

II.M.Sc.,CHEMISTRY
ORGANIC CHEMISTRY -III
SEMESTER-III

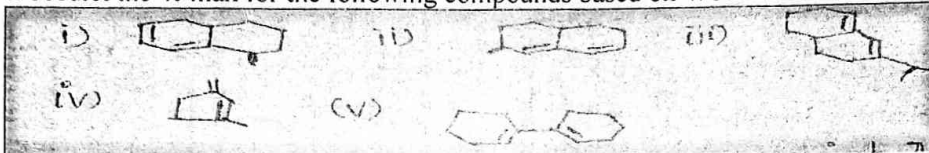
QUESTION BANK

By,
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CUDDALORE – 1.

M.SC 3 rd SEM- ORGANIC CHEMISTRY (PCH31)

UNIT-1

1. Define finger print region? Mention its significance. (4)
2. What is auxochrome? Explain how an auxochrome exert a bathchromic shift on a chromophoric group (6)
3. Differentiate inter and intramolecular hydrogen bonding by IR spectroscopy (6)
4. Predict the λ -max for the following compounds based on Woodward-fieser rules (10)



5 What do you mean by finger print region? (5)

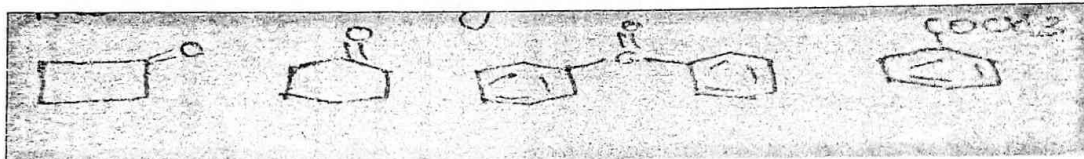
6. Define chromophore and identify chromophoric group in the following compounds (6)

Cyclopentene

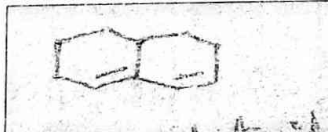
Toluene

Butanone

7. Arrange the following compounds in the order of their increasing carbonyl stretching frequency.



8. Explain the effect of solvent on λ -max in UV spectroscopy (6)
9. How will you determine the nature and strength of hydrogen bonding by IR spectroscopy. (5)
10. Define the terms hyperchromic and hypochromic shift (4)
11. Write notes on chromophore and auxochromes. (4)
12. Write a note on Fermi resonance. (4)
13. Write the Woodward-fieser rule for calculation of adsorption maxing of unsaturated hydrocarbon (10)
14. Apply this to calculate λ -max for the following compound



