, the values of m_1 and m_2 are
   (a) $m_1 > 0$ and $m_2 > 0$ (b) $m_1 > 0$ and $m_2 < 0$ (c) $m_1 < 0$ and $m_2 < 0$ (d) $m_1 < 0$ and $m_2 > 0$

4. The rate constant of a reaction is 1.25×10^{-4} mol L^{-1} s^{-1}. If the initial concentration of the reactant is 0.250 mol L^{-1}, the total time (in seconds) required for complete conversion is _____

5. Consider an ideal gas of volume V at temperature T and pressure P. If the entropy of the gas is S, the partial derivative $(\partial P/\partial S)_V$ is equal to
   (a) $(\partial T/\partial P)_S$ (b) $(\partial T/\partial V)_P$ (c) $-(\partial T/\partial V)_S$ (d) $(\partial T/\partial S)_P$

6. The wavelength associated with a particle in one-dimensional box of length L is (n refers to the quantum number)
   (a) $2L/n$ (b) L/n (c) nL (d) $L/2n$

7. The dependence of rate constant k on temperature T(in K) of a reaction is given by the expression
   $$\ln k = [(-5000 \text{ K})/T] + 10$$
   The activation energy of the reaction (in kJ mol^{-1}) is _____ (up to two decimal places)

8. The lowest energy of a quantum mechanical one-dimensional simple harmonic oscillator is 300 cm^{-1}. The energy (in cm^{-1}) of the next higher level is _____

9. The electronic ground state term for the chromium ion in $[Cr(CN)_6]^{4-}$ is
   (a) ^3F (b) ^3H (c) ^3G (d) ^5D

10. The VO_4^{3-}, CrO_4^{2-} and MnO_4^- ions exhibit intense ligand to metal charge transfer transition. The wavelengths of this transition follow the order
    (a) $CrO_4^{2-} < VO_4^{3-} < MnO_4^-$ (b) $MnO_4^- < VO_4^{3-} < CrO_4^{2-}$
    (c) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ (d) $CrO_4^{2-} < MnO_4^- < VO_4^{3-}$

11. The lanthanide ion the exhibits color in aqueous solution is
    (a) La(III)   (b) Eu(III)   (c) Gd(III)   (d) Lu(III)

12. The hapticity of cycloheptatriene, (C_7H_8), in $Mo(C_7H_8)(CO)_3$ is _____

13. The v_{O-O} resonance Raman stretching frequency (in cm^{-1}) of the O_2 coordinated to iron centre in oxy-hemoglobin is nearly
    (a) 1100   (b) 850   (c) 1550   (d) 1950

14. The energy band diagram for magnesium is

(The hatched and unhatched regions in the figure correspond to filled and unfilled regions of the band, respectively.)

(a)   (b)

(c)   (d)
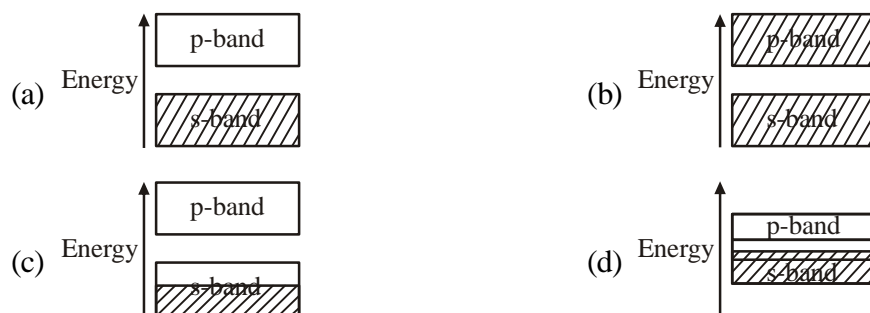
15. P, F and I represent primitive, face-centered and body-centered lattices, respectively. The lattice types of NaCl and CsCl, respectively, are
   (a) F and I   (b) F and P   (c) I and P   (d) P and I

16. The characteristic feature of an electron spin resonance (ESR) spectrum of frozen aqueous solution of $CuSO_4 \cdot 5H_2O$ at 77 K is

