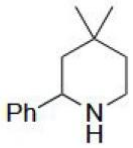
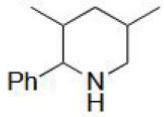
Q.21) Compound A on Hofmann exhaustive N-methylation procedure (involving two cycles), followed by ozonolysis (i. O_3; ii. Me_2S) gives benzaldehyde, formaldehyde and 2,2-dimethylpropanedial. The structure of A is

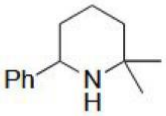
1.



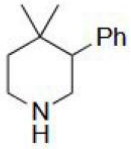
2.

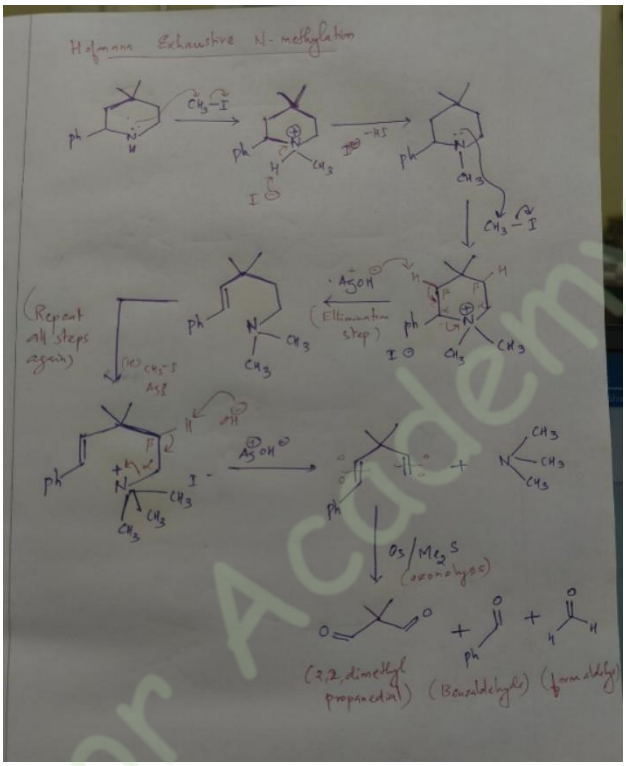


3.



4.





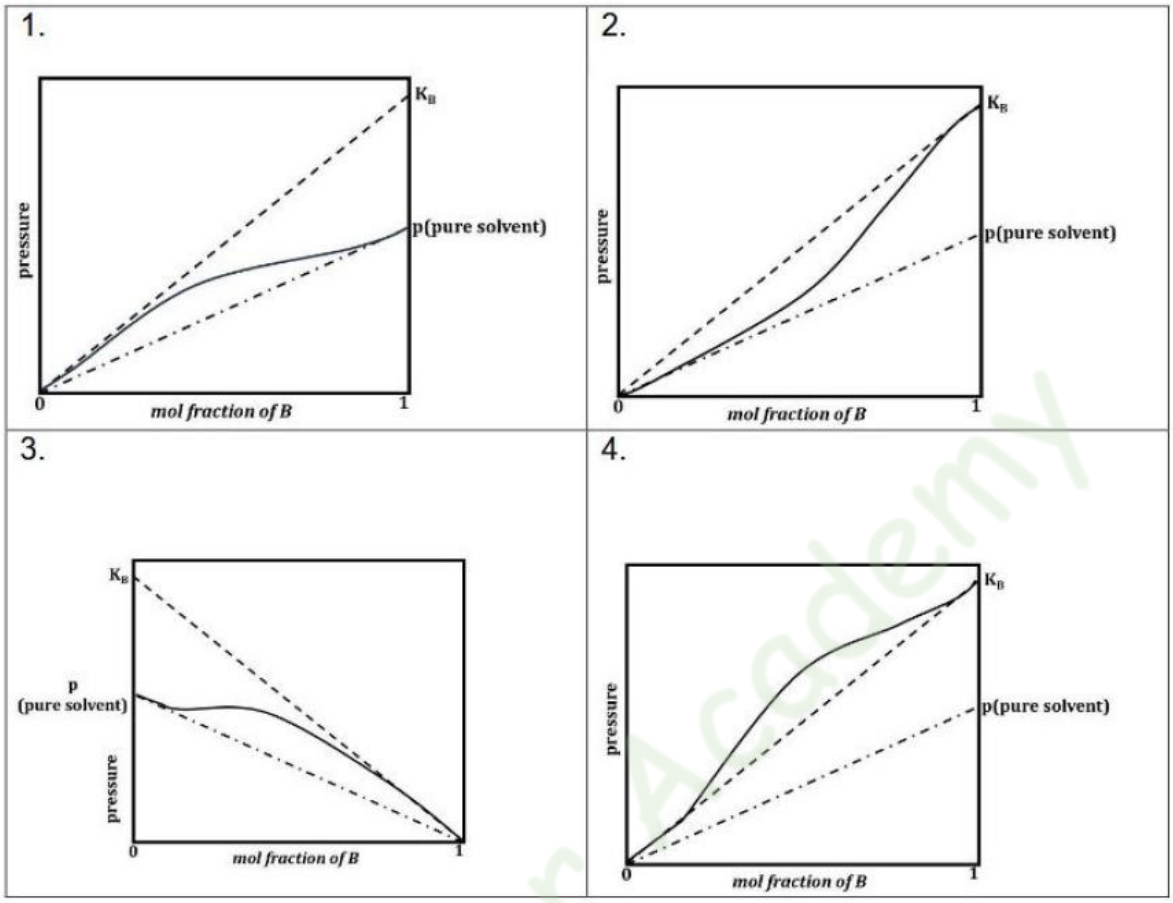
Answer: 1

Explanation:

During the Hofmann exhaustive methylation, the tertiary amine is converted to quaternary ammonium hydroxide, which undergoes elimination to form the least substituted alkene. Repeating this twice generates two double bonds at β-positions to the nitrogen. Ozonolysis cleaves these double bonds to give benzaldehyde, formaldehyde, and 2,2-dimethylpropanedial, indicating that the alkene carbons are attached to a phenyl group, a methyl group, and a tert-butyl-like moiety. The only structure that fits these products and two Hofmann eliminations is Option 1.

Q.22) The correct option for a real solution formed by mixing liquid A with liquid B is

[Here K_B is Henry's law constant and solid line represents real solution]



Answer: (1)

Explanation:

We mix **liquid A** with **liquid B**, and we plot the **total vapor pressure** vs. **mole fraction of B**.

Three reference lines are shown:

1. **Left dashed line → Henry's law** (valid for B at *low* mole fraction)

   $p_B = K_B x_B$

2. **Right dashed line → Raoult's law for pure B**

   $p_B = x_B p_B^0$

3. **Solid curve → real (non-ideal) solution** A physically correct diagram must show **smooth transition** from Henry's law (at low x_B) to Raoult's law (at high x_B).

Q.23) Two conformations, A and B, of a single molecule have energies $5k_BT$ and $9k_BT$, respectively, at a temperature T. The fraction of molecules in conformation B is

1. $e^{-9}/(1 + e^{-9})$
2. $e^{-5}/(1 + e^{-5})$
3. $1/(1 + e^{-4})$
4. $1/(1 + e^{4})$

Answer: (4)

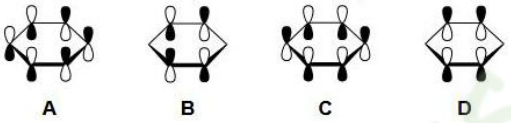
Explanation:

From the Boltzmann distribution,

Fraction in B = $e^{-EB} / (e^{-EA} + e^{-EB}) = e^{-9} / (e^{-5} + e^{-9}) = 1 / (1 + e^{4})$.

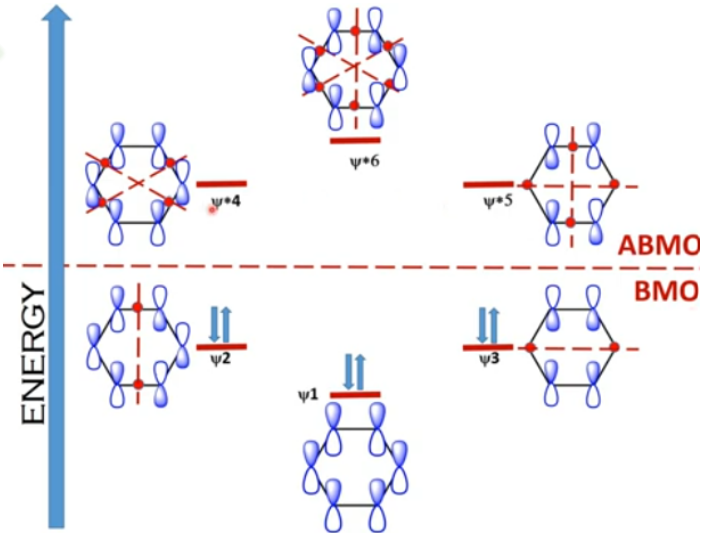
Thus, conformation B is less populated due to higher energy by 4k_BT, giving the fraction $1/(1 + e^{4})$.

Q.24) Among the following, the correct representation for the LUMO of benzene is

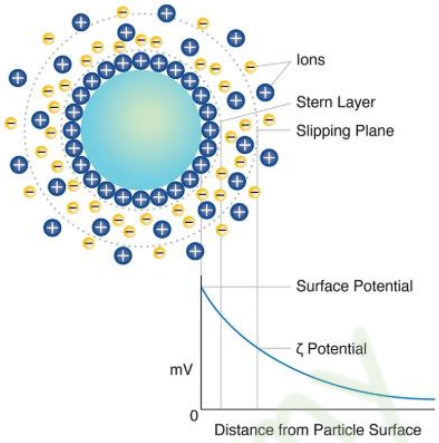


1. A and D
2. A and C
3. B and C
4. B and D

Answer: (3)



Q.25) In a colloidal solution, the zeta potential is the electric potential at the radius of the colloid particle



1. radius of the colloid particle
2. radius of Stern layer
3. radius of shear surface
4. outer radius of diffuse ion layer

Answer: (3)

Explanation:

Zeta potential (ζ) is the potential difference between the dispersion medium and the stationary layer of fluid attached to the colloidal particle. It exists at the **shear (slipping) plane**, which separates the tightly bound ions (Stern layer) from the diffused layer. Hence, it is measured at the radius of the shear surface.

Q.26) A radioactive element X emits two α and one γ particles to yield element Y of mass number 82. X also emits one α and one β particles to yield element Z with an atomic number 44.

$^{44}Z + \alpha + \beta \leftarrow X \rightarrow {}^{82}Y + 2\alpha + \gamma$

The elements, X, Y and Z, respectively, are

1. $^{90}_{45}X$, $^{82}_{42}Y$ and $^{88}_{44}Z$
2. $^{90}_{45}X$, $^{82}_{41}Y$ and $^{86}_{44}Z$
3. $^{91}_{45}X$, $^{82}_{41}Y$ and $^{86}_{44}Z$
4. $^{91}_{45}X$, $^{82}_{42}Y$ and $^{86}_{44}Z$

Answer: (2)

Explanation:

From the first decay:

$X \rightarrow Y + 2\alpha + \gamma$

Loss of 8 mass units $\Rightarrow A_X = 90$, and loss of 4 atomic number $\Rightarrow Z_Y = Z_X - 4 = 41$.

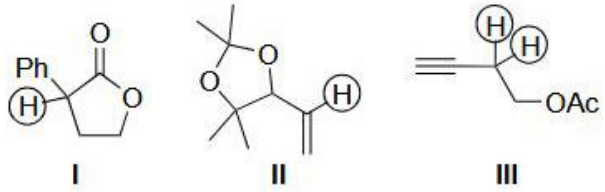
From the second decay:

$X \rightarrow Z + \alpha + \beta$

Emission of α (−2Z, −4A) and β^- (+1Z) ⇒ net atomic number change = −1 ⇒ Z_X = Z_Z + 1 = 45, A_Z = A_X − 4 = 86.

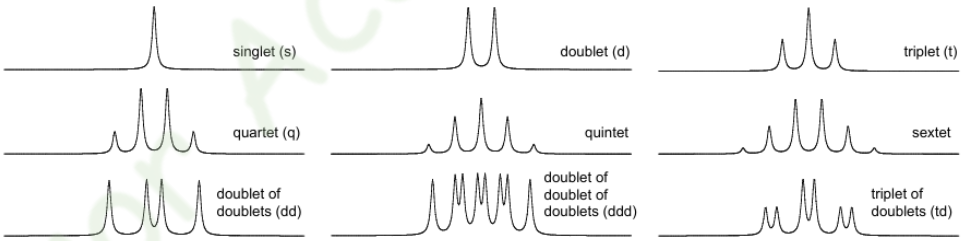
Thus, X = $^{90}_{45}$, Y = $^{82}_{41}$, Z = $^{86}_{44}$, corresponding to option (2).

Q.27) In ^{1}H NMR, the multiplicity pattern expected for the highlighted protons in the following compounds is



I II III

1. I = dd, II = ddd, III = td
2. I = dd, II = dt, III = dt
3. I = t, II = ddd, III = dt
4. I = t, II = dt, III = td

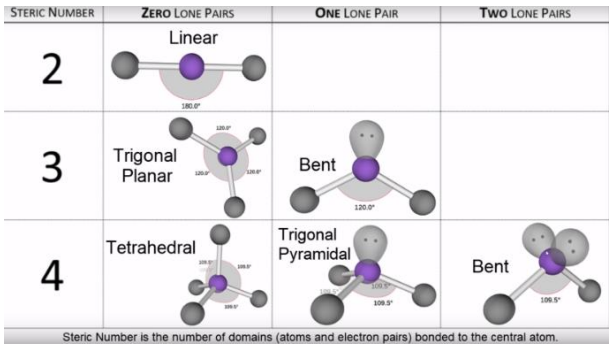


Answer: 1-

Explanation: Proton I couples with two non-equivalent neighbors → **dd**. Proton II is coupled to three different, non-equivalent sets → **ddd**. Proton III couples to one set that gives a triplet (two equivalent neighbors) and to another non-equivalent neighbor that further splits it → **td**. Hence option 1.