15. Define the following terms (4) (REPEAT)

(i) Bathchromic shift

(ii) Hypochromic shift

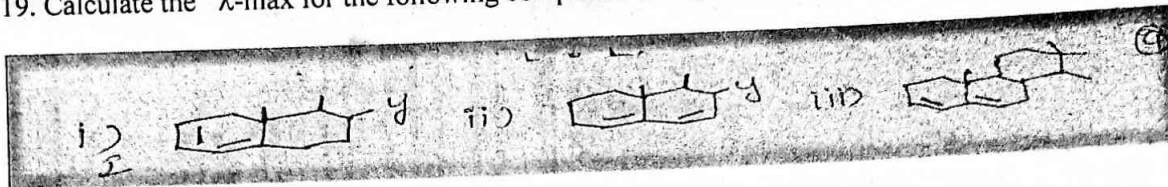
(iii) Hyper chromic shift

16. Briefly explain the item: (4)
 chromophore
 auxochrome

17. How is infrared spectroscopy useful in distinguishing between intermolecular hydrogen bonding?

18. Bring out the significance of the finger print region. (4)

19. Calculate the λ -max for the following compound using Woodward-Fieser rule (3+3+4)



20. Explain the terms.

a) chromophore

b) finger print region

21. List the electronic transition possible for the following compounds.

1) CCl4 (2) HCHO (3) C=O (4) CH3CH2OH (5) CH2=CHCl

22. Use IR to distinguish between

i. A primary amide and a primary amine

ii. A primary secondary and tertiary amine

23. Which of the following vibrational modes shows no IR absorption band?

Symmetric CO2 stretch

Symmetric O=C=S

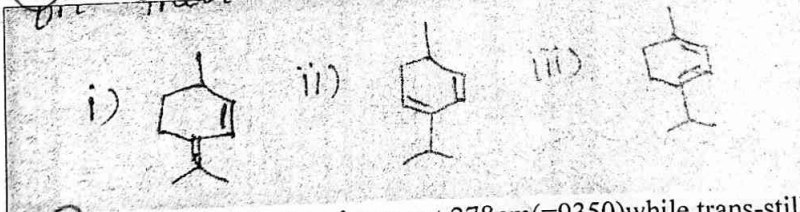
Antisymmetric CO2 stretch

Symmetric stretch NC-CN (C-C).

24. Give the characteristic IR absorption frequencies of the following group.

-O-H, =N-H, =C-H, \equiv C-H, =C=O of ketones

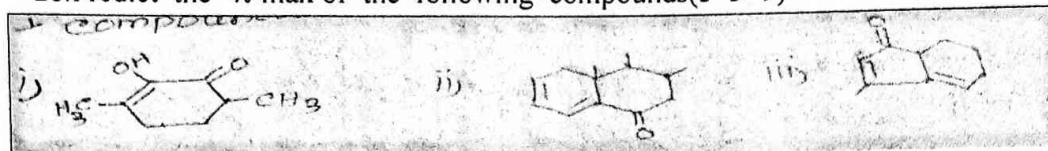
25. Distinguish the following three isomers based on their λ -max values



26. Cis-stilbene has λ -max at 278nm (=9350) while trans-stilbene has λ -max at 294nm (=24000) explain

27. Explain the bend in carbonyl stretching frequency of cyclopropane, cyclopentanone and cyclohexane in IR (6)

28. Predict the λ -max of the following compounds (3*3=9)



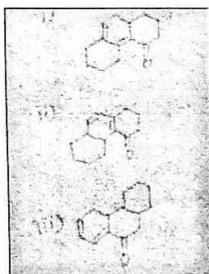
29. Write notes on chromophore and auxochromes. (4)

Write a note on Fermi resonance (4)

30. Write the Woodward-Fieser rules for calculation of absorption maxima of Unsaturated hydrocarbons. (10)

31. Explain the importance of IR spectroscopy in finger print region.

32. Using Woodward-Fieser rules calculate the values of absorption maximum for the following compounds



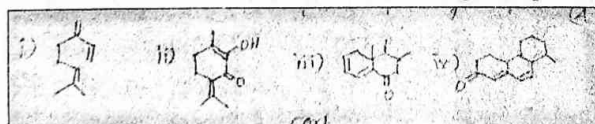
33. How will you distinguish intra and inter molecular hydrogen bonding? (7)

34. Define the following terms (8)

- i. bathochromic shift
- ii. hypsochromic shift
- iii. A chromophore
- iv. Hyperchromic effect

35. Distinguish between the

- i. o-nitrophenol and p-nitrophenol by IR
- ii. calculate λ -max value for the following compounds



36. Define λ -max, Σ max and transmittance (4)

37. Explain how the IR spectra neat samples of phenol and cyclohexanol

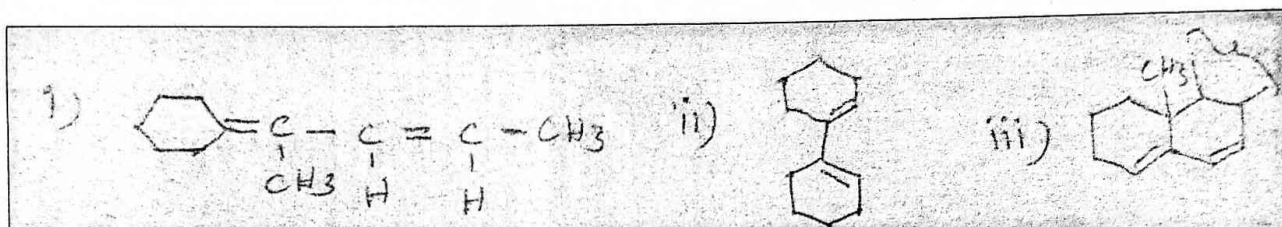
would defer(4)