   (a) $g_{\parallel} > g_{\perp}$ (b) $g_{\parallel} < g_{\perp}$ (c) $g_{\parallel} = g_{\perp}$ (d) $g_x \neq g_y \neq g_z$

17. The most suitable reagent for the following transformation is
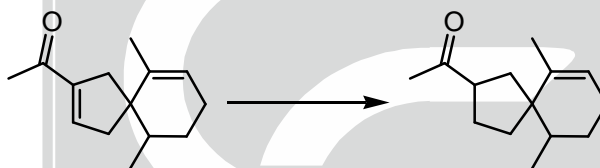
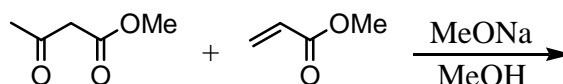   (a) $Li / Liq. NH_3$ (b) PtO_2 / H_2 (c) $LiAlH_4$ (d) B_2H_6

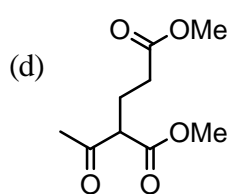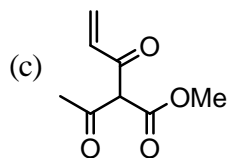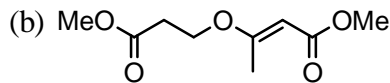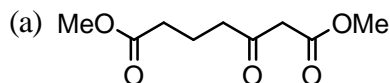18. The major products M and N formed in the following reactions are

(a)

(b)

(c)

(d)
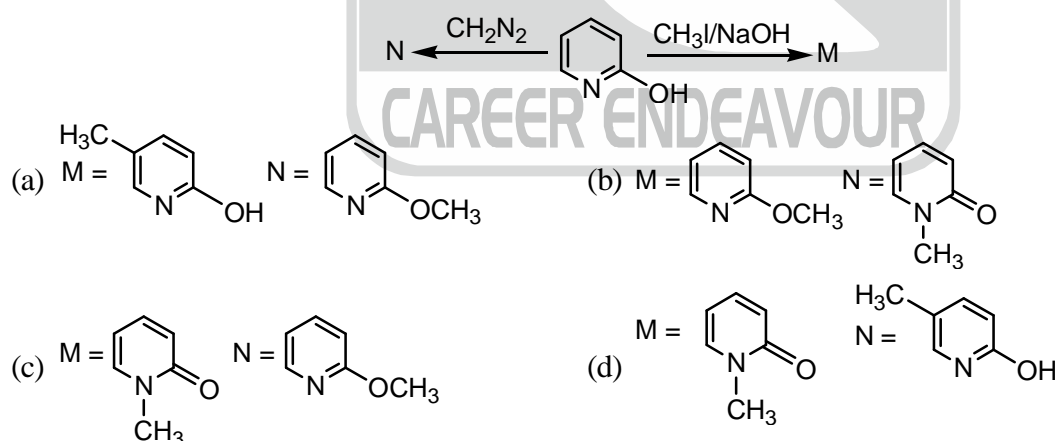
19. The $^{13}C \ NMR$ spectrum of acetone-d_6 has a signal at 30 ppm as a septet in the intensity ratio
   (a) 1 : 6 : 15 : 20 : 15 : 6 : 1   (b) 1 : 3 : 6 : 7 : 6 : 3 : 1
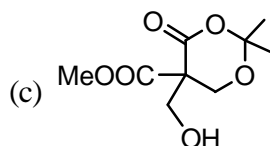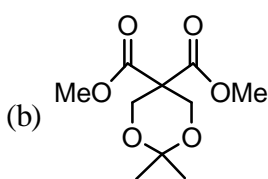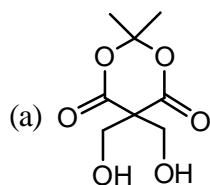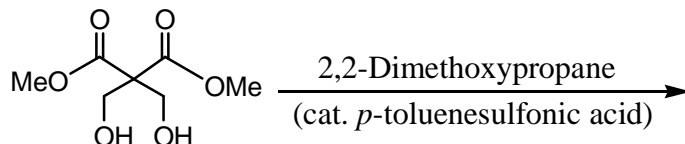   (c) 1 : 2 : 3 : 5 : 3 : 2 : 1   (d) 1 : 3 : 7 : 10 : 7 : 3 : 1