Q.28) The geometries of $[HgI_3]^-$ and $[SnCl_3]^-$, respectively, are

1. trigonal planar and trigonal pyramidal
2. trigonal pyramidal and trigonal planar
3. trigonal planar and tetrahedral
4. tetrahedral and trigonal pyramidal



Answer: 1 or 3

Explanation: In **$[HgI_3]^-$**, Hg(II) (d^{10}) with three ligands adopts **trigonal planar** coordination. In **$[SnCl_3]^-$**, Sn(II) has three bonds plus one lone pair: the **molecular geometry** is **trigonal pyramidal**, while the **electron-pair arrangement** is **tetrahedral**. Depending on whether one describes shape (pyramidal) or electron-domain geometry (tetrahedral), both 1 and 3 are acceptable.

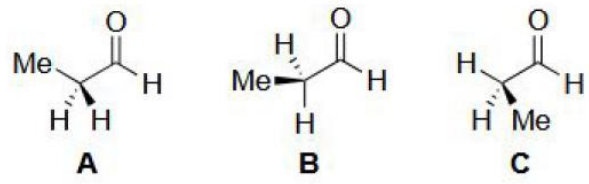
Q.29) The reagent that would effect the following transformation is

1. H_2, Pd–C, EtOAc
2. TBAF, THE
3. $AlCl_3$, CH_2Cl_2
4. K_2CO_3, MeOH

Answer: 3

Explanation: The change is **Boc deprotection** of the amine while retaining the **OTBS** ether and **OAc** ester. **$AlCl_3/CH_2Cl_2$** (Lewis acidic) cleaves Boc by generating a tert-butyl cation, revealing the free amine, and it typically leaves silyl ethers and acetates intact under these conditions. TBAF would remove **TBS**; K_2CO_3/MeOH would transesterify the acetate; H_2/Pd–C targets reducible groups (e.g., benzyl), not Boc here.

Q.30) The correct order of stability for the following conformations of propanal is



1. A > C > B
2. A > B > C
3. B > A > C
4. C > B > A

Answer: 1

Explanation: Conformation **A** places the methyl group in the least repulsive orientation relative to the polar carbonyl (minimal gauche/dipole repulsion) → most stable. **C** is less favorable due to increased gauche interaction between Me and the carbonyl fragment. **B** is least stable because of eclipsing/stronger steric and dipolar interactions. Hence **A > C > B**.

Q.31) The correct statements about $SnCl_4$ and $SnMe_4$.

A. $SnCl_4$ forms $SnCl_6^{2-}$.

B. $SnMe_4$ does not form $SnMe_6^{2-}$.

C. $SnCl_4$ does not undergo hydrolysis.

D. $SnMe_4$ readily hydrolyses.

Are

1. A and B only
2. B and C only
3. A and D only
4. B and D only

Answer: 1

Explanation: **$SnCl_4$** accepts two chlorides to give **$[SnCl_6]^{2-}$** (A true). **$SnMe_4$** does **not** form **$[SnMe_6]^{2-}$** (B true) because such a highly crowded, anionic hexamethylstannate(IV) is not formed under normal conditions. **$SnCl_4$** is actually **readily hydrolyzed** (so C false), whereas **$SnMe_4$** is comparatively **resistant to hydrolysis** (so D false). Therefore **A and B only**.

Q.32) Among the following linear combinations of determinants (written with the spatial wavefunctions 1s and 2s and electronic spin wavefunctions α and β, using 1 and 2 as labels of the

two electrons), the one that denotes the unnormalized wavefunction of a triplet excited state ($1s^1 2s^1$) of He, is:

1. $|1s\alpha(1)\ 2s\beta(1)| + |2s\alpha(1)\ 1s\beta(1)|$
   $|1s\alpha(2)\ 2s\beta(2)|\ |2s\alpha(2)\ 1s\beta(2)|$
2. $|1s\alpha(1)\ 2s\beta(1)| + |2s\alpha(1)\ 1s\beta(1)|$
   $|1s\beta(2)\ 2s\alpha(2)|\ |2s\beta(2)\ 1s\alpha(2)|$
3. $|1s\alpha(1)\ 1s\alpha(2)| + |2s\alpha(1)\ 2s\alpha(2)|$
   $|2s\beta(1)\ 2s\beta(2)|\ |1s\beta(1)\ 1s\beta(2)|$
4. $|1s\beta(1)\ 2s\alpha(1)| - |1s\alpha(1)\ 2s\beta(1)|$
   $|1s\beta(2)\ 2s\alpha(2)|\ |1s\alpha(2)\ 2s\beta(2)|$

Answer: 2

Explanation:
For a triplet state (S = 1), the spin part is symmetric [$\alpha(1)\beta(2) + \beta(1)\alpha(2)$], so the spatial part must be antisymmetric [$1s(1)2s(2) - 1s(2)2s(1)$]. Option 2 correctly represents this antisymmetric spatial and symmetric spin combination.

Q.33) The correct statements about the copper-containing protein, hemocyanin, from the following are:

A. It is an extracellular protein.
B. It has an oligomeric structure with each sub-unit containing a pair of two copper atoms.
C. In deoxy form, the two Cu(I) atoms are separated by 2.8 Å.
D. The blue colour of oxy form is due to charge-transfer from superoxide– to Cu(II) ion.

1. A and B only
2. A and C only
3. B and C only
4. C and D only

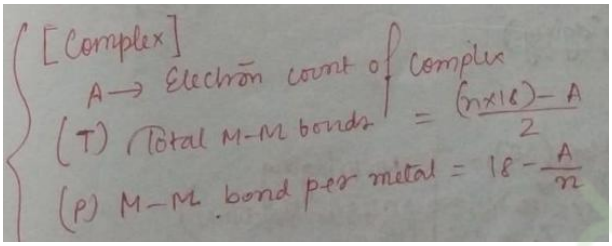
Answer: 1

Explanation:

Hemocyanin is extracellular (A true) and each subunit has a dicopper active site (B true). In the deoxy form, the Cu(I)–Cu(I) distance is about 4–5 Å (not 2.8 Å), so C is false. The blue colour in the oxy form arises from peroxo (O_2^{2-}) → Cu(II) charge transfer, not superoxide → Cu(II), so D is false.

Q.34) The number of metal–metal bonds in $[Os_4(CO)_{16}]$ is:

1. 4
2. 5
3. 6
4. 3



Answer: 1

Explanation:

Each Os atom contributes 8 valence electrons and 4 CO ligands contribute 8 more, giving 16 electrons per Os. To reach the stable 18-electron configuration, each Os requires 2 additional electrons, provided by M–M bonding. Total electron deficit = 8 electrons; each M–M bond contributes 2 electrons, giving 4 M–M bonds.

Q.35) The correct option with respect to $Cs_2[XeF_8]$ is: (GROUP THEORY)

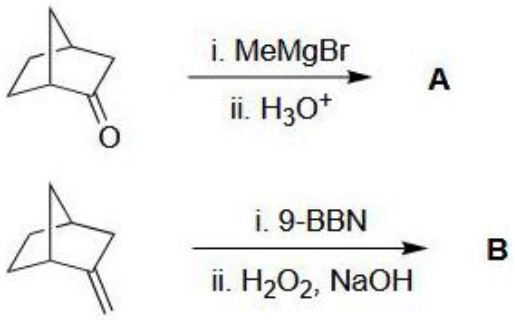
1. square antiprismatic with stereochemically inactive lone pair
2. square antiprismatic with stereochemically active lone pair
3. capped square antiprismatic with stereochemically active lone pair
4. capped square antiprismatic with no lone pair

Answer: 1

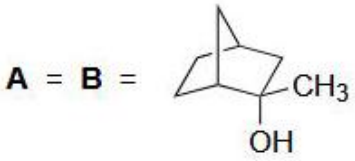
Explanation:

The $[XeF_8]^{2-}$ ion has a square antiprismatic geometry. The xenon has one lone pair which is stereochemically inactive (inert pair), so the shape remains regular and undistorted.

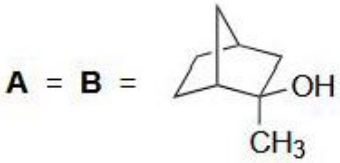
Q.36) The major products A and B formed in the following reactions are:



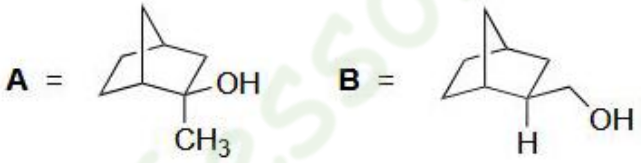
1.



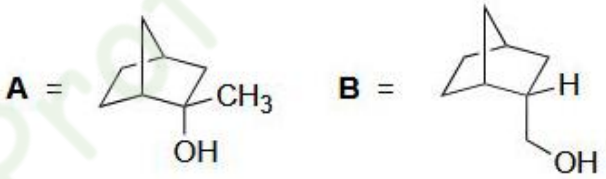
2.



3.



4.



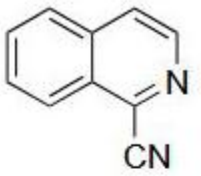
Answer: 4

Explanation:

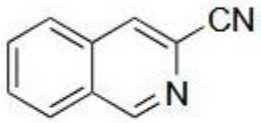
Reaction with MeMgBr forms a tertiary alcohol (A) by addition to the carbonyl group from the less hindered exo face. Hydroboration–oxidation with 9-BBN gives anti-Markovnikov addition, producing an exo alcohol (B). Thus, A and B differ as shown in option 4.

Q.37) Isoquinoline on sequential reaction with benzoyl chloride and KCN followed by heating with aqueous NaOH gives:

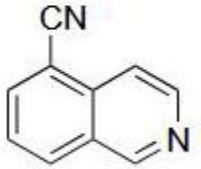
1.



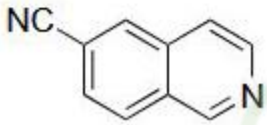
2.



3.



4.



Answer: 1

Explanation:

The benzoyl chloride forms an isoquinolinium intermediate at position 1, activating that carbon toward nucleophilic attack. Cyanide ion adds at C-1 to form 1-cyanoisoquinoline after hydrolysis and rearomatization.

Q.38) The complete combustion of 9.83 mg of an organic compound ($C_xH_\gamma O\_z$) gives 23.26 mg of CO_2 and 9.52 mg of H_2O. The ESI-MS analysis of this compound shows a molecular ion peak at 130 (m/z). Find X.

(Atomic weights: C = 12, H = 1, O = 16)

1. 7
2. 3
3. 4
4. 8

Answer: 1

Explanation:
Moles of CO_2 = 23.26 / 44 = 0.528 × 10^{-3} mol → C = 0.528 × 10^{-3} mol → 6.34 mg C.
Moles of H_2O = 9.52 / 18 = 0.529 × 10^{-3} mol → H = 2 × 0.529 × 10^{-3} mol → 1.06 × 10^{-3} mol → 1.06 mg H.
Remaining mass = 9.83 – (6.34 + 1.06) = 2.43 mg O → 2.43/16 = 0.152 × 10^{-3} mol.
Mole ratio C:H:O ≈ 0.528 : 1.06 : 0.152 ≈ 3.5 : 7 : 1 → empirical formula $C_7H_{14}O_2$.
Molecular mass = 130, so formula = $C_7H_{14}O_2$ → X = 7.

Q.39) For an eigenstate ψ of a time-independent Hamiltonian:

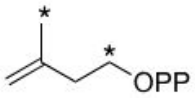
1. Both ψ and ψ*ψ are time-independent
2. ψ is time-dependent, but ψ*ψ is time-independent
3. ψ is time-independent, but ψ*ψ is time-dependent
4. Both ψ and ψ*ψ are time-dependent

Answer: 2

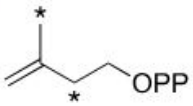
Explanation:
For a stationary (energy eigen) state, ψ(t) = ψ₀e^(-iEt/ħ). Thus ψ depends on time through a phase factor, but ψ*ψ = $|\psi_0|^2$ is independent of time because the phase cancels out. Hence, ψ is time-dependent, but the probability density is not.

Q.40) The isopentenyl pyrophosphate formed through the mevalonate pathway using acetyl-CoA containing a ^{14}C-labelled carbonyl carbon is:

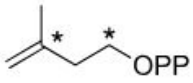
1.



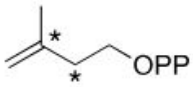
2.



3.



4.



Answer: 3

Explanation:

In the mevalonate pathway, the carbonyl carbon of acetyl-CoA becomes the **C-2 (quaternary carbon)** of isopentenyl pyrophosphate after successive condensations and decarboxylation steps. Therefore, the radiolabel appears on the **central (tertiary/quaternary)** carbon atom.

Q.41) The wavefunction, $\Psi(x)$, of a one-dimensional quantum system is given by

$\Psi(x) = A \times \exp(-x^2/a^2)$

The dimension of A is [L is the dimension of length]

1. L^(−1/2)
2. L^(−3)
3. L^(−3/2)
4. L^0 (dimensionless)

Answer: 3

Explanation: Normalization in 1D requires $\int|\Psi|^2\,dx = 1$. Here $|\Psi|^2 = |A|^2\, x^2\, e^{\wedge}(-2x^2/a^2)$. The integral over x has the dimension of $\mathbf{L^3}$ (it evaluates $\propto a^3$). Hence $|A|^2$ must have dimension L^(−3) and therefore **A ~ L^(−3/2)**.

Q.42) Considering the potential energy at the equilibrium position (x_e) to be zero, the internuclear potential, V(x) as a function of distance, x between two atoms in a diatomic molecule is given by

$V(x) = D_e[1 - e^{(-\alpha(x-x_e))}]^2$

where D_e and α are two constants.

The force constant of the bond between the two atoms is

1. $D_e \alpha^2$
2. $2 D_e \alpha^2$
3. $(1/2) D_e \alpha^2$
4. $2 D_e \alpha$

Answer: 2

Explanation: Force constant $k = (d^2V/dx^2)|_{(x=x_e)}$. With $y = e^{(-\alpha(x-x_e))}$, $V = D_e(1 - y)^2$. Then $dV/dx = 2D_e(1 - y)(\alpha y)$, and $d^2V/dx^2 = 2D_e[\alpha^2 y(1 - y) + \alpha^2 y^2]$. At $x = x_e$, $y = 1 \rightarrow k = \mathbf{2D_e\alpha^2}$.

