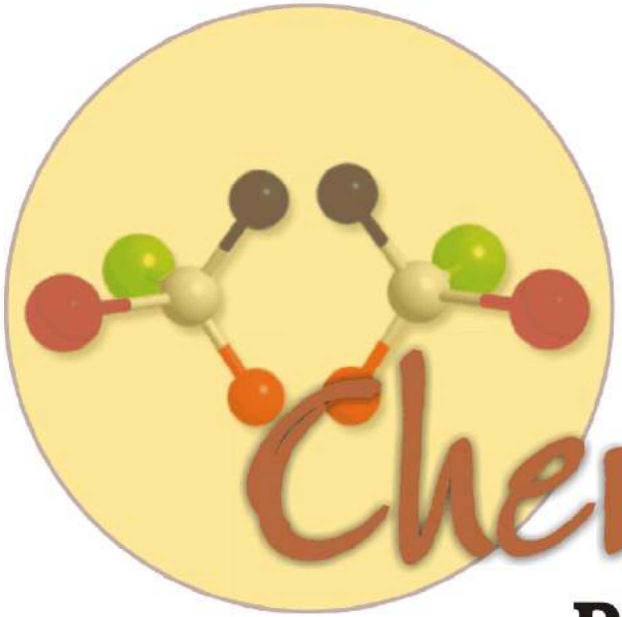


Chemistry

Part II

Textbook for Class XII

राष्ट्रीय शैक्षिक अनुसंधान और प्रशिक्षण परिषद्
NATIONAL COUNCIL OF EDUCATIONAL RESEARCH AND TRAINING

First Edition
April 2007 Chaitra 1929

Reprinted
November 2007 Kartika 1929
December 2008 Pausa 1930
January 2010 Magha 1931
January 2011 Magha 1932
January 2012 Magha 1933
November 2012 Kartika 1934
November 2013 Kartika 1935

PD 400T RNB

₹ 95.00

Printed on 80 GSM paper with NCERT watermark

Published at the Publication Division by the Secretary, National Council of Educational Research and Training, Sri Aurobindo Marg, New Delhi 110 016 and printed at Jagannath Industries, C-146 (Back Side) Naraina Industrial Area, Phase I, New Delhi 110 028

ISBN 81-7450-648-9 (Part I)
81-7450-716-7 (Part II)

OFFICES OF THE PUBLICATION DIVISION, NCERT

NCERT Campus
Sri Aurobindo Marg
New Delhi 110 016 **Phone : 011-26562708**

108, 100 Feet Road
Hosdakere Halli Extension
Banashankari III Stage
Bengaluru 560 085 **Phone : 080-26725740**

Navjivan Trust Building
P.O.Navjivan
Ahmedabad 380 014 **Phone : 079-27541446**

CWC Campus
Opp. Dhankal Bus Stop
Panihati
Kolkata 700 114 **Phone : 033-25530454**

CWC Complex
Maligaon
Guwahati 781 021 **Phone : 0361-2674869**

Publication Team

Head, Publication Division	: *Ashok Srivastava*
Chief Production Officer	: *Shiv Kumar*
Chief Business Manager	: *Gautam Ganguly*
Chief Editor (Contractual Service)	: *Naresh Yadav*
Editor	: *R. N. Bhardwaj*
Production Assistant	: *Rajesh Pippal*

Cover and Layout
Blue Fish

FOREWORD

The National Curriculum Framework (NCF), 2005 recommends that children life at school must be linked to their life outside the school. This principle marks a departure from the legacy of bookish learning which continues to shape our system and causes a gap between the school, home and community. The syllabi and textbooks developed on the basis of NCF signify an attempt to implement this basic idea. They also attempt to discourage rote learning and the maintenance of sharp boundaries between different subject areas. We hope these measures will take us significantly further in the direction of a child-centred system of education outlined in the National Policy on Education (1986).