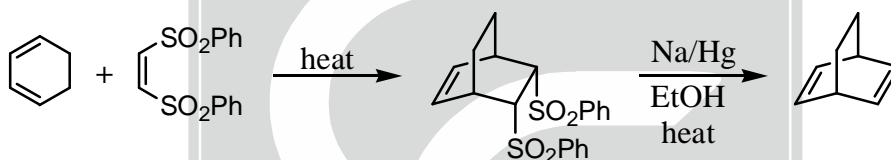20. The major product formed in the following reaction is

(a) MeO ... OMe

(b) MeO ... OMe

(c) ... OMe

(d) ... OMe

21. The major product obtained in the following reaction is

MeO—C(=O)—C(CH₂OH)₂—C(=O)—OMe $\xrightarrow{\text{2,2-Dimethoxypropane}}$ (cat. *p*-toluenesulfonic acid)

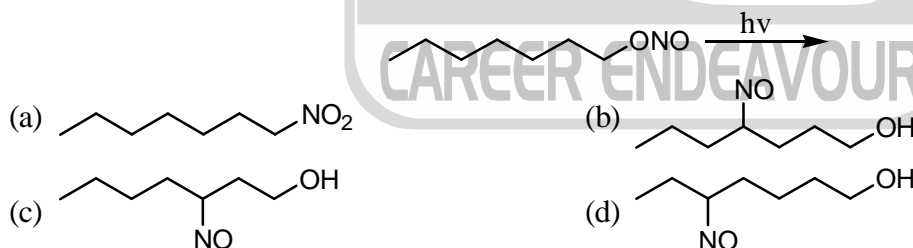(a)   (b) MeO ... OMe   (c) MeOOC ... OH   (d)
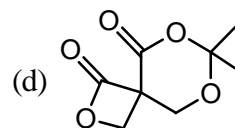
22. In the two step reaction sequence given below, the starting bis-sulfone acts as

(structure) + (structure with SO₂Ph, SO₂Ph) $\xrightarrow{\text{heat}}$ (structure with SO₂Ph, SO₂Ph) $\xrightarrow[\substack{\text{EtOH} \\ \text{heat}}]{\text{Na/Hg}}$ (structure)
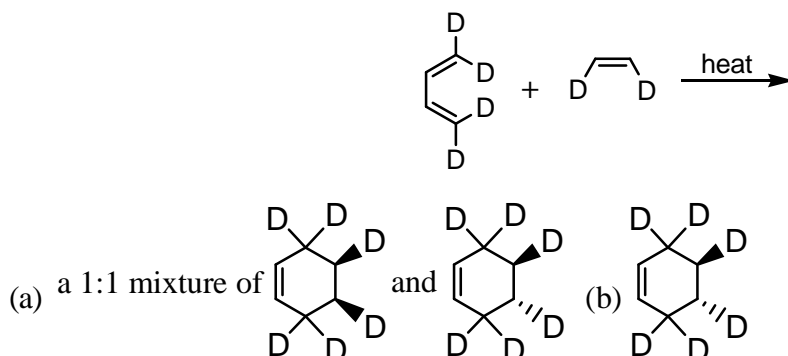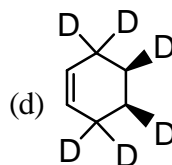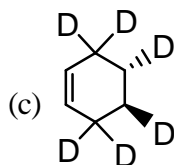
(a) a dienophile and synthetic equivalent of acetylene
(b) a dienophile and synthetic equivalent of ethylene
(c) a dipolarophile and synthetic equivalent of acetylene
(d) a dipolarophile and synthetic equivalent of ethylene

23. The major product formed in the following photochemical reaction is

(structure)—ONO $\xrightarrow{h\nu}$

(a) (structure)—NO₂

(b) (structure with NO)—OH

(c) (structure with NO)—OH

(d) (structure with NO)—OH

24. The product formed in the following reaction is

(structure with D's) + (structure with D's) $\xrightarrow{\text{heat}}$

(a) a 1:1 mixture of (structure) and (structure)

(b) (structure)

(c)   (d)

25. The number of possible stereoisomers for cyclononene is _____

Q.26 – Q.55 : Carry TWO marks each.

