

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Second Semester M.Sc Chemistry Degree Examination, March 2017

CH2C05 – Applications of Quantum Mechanics & Group Theory

(2016 Admission onwards)

Max. Time: 3 hours

Max. Weightage : 36

Section A*(Answer all questions; each question carries 1 weight)*

1. Write the Schrödinger equation for helium atom
2. What are linear and non linear variation functions
3. What is Roothan's concept of basis function?
4. What is the difference between STO and GTO
5. What is Born Oppenheimer approximation?
6. Write the term symbol of N₂ molecule
7. Write the Huckel determinant for benzene
8. What is meant by free valence
9. Draw normal modes of H₂O
10. What is meant by vanishing and non vanishing integrals
11. Write a short note on group orbitals
12. What is meant by projection operator?

(12x1=12 weights)**Section B***(Answer any eight questions; each question carries 2 weights)*

13. Apply perturbation method to He atom
14. Find the ground state energy for particle in 1D box ($\hat{H} = \frac{-h^2}{8\pi^2m} \frac{d^2}{dx^2}$) using the trial function(x-a); x varies from 0 to a
15. Write the STO of Fe atom
16. State and explain Pauli's anti symmetry principle
17. Write a short note on correlation diagrams
18. Draw the MO diagram of HF and name the MO's.
19. Obtain the normalised functions of sp hybridisation and show that the orbitals are linear
20. Write a short note on Frost - Huckel circle mnemonic device for cyclic polyenes
21. $A = \begin{bmatrix} 1 & 3 \\ 2 & 1 \end{bmatrix}$ and $B = \begin{bmatrix} -1 & 0 & 1 \\ 1 & -2 & 0 \\ 3 & 1 & 4 \end{bmatrix}$. Show that $\chi(AB) = \chi(BA) = \chi(A)\chi(B)$
22.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	3	0	1	3	0	1

Show that $\Gamma = A'_1 + E'$

23. Predict the Raman and IR active vibrations in BF₃. Use D_{3h} character table.
24. Give an outline of MO treatment of HCHO according to group theoretical method.

(8 x 2=16 weights)

Section C

(Answer any two questions; each question carries 4 weights)

25. Explain the Hartree – Fock self consistent field method for the treatment of many electron systems
26. Give the VB treatment hydrogen molecule. Also obtain singlet and triplet state functions of the molecule.
27. Explain the important features of HMO treatment. Apply the method to butadiene molecule
28. Predict the hybridisation in BF_3 and obtain the hybrid orbitals by SALC and projection operator method.

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		

(2 x 4 = 8 weights)

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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE
 Second Semester M.Sc Chemistry Degree Examination, March 2017
 CH2C06 – Coordination Chemistry
 (2016 Admission onwards)

Max. Time: 3 hours

Max. Weightage : 36

Section A

(Answer all the questions. Each question has 1 weightage)

1. Illustrate stepwise and overall formation constant
2. Differentiate macrocyclic and template effect
3. What are the reasons for the smaller Δ_t over Δ_o ?
4. What is spectro-chemical series? Splitting energy of d orbital by CN^- is greater than F^- ligand, why?
5. Arrive the ground term symbol of high spin V^{3+} and Co^{2+} ions
6. Differentiate nephelauxetic effect and racah parameter
7. Explain with examples MLCT and LMCT transitions
8. How Mossbauer spectra can be used to identify $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_5\text{NH}_3]^{4-}$ complexes
9. What you mean by Cis-effect?
10. Explain with example photo-substitution reactions in transition metal complexes.
11. State and explain remote and adjacent attacks of bridged ligands in inner sphere mechanism.
12. What you mean by spin-orbit coupling?