The success of this effort depends on the steps that school principals and teachers will take to encourage children to reflect on their own learning and to pursue imaginative activities and questions. We must recognise that, given space, time and freedom, children generate new knowledge by engaging with the information passed on to them by adults. Treating the prescribed textbook as the sole basis of examination is one of the key reasons why other resources and sites of learning are ignored. Inculcating creativity and initiative is possible if we perceive and treat children as participants in learning, not as receivers of a fixed body of knowledge.

These aims imply considerable change in school routines and mode of functioning. Flexibility in the daily time-table is as necessary as rigour in implementing the annual calender so that the required number of teaching days are actually devoted to teaching. The methods used for teaching and evaluation will also determine how effective this textbook proves for making children school a happy experience, rather than a source of stress or boredom. Syllabus designers have tried to address the problem of curricular burden by restructuring and reorienting knowledge at different stages with greater consideration for child psychology and the time available for teaching. The textbook attempts to enhance this endeavour by giving higher priority and space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience.

The National Council of Educational Research and Training (NCERT) appreciates the hard work done by the textbook development committee responsible for this book. We wish to thank the Chairperson of the advisory group in science and mathematics, Professor J.V. Narlikar and the Chief Advisor for this book, Professor B. L. Khandelwal for guiding the work of this committee.

Several teachers contributed to the development of this textbook; we are grateful to their principals for making this possible. We are indebted to the institutions and organisations which have generously permitted us to draw upon their resources, material and personnel. As an organisation committed to systemic reform and continuous improvement in the quality of its products, NCERT welcomes comments and suggestions which will enable us to undertake further revision and refinement.

Director
National Council of Educational
Research and Training

New Delhi
20 November 2006

PREFACE

Chemistry has made a profound impact on the society. It is intimately linked to the well-being of human kind. The rate of advancements in chemistry is so high that curriculum developers continuously look for strategies to cope with these advancements. Also, the students have to be inspired to be the future leaders who would make fundamental contributions. The present textbook is a sincere effort in this direction.

The textbook, presented in two parts, comprises of sixteen Units. Although the titles of various Units indicate a sort of compartmentalisation into physical, inorganic and organic chemistry, readers will find that these sub-disciplines have been intermingled, at least to a certain extent, to have a unified approach to the subject. First nine Units covering physical and inorganic chemistry portions are included in Part I while organic chemistry portion comprising of seven Units is included in Part II of the book. The approach of presentation of the subject matter discourages students from rote memorisation. The subject has in fact, been organised around the laws and principles of chemistry. As students master these laws and principles, they will soon get to the point where they can predict much of what will come.

Efforts have been directed towards making the subject stimulating and exciting by references to the historical developments and its usefulness to our lives, wherever appropriate. The text is well illustrated with examples from surrounding environment to facilitate grasping of the qualitative and quantitative aspects of the concept easily. Physical data are given in SI units throughout the book to make comparison of various properties easier. IUPAC system of nomenclature has been followed along with the common names. Structural formulae of chemical compounds showing functional/coordinating groups in different colours are drawn using electronic system. Each Unit has a good number of examples, as illustrations, with their solutions and some intext questions, the answers of some of which are given at the end of the Unit. The end of Unit exercises are designed to apply important principles and provoke thinking process to solve them. Answers of some of these exercises are given at the end of the book.

A variety of materials, e.g., biographical sketches of some scientists, additional information related to a particular topic, etc., is given in boxes with a deep yellow coloured bar. This boxed material with a 'deep yellow bar' is to bring additional life to the topic. However, it is non-evaluative. The structures of some of the more complex compounds incorporated in the book are for understanding their chemistry. As their reproduction would lead to memorisation, it is also a non-evaluative portion of the text.

The information part has been significantly reduced and, wherever possible, it has been substantiated with facts. However, it is necessary for students to be aware of commercially important chemicals, their processes of manufacture and sources of raw materials. This leads to descriptive material in the book. Attempts have been made to make descriptions of such compounds interesting by considering their structures and reactivity. Thermodynamics, kinetics and electrochemical aspects have been applied to a few chemical reactions which should be beneficial to students for understanding why a particular reaction happened and why a particular property is exhibited by the product. There is currently great awareness of environmental and energy issues which are directly related to chemistry. Such issues have been highlighted and dealt with at appropriate places in the book.

