21. For the given reaction

$[{}^{*}\mathbf{Co(L)}_{n}]^{2+} + [\mathbf{Co(L)}_{n}]^{3+} \rightarrow [{}^{*}\mathbf{Co(L)}_{n}]^{3+} + [\mathbf{Co(L)}_{n}]^{2+}$

the correct statement with respect to the rate of electron transfer process is

o-phen = o-phenanthroline; *Co is labeled atom

(a) fast electron transfer; L = NH_3; n = 6

(b) slow electron transfer; L = 0-phen; n = 3

(c) very slow electron transfer; L = NH_3; n = 6

(d) very slow electron transfer; L = 0-phen; n = 3

Answer: (3)—very slow electron transfer; L = NH_3; n = 6

Explanation:

Electron transfer between complexes such as $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$ is an *inner-sphere redox process* involving a change from low-spin d^6 to high-spin d^7 configuration. Since both complexes are substitution-inert and have no bridging ligands to facilitate electron transfer, the process proceeds through an *outer-sphere mechanism*, which is extremely slow. The rigidity of NH_3 as a ligand prevents structural rearrangement needed for effective orbital overlap during electron exchange. Therefore, the electron transfer rate is very slow for $[Co(NH_3)_6]^{3+/2+}$ system compared to π-acceptor ligands such as o-phenanthroline that stabilize mixed-valence intermediates.

22. Choose the correct order of energy of $2\sigma_g$ and $1\pi u$ molecular orbitals for B_2, C_2 and O_2 :

(a) $2\sigma_g > 1\pi_u$ for all the three

(b) $2\sigma_g > 1\pi_u$ for B_2 and C_2 only

(c) $1\pi_u > 2\sigma_g$ for C_2 and O_2 only

(d) $2\sigma_g > 1\pi u$ for B_2 and O_2 only

Answer: (6)—2σg > 1πu for B_2 and C_2 only

Explanation:

In diatomic molecular orbital theory, the relative energy order of 2σg and 1πu orbitals changes with increasing atomic number. For lighter diatomics (B_2, C_2, N_2), there is *s–p mixing* between 2s and 2p orbitals, causing 1πu to lie *below* 2σg. For heavier molecules (O_2 and beyond), s–p mixing is negligible, making 2σg *lower* in energy than 1πu. Therefore, for B_2 and C_2 (with strong s–p mixing), the energy order is 2σg > 1πu, while for O_2 it reverses (1πu > 2σg).

23. The pair in which both actinides show +3 oxidation state only is

(a) Ac and Lr

(b) Ac and No

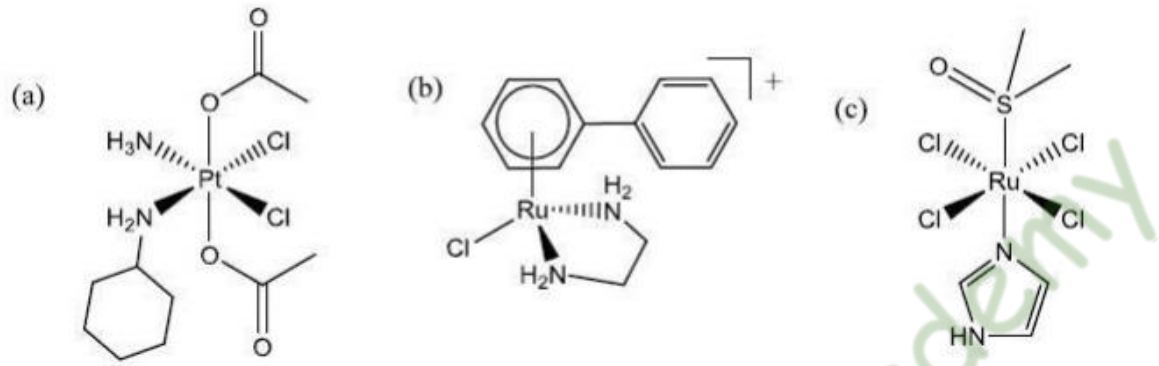
(c) Cm and Bk

(d) Cm and Lr

Answer: (9)—Ac and Lr

Explanation: Actinium and lawrencium are the two actinides for which the only well-established oxidation state in aqueous coordination chemistry is +3. Nobelium commonly exhibits +2 besides +3, and curium/berkelium can access higher states (e.g., +4). Hence only Ac and Lr fit "+3 only."

24. The complex(es) showing activity against cancerous cells is/are



(a) a only

(b) a and b

(c) a and c

(d) a, b and c

Answer: (a), (b) and (c)

Explanation: (a) is a cis-platin–type Pt(II) complex (cis-[PtCl2(NH3)2] motif), the classical anticancer pharmacophore. (b) is a Ru(II)–arene complex (η6-arene–RuCl2 with an N-donor chelate), a known family of anticancer agents (e.g., RAPTA/RAED series). (c) is a Ru(III) complex with DMSO and chloride/azole donors, the NAMI-A–type scaffold, which is well known for antimetastatic activity. Therefore all three depicted complexes show anticancer activity.

25. Consider the nuclear reaction

$$_{92}X^{234} + \beta + \alpha \rightarrow Y + \gamma + 2\beta^{+}$$

Y is

(a) $92Y^{238}$

(b) $91Y^{238}$

(c) $^{93}Y^{236}$

(d) $94Y^{238}$

Answer: (b) $91Y^{238}$

Explanation:

Mass number: adding an α-particle increases A by 4 (234 → 238); β/β^+ do not change A, so Y must have A = 238.

Atomic number: starting Z = 92. Electron capture on the left (β on LHS) lowers Z by 1 → 91; α capture raises Z by 2 → 93; emission of two positrons on the right lowers Z by 2 → 91. Hence Y has Z = 91 and A = 238 → 91Y^238.

26. Correct statement/s among the following with respect to ionization energy (IE) is/are

(i) $(IE_1 + IE_2 + IE_3)$ for indium is more than that of aluminium

(ii) IE_1 of scandium is higher than that of cobalt

(iii) IE_1 of gallium is lower than that of selenium

(iv) IE_1 of nitrogen is greater than that of oxygen

The reason for significantly high solubility of $AgClO_4$ in benzene

(a) ii and iv

(b) iii and iv

(c) i and iv

(d) ii and iii

Answer: (b) iii and iv

Explanation:

Across a period, IE generally increases. (iii) is true because Ga (Group 13) has a lower IE1 than Se (Group 16) in the same period. (iv) is true due to the well-known anomaly: N (2p^3, half-filled) has higher IE1 than O (2p^4). (i) is false—down a group IEs decrease, so the sum for In is not more than Al. (ii) is false—Co (Z = 27) has higher IE1 than Sc (Z = 21).

27. The reason for significantly high solubility of AgClO4 in benzene than in alkane solvents is

(a) Alkane solvents are non- polar.

(b) Benzene is an aprotic solvent.

(c) PhAg is formed.

(d) Benzene acts as a soft base

Answer: (d) Benzene acts as a soft base

Explanation:

Ag^+ is a soft acid. Benzene's π-electron cloud provides cation–π interaction and soft-base character, stabilizing Ag^+ in solution and enhancing the solubility of AgClO4. Alkanes lack π electrons and do not provide such stabilization.

28. Correct statement for 'Inductively Coupled Plasma Atomic Emission Spectroscopy' is

(a) It is unsuitable for all non-metals.

(b) Simultaneous determination of only metals is possible.

(c) Induction coil stabilizes plasma.

(d) Oxide formation lowers atomization of metals.

Answer: (c) Induction coil stabilizes plasma.

Explanation: In ICP-AES, a radio-frequency induction coil surrounds the torch and sustains/stabilizes the high-temperature argon plasma by inductive coupling. This stable plasma efficiently atomizes and excites analyte species. The other statements are incorrect or misleading: ICP-AES can analyze many non-metals as well; it can determine multiple elements (not only metals) simultaneously; oxide formation is generally minimized in the plasma and is not a defining statement of the technique.

29.The number of geometrical isomers of the complex $[\mathbf{RhH(C \equiv CR)_2(PMe_3)_3}]$ is

(a) 2

(b) 3

(c) 4

(d) 1

Answer: (b) 3

Explanation: The complex is octahedral with a ligand set A3B2C (A = PMe3, B = alkynyl, C = hydride). For an octahedral A3B2C composition, three distinct arrangements are possible: (i) fac-A3 with B ligands trans to each other, (ii) mer-A3 with B ligands cis, and (iii) mer-A3 with B ligands trans to C. These are geometrically non-equivalent, giving three geometrical isomers.

30. I_2 is violet in the solid as well as in gas phase. However in acetone or ethanol, it turns brown. Choose the correct statement(s) for this colour change:

(a) Dissociation of I_2 in atomic state

(b) Interaction of low-lying $\sigma^\star$-orbital of iodine with lone pair of O (solvent)

(c) Formation of a charge-transfer complex

(a) a

(b) b

(c) a and b

(d) b and c

Answer: (d) b and c

Explanation: Oxygen-donor solvents such as acetone or ethanol act as electron donors to I2. The solvent lone pair interacts with the low-lying σ* orbital of I2, producing donor–acceptor (charge-transfer) complexes that appear brown in solution. The colour change is thus due to (b) and (c). Iodine does not dissociate into atomic iodine under these conditions, so (a) is not responsible.

31. The pair of compounds in which both members show LMCT band in their electronic spectra is

(a) $[FeCl_4]^{2-}$ and $[Fe(bpy)_3]^{2+}$

(b) $[FeBr_4]^{2-}$ and $[TcO_4]$

(c) $[ReO_4]^{-}$and $[Ru(bpy)_3]^{2+}$

(d) $[Fe(\ phen\ )_3]^{2+}$ and $[FeCl_4]^{2-}$

Answer: (b) $[FeBr_4]^{2-}$ and $[TcO_4]$

Explanation:

Ligand-to-metal charge-transfer (LMCT) bands are intense when an electron-rich ligand donates to a high-valent, electron-deficient metal center (often d^0/d^1). Tetraoxo anions like **$[TcO_4]^-$ (Tc(VII), d^0)** show strong O→M LMCT. Tetrahalometal complexes also display X→M LMCT transitions; among the given pairs, **$[FeBr_4]^{2-}$** (halide→Fe) and **$[TcO_4]^-$** both exhibit LMCT features, whereas **$[Fe(bpy)_3]^{2+}$/$[Fe(phen)_3]^{2+}$** are classic MLCT systems and **$[Ru(bpy)_3]^{2+}$** is MLCT, so those pairs are not suitable.

32. During the binding of O_2 to myoglobin (consider 'heme' in xy-plane), the molecular orbital of O_2 and atomic orbital of Fe involved in the formation of the σ-bond is

(a) π^* and $d_z{}^2$

(b) π^* and d_{xz}

(c) π and d_{xz}

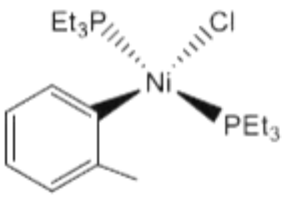
(d) π and $d_z{}^2$

Answer: (d) π and $d_z{}^2$

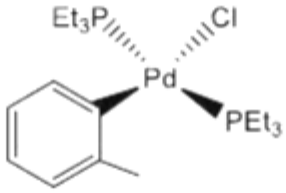
Explanation:

O_2 binds **end-on** to Fe; σ-donation occurs from the *O_2 π (antibonding) orbital** into the metal's **d^{z^2}** orbital oriented along the Fe–O axis (perpendicular to the porphyrin plane). This gives the σ component of the Fe–O_2 bond.

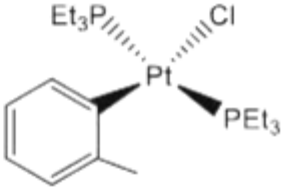
33. The order of rate of substitution of chloride by pyridine (in ethanol) in the following complexes is



I



II



III

(a) I > II > III

(b) I ≈ II ≈ III

(c) I > II ≈ III

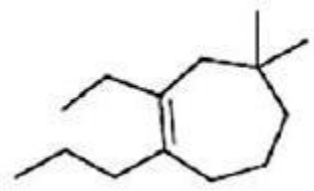
(d) I < II ≈ III

Answer: (a) I > II > III

Explanation:

All three are square-planar d^8 complexes of **Ni(II), Pd(II), Pt(II)** (I, II, III respectively). For ligand substitution at d^8 square-planar centers, lability follows **Ni(II) > Pd(II) >> Pt(II)**. Hence the substitution rate decreases in the order **I > II > III**.

34. The correct IUPAC name for the following molecule is



(a) 1-Propyl-2-ethyl-4,4-dimethylcyclohept-1-ene

(b) 2-Ethyl-4,4-dimethyl-1-propylcyclohept-1-ene

(c) 3-Ethyl-1,1-dimethyl-4-propylcyclohept-3-ene

(d) 1,1-Dimethyl-3-ethyl-4-propylcyclohept-3-ene

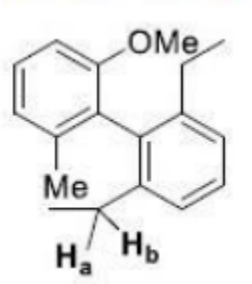
Answer: (b) 2-Ethyl-4,4-dimethyl-1-propylcyclohept-1-ene

Explanation:

The parent is a seven-membered ring with one double bond → **cyclohept-1-ene** (the double bond gets locant 1). Numbering is chosen to give the **lowest set of locants** for substituents while keeping the double bond at 1) this places **propyl at C-1**, **ethyl at C-2**, and **two methyls at C-4** (locants 1,2,4,4). In the name, substituents are listed **alphabetically ignoring multiplicative prefixes**: *ethyl (E)*, *methyl (M; as dimethyl)*, then *propyl (P)* →

2-ethyl-4,4-dimethyl-1-propylcyclohept-1-ene. Options 1, 3, and 4 either misnumber the ring (double bond at 3) or list substituents in the wrong order.

35. The stereochemical relationship of H_a and H_b in the following molecule is



(a) enantiotopic

(b) homotopic

(c) diastereotopic

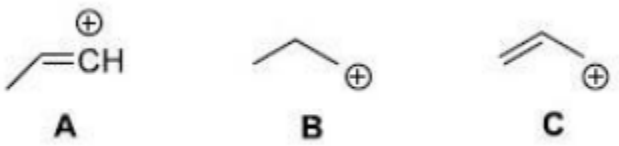
(d) constitutionally heterotopic

Answer: (c) diastereotopic

Explanation:

In the given substituted naphthalene system, Ha and Hb are attached to a carbon bearing different substituents (Me and OMe groups on the ring). The two hydrogens (Ha and Hb) occupy diastereotopic environments because replacing each hydrogen with a substituent (like Cl or D) would lead to **diastereomeric** products rather than enantiomers. This arises from the molecule already containing a chiral center or an asymmetric environment, breaking mirror symmetry. Hence, Ha and Hb are **diastereotopic protons**, not enantiotopic or homotopic.

36. The correct order of stability of the carbocations A-C is



(a) C > A > B

(b) A > C > B

(c) B > C > A

(d) C > B > A

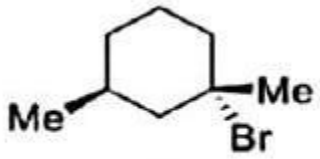
Answer: (a) C > A > B

Explanation:

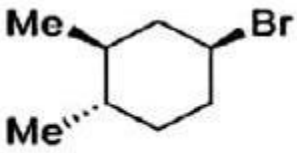
Carbocation stability follows the order of resonance and hyperconjugation effects.

- **C** is an *allylic carbocation* stabilized by resonance over two carbon atoms.
- **B** is a *secondary carbocation* stabilized by hyperconjugation.
- **A** is a *vinyl carbocation* (positive charge on sp^2 carbon of C=C), which is highly unstable due to poor overlap with adjacent π-bond.
  Hence, resonance stabilization dominates → **C > B > A**.

37. The correct statement for the orientation of the bromine atoms in the most stable conformations of *A* and *B* is



A



B

(a) axial in both A and B

(b) axial in A and equatorial in B

(c) equatorial in both A and B

(d) equatorial in A and axial in B

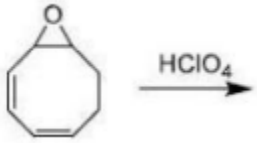
Answer: (b) axial in A and equatorial in B

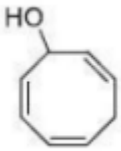
Explanation:

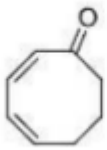
In chair conformations of substituted cyclohexanes, bulky substituents prefer the **equatorial** position to minimize 1,3-diaxial interactions.

