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(Questions and Answers)

REVISED EDITION

ORGANIC CHEMISTRY

For B.Sc. I, II and III Year

As per UGC
Model Curriculum

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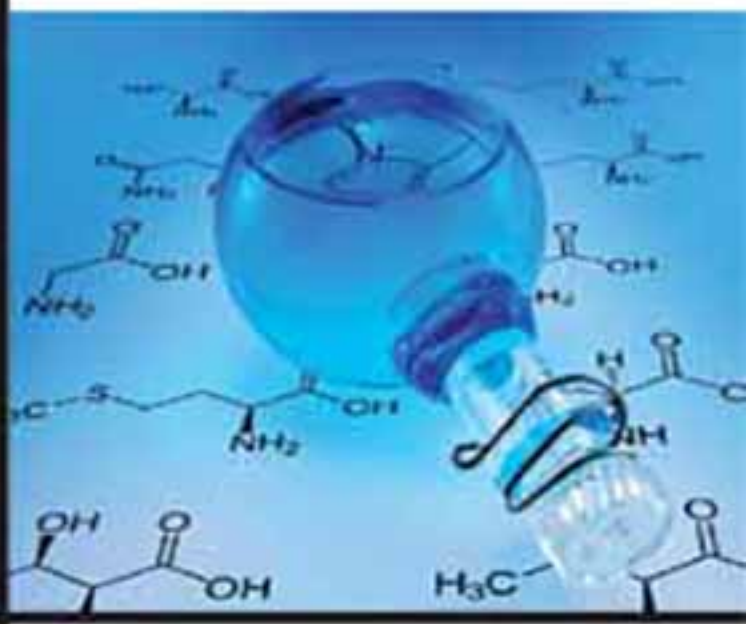
- Including Solved Long Answer Type, Short Answer Type Questions and Numerical Problems
- Authentic, simple, to the point and modern account of each and every topic
- Relevant, clear, well-labelled diagrams
- Easy-to-understand analysis of difficult and intricate topics
- Questions from university papers of various Indian Universities have been included



Dr. R.L. MADAN

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THOROUGHLY UPDATED EDITION

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PREFACE TO THE REVISED EDITION

Overwhelming response to previous editions and reprints has encouraged me to prepare this third revised edition of the book. I hope the book in the present form will be found even more useful to the students. A book in the question-answer form has its own advantages. It guides the students about the type of questions that are expected and how to answer them appropriately. It instils a sense of confidence in the students and helps them get maximum score.

Some noteworthy additions to various chapters are :

Ch 4: Assigning formal charge on intermediates and ionic species.

Ch 6: Threo and erythro diastereomers, geometric isomerism in oximes and alicyclic compound. Fischer and flying wedge formula.

Ch 11: Role of σ-and π-complexes, Birch reduction, Methods of formation and chemical reactions of alkylbenzenes, alkenyl benzenes and alkynylbenzenes.

Ch 12: Dichloroethenes, chloroform, iodoform and carbon tetrachloride.

Ch 14: Organozinc compounds

Ch 15: Synthesis of epoxides. Reactions with epoxides

Ch 16: Hauben-Hoesch and Lederer-Mannase reactions

Ch 17: Epoxidation, Ziesel method

Ch 19: Ketenes

Ch 21: Urea

Ch 24: Detergents

Ch 28: Preparation and synthetic uses of diazomethane

Ch 30: Methods of formation and reactions of cycloalkenes.

Ch 34: Bischler-Napieralski synthesis, Mechanism of electrophilic substitution reactions of indole, quinoline and isoquinoline.

Questions from latest papers of different universities have been added. Suggestions for further improvement of the book are welcome.

Dr. R. L. MADAN

PREFACE

It gives me pleasure to place, at the hands of students and teachers, Simplified Course in Organic Chemistry for B.Sc. I, II, III (Pass and Honours) Students of Indian Universities. In my long teaching career, I have noticed that students are scared of this branch of chemistry because of tough nomenclature of organic compounds and unique mechanistic steps involved in the reactions. I have tried to present the matter in a lucid style using the simplest possible language.

A large number of well-labelled diagrams and sketches have been provided to enable the students to follow the subject easily. My aim has been to create interest in the study of organic chemistry. One chapter has been devoted to nomenclature of organic compounds, so that the student feels comfortable in dealing with them. Mechanisms of reactions, which form a sizeable part of a University question paper, have been explained in an easy-to-understand manner. Structures of compounds in natural products have been discussed stepwise in a lucid style.

