OLD & NEW

2017

M.Sc. Part-II Examination

CHEMISTRY

PAPER—V

Full Marks : 75

Time : 3 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)

Old Syllabus

F.M. – 75 Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. – 100 Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer *five* questions from group C.

Group—A

1. (a) What is idempotent, nilpotent matrix? Find out eigen value and trace of the matrix

$$A = \begin{bmatrix} +0 & +1 \\ -2 & -3 \end{bmatrix}.$$ 1+1+4+1

(b) Derive the matrix representation of $\hat{L}^2$ and $\hat{L}_z$ operator using the basis set Y_{lm} where $l = 1$. 6

(c) What is Slater type orbitals (STO) ? 2

2. (a) Using the trial function $\phi = N \exp(\lambda r^2)$. Calculate ground state energy of H-atom. λ = variational parameter, N = normalization constant. 9

(b) Write down the basic assumption of Huckel molecular orbital (HMO) theory. 3

(c) Explain Pauli Principle of Antisymmetric wave function. 3

3. (a) Show that in Hartree model the total Electronic energy of a many electron atom is not equal to the sum of occupied orbital energies but less that this. 6

(b) Explain Koopman's theorem in the Hartree model. 4

(c) Discuss the Stark effect in the 1s-2s transition in H-atom. 5

4. (a) Use the time independent perterbation theory to explain the possible transitions in hydrogen atom in presence of an external electric field in the z-direction. 12

(b) Calculate the first order correction to energy for the n^{th} state of harmonic oscillator in presence of a perterbation $H' = \lambda x^3$. 3

Group—B

5. (a) What is projection operator ? 2

(b) Find the group orbitals (LGO) involved for the SALC in $PtCl_4^{2-}$ using projection operator method. Character table of D_{4h} poing group is given below : 10

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_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	-	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)	

(c) State the selection rules for the electric-dipole transition of the vibration modes of I.R active and Raman active molecules. 3

6. (a) Find the hybridisation of CH_4 molecule and construct the qualitative M.O diagram of methane molecule. 6

(b) Find the I.R and Raman actial vibrational modes of NH3 molecule. 4

(c) Show that the direct product matrix forms a representations of the point group.

Character Table for C_{3v} & Td are given below : 5

Td	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, xz, yz)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	Rz	
E	2	−1	0	(x, y) (R_x, R_y)	$(x^2-y^2,\ xy)$ (xz, yz)

7. (a) State and prove Laue equation. 6

(b) Calculate the geometrical structure factor, F_{hkl} for fcc lattice. 5

(d) How is drift velocity related to applied electric field ? 4

8. (a) Calculate the number of vacancies per mole of metal atoms at a given temperature. 4

(b) Explain the failures of Drude-Lorentz classical theory. 4

(c) Explain the properties of p-n junction. 3

(d) What are Exciton ? 2

(e) Give the definition of Hall effect. 2

Group—C

9. Answer any *five* of the following : 5×5

(i) Explain the conductivity of n-type and p-type semiconductor in the light of band theory.

(ii) Draw band diagram for conductor, insulator and semiconductor indicating the band gap in each case.

(iii) (a) What are F centres ?

(b) What are the differences between Schottky and Frenkel defects ?

(iv) From quantum theory of free electrons give example of degenerate eigen values.

(v) Evaluate the commutator, $\left[\hat{L}^2, \hat{L}_z\right]$.

(vi) Starting from appropriate expression for the time dependent coefficient obtain Fermi's Golden rule.

(vii) Show that a non-degenerate Hermitian matrix can be diagonalized by the matrix of its eigen vector.

(*Organic Special*)

Old Syllabus

F.M. – 75 Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

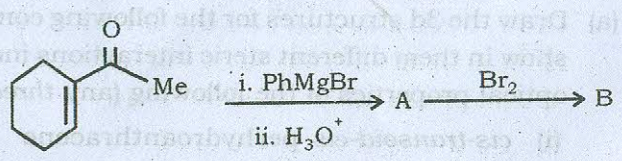
F.M. – 100 Time : 4 Hrs.

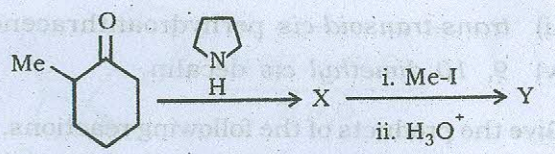
Answer any *five* questions
taking at least *two* from each group (A and B)
and answer group C.