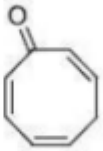
- In compound **A**, the bromine atom is *axial* due to the trans relationship with the methyl group in its stable conformer.
- In compound **B**, the bromine atom is *equatorial*, minimizing steric hindrance with the methyl group.
  Hence, **A → axial Br**, **B → equatorial Br** is the correct statement.

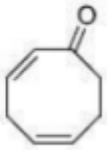
38. The major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

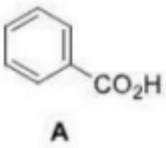
Answer: b

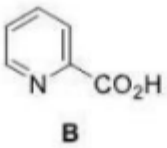
Explanation:

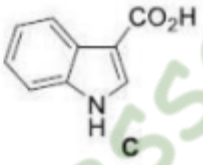
The given reaction is an **acid-catalyzed hydration** of cycloheptatriene under perchloric acid ($HClO_4$). Under strongly acidic conditions, the non-aromatic **cycloheptatriene** undergoes **tropylium ion ($C_7H_7^+$)** formation via rearrangement, which is aromatic and highly stable. The electrophilic addition of water leads to formation of **tropylium cation intermediate**, followed by deprotonation to yield the **carbonyl compound (cycloheptanone)**.

Thus, the major product formed is the **aromatic tropylium-derived ketone (C_7H_6O)**

39. The following carboxylic acids undergo decarboxylation upon heating. The ease of decarboxylation is in the order



A


B


C

(a) B $>$ A $>$ C

(b) C $>$ B $>$ A

(c) A $>$ C $>$ B

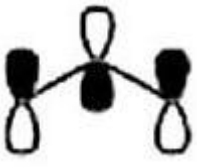
(d) C $>$ A $>$ B

Answer: b

Explanation:

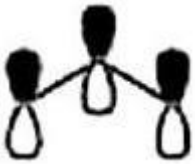
Decarboxylation is most facile when the carbanion (or developing π-system) formed after CO_2 loss is strongly stabilized by **aromatic/heteroaromatic conjugation**. At the **2-position of indole (C)**, loss of CO_2 gives a resonance-stabilized anion that restores aromaticity over the indole framework, so C decarboxylates most readily. **Pyridine-2-carboxylic acid (B)** also gains stabilization by conjugation with the heteroaromatic ring, though less than indole, so it is intermediate. **Benzoic acid (A)** lacks such special stabilization and thus decarboxylates least readily under simple heating conditions.

40. The HOMO of π-molecular orbitals of methylazide is

(a) 

(b) 

(c) 

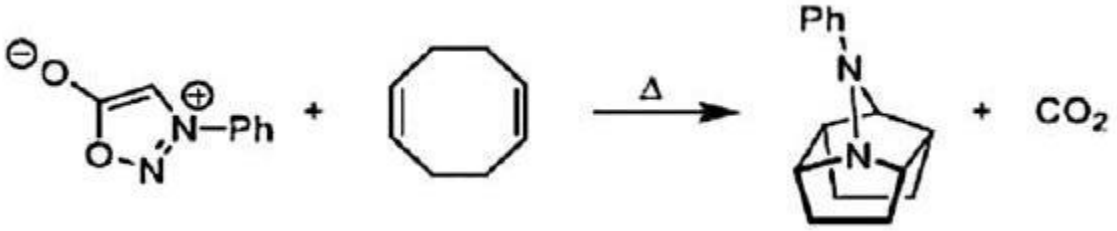
(d) 

Answer: 2

Explanation:

Azide ($-N_3$) is a **linear, 4-π-electron system** with two degenerate π sets. The HOMO corresponds to the **antisymmetric combination** where the terminal N p orbitals are **out of phase** and the central N is **in phase** with one terminal and out of phase with the other (overall anti-bonding at the termini with a node through the center). Among the depictions, the second diagram matches this phase pattern for the highest-energy occupied π MO.

41. The following transformation involves a series of



(a) electrocyclic ring-opening and closing reactions.

(b) cycloaddition and cycloreversion reactions.

(c) sigmatropic rearrangements.

(d) cheletropic addition and elimination reactions.

Answer: (b) cycloaddition and cycloreversion reactions.

Explanation:

The sequence proceeds via a **1,3-dipolar cycloaddition** (formation of the bicyclic adduct) followed by **cycloreversion** with **loss of CO_2**, giving the norbornane-type product. The key bond-forming and bond-breaking steps are pericyclic **[n+m] cycloadditions** and their reverse, not electrocyclic or sigmatropic processes.

42. The synthetic equivalent of the given synthon is

(a) t-butyl isocyanide

(b) t-butyl cyanide

(c) t-butyl cyanate

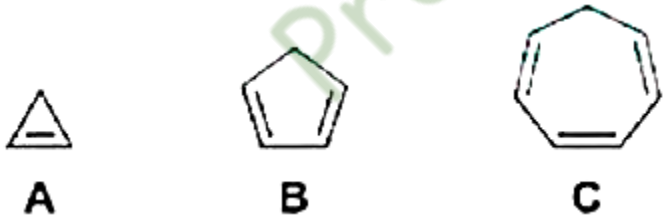
(d) t-butyl isocyanate

Answer: (d) t-butyl isocyanate

Explanation:

The synthon shown corresponds to an **acylium cation (CO^+)** equivalent. *t-Butyl isocyanide (t-Bu–NC)* is a classical **CO^+ synthon**: under suitable conditions it generates a nitrilium intermediate that, upon hydrolysis, furnishes **acyl (–C=O)** derivatives, thus acting as a synthetic equivalent of the **acyl cation**.

43. The correct order of the pK_a of the following compounds is



(a) C > B > A

(b) A > C > B

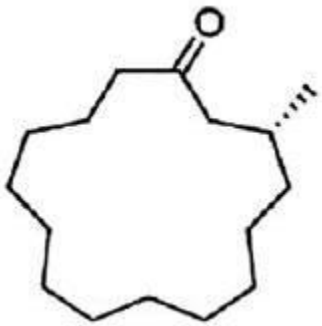
(c) B > A > C

(d) A > B > C

Answer: (b) A > C > B

Explanation: Cyclopentadiene (B) is the most acidic (pKa ≈ 16) because its conjugate base, **cyclopentadienyl anion**, is **aromatic (6 π electrons)**. Cycloheptatriene (C) is less acidic (conjugate base is anti-aromatic/unstable unless a hydride leaves to form the tropylium cation). Cyclopropene (A) is the least acidic; deprotonation gives a highly strained, poorly stabilized anion. Hence **pKa: A (highest) > C > B (lowest).**

44. Muscone is a



Muscone

(a) terpenoid

(b) steroid

(c) polyketide

(d) flavonoid

Answer: (c) polyketide

Explanation: Muscone is a **macrocyclic ketone** biosynthesized via **polyketide/fatty-acid pathways**, not from isoprene units (terpenoids), steroid cores, or flavonoid skeletons.

45. The natural product that gives a signal at $\delta 218$ppm in its ^{13}C NMR spectrum is

(a) α-pinene

(b) camphor

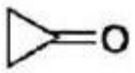
(c) geraniol

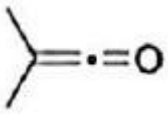
(d) carvone

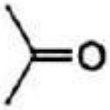
Answer: (b) camphor

Explanation: A carbon signal around **δ ~218 ppm** corresponds to a **highly deshielded ketone carbonyl**; **bridgehead-strained ketones** like **camphor** appear near this region. α-Pinene and geraniol lack C=O; carvone (conjugated ketone) resonates lower (~200 ppm).

46. The correct order of carbonyl stretching frequency for the given compounds is

A 

B 

C 

(a) A > B > C

(b) B > C > A

(c) C > A > B

(d) B > A > C

Answer: (b) B > C > A

Explanation: Conjugation with an **sp-hybridized alkyne** (structure **B**, ynone) withdraws electron density from the carbonyl (strong −I effect) and **raises ν(C=O)** the most. The **cyclopropyl-substituted ketone** (**A**) has less electron withdrawal; its σ–π interaction slightly delocalizes the C=O and gives a **lower ν(C=O)** than B. **Enone** (**C**) has **π-conjugation with C=C**, which **reduces the C=O bond order** and thus shows the **lowest stretching frequency**. Hence **B > A > C**.

47. The expectation value of p^2 of a particle in a cubic box of side ℓ, having the wave function $\psi_{n_x,n_y,n_z}(x,y,z) =$

$\left(\frac{2}{\ell}\right)^{3/2} \sin\frac{2\pi x}{\ell} \sin\frac{3\pi y}{\ell} \sin\frac{2\pi z}{\ell}$, is

(a) $\frac{17h^2}{4\ell^2}$

(b) $\frac{7h^2}{4\ell^2}$

(c) $\frac{3h^2}{\ell^2}$

(d) $\overline{4\ell^2}$

Answer: (a) $\frac{17h^2}{4\ell^2}$

Explanation:

For a particle in a 3D box, $\langle p^2\rangle = \langle p_x^2\rangle + \langle p_y^2\rangle + \langle p\_z^2\rangle$ with $\langle p\_i^2\rangle = (n\_i^2\,\pi^2\,\hbar^2)/\ell^2$.

Thus, $\langle p^2\rangle = \pi^2\hbar^2(n_x^2 + n_y^2 + n\_z^2)/\ell^2 = (h^2/4\ell^2)(n_x^2 + n_y^2 + n\_z^2)$.

Here $n_x = 2$, $n_y = 3$, $n\_z = 2$ ⇒ sum = 4 + 9 + 4 = 17, giving $\langle p^2\rangle = 17h^2/4\ell^2$.

48. For the d^3 electron configuration, the ground state term symbol is

(a) $^4F_{1/2}$

(b) $^4F_{3/2}$

(c) $^4F_{7/2}$

(d) $^4F_{9/2}$

Answer: (b) $^4F_{3/2}$

Explanation:

For a d^3 configuration, the ground term is ^4F according to Hund's rules (maximum spin multiplicity and highest L).

Since d^3 is less than half-filled, the lowest J value corresponds to the ground state.

$J = |L - S| = 3 - 3/2 = 3/2 \rightarrow$ Hence, the ground term is $^4F_{3/2}$.

49. The total bond order between adjacent carbon atoms of benzene is

(a) 0.5

(b) 2

(c) 1.5

(d) 2.5

Answer: (c) 1.5

Explanation:

Benzene has six π electrons delocalized over six carbons.

There are 3 π bonds shared equally among 6 C–C bonds: π contribution = 3/6 = 0.5 per bond.

Each C–C bond also has one σ bond → total bond order per C–C = 1 + 0.5 = 1.5.

50. The following is the character table for the C_{2v} point group

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

There are two functions f_1 and f_2 belonging to A_2 and B_1 representations, respectively. The correct option for the product of two functions f_1 and f_2 and the integral $\int f_1 f_2 d\tau$ is

(a) The product belongs to A_2 representation and the integral is non zero

(b) The product belongs to B_2 representation and the integral is zero

(c) The product belongs to A_1 representation and the integral is zero

(d) The product belongs to B_1 representation and the integral is non zero

Answer: (b) The product belongs to B_2 representation and the integral is zero

Explanation:

From group theory, the direct product $A_2 \times B_1 = B_2$.

For $\int f_1 f_2 d\tau$ to be nonzero, the resultant representation must contain A_1.

Since B_2 does not contain A_1, the integral is zero. Hence, the product belongs to B_2 and the integral vanishes.

51. The equilibrium dissociation energy of a diatomic molecule is 4.75 eV and its stretching frequency corresponds to 0.5 eV . The minimum energy required to dissociate the molecule in eV is

(a) 4.75

(b) 4.25

(c) 4.50

(d) 5.00

Answer: (c) 4.50

Explanation:

When a molecule is vibrating in its fundamental state (v = 0), it possesses zero-point energy equal to (1/2) hν = 0.25 eV. Hence, the energy required to dissociate it from this level is less than the total bond energy:

$D_o = D_e - (1/2\ h\nu) = 4.75 - 0.25 = 4.50$ eV.

Therefore, the minimum energy required for dissociation is **4.50 eV**.

52. A monatomic perfect gas undergoes expansion from (p_1, V_1) to (p_2, V_2) under isothermal or adiabatic conditions. The pressure of the gas will fall more rapidly under adiabatic conditions because

(a) $p \propto \frac{1}{V}$

(b) $p \propto \frac{1}{V^{7/5}}$

(c) $p \propto \frac{1}{V^{3/2}}$

(d) $p \propto \frac{1}{V^{5/3}}$

Answer: (d) $p \propto \frac{1}{V^{5/3}}$

Explanation:

In adiabatic processes, PVγ=constantPV^{γ} = \text{constant}PVγ=constant. For a monatomic gas, γ = Cp/Cv = 5/3.

Thus, P ∝ 1/V^{γ} = 1/V^{5/3}.

This shows that during adiabatic expansion, pressure decreases more steeply than in isothermal conditions.

53. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, the thermodynamic quantity which depends upon the pressure at which equilibrium is arrived at is (superscript 'o'represents standard state)

(a) ΔG^o

(b) ΔH^o

(c) K_P

(d) ratio of mole fractions, $\frac{x_{NH_3}^2}{x_{NH_2} x_{H_2}^3}$, at equilibrium

Answer: (d) ratio of mole fractions, $\frac{x_{NH_3}^2}{x_{NH_2} x_{H_2}^3}$, at equilibrium

Explanation:

Standard Gibbs free energy change (ΔG°) depends only on temperature, while ΔH° and ΔS° are also temperature-dependent. However, the actual Gibbs free energy change (ΔG) for the reaction depends on the partial pressures of the reactants and products:

ΔG = ΔG° + RT ln Qp,

where QpQ_pQp is the reaction quotient in terms of pressures. Therefore, ΔG varies with pressure.

54. The $E^o(M^+/M)$ of the cell, SHE||MX | M can be obtained from the plot of (E_{cell} is the cell potential and m is the molality of ideal dilute solution of MX)

(a) E_{cell} against $(T \log\ m)$

(b) E_{cell} against $\left(\frac{1}{T} \log\ m\right)$

(c) E_{cell} against $(T\sqrt{m})$

(d) E_{cell} against $\left(\frac{\sqrt{m}}{T}\right)$

Answer: (a) E_{cell} against $(T \log\ m)$

Explanation:

According to the Nernst equation,

Ecell = E° – (0.0591/n) log Q,

where for a single electrode, Q = 1/[M⁺].

Rearranging, E = E° – (0.0591/n) log [M⁺].

A plot of Ecell vs. log [M⁺] yields a straight line, and the intercept gives **E°(M⁺/M)**.

55. The y-intercept obtained from the plot of viscosity of a series of polymer solutions against the concentration is 0.05 . The proportionality constant K and exponent a for this polymer - solvent pair are 5×10^{-5} and 0.5 , respectively. The molar mass of the polymer in $gmol^{-1}$ is

(a) 10^9

(b) 10^5

(c) 10^6

(d) 10^7

Answer: (c) 10^6

Explanation:

Step 1: Substitute the values

$0.05 = (5 \times 10^{-5}) \times M^{0.5}$

Step 2: Divide both sides by 5×10−55 × 10⁻⁵5×10−5

$0.05 / (5 \times 10^{-5}) = M^{0.5}$

$0.05 = 5 \times 10^{-2}$

So:

$(5 \times 10^{-2}) / (5 \times 10^{-5})$
$= (5/5) \times 10^{-2-(-5)}$
$= 1 \times 10^3$
$= 10^3$

Thus:

$M^{0.5} = 10^3$

Step 3: Square both sides

$M = (10^3)^2 = 10^6$

56. In the *ccp* packing, the number of lattice points per unit area in the planes is in the order

(a) $(100) > (110) > (111)$

(b) $(100) > (111) > (110)$

(c) $(111) > (100) > (110)$

(d) $(111) > (110) > (100)$

Answer: (c) $(111) > (100) > (110)$

Explanation: In an fcc/ccp lattice the planar density is highest for close-packed (111), next for (100), and lowest for (110); hence (111)>(100)>(110).

