Ph. D. Chemistry Entrance Examination – 2010

Time: 2 hours **Maximum marks: 75**

HALL TICKET NUMBER:

Read the following instructions carefully before answering the paper

1. Enter your hall ticket number in the space provided above. DO NOT write your name or hall ticket number anywhere else on the question paper.
2. Verify that this booklet contains **36** pages (including the space provided for rough work) with **25 (Section A)** + **30 (Section B)** questions.
3. Answer **ALL** the questions in **Section A**, and **ANY TEN** in **Section B**.
4. Each question in **Section A** carries **one mark**. Each question in **Section B** carries **five marks**.
5. There will be negative marking in **Section A**. For each wrong answer, ⅓ mark will be deducted. In case of a tie, marks obtained in Section A will be used to break it.
6. In **Section A**, write only your choice A, B, C or D in the space provided. In **Section B**, answers should be written in the space provided following each question. No additional sheets will be provided.
7. Use of calculators is permitted.
8. After the examination is over, the entire paper must be handed over to the invigilator before leaving the examination hall.

Do not write on this page below this line

Section B

Q. No.	1	2	3	4	5	6	7	8	9	10
Q. No.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Q. No.	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**

Section A	Correct	Incorrect	Unanswered	Section B	

U-59

SECTION A

(Answer all questions; enter your choice in the box provided against each question)

1. The conductivity of polysilanes is due to

   (A) π - delocalisation

   (B) σ - delocalisation

   (C) presence of an impurity

   (D) proton transfer **Ans.** ☐

2. Planet Mars is called a "red planet" as it contains

   (A) iron compounds

   (B) organic dyes

   (C) Mo-S compounds

   (D) V-O compounds **Ans.** ☐

3. If the bond is along the x-axis, which of the following combinations cannot form a molecular orbital?

   (A) p_x and s

   (B) p_x and p_x

   (C) p_z and p_z

   (D) p_z and s **Ans.** ☐

4. Which of the following molecules will form the strongest hydrogen bond with water?

   (A) H_2O

   (B) H_2S

   (C) I_2

   (D) PH_3 **Ans.** ☐

5. In tetragonally elongated $[Mn(acac)_3]$ (acac = acetylacetonato), the 4th d-electron of Mn resides in

   (A) $d_{x^2-y^2}$

   (B) d_{z^2}

   (C) d_{xy}

   (D) d_{yz}

   Ans. ☐

6. $SnCl_3^-$ is

   (A) triangular

   (B) pyramidal

   (C) T-shaped

   (D) tetrahedral

   Ans. ☐

7. The bronze colored potassium graphite (KC_8), which is prepared by melting potassium over graphite powder, is

   (A) an intercalation compound and a strong reducing agent

   (B) an adduct and a strong oxidizing agent

   (C) a covalent compound and a strong nucleophile

   (D) an ionic compound and a strong electrophile

   Ans. ☐

8. Using Wade's rule predict the structure of $B_9H_{14}^-$.

   (A) closo

   (B) nido

   (C) arachno

   (D) scorpionato

   Ans. ☐

9. The molecule with the smallest rotational constant (B) among the following is (the number indicated within bracket is the bond length of the molecule)

(A) LiH (0.98 Å)

(B) NaH (1.1 Å)

(C) KH (1.2 Å)

(D) CsH (1.5 Å) **Ans.** ☐

10. The number of IR and Raman active modes of OCS are respectively

(A) 4, 4

(B) 3, 1

(C) 1, 3

(D) 2, 2 **Ans.** ☐

11. Symmetry number is the total number of symmetry equivalent orientations that can be arrived at using the rotational symmetry operations of the molecule. The symmetry number of cyclopropane is

(A) 2

(B) 3

(C) 5

(D) 6 **Ans.** ☐

12. Assuming full equipartition translational and rotational contributions, but only 20% vibrational contribution at 25 °C, to the heat capacity at constant pressure (C_p), the C_p for acetylene at 25 °C is (R = gas constant)

(A) 3.9 R

(B) 4.6 R

(C) 4.9 R

(D) 6.0 R **Ans.** ☐

13. What is the maximum wavelength of the X-ray that can be used to obtain Bragg reflection from (100) plane of a simple cubic crystal with edge 1.5 Å?

