

**M.Sc. 3rd Semester Examination, 2019**

**CHEMISTRY**

PAPER – CEM-302

*Full Marks : 40*

*Time : 2 hours*

*The figures in the right hand margin indicate marks*

**Write the answers to questions of each Paper  
in separate books**

*(Physical Special)*

**GROUP—A**

Answer any **four** of the following : 2 × 4

1. What is meant by linear vector space ? Give one example.
2. Calculate the first order correction to ground state energy of a simple Harmonic Oscillator perturb by the following function,

$$H' = g(x) = bx.$$

3. A three level system has energy eigenvalues  $E_1$ ,  $E_2$  and  $E_3$  ( $E_1 < E_2 < E_3$ ). After a small perturbation its Hamiltonian is given by,

$$H = \begin{pmatrix} E_1 & a & b \\ a^* & E_2 + d & 0 \\ b^* & 0 & E_3 \end{pmatrix}.$$

Write down the matrix form of the perturb term.

4. According to Hückel theory, the  $\pi$ -electron charge on the central carbon atom in propyl cation  $(\text{CH}_2\text{CHCH}_2)^+$  is (in unit of electronic charge),

(i)  $\frac{1}{2}$     (ii)  $\frac{1}{\sqrt{2}}$     (iii) 1    (iv) 2

5. Matrix form of a certain system is given below,

$$H = \begin{pmatrix} 2 & 2 \\ 5 & -1 \end{pmatrix}.$$

Find the ground state energy of the system.

6. Vibrational modes of  $\text{C}_2\text{H}_2$  belongs to the irreducible representation ( $\mathbb{R}$ ),  $2A_{1g}$ ,  $E_{1g}$ ,  $E_{1u}$ ,  $A_{1u}$ . Raman active modes of  $\text{C}_2\text{H}_2$  belong to the  $\mathbb{R}$ ,

(i)  $A_{1g}$  and  $E_{1g}$

(ii)  $A_{1g}$  and  $E_{1u}$

(iii)  $E_{1g}$  and  $A_{1u}$

(iv)  $E_{1u}$  and  $A_{1u}$

7. The highest energy  $\pi$ -molecular orbital for the allyl system is

(i)  $\frac{1}{\sqrt{2}}\phi_1 + \frac{1}{2}\phi_2 + \frac{1}{\sqrt{2}}\phi_3$

(ii)  $\frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$

(iii)  $\frac{1}{2}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$

(iv)  $\frac{1}{\sqrt{2}}\phi_1 - \frac{1}{2}\phi_2 - \frac{1}{\sqrt{2}}\phi_3$

8. A certain two level system has stationary state energies  $E_1$  and  $E_2$  ( $E_1 < E_2$ ) with normalized wave functions  $\phi_1$  and  $\phi_2$  respectively. In the presence

of a perturbation  $V$ , the second-order correction to the energy for the first state ( $\phi_1$ ) will be,

$$(i) \frac{\langle \phi_1 | V | \phi_2 \rangle}{E_1 - E_2}$$

$$(ii) \frac{\langle \phi_1 | V | \phi_2 \rangle}{E_2 - E_1}$$

$$(iii) \frac{|\langle \phi_1 | V | \phi_2 \rangle|^2}{E_1 - E_2}$$

$$(iv) \frac{|\langle \phi_1 | V | \phi_2 \rangle|^2}{(E_1 - E_2)^2}$$

### GROUP-B

Answer any **four** questions of the following :  $4 \times 4$

9. The unperturb wavefunction for the infinite square well is given by,

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} \cdot x\right)$$

Suppose one perturb the system by simply raising the floor of the square well a constant amount,  $V_0$ . Find the first order correction to energy. 4

10. A two level unperturb system is described by the Hamiltonian,

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 4 \end{pmatrix}.$$

Now a small perturbation is switched on and the perturbing potential,  $V$  is represented by,

$$V = \begin{pmatrix} a & c \\ c & b \end{pmatrix}.$$

Find the second order correction to energy eigenvalues. 2 + 2

11.  $|j, m\rangle$  are the simultaneous eigenkets of operator  $J^2$  and  $J_z$ . Find the matrix representation of  $J_z$  operator for  $j = \frac{3}{2}$ . 4
12. Deduce the expression of transformation matrix which transform one basis to another in an  $n$ -dimensional linear vector space. 4

