

Section-A

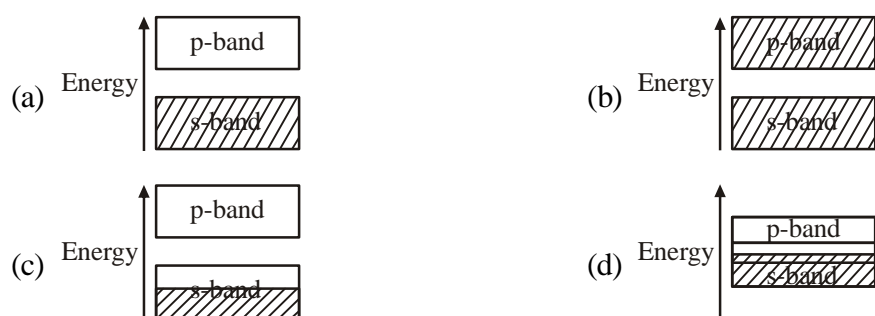
Q.1 – Q.25 : Carry ONE mark each.

- 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
- 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
- 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 $m_2 > 0$
- The rate constant of a reaction is $1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. If the initial concentration of the reactant is 0.250 mol L^{-1} , the total time (in seconds) required for complete conversion is _____
- 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) $(\partial T/\partial S)_P$
- 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) $L/2n$
- 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)
- 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 _____
- The electronic ground state term for the chromium ion in $[\text{Cr}(\text{CN})_6]^{4-}$ is
 (a) 3F (b) 3H (c) 3G (d) 5D
- 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) $\text{CrO}_4^{2-} < \text{VO}_4^{3-} < \text{MnO}_4^-$ (b) $\text{MnO}_4^- < \text{VO}_4^{3-} < \text{CrO}_4^{2-}$
 (c) $\text{VO}_4^{3-} < \text{CrO}_4^{2-} < \text{MnO}_4^-$ (d) $\text{CrO}_4^{2-} < \text{MnO}_4^- < \text{VO}_4^{3-}$
- The lanthanide ion that exhibits color in aqueous solution is
 (a) La(III) (b) Eu(III) (c) Gd(III) (d) Lu(III)
- The hapticity of cycloheptatriene, (C_7H_8) , in $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$ is _____
- The $\nu_{\text{O-O}}$ 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.)



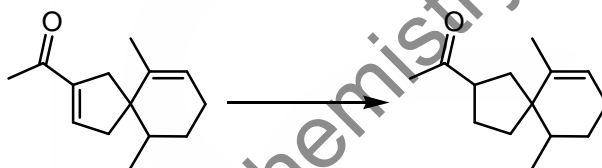
15. P, F and I represent primitive, face-centered and body-centered lattices, respectively. The lattice types of NaCl and CsCl, respectively, are

- (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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 77 K is

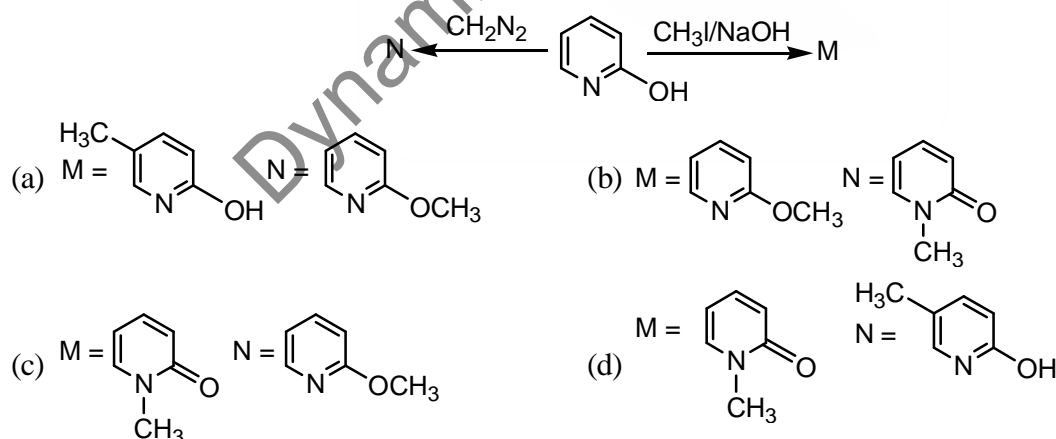
- (a) $g_{\parallel} > g_{\perp}$ (b) $g_{\parallel} < g_{\perp}$ (c) $g_{\parallel} = g_{\perp}$ (d) $g_x \neq g_y \neq g_z$

