GATE-CY 2001

Section-A

1. ***This question consists of TWENTY FIVE sub-questions (1.1 to 1.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.*** **[25×1 = 25]**

1.1. Icosahedral structure is generally exhibited by
(a) C (b) Si (c) Ge (d) B

1.2. The hybrid orbitals used by bromine atom in BrF_3 are
(a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2

1.3. The metal ion present in carbonic anhydrase is
(a) Mn (b) Zn (c) Cu (d) Fe

1.4. The most acidic aqua ion is
(a) $Fe(H_2O)_6^{3+}$ (b) $Co(H_2O)_6^{3+}$ (c) $Ti(H_2O)_6^{3+}$ (d) $Cr(H_2O)_6^{3+}$

1.5. Which one of the following metal fragments, $d^n - ML_m$, is isolobal with CH?
(a) $d^7 - ML_5$ (b) $d^8 - ML_4$ (c) $d^9 - ML_3$ (d) $d^5 - ML_6$

1.6. The softest acid amongst the following is:
(a) Al^{3+} (b) Li^+ (c) Ca^{2+} (d) Ag^+

1.7. The chromium (III) species formed soon after electron transfer between $IrCl_6^{2-}$ and $Cr(H_2O)_6^{2+}$ is:
(a) $Cr(H_2O)_6^{3+}$ (b) $Cr(H_2O)_5Cl^{2+}$ (c) $CrCl_6^{3-}$ (d) $Cr(H_2O)_3Cl_3$

1.8. The strongest reducing ion of the following is
(a) U^{3+} (b) Am^{3+} (c) Cm^{3+} (d) Cf^{3+}

1.9. The first ionization potential of Mg, Al, P and S follows the order
(a) Mg < Al < P < S (b) Al < Mg < P < S (c) Al < Mg < S < P (d) Mg < Al < S < P

1.10. As per the uncertainty principle, $\Delta x \cdot \Delta p_y =$
(a) h (b) $h/2\pi$ (c) λ (d) zero

1.11. The second lower state of particle in a cubic box is
(a) non degenerate (b) doubly degenerate (c) triply degenerate (d) six-fold degenerate

1.12. In comparision to the frequency of the EPR transition, the NMR transition frequency is
(a) much higher (b) much lower (c) almost same (d) none of these

1.13. The symmetry point group of the BF_3 molecule is:
(a) C_{3v} (b) D_{3h} (c) C_{2v} (d) D_{2h}

1.14. For an irreversible adiabatic expansion of a perfect gas from volume V_i to V_f the change in entropy of the gas is:
(a) $nR\ln(V_f/V_i)$ (b) Zero (c) less than zero (d) greater than zero

1.15. For the cell $Ag(s)|AgCl(satd)$, $NaCl(aq, m_1)|NaCl(aq, m_2)$, AgCl(satd)|Ag(s) where m_1 and m_2 are different molalities ($m_1 > m_2$), the standard cell potential is:
(a) $-RT\ln(m_1/m_2)$ (b) Zero (c) $-RT\ln(a_1/a_2)$ (d) $-FRT\ln(a_1)$

1.16. For an ideal dilute solution, which one of the following statements is correct ? (γ and x are activity coefficient and mole fraction respectively)

(a) $\gamma(\text{solvent}) \to 0$ as x $(\text{solvent}) \to 1$ (b) $\gamma(\text{solvent}) \to 1$ as x $(\text{solvent}) \to 1$

(c) $\gamma(\text{solvent}) \to 1$ as x $(\text{solvent}) \to 1$ (d) $\gamma(\text{solvent}) \to 0$ as x $(\text{solvent}) \to 1$

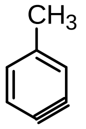
1.17. For the reaction: $Br_2(g) + BF_2(g) \to 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25. When the pressure is increased by 8-fold, the equilibrium constant.

