21. The correct order of the electron affinity for one-electron gain of the elements is

(1) F > Cl > Br

(2) P > N > As

(3) S > Se > O

(4) K > Li > Na

Answer: 3

Explanation: Electron affinity generally increases across a period and decreases down a group. However, oxygen has lower electron affinity than sulfur because of its small size, which leads to high electron–electron repulsion in its compact 2p orbital. Thus, the correct trend is **S > Se > O**, where sulfur's 3p orbitals allow better accommodation of the added electron.

22. Among the following which set of molecular/ionic species all have a planar structure?

(1) BrF_3, $FClO_2$ and $[XeF_5]^-$

(2) XeO_3, $[ClF_4]^-$ and $FClO_2$

(3) $[ClF_4]^-$, BrF_3 and $[XeF_5]^-$

(4) $FClO_2$, $[XeF_5]^-$ and XeO_3

Answer: 3

Explanation: All three species — **$[ClF_4]^-$, BrF_3, and $[XeF_5]^-$** — have a **square planar** or **distorted planar** structure according to the **VSEPR theory**.

$[ClF_4]^-$ → AX_4E_2 type → **Square planar**.

BrF_3 → AX_3E_2 type → **T-shaped (planar)**.

$[XeF_5]^-$ → AX_5E_2 type → **Square planar** due to lone pairs occupying axial positions.

Hence, all are planar in shape.

23. The total number of lone pairs of electrons on all the atoms in cyanogen azide and thiocyanogen respectively, are

(1) 4 and 6

(2) 6 and 6

(3) 3 and 4

(4) 4 and 4

Answer: 1

Explanation:

Cyanogen azide (NCN_3) has 4 lone pairs in total: nitrogen atoms contribute most due to their valence electrons and bonding pattern.

Thiocyanogen $(SCN)_2$ has 6 lone pairs — sulfur and nitrogen each contribute lone pairs as per Lewis structure. This analysis aligns with valence-shell arrangements satisfying the octet rule.

24. Of the following statements regarding dissociative substitution in an octahedral transition metal complex

(a) High steric hindrance between ligands in the metal complex favors fast dissociation of ligand.

(b) Increased charge on the metal atom/ion of the complex favours the acceptance of electron pair of the entering ligands.

(c) A pentacoordinated intermediate is observed.

(d) Nature of the entering ligand significantly influences the reaction.

Which are correct?

(1) a and d

(2) a and c

(3) a, c and d

(4) a, b, c and d

Answer: 2

Explanation:

In the **dissociative (D) mechanism**, the rate-determining step involves loss of a ligand forming a **pentacoordinate intermediate**.

(a) True: Steric crowding promotes ligand dissociation.

(b) False: Increased charge stabilizes existing bonds, reducing dissociation.

(c) True: A five-coordinate intermediate (trigonal bipyramidal/square pyramidal) forms.

(d) False: In dissociative mechanism, the entering ligand's nature does not affect the rate.

Thus, **(a) and (c)** are correct.

25. For $[Hg_2]^{2+}$, the bond order and the orbitals involved in bonding are, respectively

(1) one; s and s

(2) two; s and p

(3) one; p and p

(4) three; s and d

Answer: 1

Explanation:

In **$[Hg_2]^{2+}$**, two Hg^+ ions are linked by a **metal–metal sigma bond** formed by overlap of **6s orbitals** (one from each Hg^+).

Each Hg^{+} has configuration $[Xe]4f^{14}5d^{10}6s^{1}$. On combining, one electron from each forms the σ bond.

Bond order = ½(2 bonding – 0 antibonding) = **1**, and the orbitals involved are **s–s** overlap.

26. Consider an octahedral complex Ma_2b_2cd, where a, b, c, and d are monodentate ligands. The number of enantiomeric pairs for the complex is

(1) one

(2) two

(3) three

(4) four

Answer: 2

Explanation:

For **Ma_2b_2cd** type octahedral complexes, geometrical isomerism leads to cis–trans forms.

The **cis isomer** can show **optical isomerism**, giving **two enantiomers** (mirror images), whereas the **trans** isomer is optically inactive.

Thus, the complex exhibits **two enantiomeric pairs** in total.

27. The effective magnetic moment (in BM) for a lanthanide f^{10} ion is approximately

(1) 10.6

(2) 9.92

(3) 9.59

(4) 7.94

Answer: 1

Explanation:

For lanthanides, $\mu = \sqrt{[4S(S+1) + L(L+1)]}$ BM using **Russell–Saunders coupling**.

For **f^{10} configuration** (e.g., Ho^{3+}, Dy^{2+}), J = L – S, leading to $\mu_{eff} \approx 10.6$ BM.

This high value arises from both spin and orbital contributions to magnetism, unlike transition metals where only spin contributes.

28. Consider following statement(s) in the context of NO and CO ligands

A. In the bent mode, NO donates three electrons to the metal center.

B. In IR spectrum, the νNO for the bent nitrosyl ligand typically lies between 1525 and 1690 cm^{-1}

C. The HOMO of NO and CO are π* and σ orbitals, respectively

(1) A only

(2) B and C

(3) A and C

(4) A and B

Answer: 2

Explanation:

(A) False: In bent coordination, NO acts as a **1e⁻ donor**, not 3e⁻; in linear mode it donates 3e⁻.

(B) True: IR stretching for **bent NO** occurs at **1525–1690 cm⁻¹**, lower than linear NO due to weaker N–O bond.

(C) True: In NO, the **HOMO is π***, while in CO, the **HOMO is σ (lone pair on carbon)**.

Hence, **B and C** are correct.

29. Identify the correct statement for the two reactions given below

$Xe + PtF_6 \rightarrow [Xe^+][PtF_6^-]$

$XeOF_4 + Me_4N{\cdot}F \rightarrow [Me_4N^+][XeF_5^-]$

(1) Xe and XeF_4 both act as acids.

(2) Xe and XeF_4 both act as bases.

(3) Xe acts as an acid and XeF_4 acts as a base.

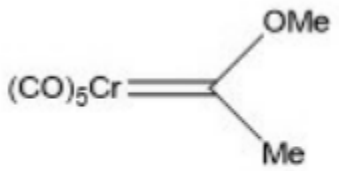
(4) Xe acts as a base and XeF_4 acts as an acid.

Answer: 4

Explanation:

In the first reaction, xenon donates an electron to platinum hexafluoride, which is a strong oxidizing agent. Hence, xenon behaves as a reducing agent (or Lewis base), while PtF_6 acts as an electron acceptor (acid). In the second reaction, $XeOF_4$ reacts with the fluoride donor $Me_4N{\cdot}F$ to form the anion $[XeF_5^-]$; here $XeOF_4$ accepts fluoride ions, showing its Lewis acid character. Therefore, Xe acts as a base and XeF_4 (or $XeOF_4$) acts as an acid.

30. Consider the following statement(s) in the context of organometallic complex (x):



X

A. The carbene ligand donates two electrons to the metal and accepts d electrons to make a π-bond.

B. The C (carbene) is nucleophilic.

C. Rotation around the Cr=C(OMe)Me double bond has a low barrier (<10 kcal/mol).

Correct statement(s) is/are:

(1) A and B

(2) A only

(3) A and C

(4) B and C

Answer: 3

Explanation:

In a Fischer carbene complex like $(CO)_5Cr=C(OMe)Me$, the carbene carbon has an electron-withdrawing substituent such as OMe, which makes the metal–carbene bond polarized as $M\delta^-–C\delta^+$. The carbene donates two electrons via a σ-bond to the metal and receives π-back donation from filled metal d-orbitals, forming a π-bond. Thus statement A is correct. The carbene carbon here is electrophilic, not nucleophilic, so B is incorrect. The π-bond between Cr and C allows free rotation with a low barrier due to weak π-back bonding, so C is also correct.

31. The penetrating power (R) and ionizing power (I) of α, β, and γ rays follow the ordering

(1) Rβ >Rγ> Rα and Iβ >Iγ> Iα or Iβ >Iγ> Iα

(2) Rγ> Rβ > Rα and Iγ> Iα > Iβ or Iβ >Iγ> Iα

(3) Rβ > Rα >Rγ and Iα > Iβ >Iγ or Iα > Iβ >Iγ

(4) Rγ> Rβ > Rα and Iα > Iβ >Iγ or Iα > Iβ >Iγ

Answer: 4

Explanation:

α-particles are heavy and highly charged, causing maximum ionization but having the least penetration because they lose energy rapidly. β-particles are lighter and less charged, hence show moderate ionizing and penetrating power. γ-rays are neutral electromagnetic radiations; they ionize weakly but penetrate deeply. Therefore, the correct trend is:

Penetrating power: γ > β > α

Ionizing power: α > β > γ.

32. For the ligand-to-metal charge-transfer (LMCT) transitions in the oxo-anions given below, the wavelength of the transitions are in the order

(1) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} < MoO_4^{2-}$

(2) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} > MoO_4^{2-}$

(3) $VO_4^{3-} > CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} < MoO_4^{2-}$

(4) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} < MoO_4^{2-}$

Answer: 1

Explanation:

In LMCT transitions, the energy of transition increases with the oxidation state of the metal and decreases with the covalency of the M–O bond. Among the given oxoanions, MnO_4^- absorbs the highest energy (lowest wavelength) because of Mn in +7 oxidation state. VO_4^{3-}, having V^{5+}, absorbs at the longest wavelength. The overall order of wavelength (λ) is therefore:

$VO_4^{3-} < CrO_4^{2-} < MnO_4^-$; and among group-6 analogues, MoO_4^{2-} has longer wavelength than WO_4^{2-} due to lower effective nuclear charge.

33. Match the items of column I with the applications given in column II

Column I:	**Column II:**
a. Zeolite	i. Solar cell
b. Indium tin oxide	ii. CO_2 capture
c. $LiCoO_2$	iii. Fuel cell
d. Pt alloy	iv. Battery

(1) a-iii; b-iv; c-i; d-ii

(2) a-i; b-iii; c-ii; d-iv

(3) a-ii; b-i; c-iv; d-iii

(4) a-iv; b-ii; c-iii; d-i

Answer: 3

Explanation:

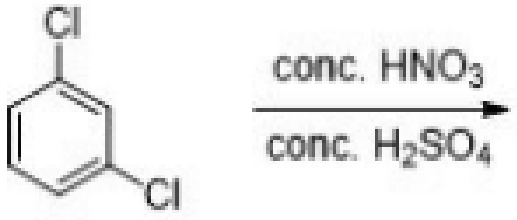
Zeolite → CO_2 capture (highly porous aluminosilicates used as adsorbents).

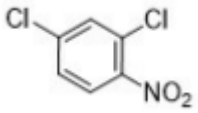
Indium tin oxide → Solar cell (ITO is a transparent conducting oxide used as electrodes).

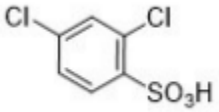
$LiCoO_2$ → Battery (cathode material in Li-ion batteries).

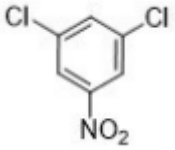
Pt alloy → Fuel cell (Pt-based catalysts for ORR/HOR in PEM fuel cells).

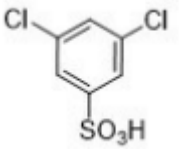
34. The major product formed in the following reaction is



(1) 

(2) 

(3) 

(4) 

Answer: 1

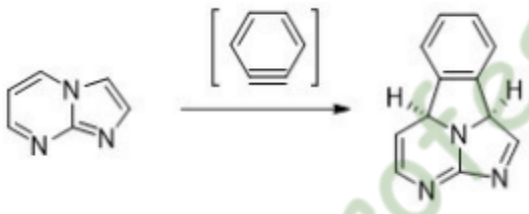
Explanation:

Nitration under conc. HNO_3/H_2SO_4 proceeds via an electrophilic aromatic substitution.

Chloro groups are deactivating but ortho/para-directing due to resonance donation.

Considering the substituent pattern in the given starting material, the most activated (least hindered) para/ortho position leads to the product shown in option (1), which dominates over the other regioisomers.