26. The mobility of a univalent ion in aqueous solution is 6.00×10^{-8} m^2 s^{-1} V^{-1} at 300 K. Its diffusion coefficient at 300 K is $X \times 10^{-9}$ m^2 s^{-1}. The value of X is _____ (up to two decimal places)

27. For the following consecutive first order reactions

$$X \xrightarrow{K_1 = 2.0\ s^{-1}} Y \xrightarrow{K_2 = 0.1\ s^{-1}} Z$$
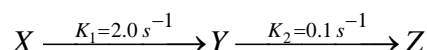
the time (in seconds) required for Y to reach its maximum concentration (assuming only X is present at time $t = 0$) is _____ (up to two decimal places)

28. Under physiological conditions, the conversion of CO_2 to bicarbonate ion by carbonic anhydrase enzyme (MW = 30,000 g mol^{-1}) has a turnover number of 4.00×10^5 s^{-1}. The minimum amount of enzyme (in μg) required to convert 0.44 g of CO_2 to bicarbonate ions in 100 seconds is _____ (up to two decimal places)

29. Assume 1,3,5-hexatriene to be a linear molecule and model the π electrons as particles in a one-dimensional box of length 0.70 nm. The wavelength (in nm) corresponding to the transition from the ground-state to the first excited-state is _____

30. The standard Gibbs free energy change of the reaction shown below is –2.7 kJ mol^{-1}.

$$Sn(s) + Pb^{2+} = Sn^{2+} + Pb(s)$$
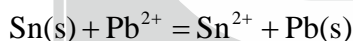
Given that $E^0(Pb^{2+}/Pb)$ is –0.126 V, the value of $E^0(Sn^{2+}/Sn)$ in V is _____ (up to two decimal places)

31. The dissociative chemisorption of $X_2(g)$ on a metal surface follows langmuir adsorption isotherm. The ratio of the rate constants of the adsorption and desorption processes is 4.0 atm^{-1}. The fractional surface coverage of X(adsorbed) at 1.0 atm pressure is _____ (up to two decimal places)

32. The ionic activity coefficients of Ca^{2+} and F^- are 0.72 and 0.28, respectively. The mean activity coefficient of CaF_2 is _____ (up to two decimal places)

33. The angle of orientation (in degrees) of the angular momentum vector with respect to z-axis for $I = 2$ and $m_\ell = +2$ state of H-atom is _____ (up to two decimal places).

34. The Gibbs free energy of mixing is denoted as ΔG_{mix}. 1.0 mole of He, 3.0 moles of Ne and 2.0 moles of Ar are mixed at the same pressure and temperature. Assuming ideal gas behavior, the value of $\Delta G_{mix}/RT$ is _____. (up to two decimal places)

35. $\Psi = \left[c\phi_1 - \left(1/\sqrt{3}\right)\phi_2 \right]$ represents a normalized molecular orbital constructed from two different atomic orbitals ϕ_1 and ϕ_2 that form an orthonormal set. The value of |c| is _____. (up to two decimal places)

36. In cyclophosphazenes, $(NPX_2)_3$ (X = F, Cl, Br and Me), the strength of P–N π-bond varies with X in the order

   (a) $F > Cl > Br > Me$ (b) $Me > F > Cl > Br$ (c) $Br > Cl > F > Me$ (d) $Me > Br > Cl > F$

37. The structure type and shape of the polyhedral (skeletal) framework of the carborane $Me_2C_2B_{10}H_{10}$, respectively, are

