M.Sc- chem. Sem III

Time: 2 hours 30 minutes **Total Marks: 60**

Instructions:

(1) All questions are compulsory.

(2) Figures to the right indicate full marks.

1. A. Attempt **any two** of the following: **8**
   - i) Discuss the following physical and chemical parameters in drug distribution: (a) Solubility (b) Ionization.
   - ii) Explain the use of functional groups in prodrugs with advantages.
   - iii) Discuss structure modification to increase potency and therapeutic index of a drug.
   - iv) Discuss how penicillin was discovered without a lead.

   B Attempt **any one** of the following: **4**
   - i) Give details of factors affecting bioactivity.
   - ii) Discuss the basic idea regarding combinatorial synthesis.

2. A Attempt **any two** of the following: **8**
   - i) What is 'QSAR'? Explain Taft equation and give it's Hancock modification.
   - ii) Explain use of computers in drug design with suitable examples.
   - iii) What are soft drugs? Give their properties.
   - iv) Give the synthesis and one application of cetrizine.

   B Attempt **any one** of the following: **4**
   - i) Explain the methods used to correlate regression parameters with biological activity.
   - ii) Give the synthesis and one application of fluconazole.

3. A Attempt **any two** of the following: **8**
   - i) Discuss the biosynthesis of dimethylallyl pyrophosphate (DMAPP) from acetyl-CoA.
   - ii) How are L-Tyrosine and phenylalanine biosynthesized from chorismic acid?
   - iii) Describe the prostaglandin PGF_{2a} production mechanism.
   - iv) Describe how palmitate is produced during the biosynthesis of fatty acids from malonyl-CoA.

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B Attempt **any one** of the following: 4

i) Give the steps involved in the synthesis of Orsellinic acid *via* acetate pathway.

ii) Write a note on primary and secondary plant metabolites.

4 A Attempt **any two** of the following: 8

i) Define, Polymer supported reagents with suitable example. Give the applications of any one polymer supported reaction in Organic synthesis.

ii) Give any two examples of green oxidation catalyst promoted reactions.

iii) Define Crown Ether. Write down any one example of crown ether catalysed reaction.

iv) What are Ionic liquids? Give any one application of ionic liquid as a green solvent.

B Attempt **any one** of the following: 4

i) Why non-polar or less polar solvents are not suitable for microwave reactions? Give any one example of microwave assisted reaction.

ii) Write down the green synthesis of Ibuprofen. Give any two advantages of green synthetic method of Ibuprofen.

5 Attempt **any four** of the following: 12

a) Discuss the basic pharmacokinetics in drug absorption.

b) Define the terms: Receptor and drug potency.

c) Explain drug design via enzyme inhibition.

d) Give synthesis of Fluoxetine

e) Write a note on the biosynthesis of Shikimic Acid.

f) Discuss the mevalonate pathway for the biosynthesis of Mevalonic acid.

g) Explain in brief any three principles of Green Chemistry.

h) Write down the structure and chemical name of Aliquat 336. Give any one application of Aliquat 336 in organic synthesis.

-----X-----X-----X-----

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Time: 2 hours 30 minutes **Total Marks: 60**

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-----X-----X-----X-----

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(5)

1MSC - sem III - chemistry

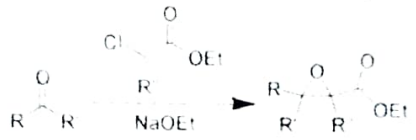
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Duration: 2.5 hours **Max. Marks: 60**

N.B. i) All questions are compulsory.
ii) Figures to the right indicate full marks.

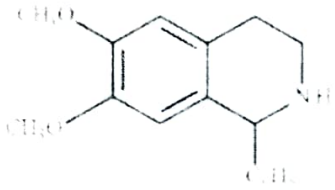
1. A. Attempt **any two** of the following: **8**

i)



a. What is the name of this reaction?
b. Write the mechanism of the reaction.

ii) The following compound is synthesised by the Pictet-Spengler reaction.



What are the components of this reaction? Explain the mechanism of this reaction.

iii) Primary or secondary alcohols on treatment with carboxylic acid in the presence of diethyl azodicarboxylate and triphenylphosphine are converted to esters. Write one example of this reaction, its name and the mechanism.

iv) What are the characteristics of a click reaction? Give an example of the Huisgen 1,3-dipolar reaction.

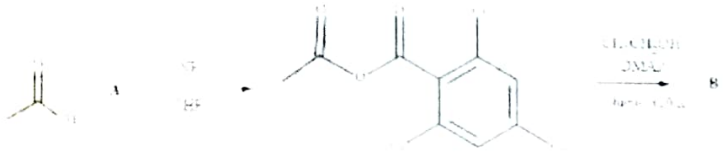
B Attempt **any one** of the following: **4**

i) Complete the following reaction and give the name.

