2017

M.Sc. 3rd Semester Examination

CHEMISTRY

PAPER—CEM-301

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(*Physical Special*)

Group—A

Answer any *one* question of the followings.

1. (a) The Hamiltonian of a three-level system is given as,

$$H_0 = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}$$

After a small perturbation, its Hamiltonian is given as,

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

Find the second order correction to energy eigen states of each of the level. 7

(b) Calculate the first order correction to energy of the n^{th} state of a Harmonic Oscillator whose centre of potential has been displaced from 0 to *l*. 3

2. Write down the magnetic interaction Hamiltonian and spin wave functions of A–X spin system. Use spin-spin coupling as perturbing potential to obtain the zero order and first order correction to energy of its first two states (in order of energy). 2+4+4

Group—B

Answer any *one* question of the followings.

3. Use time independent degenerate perturbation theory to explain the splitting of single spectral lines into three lines

during n = 1 to n = 2 transition of hydrogen atom in presence of a constant electric field along a preferred direction (Z-direction). 10

4. Deduce the energy and wavefunctions of π MO of cyclic polyene using Huckel theory. Obtain the π delocalization energy of

(i) Cyclopentadiene cation,

(ii) Cyclopentadiene radical,

(iii) Cyclopentadiene anion. 6+4

Group—C

Answer any *one* question of the followings.

5. Consider a particle in a two dimensional square well potential whose potential is defined as,

$$V(x, y) = 0 \text{ when } 0 < x < L$$

&

$$0 < y < L$$

Now a perturbation V′ is introduced such that,

$$V' = V_0 \text{ when } 0 < x < L/2$$

&

$$0 < y < L/2$$

Find the first order correction to (i) ground state and (ii) first excited state energy. 3+7

6. (a) Using perturbation theory second order energy correction can be written as,

(i) $E_K^{(2)} = \sum_L \frac{\left|\langle K|H'|L\rangle\right|^2}{E_K^0 - E_L^0}$

(ii) $E_K^{(2)} = \sum_L \frac{\left|\langle K|H'|L\rangle\right|^2}{E_L^0 - E_K^0}$

(iii) $E_K^{(2)} = \sum_L \frac{\left|\langle K|H'|L\rangle\right|^2}{E_K^0 + E_L^0}$

(iv) None of these. $2\frac{1}{2}$

(b) If V(t) is a time dependent perturbation and $\rho(E)$ is the density of energy states in the range E and E + dE, then which of the following is correctly described Fermi's Golden rule.

(i) $\Gamma = \frac{\pi}{2\hbar}|V_{fi}|^2 \rho(E)$

(ii) $\Gamma = \frac{2\pi}{\hbar}|V_{fi}|^2 \rho(E)$

(iii) $\Gamma = \frac{4\pi}{\hbar}|V_{fi}|^2 \rho(E)$

(iv) $\Gamma = \frac{2\pi}{\hbar}|V_{fi}|^2 \rho^2(E)$. $2\frac{1}{2}$

(c) An unperturb two level system has energy eigen values E_1 and E_2 and eigen functions $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$. When perturbed, its Hamiltonian is represented by, $\begin{pmatrix}E_1 & A\\ A^* & E_2\end{pmatrix}$.

Calculate first order correction to both the eigen functions. $2\frac{1}{2}+2\frac{1}{2}$

Group—D

Answer *one* question of the followings.

7. (a) What is meant by Linear vector space. Give one such example.

Deduce the general form of transformation matrix for any n-dimensional Linear Vector space.

(b) Show that the set of 'n' degenerate molecular orbitals forms a basis for the representation of an n-dimensional IR of the point group to which the molecule belongs.

2+4+4

8. Find the state of hybridization of central atom in BF_3. Obtain the hybrid orbitals as the linear combination of atomic orbitals.

