

Problems and Solutions in Organic Chemistry

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Preface

Though chemical compounds are visible to the naked eye, their constituent atoms and bonds are invisible even under a very powerful microscope. When one tries to visualize the formation of a compound, one has to depend on the information available in related literature, confirmed through time-tested experiments. Therefore, when a student comes across a new problem, the solution can only be rationalized as a 'plausible' explanation or by concluding that 'results have to be confirmed by experiments and investigations'. Organic chemistry is a mind-boggling field of chemistry, in the sense that nature has produced thousands of organic molecules with unimaginable complexities. Fascinated by this area of study, chemists are observing and following nature to synthesize many new compounds in their laboratories, many of which have changed our lifestyle in unimaginable ways.

Young learners must realize that to excel in any science course, they must develop the habit of solving problems. To gain confidence in this, they would initially need the assistance of books that contain a large number of solved problems. It is with this objective in mind that *Problems and Solutions in Organic Chemistry* was conceived. The book is designed as a self-study material, to expose students to the various facets of organic chemistry.

ABOUT THE BOOK

Problems and Solutions in Organic Chemistry is primarily written for undergraduate students who have opted for an Honours course in chemistry. It will also be useful for students pursuing postgraduation in chemistry and those preparing for competitive examinations such as the Joint Admission Test for Masters (JAM), National Eligibility Test (CSIR–UGC NET), and Graduate Aptitude Test in Engineering (GATE).

Most problems in each chapter have been discussed on the basis of traditional functional groups present in organic compounds. This will help students get an idea of the types of problems based on a particular class of compounds. For example, alcohols can participate in elimination reactions, etherification reactions, esterification reactions, and are reagents in nucleophilic substitutions as well. Therefore, if we separately discuss the problems on alcohols, we can get an idea of the different types of reactions these compounds take part in. Similarly, the properties of aliphatic carbonyl compounds and aromatic carbonyl compounds differ in many reactions. Therefore, if problems on these compounds are individually

discussed, students would get specific information on the types of reactions these two different classes of carbonyl compounds take part in. Such an approach to learning the subject is more pragmatic as it helps readers get acquainted with the relevant reactions within a class of organic compounds.

KEY FEATURES

- Problems on the nomenclature of the different classes of organic compounds based on IUPAC rules, and the answers to these
- A plethora of problems on the classes of compounds with plausible mechanisms and rationalization, where necessary
- Illustrative reaction mechanisms through well-drawn diagrams with supportive explanations and comments wherever needed
- Problems on stereochemistry, spectroscopy, and pericyclic reactions
- Over 1500 solved problems addressing various topics on the subject
- Includes 700 chapter-end exercise problems to aid self-evaluation

CONTENTS AND COVERAGE

The book has 21 chapters. A short description of the nature of problems included in each chapter is given here.

Chapter 1, *Nomenclature of Organic Compounds*, provides problems on the naming of various aliphatic, alicyclic, aromatic, fused polynuclear, spiro, heterocyclic, and bridged compounds. The nomenclature of many unique unsaturated aliphatic compounds and compounds with a variety of functional groups have been discussed. End-chapter exercises discussing certain interesting chemical structures have also been included.

Chapter 2, *Physical Organic Chemistry*, deals with problems based on the concepts and theories in organic chemistry, such as acid–base reactions, dipole moments, reaction rates, tautomerism, reaction kinetics, and aromaticities.

Chapter 3, *Stereochemistry*, includes a large number of problems on various aspects of stereochemistry involving organic molecules. Problems on both static and dynamic stereochemistry have been demonstrated.

Chapter 4, *Aliphatic and Alicyclic Hydrocarbons and their Halides*, elucidates problems on both saturated and

unsaturated compounds in addition to those on aliphatic and alicyclic hydrocarbons.

Chapter 5, *Alcohols and Ethers*, throws light on typical problems on alcohols and aliphatic ethers.

Chapter 6, *Aliphatic Carbonyl Compounds*, deals with a wide array of interesting problems on aliphatic aldehydes and ketones.

Chapter 7, *Aliphatic Acids and their Derivatives*, describes problems on aliphatic acids and their derivatives, such as esters, amides, and acid halides.

Chapter 8, *Aliphatic and Alicyclic Amines, Nitriles, Isocyanides, Ylides, Diazocompounds, and Organometallic Compounds*, discusses a host of interesting problems on these classes of compounds.

Chapter 9, *Aromatic Carbonyl Compounds*, explores the typical problems associated with these compounds.

Chapter 10, *Aromatic Acids, Amines, Nitro-compounds, and Diazo-compounds*, comprises a large number of problems on these staggering classes of compounds.

Chapter 11, *Phenolic Compounds, Benzoquinones, and Aromatic Ethers*, deals with specific and interesting problems on these compounds to understand their reactions better.

Chapter 12, *Benzenes, Polynuclear and Alicyclic Hydrocarbons*, explains problems on benzene and substituted benzenes, polynuclear aromatic hydrocarbons, and some additional problems on alicyclic compounds, which have not been discussed in Chapter 4.

Chapter 13, *Pericyclic Reactions*, deals with problems on this special class of organic reactions. These include reactions such as electrocyclic reaction, cycloaddition reaction, sigmatropic reaction, and ene-reaction.

Chapter 14, *Problems on the Uses of Spectroscopic Methods in Organic Chemistry*, illustrates the problems on the application of ultraviolet (UV), infrared (IR), nuclear magnetic resonance (NMR), and mass spectroscopic methods in the identification and determination of structures of organic molecules.

Chapter 15, *Heterocyclic Compounds*, has a large array of problems on monocyclic and bicyclic heterocycles with N, O, and S as heteroatoms.

Chapter 16, *Carbohydrates*, has problems dealing with naturally occurring typical monosaccharides, disaccharides, and polysaccharides.

Chapter 17, *Amino Acids, Proteins, and Nucleic Acids*, deals with a variety of problems on important biomolecules such as amino acids, proteins, and nucleic acids.

Chapter 18, *Molecular Rearrangements*, analyses problems associated with molecular rearrangements encompassing all the classes of organic compounds.

Chapter 19, *Conversions and Syntheses of Organic Compounds*, gives a clear picture on the mechanisms related to conversions among organic molecules and also talks about the synthesis of organic molecules from typical compounds and reagents.

Chapter 20, *Constitutional Problems on Organic Compounds*, has a diverse range of problems on the identification of compounds based on a sequence of reactions.

Chapter 21, *Miscellaneous Problems*, presents a large number of interesting problems based on the different classes of organic compounds and a variety of organic reactions we encounter in organic chemistry.

Appendix A, *Abbreviations of a Few Reagents Used in Chemical Literature*, lists out the abbreviations and the corresponding chemical structures of some frequently used reagents in organic reactions.

Appendix B, *Reducing and Oxidizing Agents Commonly Used in Organic Chemistry*, lays emphasis on the various reducing and oxidizing agents, along with their chemical composition, preferred solvent, and reaction mixture.

ACKNOWLEDGEMENTS

I express my deepest gratitude to Oxford University Press India for accepting this book for publication. I am particularly thankful to the members of the editorial team for their diligent guidance and cooperation in this endeavour.

I also appreciate the support and encouragement I received from my wife, Mrs Arundhati Sen Gupta, and my son, Dr Anirban Sen Gupta, during the preparation of this book.

Suggestions and feedback are welcome and can be sent to me at pushpal_@hotmail.com and pushpal314@data-one.in.

Subrata Sen Gupta



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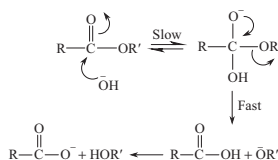
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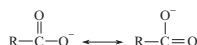
FEATURES OF

7.13 Give the B_{AC}2 mechanism of ester hydrolysis.

Ans B_{AC}2 mechanism of ester hydrolysis can be shown as follows:



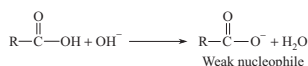
B_{AC}2 stands for 'base catalysed acyl oxygen fission bimolecular (2)'. The B_{AC}2 hydrolysis is irreversible because the carboxylate ion R-COO⁻ is resonance stabilized and consequently is a poor nucleophile. It cannot displace OH⁻ from R'-OH by S_N2 type displacement.



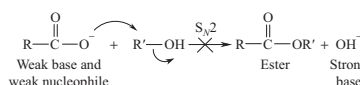
7.15 Esterification reaction is always catalysed by acids but de-esterification is catalysed by both acid and alkali and the latter is preferred. Explain with suitable examples.

Ans Esterification is always acid catalysed because when base is used, it reacts with carboxylic acid (RCOOH) to form an acid anion having poor nucleophilicity and therefore, cannot react with an alcohol (R'OH) in an S_N2 type displacement reaction to form ester by the removal of more strong nucleophilic reagent O-H. De-esterification, however, is possible by both acid and alkali according to mechanisms shown here:

In case of base catalysed esterification:



This part of the reaction cannot occur:



Over 1500 Problems with Solutions

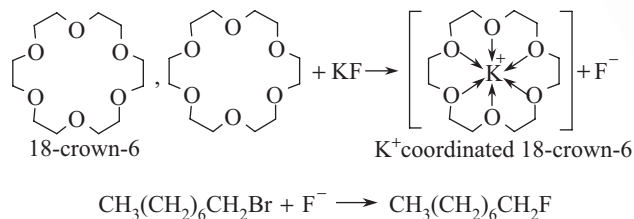
The book contains more than 1500 problems with solutions to reinforce learning through the question-and-answer format.

Illustration of Structural Formulae

The book is loaded with many structural formulae to enable visualization of the organic compounds.

Ans

(a) The structure of 18-crown is given here.



EXERCISES

5.1 Draw the structures and IUPAC names of the isomeric 2° heptanols containing one methyl side chain.

5.2 What is Lucas reagent? How is it used to distinguish three classes of alcohols?

5.3 Alcohols are neutral towards alkali but readily forms alkoxides with alkali metals such as Na and K. Offer an explanation.

5.4 Potassium *t*-butoxide is a widely used base in organic reactions but the corresponding sodium compound is unknown. Give reason.

5.5 The dehydration of *n*-BuOH with acid gives two isomeric alkenes. What are they? Which one would be the major compound?

5.6 What are three isomeric alcohols having the molecular formula C₄H₁₀O? Which of them will react first when a mixture of them is treated with one equivalent of acetic acid?