CH_3COOH $C_6H_5NH_2$ C_6H_5CHO CH_3NC ⟶

Write the mechanism of the reaction.

ii) Complete the following reaction and give the name.



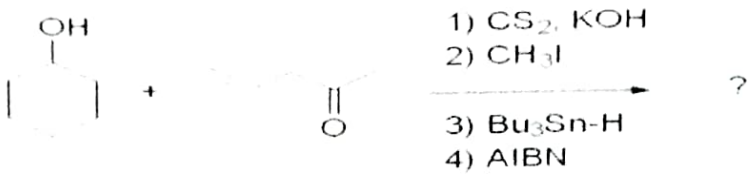
Write the mechanism of the reaction.

X51Y981BC2X51Y981BC2X51Y981BC2X51Y981BC2

2. A Attempt **any two** of the following: 8

i)

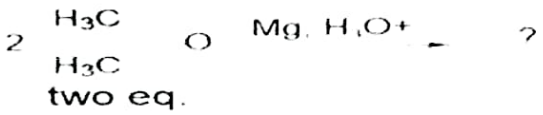
Predict the product and suggest the mechanism.



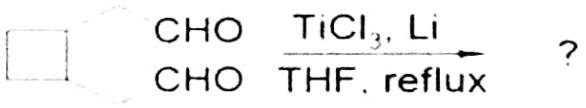
ii) Explain persistent radical with its stability and radical initiator with suitable examples.

iii)

Predict the product, name and suggest the mechanism



iv Predict the product, name the reaction and suggest the mechanism.

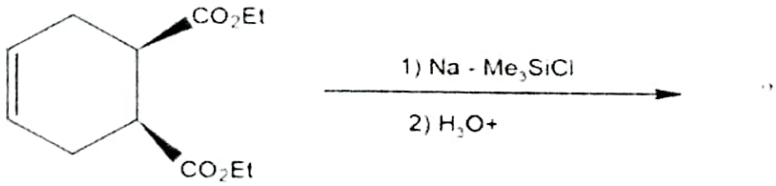


B Attempt **any one** of the following: 4

i) Discuss with example, intramolecular C-C bond formation using thiol donors.

ii)

Give the product and mechanism of the following reaction.



3. A Attempt **any two** of the following: 8

i) Give the synthesis of 2-hexene using a Witting reaction. Explain the mechanism involved.

ii) What are S-yields? How are they prepared? Give two applications of S-yield in organic synthesis.

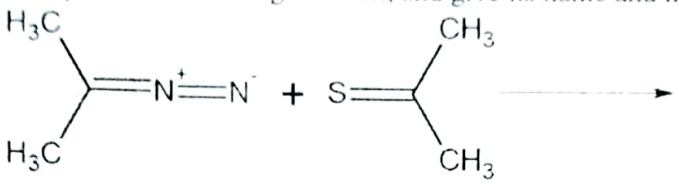
iii) What is Steven's rearrangement? Illustrate with the mechanism and one application.

iv) Explain the generation of carbanions in nitro compounds and phosphonates and give one application of each in C-C bond formation.

X51Y981BC2X51Y981BC2X51Y981BC2X51Y981BC2

B Attempt **any one** of the following: **4**

i) Complete the following reaction, and give its name and mechanism.



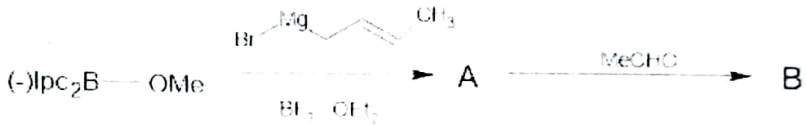
ii) Explain with mechanism, formation of enamine by condensation of secondary amine and aldehyde.

4. A Attempt **any two** of the following: **8**

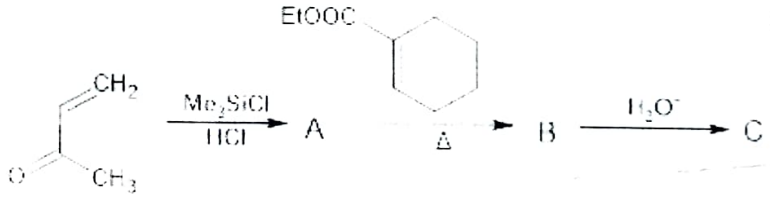
i) Give the following conversion via selenoxide.