Character table of D_{3h} point group is given below :

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$		
A'_1	1	1	1	1	1	1		$X^2 + Y^2, Z^2$
A'_2	1	1	−1	1	1	−1	R_Z	
E'	2	−1	0	2	−1	0	(x, y)	$(X^2 - Y^2, XY)$
A''_1	1	1	1	−1	−1	−1		
A''_2	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	R_X, R_Y	(XZ, YZ)

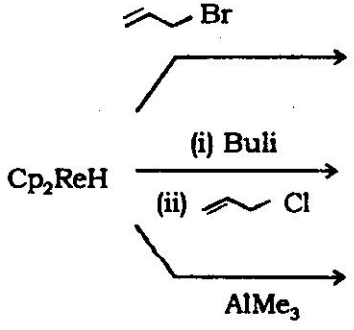
4+6

(Inorganic Special)

Group—A

Answer any *two* questions.

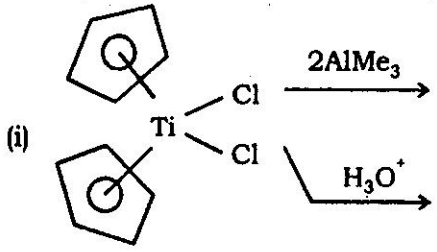
1. (a) Complete the following reactions



3

(b) Discuss the finyional behaviour of $TiCp_4$. 3

(c) Predict the product —



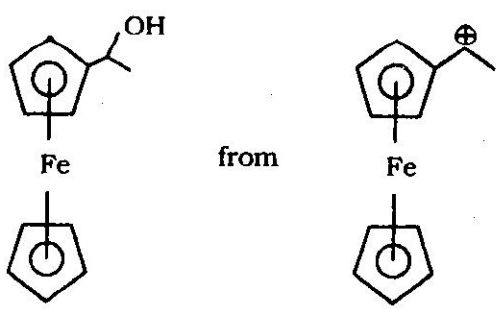
(ii) $[CpFe(CO)_2]$ $\xrightarrow[\text{(ii) } CH_3COCl]{\text{(i) Na-Hg}}$ 2+2

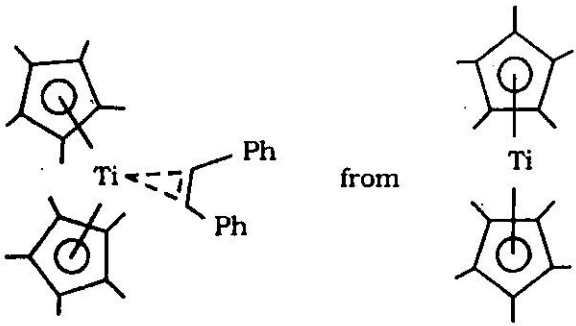
$\xrightarrow[\text{(ii) } LiCH_3]{\text{(i) } Cl_2}$

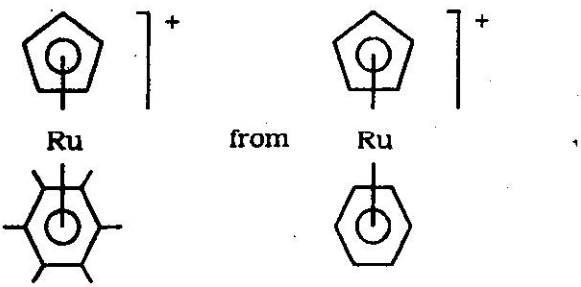
2. (a) How will you synthesis the following compounds :

2×4

(i) $Cp_3Ni_2]^+$ from Cp_2Ni

(ii) 

(iii) 

(iv) 

(b) What is orthometallation reaction ? 2

3. (a) Discuss the British Petroleum's cativa process for the production of acetic acid. Draw the catalytic cycle. 4

(b) Write down the structure of Schrock Osborn's and Mark's hydrogenation catalyst.
Draw the Catalytic Cycle of hydrogenation applying Crabtree's Catalyst. 2+4

Group—B

Answer any *two* questions.