(A) 3.5 Å

(B) 1.5 Å

(C) 3.0 Å

(D) 1.54 Å

Ans. ☐

14. When ↑ is the spin on Mn^{2+} ion and ↓ is the spin on Cu^{2+} ion, which one of the following arrangements represents ferrimagnetic ordering?

(A) ↑-↑-↑-↑-↑-↑

(B) ↑-↓-↑-↓-↑-↓

(C) ↑-↓-↑-↓-↑-↓

(D) ↑-↑-↑-↑-↑-↑

Ans. ☐

15. The electronic ground state configuration of C_2 is

(A) $^1\Pi_u$

(B) $^2\Pi_u$

(C) $^1\Pi_g$

(D) $^1\Sigma_g^+$

Ans. ☐

16. For a process at equilibrium, a plot of ln K against 1/T gave a straight line with a negative slope of 7040 K^{-1}. The ΔH° value is ($R = 8.314$ J K^{-1} mol^{-1} = 0.0821 atm dm^3 K^{-1} mol^{-1})

(A) 58.53 kJ mol^{-1}

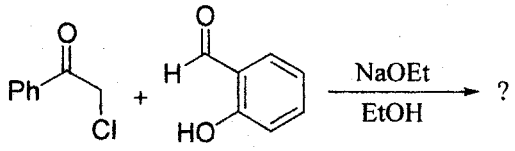
(B) 5.853 kJ mol^{-1}

(C) 5.853 kCal mol^{-1}

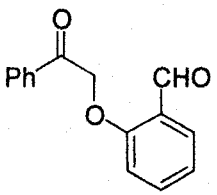
(D) 785.3 kCal mol^{-1}

Ans. ☐

17. The final product of the following reaction is



(A)



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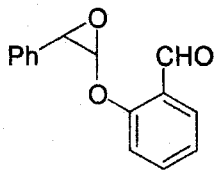

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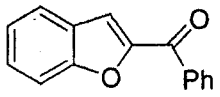

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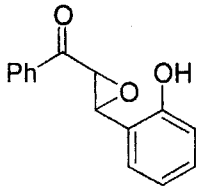
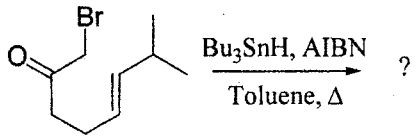
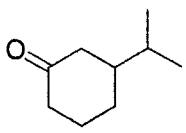


Ans. ☐

18. The product of the following reaction is



(A)



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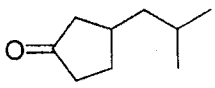

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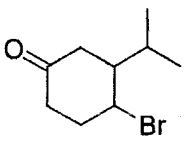
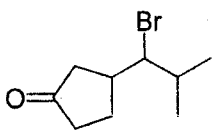


(D)



Ans. ☐

U-59

19. The characteristic peak in EI mass spectrum of $PhCH_2OH$ is at m/z =

(A) 108

(B) 77

(C) 109

(D) 91

Ans. ☐

20. The C=O stretching vibrations in aliphatic aldehyde, ketone and ester, respectively occur at the approximate wavenumbers:

(A) 1715, 1745 and 1735 cm^{-1}

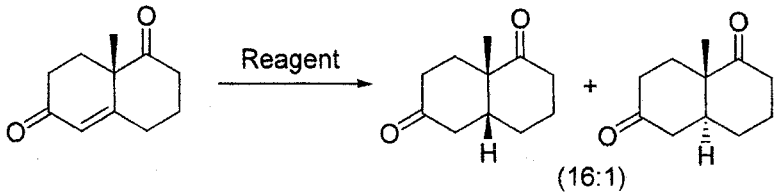
(B) 1735, 1715 and 1745 cm^{-1}

(C) 1745, 1715 and 1735 cm^{-1}

(D) 1715, 1735 and 1745 cm^{-1}

Ans. ☐

21. A suitable reagent for the following reaction is



(A) DIBAL-H

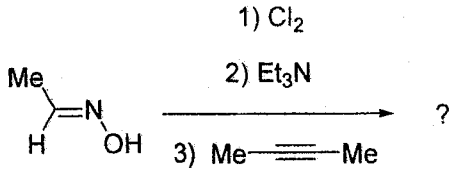
(B) B_2H_6

(C) $NaBH_4$

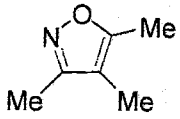
(D) $(Ph_3P)CuH$

Ans. ☐

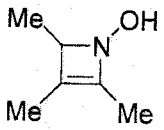
22. The product obtained in the following reaction is