17. The most suitable reagent for the following transformation is



- (a) $\text{Li} / \text{Liq. NH}_3$ (b) $\text{PtO}_2 / \text{H}_2$ (c) LiAlH_4 (d) B_2H_6

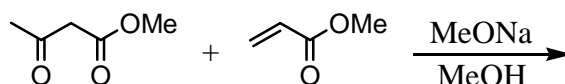
18. The major products M and N formed in the following reactions are

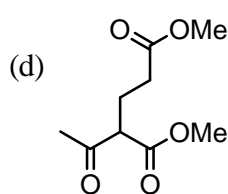
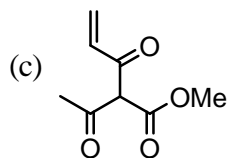
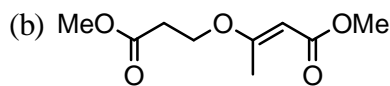
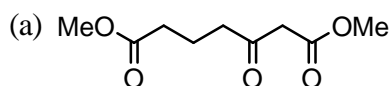


19. The ^{13}C NMR spectrum of acetone- d_6 has a signal at 30 ppm as a septet in the intensity ratio

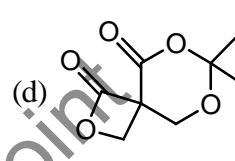
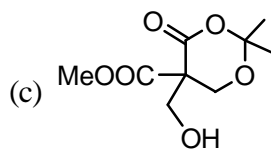
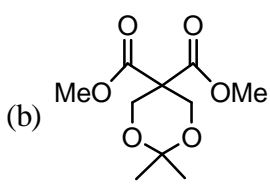
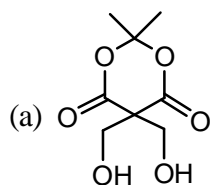
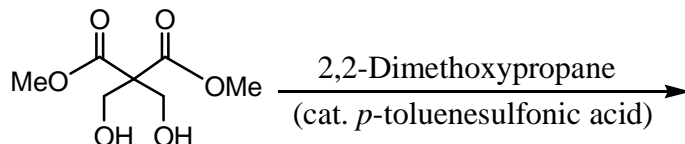
- (a) 1 : 6 : 15 : 20 : 15 : 6 : 1 (b) 1 : 3 : 6 : 7 : 6 : 3 : 1
(c) 1 : 2 : 3 : 5 : 3 : 2 : 1 (d) 1 : 3 : 7 : 10 : 7 : 3 : 1