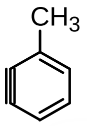
(a) Increase by a factor of 1.86 (b) Decreases by a factor of 1.86
(c) Remains same (d) Increases by a factor of 8

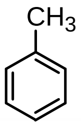
1.18. 2-Phenyl ethanol may be prepared by the reaction of phenyl magnesium bromide with

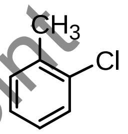
(a) HCHO (b) CH_3CHO (c) CH_3COCH_3 (d) 

1.19. o-Chlorotoluene reacts with sodamide in liquid ammonia to give o-toluidine, and m-toluidine. This reaction proceeds through an intermediate

(a) 

(b) 

(c) 

(d) 

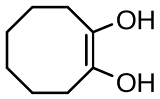
1.20. The number of signals observed in ^{1}H NMR spectrum of 3, 5-dibromotoluene is:

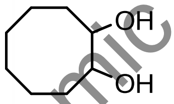
(a) 3 (b) 4 (c) 2 (d) 6

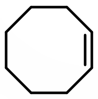
1.21. Which one of the following molecules will have $n \to \pi^*$ transition at the longest wavelength ?

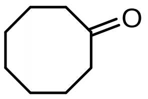
(a) HCHO (b) $CH_3COC_2H_5$ (c) $C_6H_5COC_6H_5$ (d) $CH_3COC_6H_5$

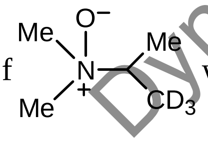
1.22. The reaction of cyclooctyne with $HgSO_4$ in the presence of aqueous H_2SO_4 gives

(a) 

(b) 

(c) 

(d) 

1.23. Pyrolysis of  would be

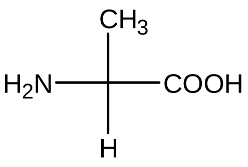
(a) A mixture of $CH_2{=}CH{-}CD_3$ and $CH_3{-}CH{=}CD_2$

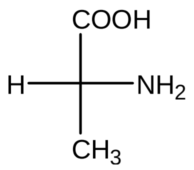
(b) $CH_3{-}CH{=}CD_2$

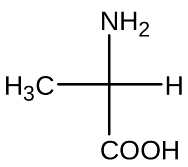
(c) $Me_2N^+{=}C(CD)_3(CH_3)$

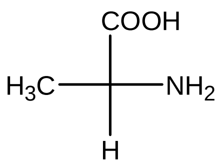
(d) $CH_2{=}CH{-}CD_3$

1.24. Amongst the following amino acids, the (R)-enantiomer is represented by

(a) 

(b) 

(c) 

(d) 

1.25. Arrange the following halides in the decreasing order of SN^1 reactivity

$CH_3CH_2CH_2Cl$, (I) $CH_2{=}CHCH(Cl)CH_3$, (II) $CH_3CH_2CH(Cl)CH_3$ (III)

(a) I > II > III (b) II > I > III (c) II > III > I (d) III > II > I

2. ***This question consists of TWENTY FIVE sub-questions (2.1 to 2.25) of ONE mark each. For each of these sub-questions, four possible answers (a, b, c and d) are given, out of which only one is correct.*** **[25×2 = 50]**

2.1. The volume of 1 N $KMnO_4$ required to reach equivalence point in the titration with 0.01 mole of ferrous oxalate dissolved in dilute H_2SO_4 is

(a) $3\ cm^3$ (b) $30\ cm^3$ (c) $10\ cm^3$ (d) $20\ cm^3$

2.2. The number of signals observed in ^1H NMR spectrum of 3, 5-dibromotoluene is:

(a) 3 (b) 4 (c) 2 (d) 6

2.3. Among the following, the paramagnetic species among the following is:

(a) B_2 (b) C_2 (c) O_2^{2-} (d) CO

2.4. The purple colour of iodine vapours is due to

(a) d-d transition (b) $\pi - \sigma^*$ transition

(c) charge - transfer transition (d) $\pi^* - \sigma^*$ transition

2.5. Amongst the following, the strongest oxidizing anion is:

(a) CrO_4^{2-} (b) VO_4^{3-} (c) FeO_4^{2-} (d) MnO_4^{2-}

2.6. ^{19}F NMR spectrum of meriodional isomer of octahedral $RhCl_3F_3$ complex, [^{103}Rh (I = ½); ^{19}F (I = ½) assuming $J_{Rh-F} > J_{F-F}$, will show