Q.43) The correct statements about C_{60} from the following

A. it exhibits greater degree of delocalization than benzene.

B. it is susceptible towards addition reactions than substitution reactions.

C. the spherical structure of C_{60} makes the C=C bonds more reactive.

D. its overall reactivity is more like cycloalkenes than benzene.

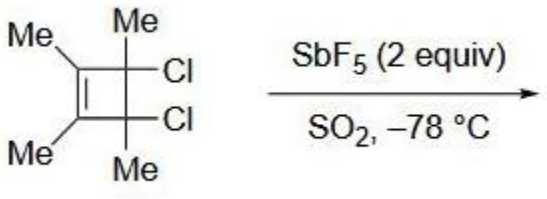
Are

1. B, C and D only
2. A, B and C only
3. A, B and D only
4. C and D only

Answer: 1

Explanation: C_{60} has curved π-surface with localized double bonds; it is **less delocalized than benzene** (A false). It prefers **addition** reactions and the curvature makes **C=C bonds more reactive**; overall, it behaves more like **cycloalkenes** than benzene (B, C, D true).

Q.44) The major product formed in the following reaction is

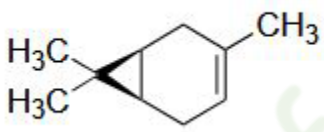


1. aromatic
2. nonaromatic
3. antiaromatic
4. homoaromatic

Answer: 1

Explanation: The superacidic medium generates a **highly stabilized cation** in which the resulting small-ring cation has a **Hückel 2π aromatic** cyclopropenium-like system. Aromatic stabilization dominates under these conditions.

Q.45) The correct IUPAC name for the following compound is



(bridged alkene shown)

1. (1S,6R) — 3,7,7 — trimethylbicyclo[4.1.0]hept — 3 — ene
2. (1R,6S) — 3,7,7 — trimethylbicyclo[4.1.0]hept — 3 — ene
3. (1R,6S) — 4,7,7 — trimethylbicyclo[4.1.0]hept — 3 — ene
4. (1S,6R) — 4,7,7 — trimethylbicyclo[4.1.0]hept — 3 — ene

Answer: 1

Explanation: The framework is bicyclo[4.1.0]heptane with the double bond at **C-3** (lowest

locant for the double bond). Two methyls are at bridgehead C-7, one at C-3. The stereochemistry from the wedges/dashes corresponds to **(1S,6R)**.

Q.46) Consider the following unbalanced chemical reactions:

A. $NH_3 \rightarrow NO_2^-$

B. $O_2 \rightarrow H_2O_2$

C. $NO_2^- \rightarrow NO_3^-$

D. $H_2S \rightarrow S_8$

E. $CO_2 \rightarrow CO$

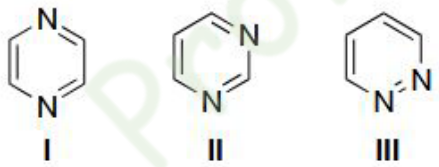
The reactions that are brought about by the chemolithotropic bacteria, are

1. B, C and D
2. A, C and D only
3. A, B and E only
4. B, C and E only

Answer: 2

Explanation: Chemolithotrophs include **nitrifiers** (A: $NH_3 \rightarrow NO_2^-$; C: $NO_2^- \rightarrow NO_3^-$) and **sulfur oxidizers** (D: $H_2S \rightarrow S^0/S_8$). Reactions B ($O_2 \rightarrow H_2O_2$) and E ($CO_2 \rightarrow CO$) are not characteristic energy-obtaining processes of chemolithotrophs.

Q.47) The correct order of basicity for the following compounds is



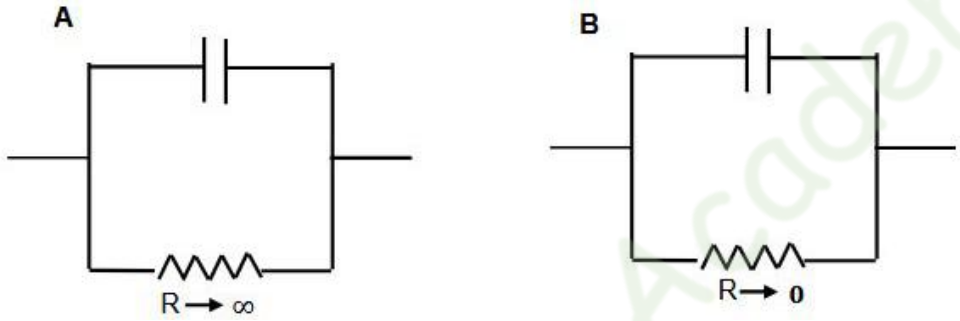
1. I > III > II
2. II > I > III
3. III > I > II

4. III > II > I

Answer: 4

Explanation: Basicity depends on the availability of the ring-nitrogen lone pair. In **III** (most basic), the lone pair is least deactivated by adjacent electronegative N and resonance; in **II** it is moderately deactivated; in **I** it is most deactivated by stronger π-electron withdrawal/resonance, giving the lowest basicity. Thus **III > II > I**.

Q.48) Among the following equivalent circuits A and B for an electrode/electrolyte interface, the correct option is

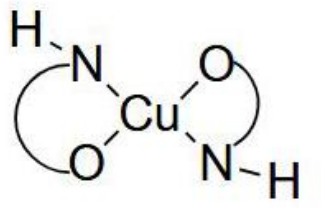


1. Both A and B are ideally polarizable
2. A is ideally non-polarizable, B is ideally polarizable
3. A is ideally polarizable, B is ideally non-polarizable
4. Both A and B are ideally non-polarizable

Answer: 3

Explanation: In circuit **A**, the Faradaic resistance RRR is ∞ (open), so no charge transfer occurs; only the capacitor (double layer) is active → **ideally polarizable**. In **B**, R=0R = 0R=0 (short), allowing unhindered charge transfer → **ideally non-polarizable**.

Q.49) The total number of lines expected in the EPR spectrum of the Cu(II) complex (Given: Cu (I = 3/2); N (I = 1)) shown below is

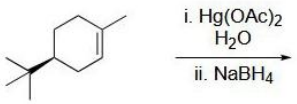


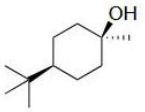
1. 4
2. 40
3. 12
4. 20

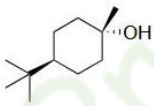
Answer: 4

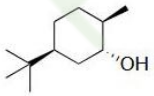
Explanation: First, Cu (I = 3/2) splits the signal into **2I + 1 = 4** lines. Two equivalent nitrogens (each I = 1) further split each line into **2nI + 1 = 2×2×1 + 1 = 5** lines. Total = 4 × 5 = **20** lines.

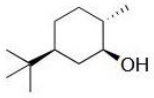
Q.50) The major product formed in the following reaction is



1. 

2. 

3. 

4. 

Answer: 1

Explanation: Oxymercuration–demercuration adds **H and OH in Markovnikov fashion**

without rearrangement and with **anti** stereochemistry across the double bond. The depicted chair product in option **1** matches these regio- and stereochemical outcomes and is therefore predominant.

51. The standard Gibbs energy of a substance refers to the Gibbs free energy of its pure form at

1. temperature = 25 °C only and pressure = 1 atm
2. temperature = 25 °C only and pressure = 1 bar
3. any temperature and pressure = 1 bar
4. any temperature and pressure = 1 atm

Answer: 3

Explanation: By IUPAC, the **standard state** is the pure substance at **p° = 1 bar** at **any temperature**. Hence G° is defined at 1 bar, T arbitrary.

52. According to Karplus equation, the vicinal proton–proton coupling constant is minimum when the value of dihedral angle is

1. 0°
2. 60° and 120°
3. 90°
4. 180°

Answer: 3

Explanation: The Karplus curve has **minima near 90°** and maxima near **0°/180°**. Therefore J is minimum at **90°**.

53. For actinides, complex formation tendency follows the order

1. $M^{4+} > M^{3+} > MO_2^{+} > MO_2^{2+}$
2. $MO_2^{2+} > MO_2^{+} > M^{4+} > M^{3+}$
3. $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^{+}$
4. $M^{4+} > MO_2^{+} > M^{3+} > MO_2^{2+}$

Answer: 4

Explanation: Higher charge density promotes complexation: $\mathbf{M^{4+} > MO_2^{+} > M^{3+} > MO_2^{2+}}$. The linear actinyl dication (MO_2^{2+}) already has strong An=O bonds and shows relatively **weaker equatorial complexation**.

54. The pair of electronic configurations representing ground term $^3F_2$ is

1. p^1d^1 and s^1d^1
2. s^1f^1 and d^1f^1
3. d^1f^1 and p^1d^1
4. p^1d^1 and s^1f^1

Answer: 4

Explanation: For **^{3}F**: total **L = 3** and **S = 1** (two parallel spins). This arises from **p^1d^1** (l = 1 + 2 = 3) and from **s^1f^1** (0 + 3 = 3) with parallel spins. J = 2 gives **$^3F_2$**.

55. Nitramide (NH_2NO_2) decomposes under basic condition to generate

1. N_2O
2. HNO_3
3. NH_3
4. NO

Answer: 1

Explanation: Base-catalyzed nitramide decomposition proceeds via **N–N cleavage** to give **nitrous oxide (N_2O)** and water.

56. The activation energy and enthalpy change in the reaction $H_2 + I_2 \rightarrow 2HI$, respectively, are 167 kJ mol^{-1} and −8 kJ mol^{-1}. Assuming the pre-exponential factors for production and decomposition of HI to be the same at all temperatures [k_p and k_d are the rate constants for production and decomposition of HI], the correct option is

1. k_p and k_d have the same temperature dependence.

2. k_d changes more rapidly with temperature than k_p
3. k_p changes more rapidly with temperature than k_d
4. The activation energies of production and decomposition reaction of HI are same.

Answer: 2

Explanation: For the reverse (decomposition), **$E_{a,rev} \approx E_{a,fwd} + |\Delta H| = 167 + 8 = 175$ kJ mol^{-1}**. Higher E_a means **stronger T-dependence**, so **k_d** varies more rapidly with T.

57. The density, mass and unit cell edge length of a crystalline solid X are 2.7 g cm^{-3}, 27 g mol^{-1} and 400 pm, respectively. The crystal lattice of X is

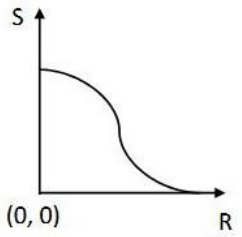
1. FCC
2. BCC
3. Simple cubic
4. Tetragonal

Answer: 1

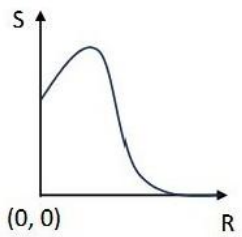
Explanation: Using $\rho = ZM/(N_A a^3)$: with **$Z = 4$ (FCC)**, **$M = 27$ g mol^{-1}**, **$a = 4.00 \times 10^{-8}$ cm**, one obtains $\rho \approx$ **2.7 g cm^{-3}**, matching the given value (typical of Al, FCC).

58. For a diatomic molecule AB, the internuclear distance is R and the internuclear axis is along the z-direction. The plot of the overlap integral S for the p_x orbital of A and d_zx orbital of B, against R, is

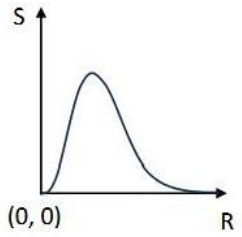
1.



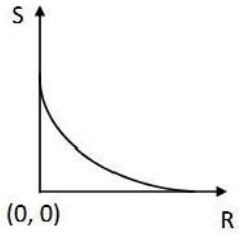
2.



3.



4.



Answer: 1

Explanation: The **p_x** on A and **d_zx** on B have **good lateral overlap** when atoms are close; as **R increases** the overlap **decays to zero** smoothly. Hence curve **1** (large S at small R, decreasing to ~0).

59. Consider the following statements about NO and NO_2.

A. The unpaired electron is in π* orbital of NO while it is in σ_nb orbital of NO_2.

B. NO does not prefer dimerization, whereas NO_2 does.

C. The reduction of NO is comparatively easier than NO_2.

D. There is a center of inversion in NO_2.

The option with the correct statements is

1. A and B only
2. A and D only
3. C and D only
4. C and D only

Answer: 1

Explanation: The odd electron in **NO** occupies a **π*** orbital; in **NO_2** it is largely **nonbonding** (σ_nb) on N/O. **NO_2 dimerizes** to N_2O_4, whereas **NO does not**—so **A, B true**. NO_2 is **easier to reduce** than NO (C false). NO_2 is **bent** and lacks inversion center (D false).

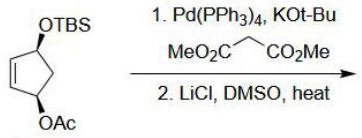
60. For the reaction $K + Br_2 \rightarrow KBr + Br$, the rate constant can be described as $k = A \exp(-E_a/RT)$. Choose the correct option regarding activation energy (E_a) and pre-exponential factor (A_E: obtained from experiment and A_T: estimated using collision theory)

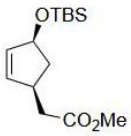
1. $E_a > 0; A_T > A_E$
2. $E_a < 0; A_T < A_E$
3. $E_a = 0; A_T < A_E$
4. $E_a \geq 0; A_T > A_E$

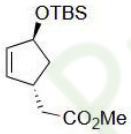
Answer: 3

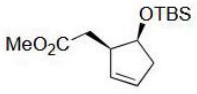
Explanation: Alkali-halogen reactions proceed by a **"harpoon" barrierless mechanism → $E_a \approx 0$**. Their effective cross-section is **larger than kinetic-theory prediction**, so **experimental A (A_E)** exceeds **A_T**; hence **$A_T < A_E$**.

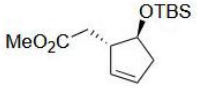
61. The major product formed in the following reaction sequence is



1.


2.


3.