13. IR active normal modes of methane belong to the irreducible representation,

(i)  $E + A_1$

(ii)  $E + A_2$

(iii)  $T_1$

(iv)  $T_2$

character table of  $T_d$  point group is given below : 4

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
$A_1$	1	1	1	1	1		$x^2 + y^2 + z^2$
$A_2$	1	1	1	-1	-1		
$E$	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$	
$T_2$	3	0	-1	-1	1	$(x, y, z)$	$(xy, yz, zx)$

14. Deduce the general expression of first order correction to wavefunction using first order time independent non-degenerate perturbation theory. 4

15. Calculate the first order correction to the ground state energy of an anharmonic oscillator whose potential is,

$$U(x) = \frac{1}{2}Kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4.$$

$$\left[ \text{given, } \int_0^{\infty} x^{2m} e^{-\alpha x^2} dx = \frac{(2m-1)!}{2^{m+1} \alpha^m} \left( \frac{\pi}{\alpha} \right)^{1/2} \right.$$

$$\left. \text{and } \psi_0(x) = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \right] \quad 4$$

16. What is meant by charge density and bond order for  $\pi$ -conjugated system? Calculate bond order for allyl cation system. 2 + 2

### GROUP-C

Answer any **two** questions of the following :  $8 \times 2$

17. Use first order time dependent perturbation theory for a two level system to obtain the following expression of probability of transition from state 'n' to 'k'.

$$P_{k \leftarrow n}^{(1)}(t) = \left| C_k^{(1)}(t) \right|^2 = \frac{1}{\hbar^2} \left| \int_0^t H'_{kn}(t) e^{i\omega_{kn}t} dt \right|^2$$

where symbols have their usual significances. Use  $H'$  as constant perturbation and then show the plot of  $P_{k \leftarrow n}^{(1)}$  Vs.  $\omega_{ka}$ . Interpret the plot. 8

18. Use Linear variational principle with Hückel approximation to obtain the energy and wave function of  $\pi$ -MO for butadiene. 8

19. Use degenerate perturbation theory to obtain the splitting of  $n = 2$  state of  $H$ -atom in presence of external electric field and also find the energies and wavefunctions of the resulting states. 8

20. Use group theoretical principle to determine the state of hybridization of central atom in  $[\text{PtCl}_4]^{2-}$ . Also obtain the hybrid orbitals as linear combination of atomic orbitals. Character table of  $D_{4h}$  point group is given below : 4 + 4

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$		
$A_{1g}$	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1		$xy$
$E_g$	2	0	-2	0	0	2	0	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	$z$	
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1		
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1		
$E_u$	2	0	-2	0	0	-2	0	2	0	0	$(x, y)$	

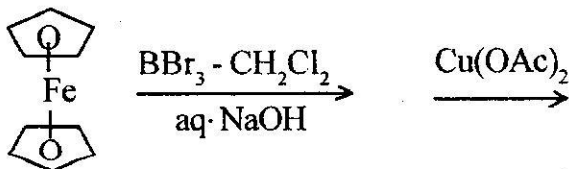


## (Inorganic Special)

## GROUP-A(a)

1. Answer any *two* questions : 2 × 2

(a) Complete the following reaction



(b) How will you synthesize  $[\text{Cp-Ni-Cp-Ni-Cp}]^+$  from nickelocene ?

(c) Comment on the structure of manganocene.

## GROUP-A(b)

2. Answer any *two* questions : 4 × 2

(a) What will be the product when  $\begin{array}{c} \text{Cp} \\ | \\ \text{Fe} \\ | \\ (\text{Co})_3 \end{array}$  is

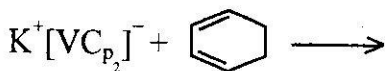
treated with  $\text{HBF}_4$ ,  $\text{CO}$  ?

If this similar kind of reaction is performed in absence of any ligand what happens ? Cite an example.