   (a) *nido* and *dodecahedron*   (b) *closo* and *icosahedron*
   (c) *nido* and *icosahedron*   (d) *closo* and *dodecahedron*

38. If Δ_o is the octahedral splitting energy and P is the electron pairing energy, then the crystal-field stabilization energy (CFSE) of $[Co(NH_3)_6]^{2+}$ is

   (a) $-0.8\Delta_o + 2\,P$ (b) $-0.8\Delta_o + 1\,P$ (c) $-0.8\Delta_o$ (d) $-1.8\Delta_o + 3\,P$

39. The rates of substitution for the following reaction vary with L in the order

$$L = CH_3^-, Cl^-, Ph^- \text{ and } H^-$$
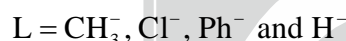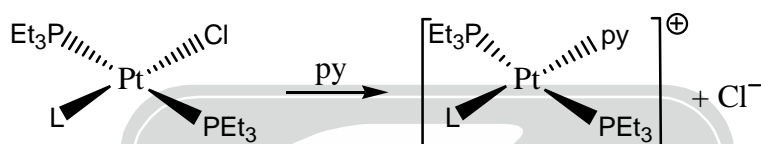
   (a) $CH_3^- > Cl^- > Ph^- > H^-$ (b) $Cl^- > Ph^- > H^- > CH_3^-$
   (c) $Ph^- > CH_3^- > H^- > Cl^-$ (d) $H^- > CH_3^- > Ph^- > Cl^-$

40. The product formed in the reaction of $MeMn(CO)_5$ with ^{13}CO is

   (a) $(Me^{13}CO)Mn(CO)_5$ (b) $(MeCO)Mn(CO)_5$
   (c) $(MeCO)Mn(CO)_4(^{13}CO)$ (d) $(Me^{13}CO)Mn(CO)_4(^{13}CO)$

41. For the following three alkenes, 1, 2 and 3, the rates of hydrogenation using Wilkinson's catalyst at 25ºC vary in the order
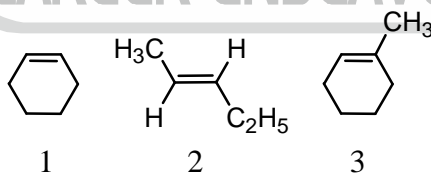

   (a) $1 > 3 > 2$ (b) $1 > 2 > 3$ (c) $2 > 1 > 3$ (d) $2 > 3 > 1$

42. ^{210}Bi undergoes β^- decay to 1/8 of its initial amount in 15 days. The time required for its decay to 1/4 of its initial amount is _____ days (up to two decimal places).

43. The metal ion and the macrocyclic skeleton present in the green pigment of plants, respectively, are
   (a) Mg(II) and chlorin   (b) Mg(II) and corrin   (c) Mn(II) and chlorin   (d) Mg(II) and porphine

44. The spinel structure of $MgAl_2O_4$ has cubic close packed arrangement of oxide ions. The fractions of the octahedral and tetrahedral sites occupied by cations, respectively, are

   (a) 1/8 and 1/2   (b) 1/4 and 1/2   (c) 1/2 and 1/4   (d) 1/2 and 1/8

45. The diffusion limiting current (I_d) at a dropping mercury electrode for an aqueous Mg(II) solution of concentration 'c' (mol L^{-1}) is 300 µA. If 'c' is increased by 0.1 mol L^{-1}, I_d increases to 900 µA. The value of 'c' (in mol L^{-1}) is _____ (up to two decimal places)
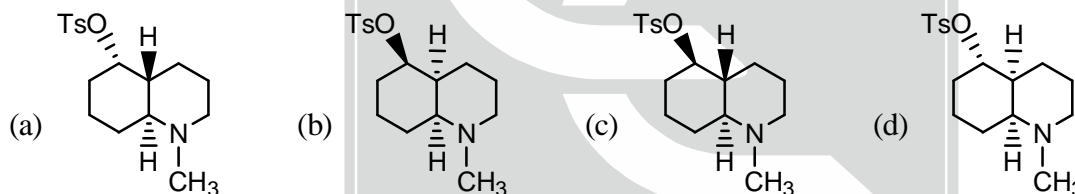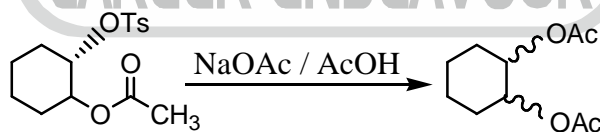
46. The major product formed in the following reaction is

