GATE-CY 2000

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.*** **[25×2 = 50]**

1.1. Which among the following molecules belong to point group C_{4v}?
(a) $[BF_4]Na^+$ (b) $XeOF_4$ (c) XeF_4 (d) $[PtCl_4]^{2-}$

1.2. The ^{19}F NMR spectrum of PCl_2F_3 (I for $^{31}P = \frac{1}{2}$, I for $^{19}F = \frac{1}{2}$) shows
(a) two triplets and two doublets (b) two triplets and one doublet
(c) two doublets and one triplet (d) three triplets and one doublet

1.3. The compound $(SiH_3)_3N$ is expected to be
(a) pyramidal and more basic than $(CH_3)_3N$
(b) planar and less basic than $(CH_3)_3N$
(c) pyramidal and less basic than $(CH_3)_3N$
(d) planar and more basic than $(CH_3)_3N$

1.4. The infrared and Raman spectrum BF_3 are expected to show
(a) the same number of peaks
(b) more absorption peaks in IR in comparison to Raman
(c) more absorption peaks in Raman in comparison with IR
(d) absorption peaks present in Raman are absent in R

1.5. The complex with maximum CFSE is
(a) $\left[CoCl_4\right]^{2-}$ (b) $\left[Co\left(H_2O\right)_6\right]^{3+}$ (c) $CoF_3\left(H_2O\right)_3$ (d) $\left[CoF_6\right]^{3+}$

1.6. The compound which has four metal-metal bonds is
(a) $Fe_2\left(CO\right)_9$ (b) $Co_2\left(CO\right)_8$ (c) $\left[Re_2Cl_8\right]^{2-}$ (d) $\left[Ru_3\left(CO\right)\right]_{12}$

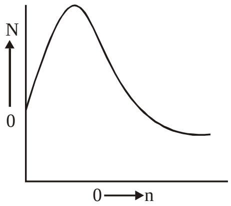
1.7. The complex with spin-only magnetic moment of ~ 4.9 B.M. is
(a) $\left[Fe\left(H_2O\right)_6\right]^{2+}$ (b) $\left[Fe\left(CN\right)_6\right]^{3-}$ (c) $\left[Fe\left(CN\right)_6\right]^{4-}$ (d) $\left[Fe\left(H_2O\right)_6\right]^{3+}$

1.8. The complex with exhibits lowest energy electronic absorption band is
(a) $\left[NiCl_4\right]^{2-}$ (b) $\left[Ni\left(H_2O\right)_6\right]^{2+}$ (c) $\left[Ni\left(CN\right)_4\right]^{2-}$ (d) $\left[Ni\left(CO\right)_4\right]$

1.9. The system for which energy (E) increases quadratically with the quantum number (n) is
(a) particle-in-a-one dimensional box (b) hydrogen atom
(c) one dimensional harmonic oscillator (d) rigid rotor

1.10. Among the following orbitals of a diatomic molecule, the bonding one is
(a) $1\sigma_u$ (b) $2\sigma_u$ (c) $1\pi_u$ (d) $1\pi_g$

1.11. The population (N) distribution over states (n) of a diatomic molecule corresponds to



(a) Translation (b) Vibration (c) Rotation (d) Electronic.

1.12. $^{2}P_{3/2}$ is the ground state of

(a) H (b) Li (c) B (d) F

1.13. The vapour pressure of pure components ‘A’ and ‘B’ are 200 torr and 100 torr respectively. Assuming a solution of these components obeys Raoult’s law, the mole fraction of component ‘A’ in vapour phase in equilibrium with a solution containing equimoles of ‘A’ and ‘B’ is

(a) 0.33 (b) 0.66 (c) 0.80 (d) 0.50

1.14. The half-life time for a reaction at initial concentrations of 0.1 and 0.4 mol^{-1} are 200s and 50s respectively. The order of the reaction is

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

1.15. The pH of a buffer solution containing 4×10^{-3} and 0.4 moles of acetic acid ($pK_a = 4.76$) and sodium acetate respectively will be

(a) 6.76 (b) 4.76 (c) 2.76 (d) 0.76

1.16. Under the equilibrium conditions for the reaction, $C(s)+CO_2(g) \rightleftharpoons 2CO(g)$, the total pressure is 12 atm. The value of K_p is