5.7 Identify the compounds A and B in the following reactions. Comment on the stereochemical aspects where necessary.

5.8 How can you use CH₃CH₂OH to get CH₃CH₂OD and CH₃CH₂D?

5.9 How can you convert (CH₃)₂CCH=O to neopentyl alcohol using HCH=O as reducing agent?

5.10 What are the compounds formed when vapour of each of the following compounds is passed through the hot copper tube? (a) Butan-1-ol, (b) Butan-2-ol (c) 2-Methylbutan-2-ol.

5.11 Describe the action of an oxidizing agent on primary, secondary, and tertiary alcohols.

5.12 Write down the action of the following reagents on ethyl and isopropyl alcohol.

- | | |
|--|---|
| (a) Na | (d) CH ₃ COOH in presence of a few drops of H ₂ SO ₄ |
| (b) POCl ₃ | (e) CH ₃ COCl |
| (c) Hot H ₂ SO ₄ | |

5.13 How can you distinguish between (a) methanol and ethanol (b) propan-1-ol and propan-2-ol.

5.14 Outline the synthesis of each of the following compounds:

Numerous Exercises

There are more than 700 exercise questions spread across chapters for self-evaluation of concepts.

THE BOOK

Exclusive Chapter on Constitutional Problems

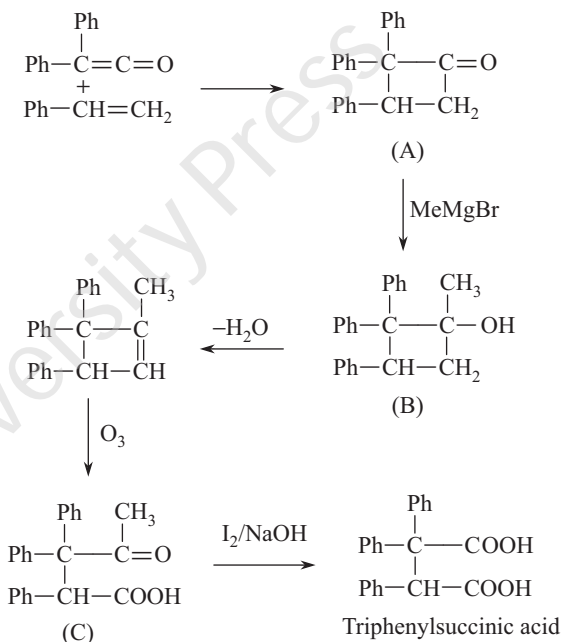
This chapter trains students to analytically think and deduce organic compounds which are represented as unknown variables in a given reaction description.

Presentation Based on Various Classes of Compounds

The text exemplifies the subject matter according to the various classes of organic compounds and their associated reactions.

20.6 The interaction of diphenylketene and styrene results in a compound 'A', $C_{22}H_{18}O$. 'A' reacts with methylmagnesium bromide to give 'B', $C_{23}H_{22}O$. Dehydration of 'B' followed by ozonolysis gives a ketoacid 'C', which with alkaline hypoiodite forms triphenylsuccinic acid. Identify the compounds 'A', 'B', and 'C' and show the reactions.

Ans



5

Alcohols and Ethers

6

Aliphatic Carbonyl
Compounds

7

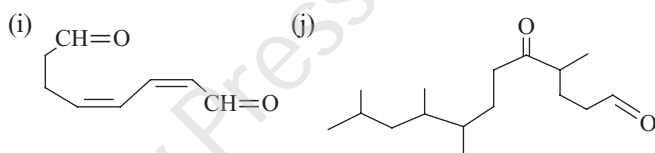
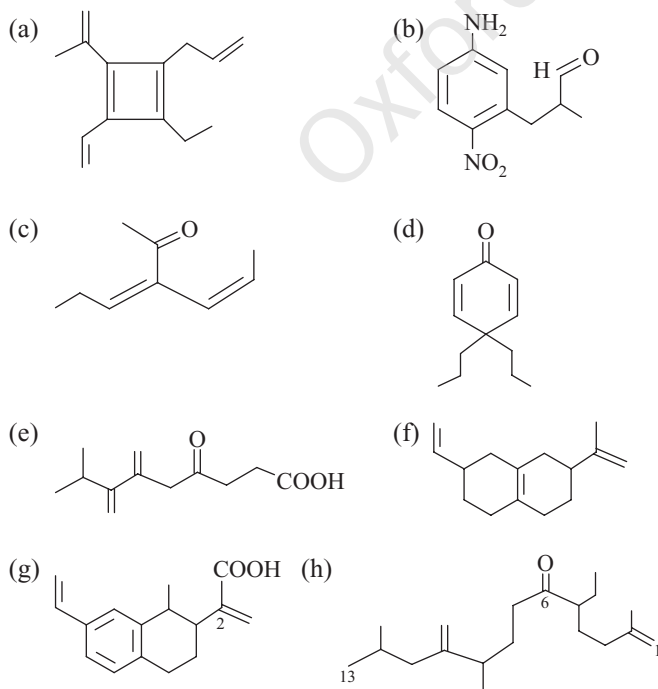
Aliphatic Acids and their
Derivatives

Nomenclature of Organic Compounds

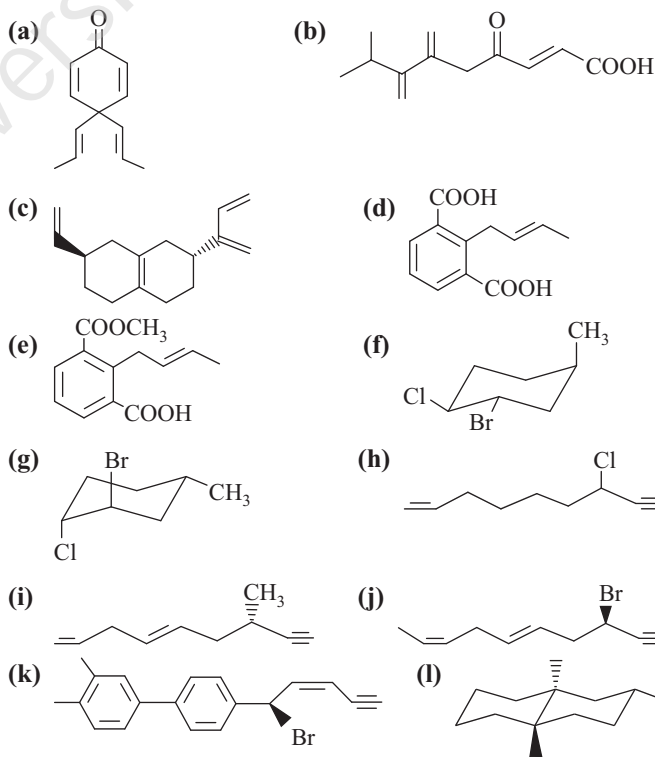
1.1 Give the structures of the following IUPAC names:

- 1-Allyl-2-ethyl-4-(prop-1-en-2-yl)-3-vinylcyclobuta-1,3-diene
- 3-(5-Amino-2-nitrophenyl)-2-methylpropanal
- 3-(Prop-1-enyl)hex-3-en-2-one
- 4,4-Dipropylcyclohexa-2,5-dienone
- 8-Methyl-6,7-dimethylene-4-oxononanoic acid
- 2-(Prop-1-en-2-yl)-7-vinyl-1,2,3,4,5,6,6,8-octahydronaphthalene
- 2-(1-Methyl-7-vinyl-1,2,3,4-tetrahydronaphthalene-2-yl)acrylic acid
- 5-Ethyl-2,9,12-trimethyl-10-methylenetridec-1-en-6-one
- Octa-2,4-dienedial
- 4,8,9,11-Tetramethyl-5-oxododecanal

Ans



1.2 Give IUPAC names of the following compounds along with the stereochemical descriptors.

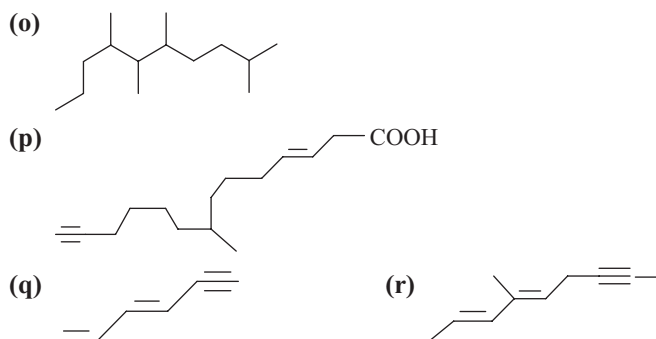
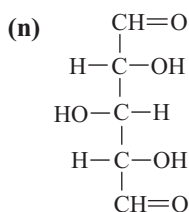
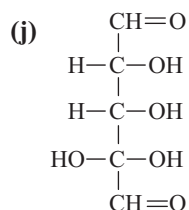
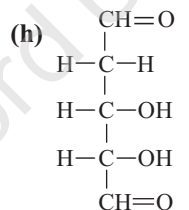
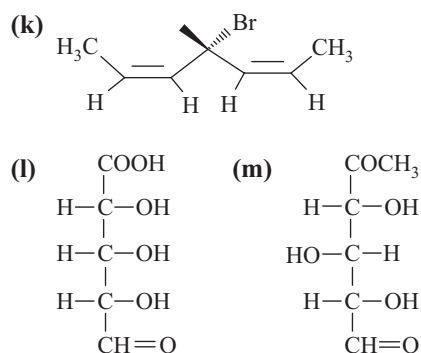
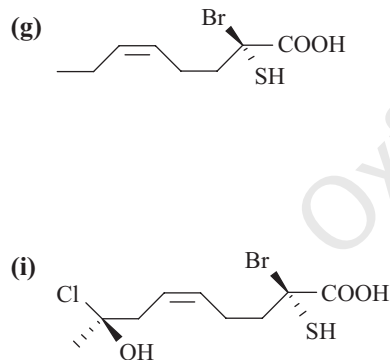
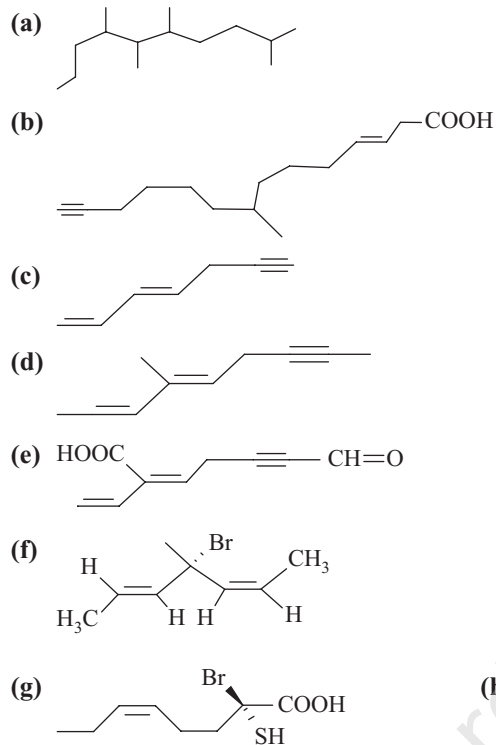