Group — A

1. (a) Deduce from the first principle the Curtain-Hammett principle (with the help of potential energy diagram) for a case where the more stable conformer given rise to predominant product. Illustrate with an example, how you can find out $\Delta G^{\neq}$. 5+2

(b) Write down the product(s) in the following reactions with stereochemistry and methanism : 3+3

(i) 

(ii) 

(c) What do you mean by kinetic quenching ? Explain with a suitable example. 2

2. (a) Write down the conformers of 9(s), 10(R) 9-methyl cis-2-decalone, give the sign of torsion angles of ring junction in both rings, and mention the sterodial and nonsteroidal conformer. 5

(b) Comment on the symmetry and chirality of cis-decalin. 3

(c) Write the two conformers of (s)-enantiomer of $\Delta^{1,9}$-octalin. Draw Newman projection showing torsion angle of ring junction (both side) in each conformer. 2+2

(d) Trans-2-decalone has a tendency to enolise to give 2, 3-double bond where as cis-2-decalone prefers enolisation to given 1, 2-double bond. Explain this observation. 3

3. (a) Draw the 3d structures for the following conformers and show in them different steric interactions including their optical properties of the following (any *three*) : 3×2

(i) *cis-transoid-cis* perhydroanthracene

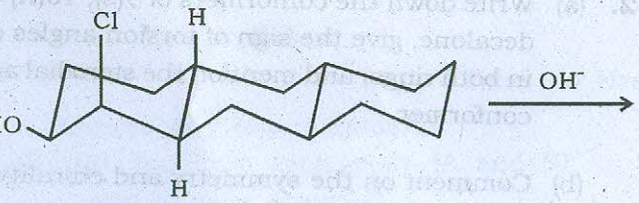
(ii) *trans-cisoid-cis* perhydrophenanthrene

(iii) *trans-transoid-cis* perhydroanthracene

(iv) *9, 10 dimethyl cis* decalin.

(b) Give the products of the following reactions. Where more than one product is likely to be formed in significant yield, indicate which will be the major product and also predict the methanism of the reaction involved (attempt any *three*) : 3×3

(i)



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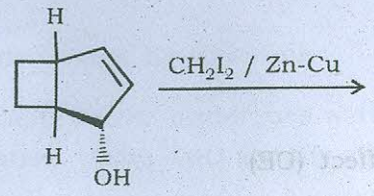

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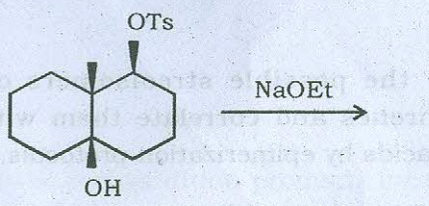

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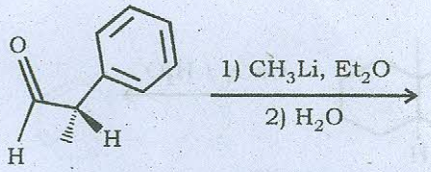


4. (a) Write in brief with *one* example in each case : 3×3

(i) Allylic 1, 2-strain

(ii) Allylic 1, 3-strain

(iii) 2-alkylketone effect

(iv) 3-alkylketone effect.

(b) Write in brief about the following terms : (any *three*) 3×2

(i) ORD

(ii) CD

(iii) Cotton Effect (CE)

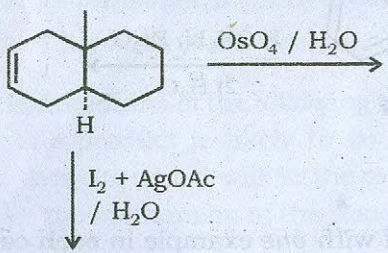
(iv) Sector rule

(v) Octant Rule.