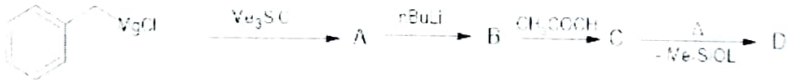
ii) Complete the following reaction with correct stereochemistry and predict the mechanism.



iii) Complete the following reaction and identify A, B and C.

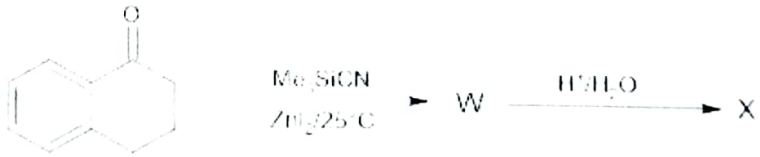


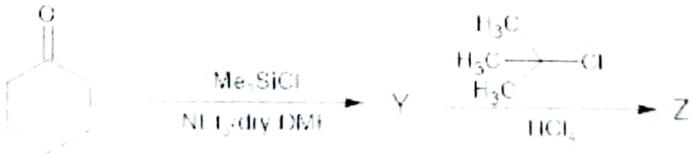
iv) Complete the following reaction by identifying A, B, C, and D.



B Attempt **any one** of the following: **4**

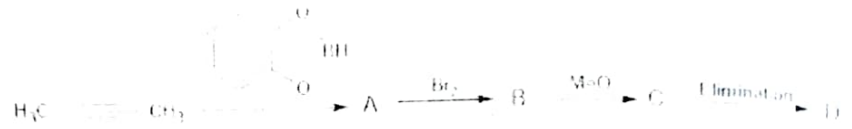
i) Complete the following reaction by identifying W, X, Y and Z.





X51Y981BC2X51Y981BC2X51Y981BC2X51Y981BC2

ii) Complete the following reaction and identify A, B, C and D



5. Answer **any four** of the following: 12

(a) Write equations to show the following reactions
Ritter reaction
Peterson olefination reaction
Strecker reaction

(b) What is a multi-component organic reaction between an aryl aldehyde, a β-keto ester and urea called? With a suitable example, explain the mechanism of this reaction.

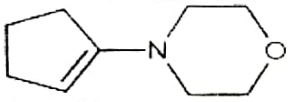
(c) Write the reagent and name the reaction.



(d) Write the reagent and byproduct and name of the following reaction.



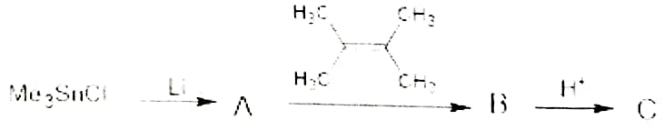
(e) What is the action of following reagents on



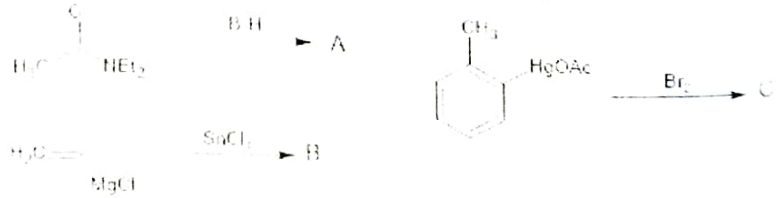
i) CH_3Br
ii) CH_3COCl
iii) CH_2=CH-CH_2Cl

(f) Write a brief note on Bestman Ohira reagent.

(g) Complete the following reaction by identifying A, B and C.



(h) Complete the following reactions by identifying A, B and C.



X51Y981BC2X51Y981BC2X51Y981BC2X51Y981BC2

(9)

M&C – chem – Sem III

(2 ½ Hours) **Marks:60**

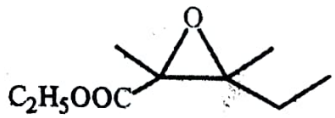
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1. A. Attempt **any two** of the following: **8**

i) What are the characteristics of a click reaction? Give an example of the Huisgen 1,3-dipolar reaction.

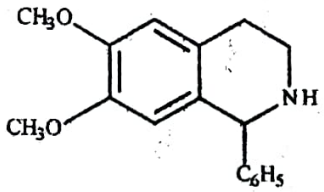
ii) Discuss the mechanism and one application of the Ugi 4-component reaction.

iii) How will you prepare the following compound by the Darzen's glycidic ester condensation?