35. The following transformation



(1) [3π+2π] cycloaddition

(2) [6π+2π] cycloaddition

(3) [8π+2π] cycloaddition

(4) [8π+4π] cycloaddition

Answer: 3

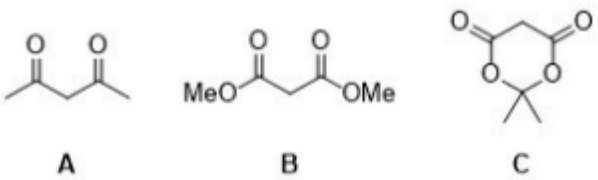
Explanation:

The reacting components comprise an 8π electron system (conjugated ring segment) and a 2π component (alkene/imine unit).

Pericyclic closure matches orbital symmetry for a concerted [8π+2π] process under thermal conditions.

The alternative [3π+2π], [6π+2π], and [8π+4π] combinations do not match the electron counts/topology in the depicted substrates.

36. The pK_a value for the following compounds



A B C

(1) B > C > A

(2) A > B > C

(3) C > B > A

(4) B > A > C

Answer: 4

Explanation:

Lower pK_a → stronger acid.

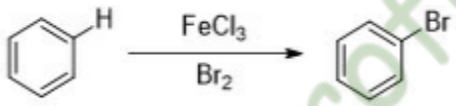
C (Meldrum's acid) is the strongest acid due to powerful inductive effects of two carbonyls embedded in a cyclic acetal framework plus excellent conjugate-base stabilization → lowest pK_a.

A (β-diketone, acetylacetone type) is next strongest via enolate resonance and chelation stabilization → intermediate pK_a.

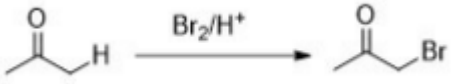
B (malonate diester) is least acidic among the three because electron-withdrawing effects are weaker than in C and conjugate base is less stabilized than A's chelated enolate → highest pK_a.

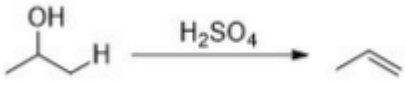
Thus pK_a order (highest → lowest): B > A > C.

37. The reaction that is expected to show a primary kinetic isotope effect for the indicated H-atom (C–H) is

(1) 

(2) 

(3) 

(4) 

Answer: 3

Explanation:

A large primary KIE appears when the C–H bond that is isotopically labeled is **broken in the rate-determining step**.

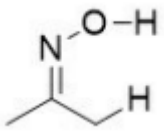
In acid-catalyzed α-bromination of a ketone (Br_2/H^+), the slow step involves **enolization**, which requires **C–H cleavage** at the α-position.

Replacing H with D at that carbon markedly changes the rate ($k_H/k_D \gg 1$), giving a primary KIE.

In the other options, the labeled C–H is not cleaved in the RDS (or hydrogen transfer is after the rate-limiting event), so a strong primary KIE is not expected.

38. The molecular orbital involved in the interaction of the oxime shown below, with a base is

(oxime structure as in the figure)



(1) σ* of O–H

(2) σ* of C–H

(3) σ of O–H

(4) σ of C–H

Answer: 1

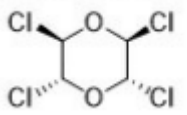
Explanation:

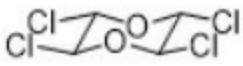
A base removes the oxime O–H proton via n(base) → σ*(O–H) interaction.

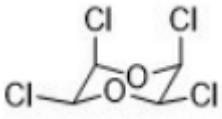
Proton transfer proceeds by donation into the **antibonding** orbital of the O–H bond, weakening it.

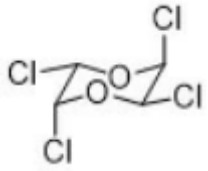
Therefore the accepting orbital is **σ*** of O–H, not σ or any C–H orbital.

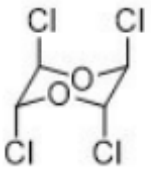
39. The structure that corresponds to the most stable conformation of the following compound is



(1) 

(2) 

(3) 

(4) 

Answer: 4

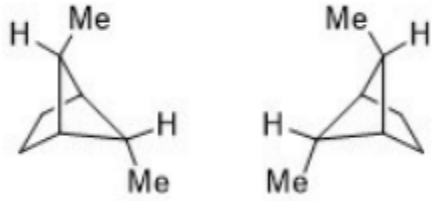
Explanation:

Chlorine substituents are bulky and strongly prefer **equatorial** positions in a chair to avoid 1,3-diaxial repulsions.

Among the depicted chairs, option **(4)** places the chlorines equatorial, minimizing steric strain.

Hence (4) represents the most stable conformation.

40. The correct relationship between the following structures is that they are



(1) identical

(2) enantiomers

(3) diastereomers

(4) constitutional isomers

Answer: 1

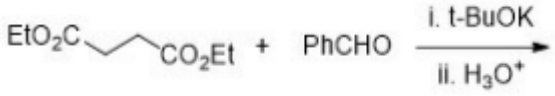
Explanation:

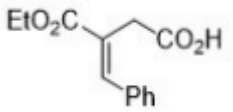
The two drawings represent the **same relative and absolute arrangement** (they are related by rotation/redrawing of the same framework).

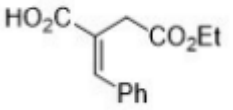
No bonds are broken/reconnected and no stereocenters invert between depictions.

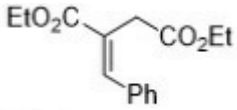
Thus the two structures are **identical**, not enantiomeric, diastereomeric, or constitutional isomers.

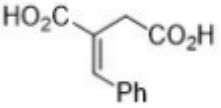
41. The major product formed in the following reaction is



(1) 

(2) 

(3) 

(4) 

Answer: 1

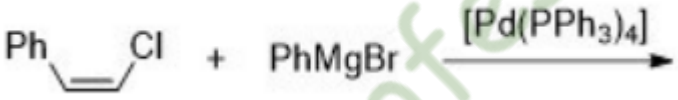
Explanation:

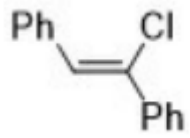
t-BuOK deprotonates the **active methylene** of the malonate to give a resonance-stabilized enolate.

The enolate undergoes **Knoevenagel condensation** with benzaldehyde, followed by **dehydration** to a conjugated alkene.

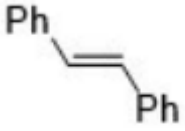
Acid workup furnishes the shown **benzylidene malonate** product with the favored (E) geometry, matching **option (1)**.

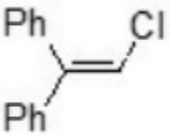
42. The major product formed in the following reaction



(1) 

(2) 

(3) 

(4) 

Answer: 2

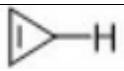
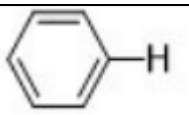
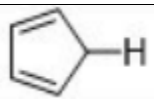
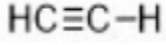
Explanation:

Under **Pd-catalysed Kumada cross-coupling**, an **allylic chloride** couples with **arylmagnesium bromide** to form the **allyl–aryl C–C bond**.

Oxidative addition of the allylic C–Cl to Pd(0) → transmetalation with PhMgBr → reductive elimination gives the **allyl–phenyl** product.

Hence the coupled, dechlorinated product shown in **option (2)** is formed.

43. The correct match for the Bond Dissociation Energies (BDE) of the C–H bonds of compounds in Column I, with the values in Column II is (As an example, the BDE for Me–H is 105.0 kcal/mol)

Column I:	**Column II BDE (kcal/mol)**
a. 	i. 110.9
b. 	ii. 71.1
c. 	iii. 132.0
d. 	iv. 90.6

(1) a – iii; b – iv; c – i; d – ii

(2) a – i; b – iii; c – ii; d – iv

(3) a – iii; b – i; c – iv; d – ii

(4) a – iv; b – i; c – ii; d – iii

Answer: 4

Explanation:

d is **HC≡C–H (sp C–H)** → strongest C–H, **~132 kcal/mol (iii)**.

b is **aromatic sp² C–H → ~111 kcal/mol (i)**.

a is **cyclopropyl (strained) C–H → ~90–91 kcal/mol (iv)**.

c is **benzylic/allylic tertiary-like C–H** (high radical stabilisation) → **lowest, ~71 kcal/mol (ii)**.

Thus **a-iv; b-i; c-ii; d-iii**.

44. The ozonolysis of a hydrocarbon in the presence of water produced pentanoic acid and carbonic acid. The hydrocarbon is

(1) 1-hexene

(2) 1-hexyne

(3) 5-decene

(4) 5-decyne

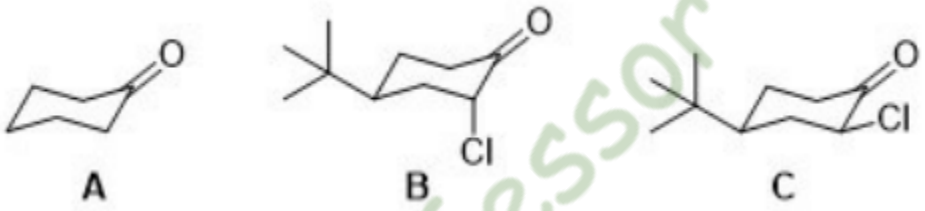
Answer: 2

Explanation:

Oxidative ozonolysis of a **terminal alkyne** gives **CO_2/H_2CO_3** from the terminal carbon and a **carboxylic acid** from the internal fragment.

For **1-hexyne**, cleavage gives **H_2CO_3 (→ CO_2)** and **pentanoic acid**, matching the products stated.

45. The correct order of C = O stretching frequency in IR spectrum for the following compounds is



A B C

(1) A > C > B

(2) B > C > A

(3) C > B > A

(4) B > A > C

Answer: 3

Explanation:

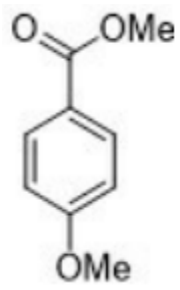
ν(C=O) increases when the carbonyl is **electron-poor** and/or **more constrained**.

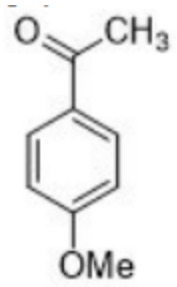
Structure **C** bears the strongest **–I/–M** effect near the carbonyl (and greater ring strain), giving the **highest ν(C=O)**.

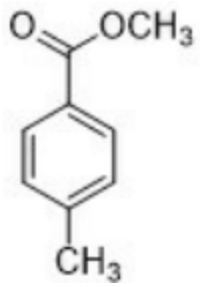
B is next; **A** has the most electron donation/least withdrawal → **lowest ν(C=O)**.

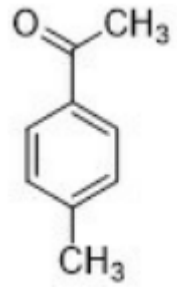
Hence **C > B > A**.

46. Which of the following compound has the ^1H NMR Spectrum ^1H NMR: δ 2.4 (s, 3H), 3.9 (s, 3H), 7.25 (d, J = 7 Hz, 2H), 7.95 (d, J = 7 Hz, 2H) ppm

(1) 

(2) 

(3) 

(4) 

Answer: 3

Explanation:

Two **doublets (2H + 2H, J ≈ 7 Hz)** indicate a **para-disubstituted benzene** (AA′BB′ pattern).

A **singlet at δ 3.9 (3H)** corresponds to an **anisylOMe** group.

A **singlet at δ 2.4 (3H)** is typical of an **Ar–CO–CH_3 (acetyl methyl)**.

Together these fit **p-methoxyacetophenone**, which corresponds to **option (3)**.

47. The combination of two reflections, σ′vσ″v about an intersecting mirror plane is equivalent to

(1) Sn

(2) Cn

(3) σh

(4) i

Answer: 2

Explanation:

The product of two reflections in planes that intersect at angle θ equals a rotation by 2θ about their line of intersection.

With vertical symmetry planes, this corresponds to a proper rotation C_n (n = 360°/2θ).

Hence σ′vσ″v≡ C_n.

