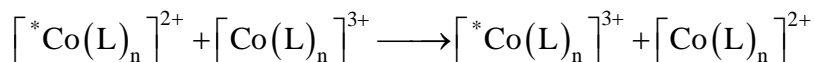


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CHEMICAL SCIENCES

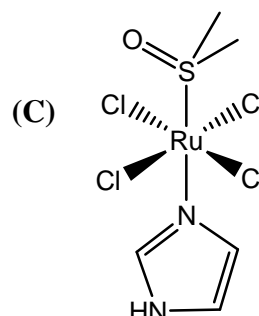
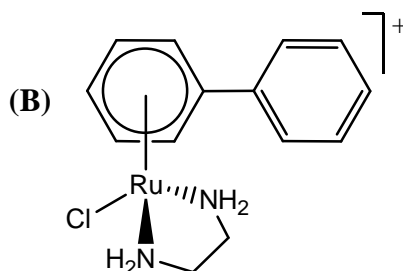
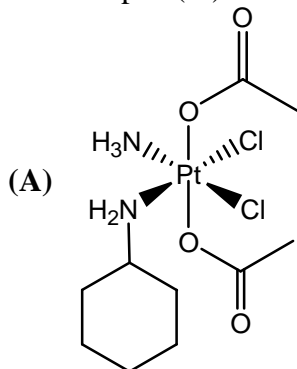
PART-B

1. For the given reaction,



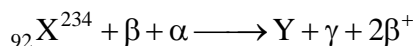
the correct statement with respect to the rate of electron transfer process is
o-phen = *o*-phenanthroline; *Co is labeled atom.

- (a) fast electron transfer; $L = NH_3$; $n = 6$
 (b) slow electron transfer; $L = o\text{-phen}$; $n = 3$
 (c) very slow electron transfer; $L = NH_3$; $n = 6$
 (d) very slow electron transfer; $L = o\text{-phen}$; $n = 3$
2. 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
 (a) (ii) and (iv) (b) (iii) and (iv) (c) (i) and (iv) (d) (ii) and (iii)
3. 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.
4. 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}
5. 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 $[FeCl_4]^{2-}$
6. 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
7. The reason for significantly high solubility of $AgClO_4$ 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
8. The complex(es) showing activity against cancerous cells is/are



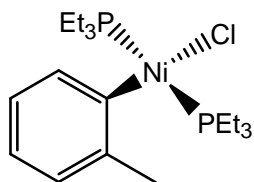
- (a) (A) only (b) (A) and (B) only (c) (A) and (C) only (d) (A), (B) and (C)

9. Consider the nuclear reaction,

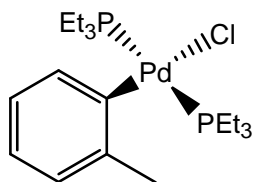


- (a) ${}_{92}\text{Y}^{238}$ (b) ${}_{91}\text{Y}^{238}$ (c) ${}_{93}\text{Y}^{236}$ (d) ${}_{94}\text{Y}^{238}$

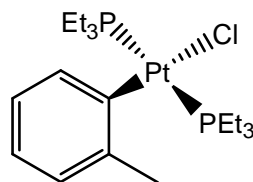
10. The order of rate of substitution of chloride by pyridine (in ethanol) in the following complexes



(I)



(II)



(III)

- (a) I > II > III (b) I ≈ II ≈ III (c) I > II ≈ III (d) I < II ≈ III

11. The number of geometrical isomers of the complex $[\text{RhH}(\text{C} \equiv \text{CR})_2(\text{PMe}_3)_3]$ is

- (a) 2 (b) 3 (c) 4 (d) 1

12. 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 σ^* -orbital of iodine with lone pair of O (solvent)

(C) Formation of a charge-transfer complex.

- (a) (A) only (b) (B) only (c) (A) and (B) only (d) (B) and (C) only

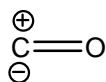
13. Choose the correct order of energy of $2\sigma_g$ and $1\pi_u$ molecular orbitals for B_2 , C_2 and O_2 .

- (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

14. The natural product that gives a signal at δ 218 ppm in its ^{13}C NMR spectrum is

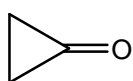
- (a) α -pinene (b) camphor (c) geraniol (d) carvone

15. The synthetic equivalent of the given synthon is

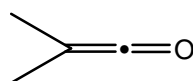


- (a) *t*-butyl isocyanide (b) *t*-butyl cyanide (c) *t*-butyl cyanate (d) *t*-butyl isocyanate

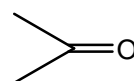
16. The correct order of carbonyl stretching frequency for the given compounds is



(A)



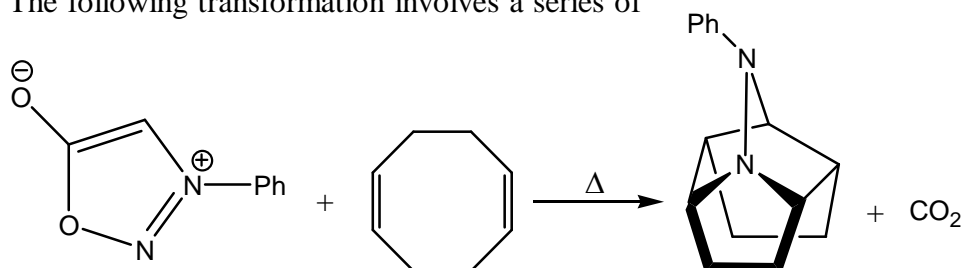
(B)



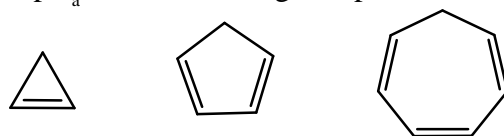
(C)

- (a) A > B > C (b) B > C > A (c) C > A > B (d) B > A > C

17. The following transformation involves a series of

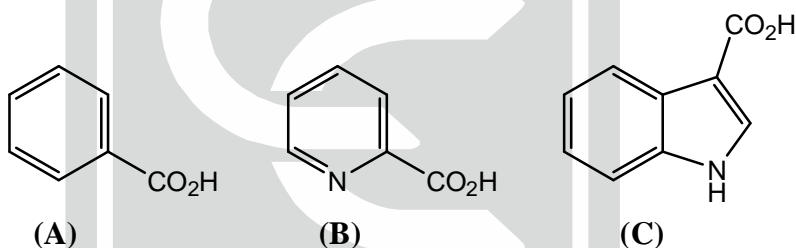


- (a) Electrocyclic ring-opening and closing reactions
 (b) Cycloaddition and cycloreversion reactions
 (c) Sigmatropic rearrangements
 (d) Chelotropic addition and elimination reactions.
18. The correct order of the pK_a of the following compounds is



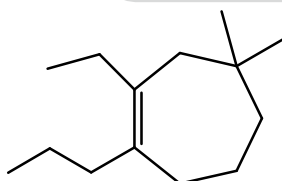
(A) (B) (C)

- (a) $C > B > A$ (b) $A > C > B$ (c) $B > A > C$ (d) $A > B > C$
19. The following carboxylic acids undergo decarboxylation upon heating. The ease of decarboxylation is in the order

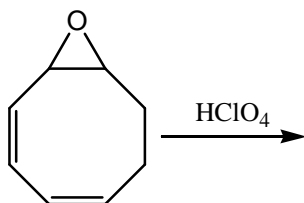


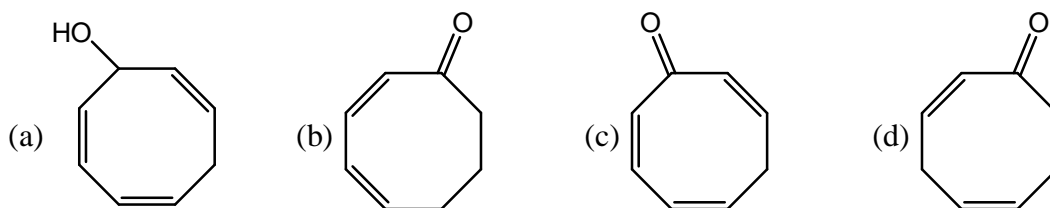
(A) (B) (C)

- (a) $B > A > C$ (b) $C > B > A$ (c) $A > C > B$ (d) $C > A > B$
20. The correct IUPAC name for the following molecule is

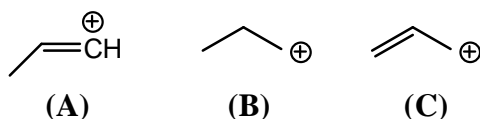


- (a) 1-Propyl-2-ethyl-4, 4-dimethylcyclohept-1-ene
 (b) 2-Ethyl-4, 4-dimethyl-1-propylcyclohept-1-ene
 (c) 3-Ethyl-1, 1-dimethyl-4-propylcyclohept-3-ene
 (d) 1, 1-Dimethyl-3-ethyl-4-propylcyclohept-3-ene
21. The major product formed in the following reaction is