(a) one doublet (b) two doublets and one triplet

(c) two doublets and two triplets (d) one singlet and two triplets

2.7. Which one of the following will show closo structure ?

(a) B_5H_9 (b) $B_{12}H_{12}^{2-}$ (c) B_4H_{10} (d) B_5H_{11}

2.8. The correct order of energy level of d-orbitals in ferrocene is:

(a) $dx^2 - y^2, dxy < dz^2 < dxz, dyz$ (b) $dz^2 < dxz, dyz < dx^2 - y^2, dxy$

(c) $dx^2 - y^2, dxy < dxz, dyz < dz^2$ (d) $dyz, dxz < dx^2 - y^2, dxy < dz^2$

2.9. Two moles of a monoatomic perfect gas initially at 4.0 bar and 47ºC undergoes reversible expansion in an insulated container. The temperature at which the pressure reduces to 3.0 bar is

(a) 200 K (b) 285 K (c) 310 K (d) 320 K

2.10. The mean ionic activity coefficient of 0.0005 mol kg^{-1} $CaCl_2$ in water at 25ºC is:

(a) 0.98 (b) 0.67 (c) 0.81 (d) 0.91

2.11. For the cell : $Cd(Hg)\,|\,CdSO_4\,(8/3)H_2O(s)\,|\,CdSO_4\,(aq,\ satd.)\,|\,Hg_2SO_4(s)\,|\,Hg$

The temperature dependence of emf in Volts is given by

$$B = 1.0185 - 4.05\times10^{-5}(T - 293) - 9.5\times10^{-7}(T - 293)^2$$

The change in entropy at 25ºC for the cell reaction is

(a) $-253\ K^{-1}\ mol^{-1}$ (b) $9.65\ J\ K^{-1}\ mol^{-1}$

(c) $8.3\times10^{-4}\ J\ K^{-1}\ mol^{-1}$ (d) zero

2.12. Two separate bulbs contain ideal gases A and B respectively. The density of gas A is twice that of gas B and molecular weight of gas A is half of that of gas B. The ratio of pressure of gas A to that of gas B is

(a) 3 (b) 6 (c) 4 (d) 1

2.13. Choose the correct criterion of spontaneity in terms of the properties of the system alone.

(a) $(dS)_{U,V} > 0$ (b) $(dS)_{T,P} > 0$ (c) $(dS)_{H,P} < 0$ (d) $(dG)_{T,V} < 0$

2.14. Compared to C_2H_6, the value of vander waal's constants 'a' and 'b' for He will be

(a) both will be smaller (b) 'a' will be larger but 'b' will be smaller

(c) 'b' will be larger but 'a' will be smaller (d) both will be larger

2.15. The number of hyperfine components observed in the electronic transition ${}^2p_{1/2} \rightarrow {}^2s_{1/2}$ of an atom with nuclear spin 1/2 is

(a) 3 (b) 4 (c) 6 (d) 5

2.16. Given than, $\psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi);\ R_{20}(r) \propto (2 - r/a_0)e^{-r/ao.},\ Y_{0,0}(\theta,\phi) = 1/\sqrt{4\pi}$

The position of radial node in the 2s orbital is at

(a) $r = a_0$ (b) $r = 2a_0$ (c) $r = a_o/2$ (d) $r = a_o/4$

2.17. Consider the following reaction and use the data given below **[GATE 2001]**

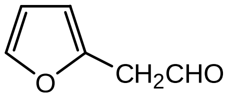
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H^0(25^o C) = -92.2 \text{ kJ}$$

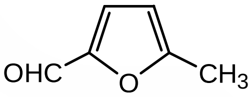
Substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$C_P / (J\ K^{-1}\ mol^{-1})$	29.1	28.8	35.1