(a)   (b)   (c)   (d)
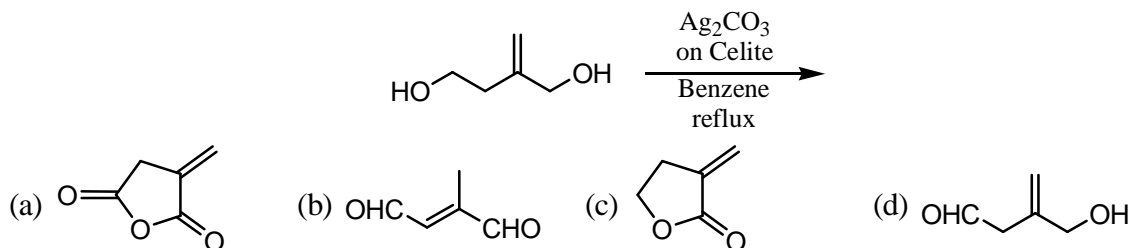
47. The product formed in the following photochemical reaction is

(a)   (b)   (c)   (d)
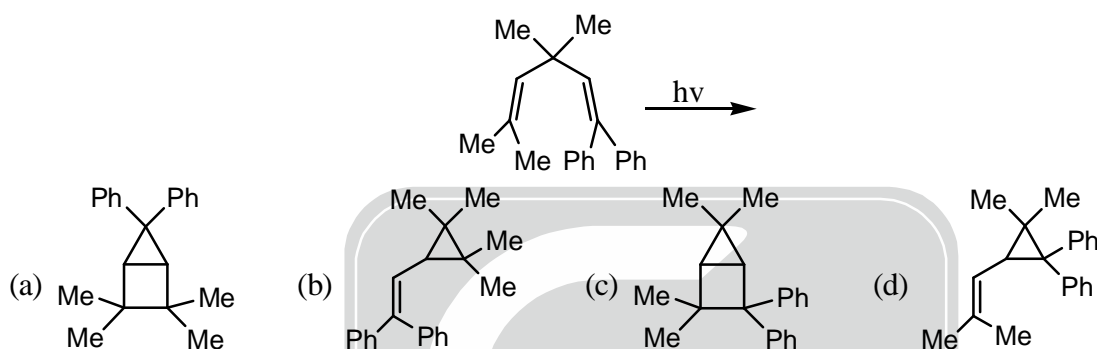
48. Among the following decahydroquinoline toluenesulfonates (Ts), the one that yields 9-methylamino-E-non-5-enal as a major product upon aqueous solvolysis is

(a)   (b)   (c)   (d)

49. The product obtained in the following solvolysis reaction is

Enantiomerically pure compound

(a) a racemic mixture of trans 1,2-diacetoxycyclohexane
(b) enantiomerically pure trans 1,2-diacetoxycyclohexane
(c) racemic cis 1,2-diacetoxycyclohexane
(d) a mixture of cis and trans 1,2-diacetoxycyclohexane

50. The spectroscopic data for an organic compound with molecular formula $C_{10}H_{12}O_2$ are given below. IR band around 1750 cm^{-1}. ^{1}H NMR δ 7.3 (m, 5H), 5.85 (q, 1H, J = 7.2 Hz), 2.05 (s, 3H), 1.5 (d, 3H, J = 7.2 Hz) ppm. the compound is

(a) methyl 2-phenylpropionate   (b) 1-(phenylethyl) acetate
(c) 2-(phenylethyl) acetate   (d) methyl 3-phenylpropionate