4

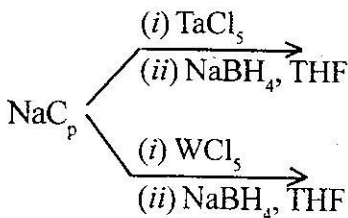
(b) (i) How electrochemical preparation (industrial) of ferrocene is carried out ? 2

(ii) Predict the product with structure 2



(c) (i) Comment on the 'stereochemistry' during the oxidative addition reaction. 2

(ii) Identify 'A' and 'B' in the following scheme : 2



GROUP-A(c)

3. Answer any *one* question : 8 × 1

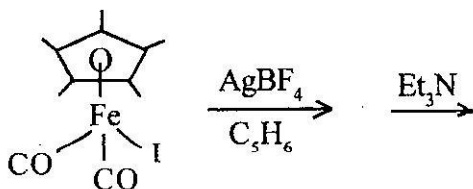
(a) (i) When  $\text{C}_{p_2}^*\text{Ti}$  is reacted with ethylene. What will be the product ? 2

(ii) Schematically present the catalytic

cycle for BP's cativa process for the production of acetic acid. 4

(iii) Mention the problems with the Monsanto processes. 2

(b) (i) Complete the following reaction : 2



(ii) Schematically present the catalytic cycle of hydrogenation using Crabtree's catalyst. 4

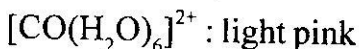
(iii) Write down the chemical composition of Schrock-Osborn's catalyst and Mark's catalyst. 2

#### GROUP-B(a)

4. Answer any two of the following questions : 2 × 2

(a) What do you mean by "vibronic polarization" ?

- (b) Using group theory how can you explain the intensity of colour of the following complex ions :



- (c) Write the all possible term symbols for  $d^2$  electronic configuration. How these terms will split in presence of tetrahedral crystal field ?

### GROUP-B(b)

5. Answer any *two* of the following questions :  $4 \times 2$

- (a) With the help of group theory determine the symmetry of vibrational modes of  $\text{cis-}[\text{ML}_4\text{X}_2]$  molecule using Cartesian coordinate method. Identify the symmetry of IR and Raman active modes in this molecule. (Given below the character table for  $C_{2v}$ ).

4

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

- (b) Explain why the intensity of  $A_2 \rightarrow T_2$  transition around 100 times less than the intensity of  $A_2 \rightarrow T_1$  transition in  $[\text{COCl}_4]^{2-}$  anion. Given below the character table for  $T_d$  point group.

4

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$A_1$	1	1	1	1	1	$x^2 + y^2 + z^2$
$A_2$	1	1	1	-1	-1	
$E$	2	-1	2	0	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$
$T_2$	3	0	-1	-1	1	$(x, y, z)$ $(xz, yz, xy)$

- (c) With the help of group theory determine the symmetries of the group of orbitals of  $F$  atoms which are effective for  $\sigma$ -bond formation in  $\text{PF}_5$  molecule. Write the

appropriate SALCs for these symmetries. Construct a qualitative  $\sigma$ -bonding molecular orbital energy level diagram for  $\text{PF}_5$  molecule. (Given below the character table for  $D_{3h}$  point group).

4

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$		
$A_1'$	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	$(R_x, R_y)$	$(xz, yz)$

## GROUP-B(c)

6. Answer any *one* of the following questions :  $8 \times 1$

- (a) (i) With the help of group theory determine the symmetry of vibrational modes of trans-[ $\text{ML}_4\text{X}_2$ ] molecule using Cartesian coordinate method. Identify the symmetry of IR and Raman active

modes in this molecule. Given below the character table for  $D_{4h}$  point group.

5

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$		
$A_{1g}$	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1		$xy$
$E_g$	2	0	-2	0	0	2	0	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	$z$	
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1		
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1		
$E_u$	2	0	-2	0	0	-2	0	2	0	0	$(x, y)$	

(ii) For trans-dichloro bis-ethylenediamine cobalt (III) complex the ground state is  ${}^1A_{1g}$  and excited singlet states are  ${}^1A_{2g}$ ,  ${}^1E_g$  and  ${}^1B_{2g}$ . Show that  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transition is vibronically allowed with  $(x, y)$  polarized light but forbidden with  $z$ -polarized light.

3

(b) Establish a correlation diagram for a  $d^2$  ion in an octahedral environment. (Given below the character table for  $O_h$  point group).