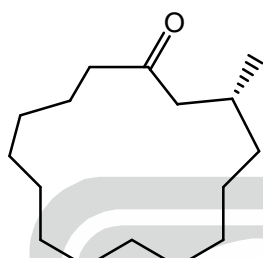


22. The correct order of stability of the carbocations **A-C** is



- (a) $C > A > B$ (b) $A > C > B$ (c) $B > C > A$ (d) $C > B > A$

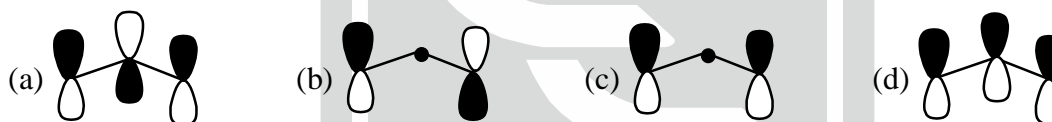
23. Muscone is a



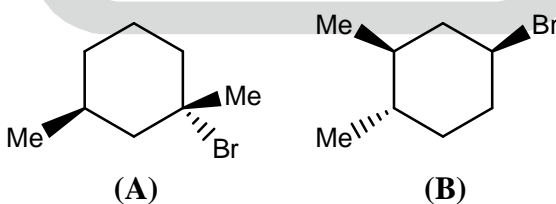
Muscone

- (a) terpenoid (b) steroid (c) polyketide (d) flavonoid

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

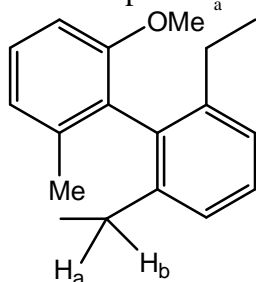


25. The correct statement for the orientation of the bromine atoms in the most stable conformations of A and B is



- (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)

26. The stereochemical relationship of H_a and H_b in the following



- (a) enantiotopic (b) homotopic (c) diastereotopic (d) constitutionally heterotopic



32. 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

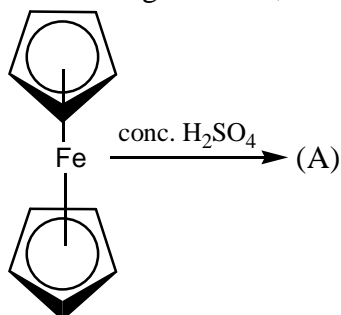
- (a) -0.2 (b) -0.1 (c) 0 (d) 0.2
33. The total bond order between adjacent carbon atoms of benzene is
(a) 0.5 (b) 2 (c) 1.5 (d) 2.5
34. The equilibrium dissociation energy of a diatomic molecule is 4.75 eV and its stretching frequency corresponds to 0.5 eV. The minimum energy required to dissociate the molecule in eV is
(a) 4.75 (b) 4.25 (c) 4.50 (d) 5.00
35. 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)
36. 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) $p \propto \frac{1}{V^{5/3}}$
37. 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 g mol^{-1} is
(a) 10^9 (b) 10^5 (c) 10^6 (d) 10^7
38. The correct statement about chemisorption is
(a) Chemisorption results in multi molecular layer adsorption
(b) Chemisorption is reversible in nature
(c) Chemisorption has lower specificity than physisorption
(d) Chemisorption occurs due to formation of chemical bonds.
39. The expectation value of p^2 of a particle in a cubic box of side ℓ , having the wavefunction $\psi_{n_x, n_y, n_z}(x, y, z) = \left(\frac{2}{\ell}\right)^{3/2} \sin \frac{2\pi x}{\ell} \sin \frac{3\pi y}{\ell} \sin \frac{2\pi z}{\ell}$, is
(a) $\frac{17h^2}{4\ell^2}$ (b) $\frac{7h^2}{4\ell^2}$ (c) $\frac{3h^2}{\ell^2}$ (d) $\frac{13h^2}{4\ell^2}$
40. The $E^0(M^+/M)$ 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 $\left(\frac{\sqrt{m}}{T}\right)$

PART - C

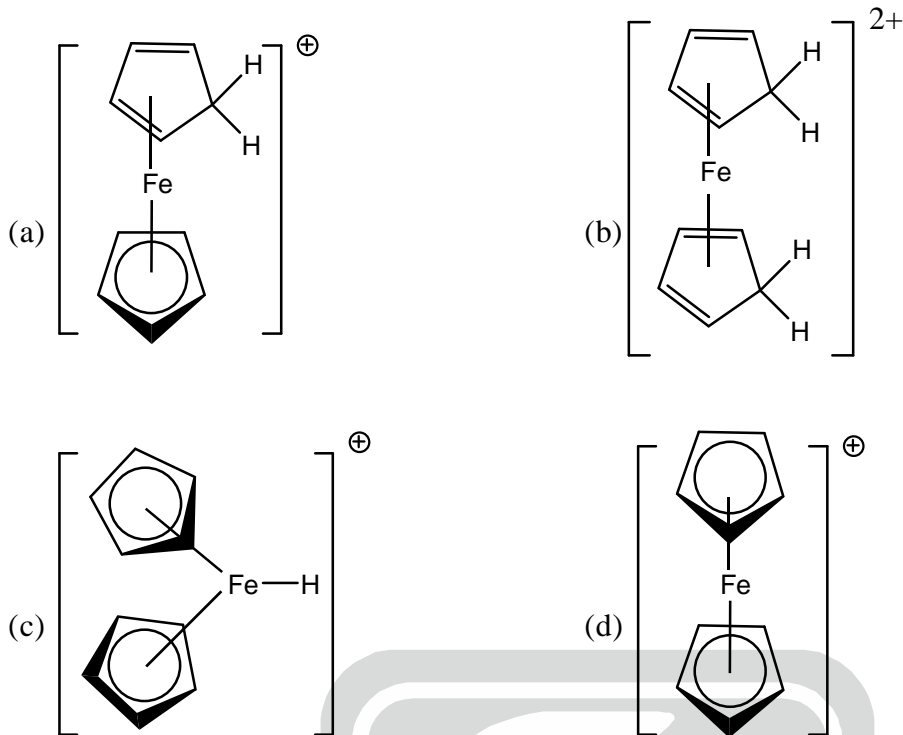
- The reaction of XeF_6 with a limited amount of quartz gives compound A. Then on reaction with an equivalent amount of XeO_3 A gives B. The products A and B are, respectively.

(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
- The geometry/shape of the Fe_4 core of the cluster $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ is
 (a) tetrahedron (b) square pyramid (c) butterfly (d) trigonal bipyramid
- 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
- The correct electronic configuration of frontier MO's of $\text{Mn}(\eta^5\text{-C}_5\text{Me}_5)_2$ is
 (a) $e_{2g}^2 a_{1g}^1 e_{1g}^2$ (b) $e_{2g}^4 a_{1g}^1$ (c) $e_{2g}^3 a_{1g}^2$ (d) $a_{1g}^2 e_{2g}^3$
- The correct match for **Column-A** with **Column-B** is

Column-A	Column-B
(A) $f \rightarrow f$ 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) (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)
- On heating $[\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ and $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$, the products formed are respectively
 (a) $[(\eta^6\text{-PhPMe}_2)\text{Mo}(\text{PMe}_2\text{Ph})_3]$ and $[(\eta^6\text{-PhPMe}_2)\text{Re}(\text{PMe}_2\text{Ph})_3]\text{Cl}$
 (b) $[(\text{PMe}_2\text{Ph})_4\text{Mo}(\mu\text{-N}_2)_2\text{Mo}(\text{PMe}_2\text{Ph})_4]$ and $[(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-Cl})_2\text{Re}(\text{PMe}_2\text{Ph})_4]$
 (c) $[(\eta^6\text{-PhPMe}_2)\text{Mo}(\text{PMe}_2\text{Ph})_3]$ and $[(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-Cl})_2\text{Re}(\text{PMe}_2\text{Ph})_4]$
 (d) $[(\text{PMe}_2\text{Ph})_4\text{Mo}(\mu\text{-N}_2)_2\text{Mo}(\text{PMe}_2\text{Ph})_4]$ and $[(\eta^6\text{-PhPMe}_2)\text{Re}(\text{PMe}_2\text{Ph})_3]\text{Cl}$
- The product (A) of the following reaction,



is

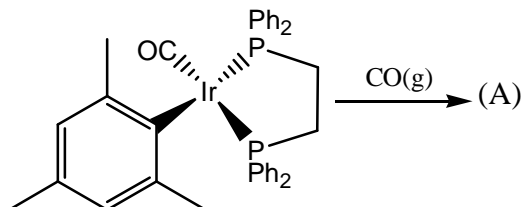


8. Consider the following statements for Allred-Rochow electronegativity (χ_{AR}):
- (I) χ_{AR} is directly proportional to Z_{eff} .
- (II) χ_{AR} is inversely proportional to Z_{eff} .
- (III) χ_{AR} is inversely proportional to $r(\text{covalent})$
- (iv) χ_{AR} is inversely proportional to $r^2(\text{covalent})$
- The correct statements are
- (a) (I) and (IV) (b) (II) and (IV) (c) (I) and (III) (d) (II) and (III)
9. 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) $(\eta^3\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (b) $(\eta^5\text{-C}_5\text{Ph}_5)\text{Mn}(\text{CO})_3$
- (c) $(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_3$ (d) $(\eta^5\text{-indenyl})\text{Mn}(\text{CO})_3$
10. In the following sequence of reactions the correct (P), (Q) and (R) are respectively
- (P) (Q) (R)
- in dil. AcOH $\xrightarrow[\text{thiourea}]{\text{solid}}$ N_2 gas \uparrow + Solution $\xrightarrow[\text{soln.}]{\text{dil. FeCl}_3}$ blood red $\xrightarrow[\text{soln.}]{\text{dil. HgCl}_2}$ Colourless
- (a) $\text{KNO}_2, \text{CO}_2, [\text{Fe}(\text{H}_2\text{O})_5(\text{S})]^+$, HgS
- (b) $\text{KNO}_2, \text{N}_2, [\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}, [\text{Hg}(\text{SCN})_4]^{2-}$
- (c) $\text{KNO}_3, \text{N}_2, [\text{Fe}(\text{H}_2\text{O})_5(\text{CN})]^{2+}, [\text{Hg}(\text{OCN})_4]^{2-}$
- (d) $\text{NaN}_3, \text{N}_2, [\text{Fe}(\text{H}_2\text{O})_5(\text{N}_3)]^{2+}, [\text{Hg}(\text{N}_3)_4]^{2-}$