Ans

- 4,4-Di((E)-prop-1-enyl)cyclohexa-2,5-dienone
- (E)-8-Methyl-6,7-dimethylene-4-oxonon-2-enoic acid
- (2R,7R)-2-(s-cis(But-1,3-dien-2-yl)-7-vinyl-1,2,3,4,5,6,7,8-octahydronaphthalene
- (E)-2-(But-2-enyl)benzene-1,3-dicarboxylic acid
- (E)-2-(But-2-enyl)-3-(methoxycarbonyl)benzoic acid

- (f) (1*S*,2*S*,4*R*)-2-Bromo-1-chloro-4-methylcyclohexane
 (g) (1*R*,2*R*,4*S*)-2-Bromo-1-chloro-4-methylcyclohexane
 (h) 7-Chloronon-1-en-8-yne
 (i) (*S*,*E*)-7-Methylnona-1,4-dien-8-yne
 (j) (*R*,5*E*,8*Z*)-3-Bromodeca-5,8-dien-1-yne
 (k) (*R*,*Z*)-4/-(1-Bromopent-2-en-4-ynyl)-3,4-dimethylbiphenyl
 (l) (2*R*,4*aS*,8*aS*)-2,4*a*,8*a*-Trimethyldehydronaphthalene

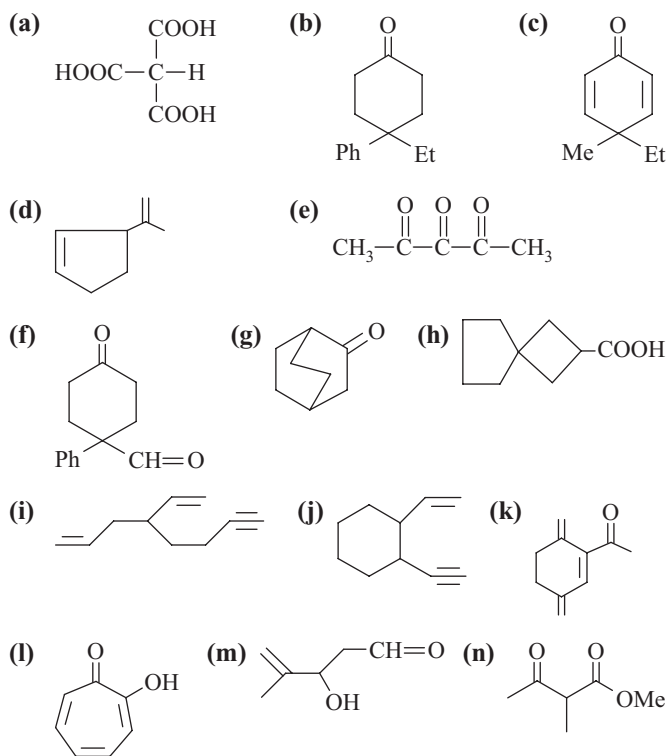
1.3 Give IUPAC names of the following compounds along with the stereochemical descriptors wherever applicable.

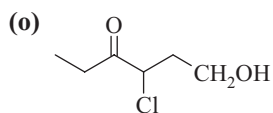


Ans

- (a) 2,5,6,7-Tetramethyldecane
 (b) (*E*)-8-Methyltetradec-3-en-13-ynoic acid
 (c) (*E*)-Hepta-1,3-dien-6-yne
 (d) (4*E*)-4-Methylnona-2,4-dien-7-yne
 (e) (2*Z*)-7-Oxo-2-(prop-1-enyl)hept-2-en-5-ynoic acid
 (f) (*S*,2*Z*,5*E*)-4-Bromo-4-methylhepta-2,5-diene
 (g) (*R*,*Z*)-2-Bromo-2-mercaptooct-5-enoic acid
 (h) (2*R*,3*r*,4*S*)-2,3,4-Trihydroxypentanedial
 (i) (2*R*,8*S*,*Z*)-2-Bromo-8-chloro-8-hydroxy-2-mercaptanon-5-enoic acid
 (j) (2*R*,4*R*)-2,3,4-Trihydroxypentanedial
 (k) (2*Z*,5*Z*)-4-Bromo-4-methylhepta-2,5-diene
 (l) (2*R*,3*R*,4*S*)-2,3,4-Trihydroxy-4-formylpentanoic acid
 (m) (2*S*,3*S*,4*R*)-2,3,4-Trihydroxy-5-oxohexanal
 (n) (2*R*,3*s*,4*S*)-2,3,4-Trihydroxypentanedial
 (o) 2,5,6,7-Tetramethyldecane
 (p) (*E*)-8-Methyltetradec-3-en-13-ynoic acid
 (q) (*E*)-Hexa-1,3-dien-6-yne
 (r) (2*E*,4*E*)-4-Methylocta-2,4-dien-6-yne

1.4 Write the IUPAC names of the following compounds.





Ans

- Methanetricarboxylic acid
- 4-Ethyl-4-phenylcyclohexanone
- 4-Ethyl-4-methylcyclohexa-2,5-dienone
- 3-(Prop-1-en-2-yl)cyclopent-1-ene
- Pentane-2,3,4-trione
- 4-Oxo-1-phenylcyclohexanecarbaldehyde
- Bicyclo[2.2.2]octan-2-one
- Spiro[3.4]octane-2-carboxylic acid
- 4-Vinyloct-1-en-7-yne
- 1-Ethynyl-2-vinylcyclohexane
- 1-(3,6-Dimethylenecyclohex-1-enyl)ethanone
- 2-Hydroxycyclohepta-2,4,6-trienone
- 3-Hydroxy-4-methylpent-4-enal
- Methyl 2-methyl-3-oxobutanoate
- 4-Chloro-6-hydroxyhexan-3-one

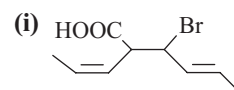
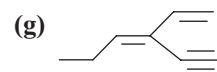
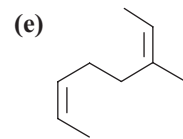
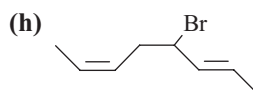
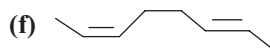
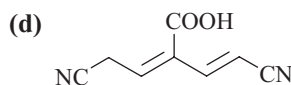
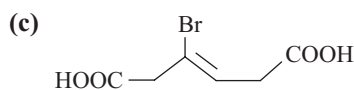
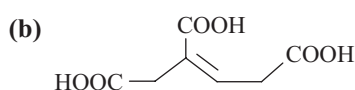
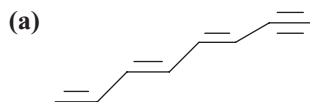
1.5 Are the following IUPAC names correct? If not, give their correct IUPAC names.

- 1,3,4,5,6-Pentabromo-1,2,6-trichlorohexane
- 5-Ethoxy-2-methyl-5-oxopentanoic acid
- 2-Methyl-4,6-dioxoheptanal
- Biacetyl
- Butane-1,3-dione
- Diethyl oxalate
- 4-Nitropentanenitrile
- Octa-5,7-dien-1,3-diyne
- Butane-1,2,4-tricarboxylic acid
- 4-Cyano-2-(2-cyanoethyl)butanoic acid
- 3-Propylenepent-1-en-5-yne

Ans

- Incorrect (Correct name: 1,2,3,4,6-Pentabromo-1,5,6-trichlorohexane)
- Incorrect (Correct name: 4-Carboxy-2-methylbutanoic acid)
- Correct
- Incorrect (Correct: Butane-2,3-dione)
- Incorrect (Correct: 3-Oxobutanal)
- Incorrect (Correct: Diethyl ethanedioate)
- Correct
- Incorrect (Correct: Octa-1,3-diene-5,7-diyne)
- Correct
- Correct
- Incorrect (3-Ethynylhexa-1,3-diene)

1.6 Give the E,Z nomenclature of the following compounds.



Ans

- (3E,5E)-Octa-1,3,5-trien-7-yne
- (E)-But-2-ene-1,2,4-tricarboxylic acid
- (Z)-4-Bromohex-2-enedioic acid
- (Z)-4-Cyano-2-[(E)-2-cyanovinyl]but-2-enoic acid
- (2Z,4Z)-3-Methylocta-2,6-diene
- (2Z,6E)-Octa-2,6-diene
- (Z)-3-Ethynylhexa-1,3-diene
- (2E,6Z)-4-Bromoocta-2,6-diene
- (E)-3-Bromo-2-[(Z)-prop-1-enyl]hex-4-enoic acid

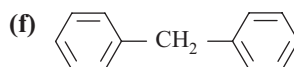
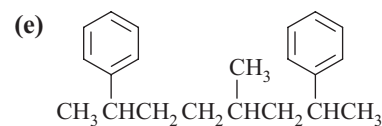
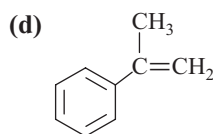
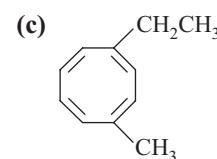
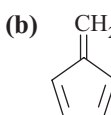
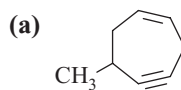
1.7 Give the IUPAC names of the following monovalent radicals.