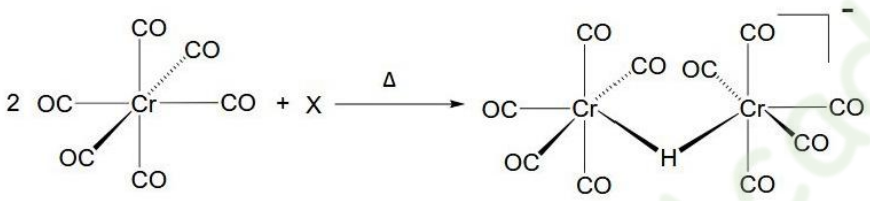
4.


Answer: 1

Explanation: Step-1 is a **Tsuji–Trost allylic substitution**: malonate anion does **SN2′ attack** at the allylic acetate to give the **terminally substituted allyl malonate** at the less hindered position (retaining the O-TBS elsewhere). Step-2 (**LiCl/DMSO, heat**) effects **Krapcho decarboxylation**, converting the malonate to the mono-ester without changing the C–C connectivity. The structure corresponding to this outcome is **option 1**.

62. Consider the following reaction (two $Cr(CO)_5$ fragments give a hydrido-bridged dimer on heating with X).

X is



1. H^+
2. H^-0
3. HO^-
4. H_2O

Answer: 3

Explanation: Hydroxide acts as a **nucleophile** toward a metal carbonyl (attack at CO), generating a **formyl/hydrido equivalent** that **couples two M–CO units** under thermal conditions to the observed **μ-H/alkyl-bridged** dimer. Such carbonylate chemistry is characteristic for **HO^-**, not $H^+/H^-/H_2O$.

63. The XRD pattern of a crystalline material (Cu Kα, λ = 1.54 Å) shows 2θ = 38.43°, 44.65°, 65.02°, 78.13°. Considering a cubic cell (a ≈ 4 Å), the Miller indices and Bravais lattice are

1. (111) (200) (22 3 1), BCC
2. (111) (200) (220) (311), FCC

3. (110) (200) (211) (220), BCC
4. (110) (200) (211) (220), FCC

Answer: 2

Explanation: For cubic systems, the ratio of $\mathbf{\sin^2\theta}$ values is proportional to $\mathbf{h^2+k^2+l^2}$. From the angles, $\sin^2\theta$ ratios ≈ **3 : 4 : 8 : 11**, which exactly matches the **FCC allowed set** (all even or all odd): **(111), (200), (220), (311)**. Hence **FCC** and **option 2**.

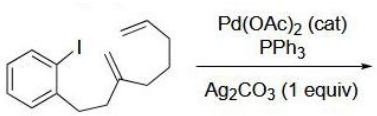
64. The number of microstates, the ground term, the energy separation between the ground term and the next excited state term of identical multiplicity, and the j value for the lowest-energy spin–orbit state for the ground state for a d^3 configuration, respectively, are

1. 120, ^{4}F, 15B, 3/2
2. 120, ^{4}F, 15B, 9/2
3. 156, ^{4}F, 15B + C, 3/2
4. 156, ^{4}F, 15B, 9/2

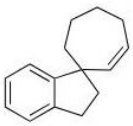
Answer: 1

Explanation: For $\mathbf{d^3}$, number of microstates = **C(10,3) = 120**. Hund's rules give ground term $\mathbf{^4F}$ (S = 3/2, L = 3). The energy gap to the next term of the same multiplicity (^{4}P) in the Racah scheme is **15B**. For **less than half-filled**, lowest J = |L − S| = **3 − 3/2 = 3/2**.

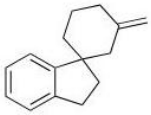
65. The major product formed in the following reaction is



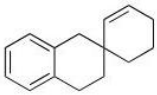
1.



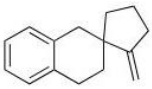
2.



3.



4.

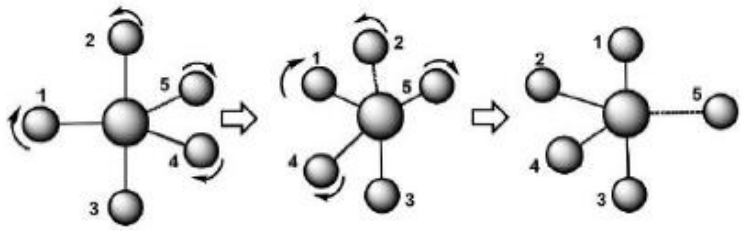


Answer: 2

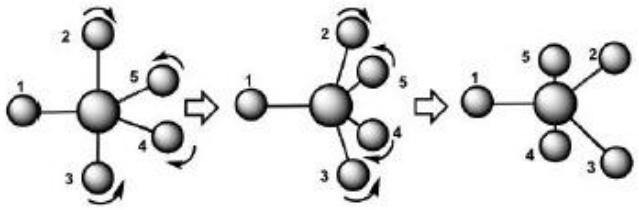
Explanation: This is an **intramolecular oxidative Heck** process: Pd(0/II) performs **oxidative addition** into Ar–I, **migratory insertion** into the tethered alkene (5-exo-trig cyclization favored), then **β-hydride elimination**, giving the **fused bicyclic alkene** depicted in **option 2**.

66. The option showing the correct Berry pseudo-rotation is

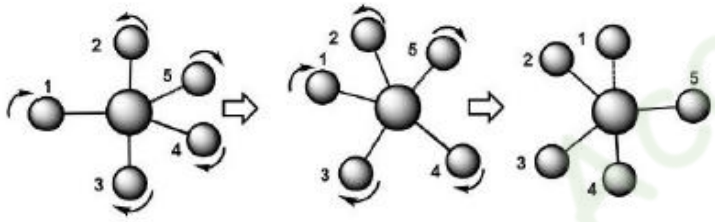
1



2



3



4

Answer: 2

Explanation: In **Berry pseudo-rotation** for a **trigonal bipyramidal (TBP)** geometry, two **equatorial** ligands move to **axial** positions while the two axial ligands move to equatorial through a **square-pyramidal** transition. **Option 2** correctly shows the **axial⇌equatorial interchange** preserving relative identities; the others do not.

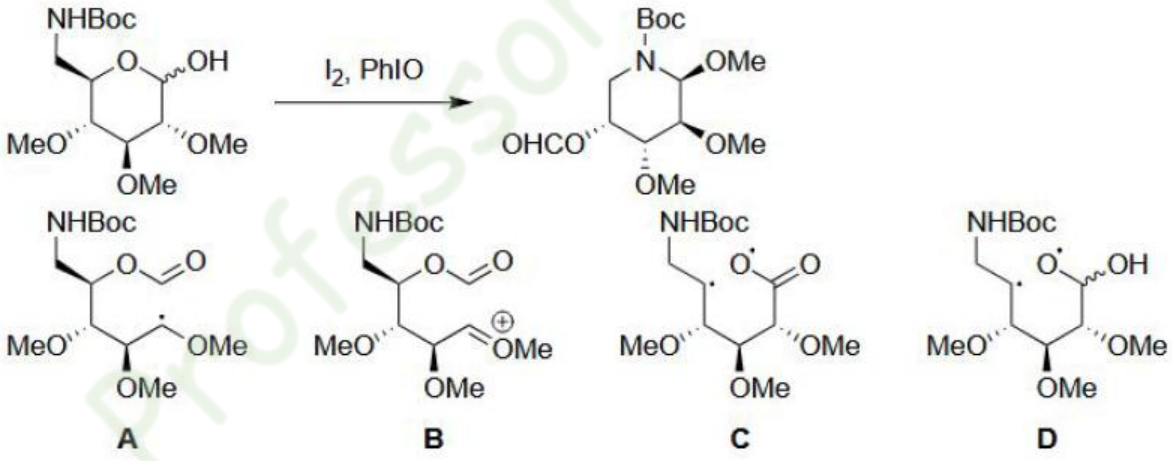
67. The unnormalized probability density distribution of a continuous variable x is given by $p(x) = e^{-ax^2}$, $-\infty \leq x \leq \infty$ (a is a constant). The average of x^2 over the normalized distribution is

1. a^2
2. 2a
3. $a^2/2$
4. 1/(2a)

Answer: 4

Explanation: The normalized Gaussian function is $p_n(x) = \sqrt{(a/\pi)}\, e^{-ax^2}$. Therefore, the expectation value $\langle x^2 \rangle = \int x^2 p_n(x) dx = \sqrt{(a/\pi)} \int x^2 e^{-ax^2} dx$ = **1/(2a)**. Hence, the average of x^2 over the normalized distribution is **1/(2a)**.

68. The intermediates involved in the following reaction are (reaction involves oxidation using I_2 and PhIO):



1. A and B
2. B and C
3. C and D
4. A and D

Answer: 1

Explanation: In this oxidation, **I_2 and PhIO** generate an electrophilic iodine species. The alcohol forms a **hypoiodite intermediate (A)**, which rearranges to a **cationic iodonium/oxocarbenium intermediate (B)** that cyclizes to the final product. Therefore, intermediates **A and B** are involved.

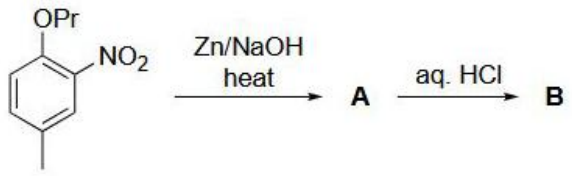
69. For a heteronuclear diatomic molecule AB, the un-normalized wavefunctions for HOMO and one of the two degenerate LUMOs, respectively, are $\psi\_HOMO = 0.9(\varphi_2s^A + 3\varphi_2p\_z^A) + 0.1\varphi_2p\_z^B$. (Atomic orbitals of A and B are denoted by φ. The internuclear axis is along the z-direction.) AB is a

1. σ-donor through A, π-acceptor through A
2. σ-donor through B, π-acceptor through B
3. σ-donor through A, π-acceptor through B
4. σ-donor through B, π-acceptor through A

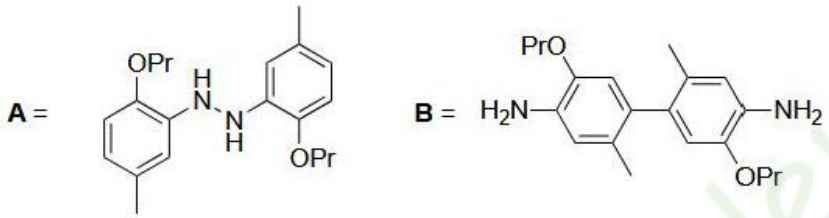
Answer: 3

Explanation: The **HOMO** is dominated by orbitals on **A** (2s and 2p_z), indicating σ-donation from **A**, while the **LUMO** is localized on **B** with p-character, showing **π-acceptor** behavior. Hence, AB acts as a **σ-donor through A and π-acceptor through B**.

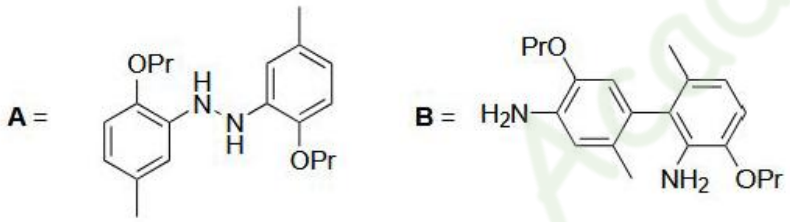
70. The major products A and B formed in the following reaction sequence are



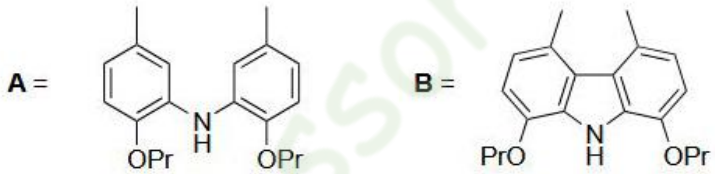
1.



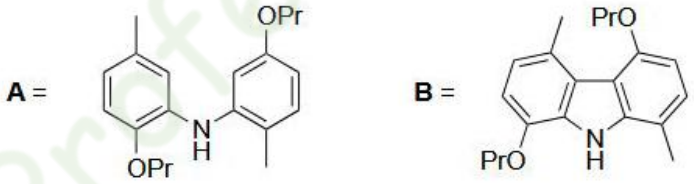
2.



3.



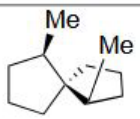
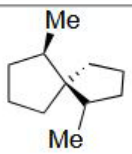
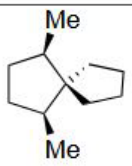
4.



Answer: 1

Explanation: Reduction of the **nitro group by Zn/NaOH** gives an intermediate anilide which, upon **intramolecular N-arylation**, forms a **diarylamine (A)**. On further treatment with **aqueous HCl**, protonation yields the stable ammonium compound **(B)**. Thus, the correct pair corresponds to **option 1**.

71. The correct match for methyl groups of molecules in Column P with their topicity in Column Q is

	Column P		Column Q
A.		**i.**	Enantiotopic
B.		**ii.**	Homotopic
C.		**iii.**	Diastereotopic

1. A–ii; B–i; C–iii
2. A–iii; B–ii; C–i
3. A–i; B–ii; C–iii
4. A–ii; B–iii; C–i

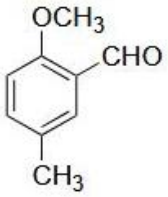
Answer: 2

Explanation: In molecule **A**, the methyl groups are *diastereotopic* as replacement of one produces diastereomers. In **B**, they are *homotopic* since both are identical by symmetry. In **C**, the methyl groups are *enantiotopic*, as replacing one gives enantiomers. Therefore, the correct correspondence is **A–iii, B–ii, C–i**, matching **option 2**.

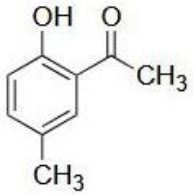
72. The compound that gives the following ^{1}H NMR spectral data is

^{1}H NMR ($CDCl_3$): δ 11.80 (s, 1H), 7.69 (d, J = 2.3 Hz, 1H), 7.35 (dd, J = 8.5, 2.3 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 2.63 (s, 3H), 2.28 (s, 3H) ppm.

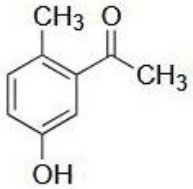
1.



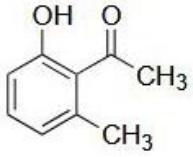
2.



3.



4.