38. List the possible electronic transition in vinyl chloride which transition would be expected to be observed in the UV visible region of the spectrum(3)

39. Explain how the auxochrome exerts the bathochromic shift on the chromophore such as C=C (3)

40. Discuss the type of absorption band in electronic spectroscopy

41. Calculate the λ_{max} for the following.



42. Explain the instrumentation of UV spectroscopy with suitable diagram(6)

43. Write the Woodward Feiser rules for calculating λ_{max} of alpha and beta unsaturated ketones (6)

44. Assign the expected infra red peaks for the following (3)

- acetophenone
- benzamide
- methanol

45. What is meant by $n-\pi^*$, $\pi-\pi^*$ and $\sigma-\sigma^*$ excitation? Arrange them in the order of increasing energy?

46. Using IR spectroscopy how will you distinguish

- cis-cinnamic acid and trans cinnamic acid
- inter and intramolecular hydrogen bonding

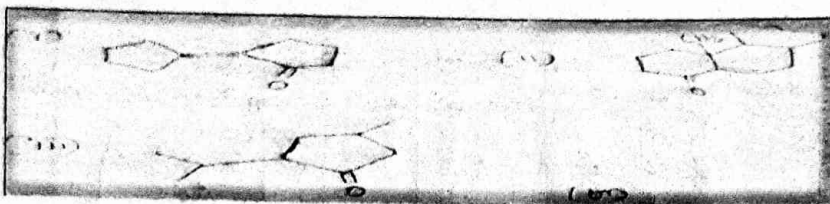
47. Explain how the presence of two chromophores in a molecule shift both in the λ_{max} and Σ_{max} to higher values (5).

48. Using Woodward-Fieser rule calculate λ_{max} of UV absorption for the following compounds(5)



49. What do you understand by fingerprint region give its applications. (5)

50. The following alpha and beta unsaturated ketones have λ_{max} in ethanol at 241m(Σ 4,700), 254m(Σ 9,550) and 259m(Σ_{max} 10,790) in ethanol which is which?



51. Write the Woodward-Fieser rules for calculating λ_{max} of dienes and polyenes

52. Account for the following

- polar solvents usually shift by $\pi-\pi^*$ transition to longer wavelength and $n-\pi^*$ transition shorter wavelength
- the λ_{max} for o-methylacetophenone is 243 nm while that for the p-isomer is 252 nm (4)

53. Which of the following would exhibit lower C=O stretching frequency? Why?

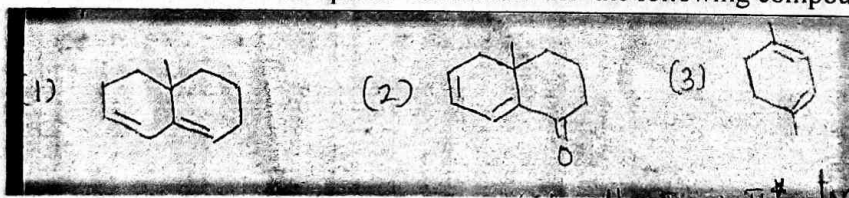
- cyclopentanone or cyclohexanone
- acetyl chloride or acetamide

54. Discuss the various factors that affect the position and intensity of UV absorption bands. (10)

55. How are the following distinguished by IR spectroscopy? (6)

- o-nitrophenol and p-nitrophenol
- Methylbenzoate and phenyl acetate
- Cyclopentanone and cyclohexanone