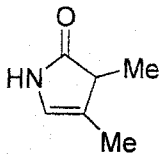
(A)



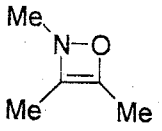
(B)



(C)



(D)



Ans. ☐

23. *S*-Mandelic acid has a specific rotation of +158°. The specific rotation of a mixture of (*R*)-mandelic acid and (*S*)-mandelic acid (mole ratio = 8:1) would be

(A) +122.9°

(B) −122.9°

(C) +35.1°

(D) −35.1°

Ans. ☐

24. Arrange the following intermediates in the order of decreasing basicity (strongest to weakest):

I : $H_2C{=}CH^-$ II : $CH_3CH_2^-$ III : $CH_3CH_2O^-$ IV : $HC{\equiv}C^-$

(A) IV > I > II > III

(B) III > II > I > IV

(C) III > IV > I > II

(D) II > I > IV > III

Ans. ☐

25. Name the following reaction:

U-59

(A) Hofmann-Loffler reaction

(B) Barton reaction

(C) Hofmann-Loffler-Freytag reaction

(D) Cope reaction

Ans. ☐

END OF SECTION A

SECTION B

(Answer any 10 questions)

1. In an adsorption experiment, the fractional coverage on surface was found to be 0.67 and 0.8 when the external pressure of the adsorbate was 1.0 and 2.0 atm., respectively. Determine the Langmuir coefficient, K. [5]

2. Given the chemical reaction, $A + B \rightarrow P + 2B$, with a rate constant k,
   (a) write down the rate law for the disappearance of A.
   (b) Determine the concentration of A as a function of time when $[A] = [B] = 1.0$ mol L^{-1} at $t = 0$. [2+3]

3. Consider the cell, $Ag \mid Ag_2SO_4 \mid H_2SO_4$ (aq, 0.1 m) $\mid H_2$ (g, 1 atm) $\mid$ Pt.

   (a) Write the half cell and full cell reactions.

   (b) If the standard EMF, E^0 of the cell at 25 °C is –0.63 V, calculate the standard potential of the left hand electrode.

   (c) If the EMF, E of the cell at 25 °C is –0.7 V, calculate the value of $(E - E^0)$ at 35 °C.

   Assume ideal behaviour for the solution and the gas. [2+1+2]

4. (a) Show that the transition $^1A_2 \leftarrow {}^1A_1$ is electronic dipole forbidden in H_2O molecule.
   (b) The series of lines in the microwave spectrum of $^1H\ ^{127}I$ are spaced 12.8 cm^{-1} apart. Calculate its bond length. [m(^{127}I) = 126.9045 au] [2+3]

5. Given the Hamiltonian, $H = -(h^2/8\pi^2 I)\, d^2/d\varphi^2 + i.B\, d/d\varphi$, corresponding to a particle on a ring in an external magnetic field B perpendicular to the plane of rotation, state the boundary conditions on the wave function and determine its eigenvalues and eigenfunctions. [1+2+2]

6. Blood is said to be isotonic with 0.85% (w/v) NaCl solution at 40 °C. Assuming complete dissociation of NaCl, calculate total concentration of various solutes in blood. What is its approximate freezing point? (Given $K_f = 1.86$ K/(mol kg^{-1})) [5]

7. The Debye temperature of two isomorphous ionic solids AB and XY are 300 K and 250 K, respectively. The lattice heat capacity of AB at 5 K is 0.05 J mol^{-1} deg^{-1}. Estimate the heat capacity of XY at 5 K and that of AB at 2 K. [5]

8. (a) Draw a schematic diagram of the crystal structure of potassium chloride.

(b) If the unit cell length is 6.295 Å, calculate the density (in g cm^{-3}) of crystalline KCl. Atomic weights: K = 39.098, Cl = 35.453

(c) What is Schottky defect ? If Schottky defect in the KCl crystal reduces its density by 6.25%, show a schematic representation of the defect in the unit cell. [2+1+2]

U-59

9. Write the partition function for a 2-level system with the lower state of energy zero and the upper state of energy ε. Plot the partition function and fraction of molecules in the i^{th} state as a function of temperature, with temperature varying from zero to infinity. [5]

10. (a) The vibrational frequency of a diatomic molecule AB is ν. If another molecule CD has the same force constant and the mass of C and D are respectively twice that of A and B, express the vibrational frequency of CD in terms of ν.