48. For a microcanonical system, the correct probability distribution function for energy is given by

(1) Exponential distribution function

(2) Gaussian distribution function

(3) Poisson distribution function

(4) Uniform distribution function

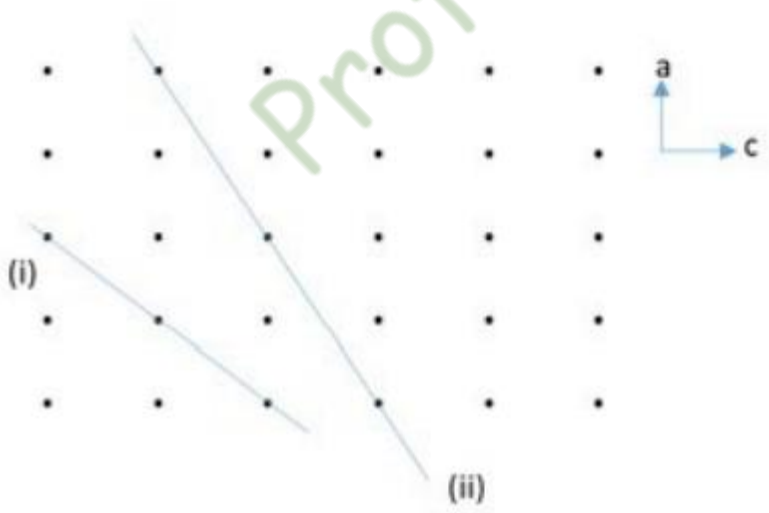
Answer: 4

Explanation:

In the microcanonical ensemble, all accessible microstates at the fixed energy are equally probable (equal a priori probabilities).

Therefore, the energy distribution is uniform over the allowed shell.

49. The Miller indices of the planes parallel to the b axis and intersecting the a and c axes, as shown in the figure, are



(1) (i) 101, (ii) 102

(2) (i) 102, (ii) 101

(3) (i) 100, (ii) 101

(4) (i) 100, (ii) 102

Answer: 1

Explanation:

Parallel to b ⇒ k = 0.

Plane (i): cuts a and c at 1 each ⇒ (101).

Plane (ii): cuts a at 1 and c at 1/2 ⇒ l = 2 ⇒ (102).

50. The volume of nitrogen gas adsorbed at STP to form a monolayer on a porous solid surface is 22.4 cm^3 g^{-1}. If the area occupied by one nitrogen gas molecule is 16.2 $Å^2$, then the surface area (in cm^2 g^{-1}) of the solid is close to

(1) 1.2×10^7

(2) 9.8×10^5

(3) 1.2×10^5

(4) 9.8×10^8

Answer: 2

Explanation:

Moles = 22.4/22400 = 1×10^{-3} mol; molecules = 6.022×10^{20}.

Area per molecule = 16.2×10^{-16} cm^2.

Total area = $6.022\times10^{20} \times 16.2\times10^{-16} \approx 9.8\times10^5$ cm^2 g^{-1}.

51. The amount of $Ba(NO_3)_2$ (molecular weight 261.32 amu) required to be added to 500 g of a 0.11 mol kg^{-1} solution of KNO_3 in order to raise its ionic strength to 1.00 is approximately

(1) 38.8 g

(2) 19.4 g

(3) 76.2 g

(4) 126.5 g

Answer: 1

Explanation:

$I = \frac{1}{2}\Sigma m_i z_i^2$. For KNO_3: $I_0 = 0.11$. $Ba(NO_3)_2$ adds 3x.

0.11 + 3x = 1 ⇒ x = 0.2967 mol kg^{-1}.

For ~0.5 kg solvent: n ≈ 0.148 mol ⇒ mass ≈ 0.148×261.32 ≈ 38.8 g.

52. The commutator, $[\hat{x}, \hat{p}_x^2]$ is equivalent to

(1) $-2i\hbar\,\hat{p}_x$

(2) $2i\hbar\,\hat{p}_x$

(3) $-i\hbar\,\hat{p}_x$

(4) $i\hbar\,\hat{p}_x$

Answer: 2

Explanation:

$[x, p^2] = [x,p]p + p[x,p] = (i\hbar)p + p(i\hbar) = 2i\hbar p$.

Hence $[\hat{x}, \hat{p}_x^2] = 2i\hbar\,\hat{p}_x$.

53. The number of micro states corresponding to the atomic term symbol ^{4}F is

(1) 7

(2) 12

(3) 28

(4) 42

Answer: 3

Explanation:

For ^{2}S+1L: multiplicity = 2S+1 = 4 ⇒ S = 3/2; L = F = 3.

Microstates = (2S+1)(2L+1) = 4×7 = 28.

54. When yellow phosphorus is converted to red phosphorus, the entropy and volume of the system do not change. The order of this phase transition is most likely to be

(1) 3

(2) 2

(3) 1

(4) 0

Answer: 2

Explanation:

First-order transitions show discontinuities in S and V (first derivatives of G).

Given S and V unchanged, the transition is second order (discontinuity in second derivatives like C_p).

55. When three of the phases of a two component system are simultaneously in equilibrium the number of degrees of freedom is

(1) 0

(2) 1

(3) 2

(4) 3

Answer: 2

Explanation:

Gibbs phase rule: $F = C - P + 2$.

With $C = 2$ and $P = 3$, $F = 1 \rightarrow$ corresponds to option (2).

56. The hypothetical NMR spectrum of 1H in 1H–C–2H would consist of (spin of the 2H is 1) a

(1) Singlet

(2) Doublet of 1:1 ratio

(3) Triplet of 1:1:1 ratio

(4) Triplet of 1:2:1 ratio

Answer: 3

Explanation:

Deuterium has spin $I = 1$, so a directly coupled 1H is split into $(2I+1) = 3$ lines.

For $I = 1$ the three mI states are equally populated, giving intensities 1:1:1.

57. The total π-electron density on the four carbon atoms of trans-butadiene are in the ratio

(1) 1:1:1:1

(2) 1:2:2:1

(3) 1:√2:√2:1

(4) 1:3:3:1

Answer: 1

Explanation:

Summing densities from the two filled π-MOs in Hückel theory gives equal total π-electron density at all four carbons → 1:1:1:1.

58. The reactive cross section is expected to be the largest for the reaction

(1) $Li + Cl_2 \rightarrow LiCl + Cl$

(2) $Na + Cl_2$

(3) $K + Cl_2$

(4) $Rb + Cl_2$

Answer: 4

Explanation:

Down the alkali metal group ionization energy decreases and polarizability increases, enhancing electron transfer to Cl2; Rb is the most reactive, giving the largest cross section.

59. The rate of decomposition of a gas is 10 mM s−1 when 10% is reacted and it is 5 mM s−1 when 40% is reacted. The order of the reaction is:

(1) 2

(2) 1.71

(3) 0

(4) 2.15

Answer: 2

Explanation:

Rate r ∝C^n = [C0(1 − x)]^n.

(10 / 5) = (0.9 / 0.6)^n ⇒ 2 = (1.5)^n ⇒ n = ln 2 / ln 1.5 ≈ 1.71.

60. For a person weighing 70 kg, the minimal volume (in mL) of a fatal dose of a compound with LD50 = 80 mg·kg−1 and density = 1.45 g·mL−1 is

(1) 5.6

(2) 3.9

(3) 0.8

(4) 0.4

Answer: 2

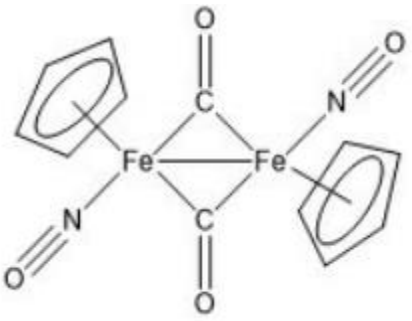
Explanation:

Mass at LD50 = 80 mg·kg−1 × 70 kg = 5600 mg = 5.6 g.

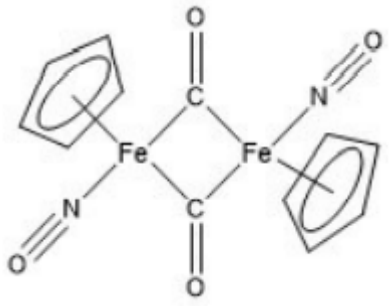
Volume = mass / density = 5.6 / 1.45 ≈ 3.86 mL ≈ 3.9 mL.

61. Identify the thermodynamically stable structure of [(η^5 – C5H5)Fe(μ2 – CO)(NO)]2

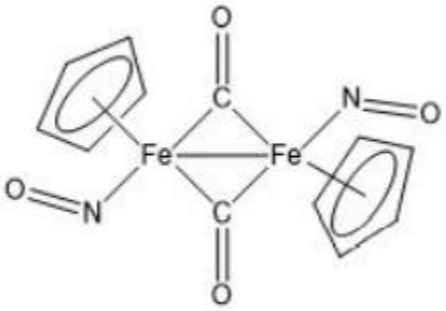
(1)



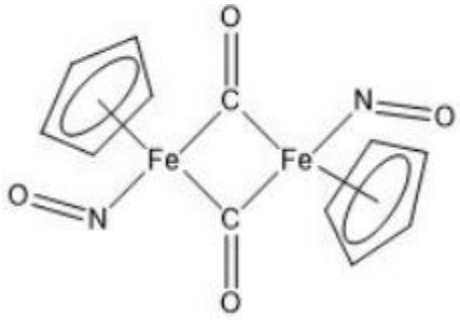
(2)



(3)



(4)



Answer: 2

Explanation: Thermodynamically favored arrangement keeps NO linear and terminal (strong π-acceptor) and the CO as the μ2-bridge between the Fe centers; this maximizes metal→ligand back-bonding and minimizes steric/electronic repulsion, matching option (2).

62. Which of the following reaction(s) do(es) NOT occur

(i) $[NPCl_2]_3 + 6\ NaF \xrightarrow[reflux]{MeCN} [NPF_2]_3 + 6\ NaCl$

(ii) $n\ PCl_5 + n\ NH_4Cl \xrightarrow[reflux]{C_6H_5Cl} [NPCl_2]_n + 4\ n\ HCl\ [n = 3, 4, 5...]$

(iii) $n\ PF_5 + n\ NH_4F \xrightarrow[reflux]{C_6H_5Cl} [NPF_2]_n + 4\ n\ HF\ [n = 3, 4, 5..]$

(1) (i) and (iii)

(2) (i) and (ii)

(3) (i) only

(4) (iii) only

Answer: 4

Explanation: (i) halogen-exchange to give NPF2 from NPCl2 proceeds; (ii) ammonolysis/condensation of PCl5 gives cyclo/linear phosphazenes NPCl2)n; (iii) analogous formation from PF5 with NH4F does not occur because PF5 is too inert toward F-based ammonolysis; formation of –NPF2– chains requires special fluoride activation (not NH4F/C6H5Cl), so (iii) fails.

63. Consider the following statements for the self-exchange electron transfer reaction in [Cr(H2O)6]2+/3+

a. σ* orbitals are only involved in electron transfer

b. It involves large inner-sphere reorganization energy

c. It involves no change in M–L bond lengths

d. Rate of self-exchange electron transfer is fast

The correct statements are

(1) a, b and d

(2) a and d

(3) a and c

(4) b and d

Answer: 2

Explanation: In aquo ions the electron resides in t2g (non-bonding relative to σ); overlap occurs through ligand σ* pathways (outer-sphere). The self-exchange Cr(II)/Cr(III) aquo couple is relatively fast; large inner-sphere reorganization and no bond-length change are both incorrect (there is some but not “large”, and not zero).

64. The type of molecular orbitals in the allyl ligand (CH2=CH–CH2–) that are used for σ-donation and π-back donation with metal d-orbitals, respectively are

(1) 2π and 3π

(2) 1π and 3π

(3) 3π and 2π

(4) 1π and 2π

Answer: 2

Explanation: The η^3-allyl set forms three π-MOs (ψ1 bonding = 1π, ψ2 non-bonding/symmetric, ψ3 antibonding = 3π). σ-type donation into the metal uses the symmetric low-energy allyl π-combination (often denoted 1π/ψ2 depending on convention), while metal→ligand back-bonding goes into the antibonding 3π.

65. Consider following terms. Identify those which are relevant to d.c. polarography

A. Thermal current

B. Supporting electrolyte

C. Depolarization

D. Gelatin

Correct answer is

(1) A, B and C

(2) A, B and D

(3) B, C and D

(4) C and D only

Answer: 3

Explanation: In dc polarography a high-concentration supporting electrolyte suppresses migration current; the electroactive species is the depolarizer; gelatin (maximum suppressor) is used to dampen adsorption/maxima at the dropping mercury electrode. “Thermal current” is not a standard component in dc polarography.