56. Calculate UV absorption maximum for the following compound? (3)



57. Discuss the various factors that affect the position and intensity of UV absorption bands (8)

58. Write notes on

- Fermi resonance
- Finger print region
- Metal-ligand stretching vibrations

unit-2

1. What are the factors influencing a chemical shift in PMR? Explain them? (6)

2. What are the factors influencing a chemical shift in NMR? Explain them? (6)

3. What is pascal triangle ? mention its significance PMR spectroscopy?(4)

4. Discuss p-cresol and m-cresol by ^{13}C NMR?(6).

5. A molecular formula of the organic compound is $\text{C}_2\text{H}_4\text{O}$. Draw the NMR spectrum of this compound

6. Illustrate how off-resonance techniques help in the assignment of peak in ^{13}C NMR. How it is affected(5)

7. Explain shielding and deshielding of a nucleus(5).

8. Explain the N.O.E ?(6)

9. What are the factors that affect vicinal coupling constant (6).

10. Write note on the factors that affect coupling constant in ^1H NMR (8).

11. How will you differentiate o,m and p-xylene on the basis of their proton decoupled ^{13}C NMR spectra?(7)

12. Explain the following (4)

- i. Radio frequency oscillator
- ii. Radio frequency receiver

13. Give a brief account of the commonly used NMR solvent(4)

13.a Briefly describe the ^{13}C nmr spectroscopy(4)

13.b Write notes on N.O.E ?(4)

14. What do you understand by terms double resonance and spin tickling? How these are helpful in simplifying the spectra?(10)

15. A compound having the molecular formula $\text{C}_{10}\text{H}_{14}$ gave the following (PMR data:

0.88 δ (9H,S) 7.28 δ (5H,S aromatic proton) assign the structural formula to the compound(10)

16. The proton decoupled ^{13}C NMR spectrum of a tribromobenzene ($\text{C}_6\text{H}_3\text{Br}_3$) consists of two signals only which tribromo benzene is it?(7)

17. Explain the origin chemical shift in NMR spectroscopy?(4)

18. Discuss the various factors which affect the value of chemical shift?(4)

19. An organic compound with molecular formula $\text{C}_3\text{H}_3\text{O}_5$ gave the following PMR data. A triplet -4.52 δ , A triplet -6.07 δ , Assign the structural formula of the compound .

20. Write short notes on spin-spin coupling ?(4)

21. Write notes on the following(10)

- i. N.O.E
- ii. Spin-decoupling

22. Give the spin multiplicity in each of the following compounds

- i. $\text{CH}_3\text{CH}_2\text{COCH}_3$
- ii. $\text{CH}_3\text{CH}_2\text{CHO}$
- iii. $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$
- iv. $(\text{CH}_3)_3\text{CHOH}$
- v. $\text{H}_3\text{C}-\text{C}_6\text{H}_5-\text{CH}-(\text{CH}_3)_2$

23. Explain the terms a) Chemical shift, b) Describe the relationship between the values of various coupling constants and stereochemical structure (5)

24. How many kinds of protons are there in

- i. CH_3COCH_3
- ii. $\text{CH}_3\text{CH}_2\text{CH}_3$
- iii. $\text{H}_2\text{C}=\text{CH}_2$
- iv. $\text{CH}_3\text{CH}=\text{CH}_2$
- v. $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$

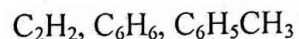
25. What is the chemical shift? what are the factors which influence proton chemical shift?

26. Discuss the phenomenon of chemical exchange and how would you overcome this differently in the interpretation of NMR spectra.

27. Explain in brief the following.

- a) AX splitting pattern
- b) Vicinal coupling
- c) Nuclear Overhauser effect

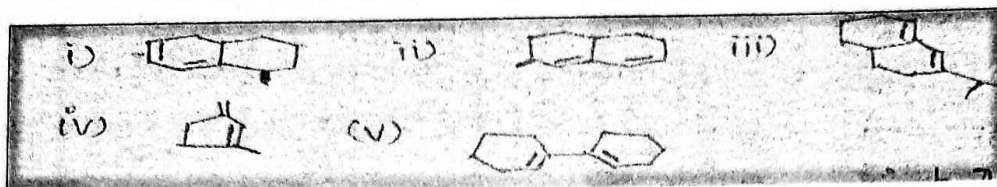
28. How do you explain the chemical shift (δ) values shown for the hydrogen's in the following compounds(5)