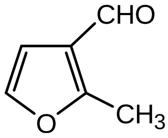
Assuming C_p to be independent of temperature, the reaction at 100ºC compared to that at 25ºC will be

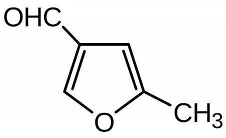
(a) Endothermic (b) Less exothermic (c) More exothermic (d) Having $\Delta H^0 = 0$

2.18. The reaction of 2-methylfuran with DMF–$POCl_3$ would give

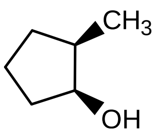
(a) 

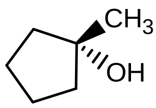
(b) 

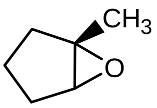
(c) 

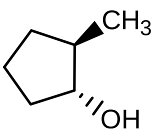
(d) 

2.19. The major product formed during the hydroboration-oxidation of 1-methyl cyclopentene is

(a) 

(b) 

(c) 

(d) 

2.20. Which one of the following carbonyl compounds will give a fragment ion at m/z = 58 in their mass spectra?

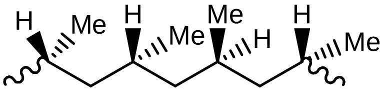
(a) $C_2H_5CH(CH_3)CHO$ (b) $CH_3CH_2CH_2CH_2CHO$

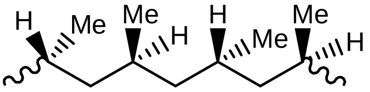
(c) $CH_3CH_2CH_2COCD_3$ (d) $(CH_3)_2CHCH_2CHO$

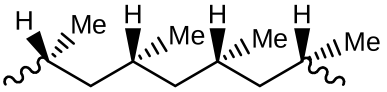
2.21. The decreasing order of reactivity of meta-nitrobromobenzene (I); 2, 4, 6-trinitrobromobenzene (II); para-nitrobromobenzene (III); and 2, 4-dinitrobromobenzene (IV) towards OH^- ions is

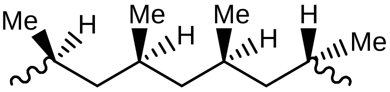
(a) I > II > III > IV (b) II > IV > III > I (c) IV > II > III > I (d) II > IV > I > III

2.22. Identify the isotactic polypropylene from the following

(a) 

(b) 

(c) 

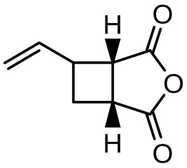
(d) 

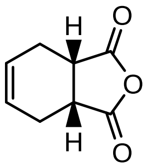
2.23. Which one of the following compounds will form an osazone derivative?

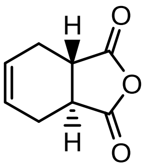
(a) $CH_3CH_2COCH_2OH$ (b) $CH_3COCH_2CH_2OH$

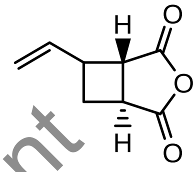
(c) $CH_3CH_2CHOHCH_2OH$ (d) $CH_3CH_2COCH_2OCH_3$

2.24. Buta-1, 3-diene on heating with maleic anhydride would give

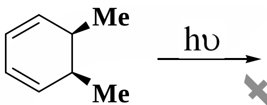
(a) 

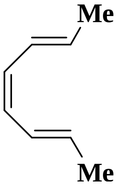
(b) 

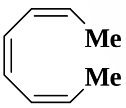
(c) 

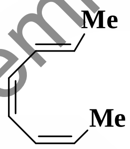
(d) 

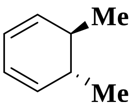
2.25. The product obtained during the following photochemical reaction is



(a) 

(b) 

(c) 

(d) 

Section-B

***This section consists of TWENTY* questions of *FIVE* marks each. *ANY FIFTEEN* out of these questions have to answered on the Answer Book provided. [75 Marks]**

3.1. There are two isomers of $Pt(NH_3)_2Cl_2$. X and Y. When X is reacted with thiourea(tu). $Pt(tu)_4^{2+}$ is formed while Y on reaction with thiourea yields $Pt(NH_3)_2(tu)_2$. Identify X and Y and explain the reaction.