(a) 16 (b) 0.5 (c) 2 (d) 32

1.17. An aqueous solution containing *m* moles of non-volatile solute freezes at –0.186°C. The elevation in the boiling point of the same aqueous solution ($K_f = 1.86^{o}$, $K_b = 0.512^{o}$) would be

(a) 0.186 (b) 0.512 (c) 0.0512 (d) 0.512/1.86

1.18. The two H’s at C-2 and C-3 in (2R, 3S) tartaric acid

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

1.19. Oxymercuration-demercuration reaction of 1-methylcyclohexene gives

(a) cis-2-methylcyclohexanol (b) trans-2-methylcyclohexanol

(c) 1-methylcyclohexanol (d) mixture of cis and trans-2-methylcyclohexanol

1.20. Bromination of (E)-2-butenedioic acid gives

(a) (2R, 3S)-2, 3-diboromosccinic acid (b) (2R, 3R)-2, 3-dibromosuccinic acid

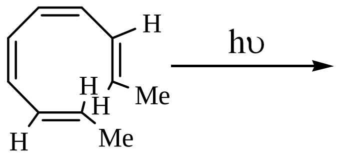
(c) 5-iodo-tetrahydropyran-2-one (d) 4-pentenoyliodide

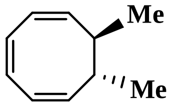
1.21. 4-Pentenoic acid when treated with I_2 and $NaHCO_3$ gives

(a) 4, 5-diiodopentanoic acid (b) 5-iodomethyl-dihydrofuran-2-one

(c) 5-iodo-tetrahydropyran-2-one (d) 4-pentenoyliodide

1.22. The following tetraene upon photolysis gives



(a)


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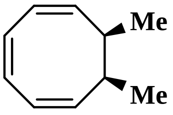

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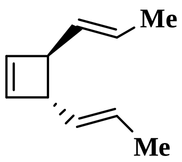
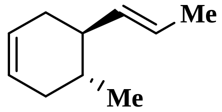
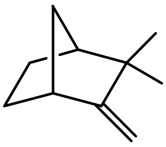
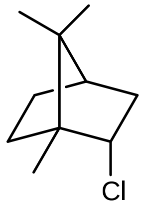
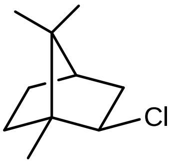
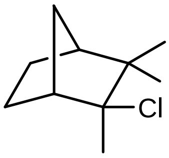
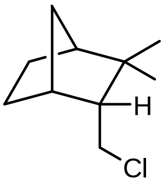


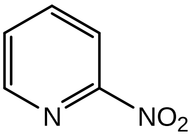
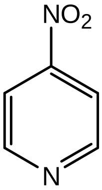
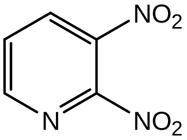
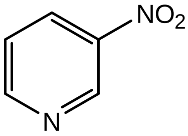
(d)


1.23. The product formed upon heating camphene with HCl is

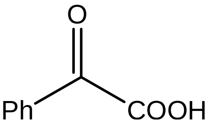
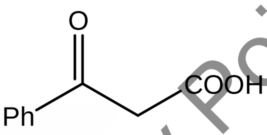

(Camphene)

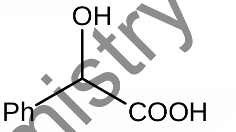
(a)  (b)  (c)  (d) 

1.24. Pyridine undergoes electrophilic nitration at elevated temperature to give the following as a major product:

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

1.25. Among the following, the acid which undergoes fastest decarboxylation is

(a)  (b) 

(c) PhCOOH (d) 

Section-B

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. Which of the following statements about the molecule NOCl is correct?
(a) It has a linear structure (b) It belongs to the point group C_s
(c) It does not have a dipole moment (d) It is a chiral molecule

2.2. Which of the following is an *arachno* borane?
(a) $[B_6H_6]^{2-}$ (b) $[B_5H_9]$ (c) $[B_2H_6]$ (d) $[B_8H_{14}]$

2.3. C_{60} has
(a) 14 pentagons and 18 hexagons (b) 12 pentagons and 20 hexagons
(c) 10 pentagons and 20 hexagons (d) 12 pentagons and 18 hexagons