- $\text{CH} \equiv \text{C}-$
- $\text{CH} \equiv \text{CCH}_2-$
- $\text{CH}_3\text{CH}=\text{CH}-$
- $\text{CH}_3\text{CH}=\text{CHCH}_2-$
- $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2-$
- $\text{CH}_2=\text{CHCH}=\text{CH}-$
- $\text{HC} \equiv \text{CCH}=\text{CHCH}_2-$

Ans

- Ethynyl
- Prop-2-ynyl
- Prop-1-enyl
- But-2-enyl
- Pent-2-enyl
- Buta-1,3-dienyl
- Pent-2-en-4-ynyl

1.8 Give the IUPAC names of the following structures.



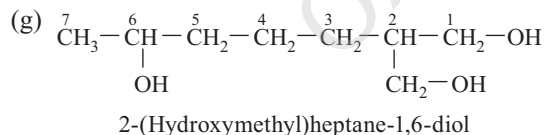
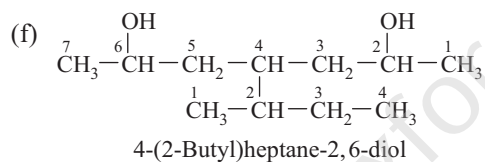
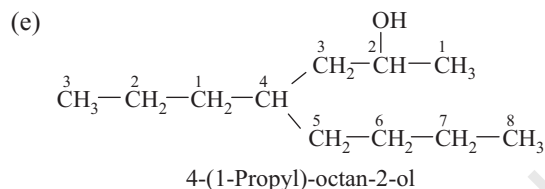
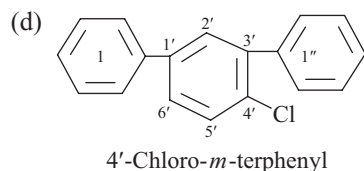
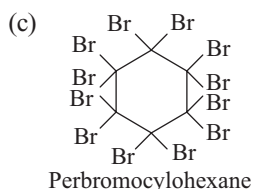
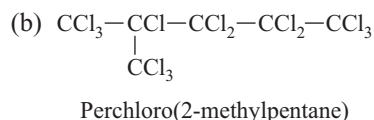
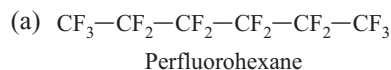
Ans

- 6-Methylcyclohepta-1-en-4-yne
- 5-Methylidenecyclopenta-1,3-diene
- 1-Ethyl-4-methylcycloocta-1,3,5,7-tetraene
- Prop-1-en-2-ylbenzene
- 4-Methyl-2,7-diphenyloctane
- Diphenylmethane

1.9 Give the structures of the following names.

- (a) Perfluorohexane
 (b) Perchloro(2-methylpentane)
 (c) Perbromocyclohexane
 (d) 4'-Chloro-*m*-terphenyl
 (e) 4-(1-Propyl)octan-2-ol
 (f) 4-(2-Butyl)heptane-2,6-diol
 (g) 2-(Hydroxymethyl)heptane-1,6-diol

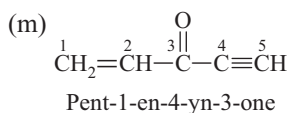
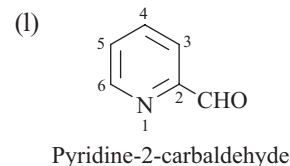
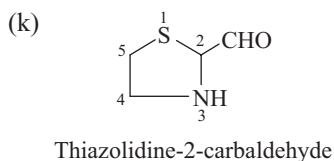
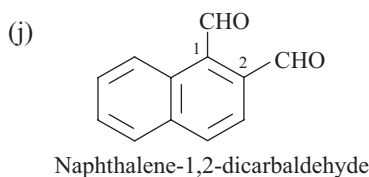
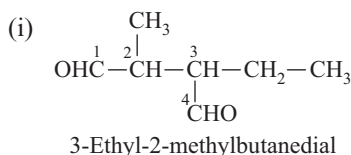
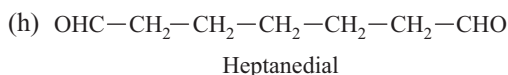
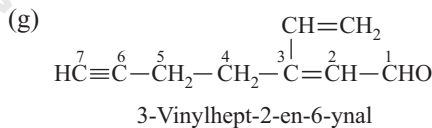
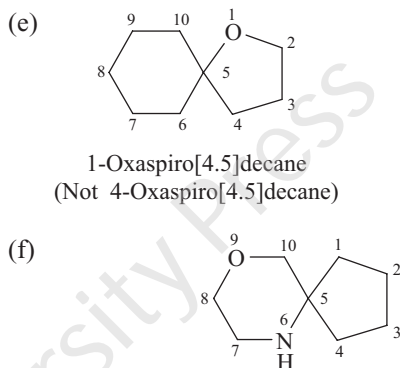
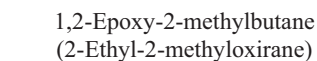
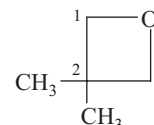
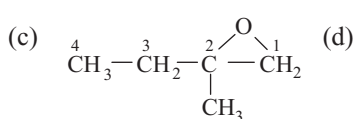
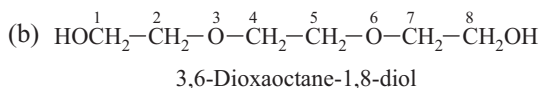
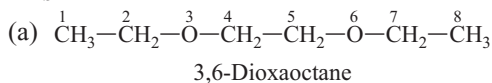
Ans



1.10 Give the structure of the following IUPAC names.

- (a) 3,6-Dioxaoctane
 (b) 3,6-Dioxaoctane-1,8-diol
 (c) 1,2-Epoxy-2-methylbutane
 (d) 1,3-Epoxy-2,2-dimethylpropane
 (e) 1-Oxaspiro[4.5]decane
 (f) 9-Oxa-6-azaspiro[4.5]decane
 (g) 3-Vinylhept-2-en-6-ynal
 (h) Heptanedial
 (i) 3-Ethyl-2-methylbutanedial
 (j) Naphthalene-1,2-dicarbaldehyde
 (k) Thiazolidine-2-carbaldehyde
 (l) Pyridine-2-carbaldehyde
 (m) Pent-1-en-4-yn-3-one

Ans

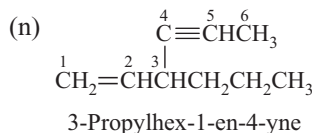
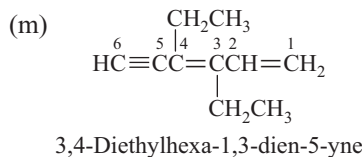
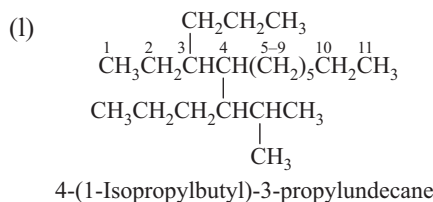
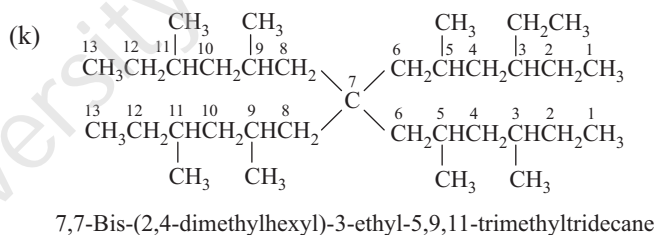
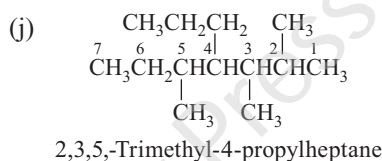
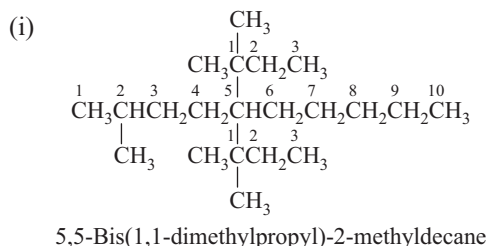
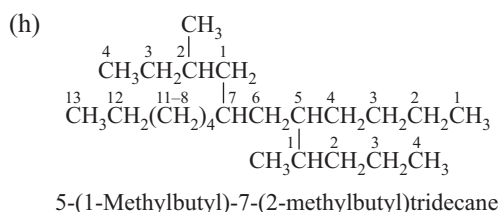


1.11 Give the structures of the following names.

- (a) 2,3,5-Trimethylhexane
 (b) 2,7,8-Trimethyldecane
 (c) 4-Ethyl-5-methylnonane
 (d) 5-Ethyl-2,2-dimethylheptane
 (e) 7-(1,2-dimethylpentyl)-5-ethyltetradecane
 (f) 4-Ethyl-5-methyloctane
 (g) 4-Isopropyl-5-propyloctane
 (h) 5-(1-Methylbutyl)-7-(2-methylbutyl)tridecane
 (i) 5,5-Bis-(1,1-dimethylpropyl)-2-methyldecane
 (j) 2,3,5-Trimethyl-4-propylheptane
 (k) 7,7-Bis-(2,4-dimethylhexyl)-3-ethyl-5,9,11-trimethyltridecane
 (l) 4-(1-Isopropylbutyl)-3-propylundecane
 (m) 3,4-Diethylhexa-1,3-dien-5-yne
 (n) 3-Propylhex-1-en-4-yne

Ans

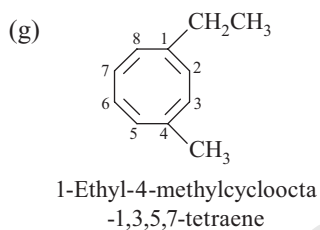
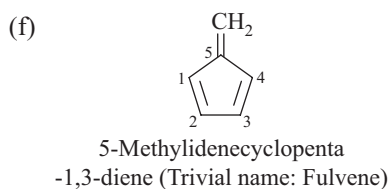
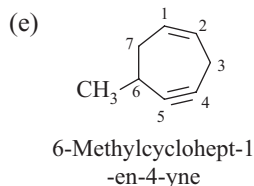
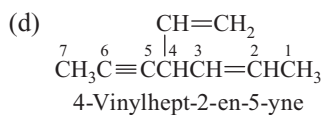
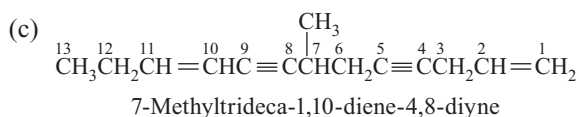
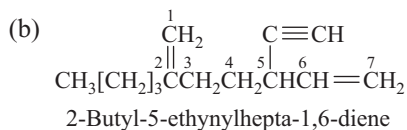
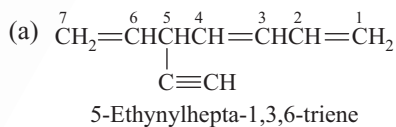
- (a)
2,3,5-Trimethylhexane
- (b)
2,7,8-Trimethyldecane
- (c)
4-Ethyl-5-methylnonane
- (d)
5-Ethyl-2,2-dimethylheptane
- (e)
7-(1,2-Dimethylpentyl)-5-ethyltetradecane
- (f)
4-Ethyl-5-methyloctane
- (g)
4-Isopropyl-5-propyloctane