(12x 1 = 12 weightage)

Section B

(Answer any 8 questions. Each question carries 2 weightage)

13. Explain excited state outer sphere electron transfer reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ ion
14. What is trans effect? Discuss the theories proposed for explaining the trans effect.
15. What are Orgal diagrams? Draw the Orgal diagram of d^3 and d^8 ions in octahedral and tetrahedral fields
16. Explain Jahn-Teller effect. Discuss its spectral consequences.
17. Discuss Valance Bond Theory and its limitation of metal complexes
18. Explain the principle involved the determination of magnetic moment by Gouy balance
19. Discuss the orbital contribution to magnetic moment and its quenching
20. Discuss the substitution reactions in octahedral complexes
21. How do you account the purple colour of the complex $[\text{Ti}(\text{H}_2\text{O})]^{3+}$?
22. What are fluxional molecules? How can we determine the structure of such molecules by proton NMR ?
23. Discuss the mechanism involved in Inner sphere redox reaction
24. Discuss the charge transfer spectra

(8 x 2 = 16 weightage)

Section C

(Answer any 2 questions. Each question carries 4 weightage)

25.
 - a. Discuss the crystal field theory of octahedral complexes
 - b. Mention the factors affecting crystal field splitting
26.
 - a. Explain the application of IR spectroscopy in the study of coordination complexes
 - b. Discuss the principle involved in ESR spectroscopy. How is it applicable in the study of the structure and bonding in Cu(II) complexes
27.
 - a. Write a note on the factors that affect the stability of metal complexes
 - b. Discuss Photo-aquation, photo-isomerisation and photo-recimization
28. Discuss MOT theory. Construct molecular orbital diagram for an octahedral complexes with sigma bonding only. Explain the larger Δ_0 value of pi bonding complexes

(2 x 4 = 8 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Second Semester M.Sc Chemistry Degree Examination, March 2017

CH2C08 – Electrochemistry , Solid State Chemistry & Statistical Thermodynamics

(2016 Admission onwards)

Max. Time: 3 hours

Max. Weightage : 36

Section A**(Answer all questions. Each question carries 1 weightage)**

1. Define thermodynamic probability? How does it differ from mathematical probability?
2. Define mean ionic activity coefficient. Write equation for the activity of an electrolyte of the type MX_2 in terms of molal concentration and mean ionic activity coefficient.
3. Give the cell reactions for Ni-Cd cell.
4. What is Wein effect?
5. Explain the term 'dilute system' with reference to statistical mechanics. Write one example for a dilute system.
6. Rationalise third law of thermodynamics using statistical concept.
7. Define Hall effect. Write one application of Hall effect.
8. Write Herman-Maugin notation for (i) C_{2h} ; (b) D_{3d} ?
9. Calculate the characteristic temperature of a solid if the fundamental vibrational frequency is 1000 cm^{-1} .
10. Explain the term non-polarisable electrode? Give one example.
11. Define piezoelectric effect. Write one application of a piezoelectric crystal.
12. What is Debye T^3 law?

(12 × 1 = 12 weightage)

Section B

(Answer any 8 questions. Each question carries 2 weightage)

13. Write the Butler-Volmer equation and explain how current density is related to over potential in electrode process.
14. Discuss Hydrogen and oxygen overvoltage with its determination method. Discuss briefly any two theories pertaining to overvoltage.
15. Write the Debye Huckel limiting law. Suggest one method to verify the law.
16. Draw the stereographic projection for a monoclinic system.
17. Prove that the five- fold axis of symmetry is not possible in crystals.
18. Explain the principle and working of dropping mercury electrode.
19. Write notes on (i) Ferromagnetism. (ii) Anti ferromagnetism (iii) colour centres and (iv) birefringence.
20. Explain Einstein's theory of heat capacities of solids.
21. Define Fermi level. Show that Fermi level is located half way between highest filled level and lowest unfilled level.
22. What are ensembles? How are they classified?
23. Derive an expression for the rotational partition function of a diatomic molecule.
24. Six particles share 6ε of energy. Quantum states are $0, \varepsilon, 2\varepsilon, 3\varepsilon, 4\varepsilon, 5\varepsilon$ and 6ε . Levels are triply degenerate. Find the most probable microstate. What is the corresponding thermodynamic probability?

(8 × 2 = 16 weightage)

Section C

(Answer any 2 questions. Each question carries 4 weightage)

25. (i) Discuss the briefly the theories related to electronic structure of solids.
(ii) Explain the Cooper theory of Superconductivity.
26. Derive Debye-Huckel equation. Explain the method to validate the equation.
27. Discuss four types of fuel cells bringing out their cell reactions, advantages and limitations.
28. Discuss the application of Fermi-Dirac statistics to electrons in metals.