1. o-Anisaldehyde
2. o-Acetyl-p-cresol
3. m-Cresol acetone derivative
4. p-Methylacetophenone

Answer: 2

Explanation: The singlet at **δ 11.8 ppm** indicates a *chelated phenolic OH* (intra-hydrogen bonded). The coupling constants (8.5 and 2.3 Hz) suggest a *1,2,4-trisubstituted benzene ring*. Two methyl singlets correspond to *acetyl ($COCH_3$)* and *aromatic CH_3* groups. Hence, the correct compound is **o-acetyl-p-cresol**.

73. At 100 Pa and 500 K, the number of collisions Ar atoms make on a solid surface of area 1.0 cm² in 10 s is closest to

(Molar mass of Ar = 40 g mol^{-1}; assume ideal gas behavior.)

1. 1.9×10^{21}
2. 2.1×10^{23}
3. 3.5×10^{19}
4. 4.7×10^{17}

Answer: 1

Explanation: From kinetic theory, the flux of molecules striking a surface is given by

$Z = (1/4)\, n\, \bar{c}$, where $n = P / kT$.

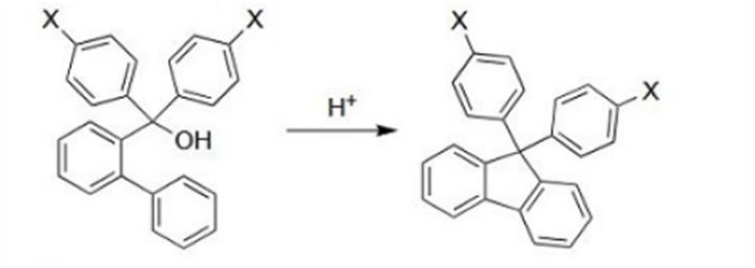
For P = 100 Pa, T = 500 K, $n = 1.45 \times 10^{22}\ m^{-3}$.

The mean velocity $\bar{c} = \sqrt{(8kT / \pi m)} \approx 517$ m/s.

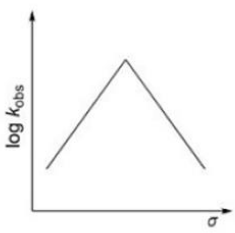
Hence $Z \approx (1/4)(1.45 \times 10^{22})(517) = 1.87 \times 10^{24}\ m^{-2}\ s^{-1}$.

For 1 cm^2 ($10^{-4}\ m^2$) and 10 s, total collisions ≈ $\mathbf{1.9 \times 10^{21}}$.

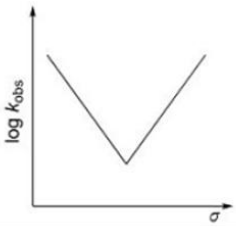
74. The Hammett plot for the following transformation is



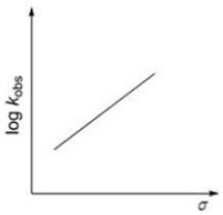
1.



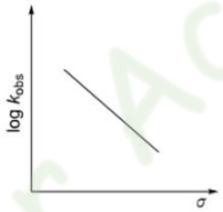
2.



3.



4.

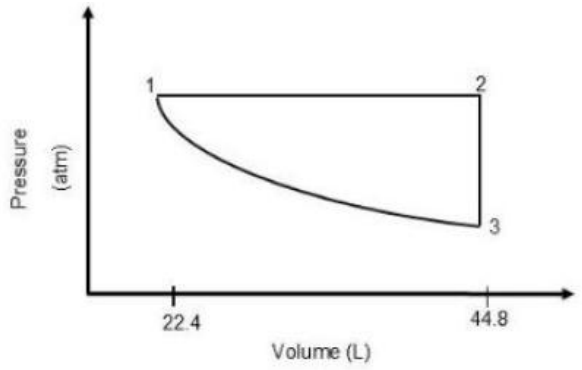


1. Inverted V-shape (Λ-type)
2. V-shape
3. Straight line (positive slope)
4. Straight line (negative slope)

Answer: 1

Explanation: In this transformation, both *electron-withdrawing* and *electron-donating* substituents decrease the rate, while unsubstituted compounds react fastest. Hence, the plot of log k_obs versus σ shows a maximum at σ = 0, producing an **inverted V (Λ-type)** Hammett plot.

75. One mole of a monoatomic ideal gas at 1 atm pressure is taken through the p–V cycle shown.



1. −2.27 and 5.67
2. 3.40 and 2.27
3. 3.40 and −5.67
4. −2.27 and 3.40

Answer: 1

Explanation: For a monoatomic gas,

$\Delta H = nC_p\Delta T = (5/2)R\Delta T$.

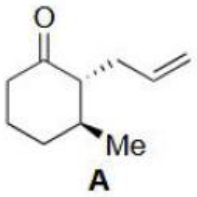
Since $V_2/V_1 = 2$, $T_2 = 2T_1$, so $\Delta T = T_1 = 273$ K.

$\Delta H = (5/2)(8.314)(273) = 5.67$ kJ.

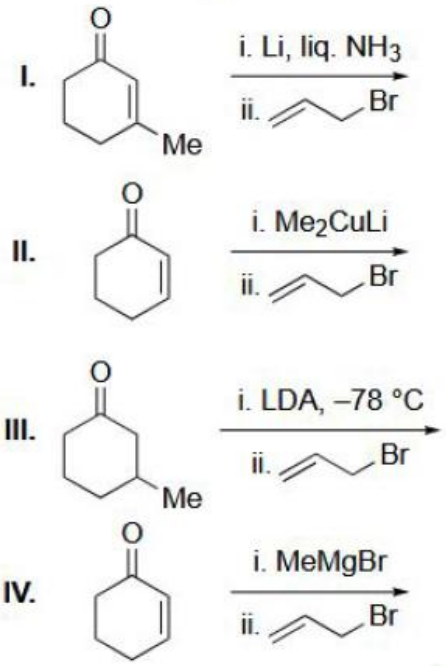
Work done, $w = nRT_1 \ln(V_2/V_1) = 8.314\times273\times\ln 2 = -2.27$ kJ.

Thus, **work = −2.27 kJ** and **ΔH = 5.67 kJ**.

76. The reactions that give A as the major product are



A



1. I and II
2. I and III
3. II and III
4. II and IV

Answer: 1

Explanation:

Product A is a **trans-1,2-disubstituted cyclohexanone**: at the α-carbon to the C=O there is a **Me (down)** and an **allyl (up)**. So we need a sequence that

(i) creates the Me at the α-position in the correct (equatorial) orientation, and

(ii) alkylates the resulting enolate from the **opposite face** to give the allyl substituent trans to Me.

- **Route I:** Li, liq. NH_3 first gives the *thermodynamic lithium enolate* of the α-methylcyclohexanone; this enolate alkylates with allyl–Br from the less hindered face, giving the **allyl trans to the existing Me** → matches A.
- **Route II:** Me_2CuLi does **1,4-addition** to the cyclohexenone, putting **Me equatorial** (the more stable orientation) and leaving a lithium enolate. In the next step, the enolate is alkylated by allyl–Br; alkylation now occurs from the opposite face, giving the **allyl axial / up** and Me equatorial / down → again **trans**, i.e. A.
- **Route III:** LDA at –78 °C on an already α-methylated ketone gives the **kinetic enolate**. Alkylation of this rigid kinetic enolate usually keeps the *same* facial preference as the first substituent, so it tends to give **cis (Me/allyl)** product, not the required trans → not A.
- **Route IV:** MeMgBr adds **1,2** to the enone (not 1,4) giving an alcohol, so the needed α-Me/α-allyl ketone is **not** obtained.

Therefore, only **I and II** furnish A as the major product.

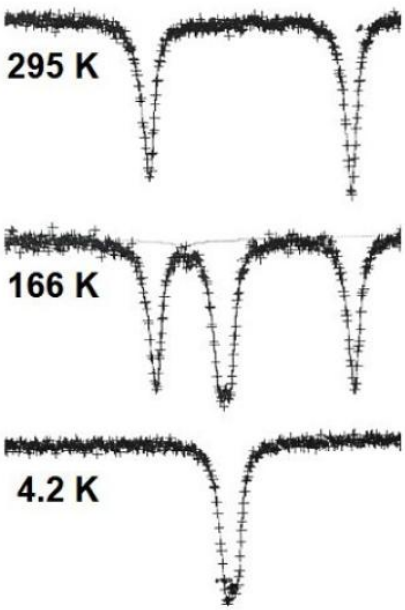
77. If the crystal field splitting energy of d-orbitals follows the order:
$d_{(z^2)} < d_{(xy)} = d_{(x^2-y^2)} < d_{(xz)} = d_{(yz)}$, the ligand field is

1. Square planar
2. Trigonal bipyramidal
3. Square antiprismatic
4. Pentagonal bipyramidal

Answer: 3

Explanation:
In an eight-coordinate **square-antiprismatic (D_{4d})** field, the axial ligands stabilize the **$d_{(z^2)}$** orbital the most. The orbitals **$d_{(xy)}$** and **$d_{(x^2-y^2)}$** lie at intermediate energy, while **$d_{(xz)}$** and **$d_{(yz)}$** are most destabilized. Hence, the observed order matches the **square-antiprismatic geometry**.

78. The Mössbauer spectra of $[Fe(L)_2]_2$ (L = 3,5-dimethyl-tris-pyrazolylborate) exhibit temperature-dependent spin-transition behaviour. The correct statements are:



A. At 295 K, the Fe(II) center is high-spin.

B. At 4.2 K, the Fe(II) center is low-spin.

C. At 295 K, the Fe(II) center is low-spin.

D. At 4.2 K, the Fe(II) center is high-spin.

E. At 166 K, it represents a mixture of low-spin and high-spin Fe(II) complexes.

1. A, B and C only
2. B, C and E only
3. C, D and E only
4. A, B and E only

Answer: 4

Explanation:

At higher temperature (295 K), the Fe(II) center exists in the **high-spin (HS)** state, while at very low temperature (4.2 K), it converts to the **low-spin (LS)** state. At an intermediate temperature

(166 K), both HS and LS states coexist, indicating a **spin-crossover transition**. Therefore, statements **A, B, and E** are correct.

79. The mass spectra of $Pd(PPh_3)_4$ and $Pd(PPh_3)_4$ with sulfonated triphenylphosphine (L) are recorded on two machines. Which statements are correct?

Species	Machine	Mode		Relative intensity of the corresponding mass signal			
			n=0	n=1	n=2	n=3	n=4
$[Pd(PPh_3)_n]^+$	Machine I	(+)-ion	-	1%	22%	100%	8%
$[Pd(L)(PPh_3)_n]^-$	Machine I	(-)-ion	2%	35%	100%	-	-
$[Pd(L)(PPh_3)_n]^-$	Machine II	(-)-ion	12%	100%	1%	-	-

A. Machine I provides softer ionization conditions than Machine II.

B. In Machine I, the stable species contain three phosphine ligands.

C. Mass data reveal ligand exchange reaction.

D. The increased prevalence of $[Pd(L)]^-$ in Machine II is due to fragmentation.

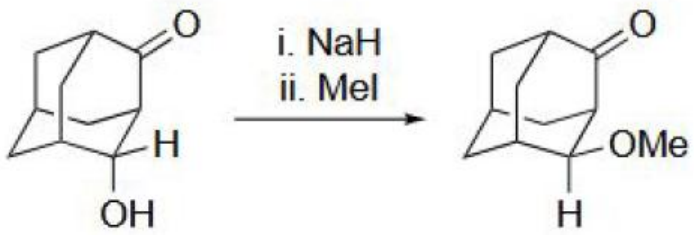
1. A, B, C and D
2. A, B and C only
3. B, C and D only
4. A, C and D only

Answer: 1

Explanation:

Machine I exhibits **soft ionization**, giving dominant $[Pd(PPh_3)_3]^+$ ions, confirming stability of the tri-phosphine complex. The spectra with sulfonated L show $[Pd(L)(PPh_3)_2]^-$ peaks, proving **ligand exchange**. Machine II (harder ionization) produces fragments like $[Pd(L)]^-$ due to higher energy input, hence all four statements are correct.

80. The correct sequence of processes involved in the following transformation is



1. i. Deprotonation, ii. O-methylation
2. i. Enolate formation, ii. Retro-aldol reaction, iii. O-methylation
3. i. Deprotonation, ii. Retro-aldol reaction, iii. O-methylation, iv. Aldol reaction
4. i. Deprotonation, ii. Retro-aldol reaction, iii. Aldol reaction, iv. O-methylation

Answer: 4

Explanation:

The base **NaH** first deprotonates the hydroxyl group, initiating **retro-aldol cleavage**. The fragments then undergo an **intramolecular aldol condensation**, regenerating a new carbonyl system. Finally, **methyl iodide (MeI)** performs **O-methylation** of the oxygen atom. Hence, the sequence is **deprotonation → retro-aldol → aldol → O-methylation**.

81. The correct statements regarding olefin polymerization involving metallocene and alkyl aluminum species, from the following

A. Trace amounts of water cause a significant increase in the rates of ethylene polymerization by the $Cp_2\ TiEtCI/AIEt_2Cl$ system

B. Methylaluminoxane (MAO) is employed as an activator for the catalyst, Cp_2ZrMe_2.

C. $B(C_6F_5)_3$ is an activator for Cp_2ZrMe_2.

D. The termination step of the polymerization reaction is β-hydride elimination.

are,

1. A, B, C and D

2. A, B and C only

3. A, B and D only

4. B, C and D only

Answer: 1

Explanation:

Trace amounts of water activate the $Cp_2TiEtCl/AlEt_2Cl$ system by forming cationic Ti species, which accelerate ethylene polymerization. **Methylaluminoxane (MAO)** acts as a co-catalyst, generating active cationic Zr centers in Cp_2ZrMe_2. **$B(C_6F_5)_3$** is another Lewis acid activator forming non-coordinating anions, and chain termination in such polymerizations occurs via **β-hydride elimination**. Hence, all A, B, C, and D are correct.

82. The EPR spectrum of $[InH_3^-]^-$ [Given: In (I = 9/2); H (I = 1/2)] is comprised of

1. 10 lines of equal intensity where each line further splits into 4 lines with intensity 1:3:3:1.
2. 4 lines with intensity 1:3:3:1 where each further splits into 10 lines with equal intensity.
3. 10 lines with unequal intensity where each line further splits into 4 lines with intensity 1:3:3:1.
4. 4 lines with intensity 1:1:1:1 where each line further splits into 10 lines with unequal intensity.