20. The major product formed in the following reaction is

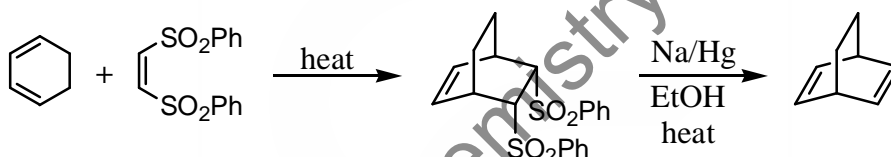




21. The major product obtained in the following reaction is

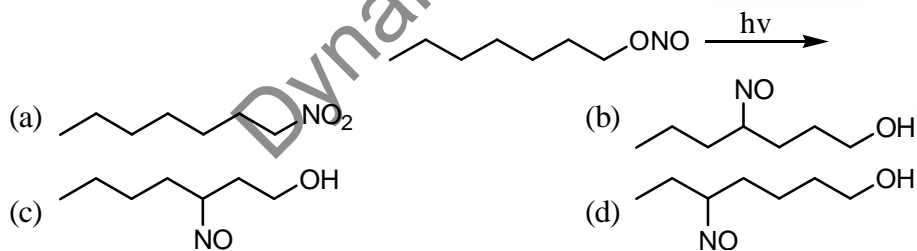


22. In the two step reaction sequence given below, the starting bis-sulfone acts as

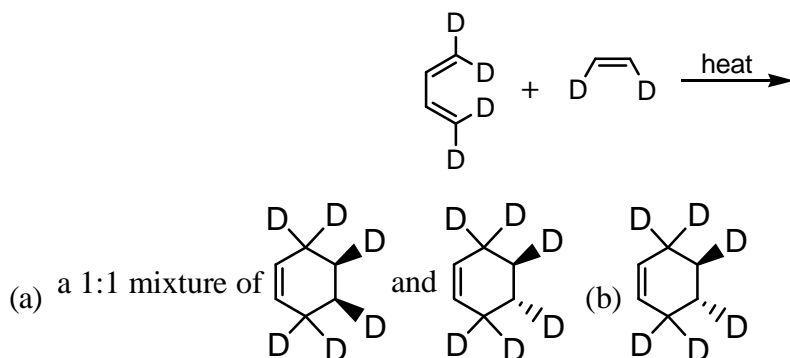


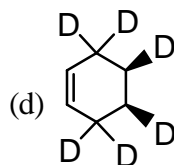
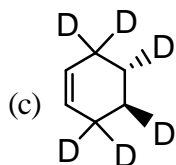
- (a) a dienophile and synthetic equivalent of acetylene
- (b) a dienophile and synthetic equivalent of ethylene
- (c) a dipolarophile and synthetic equivalent of acetylene
- (d) a dipolarophile and synthetic equivalent of ethylene

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



24. The product formed in the following reaction is



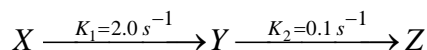


25. The number of possible stereoisomers for cyclononene is _____

Q.26 – Q.55 : Carry TWO marks each.

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

27. For the following consecutive first order reactions

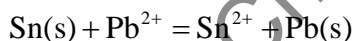


the time (in seconds) required for Y to reach its maximum concentration (assuming only X is present at time $t = 0$) is _____ (up to two decimal places)

28. Under physiological conditions, the conversion of CO_2 to bicarbonate ion by carbonic anhydrase enzyme (MW = $30,000 \text{ g mol}^{-1}$) has a turnover number of $4.00 \times 10^5 \text{ s}^{-1}$. 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} .



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

31. The dissociative chemisorption of $\text{X}_2(\text{g})$ 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)

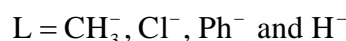
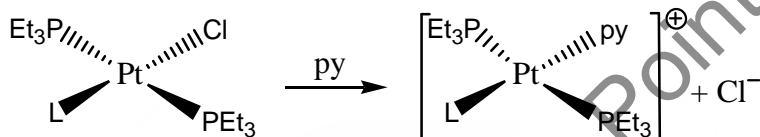
32. The ionic activity coefficients of Ca^{2+} and F^- are 0.72 and 0.28, respectively. The mean activity coefficient of CaF_2 is _____ (up to two decimal places)


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

34. The Gibbs free energy of mixing is denoted as ΔG_{max} . 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 $\Delta G_{\text{mix}}/RT$ is _____. (up to two decimal places)

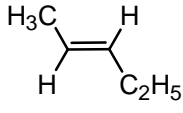
35. $\Psi = \left[c\phi_1 - (1/\sqrt{3})\phi_2 \right]$ represents a normalized molecular orbital constructed from two different atomic orbitals ϕ_1 and ϕ_2 that form an orthonormal set. The value of $|c|$ is _____. (up to two decimal places)

36. In cyclophosphazenes, $(\text{NPX}_2)_3$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ and Me), the strength of $\text{P}-\text{N}$ π -bond varies with X in the order
 (a) $\text{F} > \text{Cl} > \text{Br} > \text{Me}$ (b) $\text{Me} > \text{F} > \text{Cl} > \text{Br}$ (c) $\text{Br} > \text{Cl} > \text{F} > \text{Me}$ (d) $\text{Me} > \text{Br} > \text{Cl} > \text{F}$
37. The structure type and shape of the polyhedral (skeletal) framework of the carborane $\text{Me}_2\text{C}_2\text{B}_{10}\text{H}_{10}$, 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 $[\text{Co}(\text{NH}_3)_6]^{2+}$ is
 (a) $-0.8\Delta_o + 2P$ (b) $-0.8\Delta_o + 1P$ (c) $-0.8\Delta_o$ (d) $-1.8\Delta_o + 3P$
39. The rates of substitution for the following reaction vary with L in the order