(2 × 4 = 8 weightage)

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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE
Second Semester M.Sc Degree Examination, March 2017
CH2C06 – Organic Chemistry II
(2015 Admission onwards)

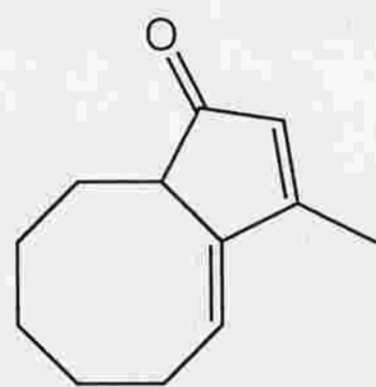
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Max. weightage :36

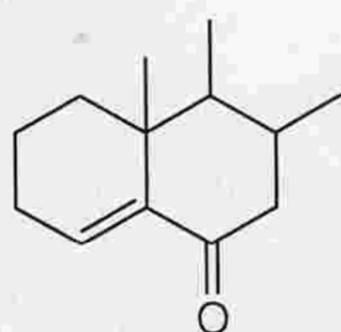
PARTA

Answer all questions. Each question carries 1weightage

1. Using Woodward Fieser rules, calculate the λ_{\max} for the following two compounds?

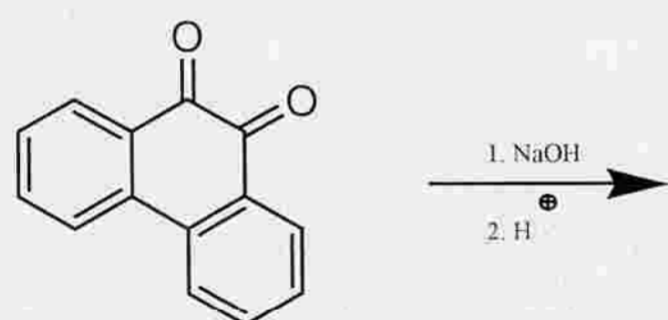


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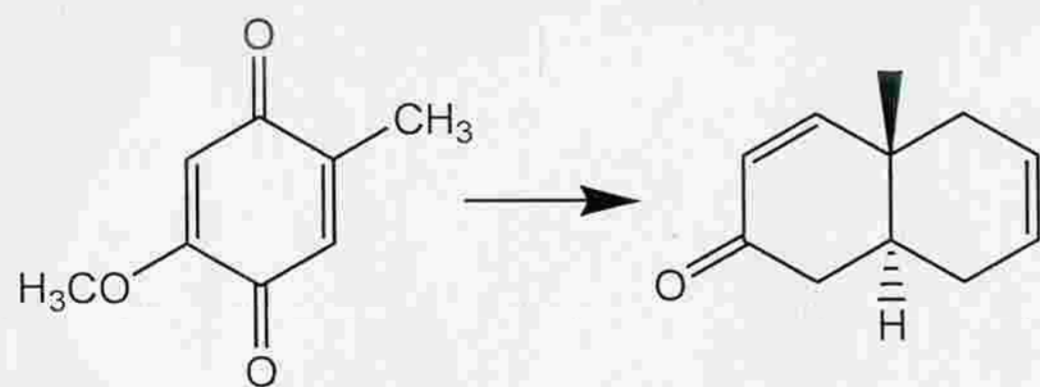