A large number of questions set in University examinations have been solved in order to apprise the students of the type of questions generally asked and the appropriate answers to them.

I hope that the book will satisfy the long-felt need of the students for a friendly book on Organic Chemistry. Any suggestions for the improvement of the book are welcome and will be gratefully acknowledged.

I express my thanks to the editorial staff of S. Chand & Company Ltd., New Delhi for the cooperation extended to me in bringing out the book.

Dr. R. L. MADAN

CONTENTS

1

OCCURRENCE AND CHARACTERISTICS OF ORGANIC COMPOUNDS

Q. 1. What is vital force theory of organic compounds? How was this theory discounted?

Ans. Berzelius, a Swedish Chemist postulated in 1815 that there exists a mysterious force, called *vital force*, in living organism, which is responsible for the formation and properties of organic compounds in plants and animals. At that time, Berzelius ruled that organic compounds can only be obtained from plants and animals, they cannot be synthesised in the laboratory. This is called *vital force theory*.

This belief was, however, shattered by a German Chemist, Wohler, who was a student of Berzelius. He prepared urea, an organic compound by heating ammonium cyanate, an inorganic compound.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\Delta} \underset{\text{Urea}}{NH_2CONH_2}$$

Vital force theory of Berzelius was thus disproved.

Q. 2. List some important characteristics of organic compounds.

Ans. Some important characteristics of organic compounds are given below:

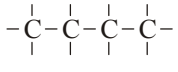
1. Composition. Organic compounds are made up of a few elements viz., C, H, O, N, S, P and halogens. This differentiates them from inorganic compounds which are made up out of 109 elements approximately.

2. Large number. The number of organic compounds exceeds the number of inorganic compounds despite the fact that organic compounds are constituted of a few elements.

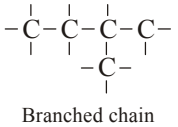
3. Type of linkage. Most of the organic compounds contain covalent bonds in contrast to inorganic compounds which are generally electrovalent.

4. Complex nature. Organic compounds are highly complex and possess higher molecular weights. For example, molecular formula for starch is $(C_6H_{10}O_5)_{200}$.

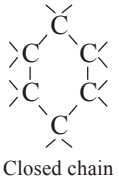
5. Catenation (self-linkage). Carbon has a unique property of combining with other carbon atoms to form long chains and rings of different sizes. *This property of carbon to combine with other carbon atoms to form long chains or large rings is called* **catenation** and is illustrated below:



Straight chain compound



Branched chain compound



Closed chain compound

6. Melting points and boiling points. Organic compounds are usually volatile having low melting and low boiling points. This is because various atoms in the molecule are held together by covalent bonds.

7. Solubility. These compounds have generally *low solubility in water and high solubility in organic solvents.* Some of the organic compounds such as lower alcohols, sugar, etc., dissolve freely in water.

8. Conductance. Aqueous solutions of organic compounds have *lower conductances*, which is explained in terms of the bonding.

9. Rates of reactions. Reactions involving organic compounds are generally *slower* than those involving inorganic compounds. This is because of the formation of intermediate compounds.

10. Combustibility. Organic compounds are combustible and they generally leave no residue on burning.

11. Isomerism. Organic compounds exhibit the phenomenon of *isomerism i.e*., compounds with the same molecular formula possess widely different physical and chemical properties. This is due to the difference in the arrangement of their atoms.

Q. 3. What is meant by homologous series?

Ans. A homologous series *is a group of related compounds in which the formula of each member differs from that of its preceding or succeeding member by one CH_2 group*. The individual members of a homologous series are called homologues. The phenomenon is known as homology. Consider, simple hydrocarbons of *alkane series* viz., CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), C_4H_{10} (butane), C_5H_{12} (pentane). Each member differs from the preceding or following member in composition by —CH_2. It is also evident that all members of the same series have the same general formula. Thus, the general formula of the alkane series is C_nH_{2n+2} where n is the number of carbon atoms.

Similarly, there are other homologous series such as alcohols, aldehydes, ketones, fatty acids, amines, etc. Study of exceedingly large number of compounds becomes easier by grouping them into homologous series.