(b) Classify BCl_3 and CH_3I as either a prolate or an oblate symmetric top. [3+2]

11. What are the possible products when hexafluoro cyclotriphosphazene is reacted with dilithium salt of 1,3-propane diol in 1:1 mol ratio? Draw all the structures. [5]

12. Along with appropriate equations describe what happens

a) When metallic potassium is dissolved in ammonia to form a dilute solution.

b) When more potassium is added to form a concentrated solution.

c) When solution (a) and (b) are evaporated carefully in vacuo.

d) When (a) is treated with Fe_2O_3

e) How can (d) be considered a leveling reaction [5x1]

13. (a) Formulate neutral 18 electron complexes of chromium which contain only i) cyclopentadienyl and nitrosyl ligands and ii) cyclopentadienyl, carbonyl and nitrosyl ligands

b) Predict the structure of $[W(CO)_2(C_5H_5)_2]$

c) Show by electron counting that $Co_4(CO)_{12}$ obeys 18 electron rule. [2+2+1]

14. (a) Calculate the spin only magnetic moment of $Mn(CN)_6^{2-}$ ion, making any reasonable assumptions about the ligand field.

(b) The magnetic moment of a four coordinate complex of Ni^{2+} in a magnetically dilute crystalline substance is found to decrease from 2.8 B.M. at 300 K to about 0.1 B.M. at 77 K. Suggest a possible explanation for this observation. [2+3]

15. (a) Draw an octahedron indicating clearly one of the 3-fold rotation (C_3) axes. There is also an improper rotation axis coincident with the C_3 axis. What is the order of this improper axis?

(b) Draw the structures of all possible isomers of $[Cr(oxalate)_2Cl_2]^{3-}$ and label them.[2+3]

16. (a) Using the following standard potentials, calculate the solubility product of TlCl.

$$Tl^+ + e^- \longrightarrow Tl \qquad E° = -0.34\ V$$

$$TlCl + e^- \longrightarrow Tl + Cl^- \qquad E° = -0.56\ V$$

(b) Estimate the minimum potential difference needed for the electrolytic reduction of Al_2O_3 to Al using the free energy given for the following decomposition at 500°C.

$$2/3\ Al_2O_3 \longrightarrow 4/3\ Al + O_2 \qquad \Delta G° = 229\ kcal\ mol^{-1}$$ [3+2]

17. Violet Iodine Vapour **A** $\xrightarrow{\text{in coordinating solvents}}$ Brown **B** $\xrightarrow{\text{heat}}$ Violet **C** $\xrightarrow{\text{cool}}$ Brown **D**

Explain the above observation (**A-D**) using M.O. energy level diagram for diatomic iodine molecule. [5]

18. (a) The spin orbit coupling constant for Eu^{3+} is ~300 cm^{-1}. Explain the room temperature magnetic moment of 3.40 – 3.60 B.M. for this ion.

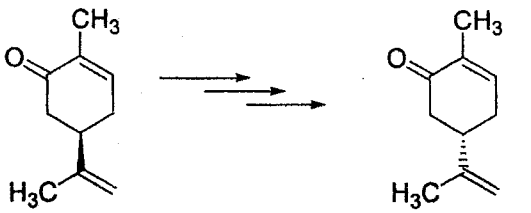
(b) Explain why carbonyl complexes of lanthanides are difficult to prepare. [3+2]

19. (a)Write the structures of (i) the anion in $Na_2[B_2(O_2)_2(OH)_4].6H_2O$ (ii) cation in $[OCNCO]^+[Sb_3F_{16}]^-$ and (iii) discrete anion in $[Me_2NH_2]_3[As_2Cl_9]$ (hint: C.N. of As is 6).