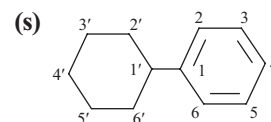
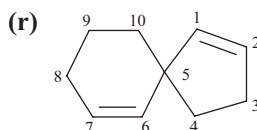
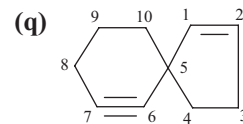
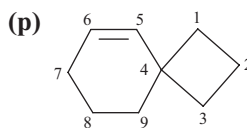
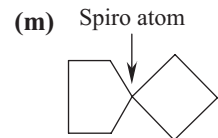
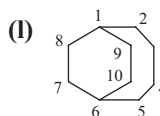
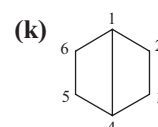
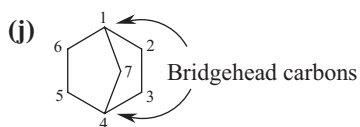
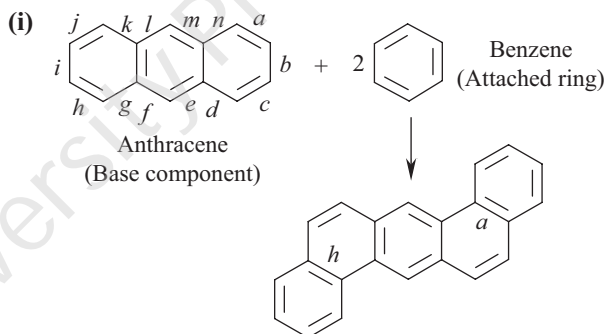
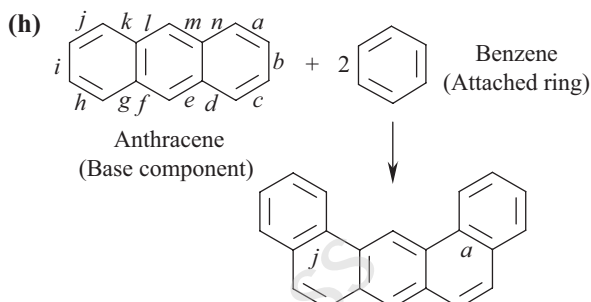
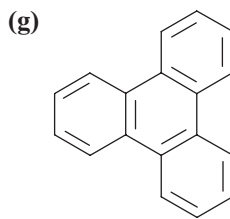
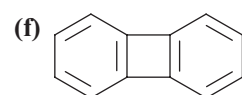
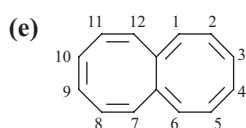
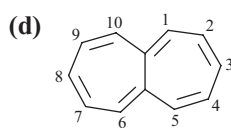
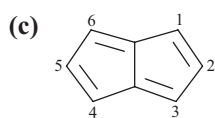
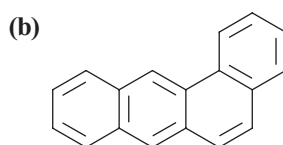
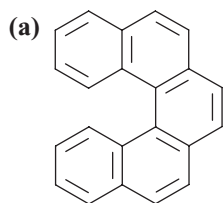
1.12 Give the structures of the following names.

- (a) 5-Ethylhepta-1,3,6-triene
 (b) 2-Butyl-5-ethynylhepta-1,8-diene
 (c) 7-Methyltrideca-1,10-diene-4,8-diyne
 (d) 4-Vinylhept-2-en-5-yne
 (e) 6-Methylcyclohept-1-en-4-yne
 (f) 5-Methylidenecyclopenta-1,3-diene
 (g) 1-Ethyl-4-methylcycloocta-1,3,5,7-tetraene

Ans



1.13 Give the names of the following fused ring hydrocarbons.



Ans

- (a) Dibenzophenanthrene
 (b) Benzanthracene
 (Not Benzoanthracene)
 (c) Pentalene
 (d) Heptalene
 (e) Octalene
 (f) Biphenylene
 (Not Diphenylene; two benzene rings are ortho-fused to the central ring of four carbon atoms)
 (g) Triphenylene
 (Three benzene rings are ortho-fused to the central ring of six carbon atoms)
 (h) Dibenzo[a,j]anthracene
 (i) Dibenzo[a,h]anthracene
 (j) Bicyclo[2.2.1]heptane
 (k) Bicyclo[2.2.0]hexane
 (l) Bicyclo[4.2.2]decane
 (m) Spiro[3.4]octane
 (Total number of carbons is eight)
 (n) Spiro[4.5]decane
 (Not Spiro[5.4]decane; total number of carbons is ten)
 (o) Spiro[3.3]heptane
 (Total number of carbons is seven)
 (p) Spiro[3.5]non-5-ene
 (q) Spiro[4.6]dec-1-en-6-yne
 (r) Spiro[4.5]deca-1,6-diene
 (Not Spiro[4.5]deca-1,9-diene; 1,6 is lower than 1,9)
 (s) Cyclohexylbenzene

1.14 Are the following IUPAC names correct? If not, give the correct name along with the structures. Give your reasons in brief.

- (a) 1,5-Dibromohexa-3,5-dien-1-yne
 (b) Hexane-1,6-dicarboxylic acid
 (c) 3-Ethynylhexa-1,4-diene
 (d) 4-Formylbutan-2-one
 (e) Hepta-2-en-5-ynedioic acid
 (f) 5-Formyl-2-oxohexanedioic acid
 (g) Propane-1,2,3-tricarboxylic acid
 (h) 3-Isocyanatopropylcyanate
 (i) Isopropanol
 (j) Diaziridine-1-carboxylic acid
 (k) 7-Bromo-hept-4,6-dien-2-ynoic acid
 (l) Octa-4,6-dien-2-ynedioic acid

Ans

- (a) Incorrect (e) Correct (i) Incorrect
 (b) Correct (f) Incorrect (j) Incorrect
 (c) Correct (g) Correct (k) Correct
 (d) Incorrect (h) Correct (l) Incorrect

The correct names and the corresponding structures are given here, with explanations as necessary.

- (a) $\text{Br}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{Br}$
 1,6-Dibromo-2,3-dien-5-yne
 (Numbering should start from the left-hand side according to IUPAC rule)

- (b) $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$

Hexanedioic acid

(In the case of saturated dicarboxylic acid with no branching, one need not give any number to indicate the positions of COOH groups)

- (c)
$$\begin{array}{c} \text{CH}=\text{CH}_2 \\ | \\ \text{CH}_3-\text{CH}=\text{CH}-\text{CH}-\text{C}\equiv\text{CH} \end{array}$$

3-Ethynylhexa-1,4-diene

(In the case of compounds having double bonds and triple bonds, the base name should include the maximum number of double bonds)

- (d)
$$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{O} \end{array}$$

4-Oxopentanal

($-\text{CH}=\text{O}$ group gets preference over $\text{C}=\text{O}$ group in numbering the chain. The position of the terminal $-\text{CH}=\text{O}$ group need not be given any number)

- (e) $\text{HOOC}-\text{CH}=\text{CH}-\text{CH}_2-\text{C}\equiv\text{C}-\text{COOH}$

Hept-2-en-5-ynedioic acid

(Since we have the option of numbering the carbon chain, the double bond gets a lower number)

- (f)
$$\begin{array}{c} \text{CH}=\text{O} \qquad \qquad \text{O} \\ | \qquad \qquad \qquad || \\ \text{HOOC}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}-\text{COOH} \end{array}$$

2-Formyl-5-oxohexanedioic acid

($-\text{CH}=\text{O}$ group gets preference in citation over $\text{C}=\text{O}$ group, when there is an option)

- (g)
$$\begin{array}{c} \text{CN} \\ | \\ \text{NC}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CN} \end{array}$$

Propane-1,2,3-tricarbonitrile

($-\text{CN}$ group is named as carbonitrile when they are supposed to yield carboxylic acid on hydrolysis in an aliphatic chain)

- (h) $\text{NCO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NCO}$

3-Isocyanatopropylcyanate

[$-\text{NCO}$ group (cyanate) gets preference over $-\text{OCN}$ (isocyanate group)]

- (i)
$$\begin{array}{c} \text{OH} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$$

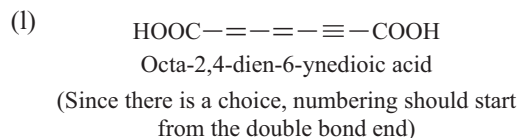
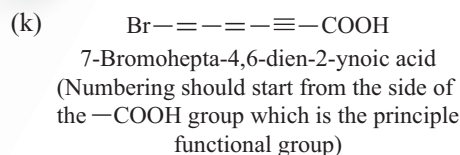
Propan-1-ol

(Isopropanol is a wrong name because there is no hydrocarbon like isopropane)

- (j)
$$\begin{array}{c} \text{HN} \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{COOH} \end{array}$$