4. For $[Co(NH_3)_6]^{3+}$, the ground electronic state belongs to $^1A_{1g}$ representation and two excited states belong to $^1T_{1g}$ and $^1T_{2g}$ representations. Show that pure electronic transitions from the ground state to these excited states are not allowed, but the transitions are vibronically allowed.

(Given below the character table for O_h point group). 10

O_h	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		$(2x^2-x^2-y^2,$ $x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
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		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

(Continued)

5. Establish the relation

$$\chi(\alpha) = \frac{\sin\left(l + \frac{1}{2}\right)\alpha}{\sin\left(\frac{\alpha}{2}\right)} \qquad (\alpha \neq 0)$$

where the terms have usual significance.

Use group theoretical principal to obtain the splitting of d-orbitals of Ni(II) ion in $[Ni(CN)_4]^{2-}$ anion. (Given below the character table for rotational subgroup D_4). 5+5

D_4	E	$2C_4$	$C_2\ (=C_4^2)$	$2C'_2$	$2C''_2$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	−1	−1	z, R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	(x, y) (R_x, R_y)	(xz, yz)

6. Construct a correlation diagram for a d^2 ion in an octahedral environment. (Use the character table of O_h group given in Q. No. 4) 10

(*Organic Special*)

Answer any *five* questions,
taking at least *two* from each group.

Group—A

1. (a) Define 'substituent constant' (σ) and 'reaction constant' (p) of Hammett equation and also indicate the reason why benzoic acid and its derivatives were chosen as standard in deducing Hammett equation.

   (b) What is the significance of the orienting power of the following groups in aromatic substitution reaction with reference to their substituent constant value ? Explain and rationalise with reason.

Group	σ_m	σ_p
– OMe	+ 0.12	– 0.27
– F	+ 0.34	+ 0.06
– NO2	+ 0.71	+ 0.78

4+4

2. (a) The acid catalysed hydrolysis of ethyl benzoate has a 'p' value (+ 0.144). What would be the effect of (–I) group on the rate of the reaction ? Explain indicating the mechanism.

(b) The saponification of methyl benzoate has p = 2.229. What would be the effect of introducing election withdrawing group on the rate of the reaction ? Show the rate determing step and transition state of the reaction. Do you expect a good linear Hammett plot or its deviation in presence of electron donating group ? Explain with reasoning.

(c) "Acid hydrolysis of ethyl benzoate with (99.9% H_2SO_4) proceeds with electron withdrawing group having p = +1.4". Explain this statement indicating mechanistic pathway of the reaction. 2+4+2

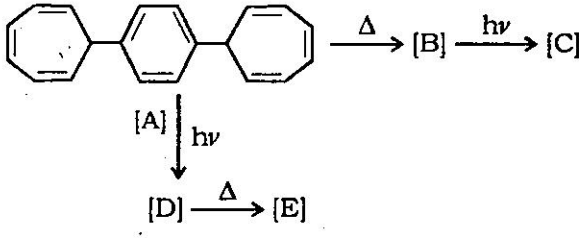
3. (a) The alkaline hydrolysis of meta/paranitro ethyl benzoate undergoes 63.5 times faster than ethyl benzoate. What would be the rate of hydrolysis of para methoxy ethyl benzoate under the same condition of reaction where,

$\sigma_{m-NO_2} = 0.71$, $\sigma_{p-OMe} = -0.268$?

(b) Calculate the relative rate of ionisation in water of p-nitro phenol, (whose p = 0.78, $\sigma_{NO_2} = 2.1$) with respect to phenol using Hammet equation. But the experimental value of which shows that p-nitro phenol is ionised 680 times faster than phenol. Explain this deviation indicating the reason. 4+2+2

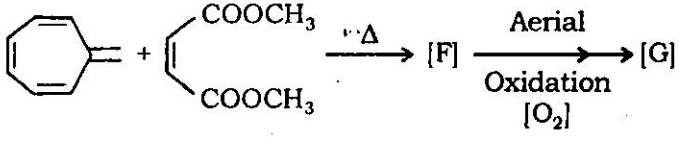
4. Complete the following transformation indicating Woodward Hoffmann Rule in each of the following reactions :

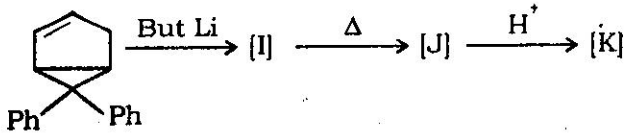
(i)



Indicate which of the products are same.