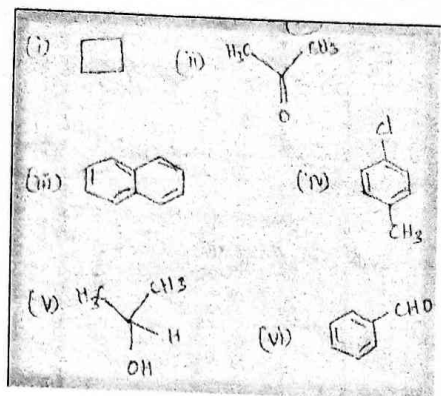
2.9 7.4 2.3

29. PMR spectrum of DMF shows two signals for methyl protons at room temperature but only one signal at higher temperatures. Explain (2)

30. Calculate λ_{max} values for the following compounds(4)



31. Explain why TMS is chosen as a reference in NMR (4)
32. Deduce the structure of the compound from the given in NMR data (3)
 C_4H_9Br : δ ppm 1.04, doublet, 6H; 1.95, multiple, 1H; 3.33, doublet, 2H
33. List the possible electronic transitions in vinyl chloride which transition would be expected to be observed in the UV, visible region of the spectrum? (3)
34. Explain how the factors electro negativity and anisotropy influence the chemical shift values (5)
35. Account for the following (4)
- i. Spin-spin splitting is observed in 2-methylpropene but not in neopentyl chloride
36. Explain the terms "chemical shift". Why TMS is used as standard reference in spectroscopy?.
37. Briefly write about off-resonance decoupling technique in ^{13}C NMR spectroscopy
38. Discuss the NOE in with example.
39. Explain the factors affecting the ^{13}C chemical shift
40. Taking CH_3CH_2Cl as an example explain the phenomenon of spin-spin splitting
41. Explain anisotropic effect in NMR spectroscopy with an example.
42. Write explanatory notes on:
- I. Spin-decoupling
 - II. Nuclear overhauser effect (NOE)
43. Discuss the importance of off-resonance decoupling in ^{13}C NMR
44. Explain the instrumentation of NMR spectroscopy
45. Predict the number of NMR signals for following



46. Discuss in factors affecting the various coupling constant 'J' in NMR spectroscopy(15)

47. Which of the following compounds would be expected to show only a single in PMR.

1. Acetone
2. Methylacetate
3. 1,2-dibromoethene
4. 1,1- dibromethene

48. Define the term chemical shift and describe any four factors which influence it.(6)

49. How is PMR spectroscopy distinguishing the following pairs of compounds.

1. N-propyl bromide and iso-propylbromide
2. Ethylbenzene and p-xylene (4)

50. Write a note on Nuclear overhauser effect(4)

51. An organic compound with molecular formula C_8H_{12} shows the following spectral features PMR :
1.3(d,6h),5.3(spectral)

Unit-3

1. How can you find out the meta peak in a mass spectroscopy ?

2. Mass spectroscopy of arise gives ions f m/z 108,93,78,77and 65 explain?(7)

3. Explain the ORD and its application?(8)[repeat]

4. How chemical ionization helps in determining the accurate molecular ion peak?(4)

5. Briefly describe the advantages and disadvantages of fast atom bombardment technique?(4)

6. Discuss in detail the following cleavage patterns in mass spectroscopy?(10)

- a. Hetero cleavage
- b. α -cleavage
- c. hemolytic cleavage
- d. β -cleavage

7. Explain the terms

- a. isotope peak , b. molecular ion peak

8. Suggest the structure of a compound with molecular formula $C_{10}H_{12}O$ whose mass spectrum show peak at m/z 15,43,57,91,105 and 148

9. Define halo ketone. Explain giving one example how this rule could be used to determine the absolute configuration of an organic compound.