Diaziridine-3-carboxylic acid

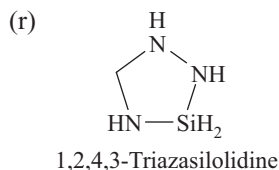
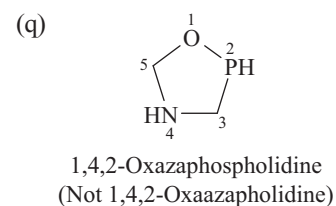
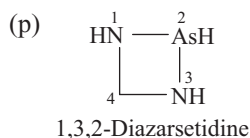
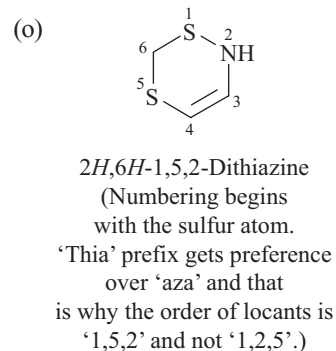
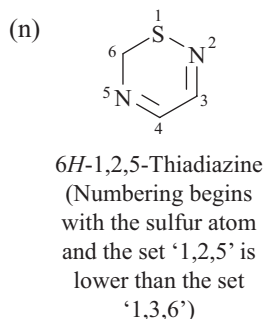
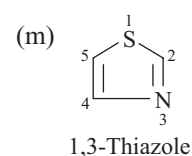
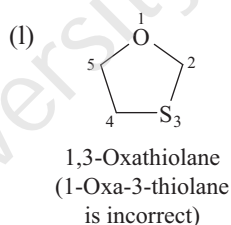
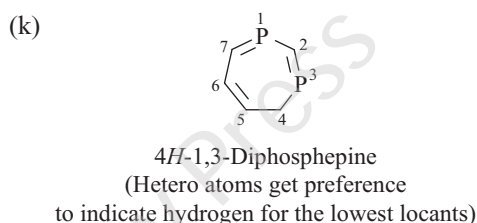
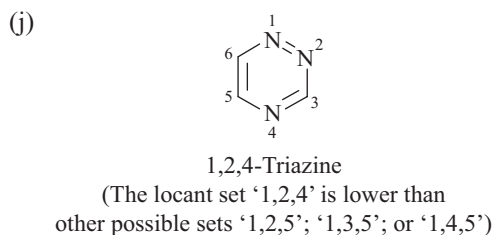
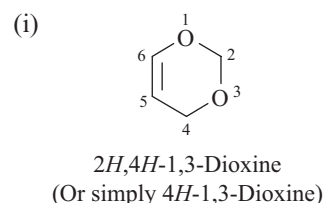
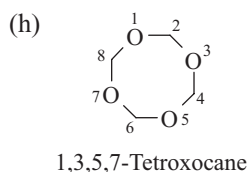
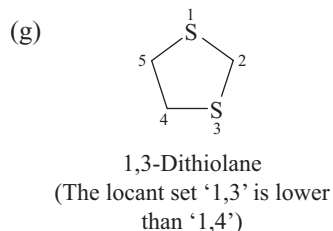
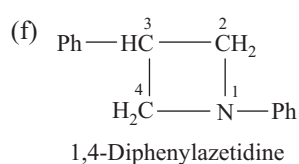
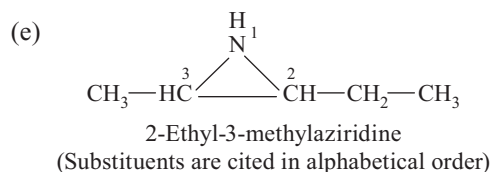
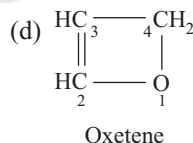
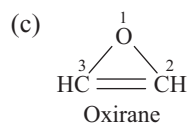
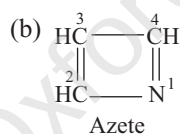
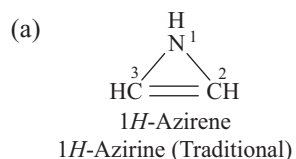
(Numbering should start from the nitrogen atoms of the ring)



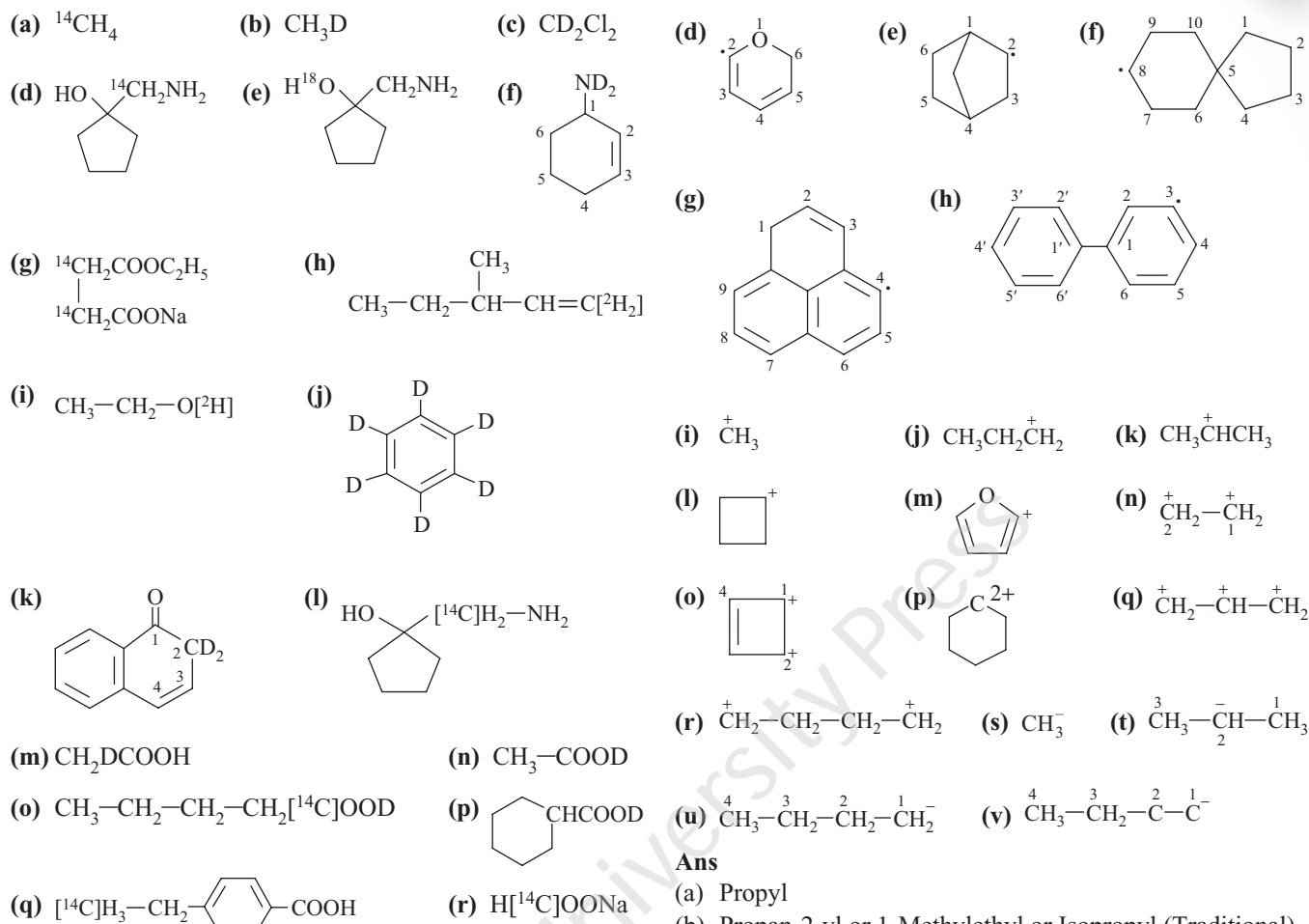
1.15 Give the names of the following heterocyclic compounds based on the Hantzsch–Widmann system.

- (a) 1H-Azirene
 (b) Azete
 (c) Oxirane
 (d) Oxetene
 (e) 2-Ethyl-3-methylaziridine
 (f) 1,4-Diphenylazetidide
 (g) 1,3-Dithiolane
 (h) 1,3,5,7-Tetroxocane
 (i) 2H,4H-1,3-Dioxine
 (j) 1,2,4-Triazine
 (k) 4H-1,3-Diphosphepine
 (l) 1,3-Oxathiolane
 (m) 1,3-Thiazole
 (n) 6H-1,2,5-Thiadiazine
 (o) 2H,6H-1,5,2-Dithiazine
 (p) 1,3,2-Diazasetidine
 (q) 1,4,2-Oxazaphospholidine
 (r) 1,2,4,3-Triazasilolidine

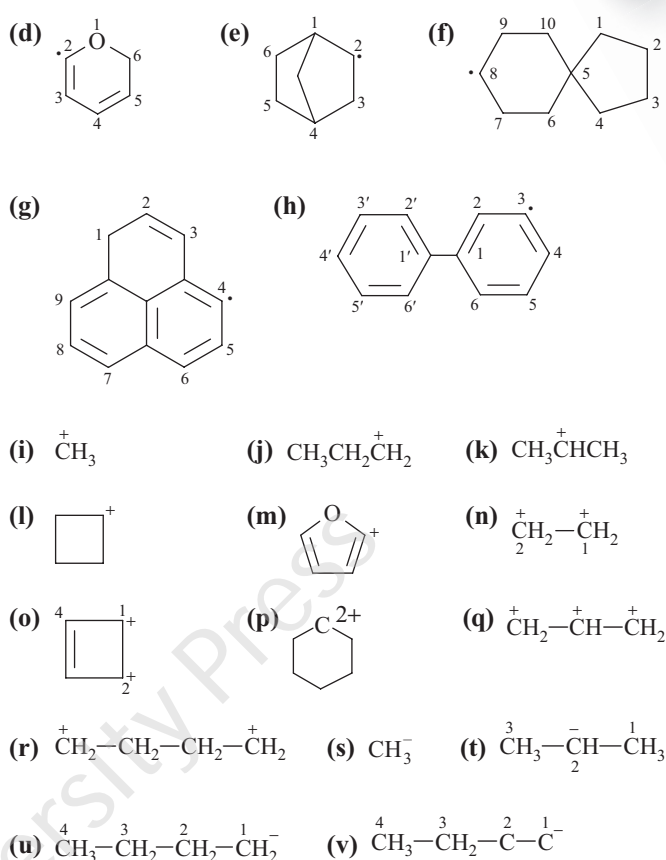
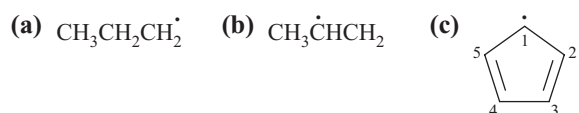
Ans The structures of the aforementioned compounds are given here.