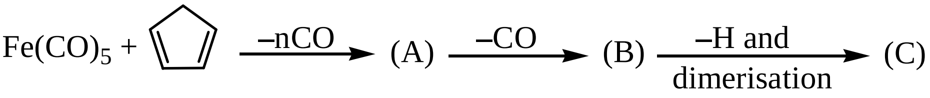
3.2. Ligand substitution reaction on metal clusters are often found to occur by associative mechanism by breaking of a M-M bond and thereby providing an open coordination site for the incoming ligand. Which one of the two clusters, $Co_4(CO)_{12}$ of $Ir_4(CO)_{12}$ is expected to undergo faster exchange with ^{13}CO ? Suggest an explanation.

4.1. Using crystal-field theory, account for the fact that in square - pyramidal $[Ni(CN)_5]^{3-}$ ion, the axial Ni—C bond (217 pm) is longer than Ni—C basal bonds (187 pm), while in trigonal bipyramidal $[CuCl_5]^{3-}$ ion, the axial Cu–Cl bonds (229 pm) are shorter than the Cu–Cl equatorial ones (239 pm).

4.2. Between complexes $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ which one should have a lower energy charge-transfer band and why?

5. Write the Russell-Saunders terms of the configuration p^1d^1 and identify the ground term. Indicate population of electrons in different d-orbitals corresponding to $^3T_{1g}$ (F), $^3T_{2g}$(F) and $^3A_{2g}$(F) states for d^2 configuration in octahedral symmetry.

6.1. Propose the structure of compounds A, B and C satisfying EAN rule in the following reactions:



6.2. Explain why 16- or 14-electron configurations are favoured over 18-electron configurations for the elements at the end of the transition series ?

7.1. Calculate spin-orbit coupling parameter (λ), for an octahedral nickel (II) complex exhibiting spin allowed d-d bands at 10,750 cm^{-1}, 17,500 cm^{-1} and 28,200 cm^{-1} respectively. The experimentally determined magnetic moment is 3.2 BM.

7.2. Explain why pKa of $(CH_3)_3SiOH(pKa \approx 11)$ is lower than that of $(CH_3)_3COH(pKa \approx 16)$.

8.1. Define capacity factor. What is the effect of large capacity factor on the separation of analytes? How can capacity factors be optimized in gas chromatography?

8.2. What prevents simple iron porphyrins from functioning as O_2 carriers like haemoglobin?

9. Identify all the symmetry operations for HCHO with rotation axis as the z-axis and plane of the molecule being the yz plane. will the transition from an a_1 to b_1 orbital be allowed in HCHO? What will be the polarization of the corresponding $b_1 \rightarrow a_1$ emission?

10.1. Using quantization condition for de Broglie wavelength on a ring, derive the expression for rotational energy levels of a rigid homonuclear diatomic rotor of bond length 2r.

10.2. Given $\psi_n(x) = (2)^{1/2}\sin(n\pi x)$, show that eigen functions $\psi_1(x)$ and $\psi_2(x)$ of a particle in a one dimensional box of length 1 are orthogonal.

11. The emf of the cell

$Ag(s) \mid AgCl(satd), KCl(0.05\ mol\ dm^{-3}) \mid AgNO_3(0.1\ mol\ dm^{-3}) \mid Ag(s)$

is 0.431 v at 298.15 K. The mean activity coefficient of KCl is 0.817 and that of $AgNO_3$ is 0.723. Calculate the solubility product of AgCl at 25ºC.