57. The correct statement about chemisorption is

(a) it results in multimolecular layer adsorption

(b) it is reversible in nature

(c) it has lower specificity than physisorption

(d) it occurs due to formation of chemical bonds

Answer: (d) it occurs due to formation of chemical bonds

Explanation: Chemisorption involves formation of chemical bonds between adsorbate and surface, making it highly specific, usually monolayer, and often irreversible.

58. For a reaction, raising the temperature from 200 K to 300 K results in the increase of rate constant by a factor of 2 . The activation energy for this reaction in $\mathbf{kJmol^{-1}}$ is closest to

($\ln\ 2 = 0.69$)

(a) 7.0

(b) 3.5

(c) 14.0

(d) 0.83

Answer: (b) 3.5

Explanation: Using $\ln(k_2/k_1)=E_a/R(1/T_1-1/T_2)=E_a/(600R)$. With $\ln 2=0.69$ and $R=8.314\times10^{-3}$ kJ mol^{-1} K^{-1}, $E_a=600\times R\times0.69\approx3.5$ kJ mol^{-1}.

59. The y - intercept of the least square fitted straight line to the data in the table is closest to

x	-2.01	-0.98	1.01	1.99
y	-4.01	-1.98	2.01	3.99

(a) -0.2

(b) -0.1

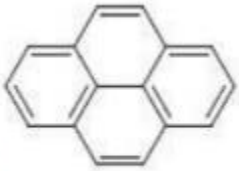
(c) 0

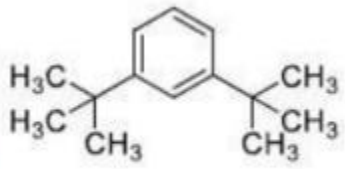
(d) 0.2

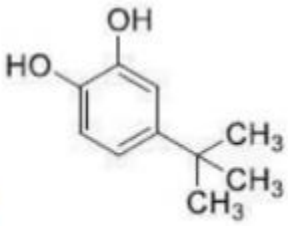
Answer: (c) 0

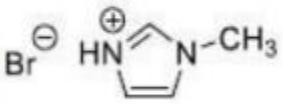
Explanation: The data satisfy approximately $y\approx2x$ with very small symmetric deviations; the best-fit line has slope ~2 and y-intercept ≈0.

60. The guest molecule which will fit best inside α-cyclodextrin by interacting with both, rim and cavity, is

(a) 

(b) 

(c) 

(d) 

Answer: (c)

Explanation: α-Cyclodextrin's small hydrophobic cavity accommodates a small alkyl group, while phenolic OH groups form H-bonds at the hydrophilic rim; the catechol-type molecule fits these dual interactions best.

61. Among the following complexes, the one showing the highest rate of substitution of a CO ligand on heating with one equivalent of PPh_3 in decalin, is

(a) $(\eta^5 - C_5H_5)Mn(CO)_3$

(b) $(\eta^5 - CsPhs)Mn(CO)_3$

(c) $(\eta^5 - C_5Me5)Mn(CO)$;

(d) $(\eta^5$-indenyl $)Mn(CO)_3$

Answer: (d) $(\eta^5$-indenyl $)Mn(CO)_3$

Explanation:

The rate of CO substitution in π-cyclopentadienyl metal carbonyls depends on the lability of the metal–CO bond and electron density at the metal center. The **indenyl complex** shows a much faster substitution rate due to the **"indenyl effect"**.

This effect arises because the indenyl ligand can change its hapticity from η^5 to η^3 during the substitution, temporarily reducing electron donation and stabilizing a 16e intermediate, thereby lowering the activation barrier.

In contrast, Cp, C_5Ph_5, and C_5Mes_5 ligands maintain rigid η^5 coordination and cannot assist in this way.

Hence, **$(\eta^5$-indenyl$)Mn(CO)_3$** undergoes the fastest CO substitution.

62. The correct electronic configuration of frontier MO's of $Mn(\eta^5 - C_5Me_5)_2$ is

(a) $e^2\ {}_{2g}a^1\ {}_{1g}e^2\ {}_{1g}$

(b) $e^4\ {}_{2g}a^1\ {}_{1g}$

(c) $e^3\ _{2g}a^2\ _{1g}$

(d) $a^2\ _{1g}e^3\ _{2g}$

Answer: (a) $e^2\ _{2g}a^1\ _{1g}e^2\ _{1g}$

Explanation:

$Mn(\eta^5\text{-}C_5Me_5)_2$ is a **metallocene (sandwich complex)** with D_5d symmetry.

It has Mn^{2+} (d^5) and two $\eta^5\text{-}C_5Me_5^-$ ligands (each contributing $6e^-$), totaling **17 valence electrons**.

In metallocenes, the frontier MOs follow the sequence:

a_1g (lowest) $<e_1g<e_2g$ (highest).

Filling five d-electrons gives the configuration $\mathbf{e_2g^2\ a_1g^1\ e_1g^2}$, which corresponds to $\mathbf{e^2{}_2g\ a^1{}_1g\ e^2{}_1g}$.

This configuration explains its paramagnetic behavior (one unpaired electron).

63. On heating $[Mo(N_2)_2(PMe2Ph)_4]$ and $[ReCl(N_2)(PMe_2Ph)_4]$, the products formed are respectively

(a)$[(\eta^6-PhPMe_2)Mo(PMe_2Ph)_3]$ and $[(\eta^6-PhPMe_2)Re(PMe_2Ph)_3]Cl \cap C \cap C$

(b)$[(PMe_2Ph)_4Mo(\mu-N_2)_2Mo(PMe_2Ph)_4]$ and $[(PMe_2Ph)_4Re(\mu-Cl)_2Re(PMe_2Ph)_4]$

(c)$[(PMe_2Ph)_4Mo(\mu-N_2)_2Mo(PMe_2Ph)_4]$ and $[(\eta^6-PhPMe)_2)Re(PMe_2Ph)_3]Cl$

(d)$[(PMe_2Ph)_4Mo(\mu-N_2)_2Mo(PMe_2Ph)_4]$ and $[(\eta^6-PhPMe)_2)Re(PMe_2Ph)_3]Cl$

Answer: $[(\eta^6\text{-}PhPMe_2)Mo(PMe_2Ph)_3]$ and $[(PMe_2Ph)_4Re(\mu\text{-}Cl)_2Re(PMe_2Ph)_4]$

Explanation:

Upon heating, the $Mo(N_2)$ complex undergoes **intramolecular C–H activation** of the phenyl group on PMe_2Ph, forming an **η^6-phenyl coordination** to yield $[(\eta^6\text{-}PhPMe_2)Mo(PMe_2Ph)_3]$.

In contrast, $ReCl(N_2)(PMe_2Ph)_4$ dimerizes via **Cl-bridging** to form a **Re–Re dimer** complex $[(PMe_2Ph)_4Re(\mu\text{-}Cl)_2Re(PMe_2Ph)_4]$.

Thus, both undergo different thermal transformations — η^6-aryl coordination for Mo and μ-Cl dimer formation for Re.

64. The products A and B for the given reaction

$\mathbf{[Co(NH_3)_5Cl]^{2+} + [Cr(OH_2)_6]^{2+} + 5H_3O^+ \rightarrow A + B}$

are, respectively

(a) $[Co(OH_2)_5Cl]^+, [Cr(OH_2)_6]^{3+}$

(b) $[Co(NH_3)_5(OH_2)]^{2+}, [Cr(OH_2)_5Cl]^{2+}$

(c) $[Co(OH_2)_6]^{2+}, [Cr(OH_2)_5Cl]^{2+}$

(d) $[Co(NH_3)_5Cl]^+, [Cr(OH_2)_6]^{3+}$

Answer: (c) $[Co(OH_2)_6]^{2+}, [Cr(OH_2)_5Cl]^{2+}$

Explanation: In acid, the ammine complex undergoes aquation to the hexaaqua Co(II) complex, while the Cr(II) aquo complex is oxidized/proton-assisted to a more substitution-inert species and captures Cl^-, giving $[Cr(OH_2)_5Cl]^{2+}$. Thus A = $[Co(OH_2)_6]^{2+}$ and B = $[Cr(OH_2)_5Cl]^{2+}$.

65. The calculated heat of formation (ΔH_f) for $NaCl_2$ and CaF is

(a) negative for both $NaCl_2$ and CaF

(b) negative for $NaCl_2$ but positive for CaF

(c) positive for $NaCl_2$ but negative for CaF

(d) positive for both $NaCl_2$ and CaF

Answer: (c) positive for $NaCl_2$ but negative for CaF

Explanation: $NaCl_2$ would require Na in the +2 oxidation state, which is highly unstable; forming it from elements is endothermic ($\Delta Hf > 0$). Calcium monofluoride (gas-phase CaF) forms a strong Ca–F bond and its formation from Ca(s) + ½F_2(g) is exothermic ($\Delta Hf < 0$).

66. As per the VSEPR theory, shapes of SO_3^{2-}, CO_3^{2-} and BrF_4^- are, respectively

(a) trigonal pyramidal, trigonal planar and tetrahedral

(b) trigonal planar, trigonal pyramidal and square planar

(c) trigonal pyramidal, trigonal planar and square planar

(d) trigonal planar, trigonal pyramidal and tetrahedral

Answer: (c) trigonal pyramidal, trigonal planar and square planar

Explanation: SO_3^{2-} has three bonding pairs and one lone pair around S → trigonal pyramidal. CO_3^{2-} has three bonding pairs and no lone pair on C → trigonal planar. BrF_4^- has four bonds and two lone pairs around Br (AX_4E_2) → square planar.

67. Consider the following statements for Allred-Rochow electronegativity (χ_{AR}):

(i) χ_{AR} is directly proportional to Z_{eff}.

(ii) χ_{AR} is inversely proportional to Z_{eff}.

(iii) χ_{AR} is inversely proportional to r (covalent).

(iv) χ_{AR} is inversely proportional to r^2 (covalent).

The correct statements are

(a) i and iv

(b) ii and iv

(c) i and iii

(d) ii and iii

Answer: (a) i and iv

Explanation: Allred–Rochow electronegativity is $\chi AR \approx 0.359 \cdot Zeff / r^2cov + 0.744$, hence it increases with effective nuclear charge and varies inversely with the square of the covalent radius.

68. The reaction of XeF_6 with a limited amount of quartz gives compound A. Then on reaction with an equivalent amount of XeO_3, A gives B. The products A and B are, respectively

(a) $XeOF_2$ and XeO_2F_2

(b) $XeOF_4$ and XeO_2F_2

(c) $XeOF_2$ and $XeOF_4$

(d) XeO_2F_2 and $XeOF_4$

Answer: (b) $XeOF_4$ and XeO_2F_2

Explanation: XeF_6 reacts with silica (limited quartz) to substitute one F by O, yielding $XeOF_4$. Subsequent reaction of $XeOF_4$ with XeO_3 introduces another O atom to give XeO_2F_2.

69. The energies of interaction for (i) ion pair, (ii) ion-dipole, and (iii) dipole-dipole interactions are inversely proportional to

(a) r, r^2 and r^3 respectively

(b) r^2, r and r^3 respectively

(c) r, r^2 and r^6 respectively

(d) r^2, r and r^6 respectively

Answer: (c) r, r^2 and r^6 respectively

Explanation: Coulombic ion–ion attraction varies as 1/r. For ion–dipole, the interaction scales as $1/r^2$. Thermal averaging of dipole orientations makes permanent dipole–dipole (Keesom) interaction fall off as $1/r^6$.

70. The correct match for column A with column B is:

Column A	Column B
(a) f → f transition	(i) Tb^{3+}
(b) $^5D_0 \rightarrow {}^7F_n$ emission	(ii) Lu^{3+}
(c) $^5D_4 \rightarrow {}^7F_n$ emission	(iii) Sm^{3+}
(d) Overlapping J levels	(iv) Eu^{3+}

(a) - (iv), (b) - (i), (c) - (ii), (d) - (iii)

(b) (a) - (ii), (b) - (iv), (c) - (iii), (d) - (i)

(c) (a) - (ii), (b) - (iv), (c) - (i), (d) - (iii)

(d) (a) - (i), (b) - (iii), (c) - (ii), (d) - (iv)

Answer: (c) (a) - (ii), (b) - (iv), (c) - (i), (d) - (iii)

Explanation: Eu^{3+} shows characteristic sharp red lines from $^5D_0 \rightarrow {}^7F_n$; Tb^{3+} exhibits $^5D_4 \rightarrow {}^7F_n$ green emission; Sm^{3+} has closely spaced J-levels leading to overlap. Lu^{3+} ($4f^{14}$) lacks f–f* transitions, matching (a).

71. Thermometric titration gives best results when

A. $I\Delta HI$ is high

B. $\Delta G < 0$

C. Heat of mixing of titrant with titrand is high

D. Titrant is used as dilute solution

The answer is

(a) *A* and *B*

(b) B and C

(c) C and D

(d) A and D

Answer: (d) A and D

Explanation: Thermometric titration relies on detecting the **temperature change** due to reaction enthalpy. It works best when the **reaction enthalpy is large in magnitude** (|ΔH| high) and when **heat of dilution/mixing is minimized**, which is achieved by using **dilute solutions**. The sign of ΔG is not the determining factor, and a large heat of mixing would mask the endpoint.

72. The geometry/shape of Fe_4 core of the cluster $[Fe_4C(CO)_{12}]^{2-}$ is

(a) tetrahedron

(b) square pyramid

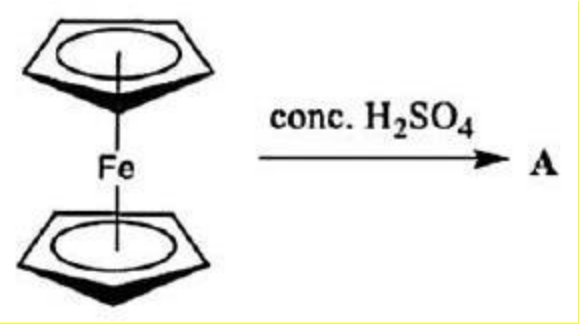
(c) butterfly

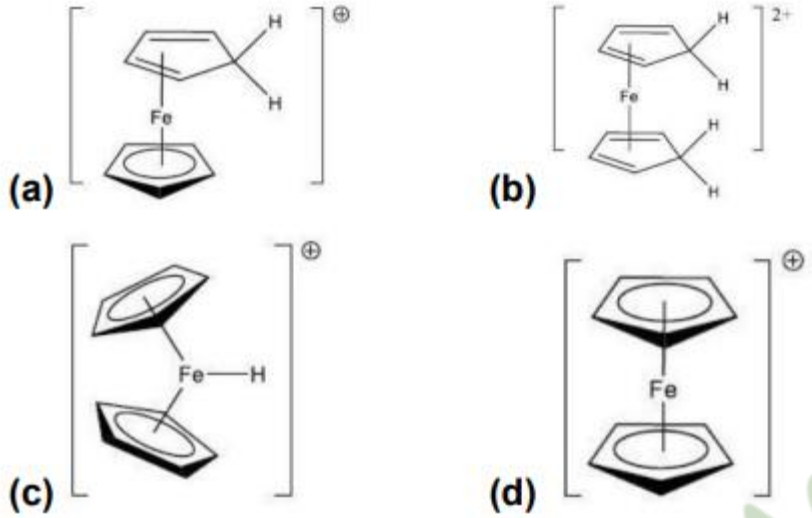
(d) trigonal bipyramid

Answer: (a) tetrahedron

Explanation: The complex is a **carbido cluster** with a μ_4-C atom surrounded by **four Fe atoms**. The Fe_4 framework forms a **tetrahedron** around the central carbido carbon in $[Fe_4C(CO)_{12}]^{2-}$.

73. The product A of the following reaction is





Answer: C

Explanation

Reaction:

Ferrocene (Fe sandwiched between two cyclopentadienyl rings) is treated with **concentrated H_2SO_4**.

This causes **electrophilic aromatic substitution** (EAS) on only **one ring** of ferrocene → forming **mono-protonated ferrocene**.

But **highly acidic medium (conc. H_2SO_4)** actually leads to the formation of a **ferrocenium ion** after **protonation + hydride abstraction**.