1.16 Give the names of the following isotope labelled compounds.

**Ans**

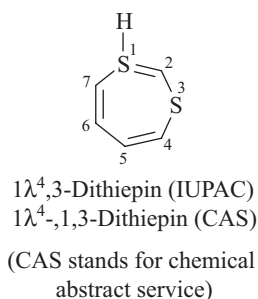
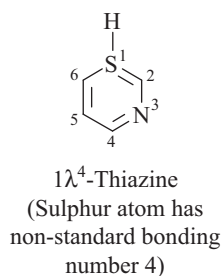
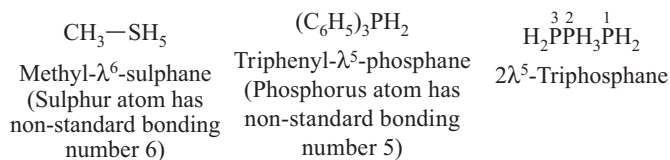
- (^{14}C)Methane
- ($^2\text{H}_1$)Methane
- Dichloro($^2\text{H}_2$)methane
- 1-[Amino(^{14}C)methyl]cyclopentanol
- 1-(Aminomethyl)cyclopentan(^{18}O)ol or 1-(Aminomethyl)(^{18}O)cyclopentanol
- (N,N - $^2\text{H}_2$)Cyclohex-2-en-1-amine
- Sodium ethyl(2,3- $^{14}\text{C}_2$)succinate
- 3-Methyl[1,1- $^2\text{H}_2$]pent-1-ene (Here the locant is part of the parent hydrocarbon name)
- Ethan[^2H]ol or [O - ^2H]Ethanol
- [$^2\text{H}_6$]Benzene
- [2,2- $^2\text{H}_2$]-1-(2*H*)-Naphthalene
- 1-(Amino[^{14}C]methyl)cyclopentanol
- [2- $^2\text{H}_1$]Acetic acid
- [O - ^2H]Acetic acid or Acetic[^2H]acid
- [1- ^{14}C]Pentan[^2H]oic acid or [1- ^{14}C , O - ^2H]pentanoic acid
- Cyclohexane[^2H]carboxylic acid
- 4-([2- ^{14}C]Ethyl)benzoic acid
- Sodium [^{14}C]formate

1.17 Give the names of the following radicals and ions.**Ans**

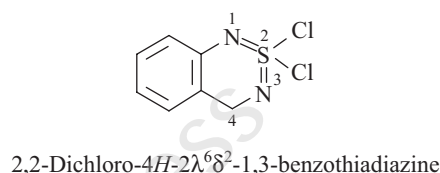
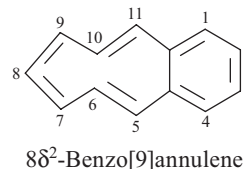
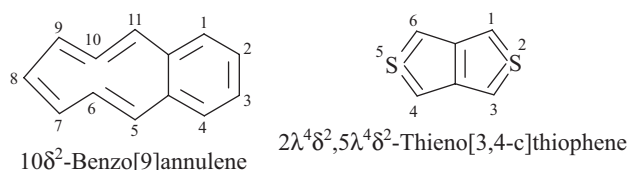
- Propyl
- Propan-2-yl or 1-Methylethyl or Isopropyl (Traditional)
- Cyclopenta-2,4-diene-1-yl
- 2*H*-Pyran-6-yl
- Bicyclo[2.2.1]heptan-2-yl
- Spiro[4.5]decan-8-yl
- 1*H*-Phenalen-4-yl
- 1,1'-Biphenyl-3-yl
- Methyl cation *Methyl cation
- Propyl cation *Propyl cation
- Propyl-2-yl cation *Propan-2-yl cation
- Cyclobutyl cation *Cyclobutyl cation
- Furan-2-yl cation *Furan-2-yl cation
- Ethane-1,2-bis(yl) cation
- Cyclobut-3-ene-1,2-bis(yl) cation
(Note that the charged carbon gets priority in numbering)
- Cyclohexane-1,1-bis(yl) dication *Cyclohexylidene dication
- Propane-1,2,3-tris(yl) cation
- Butane-1,4-bis(yl) cation
- Methanide *Methyl anion
- Propan-2-ide 1-Methylethanide
*Propan-2-yl anion
*1-Methylethyl anion
- Butan-1-ide *Butan-1-yl anion
- But-1-yn-1-ide *But-1-yn-1-yl anion

1.18 What is meant by λ , δ , and Δ conventions in naming organic compounds? Give examples.

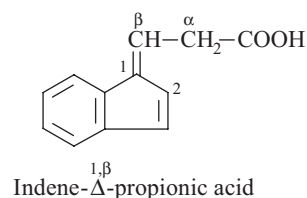
Ans λ -convention: It is a method of describing non-standard bonding numbers of skeletal atoms in parent hydrides. A non-standard bonding number of a neutral hetero atom in a structure is denoted by the symbol λ^n , where n is the number of non-standard bonds. A few examples are given here.



δ -convention: The presence of contiguous formal double bonds at a skeletal atom in a cyclic parent compound whose name normally represents the structural unit having maximum number of non-cumulative double bonds is described by the symbol ' δ^c ', where ' c ' is an Arabic numeral denoting the number of contiguous double bonds attached to that particular skeletal atom. The symbol ' δ^c ' is always preceded by the concerned locant. The hetero atom exhibiting a non-standard bonding number can be associated with contiguous formal double bonds in a cyclic parent hydride. In such cases the symbol for the non-standard bonding number is also to be incorporated in the name. Illustrative examples are given here.



Δ -convention: If the cyclic component and the side chain are linked together through a double bond, the locants of this bond are placed as superscripts to a Greek capital delta (Δ). The symbol is inserted between the cyclic and the acyclic component. The locant for the cyclic part is placed earlier.



EXERCISES

1.1 In the following pairs, state which name is correct and which isn't.

- Pentan-2-ol and Pentane-2-ol
- Pentane-2,4-dione and Penta-2,4-dione
- 1,2,*N,N*-Tetraaminobenzene and *N,N*,1,2-Tetraaminobenzene
- 1,3,5,7-Tetroxocane and 1,3,5,7-Tetraoxacane
- Thialdehyde and Thioaldehyde
- Imidoamidic acid and Imidamidic acid
- Carboximidic acid and Carboximidoic acid
- Cyclohexaneethanol and Cyclohexethanol
- Dibenz[*b,e*]oxepine and Dibenzo[*b,e*]oxepine
- Benzilmonoxime and Benzilmonooxime
- Benzophenone and Benzphenone

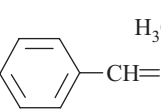
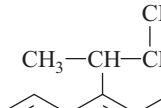
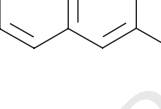
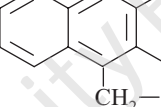
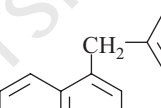
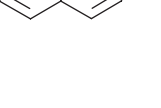
1.2 Answer these questions.

- In the following sets of combinations of locants, which set will get preference in numbering the carbon atoms of a chain.

- (2,3,6,8)-, (2,4,5,7)-, (3,4,5,6)
 - 2, 2' and 1', 2
 - (*N*, α , 1,2) and (1,2,4,6)
- What does the following letter/letters or combination of letters indicate in a structure of an organic compound?
peri, *s*, *rac*, *m*, *abeo*, *seco*, *nor*, *neo*, *friedo*, *vic*, *as*.
 - Decide which one of the following names are correct or incorrect in each pair according to IUPAC rules of naming organic compounds. Give reasons wherever necessary.
 - Neo-pentane and Neopentane
 - Isopropanol and Propan-2-ol
 - N*-Acetylated aniline and *N*-acetylated aniline
 - Spiro[5.4]decane and Spiro[4.5]decane
 - Methanoic acid and Methanoic-acid.
 - Ethylethanoate and Ethyl ethanoate
 - Ethylmethyl ketone and Ethyl methyl ketone
 - Styrene oxide and Stryreneoxide
 - Biphenyl and Diphenyl

- (b) Draw the structures of the following compounds.
- | | |
|------------------------|-----------------------|
| (i) Triapentafulvalene | (iv) Benzo[8]annulene |
| (ii) Azulene | (v) 6[Annulene] |
| (iii) 14[Annulene] | |

1.6 Give the IUPAC names of the following compounds.

- (a) 
- (b) 
- (c) 
- (d) 
- (e) 
- (f) 

(f)

$\text{CH}_3\text{---}\text{C}_6\text{H}_4\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---C}_6\text{H}_3\text{(CH}_2\text{---CH}_2\text{---CH}_2\text{---C}_6\text{H}_4\text{---CH}_3\text{)}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---C}_6\text{H}_4\text{---CH}_3$

(g)

Naphthalene
(*ortho*-fused)


(h)

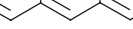
Naphthacene
(*ortho*-fused)


(i)


Chrysene
(*ortho*-fused)





- 1.7** Give the trivial names of the following compounds.

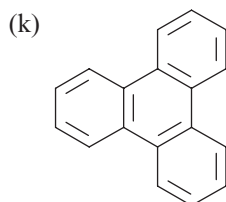
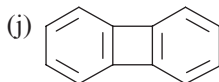
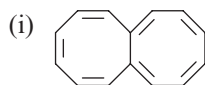
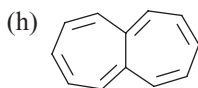
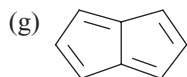
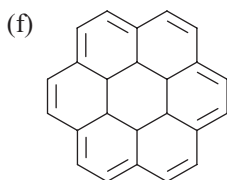
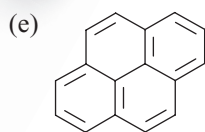
(a) 

(b) 

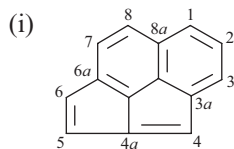
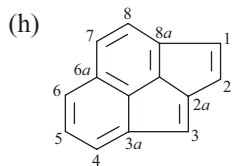
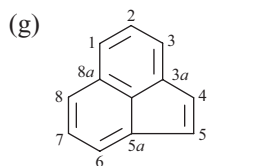
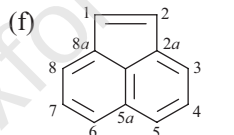
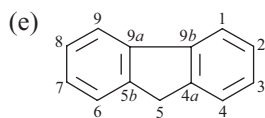
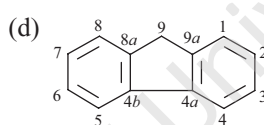
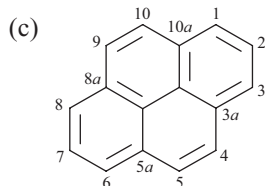
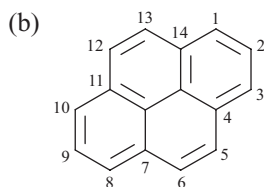
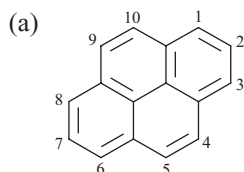
(c) 

(d) 