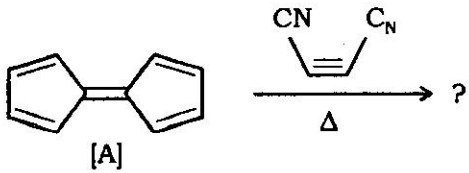
(ii)

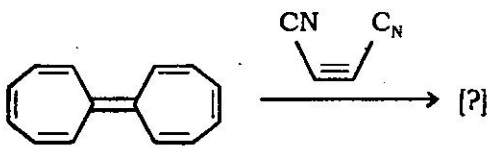


(iii) 

4+2+2

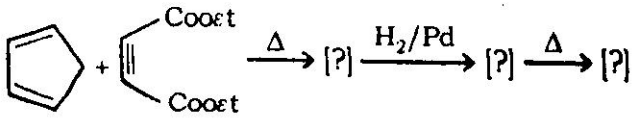
5. Predict theproduct in each case of the following :

(i) 

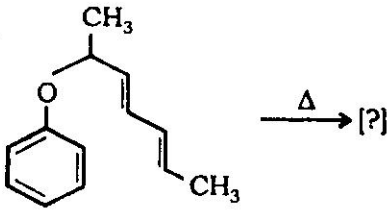


The compound [A] gives (1 : 2) adduct but the [B] gives (1 : 1). Explain indicating Frontier Orbitat interactives (F.O.I).

(ii) Complete the following transformation :



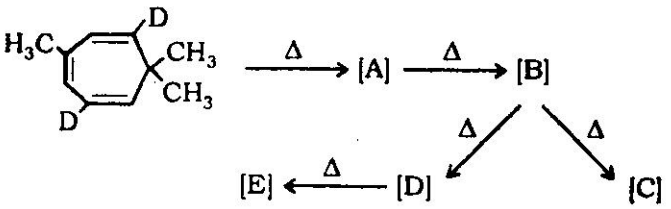
(iii) Predict the product indicating F.O.I of the following reaction :



4+2+2

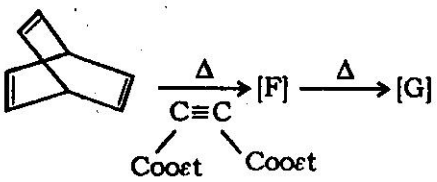
Group—B

6. (a) Complete the following transformation :

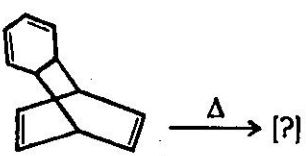


Identify A, B, C, D, E and designate each step with respect to what type of principle reaction occuring therein.

(b) Predict the product of the following reaction with mechanitic pathway :

(i) 

Identify [F] and [G]

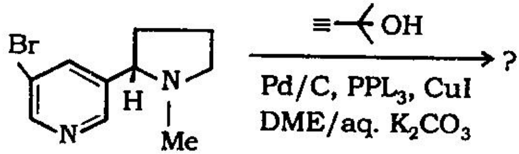
(ii) 

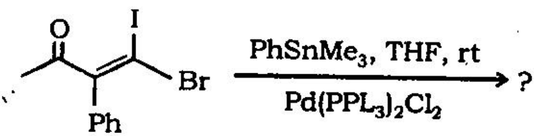
4+2+2

7. (a) Transition metal complex exibit special bounding with alkene — explain.