A team of experts constituted by the NCERT has developed the manuscript of the book. It gives me great pleasure to acknowledge the valuable contribution of all the members of this team. I also acknowledge the valuable and relentless contribution of the editors in bringing the book to the present shape. I also acknowledge with thanks the dedicated efforts and valuable contribution of Professor Brahm Parkash, who not only coordinated the entire programme but also actively involved in writing and editing of this book. Thanks are also due to the participating teachers and subject experts of the review workshop for their contribution, which has helped us to make the book learner friendly. Also, I thank the technical and administrative staff of the NCERT for their support in the entire process.

The team of this textbook development programme hopes that the book stimulates its readers and makes them feel the excitement and fascination for this subject. Efforts have been made to bring out this book error-free. Nevertheless, it is recognised that in a book of this complexity, there could inevitably be occasional errors. It will always be a pleasure to hear about them from readers to take necessary steps to rectify them.

B.L. KHANDELWAL

TEXTBOOK DEVELOPMENT COMMITTEE

CHAIRMAN, ADVISORY GROUP FOR TEXTBOOKS IN SCIENCE AND MATHEMATICS

J.V. Narlikar, *Professor Emeritus*, *Chairman*, Advisory Committee, Inter University Centre for Astronomy and Astrophysics (IUCAA), Ganeshkhind, Pune University Campus, Pune

CHIEF ADVISOR

B.L. Khandelwal, *Professor*, *Director*, Disha Institute of Management and Technology, Raipur, Chhattisgarh. Formerly *Chairman*, Department of Chemistry, Indian Institute of Technology, New Delhi

MEMBERS

A.S. Brar, *Professor*, Department of Chemistry, Indian Institute of Technology, New Delhi

A.Q. Contractor, *Professor*, Department of Chemistry, Indian Institute of Technology, Powai, Mumbai

Alka Mehrotra, *Reader*, DESM, NCERT, New Delhi

Anjni Koul, *Lecturer*, DESM, NCERT, New Delhi

Brahm Parkash, *Professor*, DESM, NCERT, New Delhi

I.P. Agarwal, *Professor*, DESM, Regional Institute of Education, NCERT, Bhopal, M.P.

K.K. Arora, *Reader*, Department of Chemistry, Zakir Hussain College, University of Delhi, New Delhi

K.N. Upadhayaya, *Head* (Retired), Department of Chemistry, Ramjas College, Delhi University, Delhi

Kavita Sharma, *Lecturer*, DEE, NCERT, New Delhi

M.P. Mahajan, *Professor*, Department of Chemistry, Guru Nanak Dev University, Amritsar, Punjab

M.L. Agarwal, *Principal* (Retired), Kendriya Vidyalaya, Jaipur, Rajasthan

Puran Chand, *Professor*, *Joint Director* (Retired), CIET, NCERT, New Delhi

R.A. Verma, *Vice Principal*, Shaheed Basant Kumar Biswas Sarvodaya Vidyalaya, Civil Lines, New Delhi

R.K. Verma, *Professor*, Department of Chemistry, Magadh University, Bihar

R.K. Prashar, *Lecturer*, DESM, NCERT, New Delhi

R.S. Sindhu, *Professor*, DESM, NCERT, New Delhi

S.K. Gupta, *Reader*, School of Studies in Chemistry, Jiwaji University, Gwalior, M.P.

S.K. Dogra, *Professor*, Dr B.R. Ambedkar Centre for Biomedical Research, University of Delhi, Delhi

Sarabjeet Sachdeva, *PGT*, (Chemistry), St. Columbas School, New Delhi

S. Badhwar, *Lecturer*, The Daly College, Indore, M.P.

V.N. Pathak, *Professor*, Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan

Vijay Sarda, *Reader*, Department of Chemistry, Zakir Hussain College, University of Delhi, New Delhi

V.K. Verma, *Professor*, (Retired), Institute of Technology, Banaras Hindu University, Varanasi, U.P.