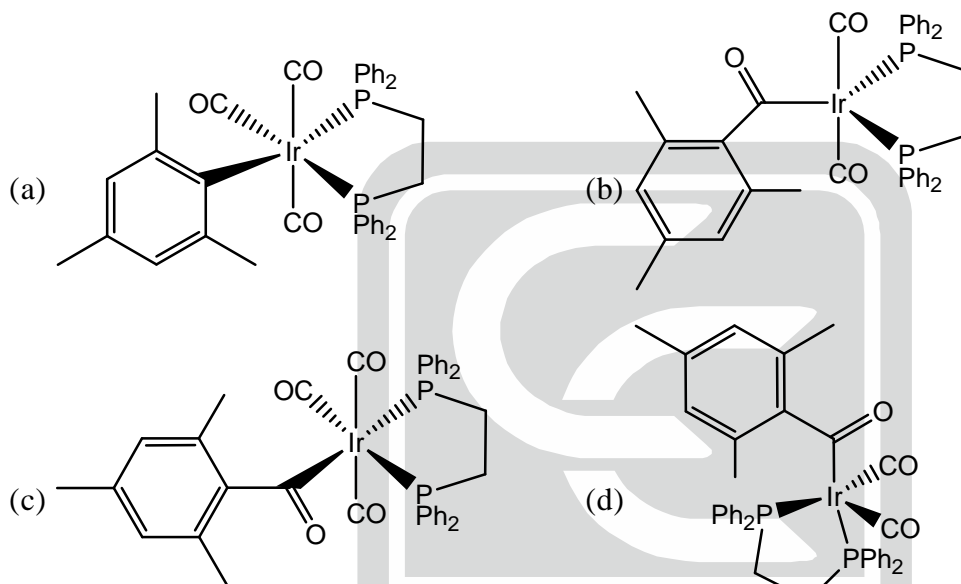
11. The value of magnetic moment will be independent of temperature for (acac = acetylacetonato; OAc = acetate; *o*-phen = *o*-phenanthroline; Pz = pyrazolyl)



12. 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



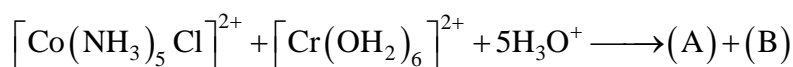
13. The calculated heat of formation (ΔH_f) for NaCl_2 and CaF is
 (a) negative for both NaCl_2 and CaF (b) negative for NaCl_2 but positive for CaF
 (c) positive for NaCl_2 but negative for CaF (d) positive for both NaCl_2 and CaF

14. Thermometric titration gives best results when
 (A) $|\Delta H|$ is high (B) $\Delta G < 0$
 (C) Heat of mixing of titrant with titrand is high
 (D) Titrant is used as dilute solution

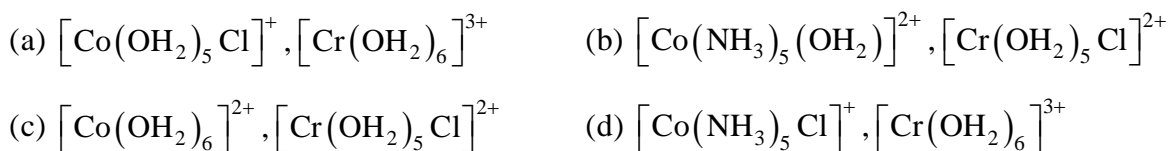
The answer is

- (a) A and B (b) B and C (c) C and D (d) A and D

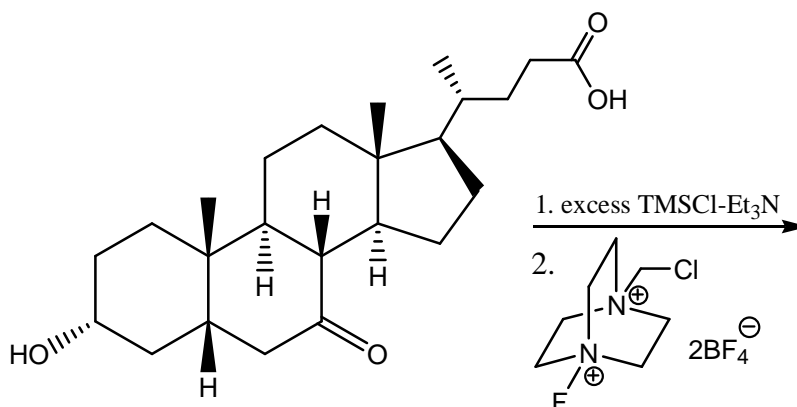
15. The products (A) and (B) for the given reaction

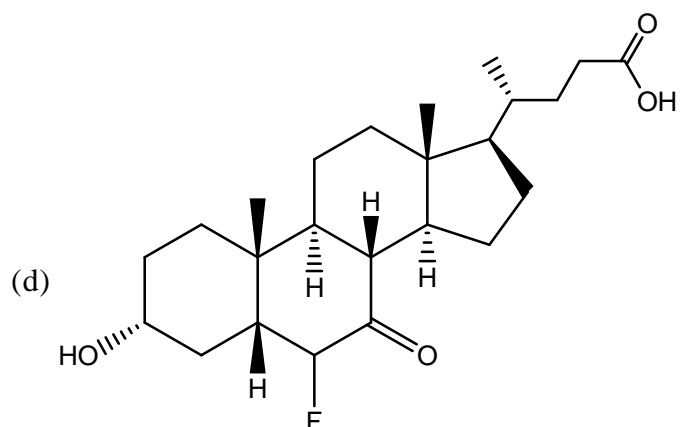
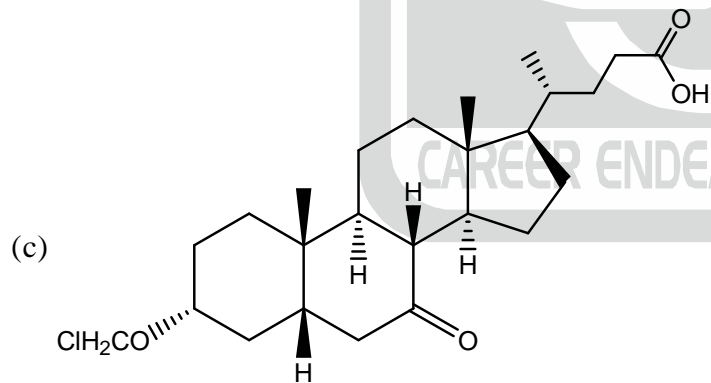
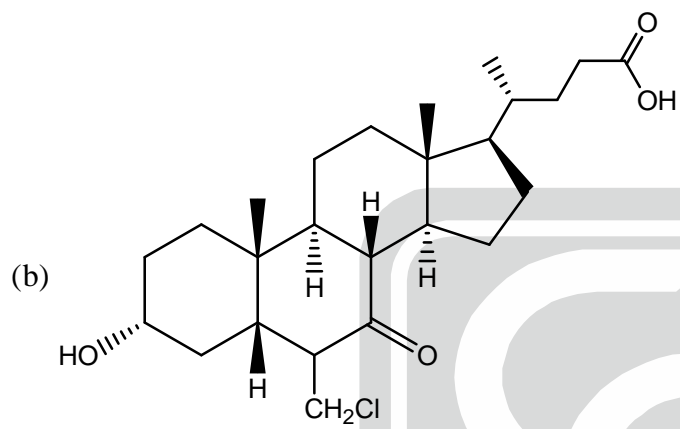
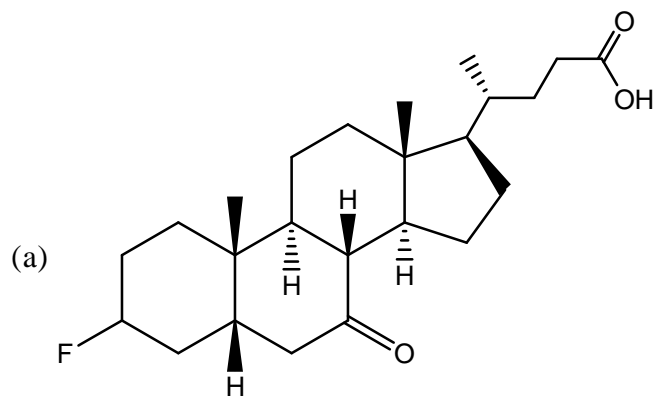