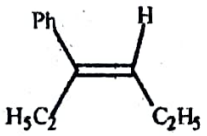


Explain the mechanism of this reaction.

iv) How will you prepare the following



by Pictet - Spengler synthesis

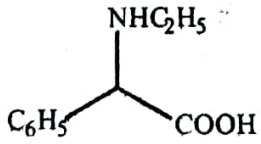


by Peterson olefination reaction

B Attempt **any one** of the following: **4**

i) Give an example each of the following
Hantzsch synthesis
Mitsunobu reaction,
Ritter reaction
Mukaiyama esterification.

ii) What are multicomponent reactions? List any two advantages of these reactions. Show the synthesis of the following compound by a suitable multicomponent reaction.

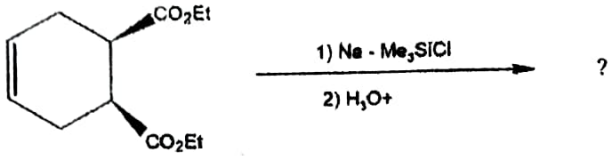


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2. A Attempt **any two** of the following: 8

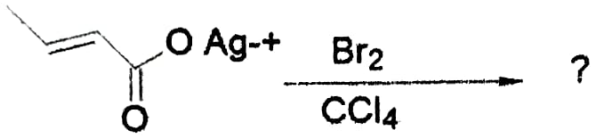
i)

Give the product and mechanism of the following reaction.



ii)

Predict the product, name the reaction and suggest the mechanism.



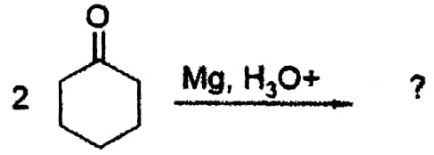
iii) Discuss with suitable examples, intramolecular C-C bond formation using tin hydride.

iv Explain persistent radical with its stability and radical initiator with suitable examples.

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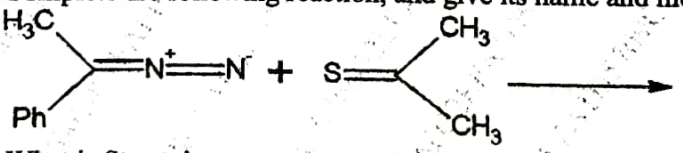


ii) Define radicals and discuss the characteristics of radicals.

3. A Attempt **any two** of the following: 8

i) How are enamines prepared using alkynes? Give one example and explain the mechanism involved.

ii) Complete the following reaction, and give its name and mechanism



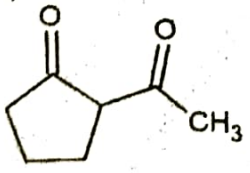
iii) What is Steven's rearrangement? Illustrate with the mechanism and one application.

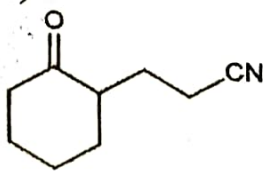
iv) Explain the generation of carbanions in nitro compounds and phosphonates and give one application of each in C-C bond formation

B Attempt **any one** of the following: 4

i) How are the following compounds prepared via enamine?

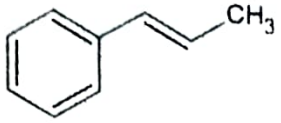
i) ii)





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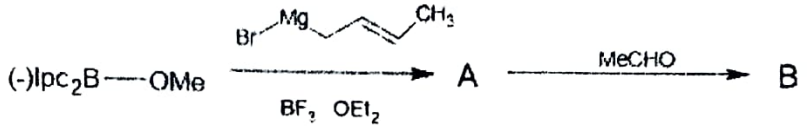
ii) Using phosphorous ylide, sugges: synthesis of the following compound. Name the reaction involved and provide a mechanism for the same.



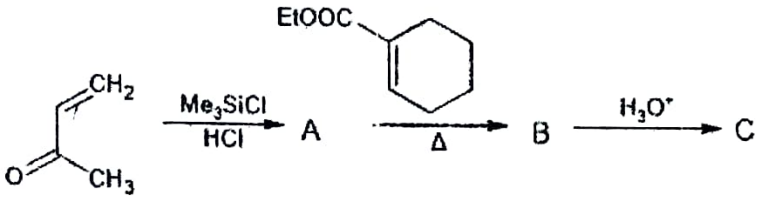
4. A Attempt **any two** of the following: 8

i) Give the synthesis of 1,3-butadiene using $PhSeCH_3$.

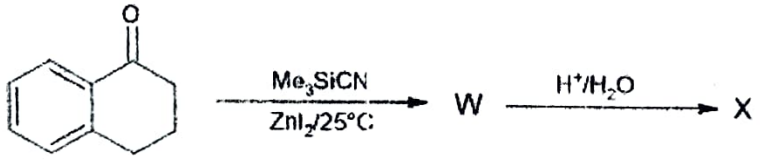
ii) Complete the following reaction with correct stereochemistry and predict the mechanism.