12.1. A paramagnetic substance $(A_2B_3 - 5H_2O)$ initially at T = 0.30 K was magnetized by application of strong magnetic field while the sample was surrounded by helium gas in contact with a cold reservoir. Subsequently, helium gas was pumped away and the magnetic field was slowly reduced to zero. Calculate the change in temperature of the sample using the data given below :

Unmagnetized sample		Magnetized sample	
T/K	S/(J K^{-1} mol^{-1})	T/K	S/(J K^{-1} mol^{-1})
0.30	0.40	0.30	0.19
0.25	0.32	0.25	0.15
0.18	0.19	0.20	0.12
0.15	0.14	0.15	0.10

12.2. When 2 moles of liquid A and 4 moles of liquid B are mixed, experimental measurements give entropy of mixing as $42\ \text{J K}^{-1}$. Show whether the solution AB thus formed is ideal or not.

13.1. The LCAOs : $\phi_1 = \left(1_{sA} + 1_{sB}\right)$ and $\phi_2 = \left(1_{sA} - 1_{sB}\right)$ approximate the lowest σ and σ^* orbitals of H_2^+ respectively. Show that the σLCAO is of g-type and σ^* of u type. [1_{S_A} and 1_{S_B} are the 1s orbitals centered on H_A and H_B of $(H_A - H_B)^+$].

13.2. The fundamental vibrational frequency of HCl is $2885\ \text{cm}^{-1}$. Assuming that HCl and DCl may be treated as Simple Harmonic Oscillator, calculate the fundamental frequency of DCl.

14.1. The conversion of A to B and C goes through the following mechanism

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 1 \underset{k_4}{\overset{k_2}{\rightleftharpoons}} B + C$$

Show that the equilibrium constant (K) of the overall reaction is

$$K = \frac{k_1 k_3}{k_2 k_4}$$

14.2. The rate of the acid catalyzed hydrolysis of ethylacetate in HCl solution obeys the following rate law

$$\text{Rate} = -d[\text{ester}]/dt = k[\text{ester}][\text{HCl}]$$

where $k = 0.1\ \text{mol}^{-1}\ \text{dm}^{-3}\ \text{h}^{-1}$. Neglecting any back reaction, calculate the time required for half the ester to be hydrolyzed if the initial concentration of ester and HCl are $0.02\ \text{mol dm}^{-3}$ and $0.01\ \text{mol dm}^{-3}$ respectively.

15.1. Using the data given below, calculate the equilibrium constant and enthalpy of the following reaction at 25ºC.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Substance	$\Delta G_f^0/(\text{kJ mol}^{-1})$	$S^0/(\text{J K}^{-1}\ \text{mol}^{-1})$
$NO_2(g)$	51.31	240.06
$N_2O_4(g)$	97.89	304.29

15.2. When 1.0 mol of $CH_4(g)$ is oxidized to carbon dioxide and water according to the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

the corresponding thermodynamic parameters are : $\Delta H^o = -890\ \text{kJ mol}^{-1}$, and $\Delta S^o = -140.3\ \text{JK}^{-1}\ \text{mol}^{-1}$. Assuming ideal gas behaviour, calculate the amount of energy that can be extracted as work at 25ºC.

16. Acid catalyzed dehydration of a tertiary alcohol $A(C_6H_{14}O)$ gives one major compound B, and one minor compound C both having molecular formula C_6H_{12}. Spectroscopic data of these compounds are as follows:

Compound B : IR : 1660 cm^{-1}, 3080 cm^{-1}

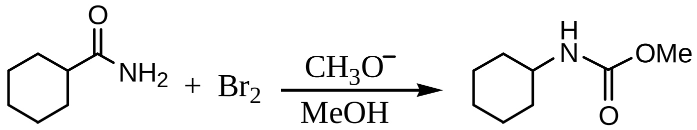
^{1}H NMR δ : 0.91(t, J = 7 Hz, 3H), 1.60 (s, 3H). 1.70 (s, 3H), 1.98 (quin, J = 7 Hz, 2H), 5.08 (t, J = 7 Hz, 1H)