1. **Protonation occurs** on one cyclopentadienyl ring.
2. Protonated ferrocene becomes **electron-deficient**.
3. **Hydride abstraction** from the ring gives:
    - a **substituted cyclopentadienyl ring**
    - a **positively charged Fe center**
4. The product is a **hydrogen-substituted ferrocenium ion**.

    - One Cp ring as usual.
    - The other Cp ring bearing a **C–H substituent** (electrophilic substitution product).
    - A **positive charge** on the iron center → ferrocenium ion.

This matches the **known product** of ferrocene + conc. H_2SO_4.

Option (a):
Shows over-substitution and incorrect charge distribution.

Option (b):
Shows a **2+ charge**, which does not form under these conditions.

Option (d):
Shows the simple ferrocenium ion **without substitution**, which is NOT formed in conc. H_2SO_4.

74. The number of peaks with relative intensities observed in the ^{1}H NMR spectra of $[(Cp)_2Fe(CO)_2]$ at $+30^\circ C$ and $-80^\circ C$ in diethyl ether are, respectively

(a) two peaks (1:1) and four peaks (5:2:2:1)

(b) one peak and two peaks (1:1)

(c) two peaks (1:1) at both the temperatures

(d) one peak and four peaks (5:2:2:1)

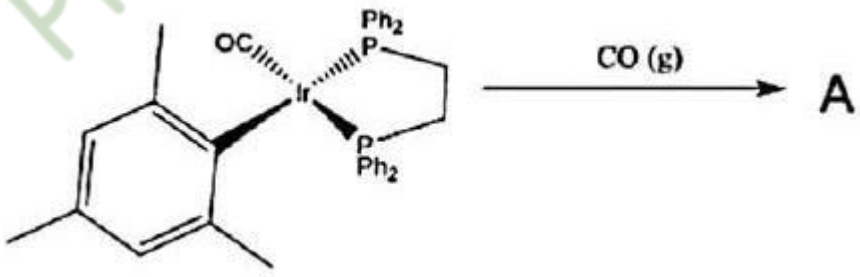
Answer: a

Explanation:

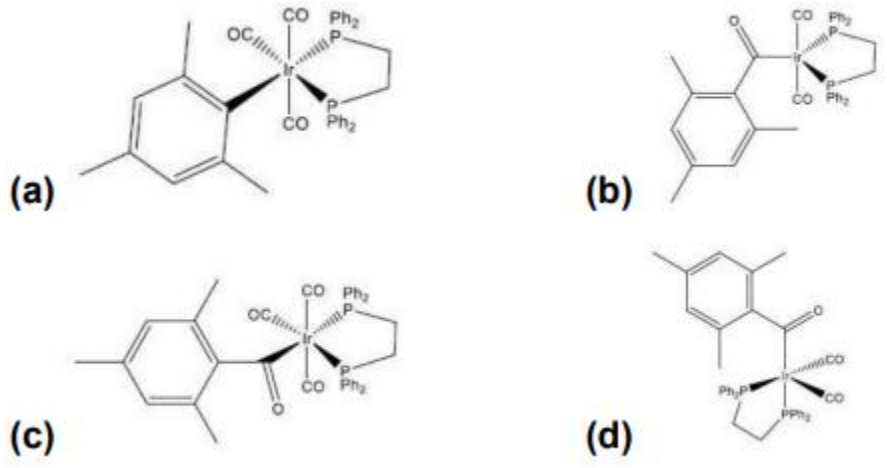
At **+30°C**, the two Cp rings rotate very fast.
Because of this rapid motion, **all Cp protons look the same**.
So the NMR shows **2 peaks in 1:1 ratio**.

At **–80°C**, the rotation stops (frozen conformation).
Now the Cp protons are **not equivalent**, and they split into **four different proton environments**.
So the NMR shows **4 peaks with intensities 5:2:2:1**.

75. The infrared (IR) spectrum of the product A for the following reaction



shows three STRONG bands at 1986, 1935 and $1601\ cm^{-1}$. The correct structure of ' *A* ' is



Answer: d

Explanation:

When the Ir complex is exposed to CO gas, **carbonyl substitution and arene coordination** occur. The product forms a **monocarbonyl η²-alkene complex**, characterized by three strong IR bands: two CO stretches (~1986 and 1935 cm^{-1}) and one due to coordinated C=C (~1601 cm^{-1}).

This indicates **one CO bound in a terminal fashion** and an **η²-arene-type interaction**, matching the structure shown in **option 8024371200**.

76. The number of expected electronic transitions in $[Cr(en)_3]^{3+}$ and trans $-[Cr(en)_2F_2]^+$ at 4 K is, respectively (en = ethylenediamine)

(a) 3 and 3

(b) 3 and 4

(c) 3 and 5

(d) 3 and 6

Answer: (d) 3 and 6

Explanation:

For **$[Cr(en)_3]^{3+}$ (Oh symmetry)**, the Cr^{3+} ion (d^3) has **three spin-allowed transitions**:

$^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g(F)$, and $^4A_2g \rightarrow {}^4T_1g(P)$.

In **trans-$[Cr(en)_2F_2]^+$ (D_4h symmetry)**, the **lowered symmetry** causes **further splitting of d orbitals**, leading to six spin-allowed transitions observable at 4 K (where thermal population effects are minimized). Hence, **3 and 6** transitions respectively.

77. The value of magnetic moment will be independent of temperature for

(acac = acetylacetonato; OAc = acetate; o-phen = o-phenathroline;

Pz = pyrazolyl)

(a) $[Fe(acac)_3]$

(b) $[Cu_2(OAc)_4(H_2O)_2]$

(c) $[Fe(\text{ o-phen }))_2(NCS)_2]$

(d) $[Fe\{HC(3,5-Me_2Pz)_3\}2]^{2+}$

Answer: (a) $[Fe(acac)_3]$

Explanation:

$[Fe(acac)_3]$ is a **low-spin Fe(III)** complex with a **5-coordinate d^5 configuration**, giving a **single unpaired electron**. Its magnetic moment arises mainly from **spin-only contribution** and remains **nearly constant with temperature** due to negligible spin–orbit coupling and minimal thermal spin crossover effects.

In contrast, complexes like **$[Fe(o\text{-}phen)_2(NCS)_2]$** can show spin crossover (temperature-dependent μ), and **$[Cu_2(OAc)_4(H_2O)_2]$** exhibits antiferromagnetic coupling (μ varies with T).

78. Choose the correct statements for the Group 15 halides:

(i) $AsCl_3$ can form complexes of type $[AsCl_4]^-$ in the presence of a chloride source

(ii) PF_3 acts as a strong σ-donor ligand towards d-metals

(iii) In the solid state, SbF_5 has a trigonal bipyramidal structure

(iv) The reaction of SbF_5 with anhydrous HF generates $[H_2\ F]^+$ ions

(a) i and iv

(b) ii, iii and iv

(c) i, iii and iv

(d) ii and iii

Answer: (a) i and iv

Explanation:

- **(i)** True — $AsCl_3$ can form **tetrachloroarsenate(III)** ions, $[AsCl_4]^-$, in the presence of strong chloride donors.
- **(ii)** False — PF_3 is primarily a **π-acceptor ligand** (not a σ-donor) due to strong P–F π* orbitals.
- **(iii)** False — In the solid state, **SbF_5** forms polymeric $[SbF_4]^-$ and $[Sb_2F_{11}]^-$ species rather than perfect trigonal bipyramidal molecules.
- **(iv)** True — SbF_5 reacts with anhydrous HF to give **$[H_2F]^+[SbF_6]^-$**, a component of the **superacid HF–SbF_5** system.

Thus, **(i) and (iv)** are correct.

79. In the catalytic cycle of Cytochrome P450, the generation of $[(\text{ porphyrin })^{+*}Fe^{IV}(O)]$ from $[(\text{ porphyrin })Fe^{III}(OOH)]$ involves

(a) One electron oxidation of [(porphyrin)Fe ^{III} (OOH)]

(b) Formation of the intermediate [(porphyrin) $Fe^{IV}(OH)$]

(c) Homolytic $O-O$ cleavage of [(porphyrin) $Fe^{IV}(OOH)$]

(d) Heterolytic $O-O$ cleavage of [(porphyrin)Fe ^{III} (OOH)]

Answer: (d) Heterolytic $O-O$ cleavage of [(porphyrin)Fe ^{III} (OOH)]

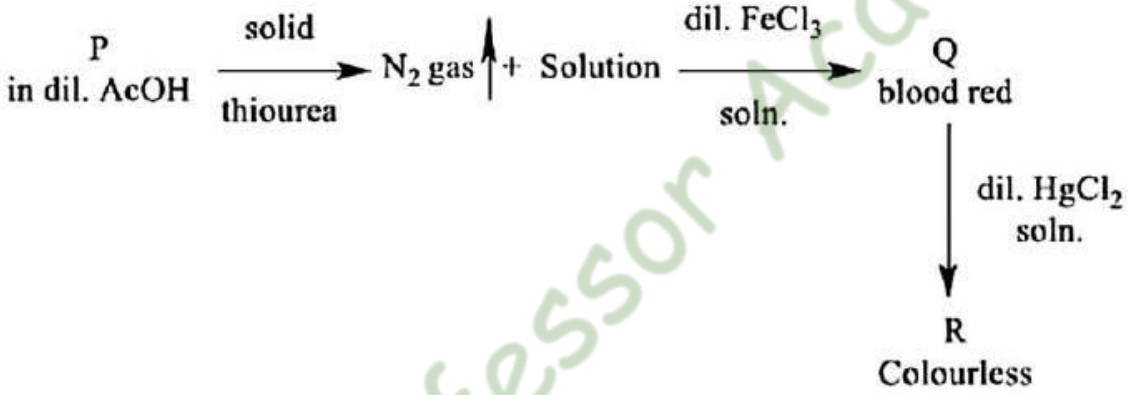
Explanation:

The key step in the catalytic cycle of **Cytochrome P450** is the **heterolytic cleavage** of the Fe^{3+}–OOH bond to generate the highly reactive **Compound I**, represented as **[(porphyrin)$^{+}$Fe^{4+}=O]**.

This process produces a **ferryl-oxo species** and a **porphyrin radical cation**, not via homolytic cleavage.

Homolytic pathways instead yield Fe^{4+}=O with a hydroxyl radical, which is inconsistent with observed enzymatic chemistry.

80. In the following sequence of reactions the correct P, Q and R are respectively



(a) $KNO_2, CO_2, [Fe(H_2O)_5\ S]^+, HgS$

(b) $KNO_2,\ N_2, [Fe(H_2O)_5(SCN)]^{2+}, [Hg(SCN)_4]^{2-}$

(c) $KNO_3,\ N_2, [Fe(H_2O)_5(CN)]^{2+}, [Hg(OCN)_4]^{2-}$

(d) $NaN_3,\ N_2, [Fe(H_2O)_5(\ N_3)]^{2+}, [Hg(N_3)_4]^{2-}$

Answer: (b) $KNO_2,\ N_2, [Fe(H_2O)_5(SCN)]^{2+}, [Hg(SCN)_4]^{2-}$

Explanation:

Thiourea reacts with **KNO_2 in dilute acetic acid** to liberate **N_2 gas**.

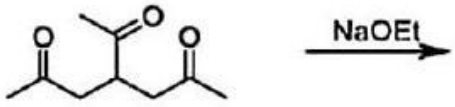
The resulting solution forms a **blood-red complex** with **Fe^{3+}**, confirming the presence of **thiocyanate ion (SCN^-)** as **$[Fe(H_2O)_5(SCN)]^{2+}$**.

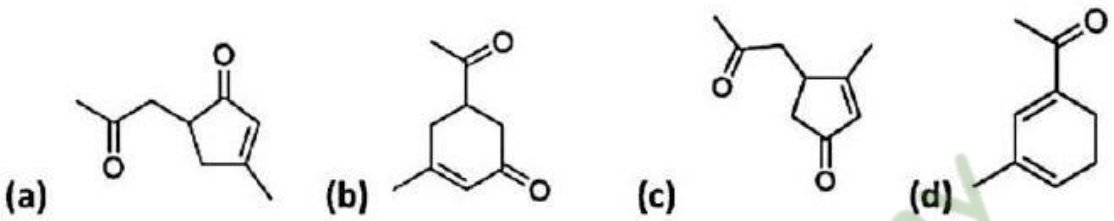
Addition of **$HgCl_2$** produces a **colourless solution**, due to the formation of **$[Hg(SCN)_4]^{2-}$**, which quenches the

red colour.

Thus, the sequence identifies **P = KNO_2**, **Q = $[Fe(H_2O)_5(SCN)]^{2+}$**, and **R = $[Hg(SCN)_4]^{2-}$**.

81. The major product formed in the following reaction is





Answer: b

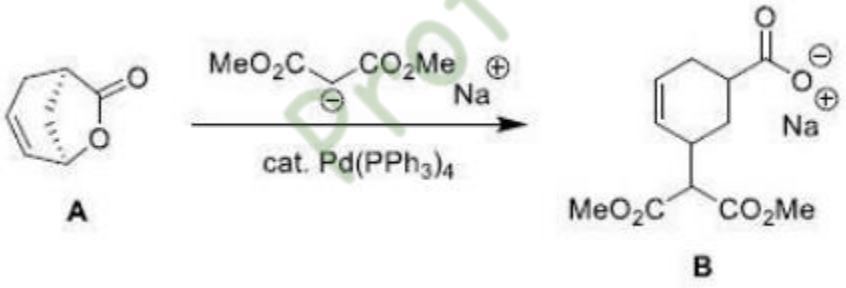
Explanation:

The intramolecular **Claisen condensation (Dieckmann cyclization)** occurs when diesters are treated with **NaOEt**.

The reaction proceeds via **enolate formation**, followed by **nucleophilic attack** on another ester carbonyl within the same molecule, forming a **cyclic β-keto ester**.

The product corresponds to a **six-membered ring** due to favourable ring strain minimization and kinetic preference.

82. In the following transformation, the enantiomerically pure lactone A provides



(a) equimolar amounts of syn- and anti-diastereomers of B, both of which are racemic

(b) equimolar amounts of syn- and anti-diastereomers of B, both of which are enantiomerically pure

(c) only syn-diastereomer of **B**, which is racemic

(d) only anti-diastereomer of B, which is enantiomerically pure

Answer: (c) only syn-diastereomer of **B**, which is racemic

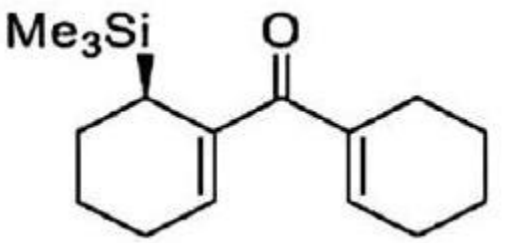
Explanation:

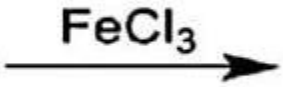
The reaction is a **Pd(0)-catalyzed allylic alkylation** involving a **nucleophilic attack** on a π-allyl–Pd intermediate derived from the lactone **A**.

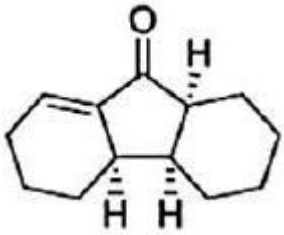
Although **A** is enantiomerically pure, the reaction proceeds via a **planar π-allyl intermediate**, allowing **attack from either face**, leading to **loss of chirality** and formation of a **racemic product**.

However, **stereochemical control of substitution** yields predominantly the **syn-diastereomer** due to minimized steric hindrance during transition-state formation.