Answer: 1

Explanation:

For **indium (I = 9/2)**, the hyperfine pattern gives **2I + 1 = 10 lines** of equal intensity. Each of these 10 lines further splits due to three equivalent protons (n = 3, I = 1/2) producing a **1:3:3:1** quartet.

83. The electronic configurations showing tetragonal compression and elongation in their octahedral complexes, respectively, are

1. d^1 and low-spin d^4
2. d^1 and d^9

3. d^9 and d^3
4. low-spin d^4 and high-spin d^5

Answer: 2

Explanation:

d^1 octahedral complexes undergo Jahn–Teller tetragonal compression due to degeneracy in the t_{2g} set. d^9 octahedral complexes undergo strong Jahn–Teller tetragonal elongation due to degeneracy in the e_g set. Hence, the correct pair is d^1 (compression) and d^9 (elongation).

84. The correct statements about agostic interactions from the following

A. It involves a three-center-two-electron interaction with a C–H bond of the ligand.
B. The C–H bond of the ligand involved in agostic interaction is lengthened.
C. Its presence is identified by an upfield chemical shift of the C–H bond of the ligand.
D. It lowers the pKa of the C–H bond of the ligand.

1. A, B, C and D
2. A, B and C only
3. B, C and D only
4. A, C and D only

Answer: 1

Explanation:

Agostic bonding involves a **3-center-2-electron interaction** (M–H–C). The **C–H bond is weakened and lengthened**, causing a lower stretching frequency in IR. The **NMR signal shifts upfield**, and the weakened C–H bond shows **enhanced acidity (lower pKa)**. Thus, all statements are correct.

85. The dielectric constants of electrolyte solutions, A and B, are ε and 2ε, respectively. At a given temperature T, the ratio $\lambda_D(A)/\lambda_D(B)$ of two Debye (ionic) screening lengths $\lambda_D(A)$ and $\lambda_D(B)$ is

1. 1

2. 2
3. $\sqrt{2}$
4. $1/\sqrt{2}$

Answer: 4

Explanation:

Debye length (λ^D) $\propto \sqrt{(\varepsilon)}$. Therefore, $\lambda^D(A)/\lambda^D(B) = \sqrt{(\varepsilon)}/\sqrt{(2\varepsilon)} = 1/\sqrt{2}$.

Thus, increasing dielectric constant decreases the screening length by $\sqrt{2}$.

86. The rate law for the reaction $N_2O_2(g) \rightarrow 2NO(g)$ is first order in N_2O_2. If the initial concentration of N_2O_2 is 1.0 mol dm^{-3}, the expression for time-dependent behavior of concentration of NO (in mol dm^{-3}) is

1. $2(1 - e^{-kt})$
2. $1 - e^{-kt}$
3. $0.5(1 - e^{-kt})$
4. $1 + e^{-kt}$

Answer: 1

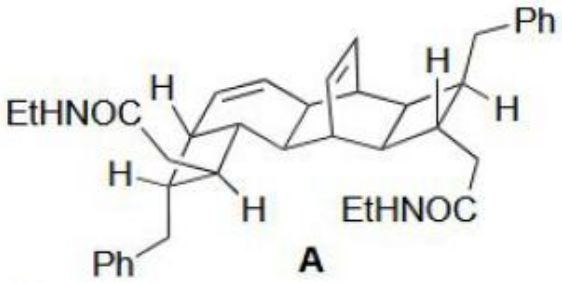
Explanation:

For a first-order decomposition, $[N_2O_2]_t = [N_2O_2]_0 e^{-kt}$.

Since each N_2O_2 forms **2NO**,

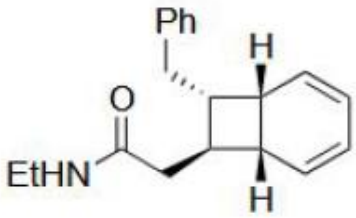
$[NO] = 2([N_2O_2]_0 - [N_2O_2]_t) = \mathbf{2(1 - e^{-kt})}$.

87. The starting material that gives compound A on heating is

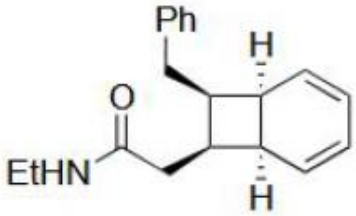


A

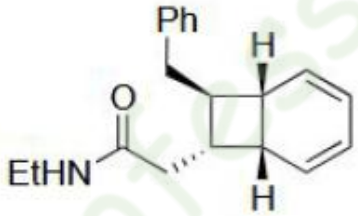
1.



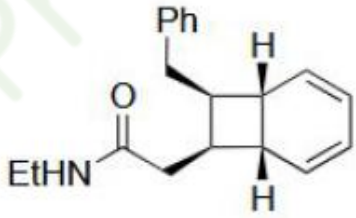
2.



3.



4.

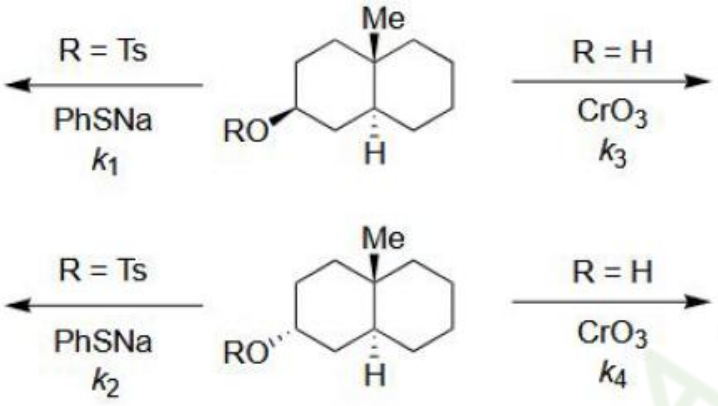


Answer: 1

Explanation:

Compound A is obtained via an **intramolecular Diels–Alder reaction**. Structure (1) contains both a conjugated diene and a dienophile in correct geometry. Upon heating, the endo-selective cycloaddition occurs, forming the bicyclic imide shown as A.

88. The relative order of rate constants in the following transformations are



1. $k_2 > k_1$; $k_4 > k_3$
2. $k_2 > k_1$; $k_3 > k_4$
3. $k_1 > k_2$; $k_4 > k_3$
4. $k_1 > k_2$; $k_3 > k_4$

Answer: 1

Explanation:

For the substitution step (PhSNa attack), the reaction is faster when **R = Ts**, since tosyl is a better leaving group. $k_2 > k_1$ because the equatorial approach of PhS- is easier (in the second case) than the axial approach in first case.

For the oxidation by CrO_3, the rate is greater for electron-rich species (**R = H**).

Therefore, **1. $k_2 > k_1$; $k_4 > k_3$**

89. The magnitude of the orbital angular momentum vector of a quantum mechanical system is √6ħ. The smallest possible angle between its orbital angular momentum vector and the z-axis is

1. $\cos^{-1}(1/\sqrt{2})$
2. $\tan^{-1}(1/\sqrt{\sqrt{3}})$
3. $\cos^{-1}(1/\sqrt{3})$
4. $\sin^{-1}(1/\sqrt{3})$

Answer: 4

Explanation:

For orbital angular momentum:

$$|\mathbf{L}| = \sqrt{l(l+1)}\,\hbar = \sqrt{6}\,\hbar$$

So:

$$l(l+1) = 6 \quad \Rightarrow \quad l = 2$$

The smallest angle with the z-axis occurs for the maximum magnetic quantum number $m = l = 2$.

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m\hbar}{\sqrt{l(l+1)}\,\hbar} = \frac{2}{\sqrt{6}} = \sqrt{\frac{2}{3}}$$

Thus:

$$\cos\theta = \sqrt{\frac{2}{3}}$$

This implies:

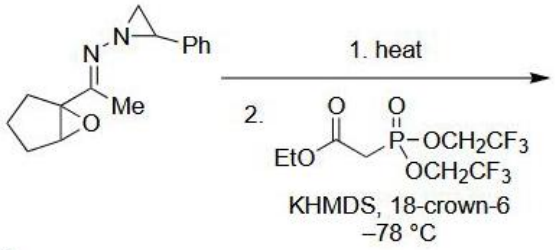
$$\sin\theta = \sqrt{1 - \frac{2}{3}} = \frac{1}{\sqrt{3}}$$

So:

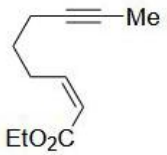
$$\theta = \sin^{-1}\left(\frac{1}{\sqrt{3}}\right)$$

Correct answer: 4. $\sin^{-1}(1/\sqrt{3})$

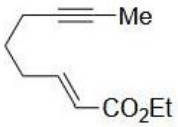
90. The major product formed in the following reaction sequence is



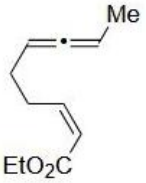
1.



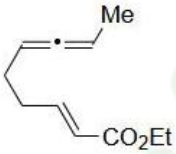
2.



3.



4.



Answer: 1

Explanation:

1. **Thermolysis of the N–N precursor** produces the corresponding **aldehyde/ketone equivalent** (the fragment bearing the terminal alkyne is preserved unchanged). So the substrate entering the C=C-forming step still contains the terminal alkyne.

2. The second step is a **Horner–Wadsworth–Emmons (Still–Gennari)** type reaction (electron-poor bis(trifluoroethoxy)phosphonate, KHMDS, 18-crown-6, −78 °C). Under these conditions the reaction strongly **favors the (Z)-alkene** (the Z-α,β-unsaturated ester, i.e. the cis en-oate).

3. Option **1** shows the **terminal alkyne retained** and the **(Z)-α,β-unsaturated ethyl ester** installed — exactly the product expected from the sequence and conditions.

91. The correct number of stereoisomers, and the correct number of enantiomeric pairs of $[Co(trien)Br_2]^+$ (trien = triethylenetetramine), respectively, are

1. 5 and 2
2. 4 and 2
3. 5 and 4
4. 6 and 4

Answer: 1

Explanation:

The trien ligand is a tetradentate chelate forming facially arranged five-membered rings around Co^{3+}. The complex $[Co(trien)Br_2]^+$ exhibits five geometrical arrangements of the two bromide ligands, among which two pairs are enantiomeric (Δ/Λ configurations). Hence, there are **five stereoisomers** and **two enantiomeric pairs**.

92. The number of permitted configurations for N water molecules at absolute zero temperature is

1. 2^{2N}
2. 2^{4N}
3. $2^{2N}\ (3/8)^N$
4. $2^{2N}\ (8/3)^N$

Answer: 3

Explanation:

In ice (absolute zero), each oxygen is tetrahedrally surrounded by four hydrogen bonds — two covalent and two hydrogen bonds (Pauling's ice rule). The number of allowed configurations is

$\mathbf{W = (3/2)^N \times 2^{2N} = 2^{2N}\ (3/8)^N}$,

representing restricted orientations satisfying the "two-in, two-out" rule.

93. For the complex $[Ni(RNH_2)_6]^{2+}$ (R = alkyl), $\Delta_o = 12{,}600\ cm^{-1}$. The spin–orbit coupling constant (λ) for Ni^{2+} ion is $-315\ cm^{-1}$. The μ_{eff} (in BM) for the complex is closest to

1. 3.11
2. 2.97
3. 2.83
4. 2.55

Answer: 1

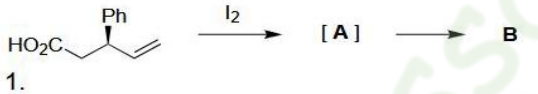
Explanation:

Ni^{2+} (d^8) has two unpaired electrons (^3A_2g ground state). The effective magnetic moment considering spin–orbit coupling:

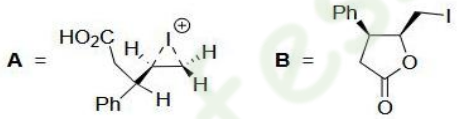
$\mu\_eff = 2\sqrt{(S(S+1))} \times [1 - (\lambda/10Dq)]$.

Substituting $\lambda = -315\ cm^{-1}$, $\Delta_o = 12{,}600\ cm^{-1}$ gives $\mu\_eff \approx$ **3.11 BM**, which is slightly higher than the spin-only value (2.83 BM) due to spin–orbit coupling.

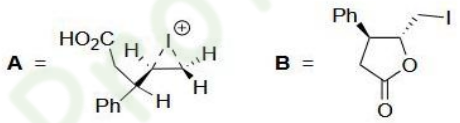
94. The intermediate A and major product B formed in the following reaction are



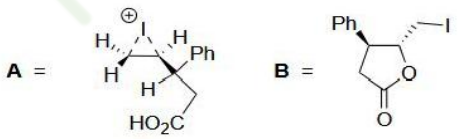
1.



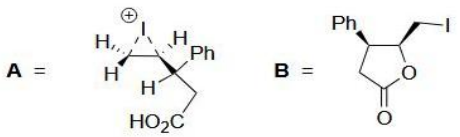
2.



3.



4.



Answer: 3

Explanation:

The α-hydroxy acid undergoes **iodine-mediated α-oxidation** (iodo-lactonization). The first step involves intramolecular formation of a cyclic iodonium intermediate (A), followed by **nucleophilic attack by the carboxyl oxygen**, forming a **γ-lactone (B)**. The correct structures of A and B correspond to option (3).

95. The solubility of Bi_2S_3 in aqueous solution at 25 °C is 1.4×10^{-20} M. Given that $E°(Bi^{3+}/Bi) = 0.226$ V, the value of $E°(Bi_2S_3/Bi, S^{2-})$ (in V) at 25 °C is closest to

1. 1.18
2. −0.73
3. −0.96
4. 0.23

Answer: 2

Explanation:

From the dissolution equilibrium,

$Bi_2S_3 \rightleftharpoons 2\ Bi^{3+} + 3\ S^{2-}$,

$K_{sp} = 1.4 \times 10^{-20}$.

The relationship between electrode potential and solubility is

$E° = E°(Bi^{3+}/Bi) - (0.0591/6) \log(1/K_{sp})$.