66. Match the iron and copper proteins with biological function in the table below:

Iron protein	**Copper protein**	**Biological function**
A: Hemerythrin	i: Azurin	X: Oxygenase
B: Cytochrome P450	ii: Hemocyanin	Y: Electron transfer
C: Rieske protein	iii: Tyrosinase	Z: O_2 transport

(1) A-ii-Z, B-iii-X, C-i-Y

(2) A-ii-Z, B-i-X, C-iii-Y

(3) A-iii-Y, B-i-Z, C-ii-X

(4) A-i-Y, B-iii-Z, C-ii-X

Answer: (1) A-ii-Z, B-iii-X, C-i-Y

Explanation:

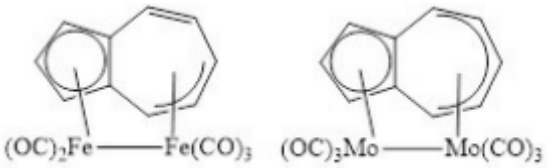
Hemerythrin (iron) and hemocyanin (copper) are oxygen transport proteins → (Z).

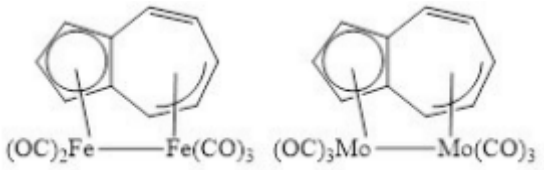
Cytochrome P450 (iron) and tyrosinase (copper) are oxygenase enzymes → (X).

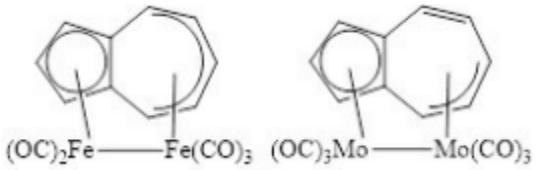
Rieske protein (iron–sulfur) and azurin (copper) are electron transfer proteins → (Y).

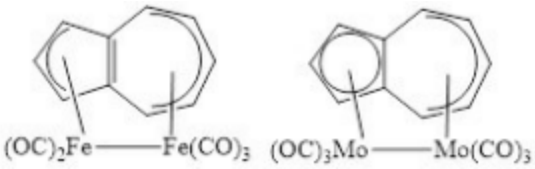
Hence A–ii–Z, B–iii–X, C–i–Y.

67. The set of structures showing the correct hapticity of azulene on the basis of the 18 e^- rule, is

(1) 

(2) 

(3) 

(4) 

Answer: (1)

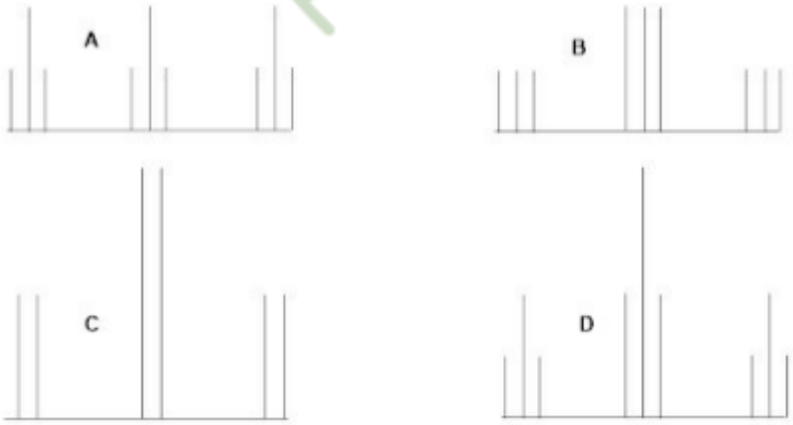
Explanation:

In the $(OC)_3Fe$ complex, η^5-coordination through the five-membered ring contributes 6 π-electrons, resulting in an 18-electron configuration for $Fe(CO)_3$.

In the $(OC)_3Mo$ complex, η^7-coordination through the seven-membered ring donates 8 π-electrons, giving an 18-electron configuration for $Mo(CO)_3$.

Therefore, the correct set of structures consistent with the 18-electron rule corresponds to option (1).

68. Which of the patterns (A, B, C or D) fits best with the ^{13}C NMR spectrum of $TiCl_3(CDH_2)$ [Given: $^1J(C–H) > {}^1J(C–D)$]



(1) A

(2) B

(3) C

(4) D

Answer: (2) B

Explanation:

The ^{13}C nucleus couples to two equivalent ^{1}H nuclei (I = ½) to form a 1:2:1 triplet with a larger coupling constant ($^{1}J(C–H)$).

Each component of this triplet further splits due to coupling with one ^{2}H nucleus (I = 1) into a 1:1:1 triplet with a smaller coupling constant ($^{1}J(C–D)$).

Hence, the resulting pattern is a triplet of triplets corresponding to pattern B.

69. The number of CO bands for isomers from sets (i) and (ii) in their IR spectra are:

Set (i): Trigonal bipyramidal isomers, axial-$Fe(CO)_4L$ (A) and equatorial-$Fe(CO)_4L$ (B)

Set (ii): Octahedral isomers, fac-$Mo(CO)_3L_3$ (C) and mer-$Mo(CO)_3L_3$ (D)

(1) A, 4 and B, 3; C, 3 and D, 2

(2) A, 4 and B, 3; C, 2 and D, 3

(3) A, 3 and B, 4; C, 3 and D, 2

(4) A, 3 and B, 4; C, 2 and D, 3

Answer: (4) A, 3 and B, 4; C, 2 and D, 3

Explanation:

For trigonal bipyramidal $Fe(CO)_4L$ isomers:

– Axial-$Fe(CO)_4L$ (C_3v symmetry) → 3 CO stretching bands.

– Equatorial-$Fe(CO)_4L$ (C_2v symmetry) → 4 CO stretching bands.

For octahedral $Mo(CO)_3L_3$ isomers:

– fac-$Mo(CO)_3L_3$ (C_3v symmetry) → 2 CO bands.

– mer-$Mo(CO)_3L_3$ (C_2v symmetry) → 3 CO bands.

70. In 3-iron ferredoxins, the number of sulfide bridges and cysteinyl ligands, respectively, are:

(1) 3, 3

(2) 4, 3

(3) 3, 4

(4) 4, 4

Answer: (2) 4, 3

Explanation:

In 3Fe–4S ferredoxins, three iron atoms are bridged by four sulfide ions forming a cubane-type cluster missing

one corner (incomplete cubane).

Each iron is also coordinated to a cysteinyl sulfur, giving three cysteine ligands.

Thus, the cluster contains four inorganic sulfides and three cysteinyl ligands — 4, 3.

71. The absorption spectrum of [Cr(NH3)6]3+ in water shows two bands around 475 and 365 nm. The ground term and the spin-allowed transitions, respectively, are

(1) 4F; 4T1g(F) → 4T2g and 4T1g → 4A2g

(2) 4F; 4A2g → 4T2g and 4A2g → 4T1g(F)

(3) 2G; 2Eg → 2T1g and 2Eg → 2T1g

(4) 2F; 2A2g → 2T2g and 2A2g → 2T1g(F)

Answer: (2) 4F; 4A2g → 4T2g and 4A2g → 4T1g(F)

Explanation:

Cr(III) is d3 (octahedral). Free-ion ground term = 4F; in Oh the ground state is 4A2g. Spin-allowed d–d bands are 4A2g→4T2g and 4A2g→4T1g(F), matching option (2).

72. Choose the correct statement(s) from the following:

(i) The trend in Lewis acidity among silicon halides is SiI4 < SiBr4 < SiCl4 < SiF4.

(ii) Tin(II) chloride can act as a Lewis acid and not as a Lewis base.

(iii) Aluminosilicates can display Brønsted acidity.

(1) (i) and (ii)

(2) (i) and (iii)

(3) (ii) and (iii)

(4) (ii) only

Answer: (2) (i) and (iii)

Explanation:

(i) Lewis acidity rises with increasing halogen electronegativity/π back-donation decrease: SiI4 < SiBr4 < SiCl4 < SiF4.

(ii) SnCl2 possesses a lone pair and can behave as a Lewis base; hence “not a Lewis base” is false.

(iii) Aluminosilicates contain Brønsted-acidic bridging Si–OH–Al sites → true.

73. Consider following statements

A. PbCl2 has low solubility in water.

B. Sulfides of As(III) and Sb(III) are soluble in ammonium sulfide.

C. SnS is soluble in yellow ammonium sulfide.

D. MnS is precipitated by passing H2S through acidic MnCl2.

Correct statements are

(1) A, B and C

(2) B, C and D

(3) A, C and D

(4) A and C only

Answer: (1) A, B and C

Explanation:

A true (sparingly soluble). B true (group II B sulfides dissolve in (NH4)2S). C true (SnS dissolves in yellow ammonium sulfide forming thio-complex). D false (MnS precipitates only in alkaline/basic medium, not acidic).

74. Which of the following statements for rubredoxin are correct?

A. Fe2+ center has a tetrahedral geometry.

B. Reduced form of iron is diamagnetic.

C. Fe2+ center undergoes Jahn–Teller distortion.

D. It is a [2Fe–2S] cluster.

(1) A, B and C

(2) A, C and D

(3) C and D only

(4) A and C only

Answer: (4) A and C only

Explanation:

Rubredoxin contains a single Fe bound to four Cys thiolates in (approx.) tetrahedral geometry (A true). The Fe2+ (high-spin d6, Td) is paramagnetic, so B is false. Distortion from ideal Td due to electronic degeneracy/ligand field effects is observed (C taken as true). It is not a [2Fe–2S] cluster (D false).

75. The correct geometries for the metal carbonyl clusters, A–C, are

A. [Ru6(CO)17B]–

B. [Os6(CO)18P]–

C. [Os4(CO)16]

(1) A: pentagonal bipyramidal, B: trigonal prismatic, and C: tetrahedral

(2) A: pentagonal bipyramidal, B: octahedral, and C: square

(3) A: octahedral, B: trigonal prismatic, and C: tetrahedral

(4) A: octahedral, B: trigonal prismatic, and C: square

Answer: (4) A: octahedral, B: trigonal prismatic, and C: square

Explanation:

Carbido/heteroatom-centred Ru6 clusters adopt octahedral metal frameworks; [Os6(CO)18P]– is trigonal prismatic; the tetranuclear Os4(CO)16 has a square metal core.

76. Which of the statements (A–D) given below are correct for B2H6 molecule:

A. Addition of Et2O·BF3 to NaBH4 in a polyether solvent produces B2H6.

B. It has D2d symmetry.

C. Reaction of B2H6 with NMe3 gives Me3N·BH3.

D. It is diamagnetic.

(1) A, B and C

(2) A, C and D

(3) A and B only

(4) B and D only

Answer: (2) A, C and D

Explanation:

Diborane is produced from NaBH4/Et2O·BF3; it adducts with tertiary amines to give amine–borane (Me3N·BH3); all electrons are paired → diamagnetic. Its symmetry is D2h (not D2d), so B is false.

77. Match the following

Measurement	**Spectroscopic Technique**
a. Binding energy	i. NMR spectroscopy
b. Quadrupole splitting	ii. Energy – dispersive X-ray spectroscopy (EDS)
c. Contact shift	iii. X-ray photoelectron spectroscopy (XPS)
d. Elemental analysis	iv. Mossbauer spectroscopy

(1) (a) – (iii), (b) – (iv), (c) – (i), (d) – (ii)

(2) (a) – (iv), (b) – (iii), (c) – (i), (d) – (ii)

(3) (a) – (i), (b) – (iv), (c) – (ii), (d) – (iii)

(4) (a) – (i), (b) – (iv), (c) – (ii), (d) – (iii)

Answer: 1

Explanation:

NMR (Nuclear Magnetic Resonance) spectroscopy is helpful in determining the purity of the compound. It is based on the fact that every nuclei has charge and spin, which cause generation of magnetic field. The magnetic

field of the one nuclei can get affect by external magnetic field as well as the magnetic field of neighbouring nuclei.

EDS (Energy dispersive X-ray spectroscopy) is based on the emission of characteristic X-rays. The detection of x-ray energy gives the idea about elements present in the sample.

Principle of XPS(X-ray Photoelectron spectroscopy) relies on the photoelectric effect. The incident radiation knocks off the inner shell electrons and the photoelectron received posses some kinetic energy which further helps in calculation of Binding energy.