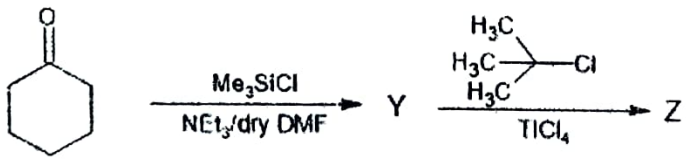


iii) Complete the following reaction and identify A, B and C.



iv) Complete the following reaction by identifying W, X, Y and Z.

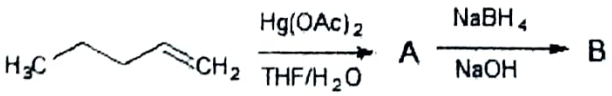




B Attempt **any one** of the following: 4

i) Trialkylborane when reacted with NaCN in presence of $(CF_3CO)_2O$ at low temperature gives ketone while in excess of $(CF_3CO)_2O$, H_2O_2/OH^- and higher temperature gives tertiary alcohol. Explain with a suitable example.

ii) Complete the following reaction and predict its name and mechanism.

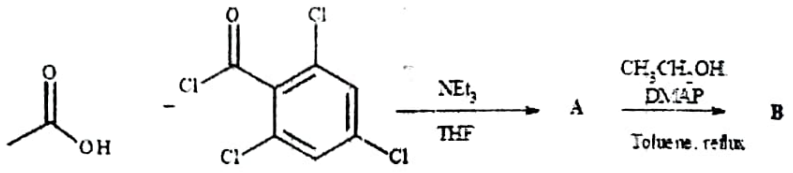


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5. Answer **any four** of the following: 12

(a) What is a multi-component organic reaction between an aryl aldehyde, a β-keto ester and urea called? Illustrate this reaction with a suitable example.

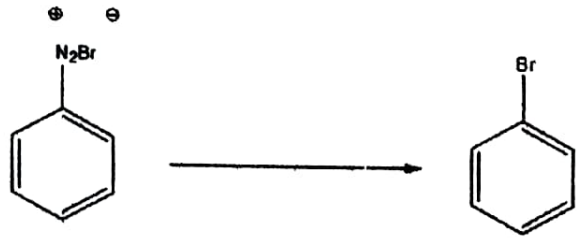
(b) Complete the following reaction by drawing suitable structures for A and B.



What is the name of this reaction?

(c) With a suitable example, explain the mechanism of McMurry coupling.

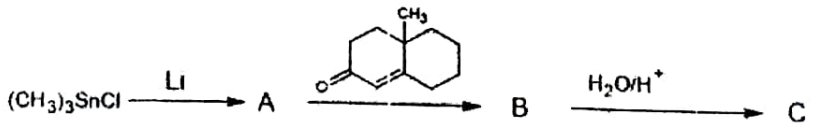
(d) Write the reagent, by-product and name of the following reaction.



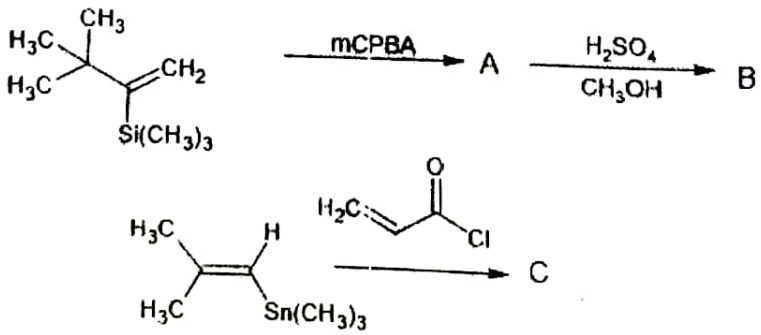
(e) Write the structures of phosphorus and nitrogen ylide. Which ylide is most stable. Justify the answer.

(f) What is Bestmann Ohira reagent? How is it prepared? What is its advantage?

(g) Identify A, B and C in the following reaction.



(h) Identify A, B and C in the following reaction.



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CEC6AEEB608081FAE076D32EFA1D5709

(13)

Time: 2 ½ hours **Total Marks: 60**

N.B. (1) All questions are **compulsory.**

(2) **Figures** to the **right** indicate **full** marks.

Q.1 A Attempt any two of the following: **8**

a Explain structural features and applications of inositol and heparin.

b Give structural features and biological importance of carotenoids and quinones.

c Give synthesis of β-carotene.

d Write a short note on deoxy sugars and branched sugars.