5. (a) Write all the possible streoisomers of perhydrophenanthrenes and correlate them with perhydrodiphenic acids by epimerization protocols. 7

(b) Predict the product with appropriate methanism and product's sterochemistry : 4×2

(i)



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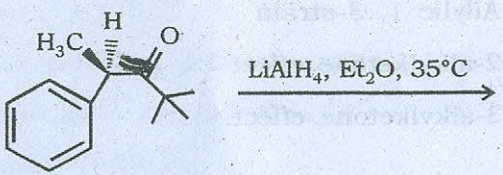
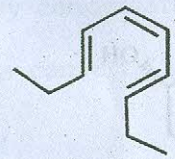


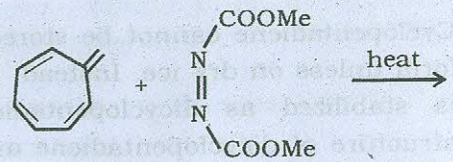
Group — B

6. Attempt any *three* of the following : 3×5

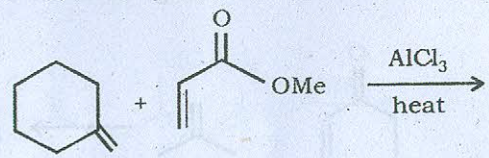
(a) The triene below undergoes a thermal electrocyclic cyclisation. Using FMO identify all the products.



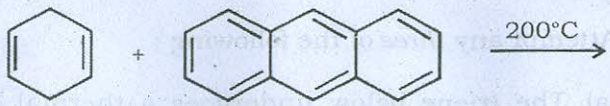
(b) Predict the cycloaddition products formed from the following pairs of starting materials. State the number of 'pi' electrons involved.



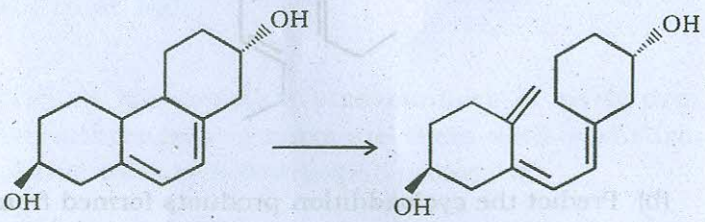
(c) Predict the product with MO diagrams and methanisms :



(d) Predict the product with MO diagrams and mechanisms :



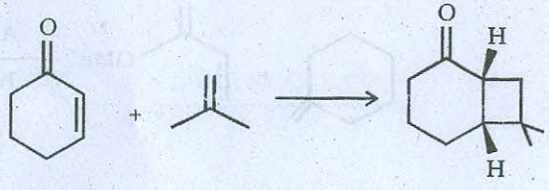
(e) How will you convert the following starting material to product ?



7. (a) Attempt any *four* of the following :

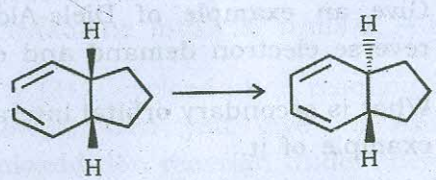
(i) Cyclopentadiene cannot be stored in monomeric form unless on dry ice. Instead, cyclopentadiene is stabilized as dicyclopentadiene. Draw the structure of dicyclopentadiene and show how it is formed. Be sure to indicate the stereochemistry of the product. 4×2

(ii) Consider the following reaction :



Classify this cycoaddition reaction (e.g. it is a [X + Y] reaction), Is this reaction more likely to occur thermally or photochemically ? Will this reaction proceed with suprafacial or antarafacial stereochemistry ? Draw MO diagram and explain the symmetry condervation of the orbitals.

(iii) How will you convert :

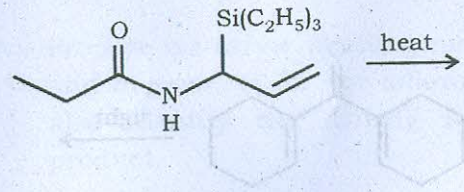


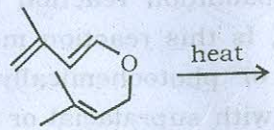
(iv) Give one example of [1, 5] sigmatropic reaction with MO diagrams.

(v) What is "Group Transfer Reaction" explain with one example.