51. The structures of the intermediate [P] and major product Q formed in the following reaction sequence are
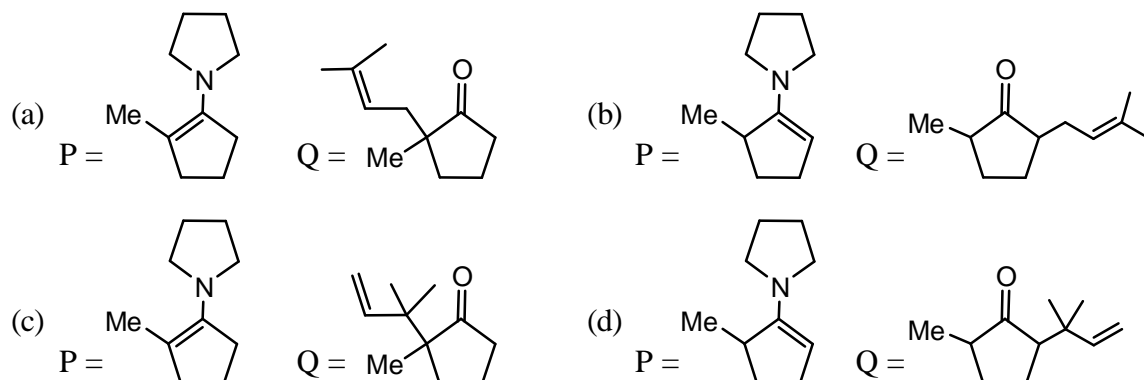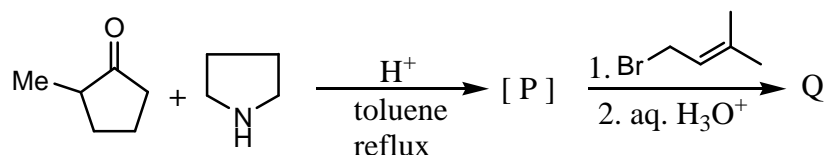

52. Hydration of fumaric acid gives malic acid as shown below. Assume that addition of water takes place specifically from A face or B face. The correct statement pertaining to stereochemistry of malic acid formed is
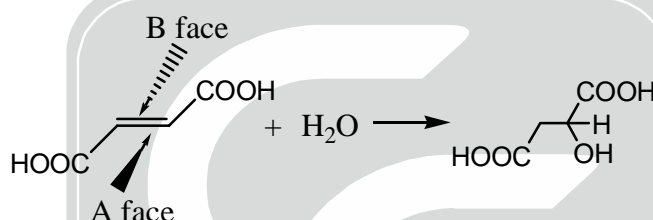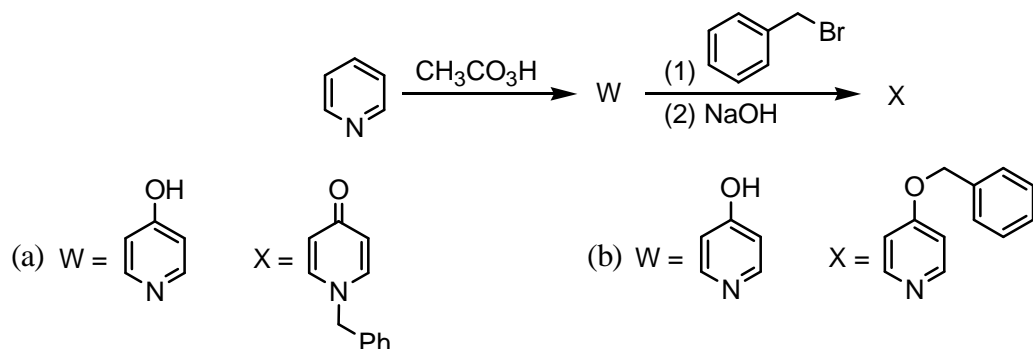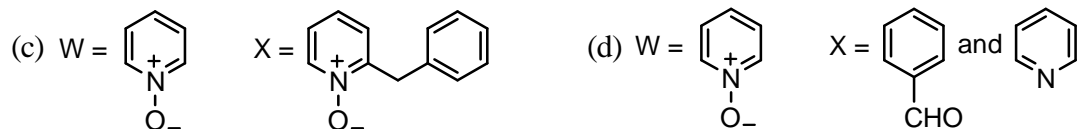