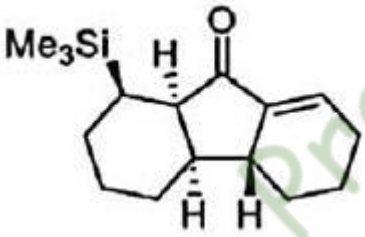
83. The major product formed in the following transformation is



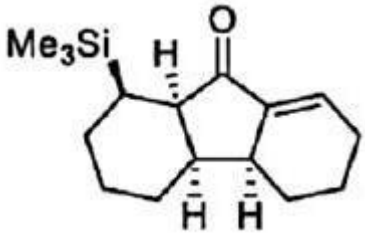




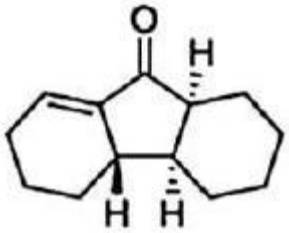
(a)



(c)



(b)



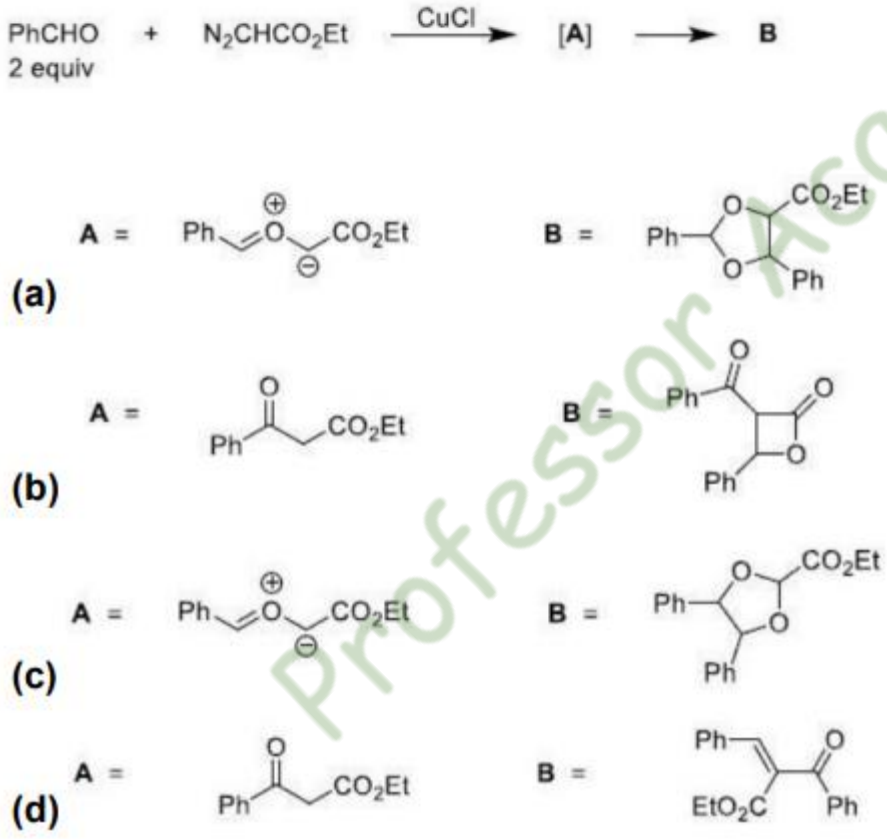
(d)

Answer: d

Explanation:

$FeCl_3$ promotes intramolecular Friedel–Crafts type electrophilic cyclization via the silyl-substituted aryl/alkyl unit. Ring closure gives a fused bicyclic ketone after loss of the silyl group, with the specific relative stereochemistry shown in option 8024371232.

84. In the given transformation, the intermediate [*A*] and the major product B are

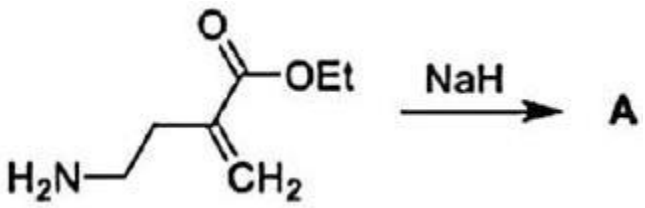


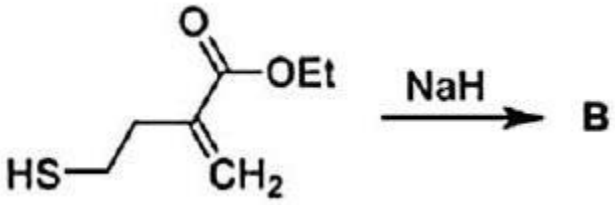
Answer: a

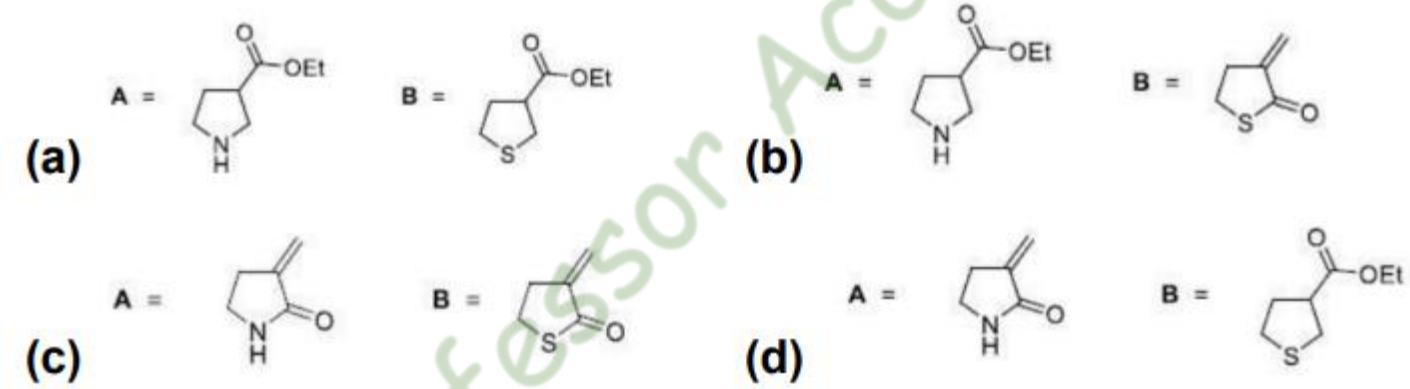
Explanation:

The Cu-catalyzed reaction of an aldehyde with an α-diazocarbonyl generates an α-oxo carbenoid / acyl-diazomethyl intermediate of the type shown in 8024371233, which then undergoes intramolecular acetalization with the second equivalent of benzaldehyde to give the benzylic acetal (five-membered dioxolane ring with two Ph substituents and CO_2Et).

85. The major products A and B formed in the following transformations are







Answer: d

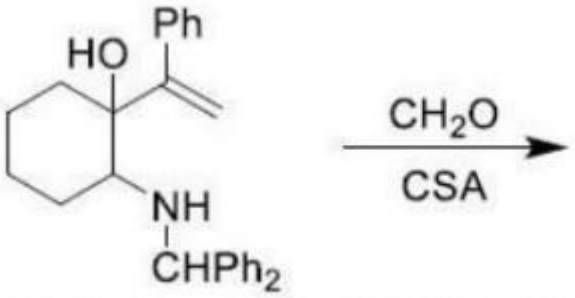
Explanation:

NaH deprotonates $–NH_2$ and –SH to give intramolecular nucleophiles.

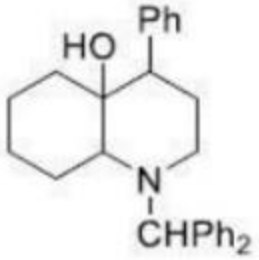
For the amino ester, intramolecular attack on the ester gives a 5-membered γ-lactam and expels EtO^-, so A is the lactam without the ethyl ester group.

For the thio analogue, intramolecular cyclization gives a thioester ring that still bears the $–CO_2Et$ substituent.

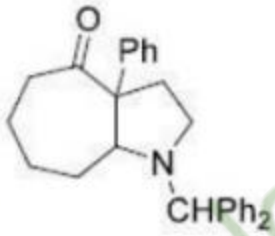
86. The major product formed in the following reaction is



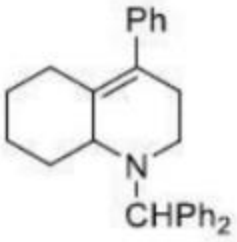
CSA = camphorsulfonic acid



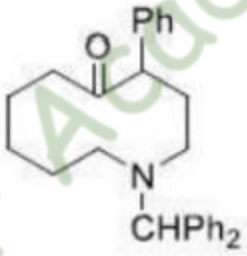
(a)



(b)



(c)



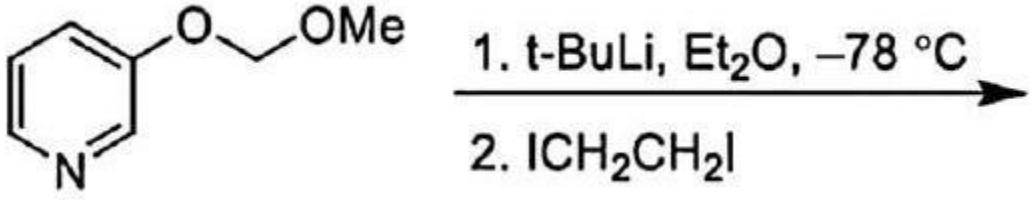
(d)

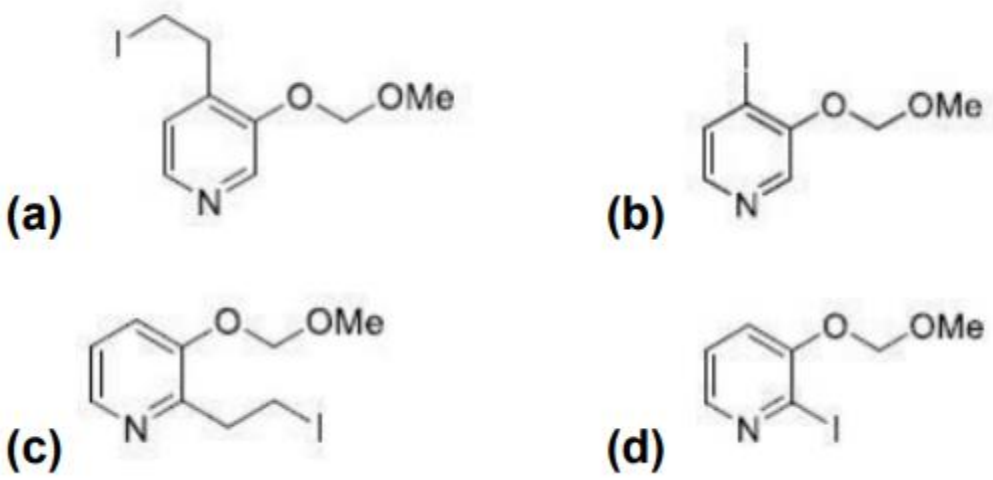
Answer: b

Explanation:

Under CH_2O and CSA, the amine reacts with formaldehyde to form an iminium species. The tethered alcohol then attacks intramolecularly, followed by dehydration and stabilization. This gives a locked bicyclic system in which the nitrogen (bearing $CHPh_2$) is incorporated and a new carbonyl is present. That matches the bridged bicyclic carbonyl-containing product.

87 .major product formed in the following reaction sequence is



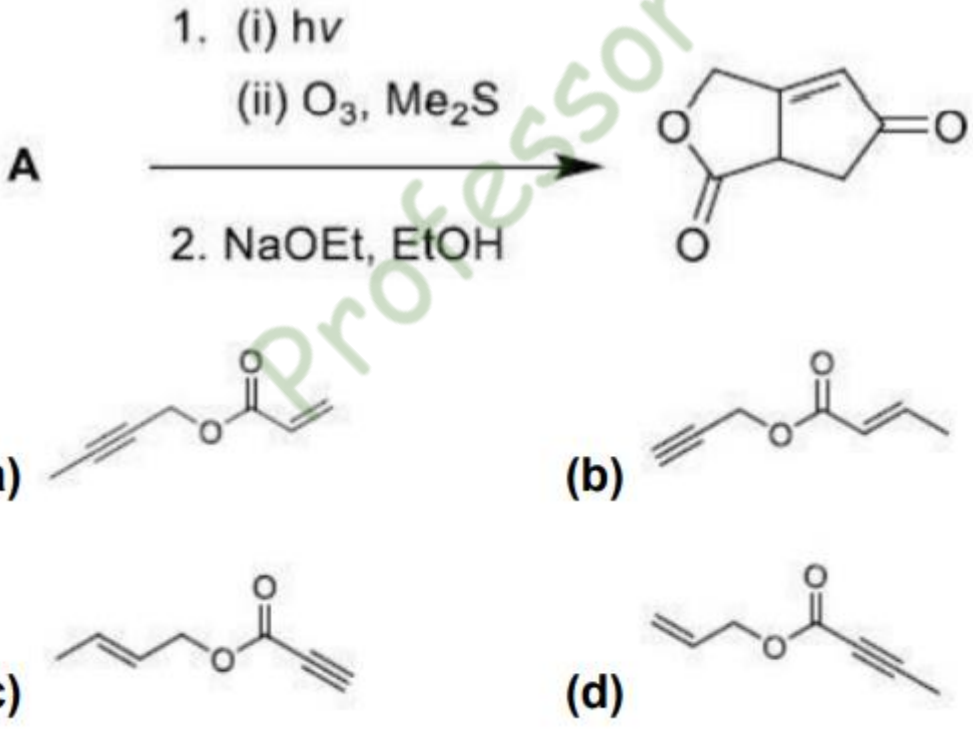


Answer: b

Explanation:

t-BuLi lithiates the most acidic benzylic site adjacent to the oxygen substituent. That carbanion then attacks diiodoethane, displacing iodide and installing an ethyl fragment. The product is the pyridine derivative where that benzylic/ortho position is now alkylated. We do not end up with iodine still attached, and we do not directly iodinate the aromatic ring.

88. The structure of A in the following reaction is



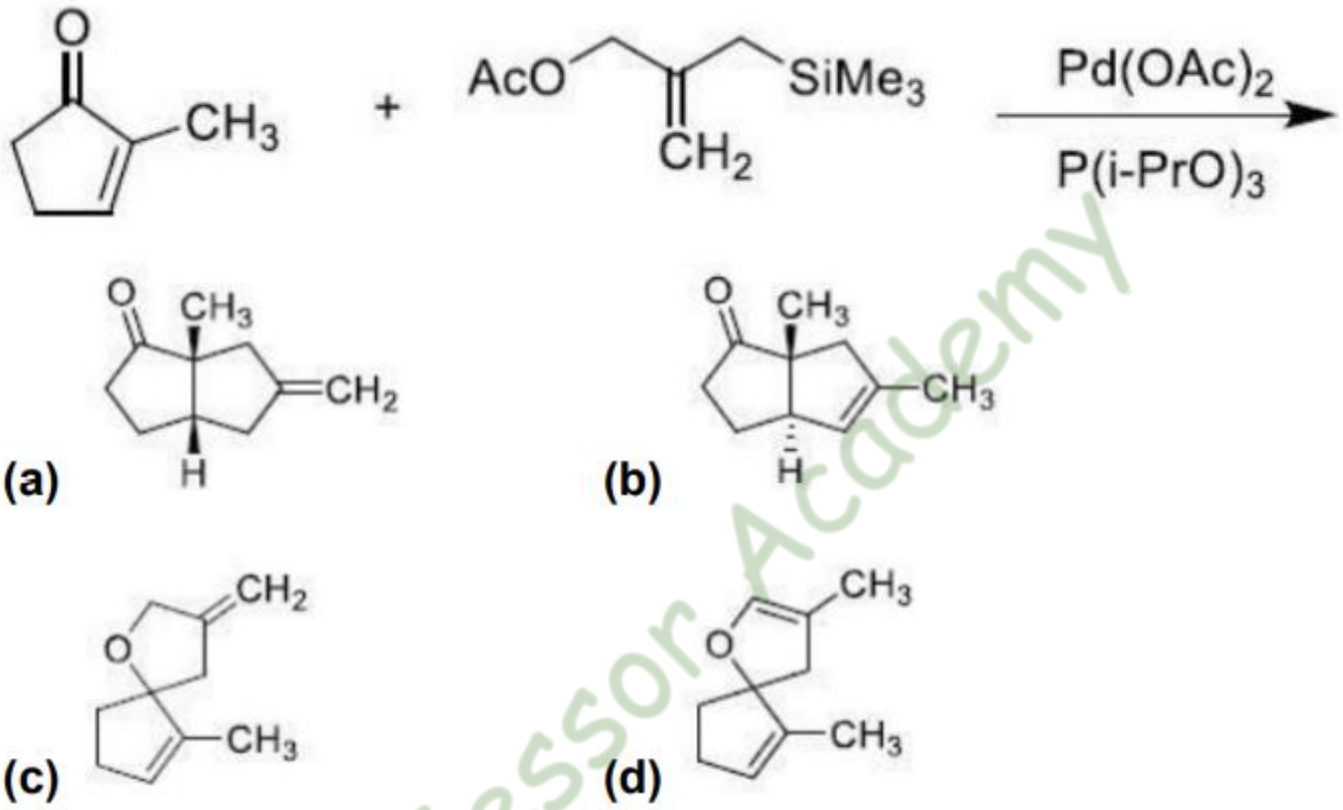
Answer: a

Explanation:

The observed bicyclic anhydride arises after photochemical activation, oxidative cleavage (ozonolysis), and

base-induced intramolecular condensation. To reach that arrangement of two adjacent carbonyls ready to cyclize, the starting material must position unsaturation so that oxidative cleavage yields two carbonyl fragments on the same tether. An enyne-ester does this: the alkene/alkyne framework breaks down into the needed carbonyl pattern, which then cyclizes under base to the bicyclic anhydride.