2.4. The order of acidity in boron trihalides is
(a) $BF_3 > BCl_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$
(c) $BF_3 > BBr_3 > BCl_3$ (d) $BBr_3 > BF_3 > BCl_3$

2.5. The compound which obeys 18-electron rule is:
(a) $Mn(CO)_3$ (b) $Fe(CO)_4$ (c) $V(CO)_6$ (d) $Cr(CO)_6$

2.6. The Si–O–Si bond angle in $Me_3SiOSiMe_3$ is
(a) ~ 120° (b) ~ 180° (c) ~ 90° (d) ~ 109°

2.7. The compound which exhibits Jahn-Teller distortion is:
(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{3+}$ (c) $[Cr(H_2O)_6]^{3+}$ (d) $[Fe(CN)_6]^{4-}$

2.8. The orange colour of $Cr_2O_7^{2-}$ is due to
(a) metal to ligand charge transfer transition (b) ligand to metal charge transfer transition
(c) crystal-field transition (d) charge-transfer complex formation

2.9. Among the following diatomic molecules, the shortest bond length is to be found in
(a) C_2 (b) N_2 (c) O_2 (d) F_2

2.10. Among the following diatomic molecules, the one that shows EPR signal is
(a) Li_2 (b) B_2 (c) C_2 (d) N_2

2.11. Among the following elements, the one that acts as the major component in a semiconductor is
(a) C (b) Si (c) Ga (d) As

2.12. Among the singlet (S), doublet (D) and triplet (T) electronic states, phosphorescence involves transition between
(a) S and S (b) D and D (c) T and T (d) S and T

2.13. In a system, when the chemical potential of each component is the same for all the phases, the equilibrium is said to be
(a) metastable equilibrium (b) thermal equilibrium
(c) composition equilibrium (d) mechanical equilibrium

2.14. The number of molecules of an ideal gas in a 8.21 container at 380 torr and 27ºC will be
(a) 1.0×10^{23} (b) 1.0×10^{22} (c) 6.02×10^{23} (d) 12.04×10^{23}

2.15. The criterion for the spontaneity of a process is:
(a) $\Delta S_{sys} > 0$ (b) $\Delta S_{surr} > 0$ (c) $\Delta S_{sys} + \Delta S_{surr} > 0$ (d) $\Delta S_{sys} - \Delta S_{surr} > 0$

2.16. ΔH and ΔE for the reaction $Fe_2O_3(s) + 3H_2(s) \longrightarrow 2Fe(s) + 3H_2O(\ell)$ at constant temperature are related as
(a) $\Delta H = \Delta E$ (b) $\Delta H = \Delta E + RT$ (c) $\Delta H = \Delta E + 3RT$ (d) $\Delta H = \Delta E - 3RT$

2.17. For an ideal gas following adiabatic reversible expansion, plot of log P versus log$V$ is linear with a slope equal to $(\gamma = C_P / C_V)$:
(a) $1/\gamma$ (b) $-1/\gamma$ (c) γ (d) $-\gamma$

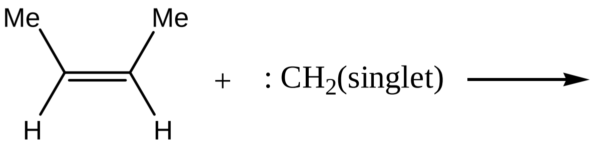
2.18. Toluene when refluxed with Br_2 in the presence of light mainly gives
(a) o-bromotoluene (b) p-bromotoluene
(c) mixture of o- and p-bromotoluene (d) benzyl bromide

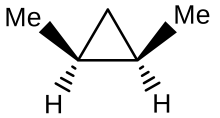
2.19. Optically active 2-octanol rapidly loses its optical activity when exposed to
(a) dilute acid (b) dilute base (c) light (d) humidity

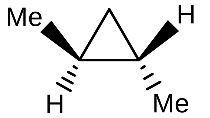
2.20. 1-Hexyne upon treatment with disiamylborane followed by oxidation with H_2O_2 gives
(a) hexanoic acid (b) hexenol (c) hexanal (d) hexanol