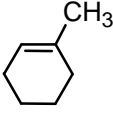


- (a) $\text{CH}_3^- > \text{Cl}^- > \text{Ph}^- > \text{H}^-$ (b) $\text{Cl}^- > \text{Ph}^- > \text{H}^- > \text{CH}_3^-$
 (c) $\text{Ph}^- > \text{CH}_3^- > \text{H}^- > \text{Cl}^-$ (d) $\text{H}^- > \text{CH}_3^- > \text{Ph}^- > \text{Cl}^-$
40. The product formed in the reaction of $\text{MeMn}(\text{CO})_5$ with ^{13}CO is
 (a) $(\text{Me}^{13}\text{CO})\text{Mn}(\text{CO})_5$ (b) $(\text{MeCO})\text{Mn}(\text{CO})_5$
 (c) $(\text{MeCO})\text{Mn}(\text{CO})_4(^{13}\text{CO})$ (d) $(\text{Me}^{13}\text{CO})\text{Mn}(\text{CO})_4(^{13}\text{CO})$
41. For the following three alkenes, 1, 2 and 3, the rates of hydrogenation using Wilkinson's catalyst at 25°C vary in the order
- 

1



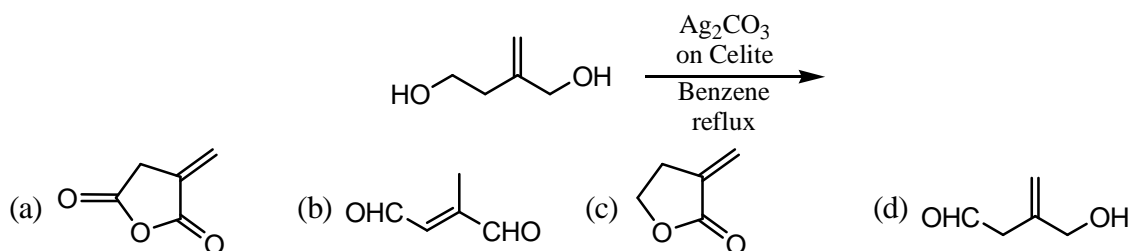
2



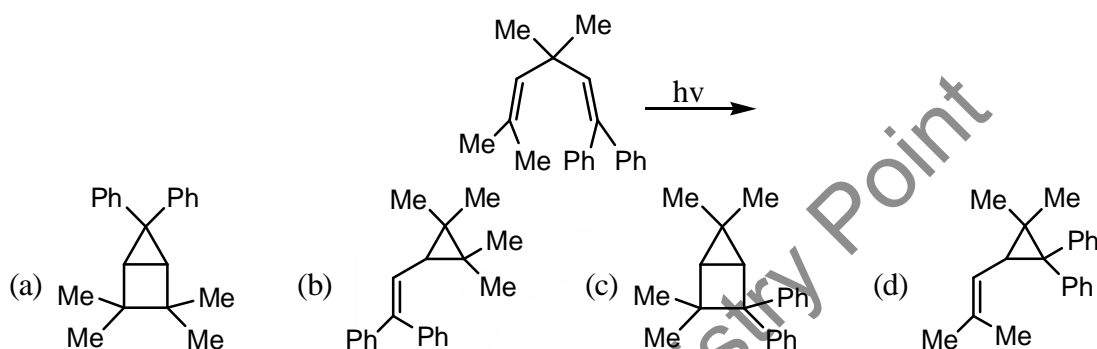
3
- (a) $1 > 3 > 2$ (b) $1 > 2 > 3$ (c) $2 > 1 > 3$ (d) $2 > 3 > 1$
42. ^{210}Bi undergoes β^- decay to $1/8$ of its initial amount in 15 days. The time required for its decay to $1/4$ of its initial amount is _____ days (up to two decimal places).
43. The metal ion and the macrocyclic skeleton present in the green pigment of plants, respectively, are
 (a) $\text{Mg}(\text{II})$ and chlorin (b) $\text{Mg}(\text{II})$ and corrin (c) $\text{Mn}(\text{II})$ and chlorin (d) $\text{Mg}(\text{II})$ 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 $300 \mu\text{A}$. If 'c' is increased by 0.1 mol L^{-1} , I_d increases to $900 \mu\text{A}$. The value of 'c' (in mol L^{-1}) is _____ (up to two decimal places)