Mössbauer spectroscopy uses gamma radiations of lower energy. It is used in study of oxidation state of metals in bioinorganic compounds, especially F and Sn.

78. Consider the following statements regarding EPR spectra.

(a) For allowed transitions, $\Delta M_s = \pm 1$ and $\Delta M^I = 0$

(b) For allowed transitions $\Delta M_s = 0$ and $\Delta M^I = \pm 1$

(c) Tetragonally elongated Cu(II) complexes have $g\| > g\perp$

(d) The orbital considered as ground state for tetragonally compressed Cu(II) complexes is $d_{x^2-\gamma^2}$.

The correct statements are

(1) (a), (c) and (d)

(2) (b), (c) and (d)

(3) (a) and (c) only

(4) (b) and (d) only

Answer: 3

Explanation:

EPR selection rule is $\Delta M_s = \pm 1$ with $\Delta M^I = 0 \Rightarrow$ (a) true.

$\Delta M_s = 0$, $\Delta M^I = \pm 1$ corresponds to NMR-type hyperfine transitions, not allowed in EPR $\Rightarrow$ (b) false.

Cu(II) (d^9) with tetragonal elongation (Jahn–Teller) gives $g\| > g\perp \Rightarrow$ (c) true.

Tetragonal compression favors d_z^2 ground state, not $d_{x^2-\gamma^2} \Rightarrow$ (d) false.

79. For trigonal bipyramidal coordination complex (ML_5) the correct point group symmetry and the relative order of the energies of the 3d orbitals in that crystal field, respectively are

(1) $D3h^-$, $d_{x^2-\gamma^2} > d\_z^2$, d_xy>d_xz, d_yz

(2) $D3h^-$, $d\_z^2 > d\_z^2$, $d_{x^2-\gamma^2}$ >d_xz, d_yz

(3) $D3h^-$, $d_{x^2-\gamma^2} > d\_z^2$, d_xy>d_xz, d_yz

(4) $D3h^-$, $d\_z^2 > d_{x^2-\gamma^2}$, d_xy>d_xz, d_yz

Answer: 4

Explanation:

Trigonal bipyramidal ML_5 has D_3h symmetry. The axial ligands interact strongly with d_z^2 (highest). Equatorial interactions raise $d_{x^2-y^2}$ and d_xy next, while d_xz and d_yz (with nodal orientation toward ligands) are lowest → d_z^2 > ($d_{x^2-y^2}$, d_xy) > (d_xz, d_yz).

80. The ore (X) gives a d-block metal (M) in the elemental form, following a chemical process. Which of the sets X/ M/ Chemical process below is correct?

(1) Ilmenite/ Titanium/ $2FeTiO_3 + Mg + O_2 \rightarrow 2TiO_2 + MgO + Fe_2O_3$ followed by reduction of TiO_2 with Mg.

(2) Rutile/ Titanium/ $TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$ followed by reduction of $TiCl_4$ with Na or Mg.

(3) Rutile/ Titanium/ $TiO_2 + 4HCl(conc.) \rightarrow TiCl_4 + 2H_2O$ followed by electrolytic reduction of $TiCl_4$.

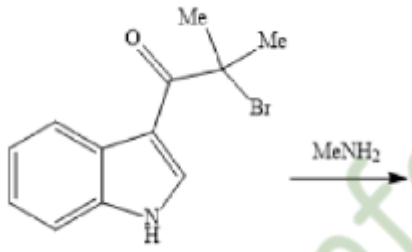
(4) Molybdenite/ Molybdenum/ $2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$ followed by reduction of MoO_3 with carbon.

Answer: 2

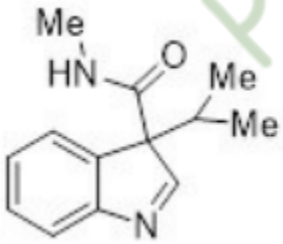
Explanation:

Titanium is produced industrially from rutile by chlorination of TiO_2 with C/Cl_2 to $TiCl_4$, then Kroll reduction with Na/Mg → Ti^0.

81. The major product formed in the following reaction is ($MeNH_2$ on the given indole-derived bromoimide).



(1)



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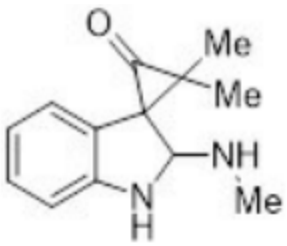
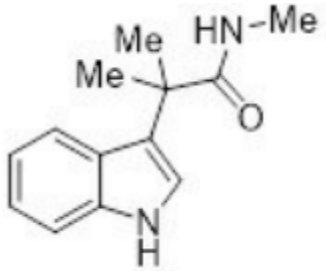
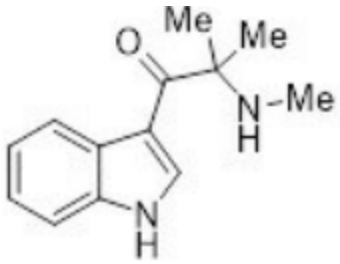


(3) 

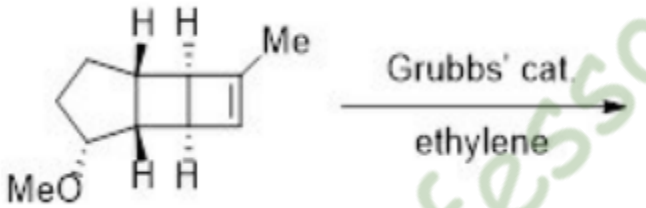
(4) 

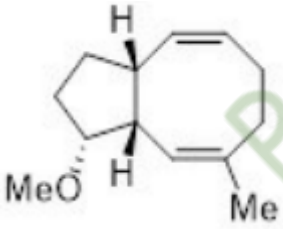
Answer: 3

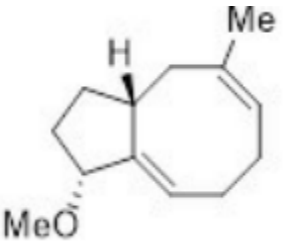
Explanation:

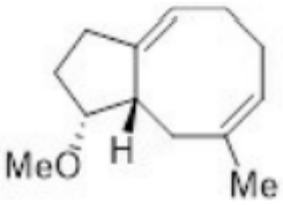
$MeNH_2$ first substitutes the benzylic bromide (SN2) giving a secondary amine, which intramolecularly cyclizes onto the imide carbonyl (aminolysis → imide ring). The stable N-methyl lactamated product corresponds to structure (3).

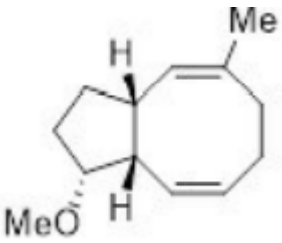
82. The major product formed in the following reaction is



(1) 

(2) 

(3) 

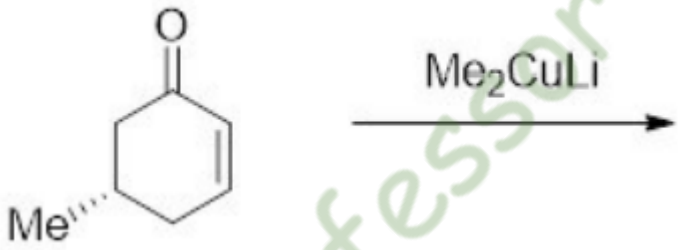
(4) 

Answer: 4

Explanation:

RCM with ethylene removes terminal fragments to the thermodynamically favored internal alkene. The tether length/orientation in the bicyclic system closes to the depicted bicyclic alkene in option (4); ethylene atmosphere drives the equilibrium.

83. The major product formed in the following reaction is



(1) cis-3,5-dimethylcyclohexanone, which is chiral

(2) trans-3,5-dimethylcyclohexanone, which is chiral

(3) cis-3,5-dimethylcyclohexanone, which is achiral

(4) trans-3,5-dimethylcyclohexanone, which is achiral

Answer: 2

Explanation:

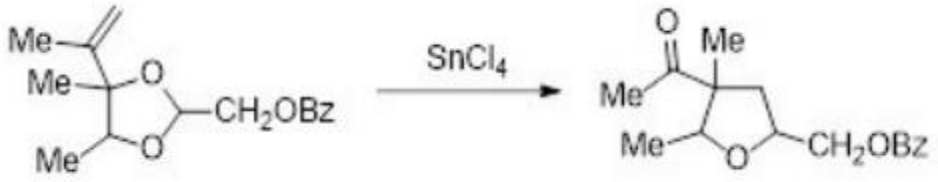
Me_2CuLi performs conjugate (1,4-) addition to an α,β-unsaturated cyclohexenone.

The cuprate adds Me at C-3; the carbonyl survives (no 1,2-addition).

Chair control places the incoming Me equatorial; the pre-existing Me prefers equatorial on the opposite face → trans-1,3 relationship.

A trans-1,3-disubstituted cyclohexanone lacks any mirror plane here, so the product is chiral.

84. The correct sequence of mechanistic steps involved in the formation of product in the following reaction is



(1) Prins cyclization, formation of oxonium ion, pinacol rearrangement

(2) pinacol rearrangement, Prins cyclization and formation of oxonium ion

(3) formation of oxonium ion, Prins cyclization and pinacol rearrangement

(4) pinacol rearrangement, formation of oxonium ion and Prins cyclization

Answer: 3

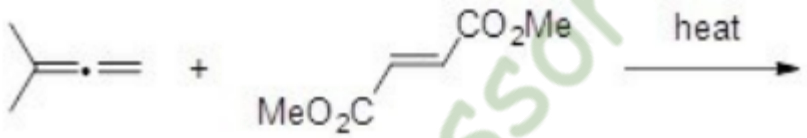
Explanation:

First, the alcohol is protonated → oxonium ion (activates the system).

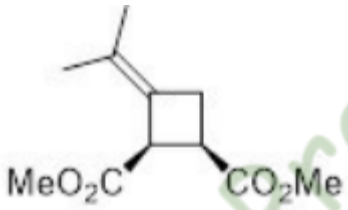
Then the tethered alkene undergoes a Prins cyclization to give a carbocation.

Finally, a 1,2-shift occurs (pinacol rearrangement) to deliver the rearranged product.

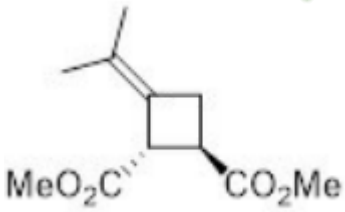
85. The major product formed in the following reaction is

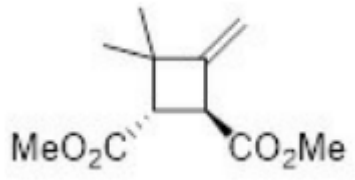


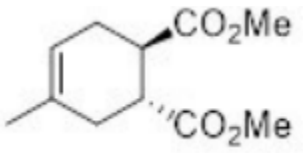
(1)



(2)



(3) 

(4) 

Answer: 2

Explanation:

Heating the diene–dienophile tether triggers an intramolecular Diels–Alder reaction.

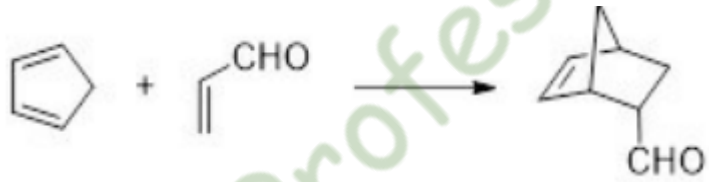
The endo rule governs, placing the two CO_2Me groups syn on the newly formed ring junction.

The tether geometry leads to the bicyclic adduct corresponding to option (2) as the thermodynamically favored product.