- (i) 
- (ii) 
- (iii) 
- (iv) 

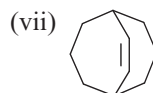
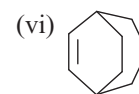
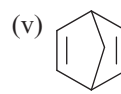
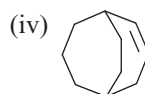
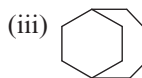
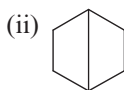
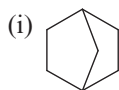


1.8 Identify the correct numbering of the carbon atoms of the following sets of compounds.

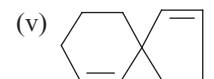
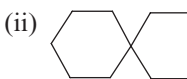
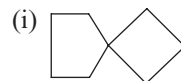


1.9 Answer these questions on the naming of structures.

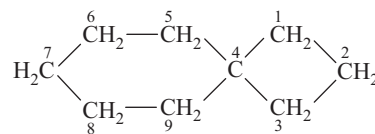
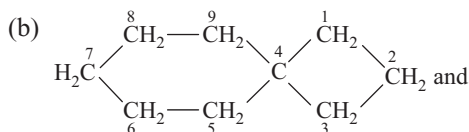
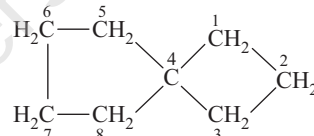
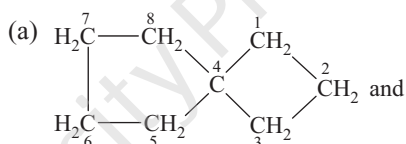
(a) Number the carbons and give the correct name of each of the following bridged hydrocarbons.



(b) Give the IUPAC names of the following spiro hydrocarbons. Show the numbering of the carbon atoms.



1.10 Identify the correct numbering of the following pairs of spiro compounds and give its IUPAC names.



1.11 Answer these questions on IUPAC names and structures.

(a) Give the structure of the following compounds.

(i) 1,1'-Bicyclopentadienylidene

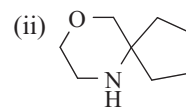
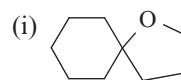
(ii) Bi(cyclopentylidene)

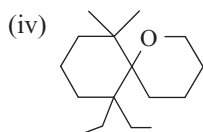
(iii) Biphenyl

(iv) Tercyclopropane

(b) Give the structures of *alternate* acyclic and cyclic hydrocarbons and *non-alternate* cyclic hydrocarbons and mention the necessary rules for such definitions.

(c) Give the IUPAC names of the following heterocyclic spiro compounds.

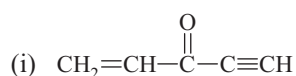
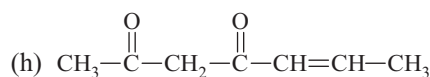
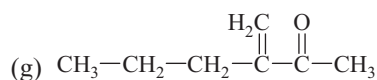
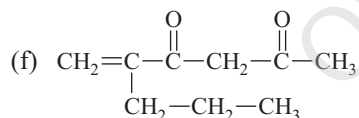
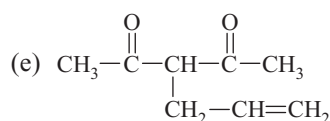
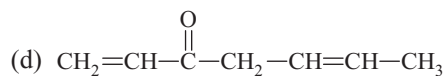
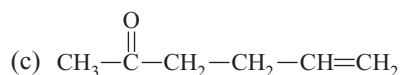
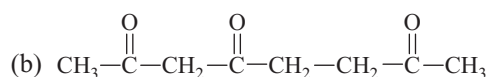
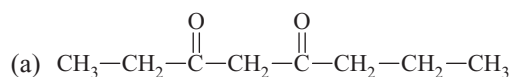




1.12 Draw the structures of the following compounds.

- Perchloro(2-methylpentane)
- 2-(Hydroxymethyl)heptane-1,6-diol
- Aluminium tri(2-propanolate)
- Ethoxyethylene
- Bis(2-bromoethyl) ether
- 2,2'-Oxydiethanol
- 3-Formylhept-2-enal
- 3-Vinylhept-2-en-6-ynal
- Pyridine-2-carbaldehyde
- Benzenecarbothialdehyde
- Benzenhexol

1.13 Give the IUPAC names of the following compounds.

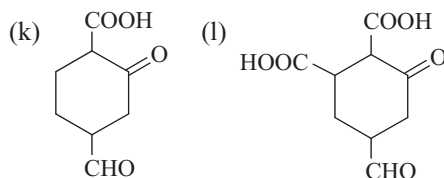
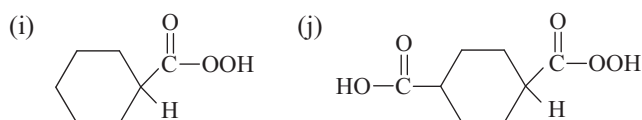
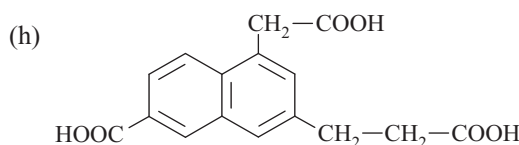
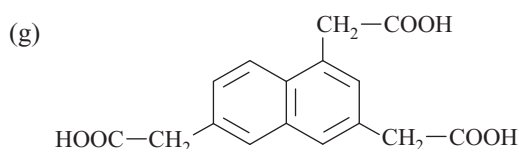
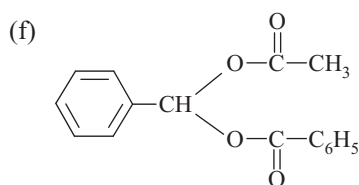
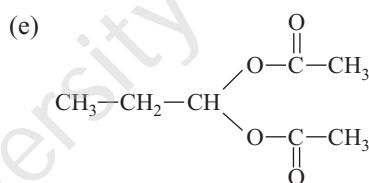
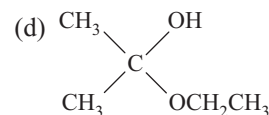
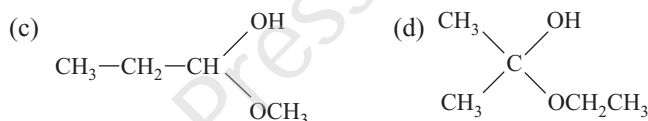
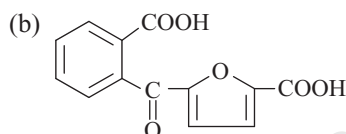
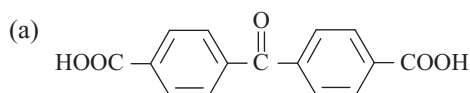


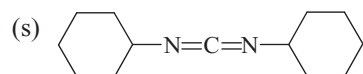
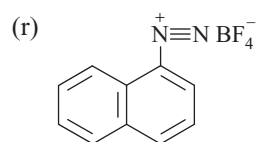
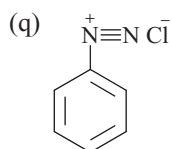
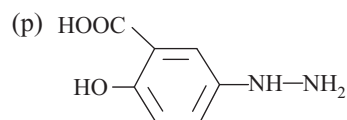
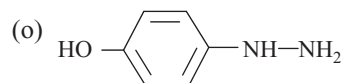
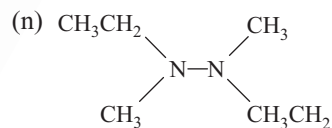
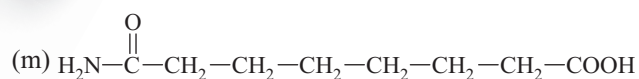
1.14 Draw the structures of the following compounds.

- Hepta-2,5-dienoic acid
- Hex-2-en-4-ynedioic acid
- Pent-4-en-2-ynoic acid

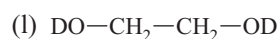
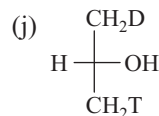
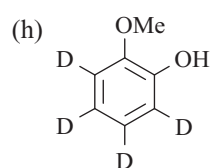
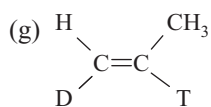
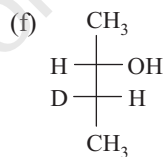
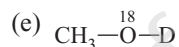
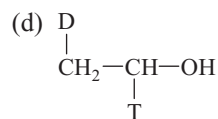
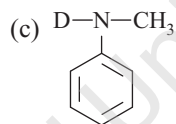
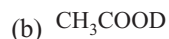
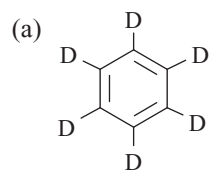
- 3-(carboxymethyl)heptanedioic acid
- Biphenyl-3-carboxylic acid
- Naphthalene-1,3,5-tricarboxylic acid
- o*-(2-Oxobutyl)benzoic acid
- p*-Benzoylbenzoic acid
- 4-Methylbenzene-1,3-disulphonic acid

1.15 Give the IUPAC names of the following compounds.



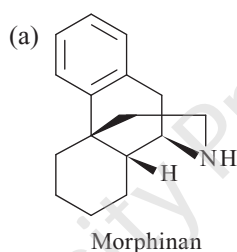


1.16 Give the IUPAC names of the following isotopically labelled compounds.

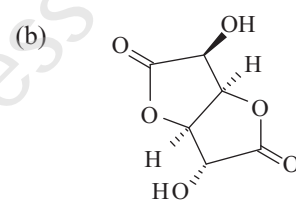


D = Deuterium, T = Tritium

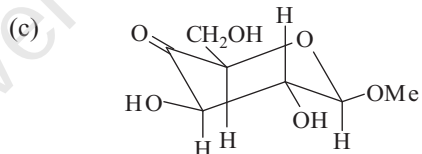
1.17 Give the method of numbering the carbon atoms in the following compounds.



Morphinan



D-Glucaro-1,4 : 6,3-dilactone



Methyl β -D-xylo-Hexopyranoside-4-uloside

1.18 Draw the Fischer projection formula of (a) 4-O- α -D-Glucopyranosyl- α -D-glucopyranose and Haworth structure of (b) β -D-Galactopyranosyl(1 \rightarrow 4)- α -D-glucopyranose.

1.19 Draw the structures of (a) [(Z,Z,Z,Z)-Eicosa-5,8,11,14-tetraenoic acid] and (Z)-Octadec-9-enoic acid. What are the trivial names of these two compounds?