II

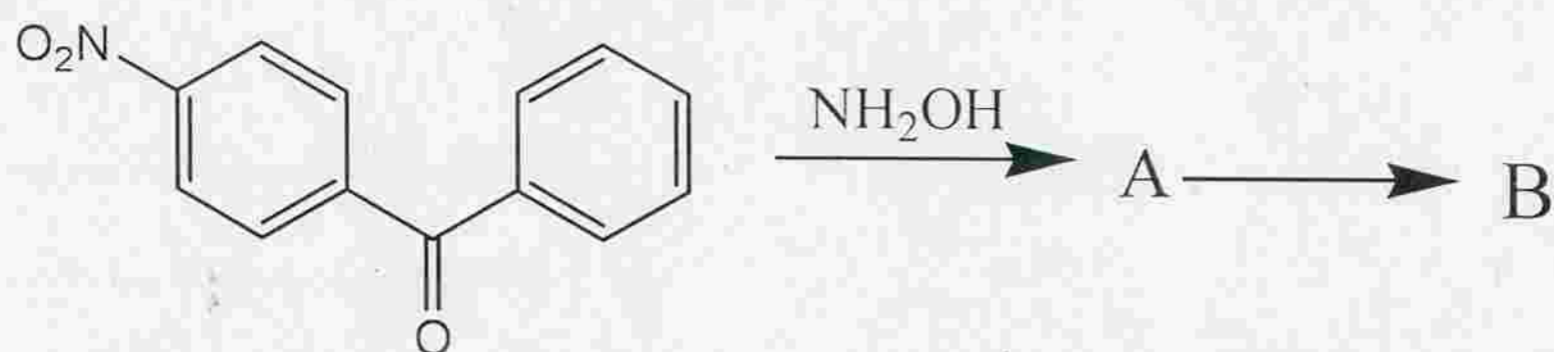
2. Complete the following reaction. Explain the mechanism



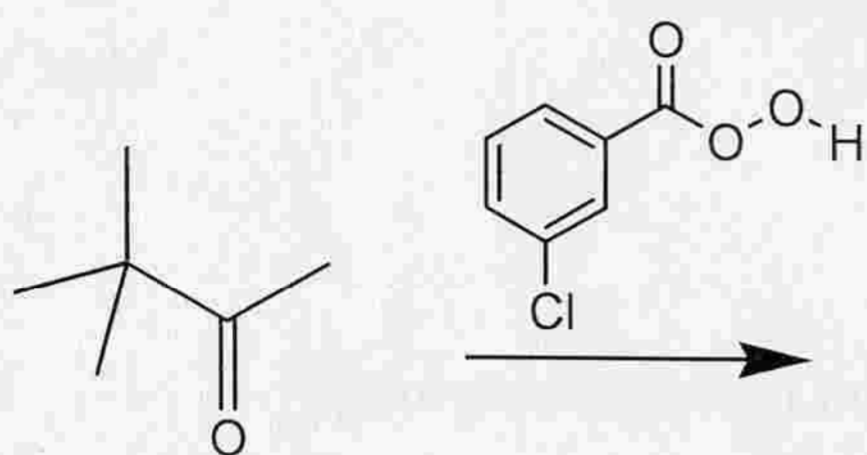
3. Explain how the following conversion is achieved in the Woodward synthesis of cholesterol



4. Explain the stereochemistry of Diels Alder reaction with any two examples
5. Discuss the chemical classification of alkaloids with one example for each class.
6. What is Ziesel's method? What is its use?
7. Identify the structure of A and B in the following reaction



8. Illustrate the Norrish type II cleavage with an example
9. What is the product formed in the following reaction and explain the mechanism