(b) Predict the product of the reactions with mechanism :

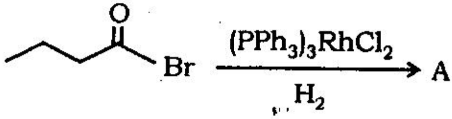
(i) $$Me_3C-\equiv N \xrightarrow[\substack{(2)\ Me_3C-\equiv N \\ (3)\ HCl-H_2O}]{(1)\ Cp_2Ti=} ?$$

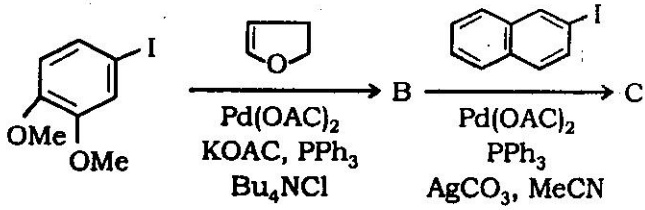
(ii) 

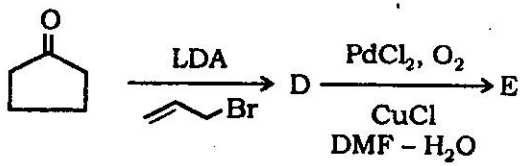
(iii) 

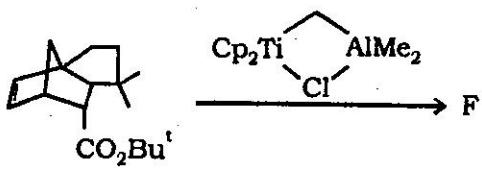
2+3×2

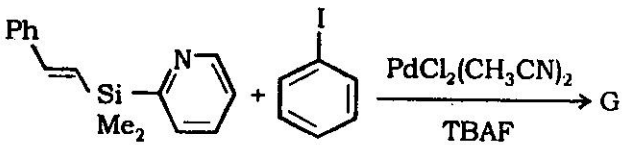
8. (a) Write down the structure of the products (A → H) in the following reactions (any *four*) :

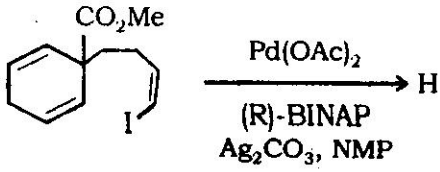
(i) 

(ii) 
I
OMe
OMe
O
B
I
C
Pd(OAC)2
KOAC, PPh3
Bu4NCl
Pd(OAC)2
PPh3
AgCO3, MeCN

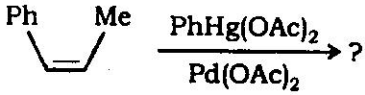
(iii) 
O
LDA
Br
D
PdCl2, O2
CuCl
DMF – H2O
E

(iv) 
Cp2Ti
AlMe2
Cl
CO2But
F

(v) 
Ph
Si
Me2
N
+
I
PdCl2(CH3CN)2
TBAF
G

(vi) 

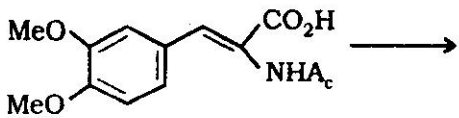
(b) Predict the product (Major) with proper stereochemistry

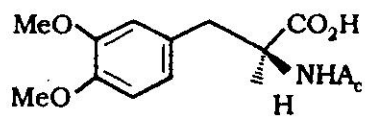


(c) How would you prepare Quinoline from 2-Iodoaniline using palladium catalyst. 4+2+2

9. (a) What is the migratory insertion ? Show a migratory insertion with reference to transition metal complex.