Q. 4. List some characteristics of homologous series.

Ans. (*i*) Various members of the series conform to the same general formula.

(*ii*) Different members of the series contain the same functional group and, therefore, show similar chemical reactions.

(*iii*) Physical properties such as melting point, boiling point, density, etc., change gradually as we move from lower to higher members or vice-versa.

(*iv*) The members of a series can be prepared by common methods.

Consider the homologous series of alcohols:

CH_3OH	*Methyl alcohol*
C_2H_5OH	*Ethyl alcohol*
C_3H_7OH	*Propyl alcohol*
C_4H_9OH	*Butyl alcohol*

Any two adjacent members of the series differ by — CH_2.

The members can be represented by the general formula $C_nH_{2n+1}OH_3$ have the same functional group, *i.e*., hydroxy group (OH), and can be prepared by similar methods of preparation.

Q. 5. Describe the occurrence of organic compounds.

Ans. Principal natural sources of organic compounds are listed below:

1. Plants. These form the richest sources of organic compounds. Substances like starch, sugar, cellulose, oils, etc., are isolated from various plants, their leaves, fruits and bark. Distillation of wood also yields organic compounds like methanol, acetic acid and acetone.

2. Animals. Many organic compounds like milk, fats, proteins, urea, uric acid, etc. are obtained from animals.

3. Petroleum. Petroleum is a mixture of liquid hydrocarbons, which can be separated into various fractions, such as petroleum ether, gasoline, kerosene oil, lubricating oil, etc. by distillation of petroleum at different temperatures. These fractions are used for various purposes.

4. Coal. The destructive distillation of coal gives a very large number of organic compounds such as benzene, toluene, naphthalene, pyridine, and so on. These products are further used in the manufacture of dyes, drugs, perfumes, explosives and plastics.

5. Fermentation. Some organic reactions take place with the help of bacteria and enzymes. Such a reaction is called **fermentation**. Fermentation forms an important source of many organic compounds. Thus, ethyl alcohol is prepared by fermentation of sugar and acetic acid is made by fermentation of ethyl alcohol. *Antibiotics* such as penicillin, streptomycin, aureomycin, tetramycin, etc., are the products of fermentation processes.

6. Natural gas. It is obtained from petroleum wells. It mainly contains methane, CH_4 which is used as household fuel. In addition to this, natural gas *i.e.*, methane is employed for the preparation of other organic compounds like methyl alcohol CH_3OH, methyl chloride CH_3Cl, chloroform $CHCl_3$, etc.

Q. 6. Name different techniques for isolation and purification of organic compounds.

Ans. The techniques used to isolate and purify the organic compounds are:

1. Crystallization. This method is used for the purification of solid organic compounds. For example, sugar is obtained from its saturated solution by crystallization.

2. Fractional Crystallization. This method is used for the separation of a mixture of solids having different solubilities.

3. Sublimation. This method is used for the purification of volatile solids from non-volatile solids. Organic compounds which can be purified by this method are naphthalene, benzoic acid, camphor, etc.

4. Simple Distillation. This method is used for the purification of those liquids which contain non-volatile impurities. For example, organic liquids like benzene, acetone, ether can be purified by this method.

5. Fractional Distillation. This method is used for the separation of a mixture of organic liquids which possess different boiling points.

6. Steam Distillation. This method is used for the purification of organic solids or liquids which are insoluble in water, volatile in steam and contain non-volatile impurities. For example, purification of aniline and nitro benzene can be done by this method.

7. Distillation under the reduced pressure. Those liquids which decompose at or below their boiling points under atmospheric pressure are purified by this method. For example, recovery of glycerol from spent lye is done by this process.

8. Extraction with solvent. Extraction of oils and fats from seeds and essences from flowers is done by using suitable organic solvents.

9. Chromatography. This is a modern technique used to separate and to purify mixtures of organic compounds.

Q. 7. What is the criteria of purity of an organic compound? (*Agra 2004*)

Ans. Criteria of purity of an organic compound

A pure substance possesses fixed physical constants and shows a variation with the impurities. *A pure solid organic substance possesses a sharp melting point, i.e., it liquefies at one fixed temperature. Similarly a pure organic liquid will boil at a fixed temperature, i.e., it will possess a sharp boiling point.*

Generally it is a common practice to check up the purity of organic solids and liquids by determining their melting and boiling points respectively.