10. Explain McLafferty rearrangement taking the example of $CH_3CD_2CN_2CH_2COCH_3$? (8)

11. How will you determine the conformation of (+)cis-10-methyl-2-decalone by an application of Cotton effect? (7)

12. Distinguish between primary, secondary, and tertiary alcohols by mass spectrum? (6)

13. Illustrate the application of octant rule in the determination of conformation of (+)3-methylcyclohexanone having R-configuration? (5)

14. The mass spectrum of $CH_3CH_2CH_2CHO$ shows an intense peak at $m/z=44$

15. Explain Cotton effect with suitable example.

16. Explain the octant rule with a cyclic ketone

17. Explain the terms (6)

i. molecular ion

ii. isotope ions

iii. fragmentation ion with odd and even electron types

18. Discuss the mass fragment pattern of alcohols? (9) *answer for 12*

19. Mass spectrum of anisole gives ions of m/z 108, 93, 78, and 65 explain?

20. Write notes on the following

i. molecular ion peak

ii. meta stable peak

iii. nitrogen rule

21. Explain McLafferty rearrangement with examples. (7)

22. Explain M+1, M+2 and M+4 ion peaks when these ions are formed.

23. Discuss the mass fragmentation pattern of 1-phenylethanol and phenol (6)

24. How axial halo ketone rule was applied for conformational analysis of cyclic and polycyclic compound. (9)
25. Define
- base peak
 - molecular ion peak
26. Write the fragmentation pattern for $C_6H_5CH_2OH$ in mass spectroscopy?(3)
27. Explain McLafferty rearrangement and retro diels-alder reaction with an example for each?(7)[repeat]
28. What are meta stable peaks? How are they produced? Explain the importance of it?(3)
29. Write a note on SIMS-FAB technique(3)
30. State octant rule and discuss its application in the of conformation and configuration of molecule?(9)
31. Write the fragmentation pattern in the mass spectra for (6)
- phenol
 - 2-butanol
32. Write the principle of optical rotatory dispersion? Mention it application?
33. An organic compound with molecular formula C_8H_8O undergoes fragmentation to give ions of m/e 120, 105, 77, 51, and 43. Identify the structure of the compound and account for the fragmentation pattern?
34. Write the short notes on following?
- Axial haloketone rule
 - Cotton effect
35. In the mass spectrum of heptan-3-one peaks at $m/e=114,85,72$, and 57 are obtained . relationalize these peaks in terms of fragmentation of the above ketones?
36. Illustrate McLafferty rearrangement with an example?
37. Write notes on
- Cotton effect
 - Axial haloketone rule
 - Octant rule
38. How will you distinguish 2-pentanone and 2-hexanone by mass spectra?
39. Explain field desorption?

40. Write briefly on isotopic peaks in mass spectrometry?
41. Discuss the mass spectrum of primary, secondary and tertiary?
42. How chemical ionization helps in determining the accurate molecular ion peak?
43. Briefly describe the advantages and disadvantages of fast atom bombardment technique?
44. Discuss in detail the following cleavage patterns in mass spectroscopy.
 - i. Heterolytic cleavage
 - ii. Homolytic cleavage
 - iii. α - cleavage
 - iv. β - cleavage
45. Describe the following technique in mass spectroscopy.
 - i. Chemical ionization technique
 - ii. Field desorption technique

UNIT-4

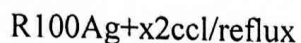
- 1) Describe how the structure of citral was established.
2. Describe how the structure of quinine was established.
3. Show that the following compounds could be synthesized from the indicating materials.
 - a) Camphor from α -pinene
 - b) Geranial from citral
 - c) α -terpineol from guaiol
4. Write the total synthesis of morphine. (10)
5. Discuss the structural elucidation of α -pinene (15)
6. Write the synthetic strategies involve in reserpine? (10)
7. What isoprene rule? Explain with example? (6)
8. Describe the classification of terpenoids?(6)
9. Describe the structural elucidation of farnesol?(10)
10. Describe the structural elucidation of linalool?(10)
11. Describe the structural elucidation of camphor?(15)
12. Write the synthies of linalool? (6)

13. Write the syntheses of camphor?(6)

UNIT-5

1. Explain how free radicals are detected by ESR spectroscopy

2. Predict the product and explain



3. Explain

- i. Phenol-coupling
- ii. Gomberg reaction

4. Write the mechanism of addition of free radical to olefinic double bond(5)

5. Explain how the ESR technique is used to detect the radicals(4)

- i. What is the chemically induced dynamic nuclear polarisation(CIDNP)?how this technique is used to find free radicals(4)

6. Write notes on the stability of free radicals

- ii. How are free radicals formed? Explain any two methods?