Q.1 B Attempt any one of the following: **4**

a Give the synthesis of ubiquinone from 3,4,5-trimethoxy acetophenone.

b Write a short note on sex pheromones and trail pheromones.

Q.2 A Answer any two of the following: **8**

a Discuss the synthetic strategy for the synthesis of Longifolene.

b Write the Structure of Gibberellic acid. Give the synthesis of Triacontanol.

c Explain the insect growth regulator. Discuss the structure features of gibberellic acid.

d How is decalinedione prepared from resorcinol? Draw the configuration of the two enantiomers of Griseofulvin.

Q.2 B Answer any one of the following: **4**

a Write the structure of reserpine. Write the biological importance of prostaglandins.

b Draw the structure of 4-demethoxydaunomycin. How is phloroglucinol converted to 4,6-dimethyl benzofuranone?

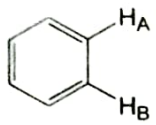
Q.3 A Answer any two of the following: **8**

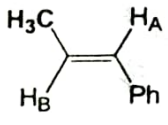
a Give one example each for compounds which exhibit the following spin systems according to Pople's nomenclature:

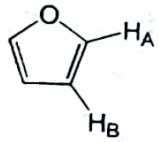
i) AB ii) AX iii) AMX iv) A_3X_2

X51YAA1165X51YAA1165X51YAA1165X51YAA1165

b Arrange the following compounds in decreasing order of coupling constant. Justify your answer.







c Calculate ^{13}C NMR chemical shifts for all the aromatic carbons using incremental shifts of all the aromatic carbon atoms from the table given below for the following compounds:

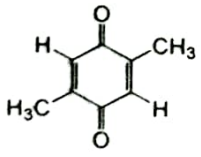
(I) *p*-bromoaniline (II) *m*-chlorophenol

Substituents	Increments in ppm			
	Ipso	*Ortho*	*Meta*	*Para*
-Cl	+6.4	+0.2	+1.0	-2.0
$-NH_2$	+19.2	-12.4	+1.3	-9.5
-OH	+26.6	-12.7	+1.6	-7.3
-Br	-5.4	+3.4	+2.2	-1.0

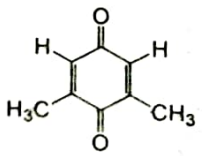
d Explain the first order and second order spin system with suitable examples.

Q.3 B Answer any one of the following: 4

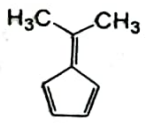
a Predict the number of signals for following compounds in ^1H and ^{13}C NMR. Justify your answer.



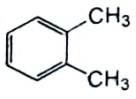
i



ii



iii



iv

b Deduce the structure of an organic compound from the following data:

Molecular formula: $C_8H_{14}O_3$,

IR (cm-1): 2900, 1820 and 1755 cm^{-1};

^1H NMR: δ: 1.0 (t), 1.7 (m) and 2.5 (t);

^{13}C NMR (δ): 12, 18 (DEPT –ve signals), 38 and 180;

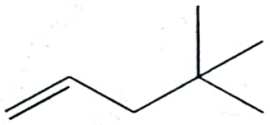
Mass: 158 (M+), 71 (base peak), 70 and 55.

X51YAA1165X51YAA1165X51YAA1165X51YAA1165

Scan

Q.4 A Answer any two of the following: **8**

a The following chemical shifts were obtained in the ^{13}C NMR spectrum of the compound.



δ(ppm): 28, 29, 49, 118, 133.

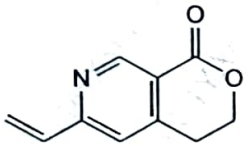
Match the chemical shifts with the appropriate carbons and draw its proton decoupled ^{13}C NMR, DEPT-45, DEPT-90, DEPT-135 spectra.

b Discuss the significance of 2D NMR spectroscopic techniques over one dimensional.

c What is Nuclear Overhauser Effect proton NMR? What significance does it have? Explain with suitable example.

d Assign the ^{13}C NMR chemical shifts to the given structure. Justify your assignments.

24 (t), 66.12(t), 120.26(t), 120.82(s), 129.44(d), 130.72(s), 144.66(s), 150.20 (d), 150.88(d), 163.46 (s).



Q.4 B Answer any one of the following: **4**

a What is HETCOR spectroscopy? With suitable example explain its significance in structure determination of organic compounds.

b Predict the probable ^{1}H NMR and ^{13}C NMR signals for 1-propanol. Using predicted signals draw a sketch of ^{1}H-^{1}H COSY spectrum and assign correlations.