Compound C : IR ; 1640 cm^{-1}, 3090 cm^{-1}

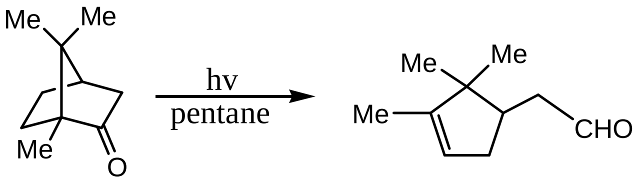
^{1}H NMR δ : 0.92 (t, J = 7 Hz, 3H), 1.40 (sextet, J = 7Hz, 2H), 1.74 (s, 3H), 2.02 (t, J = 7Hz, 2H), 4.78 (s, 2H)

Deduce the structure of A, B and C.

17.1. Suggest a plausible mechanism for the following reaction

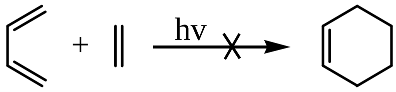


17.2. Propose a mechanism for the photochemical reaction given below.

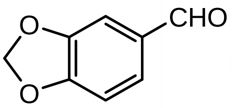


18.1. Draw π orbitals of buta-1, 3-diene and ethylene, and identify their HOMO and LUMO.

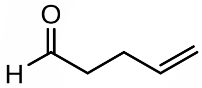
18.2. Using "frontier orbital concept", explain why the $\pi^{4s} + \pi^{2s}$ cycloaddition given below is photochemically not allowed?



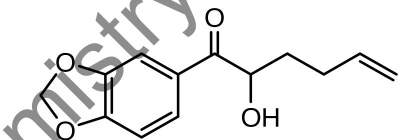
19.1. Suggest a synthetic route to the hydroxy-ketone C using A and B starting materials.



A

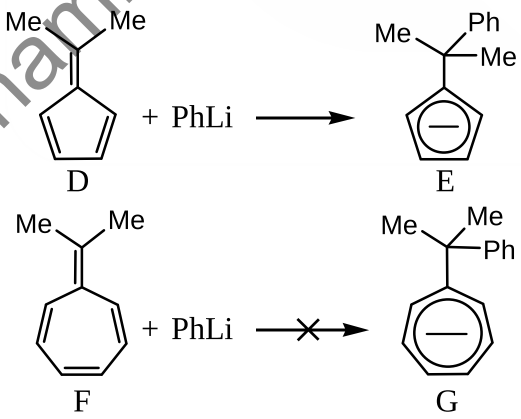


B



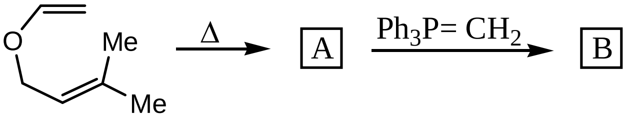
C

19.2. The reaction of dimethyl fulvene D with PhLi readily gives the anion E. However, the analogous compound F does not react with PhLi to give the corresponding anion G. Explain.

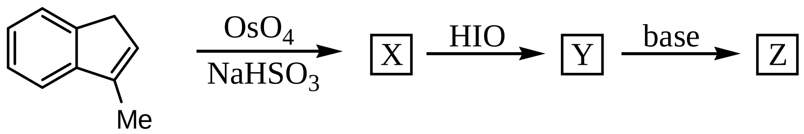


20.1. Outline a synthesis of para-nitropropylbenzene from benzene.

20.2. Predict the products in the following reactions.

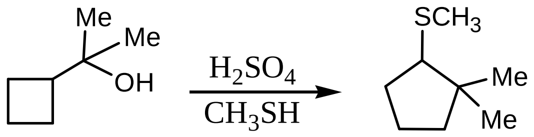


21.1. Write the structure of the products X, Y and Z in the following sequence of reactions.



21.2. D-Glucose and D-fructose interconvert into each other in aqueous alkaline solution. Suggest a mechanism for the interconversion.

22.1. Propose a mechanism of the following reaction.



22.2. Suggest a route for synthesis of the enone B from A.