are, respectively

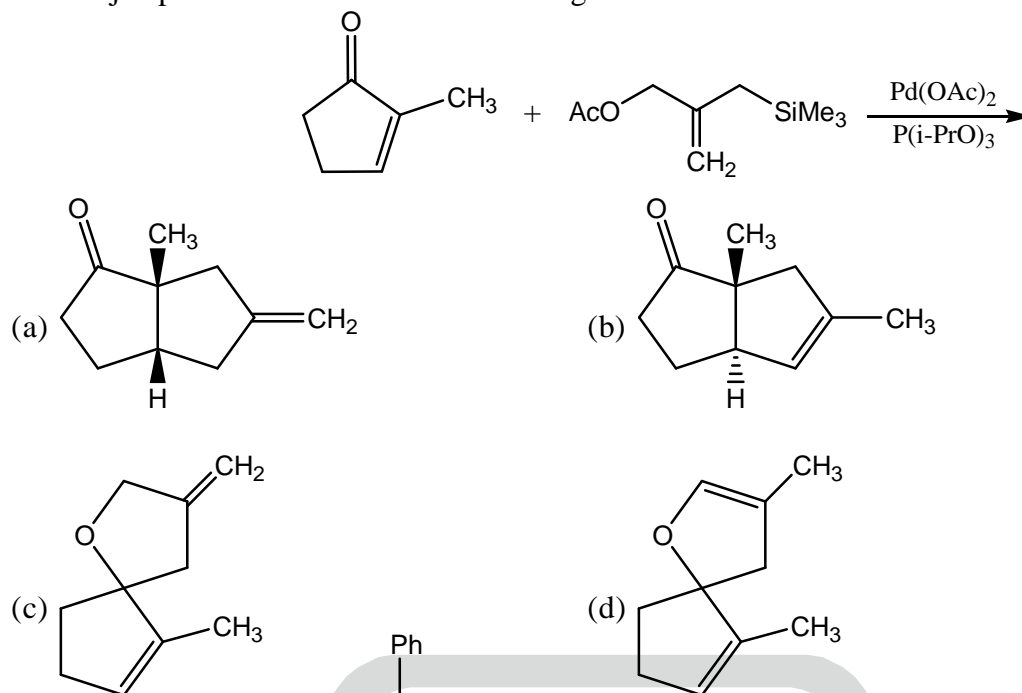


16. In the catalytic cycle of Cytochrome P450, the generation of $[(\text{porphyrin})^{+\bullet}\text{Fe}^{\text{IV}}(\text{O})]$ from $[(\text{porphyrin})\text{Fe}^{\text{III}}(\text{OOH})]$ involves
- one electron oxidation of $[(\text{porphyrin})\text{Fe}^{\text{III}}(\text{OOH})]$
 - formation of the intermediate $[(\text{porphyrin})\text{Fe}^{\text{IV}}(\text{OH})]$
 - homolytic O–O cleavage of $[(\text{porphyrin})\text{Fe}^{\text{IV}}(\text{OOH})]$
 - heterolytic O–O cleavage of $[(\text{porphyrin})\text{Fe}^{\text{III}}(\text{OOH})]$
17. The number of expected electronic transitions in $[\text{Cr}(\text{en})_3]^{3+}$ and $\text{trans}-[\text{Cr}(\text{en})_2\text{F}_2]^+$ at 4K is, respectively (en=ethylenediamine)
- 3 and 3
 - 3 and 4
 - 3 and 5
 - 3 and 6
18. As per VSEPR theory, shapes of SO_3^{2-} , CO_3^{2-} and BrF_4^- are, respectively
- trigonal pyramidal, trigonal planar and tetrahedral
 - trigonal planar, trigonal pyramidal and square planar
 - trigonal pyramidal, trigonal planar and square planar
 - trigonal planar, trigonal pyramidal and tetrahedral
19. Choose the correct statement(s) for the group 15 halides
- AsCl_3 can form complexes of type $[\text{AsCl}_4]^-$ in the presence of a chloride source.
 - PF_3 acts as a strong σ -donor ligand towards d-metals
 - In the solid state, SbF_5 has a trigonal bipyramidal structure
 - The reaction of SbF_5 with anhydrous HF generates $[\text{H}_2\text{F}]^+$ ions
- (I) and (IV)
 - (II), (III) and (IV)
 - (I), (III) and (IV)
 - (II) and (III)
20. The number of peaks with relative intensities observed in the ^1H NMR spectra of $[(\text{Cp})_2\text{Fe}(\text{CO})_2]$ at $+30^\circ\text{C}$ and -80°C in diethyl ether are respectively,
- two peaks (1: 1) and four peaks (5 : 2 : 2 : 1)
 - One peak and two peaks (1:1)
 - two peaks (1:1) at both the temperatures
 - one peak and four peaks (5 : 2 : 2 : 1)
21. The major product formed in the following reaction is