Q.5 Answer any four of the following **12**

a Give the synthesis of Grandisol.

b Prove the following :

i. Presence of secondary amine group in coniine

ii. Presence of piperidine nucleus in coniine

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M S c - sem III - chemistry

c What are lipids? Give its classification with suitable example.

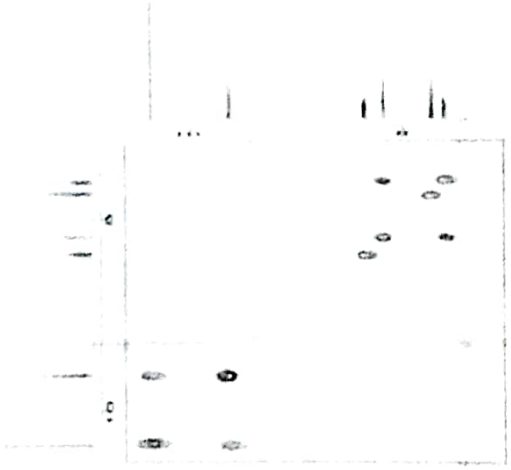
d Draw the structure of Texol. Give the applications of JH_2 and JH_3

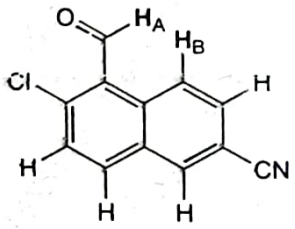
e Explain the principle and significance of double resonance technique in NMR spectroscopy.

f A compound with MF $C_6H_4N_2O_4$ shows IR at 1530, 1360 and 1600 cm^{-1}. PMR at 8.2 (s, 4H). ^{13}C NMR at 145 and 132 and DEPT-135 at 132 (up). Deduce the structure.

g Write a note on coupling constants.

h Assign the diagonal and off diagonal to protons H_A and H_B in a given NOESY spectrum and justify your answer.





X51YAA1165X51YAA1165X51YAA1165X51YAA1165

MSC-chem . sem III

Time: 2:30 Hours **Marks: 60**

Q.1 **A** **Attempt any two of the following.** **8**

a Explain structural features and applications of chitin and cellulose.

b Explain Wohl degradation studies in structural determination of lactose.

c i) Give the analytical evidence for number and position of hydroxyl groups in cyanidin chloride.

ii) Give structural features and biological importance of porphyrins.

d Give the synthesis of ubiquinone from 3,4,5-trimethoxy acetophenone.

B **Attempt any one of the following** **4**

a Give synthesis of Disparlure from 6-methyl-hept-1-ene.

b i) Give analytical evidence for the presence of n-propyl side chain in coniine.

ii) Give physiological importance and occurrence of morphine.

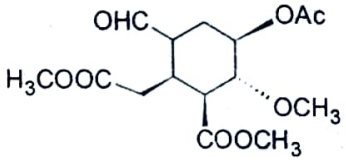
Q.2 **A** **Attempt any two of the following** **8**

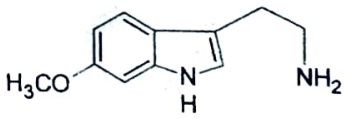
a Give the synthesis of Juvabione from Limonene.

b Give the synthesis of Caryophyllene from 2-Cyclohexenone and Isobutylene.

c Write the analytical evidences for structure elucidation of PGE_1.

d Write the synthesis of Reserpine from the following compounds.





B **Attempt any one of the following.** **4**

a What are lipids? Give its classification with suitable example.

b Write the synthesis of Griseofulvin from phloroglucinol.

Q.3 **A** Attempt any two of the following. **8**

a Using spin system notation, designate the type of spin system in the following compounds.

i) 2-Bromoethanol ii) o-dichlorobenzene iii) 2-furoic acid iv)1,1,2-trichloroethane

b Explain long range coupling in heteroaromatic and allylic compounds.

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c Calculate ^{13}C NMR shift for all aromatic carbons using incremental shifts of all the aromatic carbon atoms from the table given below for the following compounds.

i) m-nitroacetophenone ii) o-bromonitrobenzene

Substituents	Increments in ppm			
	Ipso	Ortho	Meta	Para
$-NO_2$	+19.6	-5.3	+0.9	+6.0
-Br	-5.4	+3.4	+2.2	-1.0
$-COCH_3$	+7.8	-0.4	-0.4	+2.8

d A compound with molecular formula $C_{10}H_{14}O$ with the following NMR data.