86. The reaction that will show a large increase in rate when the reaction medium is changed from a non-polar to a polar organic solvent is

(1) 

(2) 

(3) 

(4) 

Answer: 4

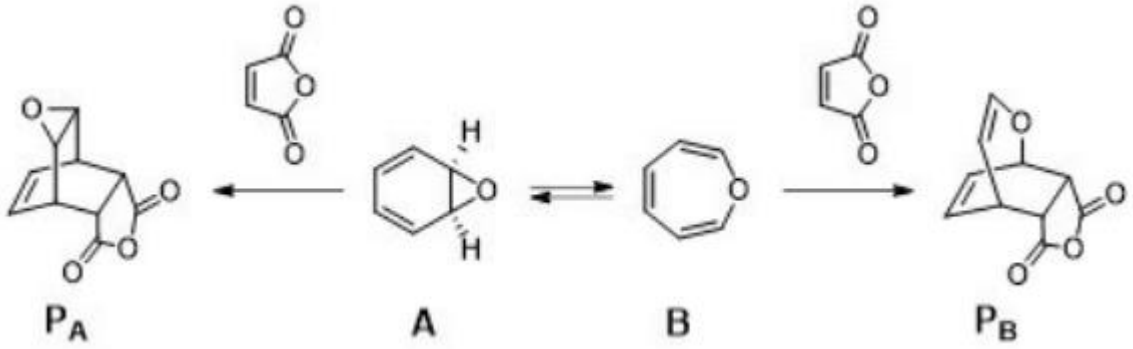
Explanation:

This is a bimolecular SN2 (Menshutkin) quaternization.

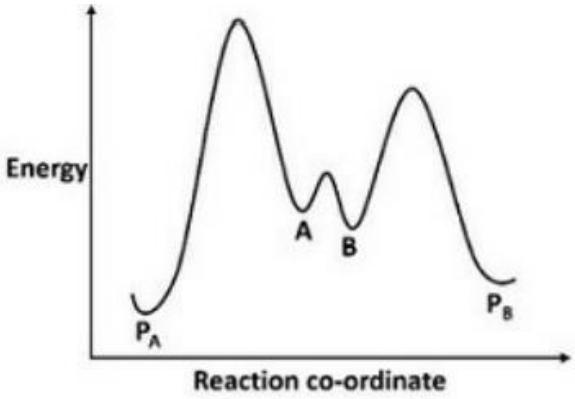
Polar aprotic solvents strongly stabilize the ionic transition state more than the non-polar medium.

Thus the SN2 rate rises markedly on switching to a polar organic solvent, making option (4) the most sensitive.

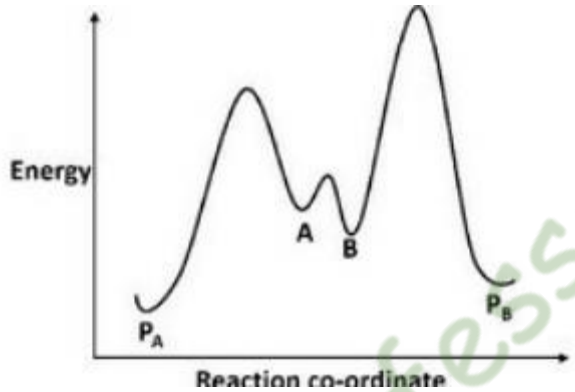
87. The correct energy-profile diagram for the above reactions is



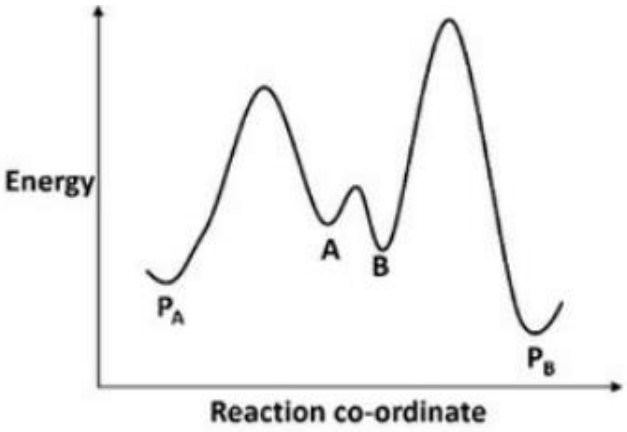
(1)



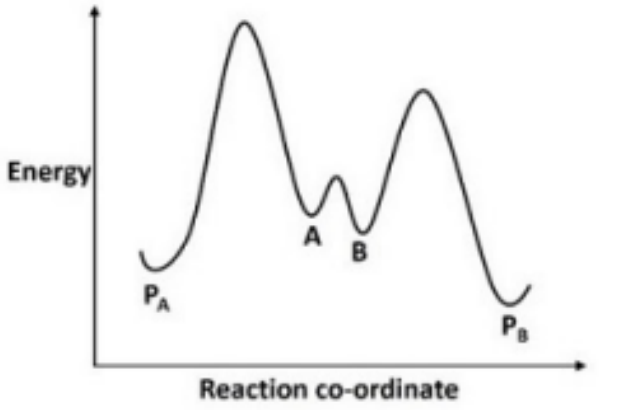
(2)



(3)



(4)



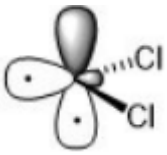
Answer: 3

Explanation:

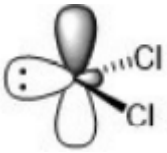
The sequence proceeds by two stepwise processes with an intermediate (A → B). The first step has the higher barrier (rate-determining) and forms a relatively high-energy intermediate A; the second step has a lower barrier to the final product PB. Among the sketches, (3) alone shows PA → A (higher barrier), then A → PB (lower barrier), with PB lower than PA.

88. The structure of the reactive intermediate generated by reaction of CHCl3 with KOH is

(1)

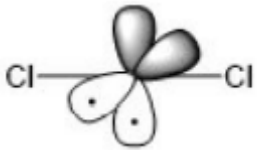


(2)



(3)

(4)

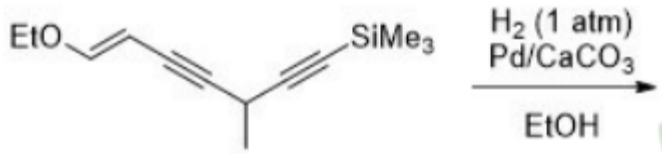


Answer: 2

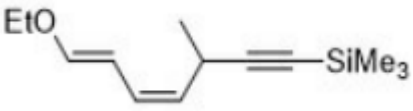
Explanation:

CHCl3/KOH gives dichlorocarbene, :CCl2. It is a singlet carbene: bent, approximately sp2 at carbon, with one lone pair in an sp2 orbital and an empty p orbital perpendicular to the plane. Option (2) depicts this bent singlet carbene with the vacant p orbital.

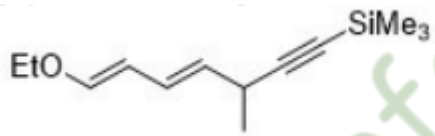
89. The major product formed in the following reaction (H2, Pd/CaCO3, EtOH) is



(1)

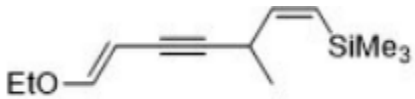


(2)



(3)

(4)



Answer: 1

Explanation:

Pd/CaCO3 (Lindlar/poisoned catalyst) reduces an alkyne selectively to a cis (Z) alkene by syn addition of H2 and stops at the alkene stage. Other groups (TMS, ether) remain intact. Hence the cis-alkene (1) is formed.

90. The reagent that effects the following selective conversion is

(1) NaOMe, MeOH

(2) TBAF, THF

(3) DDQ, CH2Cl2

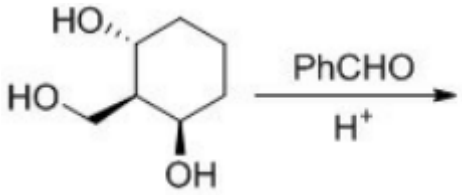
(4) Et3N, MeOH

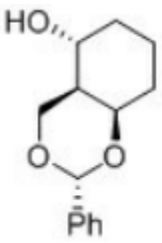
Answer: 3

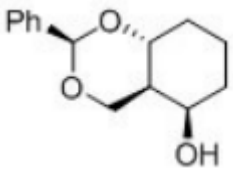
Explanation:

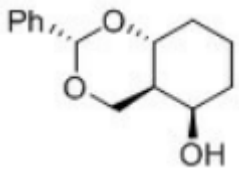
The transformation selectively removes a p-methoxybenzyl (PMB) protecting group from oxygen while leaving benzyl/acetate groups unchanged. DDQ (in CH2Cl2) is the standard reagent for oxidative PMB deprotection under mild conditions, giving the free alcohol. TBAF would remove silyl groups, not PMB; base or Et3N/MeOH would not cleave PMB selectively.

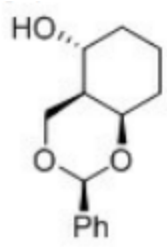
91. The major product formed in the following reaction is



(1) 

(2) 

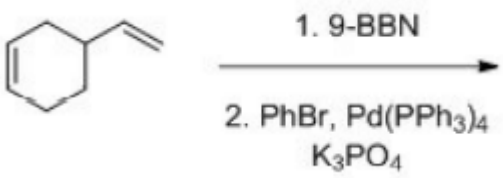
(3) 

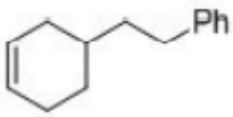
(4) 

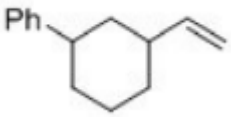
Answer: (3)

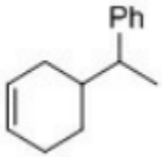
Explanation: Under acid, benzaldehyde condenses with a **1,2-diol** to give the **benzylidene acetal** (five/six-membered cyclic acetal favored). The benzylic acetal is the thermodynamically stable protecting group → structure (3).

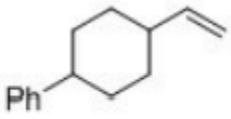
92.The major product formed in the following reaction is



(1) 

(2) 

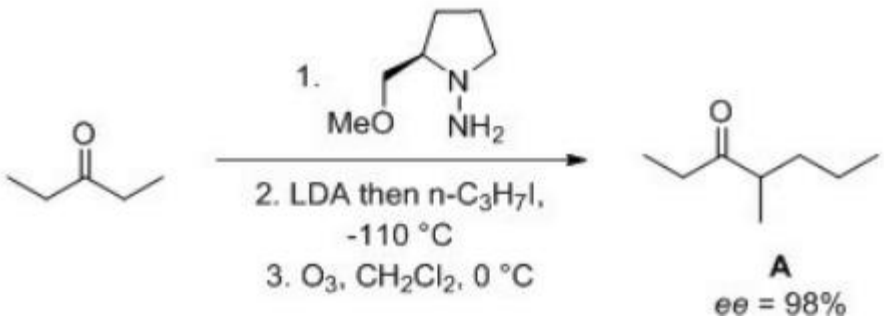
(3) 

(4) 

Answer: (1)

Explanation: 9-BBN adds **regioselectively** (anti-Markovnikov, syn) across the terminal C=C to give a **vinyl/alkyl borane**. In the second step, **Suzuki–Miyaura coupling** with **PhBr** replaces B with **Ph** at the less-hindered terminus, giving the **linear phenylated product** shown in (1), with retention of the alkene geometry set by hydroboration.

93. Given the specific rotation [α]^20_D of (S)-4-methyl-3-heptanone in hexane as +22°, the specific rotation [α]^20_D , in hexane, of the product A (ee = 98%) obtained from the following enantioselective alkylation reaction is



(1) +21.56

(2) +21.12

(3) −21.56

(4) 21.12

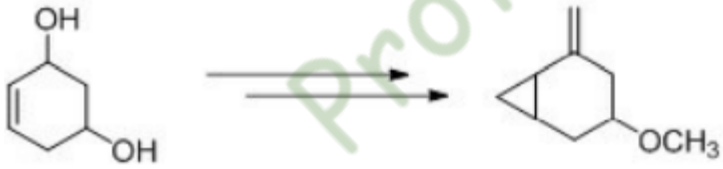
Answer: (3) −21.56

Explanation: Optical rotation of a scalemic sample = **ee × [α] of the pure enantiomer**.

ee = 0.98 ⇒ |[α]| = 0.98 × 22 = **21.56°**.

The auxiliary/enolate alkylation step **inverts the absolute configuration** of the stereogenic center relative to the listed (S) reference, hence **sign changes → −21.56°**.