(a) addition specifically from A face gives S isomer of malic acid
(b) addition specifically from B face gives S isomer of malic acid
(c) addition specifically from A face gives R isomer of malic acid
(d) addition specifically from B face gives a racemic mixture of malic acid

53. Hydroboration of 2-butyne with $(C_6H_{11})_2BH$ yields the intermediate U, which on treatment with I_2 and NaOMe at $-78^\circ C$, gives product V. The structures of U and V are
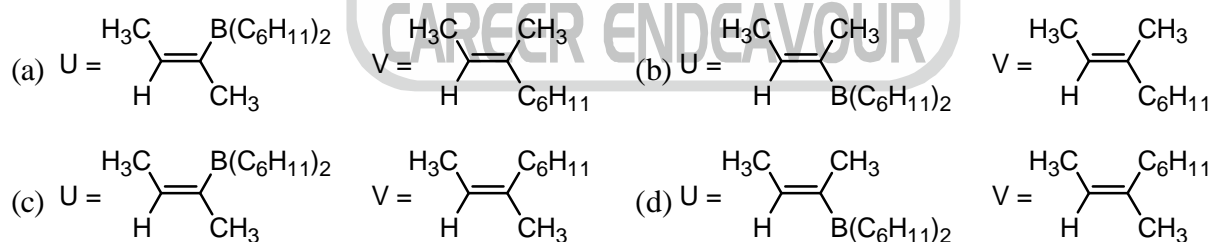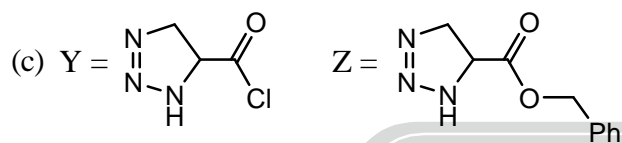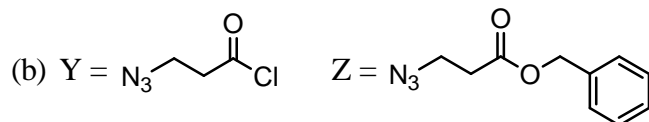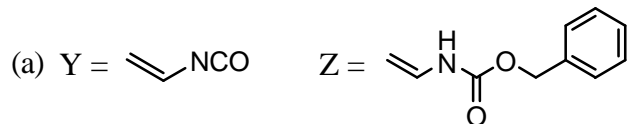
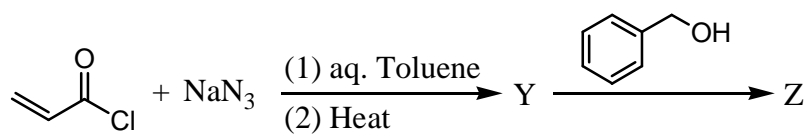

54. The structures of the major products W and X in the following synthetic scheme are

(c) W = [pyridine N-oxide structure]   X = [2-benzylpyridine N-oxide structure]

(d) W = [pyridine N-oxide structure]   X = [benzaldehyde structure] and [pyridine structure]

55. The major products Y and Z in the following reaction sequence are

[Reaction scheme: acryloyl chloride + NaN₃ → (1) aq. Toluene (2) Heat → Y → (benzyl alcohol) → Z]

(a) Y = [vinyl isocyanate, CH₂=CH–NCO] Z = [benzyl N-vinyl carbamate structure]

(b) Y = [N₃–CH₂CH₂–C(=O)Cl] Z = [N₃–CH₂CH₂–C(=O)–O–CH₂Ph benzyl ester]

(c) Y = [triazoline-carbonyl chloride structure] Z = [triazoline-carbonyl benzyl ester structure]

(d) Y = [CH₂=CH–C(=O)–N₃] Z = [Ph–CH₂–O–CH₂CH₂–C(=O)–N₃]