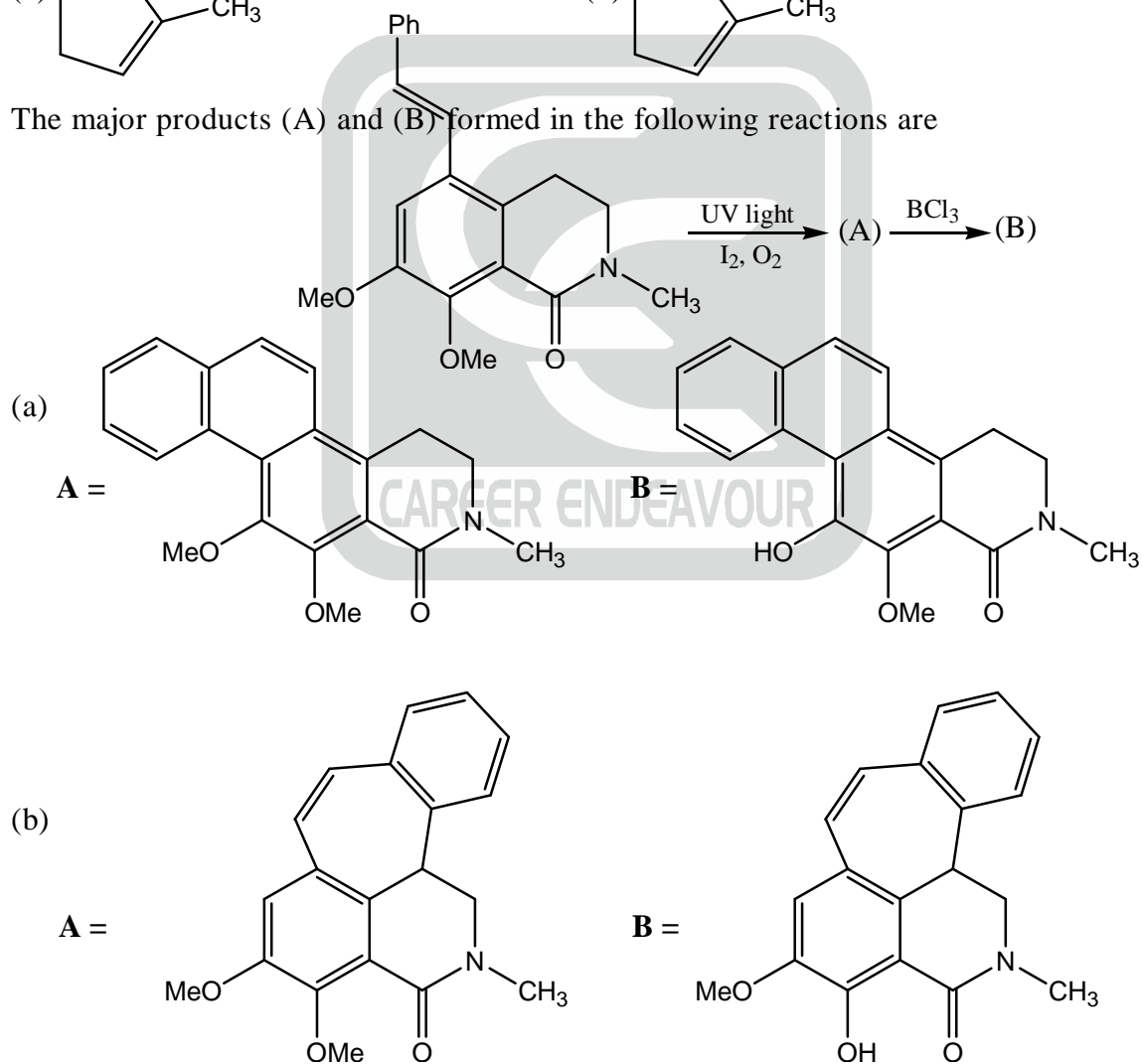


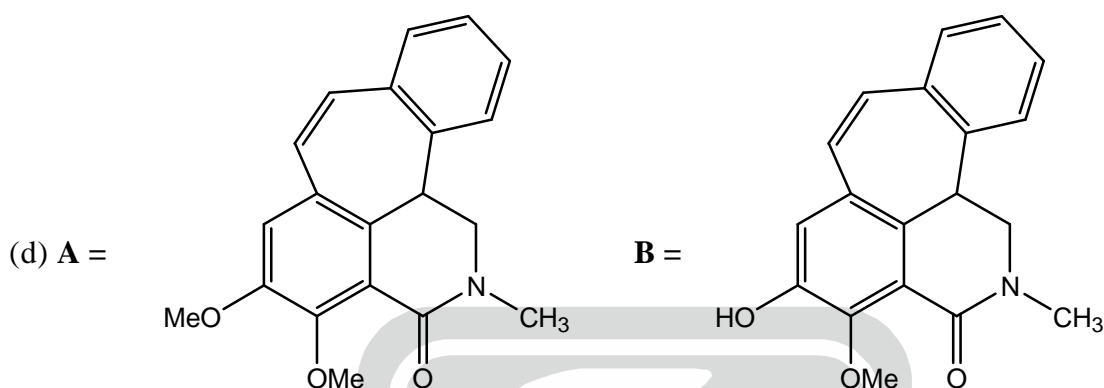
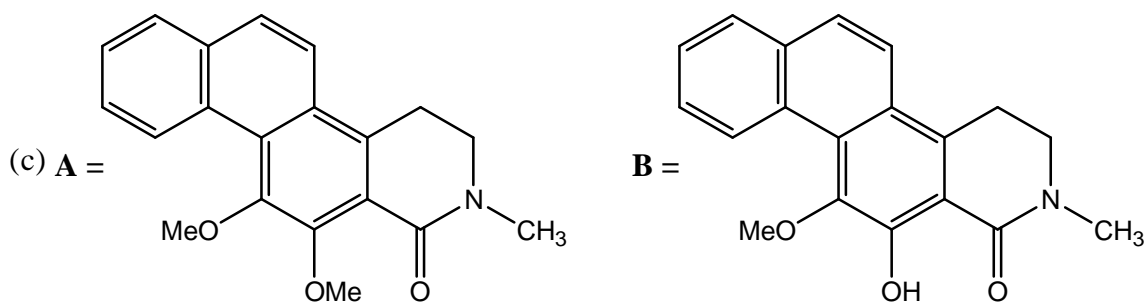


22. The major product formed in the following reaction is

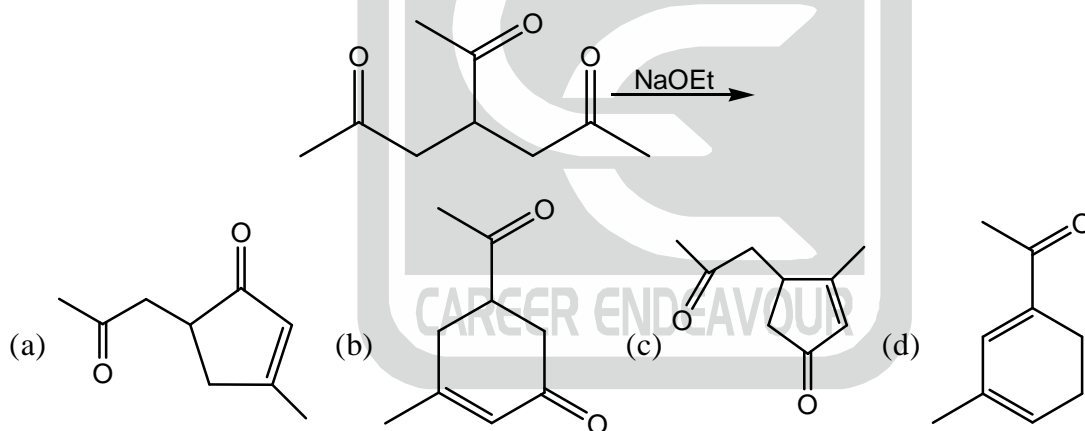


23. The major products (A) and (B) formed in the following reactions are

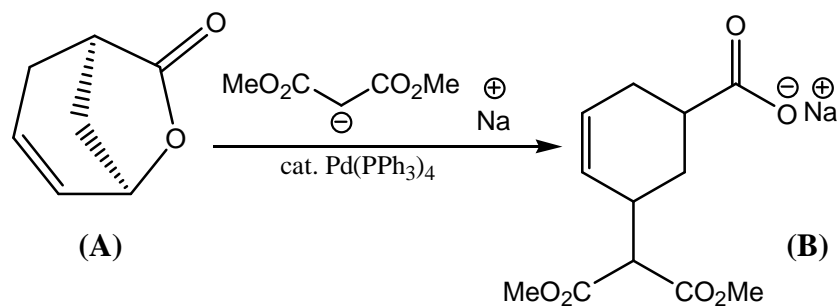




24. The major product formed in the following reaction is

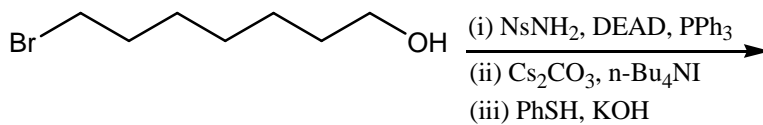


25. In the following transformation, the enantiomerically pure lactone (A) provides

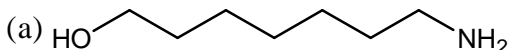
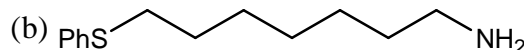
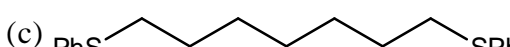
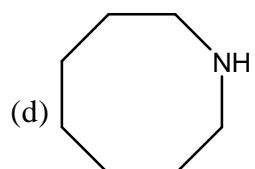


- (a) Equimolar amounts of syn- and anti-diastereomers of B, both of which are racemic
 (b) Equimolar amounts of syn- and anti-diastereomers of B, both of which are enantiomerically pure
 (c) Only syn-diastereomer of B, which is racemic
 (d) Only anti-diastereomer of B, which is enantiomerically pure

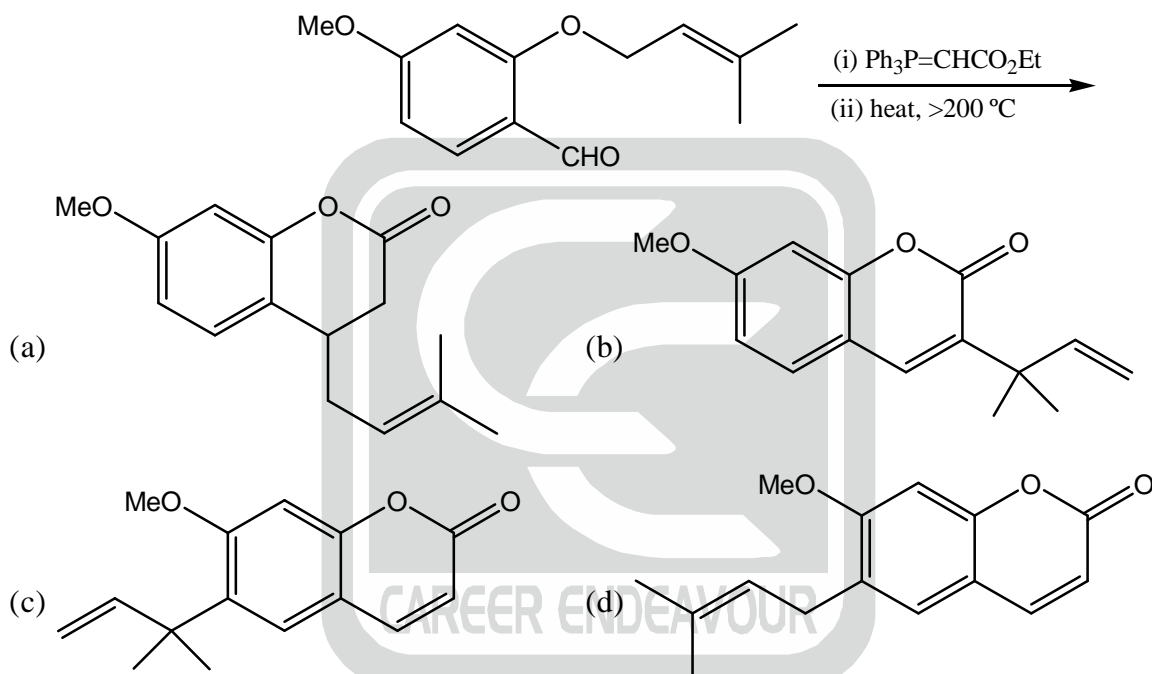
26. The major product formed in the following reaction sequence is