94. The correct sequence of reagents that will lead to the formation of the given product in the following transformation is



(1) I. active MnO_2; II. MeI, NaH; III. $Me_3S(O)I$, NaH; IV. $MePPh_3Br$, NaH

(2) I. MeI, NaH; II. active MnO_2; III. Me_3SI, NaH; IV. $MePPh_3Br$, NaH

(3) I. CH_2I_2, Zn–Cu; II. $MePPh_3Br$, NaH; III. active MnO_2; IV. MeI, NaH

(4) I. $MePPh_3Br$, NaH; II. active MnO_2; III. CH_2I_2, Zn–Cu; IV. MeI, NaH

Answer: (1)

Explanation:

(logic of sequence 1)

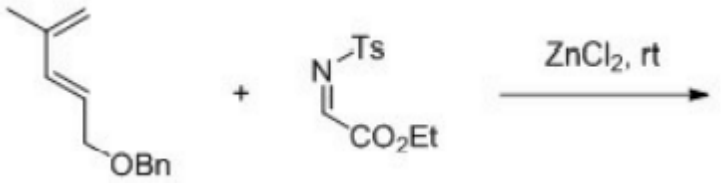
• **Active MnO_2** selectively oxidizes the **allylic alcohol** to the enone/allylic carbonyl.

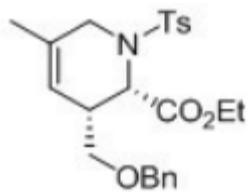
• **MeI/NaH** generates the ylide precursor needed next.

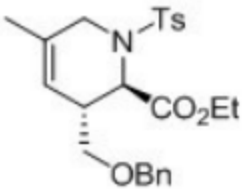
• **$Me_3S(O)I$/NaH** (sulfoxonium ylide) performs a **Johnson–Corey–Chaykovsky** epoxidation/oxonium formation on the carbonyl, setting the bicyclic framework.

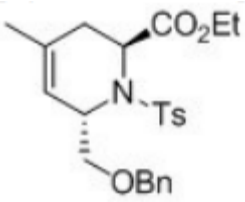
• **$MePPh_3Br$/NaH** (Wittig) finalizes the **methoxy/methylene** substitution pattern shown in the product. Overall, only sequence **(1)** maps cleanly onto the required functional-group changes.

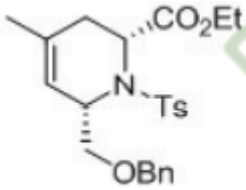
93. The major product formed in the following reaction is



(1) 

(2) 

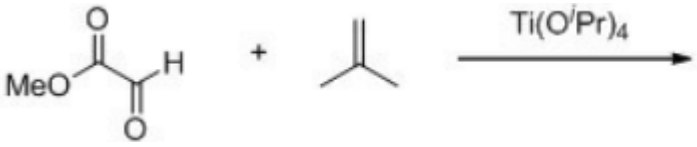
(3) 

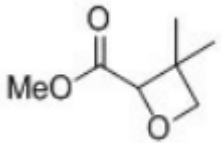
(4) 

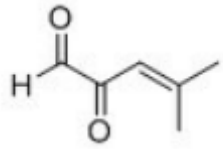
Answer: (4)

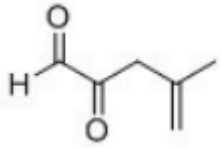
Explanation:$ZnCl_2$ forms the **iminium** from the aldehyde/amine and promotes the **Povarov (aza-Diels–Alder) reaction** of the electron-rich styrene. **Endo-selective, para-directed** cycloaddition followed by trapping gives the **dihydroquinoline**/tetrahydroquinoline isomer shown in **(4)**; this regioisomer is favored by the para orientation and HOMO(alkene)–LUMO(iminium) control.

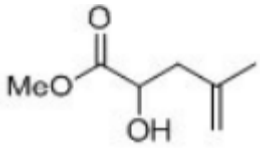
93. The major product formed in the following reaction is



(1) 

(2) 

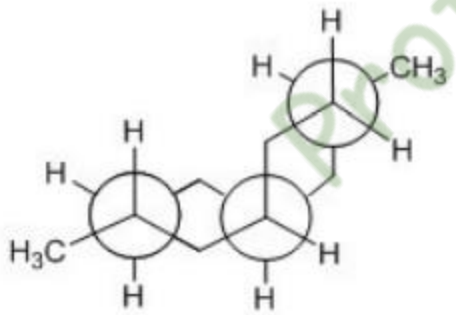
(3) 

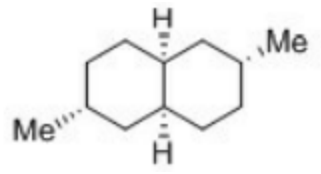
(4) 

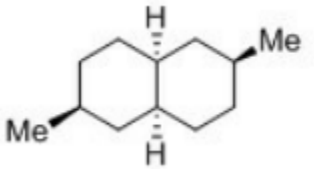
Answer: (4)

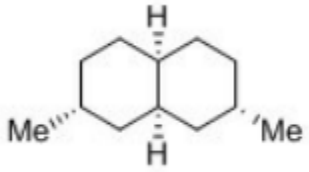
Explanation: 2,2-Dimethoxypropane in the presence of Ti(OiPr)_4 selectively converts a 1,2-/1,3-diol into the **isopropylidene acetal (acetonide)**. The ester/acid functions are untouched, so the protected acetonide product (4) is formed.

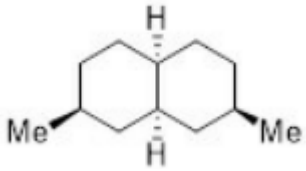
97. The Newman projection shown corresponds to the compound



(1) 

(2) 

(3) 

(4) 

Answer: (1)

Explanation: The three consecutive C–C bonds are all **staggered** with the terminal substituents **anti**. Mapping front/back substituents onto the ring places both Me groups **equatorial** in a **trans-decalin**, matching (1).

98. A compound shows MMM$^+$ at m/z 84 with a base peak at 56 and gives one ^{1}H NMR signal at δ 1.4 ppm and one ^{13}C NMR signal at δ 35 ppm. The compound is

(1) cyclobutane-1,3-dione

(2) dichloromethane

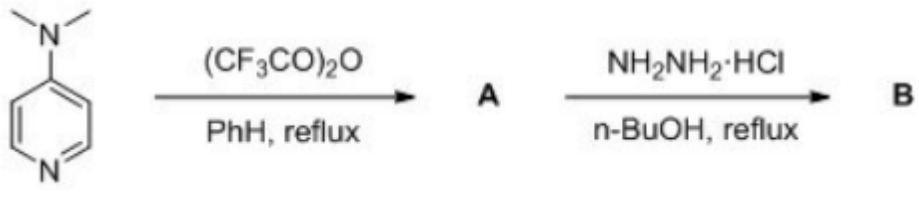
(3) cyclohexane

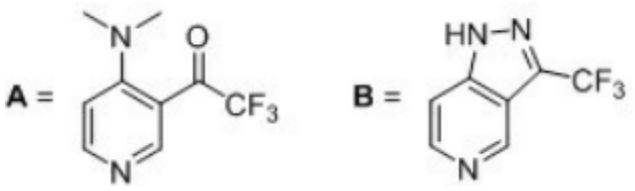
(4) 1,2,3-trimethylcyclopropane

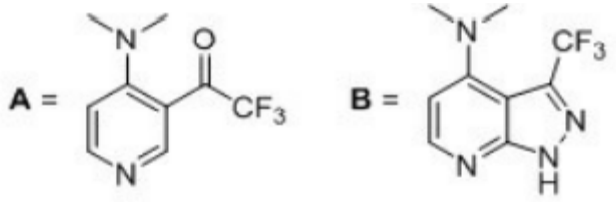
Answer: (3)

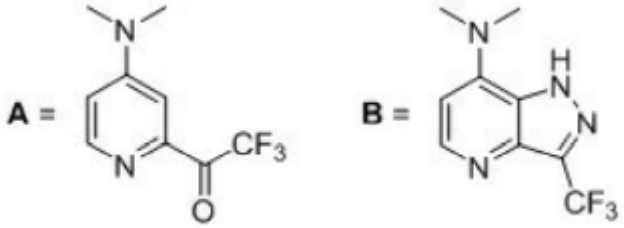
Explanation: Molecular mass 84 fits C_6H_{12} (cyclohexane). High symmetry gives **one proton** and **one carbon** environment. A common fragment at **m/z 56** ($C_4H_8^+$) matches cyclohexane cracking.

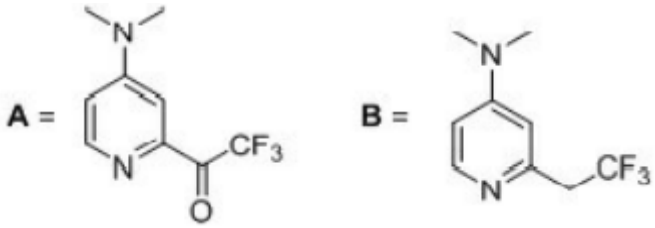
99.The major products A and B in the sequence with $(CF_3CO)_2O$ (PhH, reflux) followed by $NH_2NH_2{\cdot}HCl$ (n-BuOH, reflux) are



(1) 

(2) 

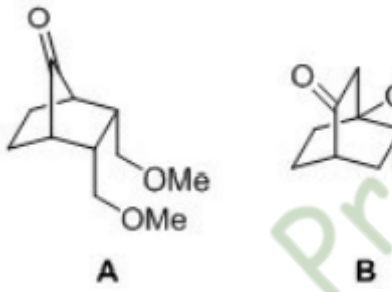
(3) 

(4) 

Answer: (1)

Explanation: Acylation of pyridine N-oxide with $(CF_3CO)_2O$ triggers a **Boekelheide/aza-acylation** giving the **2-(trifluoroacetyl) derivative (A)**. **Hydrazine hydrochloride** then condenses with the CF_3-acyl group to the **aza-heterocycle (B)** drawn in option (1).

100. The correct relationship between the two faces of the C=O group in compounds A and B is



(1) A = diastereotopic; B = enantiotopic

(2) A = B = enantiotopic

(3) A = enantiotopic; B = diastereotopic

(4) A = B = diastereotopic

Answer: (1)

Explanation: In **A**, pre-existing stereocenters make the two faces of the carbonyl **non-equivalent as diastereotopic**. In **B**, there is no element breaking enantiomeric symmetry at that carbonyl; its two faces are **enantiotopic**.

101. For every atom that is not shifted under C4 and σ symmetry operation, the characters are, respectively,

(1) -1, -1

(2) 0, 0

(3) 1, 1

(4) -1, 1

Answer: (1) -1, -1

Explanation: For a basis tied to an atom on the principal axis/plane, the character is the sum of direction cosines of its unit vectors after the operation. A C4 rotation reverses two perpendicular components (net -1), and reflection in the vertical plane inverts one component relevant to the basis used here (net -1).

102. The equivalent symmetry operation for S6^3 and S6^3 are, respectively,

(1) C3 and C2

(2) σh and i

(3) σh and E

(4) i and E

Answer: (4) i and E

Explanation: S6 = C6·σh. Thus S6^3 = (C6·σh)^3 = C6^3·σh^3 = C2·σh = i. Reapplying S6^3 again gives (S6^3)^2 = i^2 = E.

103. A system of N identical distinguishable non-interacting particles with two levels (0 and ε). The constant-volume heat capacity Cv is (β = 1/kBT):

(1) Nk_B

(2) $Nk_B \left(\frac{\epsilon\beta}{1+e^{\epsilon\beta}}\right)^2$

(3) $Nk_B \left(\frac{\epsilon\beta e^{\epsilon\beta/2}}{1+e^{\epsilon\beta}}\right)^2$

(4) $Nk_B \left(\frac{\epsilon\beta e^{-2\epsilon\beta}}{1+e^{-\epsilon\beta}}\right)^2$

Answer: (3)

Explanation: For a two-level system, ⟨E⟩ = ε/(1+e^{βε}). Then Cv = (∂⟨E⟩/∂T)_V = kB(εβ)^2 e^{βε}/(1+e^{βε})^2 = N kB (εβ e^{εβ/2}/(1+e^{εβ}))^2.

104. Plutonium (M = 244 g mol^-1) crystallizes monoclinic (a = 620 pm, b = 480 pm, c = 1100 pm, β = 102°) with 16 atoms per cell. The density (g cm^-3) is closest to (use sinβ = 0.98, sin(β/2)=0.78):

(1) 25.38

(2) 16.12

(3) 12.69

(4) 20.26

Answer: (4) 20.26

Explanation: V = a b c sinβ = (6.20×10^-8 cm)(4.80×10^-8 cm)(1.10×10^-7 cm)(0.98) ≈ 3.23×10^-22 cm^3. Mass per cell = (16×244 g mol^-1)/NA ≈ 6.48×10^-21 g. ρ = m/V ≈ 6.48×10^-21 / 3.23×10^-22 ≈ 20.1–20.3 g cm^-3.