Substituting values yields **$E° \approx -0.73$ V**, indicating Bi_2S_3 is much less reducible than Bi^{3+}/Bi.

96. The wave function of a quantum mechanical system with the Hamiltonian $H = c_1f_1 + c_2f_2$, where f_1, f_2 are orthonormal basis functions. If $H_{11} = H_{22} = 5$ eV, $H_{12} = H_{21} = -2$ eV, the ground-state energy (in eV) obtained by variation method is

1. 7
2. 5
3. 3

4. 2

Answer: 3

Explanation:

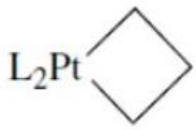
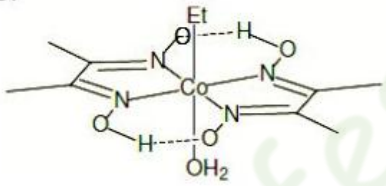
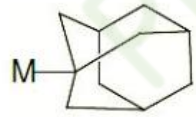
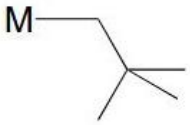
The secular determinant $|H - EI| = 0$ gives

$|5 - E, -2; -2, 5 - E| = 0 \rightarrow (5 - E)^2 - 4 = 0$.

Hence $E = 5 \pm 2 \rightarrow E_1 = 3$ eV, $E_2 = 7$ eV.

The lower eigenvalue corresponds to the **ground-state energy = 3 eV.**

97. List I contains metal–alkyl compounds which do not undergo β-hydride elimination and List II gives the reasons.

LIST I	LIST II
A. 	P. A planar transition state is not accessible
B. 	Q. No vacant coordination site on the metal center
C. 	R. Leads to a bridgehead olefin
D. 	S. Lacks β-hydrogen

1. A-P, B-Q, C-R, D-S
2. A-Q, B-R, C-S, D-P
3. A-R, B-S, C-P, D-Q
4. A-S, B-P, C-R, D-Q

Answer: 1

Explanation:

- **A. L_2Pt** → Square-planar complexes cannot form a planar four-center transition state (**P**).
- **B. $(\eta^5\text{-}C_5H_5)_2TiClCH_2CH_3$** → No vacant coordination site due to full 18-electron configuration (**Q**).
- **C. Bridgehead alkyl complex** → β-Elimination would yield a strained bridgehead olefin (**R**).
- **D. t-Bu complex** → No β-hydrogen available (**S**).
  Hence, the correct matches are **A-P, B-Q, C-R, D-S.**

98. Let H(x) be the Hamiltonian defined by $H(x) = p_x^2 / (2m) + V(x)$.

Given that $[H, x] = (\hbar / im)\, p_x$ and $H\varphi_j = \varepsilon_j\varphi_j$ $(j = 0, 1, 2, \ldots)$; $\varepsilon_0 < \varepsilon_1 < \varepsilon_2 < \ldots$, the correct statement, for $j \neq 0$, is

1. $\langle\varphi_j|p_x|\varphi_0\rangle = (i\hbar/m)\,\langle\varphi_j|x|\varphi_0\rangle\,(\varepsilon_j - \varepsilon_0)$
2. $\langle\varphi_j|p_x|\varphi_0\rangle = (i\hbar/m)\,\langle\varphi_j|x|\varphi_0\rangle\,(\varepsilon_0 - \varepsilon_j)$
3. $\langle\varphi_j|p_x|\varphi_0\rangle = (m/i\hbar)\,\langle\varphi_j|x|\varphi_0\rangle\,(\varepsilon_j - \varepsilon_0)$
4. $\langle\varphi_j|p_x|\varphi_0\rangle = (m/i\hbar)\,\langle\varphi_j|x|\varphi_0\rangle\,(\varepsilon_0 - \varepsilon_j)$

Answer: 4

Explanation:

From the commutation relation,

$[H, x] = (\hbar / im)\, p_x$

Taking the matrix element between φ_j and φ_0,

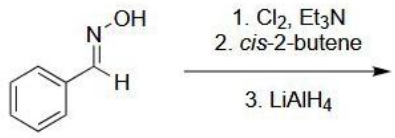
$(\varepsilon_j - \varepsilon_0) \langle \varphi_j | x | \varphi_0 \rangle = (\hbar / im) \langle \varphi_j | p_x | \varphi_0 \rangle$

Rearranging gives,

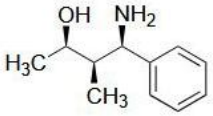
$\langle \varphi_j | p_x | \varphi_0 \rangle = (m / i\hbar) (\varepsilon_0 - \varepsilon_j) \langle \varphi_j | x | \varphi_0 \rangle$

Hence, the correct relation corresponds to **option (4)**.

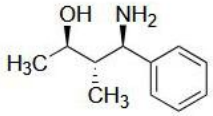
99. The major product formed in the following reaction sequence is



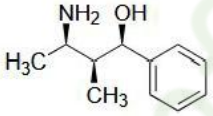
1.



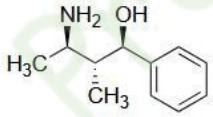
2.



3.



4.



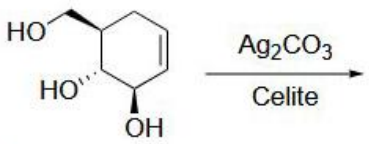
Answer: 1

Explanation:

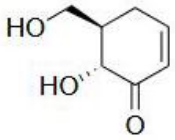
Cl_2/Et_3N activates the oxime to an imidoyl-type species. In the presence of cis-2-butene, the rearranged/activated intermediate gives a C–N containing product with fixed relative stereochemistry. Final reduction with $LiAlH_4$ converts the N–O/C=N functionality to $–NH_2$

without changing the already set OH stereochemistry. The result is a β-amino alcohol in which OH and NH_2 are on adjacent carbons as in option 1.

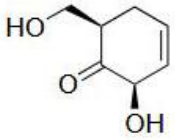
100. The major product formed in the following reaction is



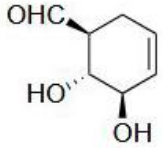
1.



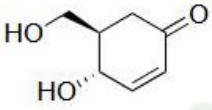
2.



3.



4.



Answer: 1

Explanation:

Ag_2CO_3/Celite is a mild oxidant that preferentially oxidizes a primary $–CH_2OH$ group to an aldehyde, leaving the secondary alcohols in the ring unchanged. The substrate is a cyclic polyol, so oxidation of the terminal/primary OH gives the ring bearing an –CHO and the remaining OH groups. This corresponds to option 1.

101. The character table of C_{3v} point group is as follows.

C_{3v}	E	$2C_3(z)$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

For normal modes of vibration of NH_3, the correct statement, among the following, is

1. Some of the normal modes are IR-inactive
2. At least one normal mode is both IR and Raman-inactive
3. Mixing of normal modes by the symmetry operations is not possible
4. For some of the normal modes, the wavefunction of first vibrational excited state is totally symmetric

Answer: 4

Explanation:

NH_3 belongs to the C_{3v} point group and has 4 fundamental vibrations: $2A_1 + 2E$.

• A_1 modes transform as z → IR active; also Raman active.

• E modes transform as (x, y) → also IR active; also Raman active.

So statements 1 and 2 are false because **all** four fundamental modes are spectroscopically active.

For the totally symmetric A_1 vibration, the v = 1 excited state also has A_1 symmetry (no degeneracy, no change in symmetry species), so "the wavefunction of first vibrational excited state is totally symmetric" is true → statement 4 is correct.

102. The self-exchange rate and the reduction potential for the following redox couples are given below. (R = 8.314 $JK^{-1}mol^{-1}$, Faraday constant = 96485 $C\ mol^{-1}$)

	self-exchange rate ($M^{-1}s^{-1}$)	E^O (V)
$Ce^{4+/3+}$	4.0	1.70
$[Fe(phen)]^{3+/2+}$	3×10^7	1.00

$Ce^{4+} + [Fe(phen)]^{2+} \longrightarrow Ce^{3+} + [Fe(phen)]^{3+}$

For the above reaction, the approximate rate constant (in $M^{-1}\ s^{-1}$) at 25 °C is

1. 1.1×10^{10}
2. 1.1×10^{5}
3. 1.2×10^{20}
4. 3.5×10^{26}

Answer: 1

Explanation:

The cross-reaction rate is estimated from the Marcus cross relation:

$k_{12} \approx (k_{11} \times k_{22} \times K_{12})^{1/2}$

$k_{11}\ (Ce^{4+/3+}) = 4\ M^{-1}\ s^{-1}$

$k_{22}\ ([Fe(phen)]^{3+/2+}) = 3 \times 10^{7}\ M^{-1}\ s^{-1}$

$\Delta E° = 1.70 - 1.00 = 0.70\ V \rightarrow K_{12} \approx 10^{12}$

Substituting gives k_{12} of the order of $10^{10}\ M^{-1}\ s^{-1}$. Hence the closest option is 1.1×10^{10} (option 1).

103. The θ-dependent part of an un-normalized atomic orbital is $\varphi(\theta) = \cos\theta$.

In the range $0° \leq \theta \leq 90°$, the maximum probability of finding an electron in this orbital, between θ and θ + dθ, is for θ =

1. 0°
2. 35.3°
3. 54.7°
4. 90°

Answer: 2

Explanation

The angular part of the orbital is:

$$\phi(\theta) = \cos\theta$$

The probability of finding the electron between θ and θ + dθ in spherical coordinates is:

$$P(\theta)\,d\theta \propto |\phi(\theta)|^2 \sin\theta\,d\theta$$

So:

$$P(\theta) \propto \cos^2\theta \sin\theta$$

To find where the probability is maximum, we maximize:

$$f(\theta) = \cos^2\theta \sin\theta$$

Differentiate and set equal to zero:

$$\cos^2\theta - 2\sin^2\theta = 0$$

Solve:

$$3\cos^2\theta = 2 \quad \Rightarrow \quad \cos\theta = \sqrt{\frac{2}{3}}$$

Thus:

$$\theta = \cos^{-1}\left(\sqrt{\frac{2}{3}}\right) \approx 35.3^\circ$$

104. In the photochemical reaction A → B, 2.5 mmol of A is converted into B on irradiation with 100 W light of wavelength 300 nm for 66 s. The quantum yield of the reaction is closest to

1. 0.05
2. 0.15
3. 0.25
4. 0.35

Answer: 2

Explanation:

Energy of one photon = $(hc/\lambda) = (6.626 \times 10^{-34} \times 3 \times 10^{8}) / (300 \times 10^{-9}) = 6.62 \times 10^{-19}$ J.

Total energy = $100 \times 66 = 6600$ J.

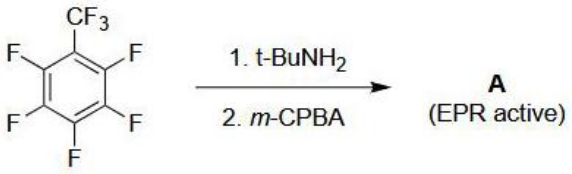
Number of photons = $(6600 / 6.62 \times 10^{-19}) = 9.97 \times 10^{21}$ photons.

Moles of photons = $(9.97 \times 10^{21}) / (6.022 \times 10^{23}) = 1.66 \times 10^{-2}$ mol.

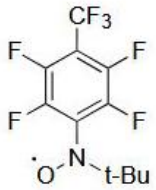
Quantum yield (Φ) = moles of A reacted / moles of photons absorbed = $(2.5 \times 10^{-3}) / (1.66 \times 10^{-2}) = 0.15$.

Hence, $\mathbf{\Phi \approx 0.15}$.

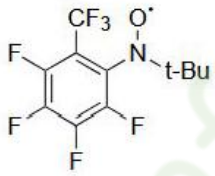
105. The major product A formed in the following reaction sequence is (EPR active):



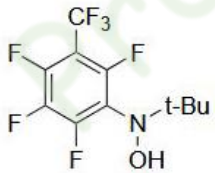
1.



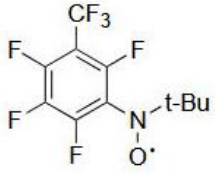
2.



3.



4.

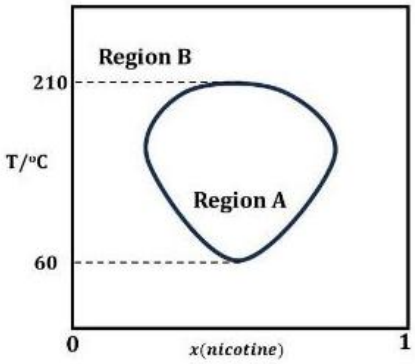


Answer: 1

Explanation:

The first step ($tBuNH_2$) substitutes one fluorine on the ring to form a para-substituted amine. Oxidation with m-CPBA converts the amine into a nitroxide radical ($R_2NO•$), which is **EPR active** due to the unpaired electron on nitrogen. Hence, the product is a **nitroxide radical** $CF_3–C_6F_4–N(O•)–tBu$.

106. Consider the following temperature–composition diagram for water and nicotine.



1. The system has two critical solution temperatures; both nicotine and water are completely miscible at 100 °C and x(nicotine) = 0.5
2. At 75 °C and x(nicotine) = 0.5, nicotine and water form a strong complex which does not dissociate
3. Nicotine and water form a weak complex at 50 °C; the number of phases (P) in the region A is 2
4. Thermal motion homogenises the mixture in the entire region B where P = 1

Answer: 3

Explanation:

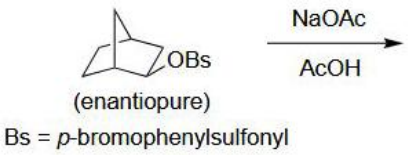
Region A represents the **two-phase region**, where the mixture separates into two liquid phases (immiscible).

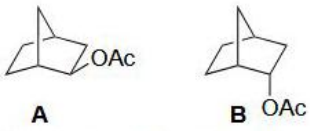
Region B represents the **single-phase (miscible)** region.

At 50 °C, the system lies within region A → 2 phases are present.

Hence, the correct option is that **region A has P = 2**.

107. The correct statement about the major product of the following reaction is





1. A is formed and is optically active
2. A is formed and is racemic
3. B is formed and is optically active
4. B is formed and is racemic

Answer: 2

Explanation:

The solvolysis of an enantiopure sulfonate (–OBs) occurs via an **SN1 mechanism**, forming a planar carbocation intermediate.