(b) The solution state ^{31}P NMR spectrum of $[HPF_5]^-$ consists of a 20-line multiplet. Explain. (Hint: I for ^1H, ^{31}P and ^{19}F is ½ and natural abundance for all the nuclei is ~ 100%) [3+2]

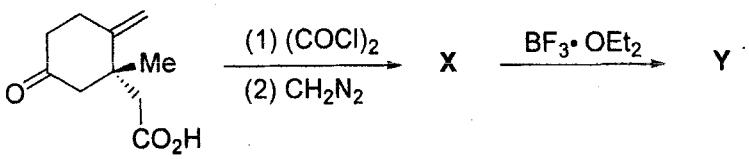
20. What is the difference between homogeneous and heterogeneous catalysis? What is Wilkinson's catalyst and how can you convert it to a heterogeneous catalyst? Explain with necessary equations. [5]

21. Write an acceptable synthetic sequence for the conversion of R-carvone to S-carvone. [5]



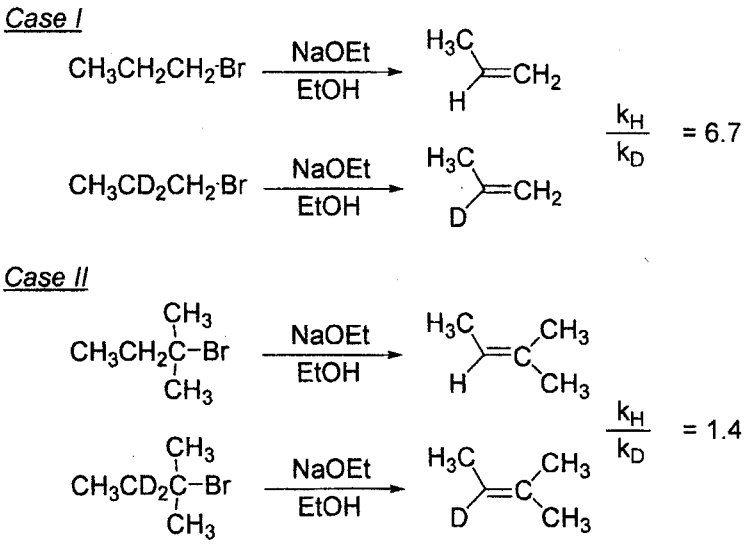
R-carvone S-carvone

22. Give the structures of products (**X** and **Y**) in the following reaction and explain briefly their formation with the intermediates and transition states. [5]

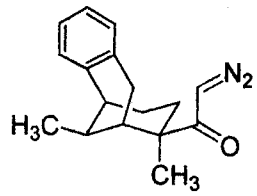


23. (a) The base-catalyzed hydrolysis of ethyl *m*-nitrobenzoate is 63.5 times faster than that of the unsubstituted ester under the same conditions. What will be the comparable rate of hydrolysis of ethyl *p*-nitrobenzoate? [$\sigma_{m\text{-}NO_2} = 0.71$ and $\sigma_{p\text{-}MeO} = -0.27$] [2]

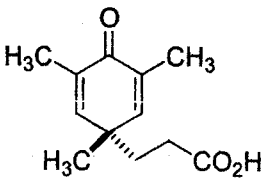
(b) Consider the following dehydrohalogenation reactions. Explain the observed kinetic isotopic effects with relevant transition states. [3]



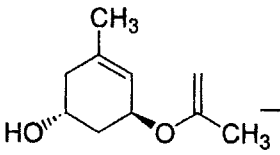
24. Provide the structures of the products with correct stereochemistry in the following reactions. [5x1]

(a) 

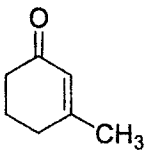
$\xrightarrow[\text{THF}]{\text{Cu (II)}}$?

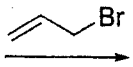
(b) 

$\xrightarrow[H_2O]{Br_2, KBr}$?

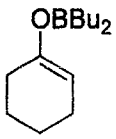
(c) 

$\xrightarrow{\text{heat}}$?

(d) 

$\xrightarrow[\text{1 equiv. } H_2O]{\text{Li, } NH_3}$ 

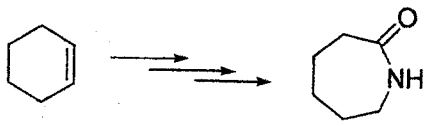
?

(e) 

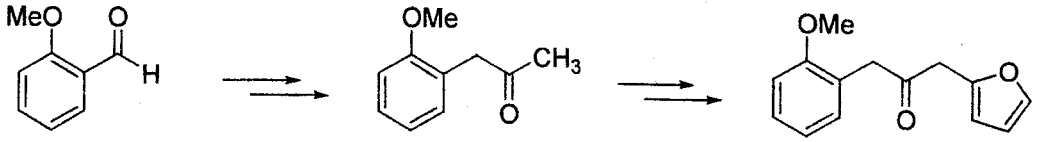
$\xrightarrow{\text{PhCHO}}$?