2.21. (E)-3-bromo-3-hexene when treated with CH_3O^- in CH_3OH gives
(a) 3-hexyne (b) 2-hexyne (c) 2, 3-hexadiene (d) 2, 4-hexadiene

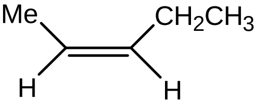
2.22. The major product formed in the following reaction is:



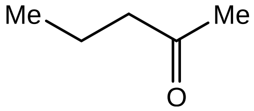
(a) 

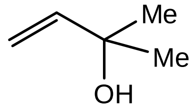
(b) 

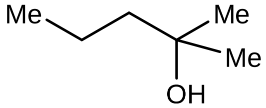
(c) 50 : 50 mixture of above two compounds

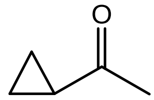
(d) 

2.23. Methyl vinyl ketone upon reaction with $LiCuMe_2$ gives a major product whose structure is

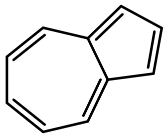
(a) 

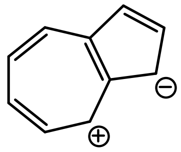
(b) 

(c) 

(d) 

2.24. The following hydrocarbon has a dipole moment of 0.8 D because



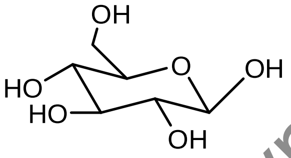
(a) It exist as  in which both the rings exhibit aromaticity.

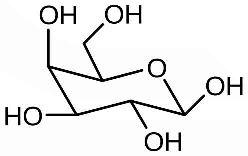
(b) Charge separation permits conformation stability

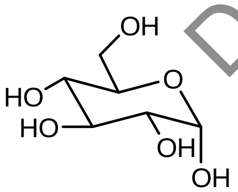
(c) The two rings are of different size

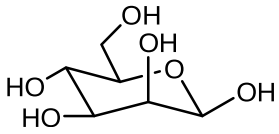
(d) The molecule obeys 4n + 2 Huckel rule

2.25. β-D-Glucose is represented as

(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. Write the structures of the following compounds

(A) S_4N_4 (B) $1,2 = B_4C_2H_6$ (C) SF_4CH_2

3.2. Account in about 10 lines the fact that the IR stretching frequency of the P-O bond increases in the order

$$(CH_3)_3PO < Cl_3PO < F_3PO$$

4. Complete the following reactions supplying the missing reactant or product

(a) $n\left[\left(CH_3\right)_2 SiO_4\right]+\left(CH_3\right)_3 SiOSi\left(CH_3\right)_3 \xrightarrow{H_2SO_4} (A)$

(b) $Al_2\left(CH_3\right)_6 + 6H_2O \longrightarrow (B)+(C)$

(c) $3BCl_3 + 3NH_4Cl \longrightarrow (D)$

(d) $E \xrightarrow[\text{hap tan e, 77K}]{\text{hv, 270 nm}} (MeS)_2\,Si = Si(MeS)_2$ (MeS = 2, 4, 6-trimethylphenyl)

(e) $SbF_5 + BrF_3 \longrightarrow (F)+(G)$

5.1. State whether the following is true or false and explain your choice in about 3 lines. “The Ni-C bond length in nickelocene is longer than the Fe-C bond length in ferrocene”.

5.2. Write the structure of $CO_4(CO)_{12}$. Using the isolobal analogy show which of the following fragments you would use to replace one of the cobalt fragments in the above cluster? Write the structure of the cluster so formed

(i) CH_2 (ii) CH (iii) NH_2 (iv) CH_3

6.1. From among the following reactions identify the type of reaction involved viz., oxidative-addition, reductive elimination, insertion or addition. Justify your choice

(i) $\left[RhI_3(CO)_2(CH)_3\right]^- \longrightarrow \left[RhI_3CO(\text{solvent})(COCH_3)\right]^-$