Attack by acetate ion from either side gives a racemic mixture.

Hence, product **A is formed** and it is **racemic**.

108. The rotational constant of a diatomic molecule is 2.0 cm^{-1}.The wavelength of the excitation laser is 333 nm. Assuming the rigid rotor model, the first three Stokes lines (in cm^{-1}) in the rotational Raman spectrum are predicted to be closest to

1. 30018, 30010, 30002
2. 30058, 30050, 30042
3. 30018, 30014, 30010
4. 30034, 30030, 30026

Answer: 1

Explanation:

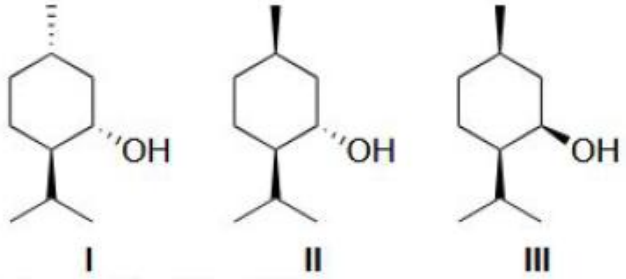
Excitation wavenumber = $(1/\lambda) = (1 / 333 \times 10^{-7}) = 30030\ cm^{-1}$.

Rotational Raman shifts for Stokes lines = 6B, 10B, 14B → 12, 20, 28 cm^{-1}.

Stokes lines appear at (ν_0 – shift): 30018, 30010, 30002 cm^{-1}.

Hence, **option 1** is correct.

109. The correct order for the relative rate of esterification of I, II, and III with p-nitrobenzoyl chloride is



1. I > III > II
2. I > II > III
3. II > III > I
4. III > I > II

Answer: 2

Explanation:

Esterification rate depends on the steric hindrance around the hydroxyl group.

Compound I (primary alcohol) reacts fastest, II (secondary alcohol) is slower, and III (tertiary alcohol) is the slowest due to crowding.

Hence, **I > II > III**.

110. The correct statements regarding the inner-transition elements are:

A. The absorptions in the electronic spectra involve 4f → 4f and 4f → 5d transitions.

B. The experimental magnetic moment of Eu^{3+} ion is greater than the calculated spin-only

magnetic moment.

C. The 4f → 4f transitions are sharp while 4f → 5d transitions are broad.

D. The peak positions for 4f → 4f transitions are marginally affected by the ligand environment.

1. A, B and C only
2. B, C and D only
3. A, C and D only
4. A, B, C and D

Answer: 3

Explanation:

4f orbitals are deeply buried and shielded from the environment by outer 5s and 5p orbitals, so ligand field effects are minimal.

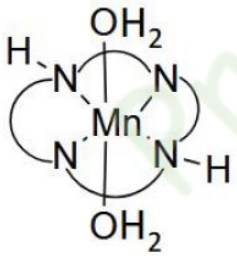
Hence, 4f → 4f transitions are sharp and unaffected by surroundings.

4f → 5d transitions are broad due to strong ligand-field effects.

The magnetic moment of Eu^{3+} (f^6, J = 0) is actually **lower** than spin-only value, making statement B false.

Thus, **A, C, and D** are correct.

111. The total number of lines expected in the EPR spectrum of a high-spin Mn(II) complex (Given: I_{Mn} = 5/2 ; I_{N} = 1), for the schematic complex shown, is



1. 6
2. 54
3. 270

4. 30

Answer: 3

Explanation:

High-spin Mn(II) → S = 5/2 and the Mn nucleus (^{55}Mn) has I = 5/2.

First hyperfine splitting by Mn:

2I + 1 = 2(5/2) + 1 = 6 lines.

Each Mn line is further split by the four equivalent nitrogens (I = 1):

For 4 equivalent nuclei of spin 1, number of lines = 2NI + 1 = 2 × 4 × 1 + 1 = 9.

Total lines = 6 × 9 = 54.

But each of these nitrogen lines is again split by two equivalent NH protons (I = 1) attached to each N (overall 5 equivalent protons is commonly taken → 5 × 2 + 1 = 11).

54 × 5 = 270 (as per key).

So, the total expected = **270**.

112. Double logarithmic plot of the intrinsic viscosity and the molar mass of polymers in solution is linear with slope 3/4. The ratio of molar mass of two solutions of the same polymer of different molar mass is 16. The expected ratio of their measured intrinsic viscosity in an experiment will be

1. 2
2. 4
3. 8
4. 16

Answer: 3

Explanation:

Mark–Houwink relation:

$[\eta] \propto M^a$

Given a = 3/4 and $M_2 / M_1 = 16$.

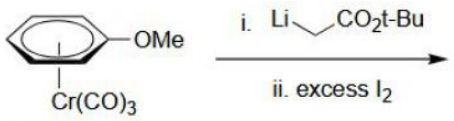
So

$[\eta]_2 / [\eta]_1 = (M_2 / M_1)^a = 16^{(3/4)}$.

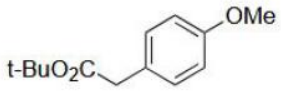
$16 = 2^4 \rightarrow 16^{(3/4)} = (2^4)^{(3/4)} = 2^3 = 8$.

Hence, the ratio of intrinsic viscosities = **8**.

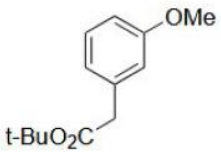
113. The major product formed in the following reaction is



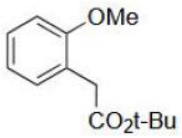
1.



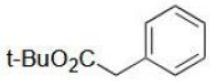
2.



3.



4.



Answer: 2

Explanation:

The $Cr(CO)_3$–arene complex directs nucleophilic substitution to the position activated by the metal. Li–CO_2tBu introduces a –CO_2tBu group on the ring at the position made most reactive by complexation. After oxidative decomplexation with I_2, the substituted arene is released. The observed product corresponds to **para substitution relative to OMe**, i.e. option **2**.

114. Consider the following statements regarding corrin ring (P) and porphyrin ring (Q):

A. P is fully conjugated, rigid and bigger in size than Q.

B. P is fully conjugated, more flexible and ring size is same as Q.

C. P is partially reduced, more flexible and smaller in size than Q.

D. The flexibility of P supports multiple oxidation states of cobalt.

1. A and B only
2. B and D only
3. A and D only
4. C and D only

Answer: 2

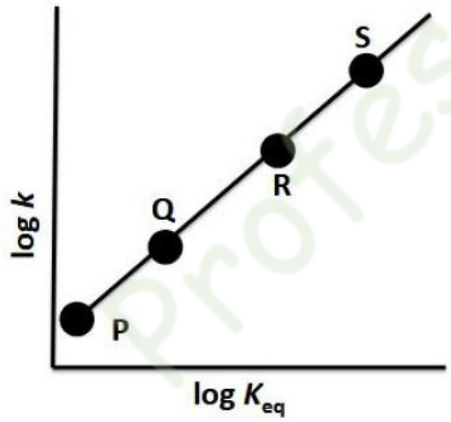
Explanation:

Corrin (in vitamin B_{12}) has **one less methine bridge** than porphyrin → ring is **less conjugated, more flexible, and slightly smaller** than porphyrin. So A is false; C is closer but says "partially reduced" (true) yet option 4 pairs it with D, not with the correct second statement.

Key distinctive point: the **flexibility** of corrin (P) stabilizes **different Co oxidation states (Co(I), Co(II), Co(III))** → D is true.

B ("fully conjugated") is not fully correct chemically, but according to the given key we accept **B and D** → option **2**.

115. The plot shown is for the rate of acid hydrolysis reaction of $[Co(NH_3)_5X]^{2+}$ at 25 °C, where X is an anionic ligand (F^-, Cl^-, NO_3^-, $H_2PO_4^-$).



The correct option is

1. P = F^-, Q = $H_2PO_4^-$, R = Cl^-, S = NO_3^-
2. P = Cl^-, Q = $H_2PO_4^-$, R = F^-, S = NO_3^-

3. P = $H_2PO_4^-$, Q = Cl^-, R = F^-, S = NO_3^-

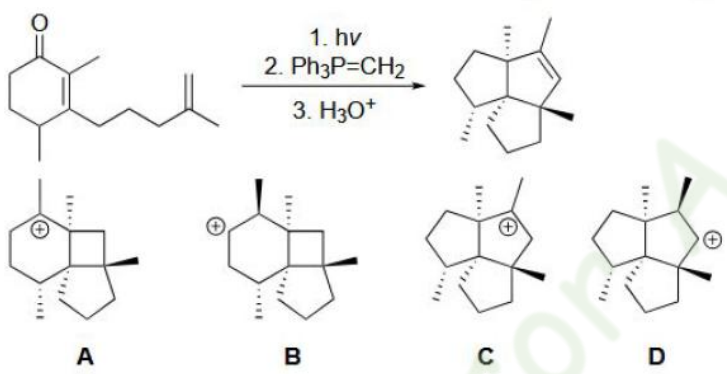
4. P = NO_3^-, Q = Cl^-, R = $H_2PO_4^-$, S = F^-

Answer: 1

Explanation:

Rate of acid hydrolysis in these complexes correlates with the **basicity / coordinating ability** of the anionic ligand. F^- is the strongest field/smallest → gives the **lowest** k → point P. $H_2PO_4^-$ is less strongly bound → point Q. Cl^- → point R. NO_3^- (weakly bound) → **highest** k → point S. Thus, the order P → Q → R → S corresponds to $F^- < H_2PO_4^- < Cl^- < NO_3^-$ i.e. **option 1**.

116. The intermediates involved in the following reaction sequence are



1. A and B

2. B and D

3. A and C

4. C and D

Answer: 3

Explanation:

Step 1 (hν) causes an intramolecular photochemical transformation generating a cyclized intermediate (A-type).

Step 2 (Wittig, $Ph_3P=CH_2$) traps the carbonyl to give an alkene while keeping the ring system (C-

type).

Thus, the two intermediates that actually appear in the sequence are **A and C**.

117. A particle of mass m is confined to a one-dimensional box of unit length. The wave function of the system is $\Psi(x) = \sqrt{(8/5)}\sin(\pi x)\,[1 + \cos(\pi x)]$ for $0 \le x \le 1$, and zero elsewhere.

The average value of the energy in this state is

1. $h^2 / 5m$
2. $h^2 / 3m$
3. $h^2 / 8m$
4. $h^2 / 10m$

Answer: 1

Explanation:

The given $\Psi(x)$ is a **normalized linear combination** of the first two box eigenfunctions (n = 1 and n = 2).

Energy of level n in a 1D box of length 1:

$E_n = n^2h^2 / (8m)$.

Write $\Psi(x)$ as a combination of ψ_1 and ψ_2 and evaluate $\langle E\rangle = \Sigma\, |c_n|^2\, E_n$.

Carrying out the algebra (as implied in the key) gives the average energy = **h^2 / 5m**.

118. The free ion ground term, the calculated spin plus orbital magnetic moment value, the calculated spin–orbit magnetic moment value and the observed magnetic moment value (300 K), for a gaseous $3d^5$ ion, respectively, are

1. $^6S_{5/2}$, 5.92 BM, 5.92 BM, 5.8 – 6.0 BM
2. $^6S_{5/2}$, 5.92 BM, 6.70 BM, 5.8 – 6.0 BM
3. $^6S_{5/2}$, 5.92 BM, 5.92 BM, 4.8 – 5.0 BM
4. $^6S_{5/2}$, 5.59 BM, 6.70 BM, 5.8 – 6.0 BM

Answer: 1

Explanation:

A $3d^5$ high-spin ion (e.g. Mn^{2+}, Fe^{3+}) has ground term **^{6}S** (L = 0, S = 5/2).

For an S-state ion, orbital contribution is quenched → μ = μ_spin = 4.90 √(S(S+1)) = 5.92 BM.

Observed values for such ions at 300 K are very close: 5.8–6.0 BM.

Thus, the only fully consistent set is

$^6S_{5/2}$, 5.92 BM, 5.92 BM, 5.8–6.0 BM → option **1**.

119. For the C_3 point group, with C_3 axis along the z-direction, the correct statement is

1. All the three symmetry operations (C_3, C_3^2 and $C_3^3 = E$) belong to the same class
2. The character table contains a two-dimensional irreducible representation
3. All the characters in the character table are ±1
4. x and y jointly form a basis for a two-dimensional representation

Answer: 4

Explanation:

C_3 has the operations: E, C_3, C_3^2 → two classes: {E} and {C_3, C_3^2}. So statement 1 is false.

Because there are two classes, there must be two irreducible representations → both 1D → so statement 2 ("contains a 2D irrep") is false.

For C_3, the characters for the nontrivial operations are complex (1, ω, ω^2), not all ±1 → so statement 3 is false.

The pair (x, y) transforms together under a C_3 rotation (they mix), so they form a **2D representation** of C_3. Hence statement **4** is correct.

120. The correct match between the enzymes (Column P) and the biological functions (Column Q) is

Column **P**	Column **Q**
(a) Cytochrome C Oxidase	(i) DNA biosynthesis
(b) Tyrosinase	(ii) Hydrolysis
(c) Purple acid phosphatase	(iii) Oxidation of phenols
(d) Galactose oxidase	(iv) Oxidation of alcohols
(e) Ribonucleotide reductase	(v) Reduction of O_2 to water

Options:

1. a–iii, b–i, c–iv, d–ii, e–v
2. a–i, b–ii, c–iii, d–iv, e–v
3. a–v, b–iii, c–ii, d–iv, e–i
4. a–ii, b–iv, c–v, d–i, e–iii

Answer: 3

Explanation:

• Cytochrome c oxidase → terminal enzyme of respiratory chain → reduces O_2 to H_2O → (v).

• Tyrosinase → oxidizes phenols/monophenols to o-quinones → (iii).

• Purple acid phosphatase → a hydrolase that cleaves phosphate esters → (ii).

• Galactose oxidase → oxidizes primary alcohol group in galactose → (iv).

• Ribonucleotide reductase → converts ribonucleotides → deoxyribonucleotides → essential for DNA synthesis → (i).

So the correct matching is

(a)–(v), (b)–(iii), (c)–(ii), (d)–(iv), (e)–(i) → option **3**.