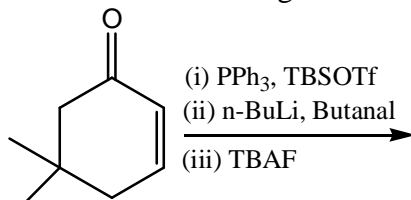
Ns = 2-Nitrobenzenesulfonyl
DEAD = Diethyl azodicarboxylate

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

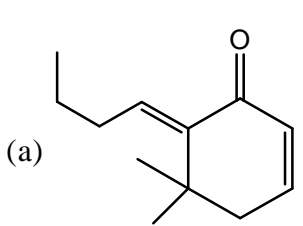
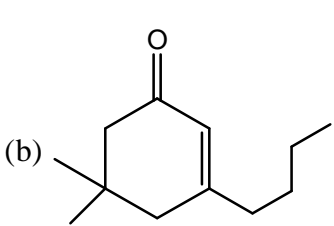
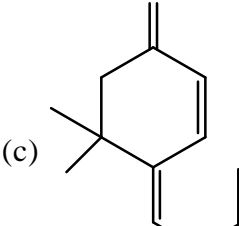
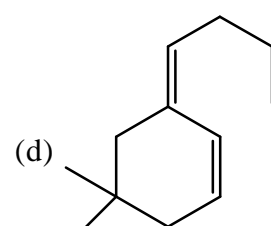
27. The major product formed in the following reaction sequence is



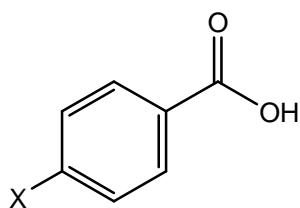
28. The major product formed in the following reaction is



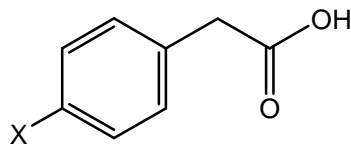
TBSOTf = t-Butyldimethylsilyl triflate
TBAF = tetra-n-butylammonium fluoride

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

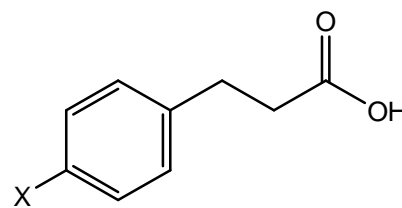
29. The correct order for the Hammett Reaction constant (ρ) for the deprotonation of the following Carboxylic acids is



(A)



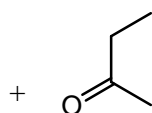
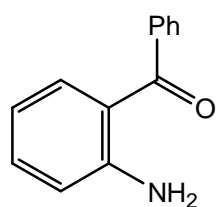
(B)



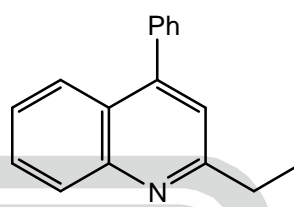
(C)

- (a) $B > C > A$ (b) $C > A > B$ (c) $A > B > C$ (d) $A > C > B$

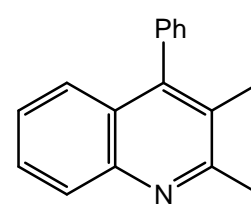
30. The correct statement for the following transformation is



Condition A or B



(P)

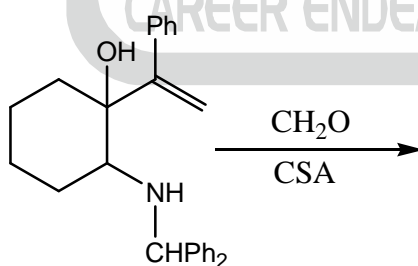


(Q)

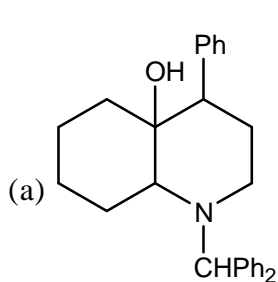
Condition A; aq. KOH, EtOH, 0°C
 Condition B; H₂SO₄, AcOH, reflux

- (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

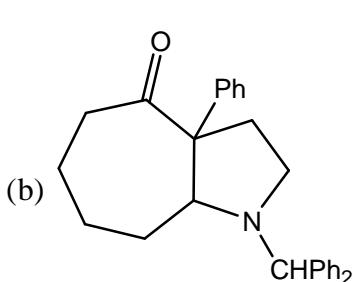
31. The major product formed in the following reaction is



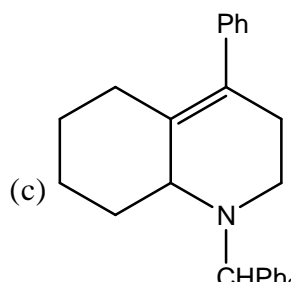
CSA = Camphorsulfonic acid



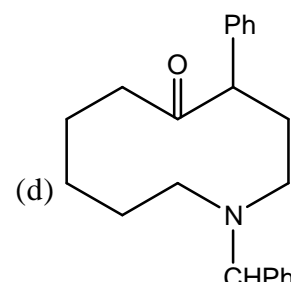
(a)



(b)

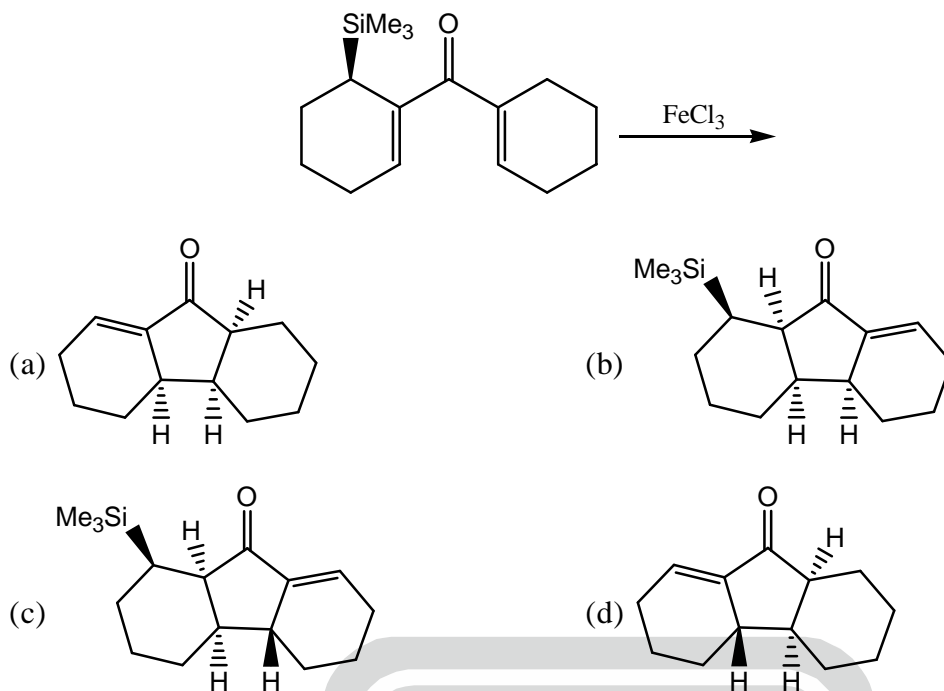


(c)



(d)

32. The major product formed in the following transformation is



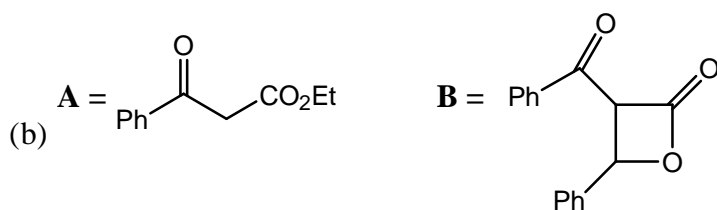
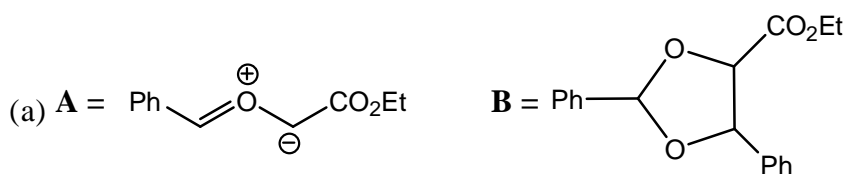
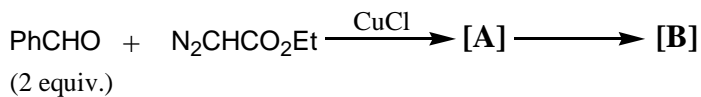
33. The compound that exhibits the following spectral data is $IR(U_{max})$: 1740 cm^{-1}