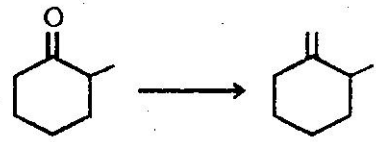
(b) Indicate the appropriate reagents in each of the following transformation :

(i) 



Optically active

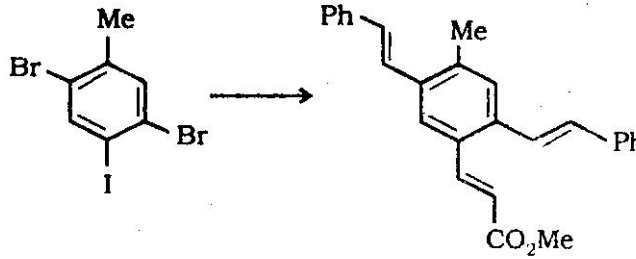
(ii)



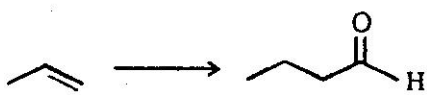
Optically active

Optically active

(iii)

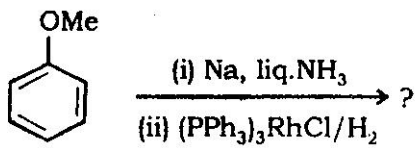


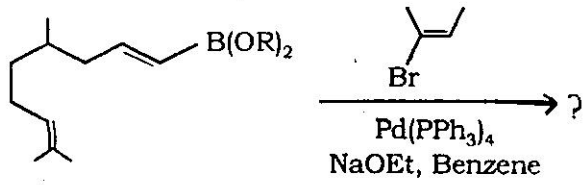
(iv)



(c) **Predict the major product of the following reactions :**

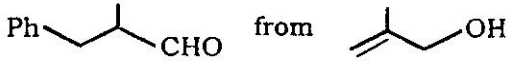
(i)

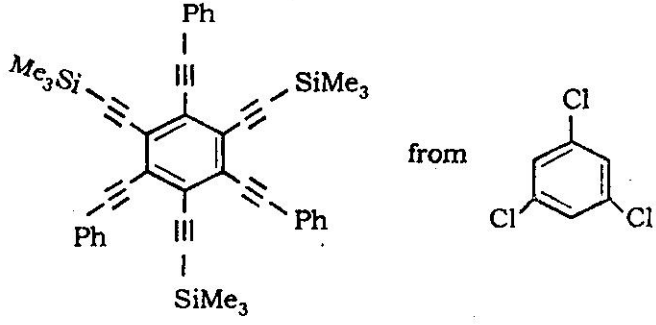


(ii) 

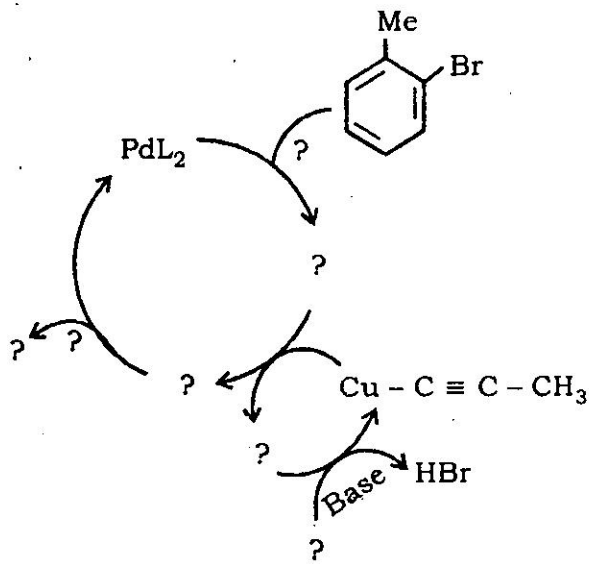
2+4+2

10. (a) How would you employ organo transition metal compounds in the synthesis of the following :

(i) 

(ii) 

(b) Complete the following cycle :



(c) Show with one example where Tebbe's reagent used for alkene metathesis. 2×2+3+1