V.P. Gupta, *Professor*, DESM, Regional Institute of Education, NCERT, Bhopal, M.P.

MEMBER-COORDINATOR

Brahm Parkash, *Professor*, DESM, NCERT, New Delhi

ACKNOWLEDGMENTS

The National Council of Educational Research and Training (NCERT) gratefully acknowledges the valuable contributions of the individuals and organisations involved in the development of Chemistry textbook for Class XII. The acknowledgements are also due to the following practicing teachers and subject experts for reviewing the draft manuscript and giving useful suggestions for its improvement in a workshop: Dr D.S. Rawat, Department of Chemistry, University of Delhi, Delhi; Dr Mahendra Nath, *Reader,* Chemistry Department, University of Delhi, Delhi; Dr Sulekh Chandra, *Reader,* Zakir Hussain College, New Delhi; Ms Ameeta K., *PGT* (Chemistry), Vidyalaya No. 3, Patiala Cantt (Pb.); Dr G.T. Bhandge, *Professor* and *Head,* DESM, Regional Institute of Education, Mysore; Dr Neeti Misra, *Senior Lecturer,* Department of Chemistry, Acharya Narendra Dev College, New Delhi; Dr S.P.S. Mehta, Department of Chemistry, Kumaun University, Nainital (UA); Dr N.V.S. Naidu, *Assistant Professor* (Chemistry), SVU College of Mathematics and Physical Sciences, S.V. University, Tirupati (A.P.); Dr A.C. Handa, Hindu College, Delhi University, Delhi; Dr A.K. Vashishtha, G.B.S.S.S. Jafrabad, Delhi; Dr Charanjit Kaur, *Head,* Department of Chemistry, Sri Sathya Sai College for Women, Bhopal, P.O. Habibganj; Ms Alka Sharma, *PGT* (Chemistry), S.L.S. DAV Public School, Mausam Vihar, Delhi; Dr H.H. Tripathy, *Reader* (Retired), Regional Institute of Education, Bhubaneswar; Shri C.B. Singh, *PGT* (Chemistry), Kendriya Vidyalaya No. 2, Delhi Cantt, Delhi; and Dr Sunita Hooda, Acharya Narendra Dev College, Delhi University, New Delhi.

The Council also thanks Professor B.L. Khandelwal, Professor Brahm Parkash, Dr K.K. Arora, Dr Vijay Sarda and Professor R.S. Sindhu, members of the Textbook Development Committee for editing the manuscript and bringing it to the present shape.

The Council also acknowledges the contributions of Shri Vijay Singh, Narender Verma and Vijay Kaushal *DTP Operators and* Dr K.T. Chitralekha, *Copy Editor* in shaping this book. The efforts of the Publication Department, NCERT are also duly acknowledged.

CONTENTS OF CHEMISTRY PART I

CONTENTS

First Edition
April 2007 Chaitra 1929

Reprinted
November 2007 Kartika 1929
December 2008 Pausa 1930
January 2010 Magha 1931
January 2011 Magha 1932
January 2012 Magha 1933
November 2012 Kartika 1934
November 2013 Kartika 1935

PD 400T RNB

₹ 95.00

Printed on 80 GSM paper with NCERT watermark

Published at the Publication Division by the Secretary, National Council of Educational Research and Training, Sri Aurobindo Marg, New Delhi 110 016 and printed at Sam Industrial Enterprises(P) Ltd., A-17 & 18, Sector

ISBN 81-7450-648-9 (Part I)
81-7450-716-7 (Part II)

OFFICES OF THE PUBLICATION DIVISION, NCERT

NCERT Campus
Sri Aurobindo Marg
New Delhi 110 016 **Phone : 011-26562708**

108, 100 Feet Road
Hosdakere Halli Extension
Banashankari III Stage
Bengaluru 560 085 **Phone : 080-26725740**