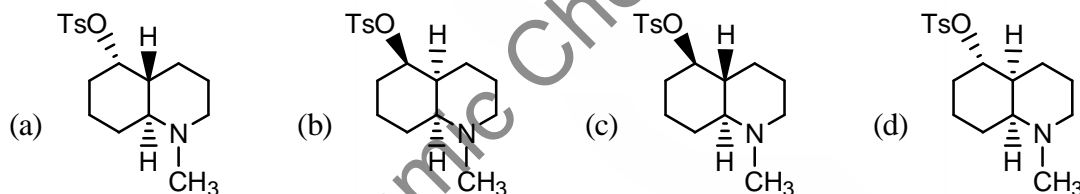
46. The major product formed in the following reaction is



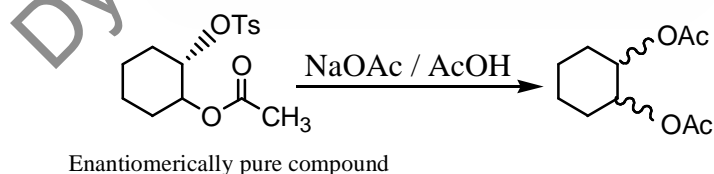
47. The product formed in the following photochemical reaction is



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



49. The product obtained in the following solvolysis reaction is

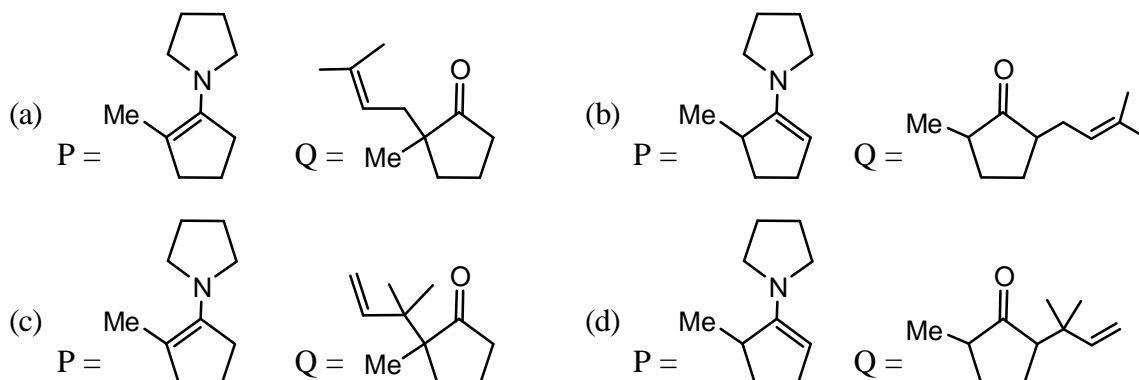
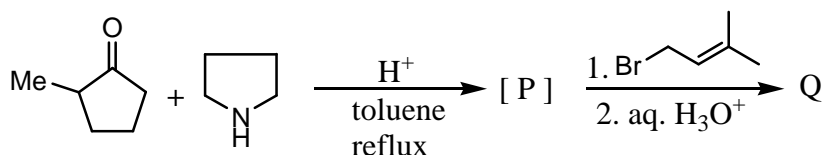


- (a) a racemic mixture of trans 1,2-diacetoxycyclohexane
 (b) enantiomerically pure trans 1,2-diacetoxycyclohexane
 (c) racemic cis 1,2-diacetoxycyclohexane
 (d) a mixture of cis and trans 1,2-diacetoxycyclohexane

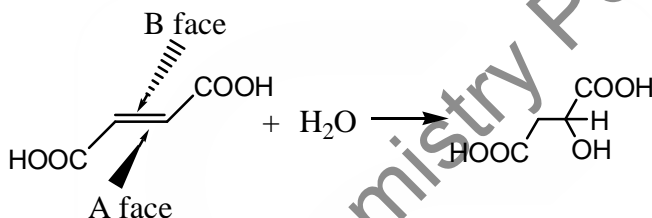
50. The spectroscopic data for an organic compound with molecular formula $\text{C}_{10}\text{H}_{12}\text{O}_2$ are given below. IR band around 1750 cm^{-1} . $^1\text{H NMR}$ δ 7.3 (m, 5H), 5.85 (q, 1H, $J = 7.2 \text{ Hz}$), 2.05 (s, 3H), 1.5 (d, 3H, $J = 7.2 \text{ Hz}$) ppm. the compound is