U-59

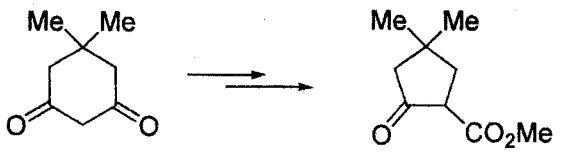
25. (a) Write the synthetic steps required to effect the following transformation. [2]



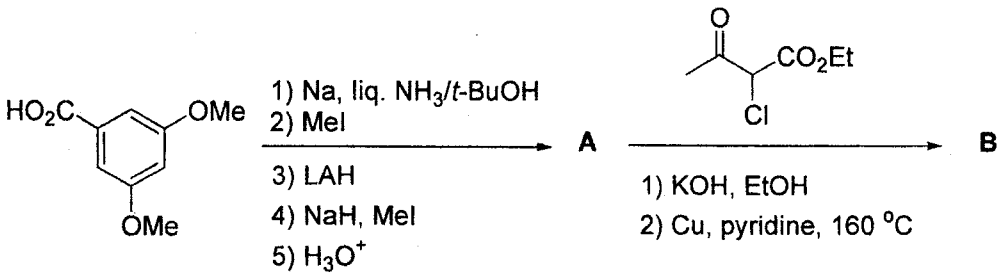
(b) Provide the detailed synthetic steps involved in the following transformation. [3]



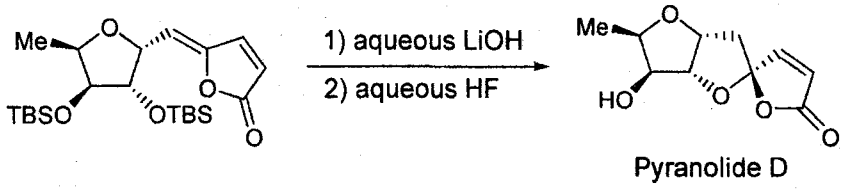
26. (a) How would you effect the following transformation? [2]



(b) Find the products **A** and **B** in the following synthetic sequence. Give the steps and intermediates of the reactions involved. [3]

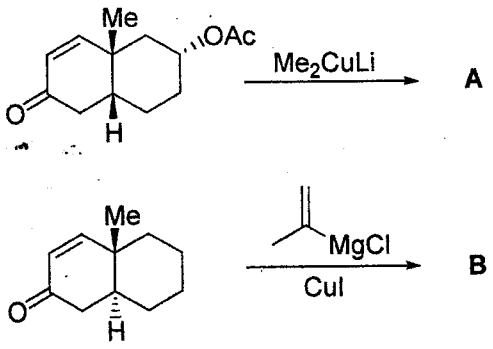


27. In the total synthesis of pyranolide D the final step involves the following reaction sequence given below. Give the intermediates involved in this conversion. [5]

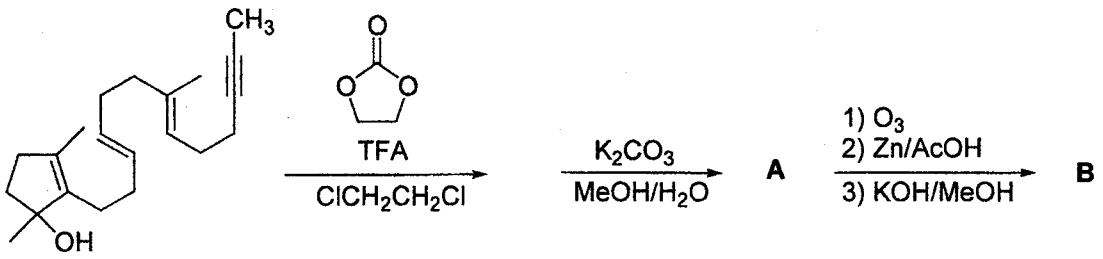


Pyranolide D

28. Give the structures of the products **A** and **B** in the following reaction with correct stereochemistry. Rationalize the stereochemical outcome with appropriate transition states. [5]