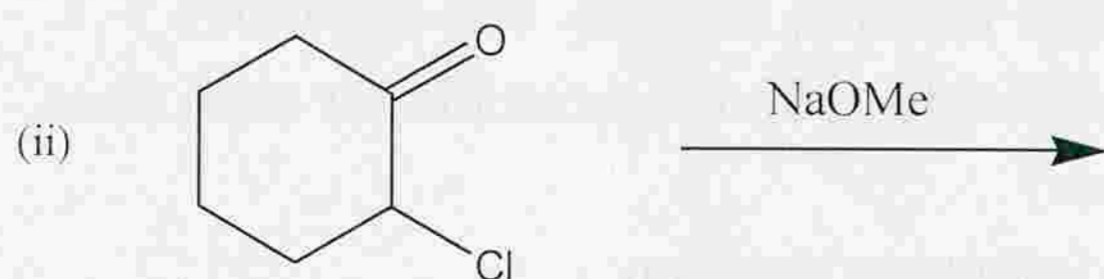
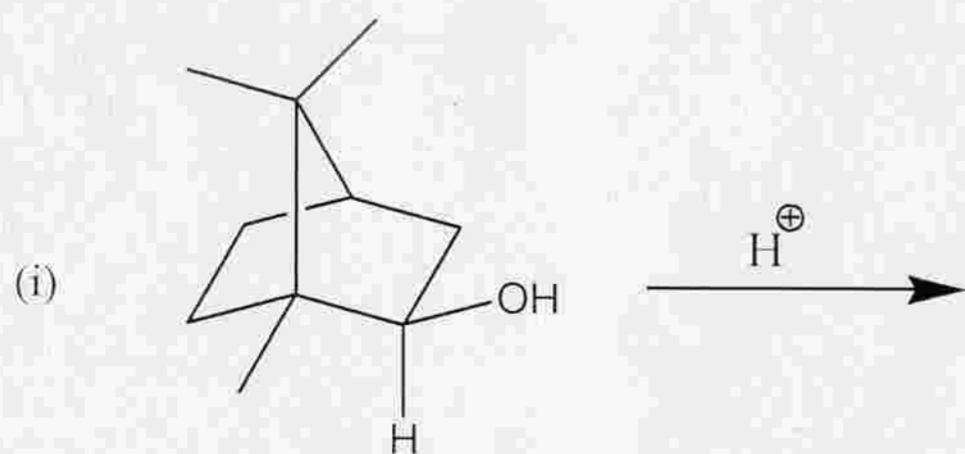
10. Draw the structures of 18-crown-6-ether and point out one of its synthetic application
11. Explain Jablonski digram.
12. Explain stereochemistry of Peterson reaction
13. What happens when 2-oxocyclohexane carboxylic acid is reduced with LiAlH_4 and NaBH_4
14. What are the molecular ion peaks in the mass spectrum of 1,2-dichloroethane . Explain their relative intensity

(14 X 1 = 14 weightage)