Q. 8. How can you use melting point property to check the purity of a substance?

Ans. Purity of a substance can be checked by using the melting point property. Every pure organic substance has a fixed melting point. These melting points of pure substances are available in literature. Two techniques may be used to check the purity of a substance:

1. Repeated crystallisation. Melting point of the substance to be checked is determined with the help of apparatus shown in Fig. 1.1. Then the substance is recrystallised using a suitable solvent. Melting point of the dry, recrystallised sample is determined again. This is repeated three times. If the melting point remains the same and does not change on recrystallisation, the substance is a pure substance.

2. Mixed melting point. Let us say we want to know whether the given sample of acetanilide is pure or not. To establish this, we shall take a pure sample of a acetanilide and mix to it, the given sample of acetanilide thoroughly. Determine the melting point of this mixture. If the melting point is the same as that of acetanilide (from the literature value), the given sample of acetanilide is pure. If it is different, the sample is impure. Impurities always change the melting point of a substance.

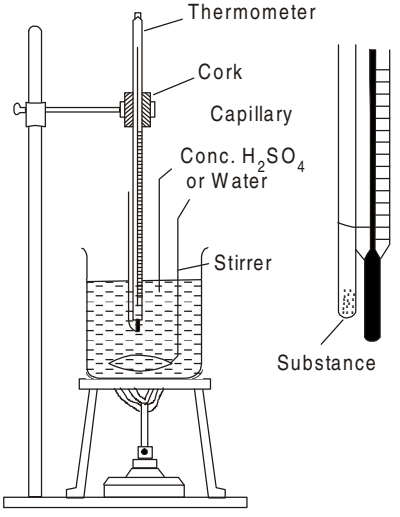


Fig. 1.1. Determination of melting point.

Q. 9. What is the criteria of purity of an organic liquid?

Ans. The purity of an organic liquid can be checked by determining its boiling point. Every liquid has a fixed characteristic boiling point. A pure liquid boils sharply at this temperature. If a liquid does not boil sharply but boils over a range, it is an impure liquid.

Boiling point is the temperature at which the vapour pressure of a liquid is equal to the atmospheric pressure.

Boiling point of a liquid is determined with the help of the apparatus shown in Fig. 1.2.

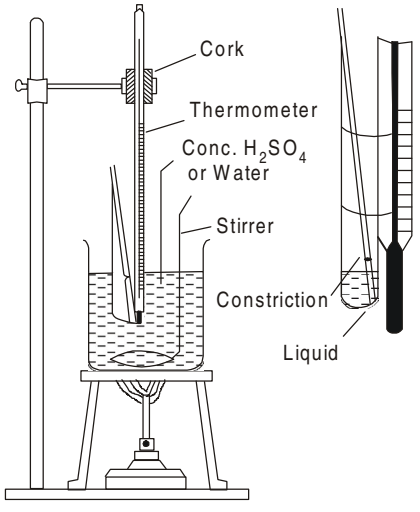


Fig. 1.2. Determination of boiling point.

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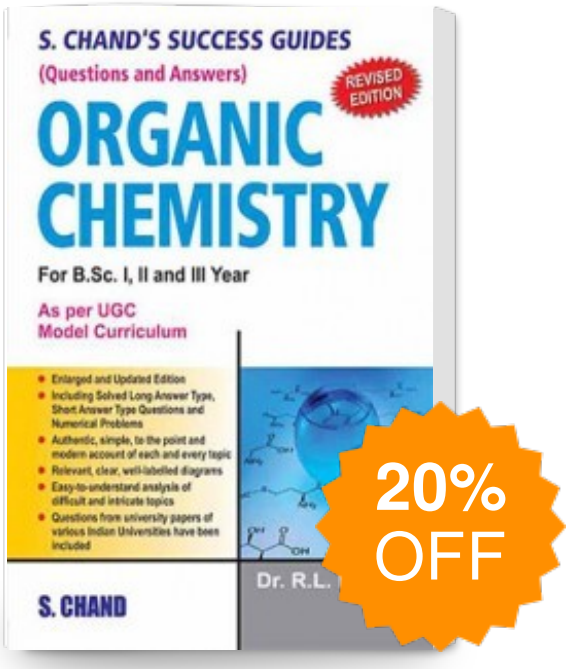

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