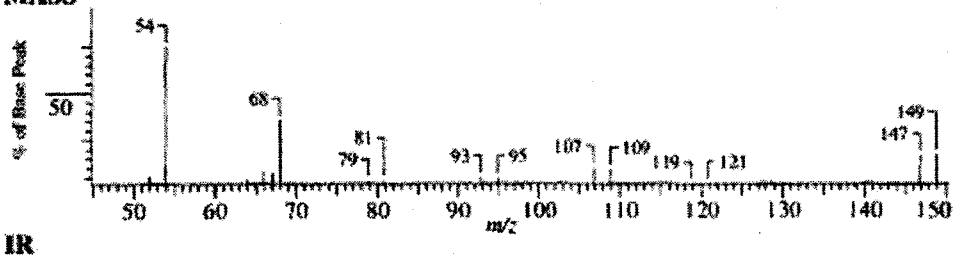


29. Identify the structures of the compounds **A** and **B** in the following reaction. Provide the detailed mechanism involved in these steps. [5]

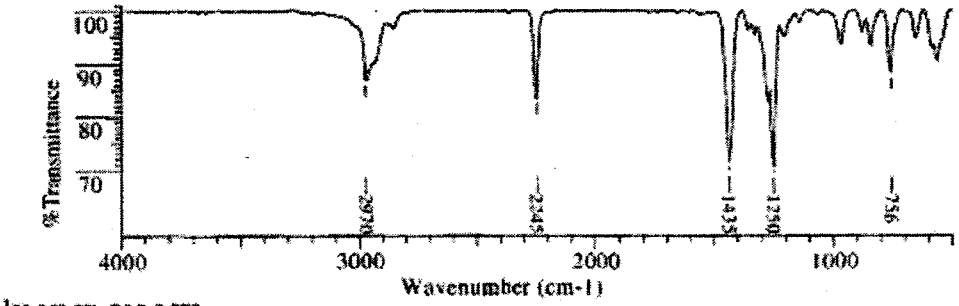


30. Identify the structure of the compound with the spectra shown on the following page (page 32) and interpret the spectral data. [5]

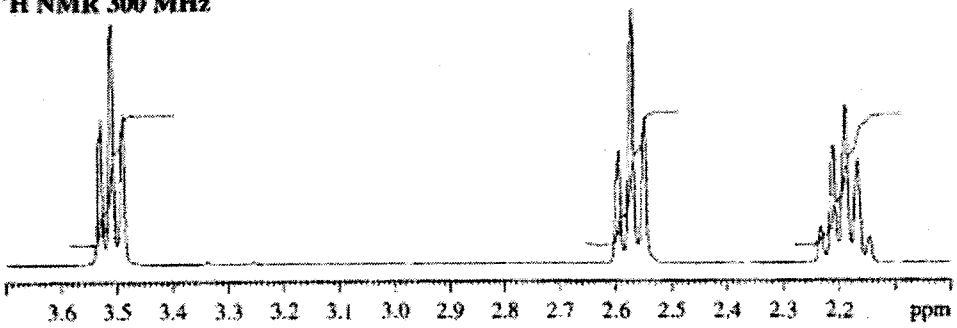
MASS



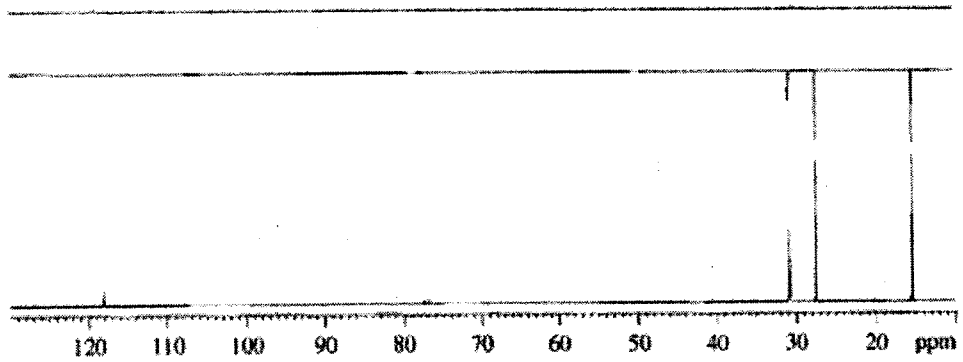
IR



^{1}H NMR 300 MHz



^{13}C/DEPT NMR 75.5 MHz



U-59