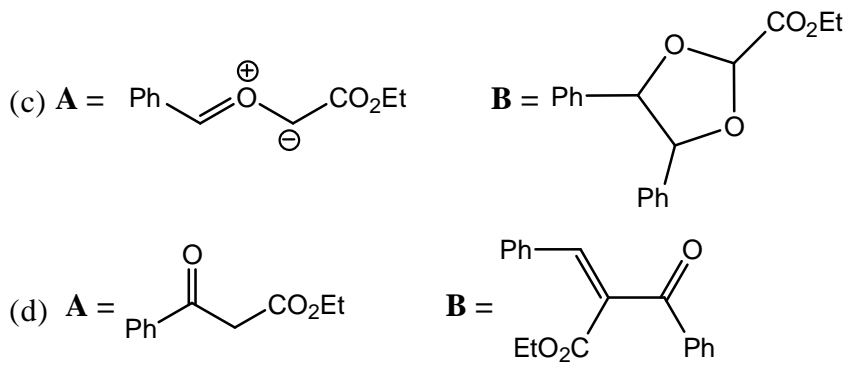
$^1\text{H NMR}$: δ 0.9(t, 3H), 1.6(sext, 2H), 2.3(t, 2H), 4.6(d, 2H), 5.2(d, 1H),
5.4(d, 1H), 5.9(m, 1H) ppm

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

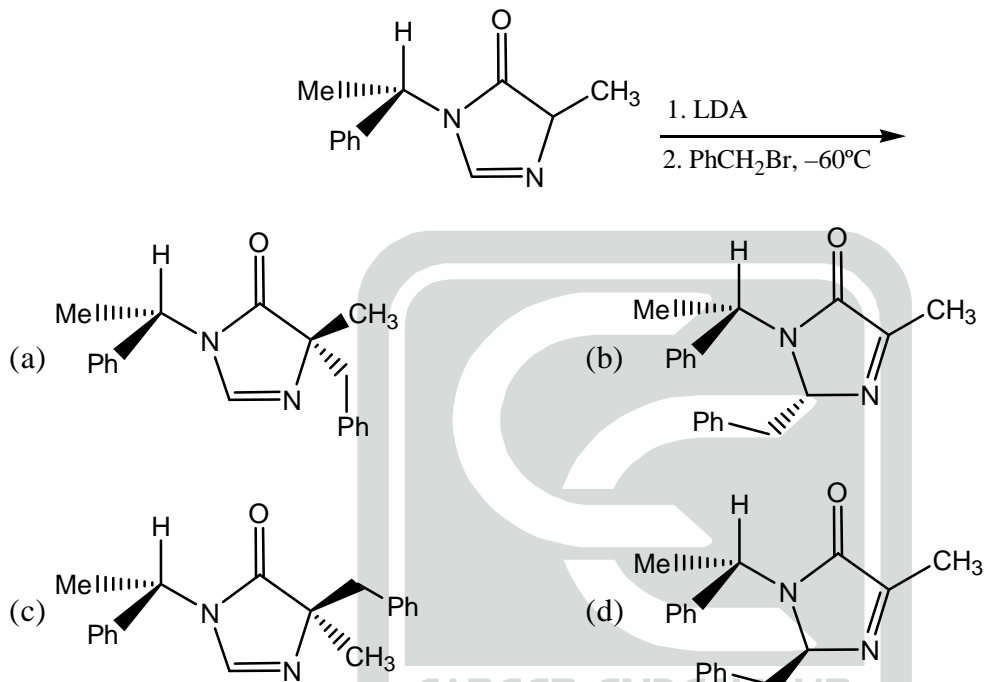


34. In the given transformation, the intermediate (A) and the major product (B) are

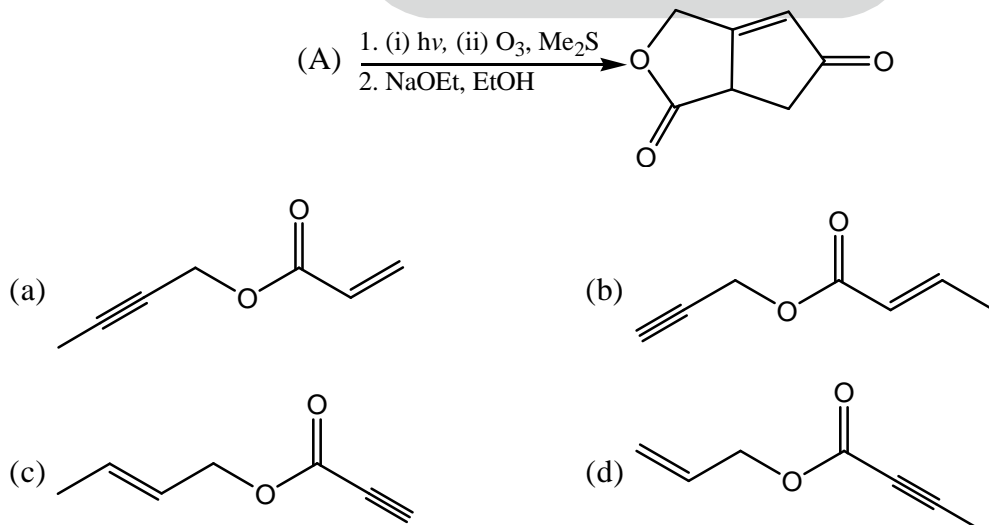




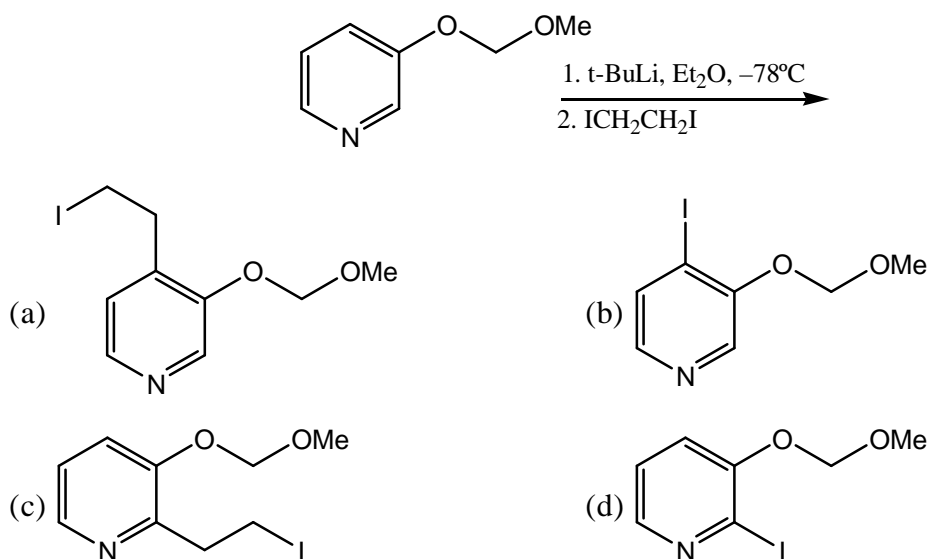
35. The major products formed in the following reaction is



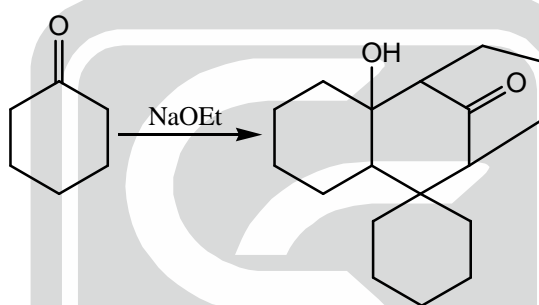
36. The structure of A in the following reaction is



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

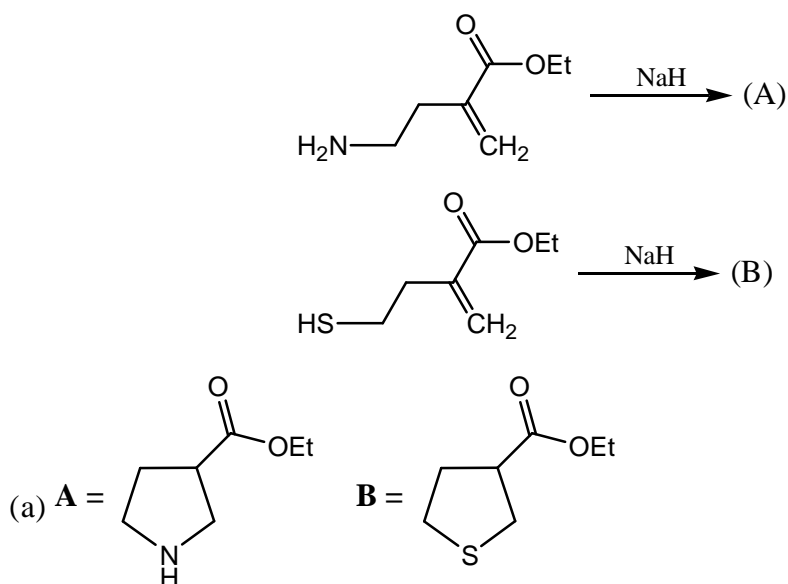


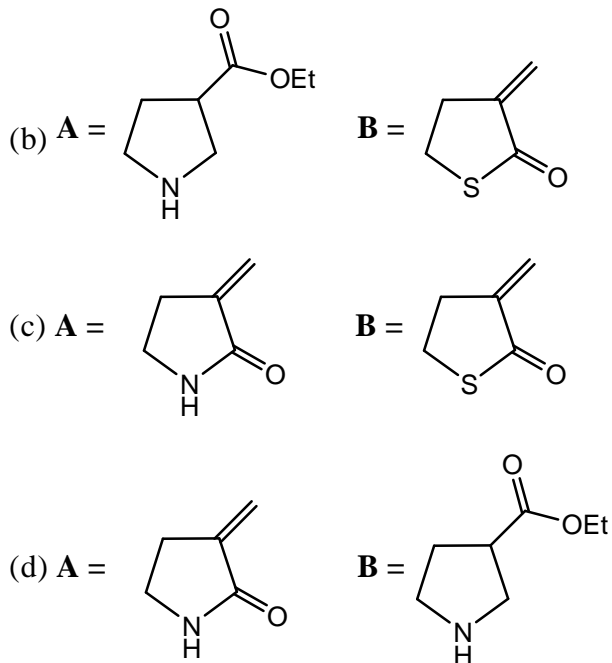
38. The correct sequence of reactions involved in the following transformation is