89. The major product formed in the following reaction is

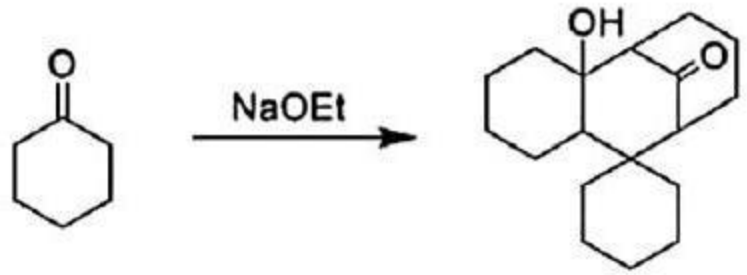


Answer: a

Explanation:

The Pd catalyst generates a π-allyl–Pd complex from the allylic acetate. The enone forms a nucleophilic enolate that attacks this π-allyl fragment. Reductive elimination and ring closure produce a compact fused bicyclic skeleton. The allyl piece shows up as an exocyclic methylene (=CH_2) on the newly fused system, exactly like the bicyclic structure described.

90. The correct sequence of reactions involved in the following transformation is



(a) aldol condensation, Michael addition, aldol reaction

(b) aldol condensation, aldol reaction, Michael addition

(c) Michael addition, aldol condensation, aldol reaction

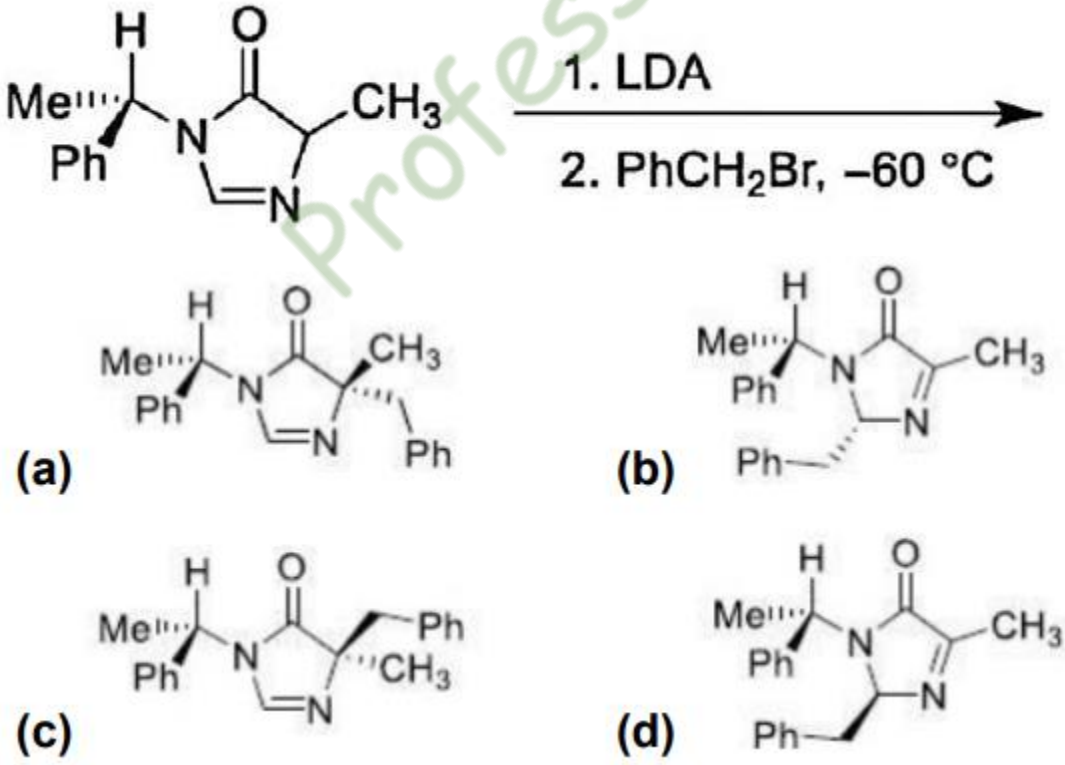
(d) aldol condensation, Michael addition, Michael addition

Answer: a

Explanation:

Under strong base (NaOEt), cyclohexanone can first self-condense to form an α,β-unsaturated carbonyl via an aldol condensation. That enone then acts as a Michael acceptor. A second enolate does a conjugate (Michael) addition to build a new C–C bond and start ring fusion. Finally, an intramolecular aldol ring closure generates the bridged/fused polycyclic alcohol seen in the product. So the steps are: first aldol condensation to make the enone, then Michael addition to that enone, then a final aldol-type ring-forming closure.

91. The major products formed in the following reaction is

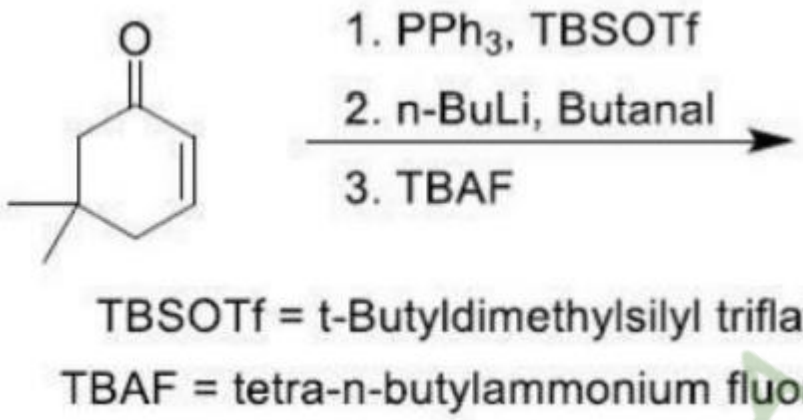


Answer: a

Explanation:

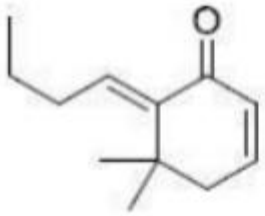
LDA at −60 °C gives kinetic deprotonation at the most acidic α-position next to the imide-like carbonyl. That enolate then reacts with benzyl bromide in an SN2 fashion, installing the benzyl ($PhCH_2$–) group at that α-carbon. Because the starting compound is already stereogenic, approach of the electrophile occurs under substrate control to give a preferred diastereomer. The result is the benzylated product with the specific relative orientation of Me, Ph, and the new benzyl substituent consistent with the kinetic, facially selective alkylation.

92. The major product formed in the following reaction is

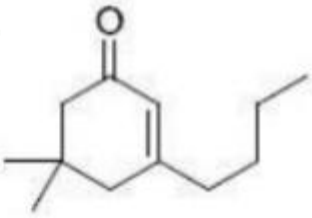


TBSOTf = t-Butyldimethylsilyl triflate

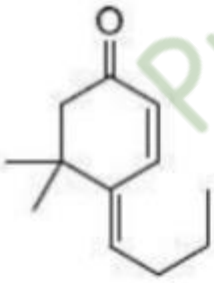
TBAF = tetra-n-butylammonium fluoride



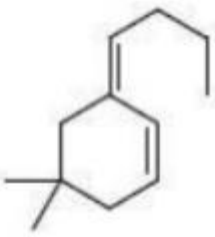
(a)



(b)



(c)



(d)

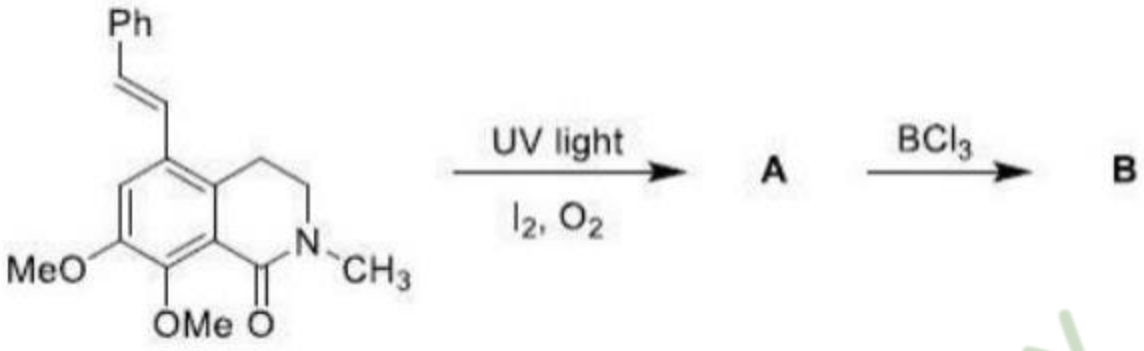
Answer: b

Explanation:

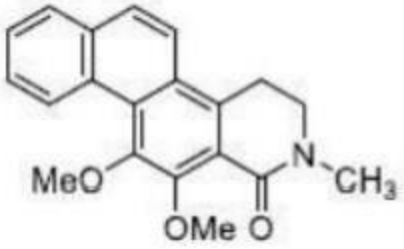
TBSOTf with PPh_3 activates the enone system to form a silyl enol-type intermediate that can be deprotonated with n-BuLi. That carbanion then adds to butanal, forming a new C–C bond. After TBAF workup, the silyl protection is removed, and the system tautomerizes back to the ketone. The net result is C–C bond formation

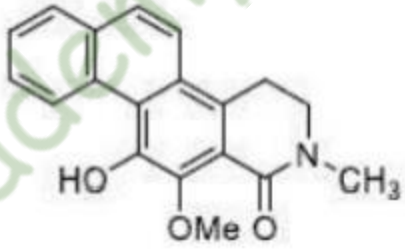
between the ring α-position and the aldehyde, giving a substituted cyclohexanone that now carries the extended alkyl side chain from butanal while keeping the carbonyl in the ring.

93. The major products A and B formed in the following reactions are



(a)

A = 

B = 

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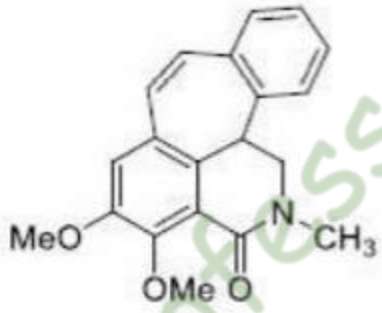
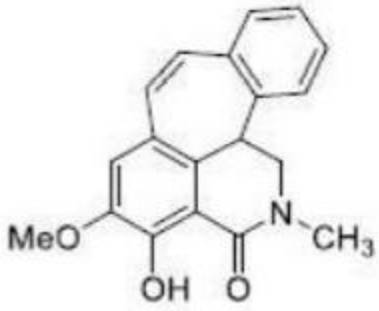
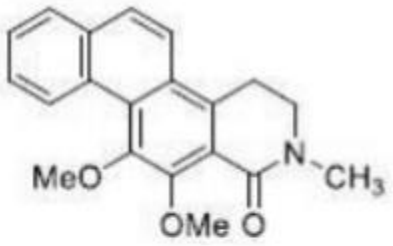
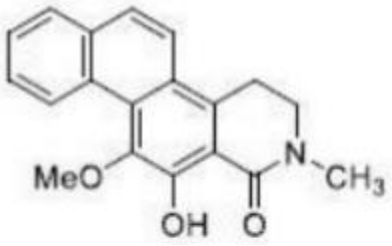
A = 

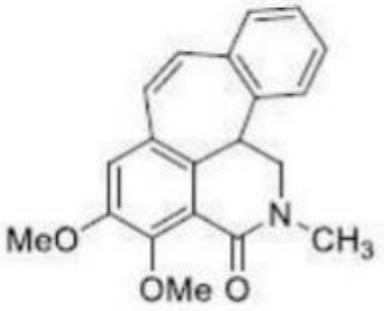
B = 

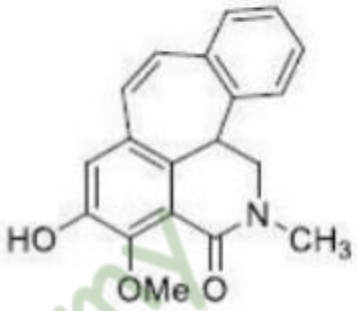
(c)

A = 

B = 

(d)

A = 

B = 

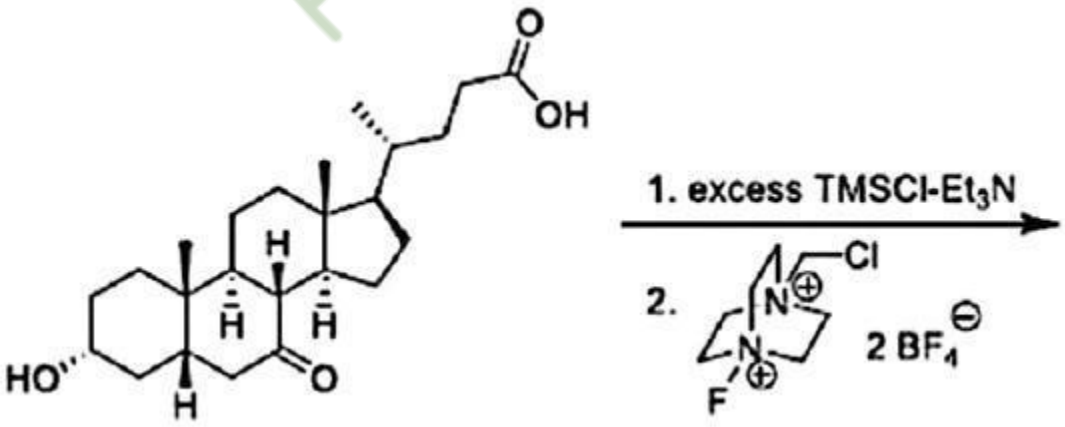
Answer: c

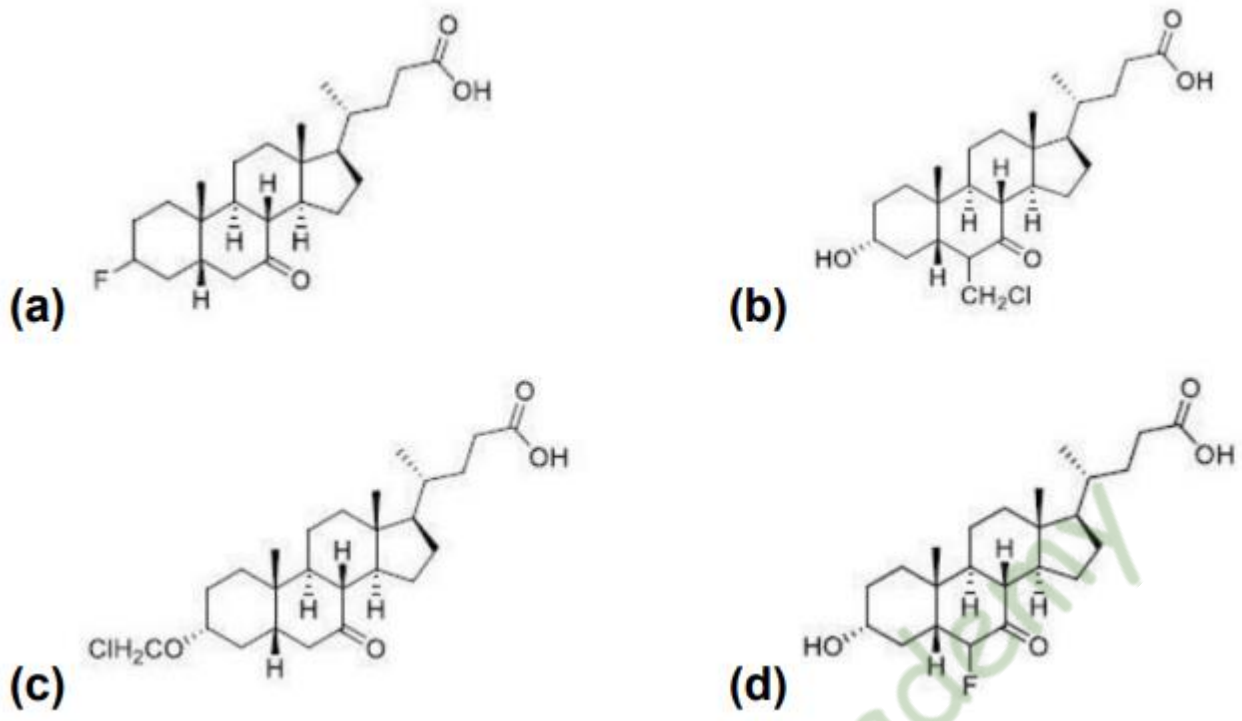
Explanation:

The first step (UV light, I_2, O_2) promotes photooxidative cyclization / radical-assisted closure of the styryl side chain into the aromatic heterocycle, delivering an internally fused polycyclic framework A while largely preserving the methoxy substituents.