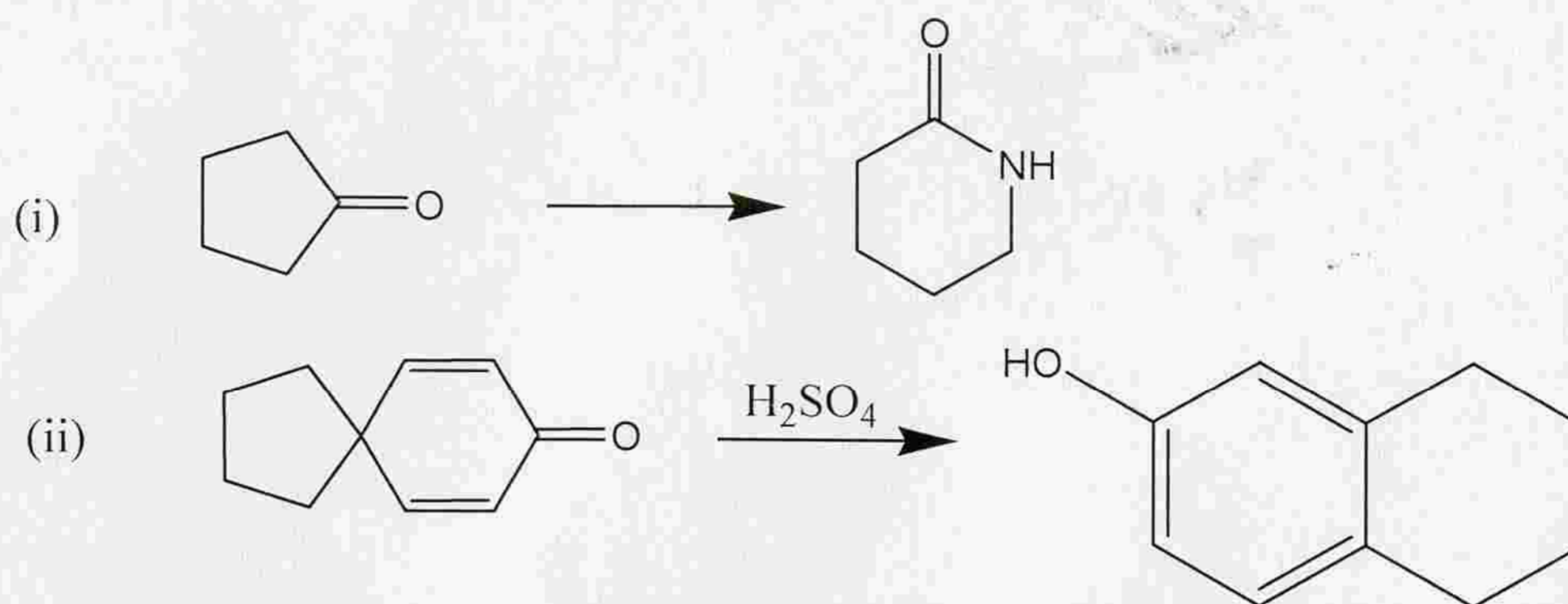
PART B

Answer any 7 questions. Each question carries a weightage 2

15. Explain activated nucleophilic substitution mechanism in aryl halides with examples.
16. Discuss the conversion of cholesterol into testosterone.
17. Explain how aniline can be converted into 1,3,5-tribromobenzene, benzoic acid , acetophenone and phenol through benzene diazonium intermediate .
18. Explain the mechanism and application of Beckmann rearrangement
19. What are the products obtained in the following reactions? Explain the mechanism.



20. Write a note on Heck reaction
21. Discuss the FMO method to interpret (4+2) cycloaddition reaction
22. Explain McLafferty rearrangement with any two examples
23. How the following transformations can be done ?



24. What are flavones and isoflavones ? Outline any one method of synthesis of isoflavone
(7 x 2 = 14 weightage)

PART C

Answer any 2 questions Each question carries a weightage 4

25. Explain the structural elucidation and total synthesis of atropine
26. Discuss the mechanism and applications of Claisen rearrangement, Wolff rearrangement, Suzuki coupling and Peterson reaction
27. Write a brief account of the applications of LDA, DDQ, Wilkinson's catalyst and diborane
28. With proper interpretation of the following spectral data deduce the structural formula of the compound

Molecular formula $C_9H_{10}O_2$

m/z ... 150, 132, 105(BP), 77

1H NMR δ 4.27(2H, quartet) 1.31(3H, triplet) 7.97(2H, multiplet),

7.47(1H, multiplet) and 7.37(2H, multiplet)

IR 1240 cm^{-1} , 1728 cm^{-1} , 3030 cm^{-1}

(2 x 4 = 8 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE
 Second Semester M.Sc Chemistry Degree Examination, March 2017
 CH2C07 – Organic Reaction Mechanism
 (2016 Admission onwards)

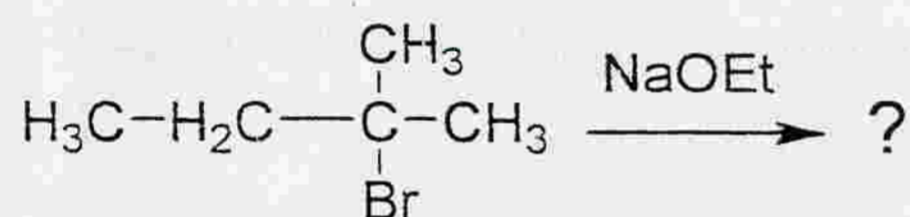
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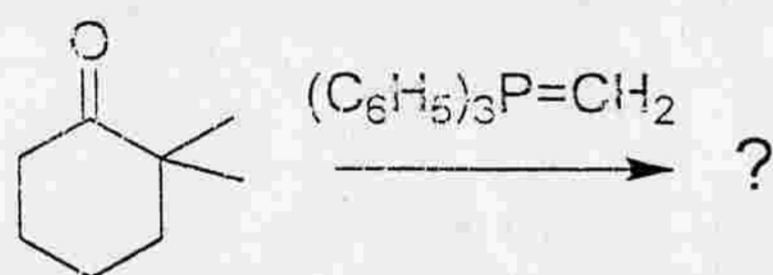
PART A

(Answer all questions. Each question carries 1 weightage)