(b) Predict the product(s) with stereochemistry of the following reactions : 3×2

(i)



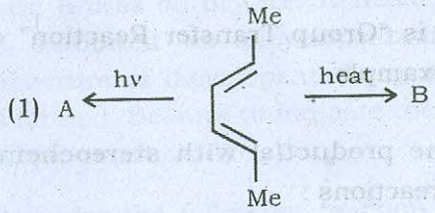
(ii) 

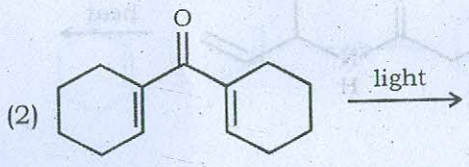
(c) Give an example of a green selvent in organic synthesis. 1

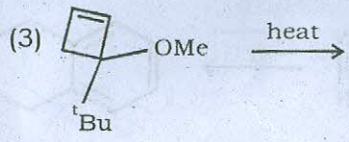
8. (a) (i) Give an example of Diels-Alder reaction with reverse electron demand and explain. 2

(ii) What is secondary orbital interaction and give an example of it. 1

(iii) Predicts the products with F.O.I. of the following (attempt any *two*) : 2×2

(1) 

(2) 

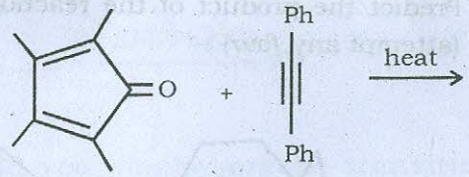
(3) 

(b) Answer the following (attempt any *four*) : 4×2

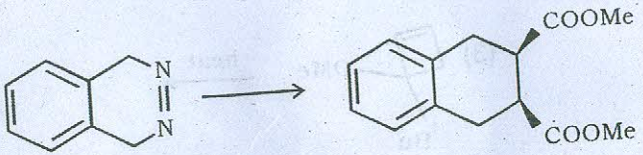
(i) Can you suggest a method for carrying out a stereospecific conversion of *trans*, *trans*-2, 4-hexadiene into *cis*, *trans*-2, 4-hexadiene ?

(ii) Why (2+2) cycloaddition reaction is not thermally allowed. Can you give an example of (2+2) cycloaddition reaction under thermal condition ? Explain with FMO and symmetry.

(iii) The following reactions proceed through two consecutive pericyclic reactions. Predict the product(s) with plausible mechanism.



(iv) Propose an arrow pushing mechanism, reagents and byproducts for the following transformation, also identify the driving force to make the product.



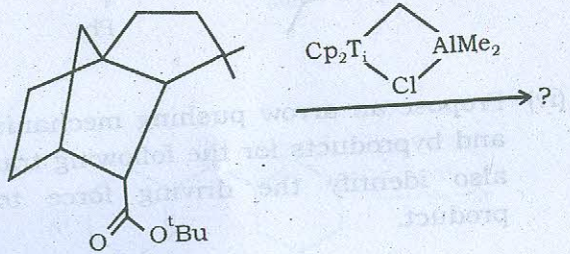
(v) How will you convert by use of your choice of reagents :

9. (a) What are the importance of organometallic chemistry. 1

(b) What is oxidative addition reaction ? Give one example. 2

(c) Predict the product of the reactions with mechanism (attempt any *four*) : 4×3

(i)



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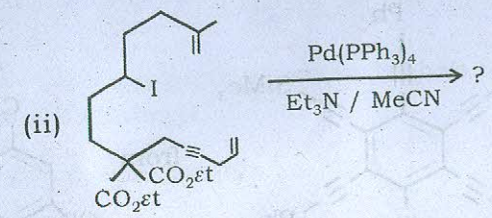
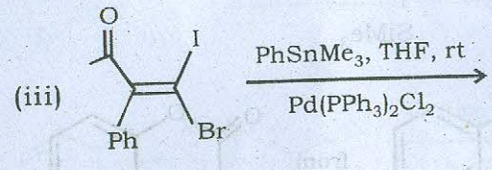


(iii)



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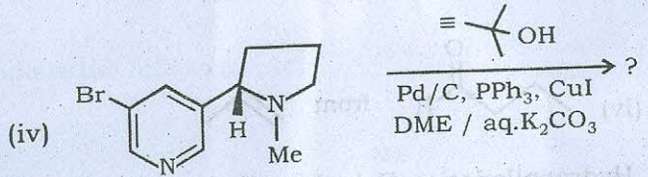
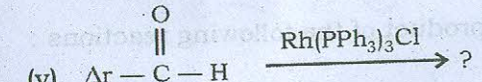
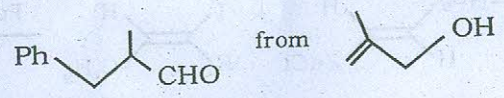