7. Illustrate Ulmann reaction with an example

8. Give a brief account of Hunsdiecker reaction (10)

9. What is Gomberg-Bachmann reaction?

10. Write notes Pschorr ring closure reaction.(10)

11. What are long short lived free radicals?

12. Discuss the mechanism Hunsdiecker reaction.

13. Write notes on

- a. Pschorr reaction
- b. Ulmann reaction
- c. Gomberg reaction
- d. Detection of free radicals by ESR.

14. Explain the mechanism of Hunsdiecker reaction with an example.

15. Write and explain the Pschorr reaction with example.

16. What are the long and short lived free radicals?
17. Give examples how to generate these radicals?
18. Explain the Sandmeyer reaction with examples(1)
19. Explain general methods of free radicals generation
20. Explain Hunsdicker reaction with example
21. Explain free radical mechanism of the following
- I. Sandmeyer reaction
 - II. Gomberg reaction
22. Explain how free radicals detected by ESR spectroscopy
23. Explain the methods of generation of free radicals
24. Write the relaxation mechanism of Gomberg reaction with example
25. Discuss the free radical addition to olefinic double bonds with example.
26. Explain the Sandmeyer reaction with examples(15)
27. What are long lived free radicals? Give two examples discuss their stability
28. Identify the product and write the mechanism for the following
- I. $C_6H_5COOAg + Br$
 - II. $CH_3-CH=CH_2 + HBr$
29. Write notes on (16)
- a. Sandmeyer reaction
 - b. Decomposition of diazo compounds
 - c. Pschorr ring closure reaction
 - d. Ullmann reaction
30. How are free radicals generated? Discuss a method for its detection
31. How are the following transformation carried out?
- i. Toluene $\xrightarrow{\text{benzoylchloride}}$ benzoylchloride(6)
32. 2-phenylethyl bromide is the major product when HBr is added to styrene in dibenzoyl peroxide account(3)
33. Write note on:
- I. Sandmeyer reaction

- II. Gomberg reaction
- III. Ullmann reaction
- IV. Decomposition of diazo compounds(12)

34. Write a note on Hunsdicker reaction?
35. What are short lived and long lived free radicals. Illustrate with example?
36. Explain the mechanism of the addition of free radicals olefin?
37. Explain with an example that sandmeyer reaction can proceed with free radical mechanism?
38. How free radicals are generated?
39. Explain the mechanism of Gomberg reaction?
40. How many lines appear for methyl radical in ESR spectrum?
41. Explain :
- i. Pschorr reaction
 - ii. Ullmann reaction
42. How free radicals are generated by photolysis?
43. Explain the following:-
- i. Radio frequency oscillator.
 - ii. Radio frequency receiver.
44. Explain how the ESR technique is used to detect polarization (CIDNP)? How this technique is used to find free radicals?
45. What is chemically induced dynamic nuclear polarization (CINP)? How this technique is used to find free radicals?
46. Write notes on the stability of free radicals?
47. How are free radicals formed? Explain any two methods?
48. Illustrate Ullmann reaction with an example?
49. Give a brief account of Hunsdicker reaction?
50. What is Gomberg Bachmann reaction?
51. Write notes on Pschorr ring closure reaction?
52. Write briefly on the stability of free radicals?
53. Discuss the general methods of generation of free radicals?

54. Discuss the mechanism of pschorr –reaction?
55. How are free radicals detected by ESR spectroscopy?
56. What is Ulmann reaction? Discuss its mechanism and scope? Can this reaction be used for ring closure? If so, in what way this is similar to or different from Pschorr ring closure?
57. Give a brief account of hunsdicker reaction?