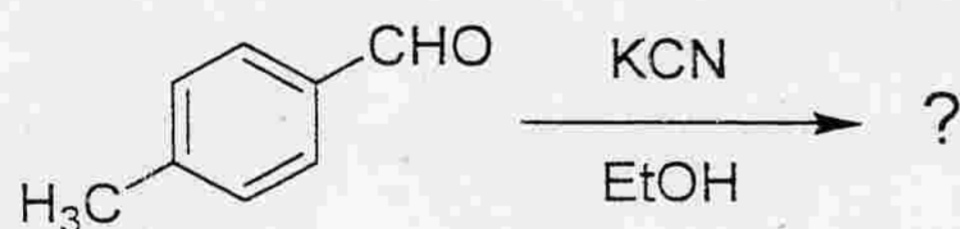
- Comment on the role of neighbouring group participation in a nucleophilic substitution reaction.
- Only 2,4-dinitrochlorobenzene undergoes nucleophilic aromatic substitution, but not 3,5-dinitrochlorobenzene. Account.
- What criteria should be satisfied for the E1cB mechanism to operate?
- Predict the product and suggest a mechanism for the following reaction:-



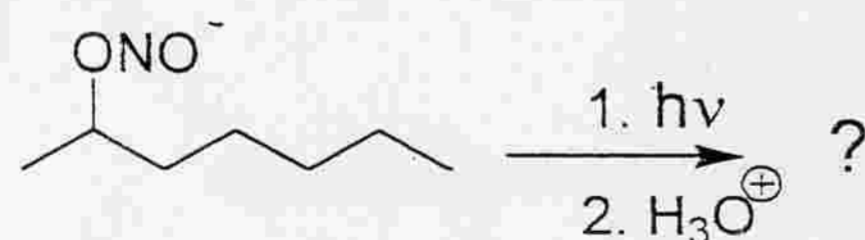
- Predict the product of the following reaction and explain its formation.



- Predict and explain the formation of the product in the following reaction:-



- Write a note on stereochemistry of Diels-Alder reaction.
- What is chelotropic reaction? Give an example.
- What product would result in the following photoreaction and how do they form?



- Explain photosensitization reaction with an example?
- Give the name and structure of one individual member from the following class of natural products:
 (i) alkaloids and (ii) flavonoids
- What are terpenoids? How are they isolated?

(12 × 1 = 12 weightage)

PART B

(Answer any 8 questions. Each question carries 2 weightage)

13. Explain with mechanism the unimolecular and bimolecular aromatic nucleophilic substitution reactions.
14. Explain the mechanism and stereochemical features of E2 eliminations.
15. Choosing appropriate examples demonstrate pyrolytic elimination of esters is a stereospecific reaction.
16. What are Mannich bases? Give their synthesis and use in organic synthesis.
17. Illustrate the mechanism of the following reactions :—
 - (a) Claisen condensation
 - (b) Dieckmann condensation
18. Discuss the $B_{AC}2$ mechanism of ester hydrolysis with suitable evidences.
19. Construct correlation diagram for disrotatory and conrotatory cyclisation of hexatriene to cyclohexadiene and state which mode of cyclisation is allowed under photochemical conditions.
20. Ethylene dimerisation takes place only under photochemical conditions but not under thermal conditions. Account it in terms of FMO approach.
21. Propose the mechanism for the di- π -methane rearrangement. Identify the stereospecific product obtained when 2, 4, 4-trimethyl-6, 6-diphenyl-2, 5-hexadiene undergoes this rearrangement.
22. Discuss the mechanism of Paterno Buchi reaction. What are the competing processes for this photochemical reaction?
23. What are the salient steps in the synthesis of cephalosporin.
24. Which step do you consider as the key step in the Corey's synthesis of longifolene? Justify.

(8 × 2 = 16 weightage)

PART C

(Answer any 2 questions. Each question carries 4 weightage)

25. Write the steps involved in the total synthesis of reserpine.
26. Describe Norrish type-I and Norrish type-II photochemical reactions with mechanism.
27. (i) Write down the explanatory notes on Cope and Claisen rearrangements.
(ii) Elucidate the selection rules for 1,3 and 1,5 sigmatropic rearrangements.
28. Discuss the factors that influence rate of S_N1 and S_N2 reactions. Comment on the factors that favour elimination over substitution.