105. In Langmuir adsorption, a solid adsorbs 0.25 mg at 50 bar and 0.2 mg at 20 bar. The percentage surface coverage at 50 bar is close to:

(1) 75

(2) 38

(3) 57

(4) 83

Answer: (4) 83

Explanation: Langmuir: x = k p θ with x ∝θ/(1-θ). Using two pressures, solve for θ: (0.25/0.2) = (θ50/(1-θ50)) / (θ20/(1-θ20)) with p50/p20 = 50/20; eliminating k gives θ50 ≈ 0.83 → 83%.

106. A polystyrene sample has weight fractions 0.20, 0.50, 0.30 with molecular weights 10,000; 40,000; 60,000. The weight-average molecular weight Mw is:

(1) 40000

(2) 55000

(3) 50000

(4) 60000

Answer: (1) 40000

Explanation: Mw = Σ(wi Mi) = 0.20×10000 + 0.50×40000 + 0.30×60000 = 2000 + 20000 + 18000 = 40000.

107. For a weak electrolyte (e.g., acetic acid), the relation among conductance λ, equilibrium constant K, and concentration C (λ° = molar conductance at infinite dilution) is:

1. $\frac{1}{\lambda} = \frac{1}{\lambda^0} - \frac{C\lambda}{K\lambda^0}$
2. $\frac{1}{\lambda} = \frac{1}{\lambda^0} + \frac{C\lambda}{K\lambda^{0^2}}$
3. $\frac{1}{\lambda^o} = \frac{1}{\lambda} + \frac{C\lambda}{K\lambda^{o^2}}$
4. $\frac{1}{\lambda} = \frac{C\lambda}{K\lambda^{0^2}}$

Answer: (2)

Explanation: From Ostwald's dilution law for weak electrolytes: K = (λ^2 C)/(λ°(λ°−λ)) ⇒ 1/λ = 1/λ° + C/(Kλ°^2) with the sign as in option (2).

108. For cell Cd|CdCl2||AgCl|Ag with E°cell = 0.675 V and (dE°/dT) = −6.5×10^-4 V K^-1 at 27 °C, the reaction Cd + 2AgCl → 2Ag + CdCl2 has ΔH (kJ mol^-1) closest to:

(1) -168

(2) -123

(3) -95

(4) -23

Answer: (1) -168

Explanation: n = 2. Use ΔH = −nF(E − T dE/dT). With T ≈ 300 K, T dE/dT = 300×(−6.5×10^-4) = −0.195 V. E − T dE/dT = 0.675 − (−0.195) = 0.870 V. ΔH ≈ −(2×96485 C mol^-1)×0.870 V ≈ −1.68×10^5 J mol^-1 ≈ −168 kJ mol^-1.

109. The rate constant for the reaction $A_2B_4O \rightarrow AB_4 + AO$ is described as log k = 14.1 – 10000K/T. The activation energy for this reaction (in kJ mol⁻¹) is closest to:

(1) 191.4

(2) 83.14

(3) 382.8

(4) 166.28

Answer: (1) 191.4

Explanation: log k = log A – (E_a / 2.303R)(1/T). Slope = –E_a / (2.303R) = –10000.

Hence E_a = 2.303 × 8.314 × 10^4 J mol⁻¹ ≈ 1.91×10^5 J mol⁻¹ = 191.4 kJ mol⁻¹.

110. For the reaction $[cis\text{-}M(en)_2(OH)_2]^+ \rightleftharpoons [trans\text{-}M(en)_2(OH)_2]^+$, K = 0.16 and $k_1 = 3.3\times10^{-4}$ s^{-1}.
If the reaction starts with pure cis form, the time required for half of the equilibrium amount of trans isomer to form is approximately:

(1) 290 s

(2) 580 s

(3) 190 s

(4) 480 s

Answer: (1) 290 s

Explanation: $k_2 = k_1/K = 3.3\times10^{-4} / 0.16 = 2.06\times10^{-3}\ s^{-1}$.

For reversible first-order reactions, B(t) = B_eq $(1 - e^{-}(k_1 + k_2)t)$.

At half equilibrium, $t = (\ln 2)/(k_1 + k_2) = 0.693 / 2.39\times10^{-3} \approx 2.9\times10^{2}$ s ≈ 290 s.

111. The stopping potential for photoelectrons emitted by light of frequency 6.0×10^{8} MHz is 0.72 V. When the stopping potential becomes 1.44 V, the new frequency is approximately:

(1) 7×10^{8} MHz

(2) 4×10^{8} MHz

(3) 2×10^{9} MHz

(4) 7×10^{14} Hz

Answer: (1) 7×10^{8} MHz

Explanation: From $e\Delta V = h\Delta\nu$, $\Delta\nu = (e/h)\,\Delta V = (2.4\times10^{14}) \times 0.72 = 1.73\times10^{14}$ Hz.

$\nu_2 = \nu_1 + \Delta\nu = 6.0\times10^{14} + 1.73\times10^{14} = 7.73\times10^{14}$ Hz ≈ 7×10^{8} MHz.

112. An electron ($m = 9.1\times10^{-31}$ kg) has energy 13.6 eV in an infinite potential well.
If the potential is zero inside the well, the expectation value of v^2 is:

(1) 3×10^{12}

(2) 4.3×10^{-18}

(3) 4.7×10^{12}

(4) 4.7×10^{31}

Answer: (3) $4.7\times10^{12}\ m^2\ s^{-2}$

Explanation: $E = \frac{1}{2} m v^2 \Rightarrow v^2 = 2E/m = (2\times13.6\times1.602\times10^{-19})/(9.1\times10^{-31}) \approx 4.8\times10^{12}\ m^2\ s^{-2}$.

113. The molecule that does not absorb in the microwave region but does absorb in the infrared is:

(1) N_2

(2) C_2H_2

(3) HCl

(4) H_2O

Answer: (2) C_2H_2

Explanation: Microwave absorption requires a permanent dipole moment.

C_2H_2 is linear and non-polar → no rotational microwave absorption.

Vibrations induce temporary dipoles → IR active.

114. From the set below, which statements are correct?

(i) If q is the displacement in harmonic motion, potential energy $\propto q$.

(ii) If $\nu(HCl) = 2990\ cm^{-1}$, zero-point energy = $1495\ cm^{-1}$.

(iii) For $O–^1H(X_1)$, $O–^2H(X_2)$, $O–^3H(X_3)$: $\nu_1>\nu_2>\nu_3$.

(iv) If fundamental transition = $1880\ cm^{-1}$, first overtone = $940\ cm^{-1}$.

(1) (i, ii, iii)

(2) (i, ii, iv)

(3) (ii, iii)

(4) (i, iv)

Answer: (3) (ii, iii)

Explanation: (i) False, $V \propto q^2$ for harmonic oscillator.

(ii) True, ZPE = $\frac{1}{2}\nu$.

(iii) True, heavier isotopes → larger μ→ smaller ν.

(iv) False, first overtone $\approx 2\nu$, not $\frac{1}{2}\nu$.

115. The following data is obtained for a light diatomic (AB) molecule from its rotational Raman spectrum:

$B = 2\ cm^{-1}$; $x_e = 0.01$; $\bar{\nu}_e = 1600\ cm^{-1}$.

If the molecule is irradiated by a laser of $20\,000\ cm^{-1}$, the expected Stokes lines (in cm^{-1}) for this molecule are:

(1) 18348, 18356, 18368, 18380, 18388

(2) 18412, 18420, 18432, 18444, 18452

(3) 18380, 18388, 18400, 18412, 18420

(4) 18416, 18424, 18430, 18440, 18452

Answer: (2)

Explanation:

The fundamental vibrational transition occurs near $\bar{\nu} = \bar{\nu}_e(1 - 2x_e) = 1600\ (1 - 0.02) = 1568\ cm^{-1}$.

Therefore, the Raman Stokes line corresponds to $20\,000 - 1568 = 18\,432\ cm^{-1}$.

Rotational Raman satellites appear at separations of about $4B = 8\ cm^{-1}$ on either side, producing Stokes lines at 18412, 18420, 18432, 18444 and $18452\ cm^{-1}$.

Hence, option (2) represents the correct set of Stokes frequencies.

116. Liquid A has half the surface tension and twice the density of liquid B at 30 °C.

Contact angles of A and B are the same. If A rises 10 cm in a capillary, the rise of B (in cm) is:

(1) 60

(2) 10

(3) 40

(4) 20

Answer: (3)

Explanation:

Capillary rise h is given by $h = 2\gamma \cos\theta / (\rho g r)$.

For the same capillary and contact angle, $h \propto \gamma/\rho$.

Given that $\gamma_a = \frac{1}{2}\gamma_\beta$ and $\rho_a = 2\,\rho_\beta$, we get $(\gamma_a/\rho_a) = (\frac{1}{2}\,\gamma_\beta)/(2\,\rho_\beta) = \frac{1}{4}\,(\gamma_\beta/\rho_\beta)$.

Thus $h_a / h_\beta = \frac{1}{4}$, so $h_\beta = 4\,h_a = 4 \times 10 = 40$ cm.

Hence, liquid B rises four times higher due to the combined effect of greater γ/ρ ratio.

117. The surface tension of a dilute soap solution is lower than that of pure water because:

(1) Soap molecules accumulate more at the surface than in the bulk solution

(2) Soap molecules accumulate more in the bulk than on the surface

(3) Soap molecules aggregate uniformly in the bulk and surface

(4) Soap molecules form micelles only at very low concentration

Answer: (1)

Explanation:

Soap molecules are amphiphilic; their hydrophobic tails repel water while hydrophilic heads attract it.

At the air–water interface, they orient with hydrophobic tails outward and heads inward, decreasing the cohesive forces among surface water molecules.

This reduces the surface free energy, thus lowering surface tension.

Micelle formation occurs only beyond the critical micelle concentration (CMC), but the major reason for the initial fall in surface tension at low concentration is the surface adsorption, not micellization.

118. The maximum number of phases that can coexist in equilibrium for a one-component system is:

(1) 1

(2) 2

(3) 3

(4) 4

Answer: (3)

Explanation:

From Gibbs' phase rule: $F = C - P + 2$.

For a one-component system ($C = 1$), equilibrium of all phases gives $F = 1 - P + 2 = 3 - P$.

When $F = 0$ (no degrees of freedom), $P = 3$.

Hence, at the triple point, three phases (solid, liquid, and vapor) coexist in equilibrium.

This is seen in water at 0.01 °C and 4.58 mm Hg, confirming that three is the maximum number of phases for a single component.

119. The quantum number corresponding to the z-component of total electronic orbital angular momentum in nitric oxide (NO) is:

(1) 0

(2) 1

(3) 2

(4) 3

Answer: (2)

Explanation:

In NO, the ground electronic state is $^2\Pi$, where the Greek letter Π represents $\Lambda = 1$, the projection of the total orbital angular momentum L on the internuclear axis (z-axis).

For diatomic molecules, $\Sigma = 0$, $\Pi = 1$, $\Delta = 2$, $\Phi = 3$, etc.

Therefore, the z-component (L_z) of L corresponds to $\Lambda = 1$, so the quantum number for L_z is 1.

120. When a hydrogen atom is subjected to a perturbation $V = E \cdot z$, the first-order correction to the wave function arises primarily from the orbital:

(1) 2_s

(2) $2p_z$

(3) $3p_y$

(4) $3d_{z^2}$

Answer: (2)

Explanation:

The perturbation $V = E \cdot z$ introduces an electric dipole field along z.

The z operator has $\Delta l = \pm 1$ and $\Delta m = 0$ selection rules.

Thus, the 1s ground state ($l = 0$, $m = 0$) can couple only to $2p_z$ ($l = 1$, $m = 0$).

Neither 2s ($\Delta l = 0$), $3p_y$ ($m \neq 0$), nor $3d_{z^2}$ ($\Delta l = 2$) satisfy these criteria.

Hence, the first-order wave-function correction comes exclusively from the $2p_z$ state due to the direction of the electric field.