(ii) $\left[Co_2(CO)_8\right] + H_2 \rightleftarrows 2\left[CoH(CO)_4\right]$

(iii) $Mn_2(CO)_{10} + Br_2 \rightarrow 2MnBr(CO)_5$

6.2. Write the structures of the products formed in the following reactions, keeping in view the 18-elecrtron rule

(i) $\eta^4C_4H_6Fe(CO)_3 + HCl \rightarrow$

(ii) $\left(\eta^5Cp\right)_2 Fe + HBF_4 \rightarrow$

7.1. Lower the symmetry of a complex, closer is its magnetic moment, to the spin-only value. Explain in 2-3 sentences.

7.2. Write the d-orbital splitting diagrams for a square pyramidal and a trigonal bipyramidal complex

8.1. Draw the active site structure of rubredoxin and two common forms of ferredoxins.

8.2. Cytochrome C is a redox protein but myoglobin is an oxygen storage protein. Justify in 2-3 sentences.

9.1. The complex $\left[Fe(H_2O)_6\right]^{2+}$ displays two overlapping absorption bands at ~1000 nm. Provide an explanation in 2-3 sentences.

9.2. Comment in 5-6 lines on the metal-olefin bonding in $K\left[PtCl_3(C_2H_4)\right]$

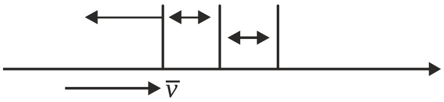
10. O_3 molecule has bent geometry in its ground electronic state. Using Huckel approximation, derive the eigen values of the π molecular orbitals of O_3 and write down the electronic configuration. Also how schematically all the three π molecular orbitals and label them bonding, non-bonding and antibonding.

11.1. Show how would you distinguish between propanal and acetone using NMR spectroscopy. Label the axes properly and schematically show all the important features in the spectrum.

11.2. Using Raman spectrum and IR spectrum, show how you will determine whether a substance is trans-or cis-1, 2-dichloroethylene (without knowing the frequencies at which different vibrational modes occur)

12.1. H_2 has one of the largest rotational constants $\left(B_e = h/8\pi^2 Ic \sim 60\text{cm}^{-1}\right)$ for a diatomic molecule. Predict the spacing between the lines in the rotational Raman spectrum indicated.

Rayleigh line



12.2. Predict the spacing between the same set of lines in the rotational Raman spectrum of HD.

13. Two half cells of hydrogen-oxygen fuel cell under basic conditions can be depicted as $OH^-/O_2(g)/Pt$ and $OH^-/H_2(g)/Pt$ and their standard electrode potentials at 25ºC are 0.4009 and –0.8279 V respectively. Write the half cell reactions and the complete cell reaction. Depict the complete cell and calculate the emf of the cell.

14. The solubility of Ag_2CrO_4 in water is 8×10^{-5} mol kg^{-1} at 25ºC and its solubility in 0.04 mol kg^{-1} $NaNO_3$ solution is 8.84×10^{-5} mol kg^{-1}. What is the mean ionic activity coefficient of Ag_2CrO_4 in 0.04 mol kg^{-1} $NaNO_3$?

15. The formation of phosgene by the reaction $CO + Cl_2 \rightarrow COCl_2$ appears to follow the mechanism:

$$Cl_2 \xrightarrow{k_1} 2Cl$$

$$Cl + CO \xrightarrow{k_2} COCl$$

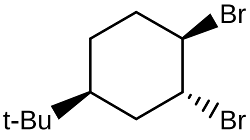
$$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$$

$$COCl \xrightarrow{k_4} CO + Cl$$

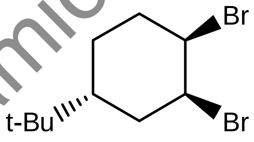
$$2Cl \xrightarrow{k_5} Cl_2$$

Assuming that the intermediates COCl and Cl are in a steady state, find the rate law for the formation of $COCl_2$.

16.1. Account for the fact that only one of the following compounds A and B give the expected elimination product with KI in acetone



(A)



(B)

16.2. Account for the fact that aniline is not a suitable substrate in the Friedel-Crafts alkylation reaction

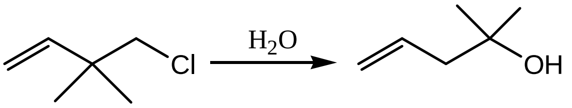
17. Suggest a suitable method and write all the steps for the following transformations

(i) anisole to 2-cyclohexenone

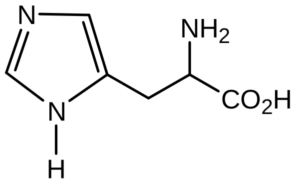
(ii) malonic ester to cyclobutanecarboxylic acid

18.1. An industrial preparation of phenol and acetone makes use of cumene and atmospheric oxygen as starting materials to produce cumene hydroperoxide which is then converted to products. Suggest what steps are involved in the process.