8

$Q_n$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ( $=C_4^2$ )	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
$A_{1g}$	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 - z^2$
$A_{2g}$	1	1	-1	-1	1	1	-1	1	1	-1		
$E_g$	2	-1	0	0	2	2	0	-1	2	0	$(R_x, R_y, R_z)$	
$T_{1g}$	3	0	-1	1	-1	3	1	0	-1	-1		
$T_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1		$(xy, xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	-1	-1	1	-1	1	-1	-1	1		
$E_u$	2	-1	0	0	2	-2	0	1	-2	0	$(x, y, z)$	
$T_{1u}$	3	0	-1	1	-1	-3	-1	0	1	1		
$T_{2u}$	3	0	1	-1	-1	-3	1	0	1	-1		

*(Organic Special)*

Answer Q. Nos. 1 and 2 and any two from  
Q. Nos. 3, 4, 5, and 6

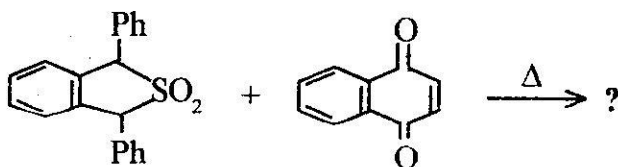
1. Answer any four of the following questions :  $2 \times 4$

(a) What do you mean by "working ligand" and 'auxiliary ligand"? Give an example for each.

(b) Give an example of a reaction with large positive  $\rho$  (reaction constant) value and also justify your answer.



- (c) The  $S_N2$  displacement of iodide from ethyl iodide by substituted phenoxide anions has a  $\rho$  value of exactly  $-1.0$ — Explain.
- (d) Give an example of [9, 9] sigmatropic rearrangement.
- (e) Complete the following reaction :



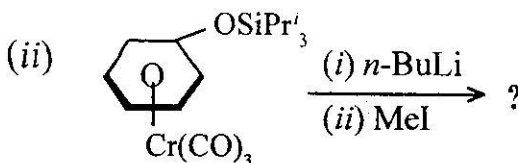
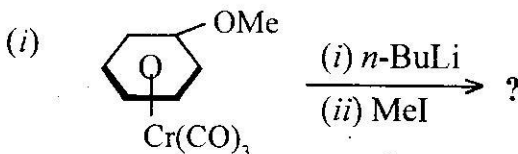
- (f) Show quantitatively that *p*-nitrophenyl-acetic acid is 2.4 times more acidic than phenyl acetic acid.  
 Given :  $\sigma_p$  for  $-\text{NO}_2$  group =  $+0.78$   
 $e$  for ionisation of phenyl acetic acid =  $+0.49$ .
- (g) What happens when chromium tricarbonyl complex of fluorobenzene is treated with *n*-butyl lithium followed by  $\gamma$ -butyrolactone ?
- (h) Give an example of Fischer carbene and also suggest the primary method for its preparation.

2. Answer any *four* questions from the following :  $4 \times 4$

(a) Using FMO and PMO method show that [1, 5] sigmatropic shift is a thermally allowed process. 4

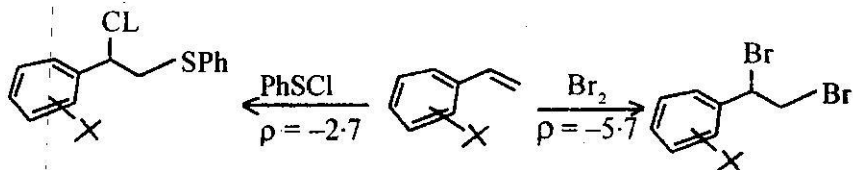
(b) What happens when arylidene derivatives derived from the condensation of chromium tricarbonyl complex of  $\alpha$ -tetralone with aromatic aldehydes is treated with ethyl acetoacetate in presence of a base ? Illustrate your answer with suitable reaction mechanism. 4

(c) Predict the products of the following reactions with proper justification : 2 + 2



- (d) How will you account for the different Hammett  $\rho$  values for the two reactions given below :

4

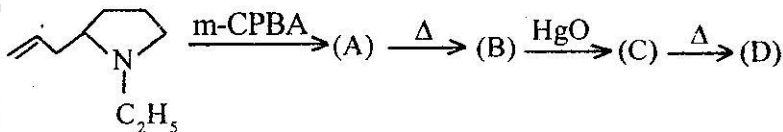


- (e) The rates of aromatic electrophilic substitution in the para-positions of monosubstituted benzenes correlate with  $\sigma^+$  values— Justify with a suitable example. Also, comment on the  $\rho$  values observed for such reaction with proper explanation.