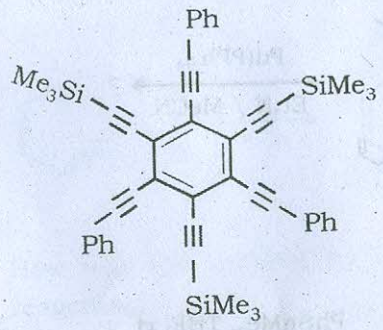
(v)

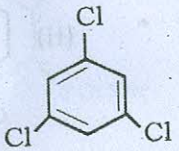


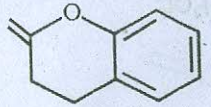
10. (a) How would you employ organo-transition metal compounds in the synthesis of the following : $2\frac{1}{2}\times4$

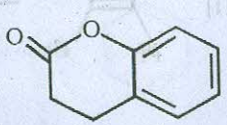
(i)

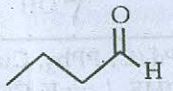


(ii) 

from 

(iii) 

from 

(iv) 

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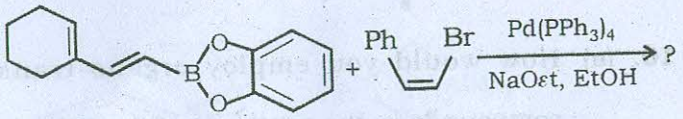
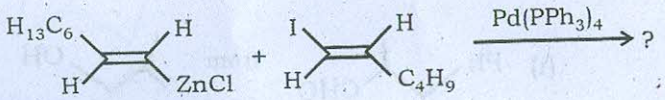
(b) Hydropalladation-Dehydropalladation can lead to alkene isomerisation — explain. 3

(c) Predict the product of the following reactions : 2

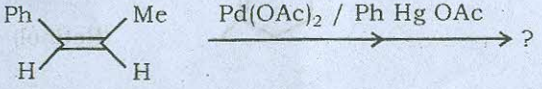
(i) 

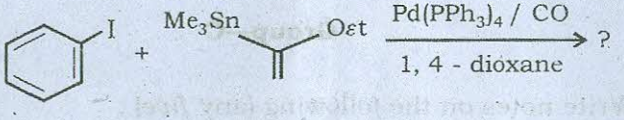
(ii) 

Or

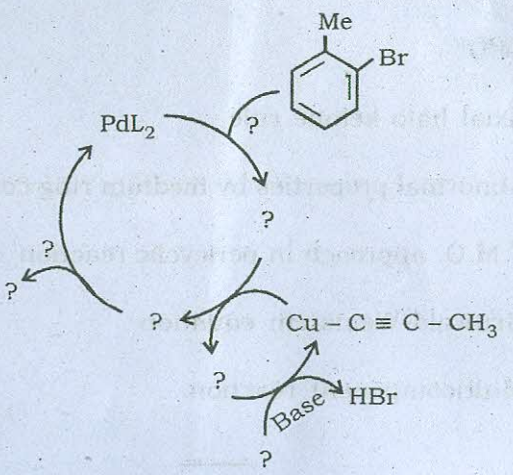
(a) Show with one example where Tebbe's reagent used for alkene metathesis. 1

(b) Predict the product(s) : 2+2

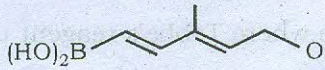
(i) 

(ii) 

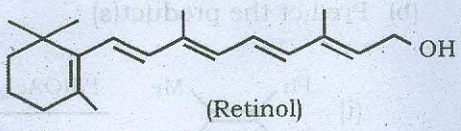
(c) Complete the following cycle : $3\frac{1}{2}$



(d) How would you prepare retinol from



$1\frac{1}{2}$



(Retinol)

Group—C

Write notes on the following (any *five*) : 5×5

(a) Burgi-Dunitz trajectory

(b) CD

(c) ORD

(d) Axial halo ketone rule

(e) Abnormal properties by medium ring compounds

(f) F.M.O. approach in pericyclic reaction

(g) Gruwald-Weinsrein equation

(h) Multicomponent reaction.

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