18.2. Suggest a plausible mechanism for the following hydrolysis reaction

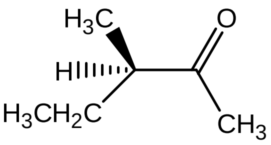


19.1. Explain briefly which nitrogen of the side chain ring of histidine is protonated in the monocationic form?

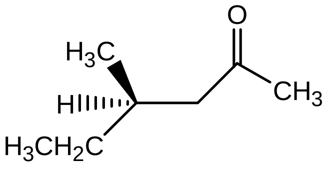


(Histidine)

19.2. Optically active ketone A undergoes racemization in basic solution. Suggest a mechanism for this process. Explain whether ketone B would also racemize in basic solution?

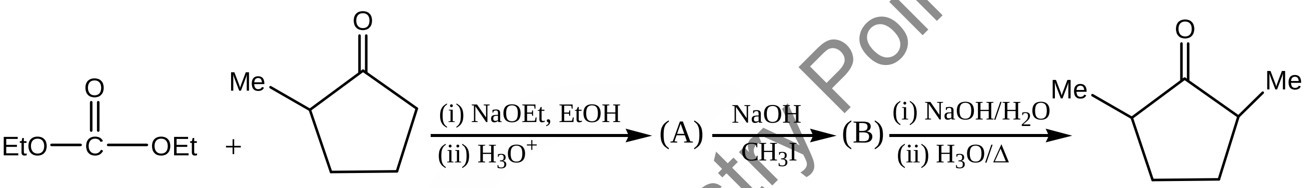


(A)



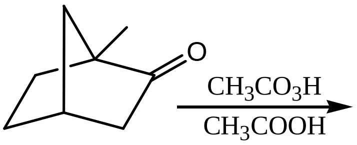
(B)

20.1. Write the missing products, A and B in the following reaction scheme

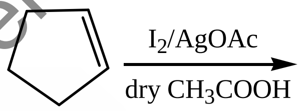


20.2. Write the structures of the major product in the following reactions.

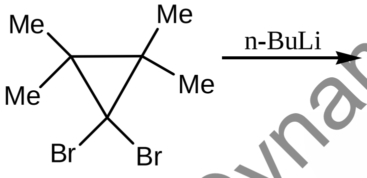
(i)



(ii)

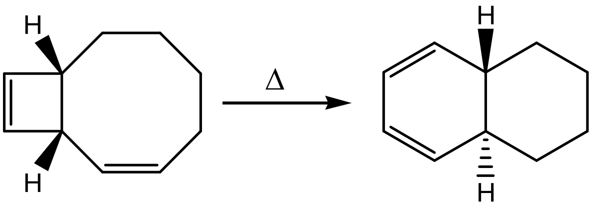


(iii)

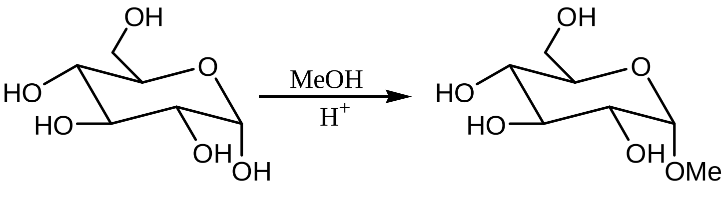


21. Suggest a suitable mechanism for each of the following reactions

(i)

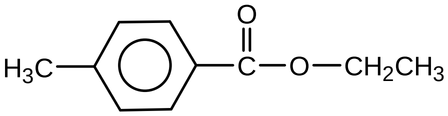


(ii)



α-D-Glucopyranose Methyl-α-D-glucoside

22.1. Predict the approximate chemical shifts and multiplicities for the absorptions in the ^{1}H NMR spectrum of the following compound.



22.2. Explain how the peaks at m/z 115, 101 and 73 arise in the mass spectrum of 3-methyl-3-heptanol.