- (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

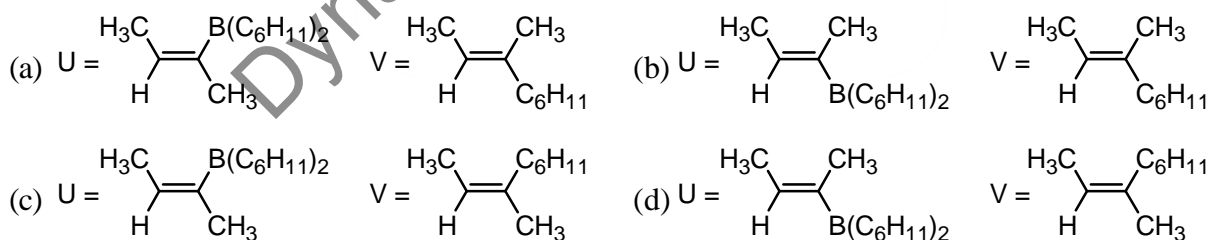


52. Hydration of fumaric acid gives malic acid as shown below. Assume that addition of water takes place specifically from A face or B face. The correct statement pertaining to stereochemistry of malic acid formed is

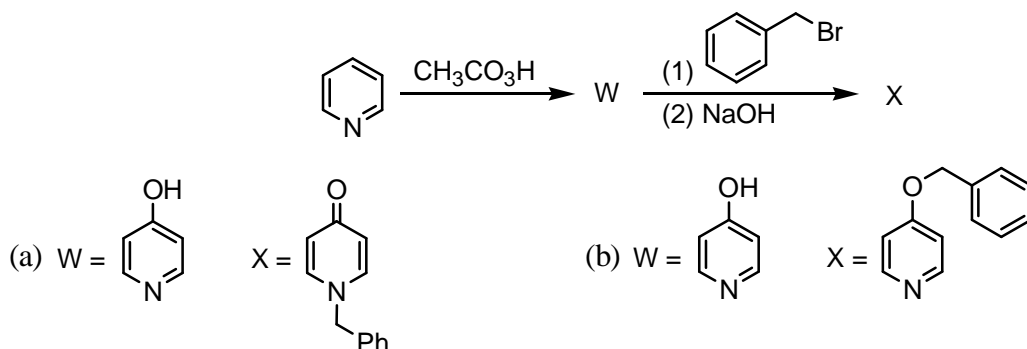


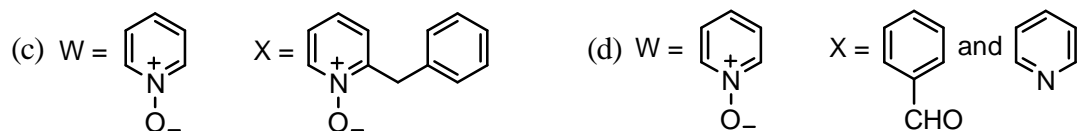
- (a) addition specifically from A face gives S isomer of malic acid
 (b) addition specifically from B face gives S isomer of malic acid
 (c) addition specifically from A face gives R isomer of malic acid
 (d) addition specifically from B face gives a racemic mixture of malic acid

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

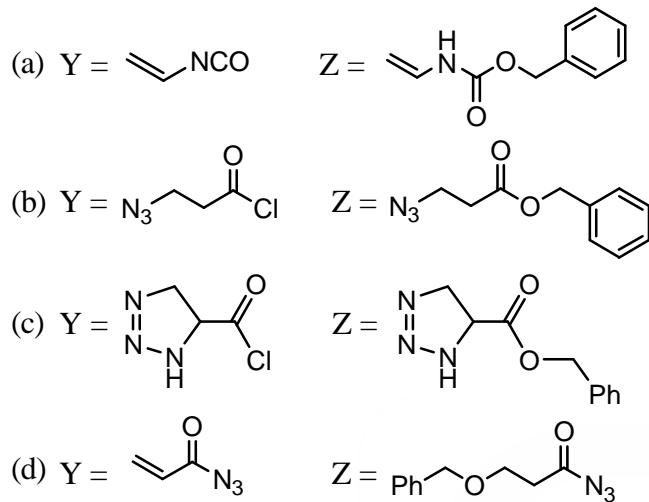
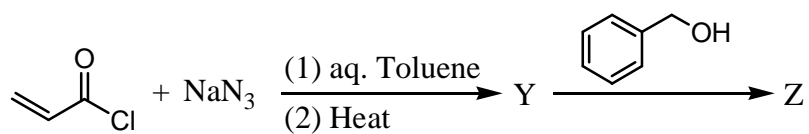


54. The structures of the major products W and X in the following synthetic scheme are





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



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