^{1}H-NMR (δ ppm) = 7.12 (doublet of doublets, integral=2) , 6.82(doublet of doublets, integral = 2), 3.74 (singlet, integral = 3), 2.84 (septet, integral = 1) , 1.21 (doublet, integral = 6)

^{13}C-NMR (δ ppm) = 157.9 (singlet), 141.1(singlet), 127.3 (doublet) , 120.9 (doublet) , 55.2 (quartet) , 33.4 (doublet) and 24.2 (quartet).

Assign the structure to the compound.

B Attempt any one of the following 4

a The following chemical shifts were obtained in the **^{13}C-NMR** spectrum of Isobutyl acetate.

^{13}C-NMR (δ ppm) = 169,70,30,24,20

Match the chemical shifts with appropriate carbons and justify your answer.

b Explain temperature effects on ^{1}H-NMR of the following compounds.
i)N,N-dimethylformamide ii) Cyclohexane

Q.4 A Attempt any two of the following. 8

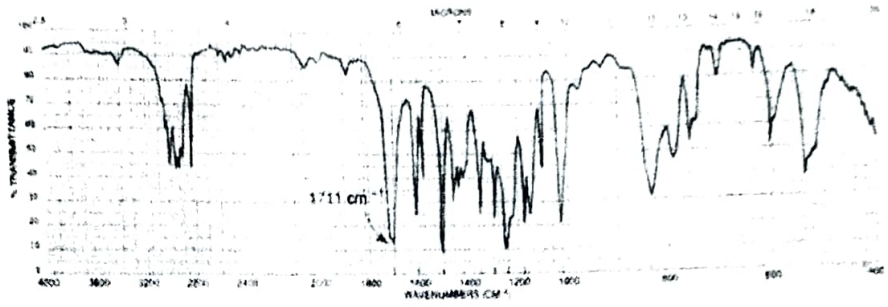
a What is NOE? Give its significance and explain it with a suitable example.

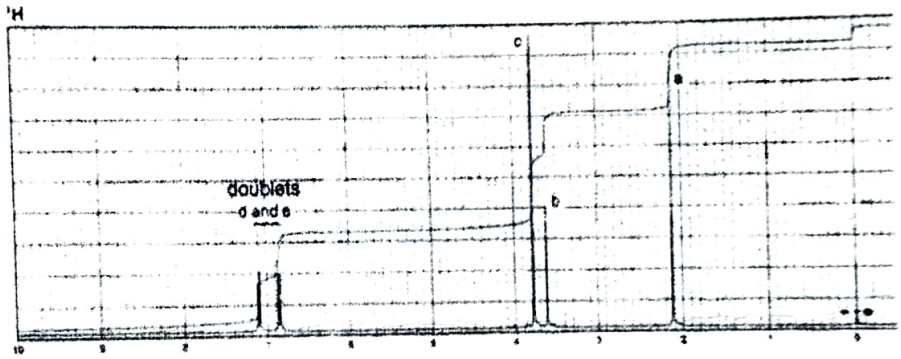
b Explain the COSY technique with a suitable example.

c What is the NOESY technique? Give its significance and explain it with a suitable example.

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d Determine the structure of the compound with a M.F. $C_{10}H_{12}O_2$. In addition to IR, ^{1}H-NMR the problem includes tabulated data for normal Carbon-NMR, DEPT-135, and DEPT-90 spectral data.





Normal Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50	Negative	No peak
55	Positive	No peak
114	Positive	Positive
126	No peak	No peak
130	Positive	Positive
159	No peak	No peak
207	No peak	No peak

B Attempt ANY ONE of the following 4

a Write the fragmentation pattern of the following molecules in Mass spectroscopy;

i) Ethyl benzene ii) 3-pentanone

b Using IR Spectroscopy how can you distinguish between

i) Phenol and Cyclohexanol ii) Ethylbenzene and o-xylene

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Q.5 **Attempt any four of the following** **12**

a i) Write a short note on deoxysugars.

ii) Draw the structure of β-Carotene.

b i) Explain aggregation pheromones.

ii) Write any two biological importances of pterins.

c Draw the structure of Taxol. Discuss the structural features of gibberellic acid.

d Draw the structures and give the applications of JH_2 And JH_3.

e How many signals you expect in the proton decoupled ^{13}C-spectra of following compounds?

i) p-Dichlorobenzene ii) Methyl acetate iii) 2-Butanone

f A compound gives following ^1H NMR spectra by using operating frequency 300 MHz. Coupling constant is 8 Hz.

^1H NMR δ (ppm) : 4.1 , 3.2

Calculate the frequency difference between these two signals. Whether the spectra is first order or second order?

g Sketch and explain the HETCOR spectrum of 1-Chloro-2-propanone.

h How to determine signals of methane, ethane, and toluene in C-13NMR?

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