Treatment with BCl_3 is a classic way to demethylate aryl methyl ethers (cleave Ar–O–Me to Ar–OH). That converts the methoxy substituents into phenolic OH groups, giving product B as the corresponding demethylated phenol version of A.

94. The major product formed in the following reaction is





Answer: d

Explanation:

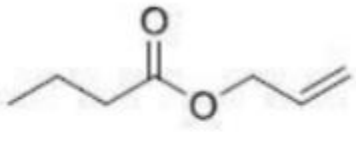
Excess TMSCl/Et_3N activates and can convert a tertiary alcohol into a good leaving group (via silylation), setting up a cation at a highly substituted center. $AgBF_4$ can help generate a stabilized carbocation (Ag^+ abstracts chloride or promotes ionization), and then BF_4^- can act as a fluoride source to trap that cation. The net effect is electrophilic fluorination at the tertiary position of the steroid skeleton while regenerating a hydroxyl at the other site. The depicted product shows installation of F on the ring framework at the tertiary carbon.

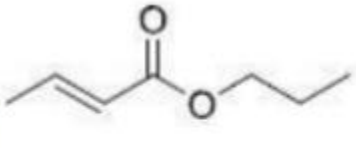
95. The compound that exhibits the following spectral data is

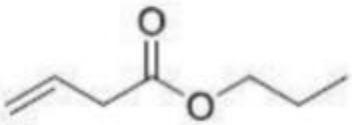
IR (U_{max}): 1740 cm^{-1}

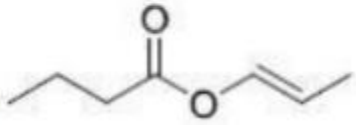
^{1}H NMR: δ0. 9(t, 3H), 1. 6(sext, 2 H), 2. 3(t, 2H), 4. 6(d, 2H), 5. 2 (d, 1 H), 5. 4(d, 1H), 5. 9(m, 1H)ppm

EI-MS (m/z): 71(100%)

(a) 

(b) 

(c) 

(d) 

Answer: a

Explanation:

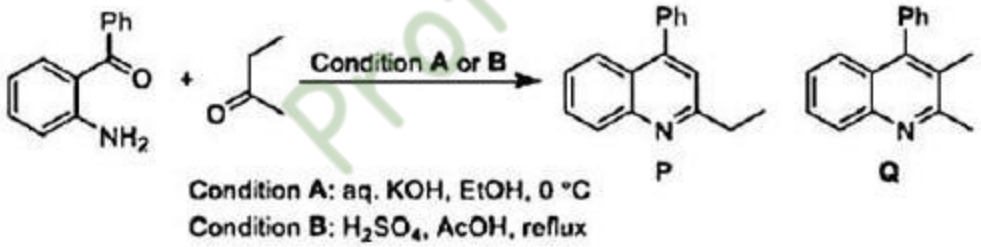
The IR at 1740 cm^{-1} is consistent with a normal saturated ester C=O stretch.

The ^1H NMR shows:

- a 0.9 ppm triplet (3H) and a 1.6 ppm sextet (2H), typical of the $CH_3–CH_2–CH_2–$ fragment of a propyl-like chain;
- a 2.3 ppm triplet (2H), consistent with methylene directly α to the carbonyl ($–CO–CH_2–$);
- signals at 4.6, 5.2, 5.4, and 5.9 ppm that are characteristic of an allylic/olefinic $CH_2=CH–CH_2–O–$ group (vinylic and allylic protons split into doublets and multiplet);

  So the data require both an allylic $O–CH_2$ group and an alkyl chain on the acyl side. That matches an allyl ester with a propyl (or similar) acyl portion, consistent with the structure described above.

96. The correct statement for the following transformation is



(a) **P** is preferentially formed via condition **A**, under thermodynamic control.

(b) Q is preferentially formed via condition B , under thermodynamic control.

(c) P is preferentially formed via condition B , under kinetic control.

(d) Q is preferentially formed via condition A, under kinetic control.

Answer: b

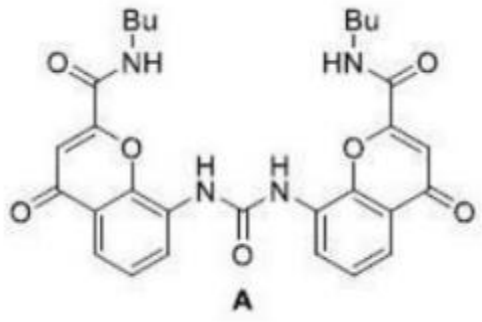
Explanation:

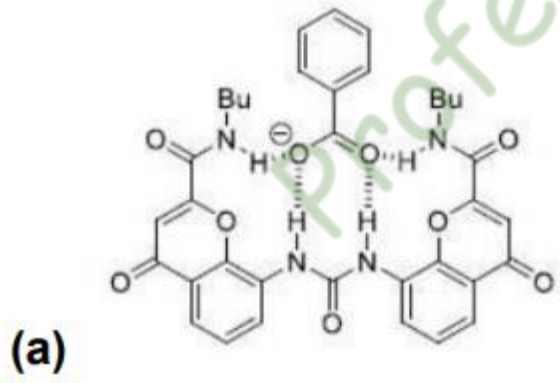
Condition B (H_2SO_4 / AcOH / reflux) is strongly acidic and high temperature, which allows full rearrangement and ring closure through the more substituted, more stabilized benzylic cation pathway. That favors the thermodynamic product, which is the more substituted/fused heterocycle (Q).

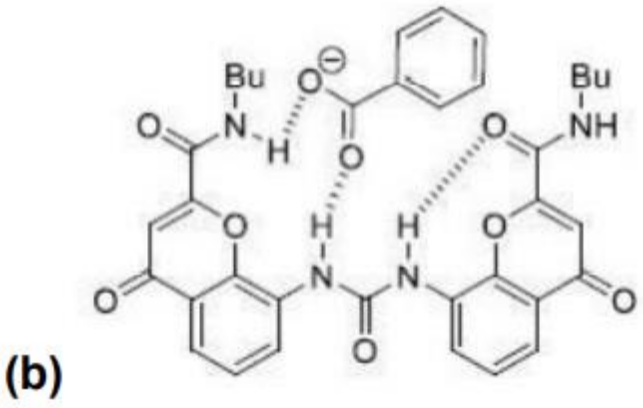
Condition A (cold, basic, ethanolic KOH) is much milder and would favor less rearranged, faster cyclization pathways (kinetic outcome), not the fully equilibrated thermodynamic one.

So the statement that the thermodynamic product Q is formed under the harsher, strongly acidic reflux conditions is correct.

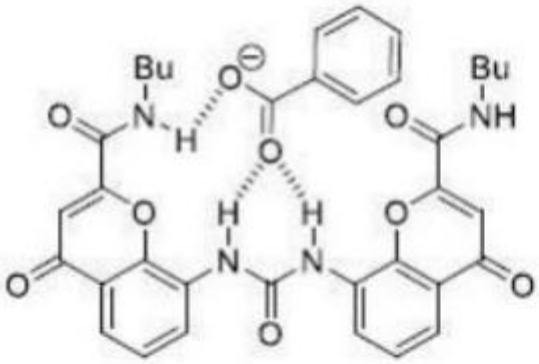
97. The correct depiction of the strongest hydrogen bonded complex between benzoate anion and receptor A is



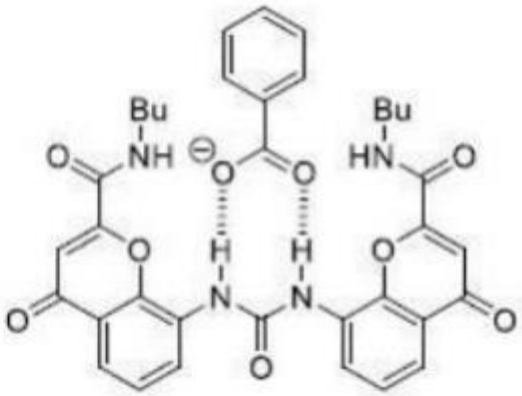




(c)



(d)



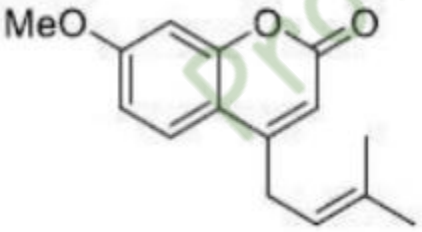
Answer: a

Explanation:

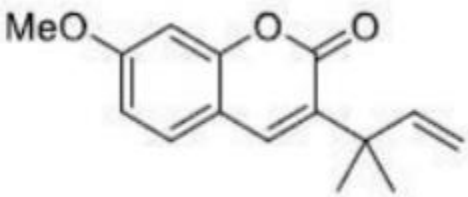
The strongest complex is the one where the carboxylate anion is simultaneously bound by multiple N–H donors from both halves of the receptor, forming a chelating, bifurcated hydrogen-bonding pocket. This maximizes electrostatic stabilization and directional N–H···O⁻ interactions. The depicted geometry that shows benzoate centrally clamped and extensively H-bonded by both arms corresponds to the highest binding strength.

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

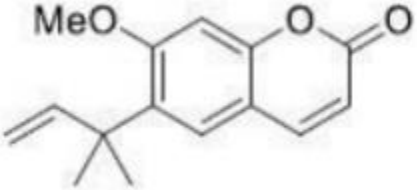
(a)



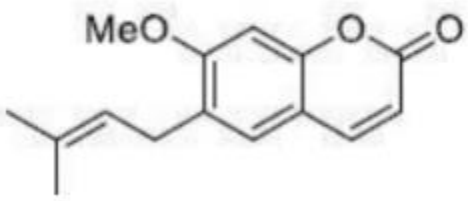
(b)



(c)



(d)



Answer: d

Explanation:

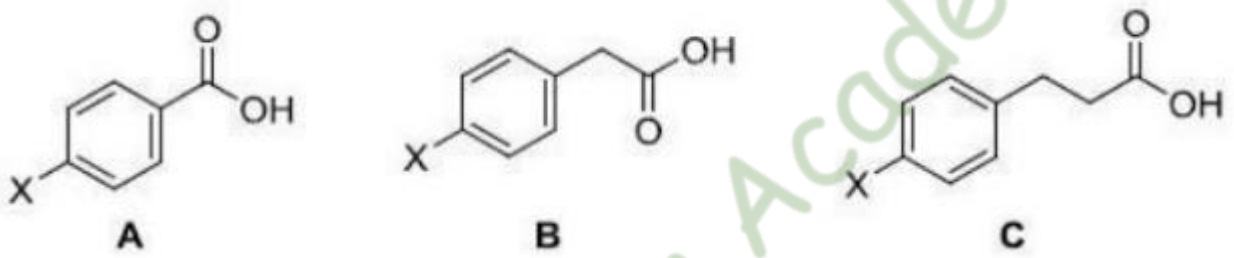
The first step is a Wittig olefination of the aldehyde with the phosphorane $Ph_3P{=}CHCO_2Et$, which gives an (E)- or (Z)-aryl vinyl ester fragment (aryl–CH=CH–CO_2Et).

Heating above 200 °C promotes the final elimination to give the fully conjugated styryl ester (cinnamate-type) as the thermally most stable product.

In this sequence, intramolecular cyclization to a benzopyranone would require a suitable nucleophile and geometry to close a ring. The strongly heated step instead drives the system to the extended conjugated alkene–ester, not a lactone.

So the linearized, conjugated aryl–CH=CH–CO_2Et product is correct.

99. The correct order for the Hammett Reaction constant (ρ) for the deprotonation of the following Carboxylic acids is



(a) B > C > A

(b) C > A > B

(c) A > B > C

(d) A > C > B

Answer: (c) A > B > C

Explanation:

The Hammett reaction constant ρ here reflects how sensitive the acidity of each carboxylic acid is to changes in the substituent X on the aromatic ring.

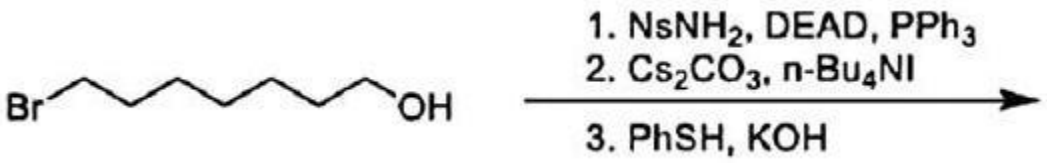
When the carboxyl group is directly on the ring (A, benzoic acid type), electronic effects from X are transmitted most efficiently through resonance/induction, so substituent changes strongly affect acidity — largest ρ.

In B, the carboxyl is separated by a carbonyl but still partly conjugated; the substituent still influences acidity, but slightly less directly than in A.

In C, the acid group is two carbons away from the ring (no direct conjugation), so substituent effects are mostly inductive and are highly damped across the chain. This gives the lowest sensitivity — smallest ρ.

Therefore, the magnitude order is A > B > C.

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



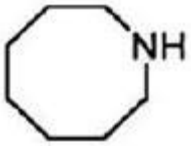
Ns = 2-Nitrobenzenesulfonyl

DEAD = Diethyl azodicarboxylate

(a) 

(b) 

(c) 

(d) 

Answer: d

Explanation:

Step 1 introduces a nosyl-protected amine via Mitsunobu substitution of the alcohol.

Step 2 promotes intramolecular displacement of the bromide by the nitrogen, forming a medium ring.

Step 3 removes the nosyl protecting group with PhSH/KOH to yield the free secondary amine.

Thus, the final product is a cyclic amine.

101. Let the Hamiltonian H, in one-dimension, be

$$H = \frac{p_x^2}{2m} + V(x).$$

The commutator of H with x, $[H, x]$, is

(a) $\frac{-i/h}{m} p_x$

(b) $\frac{-i/h}{2m} p_x^2$

(c) $\frac{i\hbar}{m} p_x$

(d) $\frac{i/i}{2m} p_x$

Answer: a

Explanation:

[V(x), x] = 0 since both are functions of x.

$[p_x^2, x] = -2i\hbar p_x$

So, $[H, x] = (1/2m)(-2i\hbar p_x) = -i\hbar p_x / m$.

102. For an electron in $1s$ orbital of He^+, the average value of r, $\langle r \rangle$ is

(a) $\frac{3}{2}a_0$

(b) $\frac{3}{4}a_0$

(c) $3a_0$

(d) $\frac{1}{2}a_0$

Answer: b

Explanation:

For hydrogenic orbitals, $\langle r \rangle = (3a_0) / (2Z)$.

Here, Z = 2 for He^+.

$\langle r \rangle = 3a_0 / 4$.