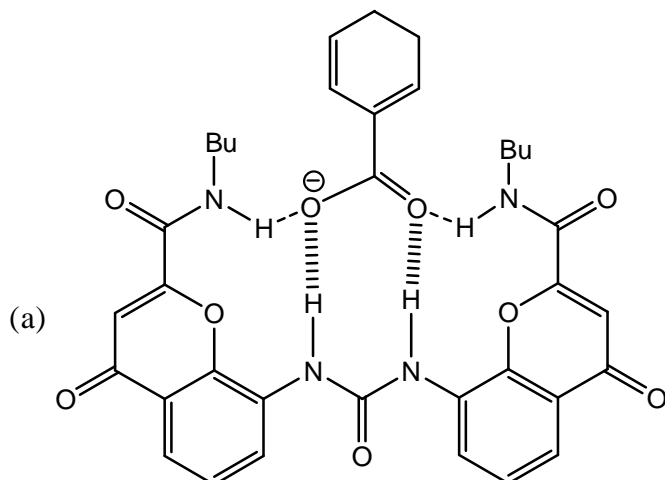
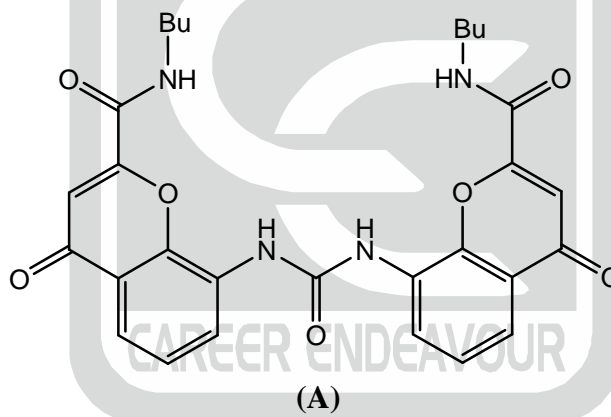
- (a) aldol condensation, Michael addition, aldol reaction
 (b) Aldol condensation, aldol reaction, Michael addition
 (c) Michael addition, aldol condensation, aldol reaction
 (d) Aldol condensation, Michael addition, Michael addition

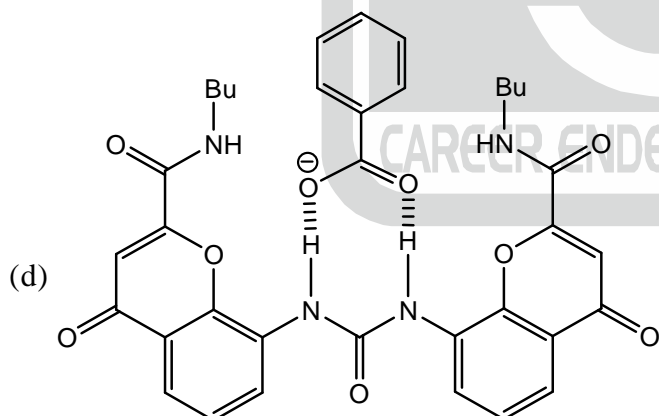
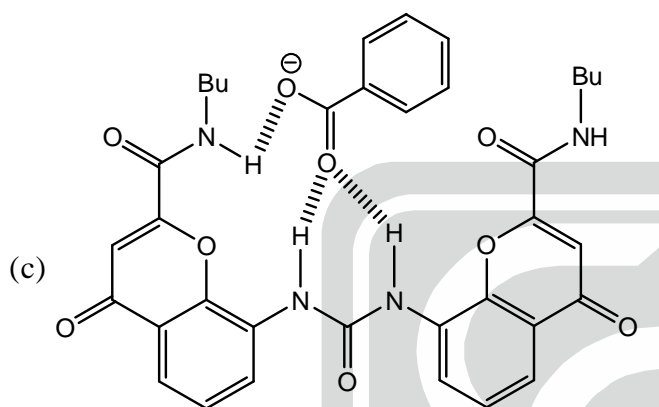
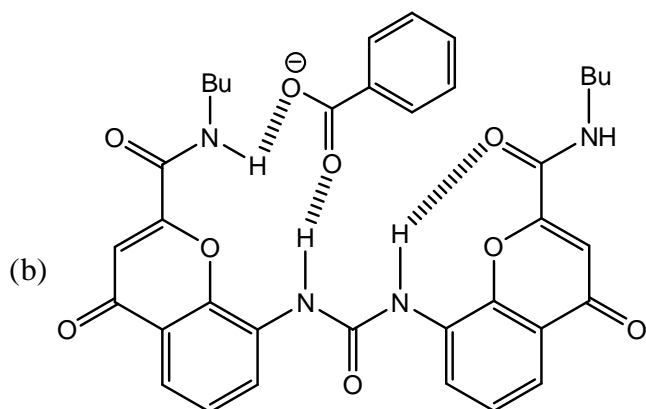
39. The major products (A) and (B) formed in the following transformations are





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





41. Molar conductivities of an electrolyte are 100 and 50 $\text{mS cm}^2 \text{mol}^{-1}$ when concentrations are 4 and 9 mM, respectively. The limiting molar conductivity of this electrolyte in $\text{mS cm}^2 \text{mol}^{-1}$ is closest to
- (a) 150 (b) 200 (c) 250 (d) 300
42. 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) $\frac{m_l^2 \hbar^2}{2} - \frac{\mu E}{\pi}$ (b) $\frac{m_l^2 \hbar^2}{2I} - \frac{\mu E}{2\pi}$ (c) $\frac{m_l^2 \hbar^2}{2I} + \frac{\mu E}{2\pi}$ (d) $\frac{m_l^2 \hbar^2}{2I}$

43. 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)
44. 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
45. 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) $\frac{a}{V_m}$
46. The degree of polymerization at $t = 10\text{h}$ of a polymer formed by a stepwise process with polymerization rate constant of $3 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ and an initial monomer concentration of 50 mM is
 (a) 55 (b) 65 (c) 550 (d) 505
47. Substance 'A' is exposed to 600 nm, 100 W light source for 6626 s, with 50% of the incident light being absorbed. 'A' decomposes according to the reaction $A \rightarrow 2B$. 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

48.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
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)

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 , $\Gamma_{\text{vib}} = A_1' + 2E' + A_2''$,

the frequency of A_1' mode in cm^{-1} is

- (a) 244 (b) 471 (c) 480 (d) 995
49. The energy separation of $^{12}\text{C}^{16}\text{O}$ rotational energy levels between $J'' = 3$ and $J'' = 9$ is 24 cm^{-1} . The rotational constant of $^{13}\text{C}^{16}\text{O}$ in cm^{-1} is closest to
 (a) 2.98 (b) 0.88 (c) 1.90 (d) 2.08
50. The concentration of (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 reaction is

- (a) 0 (b) 1 (c) 2 (d) 3



51. 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

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

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

53. 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) $-\frac{i\hbar}{m} p_x$ (b) $-\frac{i\hbar}{2m} p_x^2$ (c) $\frac{i\hbar}{m} p_x$ (d) $\frac{i\hbar}{2m} p_x$

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

(a) $^2\Pi_u$ (b) $^2\Sigma_u^-$ (c) $^2\Pi_g$ (d) $^2\Sigma_g^+$

55. The vibrational transition energies of a diatomic molecule corresponding to $\nu = 1 \leftarrow \nu = 0$ and $\nu = 2 \leftarrow \nu = 1$ are 2143.1 cm^{-1} and 2116.1 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

56. 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) $+R \ln 2$

57. Given the matrices for C_3 and σ_h below,

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

the trace of the matrix representing for S_3^2 is

(a) 0 (b) -2 (c) 1 (d) -1

58. An aqueous solution contains 0.02 mol kg^{-1} NaCl and 0.03 mol kg^{-1} $\text{Ca}(\text{NO}_3)_2$. 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) $-\sqrt{0.11}$
59. 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) $\frac{1}{2}a_0$
60. The change in chemical potential (in J) of one mole of an ideal gas, when it is compressed isothermally at 300K from 1.0 atm to 2.0 atm, is closest to ($\ln 2 = 0.69$)
- (a) 1225 (b) 1725 (c) 2425 (d) 2725