4

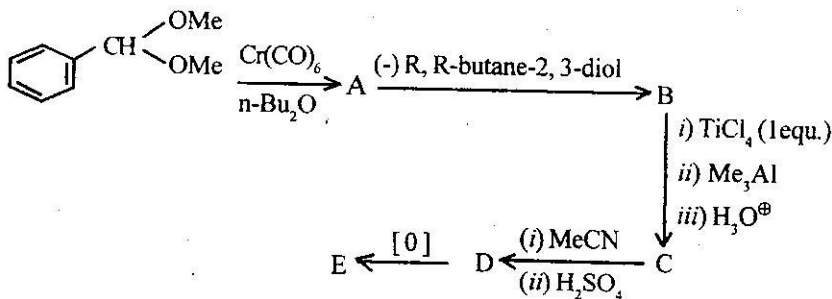
- (f) Identify the products and complete the following reaction sequence :

4



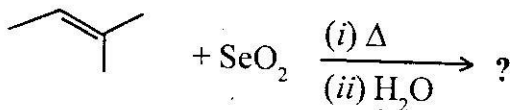
- (g) Predict the products in the following reaction sequence along with their stereochemistry wherever applicable :

4

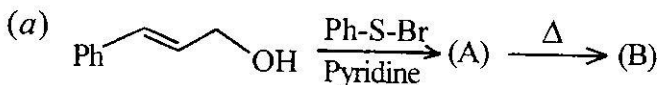


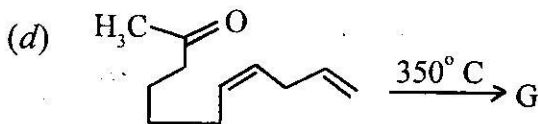
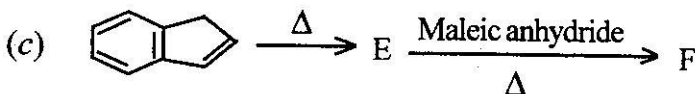
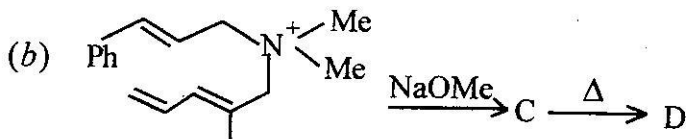
(h) (i) What happens when chromium tricarbonyl complex of *N,N*-dimethyl-1-phenylethyl amine is treated with *n*-butyl lithium and subsequently quenched with a suitable electrophile? 2

(ii) Identify the product with plausible mechanism: 2



3. Predict the products of the following reactions with plausible mechanism: 2 × 4

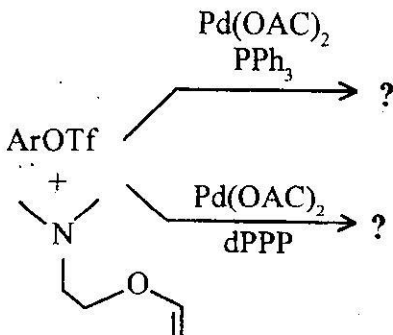




4. What were the modifications made by Taft to Roberts and Morel and work? What are the approximations involved in Taft equation? Write down the Taft equation and explain the terms involved in it. Discuss the practical validity of this equation. 2 + 2 + 2 + 2
5. (a) Suggest a suitable catalyst for Heck reaction and draw the catalytic cycle for the reaction. Arrange the following leaving groups in order of their reactivity in Heck reaction : 3 + 2  
Chloride, bromide, iodide, triflate, tosylate.

- (b) Predict the products with proper justification :

3



6. (a) The acid catalysed hydrolysis of ethyl benzoate has a  $\rho$  value of 0.144. What would be the effect of (- I) group on the rate of the reaction ?

2

- (b) The alkaline hydrolysis of methyl benzoate should be  $\rho = 2.224$ . What would be the effect of introducing electron withdrawing and electron donating groups on the reaction rate. Explain the reaction mechanism indicating the rate determining step.

3

- (c) The following compound (A) gives (1 : 2) adduct and compound (B) gives (1 : 1) adduct. Predict the products with explanation :

3