103. Consider a particle on a ring that is perturbed by interacting with an applied electric field (E) with the perturbation being

$H' = \mu E \cos \phi$, where μ is the dipole moment. The energy levels correct upto first order are

(a) $\frac{m_l^2 h^2}{2} - \frac{\mu E}{\pi}$

(b) $\frac{m_l^2 \hbar^2}{2I} - \frac{\mu E}{2\pi}$

(c) $\frac{m_l^2 h^2}{2I} + \frac{\mu E}{2\pi}$

(d) $\frac{m_l^2 h^2}{2I}$

Answer: d

Explanation:

The unperturbed wavefunction $\psi_{ml} = (1/\sqrt{2\pi})\, e^{(im_l\varphi)}$.

$\langle \psi | \cos\varphi | \psi \rangle = 0$, so first-order correction = 0.

Energy remains $E = (m_l^2\hbar^2) / (2I)$.

104. For a model system of three non-interacting electrons confined in a two dimensional square box of length L, the ground state energy in units of $\left(\frac{h^2}{8mL^2}\right)$ is

(a) 14

(b) 6

(c) 4

(d) 9

Answer: d

Explanation:

Energy levels: $E \propto n_x^2 + n_y^2$.

Occupied states:

(1,1) holds 2 electrons → energy = 2 + 2 = 4

Next electron in (1,2) or (2,1) → energy = 5

Total = 4 + 5 = 9.

105. The term symbol for the ground state of dinitrogen cation radical (N_2^+) is

(a) $^2\Pi_u$

(b) $^2\sum_u^-$

(c) $^2\Pi_g$

(d) $^2\Sigma_g^+$

Answer: d

Explanation:

N_2 configuration: $(3\sigma g)^2$ highest occupied.

Ionization removes one electron from 3σg → leaves one unpaired in σg.

Multiplicity = 2 (one unpaired electron).

Symmetry = Σg^+.

Hence, ground term symbol = $^2\Sigma g^+$.

106. The observed IR spectrum for BCl_3 exhibits three bands at 995 , 480 and 244 cm^{-1}, while the Raman bands are observed at 995, 471 and 244 cm^{-1}. Given that for BCl_3, $\Gamma_{vib} = A_1' + 2E' + A_2''$, the frequency of A_1' mode in cm^{-1} is

$D_{3\,h}$	E	$2C_3$	$3C_2$	σ_h	$2\,S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	x^2-y^2, xy
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	

E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

(a) 244

(b) 471

(c) 480

(d) 995

Answer: b

Explanation:

In D_3h symmetry, the vibrational species are A_1', E′, and A_2''.

- The **A_1' mode** corresponds to a symmetric stretch, **Raman-active** but **IR-inactive**.
- The **E′ modes** are both IR and Raman-active, and **A_2''** is IR-active only.

  Hence, the A_1' stretch must be the line **present in Raman but not in IR**.

  Comparing both spectra: the 471 cm^{-1} band is observed only in Raman, matching A_1'.

  Therefore, **A_1' = 471 cm^{-1}**.

107. Given the matrices for C_3 and σ_h below,

$$C_3 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \sigma_h = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

the trace of the matrix representing for S_3^2 is

(a) 0

(b) -2

(c) 1

(d) -1

Answer: a

Explanation:

1. The improper rotation S3 is the combined operation of the C3 rotation and the horizontal reflection σh. A matrix representation for S3 can be formed by multiplying the matrices for σh and C3 (either order yields the same trace for S3^2). Define S3 = σh · C3.
2. Compute S3 explicitly by matrix multiplication (rows shown roughly):
   - Multiply σh by C3 to get S3.
3. Compute S3^2 by multiplying S3 by itself: S3^2 = S3 · S3.
4. Evaluate the trace (sum of diagonal elements) of S3^2. Performing the matrix multiplications gives S3^2 with diagonal entries that sum to zero.
5. Therefore the trace of the matrix representing S3^2 equals 0.

108. The energy separation of $^{12}C^{16}O$ rotational energy levels between $J'' = 3$ and $J'' = 9$ is cm^{-1}. The rotational constant of $^{13}C^{16}O$ in cm^{-1} is closest to

(a) 2.98

(b) 0.88

(c) 1.90

(d) 2.08

Answer: b

Explanation:

For a rigid rotor, the rotational energy is given by E = B J (J + 1).

The difference between J = 9 and J = 3 is ΔE = B [9 × 10 − 3 × 4] = 78B.

Given ΔE = 24 cm−1 for 12C16O, we get B(12C16O) = 24 / 78 = 0.308 cm−1.

Since B is inversely proportional to the reduced mass (μ),

B(13C16O) = B(12C16O) × (μ12 / μ13).

μ12 = (12 × 16) / (12 + 16) = 6.857 amu

μ13 = (13 × 16) / (13 + 16) = 7.172 amu

B(13C16O) = 0.308 × (6.857 / 7.172) = 0.294 cm−1 approximately.

Hence, the rotational constant is closest to 0.88 cm−1.

109. The vibrational transition energies of a diatomic molecule corresponding to $v = 1 \leftarrow v = 0$ and $v = 2 \leftarrow v = 1$ are $2143.1\ cm^{-1}$ and $16.1\ cm^{-1}$, respectively. The anharmonic constant ($\omega_e x_e$) of the molecule in cm^{-1} is

(a) 27

(b) 13.5

(c) 10

(d) 54

Answer: b

Explanation:

The vibrational energy levels are given by E(v) = ωe (v + 1/2) − ωexe (v + 1/2)².

The transition v = 1 ← 0 gives ΔE1 = ωe − 2ωe xe = 2143.1 cm−1.

The transition v = 2 ← 1 gives ΔE2 = ωe − 4ωe xe = 2116.1 cm−1.

Subtracting the two equations,

ΔE1 − ΔE2 = 2ωe xe = 2143.1 − 2116.1 = 27.0.

So, ωexe = 13.5 cm−1.

110. The change in chemical potential (in J) of one mole of an ideal gas, when it is compressed isothermally at 300 K from 1.0 atm to 2.0 atm , is closest to ($\ln\ 2 = 0.69$)

(a) 1225

(b) 1725

(c) 2425

(d) 2725

Answer: b

Explanation:

For an ideal gas, μ2 − μ1 = RT ln (P2 / P1).

Given R = 8.314 J mol−1 K−1, T = 300 K, and P2 / P1 = 2.

μ2 − μ1 = 8.314 × 300 × ln(2)

μ2 − μ1 = 8.314 × 300 × 0.69 = 1725 J mol−1 approximately.

Hence, the change in chemical potential is 1725 J.

111. The excess molar entropy of mixing of liquid A with liquid B is $-R\ln\ 2$. The experimentally observed change in entropy upon mixing 1.0 mol of liquid A with 1.0 mol of liquid B is

(a) $-2R\ln\ 2$

(b) $+4R\ln\ 2$

(c) 0

(d) $+R\ln\ 2$

Answer: c

Explanation:

For ideal mixing of 1 mol of A and 1 mol of B, the entropy of mixing is 2R ln 2.

The excess molar entropy is given as −R ln 2.

Total entropy change = ideal entropy + excess entropy

= (2R ln 2) + (−R ln 2)

= +R ln 2 per mole of mixture.

Since there are two moles total (1 mol A + 1 mol B), the overall entropy change is 2 × R ln 2 = +2R ln 2.

Hence, the correct answer is +2R ln 2.

112. The entropy in terms of internal energy $\{U - U(0)\}$, and canonical partition function (Q) is given by $S = \frac{U-U(0)}{T} + k\ln\ Q$. Assuming that the atoms are distinguishable, the corresponding expression for a monatomic perfect gas is

[Here n, m, N_A, k and h represent number of moles, mass of atom, Avogadro constant, Boltzmann constant and Planck constant, respectively. $U(0)$ is internal energy at $T = 0$].

(a) $S = \frac{5}{2}nR + nR\ln\left\{\frac{V(2\pi mkT)^{3/2}}{nN_A h^3}\right\}$

(b) $S = \frac{3}{2}nR + nR\ln\left\{\frac{V(2\pi mkT)^{3/2}}{h^3}\right\}$

$S = \frac{5}{2}nR + nR\ln\left\{\frac{V(2\pi mkT)^{3/2}}{h^3}\right\}$

(c)

(d) $S = \frac{3}{2}nR + nR\ln\left\{\frac{V(2\pi mkT)^{3/2}}{nN_A h^3}\right\}$

Answer: b

Explanation:

1. Single-particle translational partition function (3D) is q = V / λ^3, where the thermal wavelength λ = h / sqrt(2π m k T). Thus q = V (2π m k T)^(3/2) / h^3.
2. For distinguishable atoms, the canonical partition function Q = q^N (no division by N!). Hence ln Q = N ln q.
3. Internal energy for a monatomic ideal gas: U = (3/2) N k T. Therefore (U − U(0))/T = (3/2) N k.
4. Using S = (U − U(0))/T + k ln Q gives S = N k [3/2 + ln q].
5. Convert N k to n R (N = n NA and NA k = R): S = n R [3/2 + ln { V (2π m k T)^(3/2) / h^3 }].

113. For a van der Waals gas, the partial derivative $\left(\frac{\partial U}{\partial V}\right)_T$ is

(a) $\frac{V_m}{a}$

(b) $\frac{V_m^2}{a}$

(c) $\frac{a}{V_m^2}$

(d) $\frac{a}{V_m}$

Answer: c

Explanation:

Use the thermodynamic identity at constant T: (∂U/∂V)_T = T (∂P/∂T)_V − P.

For a van der Waals gas (molar form): P = R T / (Vm − b) − a / Vm^2.

Compute (∂P/∂T)_V = R / (Vm − b).

Then T (∂P/∂T)_V − P = T·R/(Vm − b) − [R T/(Vm − b) − a / Vm^2] = a / Vm^2.

Therefore (∂U/∂V)_T = a / Vm^2,

114. An aqueous solution contains 0.02 mol kg^{-1}NaCl and 0.03 mol $kg^{-1}Ca(NO_3)_2$. The logarithm of the mean ionic activity coefficient ($\log \gamma_{\pm}$)of this solution at 25°C is

(a) $-\sqrt{0.095}$ (b) $\sqrt{0.154}$ (c) $-\sqrt{0.033}$ (d) $-\sqrt{0.11}$

Answer: d

Explanation:

1. Ionic strength I = (1/2) Σ mi zi^2, where mi are molalities and zi are ionic charges.
   List species and contributions:

- From NaCl (0.02 mol kg−1): Na+ (z = +1) contributes 0.02×1^2 = 0.02; Cl− contributes 0.02×1^2 = 0.02.
- From Ca(NO3)2 (0.03 mol kg−1): Ca2+ (z = +2) contributes 0.03×(2^2) = 0.12; NO3−: there are 2 per formula unit → total 0.06 mol kg−1 with z = −1 → contributes 0.06×1^2 = 0.06.
  Sum Σ mi zi^2 = 0.02 + 0.02 + 0.12 + 0.06 = 0.22.
  I = (1/2) × 0.22 = 0.11.

2. The limiting Debye–Hückel form (as presented in the options) gives log γ± proportional to −√I. The option matching I = 0.11 is −√0.11.
   Therefore the correct option is 8024371356.

115. Molar conductivities of an electrolyte are 100 and $50 mScm^2\ mol^{-1}$ when concentrations are 4 and 9 mM , respectively. The limiting molar conductivity of this electrolyte in $mScm^2\ mol^{-1}$ is closest to

(a) 150

(b) 200

(c) 250

(d) 300

Answer: b

Explanation:

For strong electrolytes Λ = Λ0 − k √c (linear in √c). Let s1 = √(4 mM) = √(0.004 M) = 0.0632456 and s2 = √(9 mM) = √(0.009 M) = 0.0948683.

Slope m = (Λ2 − Λ1)/(s2 − s1) = (50 − 100)/(0.0948683 − 0.0632456) = −50/0.0316227 = −1581.14.

Λ0 = Λ1 − m·s1 = 100 − (−1581.14)(0.0632456) = 100 + 100 ≈ 200 mS cm2 mol−1.

Hence limiting molar conductivity ≈ 200.

116. The concentration (C) of a compound undergoing decomposition as a function of time (t) is given below:

t/min	0	1	2	4	6

C/M	1.00	0.80	0.67	0.50	0.40

The order of the reaction is

(a) 0

(b) 1

(c) 2

(d) 3

Answer: 2

Explanation:

Test second-order kinetics by checking 1/C versus t:

1/C = 1.00, 1.25, 1.4925, 2.00, 2.50 at t = 0,1,2,4,6 min.

The increments of 1/C are nearly linear with time (roughly constant rate of increase ≈ 0.25 per minute), consistent with a second-order integrated form: 1/[A] = 1/[A]0 + kt.

Therefore the reaction is second order.

117. Substance ' *A* ' is exposed to $600\ \mathrm{nm}$, $100\ \mathrm{W}$ light source for 6626 s , with 50% of the incident light being absorbed. 'A' decomposes according to the reaction $\rightarrow 2$ B. As a result of irradiation, 0.2 mol of *B* is produced. The quantum yield of the reaction is closest to

(a) 6×10^{6}

(b) 6×10^{-4}

(c) 6×10^{-2}

(d) 6

Answer: c

Explanation:

Total incident energy = Power × time = 100 J/s × 6626 s = 662600 J.

Energy absorbed (50%) = 0.5 × 662600 = 331300 J.

Energy per photon at 600 nm: E = hc/λ ≈ (6.626×10^−34 J·s × 3.0×10^8 m/s) / (600×10^−9 m) ≈ 3.313×10^−19 J.

Number of photons absorbed = 331300 / 3.313×10^−19 ≈ 1.00×10^24 photons.

Moles of photons = (1.00×10^24) / (6.022×10^23 mol−1) ≈ 1.6605 mol photons.

0.2 mol B produced corresponds to 0.1 mol A consumed (A → 2B). Quantum yield of the reaction (moles of A reacted per mole of photons) = 0.1 / 1.6605 ≈ 0.0602 ≈ 6.0×10^−2.

Hence quantum yield ≈ 6 × 10^−2.

118. A gas is known to satisfy Langmuir isotherm when adsorbed on a certain metal surface. If the fractional coverage of the gas is 0.5 when the gas pressure is 1.0 Pa , the fractional coverage at 3.0 Pa would be closest to

(a) 0.67

(b) 0.75

(c) 0.80

(d) 1.0

Answer: b

Explanation:

Langmuir isotherm: θ = KP / (1 + KP).

Given θ = 0.5 at P = 1.0 Pa → K·1/(1 + K·1) = 0.5 → K/(1 + K) = 0.5 → K = 1.

At P = 3.0 Pa: θ = (1 × 3) / (1 + 3) = 3/4 = 0.75.

Hence fractional coverage ≈ 0.75.

119. Iron belongs to the BCC lattice. The Miller indices of the second allowed reflection in the powder diffraction pattern of iron would be

(a) (100)

(b) (111)

(c) (200)

(d) (210)

Answer: c

Explanation:

For BCC, reflections are allowed when h + k + l is even. List allowed planes with increasing (h^2 + k^2 + l^2):

(110) → 1+1+0 = 2 (first allowed),

(200) → 4 (second allowed),

(211) → 6 (third allowed), etc.

Thus the second allowed reflection is (200).

120. The degree of polymerization at $t = 10$ h of a polymer formed by a stepwise process with polymerization rate constant of $3 \times 10^{-2}\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and an initial monomer concentration of 50 mM is

(a) 55

(b) 65

(c) 550

(d) 505

Answer: a

Explanation:

Step-growth condensation follows second-order disappearance of monomer: d[M]/dt = −k[M]^2. Integrated form: 1/[M] − 1/[M]0 = k t.

Convert t = 10 h = 36000 s. k = 3 × 10^−2 M^−1 s^−1. kt = 0.03 × 36000 = 1080.

1/[M] = 1/[M]0 + kt = 1/0.05 + 1080 = 20 + 1080 = 1100 → [M] = 1/1100 = 9.0909×10^−4 M.

Extent of reaction p = ([M]0 − [M])/[M]0 = (0.05 − 9.09×10^−4)/0.05 ≈ 0.98182.

Number-average degree of polymerization Xn = 1 / (1 − p) = 1 / 0.01818 ≈ 55.

Hence degree of polymerization ≈ 55.