Navjivan Trust Building
P.O.Navjivan
Ahmedabad 380 014 **Phone : 079-27541446**

CWC Campus
Opp. Dhankal Bus Stop
Panihati
Kolkata 700 114 **Phone : 033-25530454**

CWC Complex
Maligaon
Guwahati 781 021 **Phone : 0361-2674869**

Publication Team

Head, Publication Division : *Ashok Srivastava*
Chief Production Officer : *Shiv Kumar*
Chief Business Manager : *Gautam Ganguly*
Chief Editor (Contractual Service) : *Naresh Yadav*
Editor : *R. N. Bhardwaj*
Production Assistant : *Rajesh Pippal*

Cover and Layout
Blue Fish

INDEX

SUPPLEMENTARY MATERIAL

UNIT XIV: *Biomolecules*

14.5 HORMONES

Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are poured directly in the blood stream which transports them to the site of action.

In terms of chemical nature, some of these are steroids, e.g., estrogens and androgens; some are poly peptides for example insulin and endorphins and some others are amino acid derivatives such as epinephrine and norepinephrine.

Hormones have several functions in the body. They help to maintain the balance of biological activities in the body. The role of insulin in keeping the blood glucose level within the narrow limit is an example of this function. Insulin is released in response to the rapid rise in blood glucose level. On the other hand hormone glucagon tends to increase the glucose level in the blood. The two hormones together regulate the glucose level in the blood. Epinephrine and norepinephrine mediate responses to external stimuli. Growth hormones and sex hormones play role in growth and development. Thyroxine produced in the thyroid gland is an iodinated derivative of amino acid tyrosine. Abnormally low level of thyroxine leads to hypothyroidism which is characterised by lethargyness and obesity. Increased level of thyroxine causes hyperthyroidism. Low level of iodine in the diet may lead to hypothyroidism and enlargement of the thyroid gland. This condition is largely being controlled by adding sodium iodide to commercial table salt (

Steroid hormones are produced by adrenal cortex and gonads (testes in males and ovaries in females). Hormones released by the adrenal cortex play very important role in the functions of the body. For example, glucocorticoids control the carbohydrate metabolism, modulate inflammatory reactions, and are involved in reactions to stress. The mineralocorticoids control the level of excretion of water and salt by the kidney. If adrenal cortex does not function properly then one of the results may be Addison

hypoglycemia, weakness and increased susceptibility to stress. The disease is fatal unless it is treated by glucocorticoids and mineralocorticoids. Hormones released by gonads are responsible for development of secondary sex characters. Testosterone is the major sex hormone produced in males. It is responsible for development of secondary male characteristics (deep voice, facial hair, general physical constitution) and estradiol is the main female sex hormone. It is responsible for development of secondary female characteristics and participates in the control of menstrual cycle. Progesterone is responsible for preparing the uterus for implantation of fertilised egg.

UNIT XVI: *Chemistry in Everyday Life*

16.4.3 Antioxidants in Food

These are important and necessary food additives. These help in food preservation by retarding the action of oxygen on food. These are more reactive towards oxygen than the food material which they are protecting. The two most familiar antioxidants are butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA). The addition of BHA to butter increases its shelf life from months to years.

Sometimes BHT and BHA along with citric acid are added to produce more effect. Sulphur dioxide and sulphite are useful antioxidants for wine and beer, sugar syrups and cut, peeled or dried fruits and vegetables.

Unit 10

Haloalkanes and Haloarenes

Objectives

After studying this Unit, you will be able to

- name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- correlate the structures of haloalkanes and haloarenes with various types of reactions;
- use stereochemistry as a tool for understanding the reaction mechanism;
- appreciate the applications of organo-metallic compounds;
- highlight the environmental effects of polyhalogen compounds.

Halogenated compounds persist in the environment due to their resistance to breakdown by soil bacteria.

The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, *chloramphenicol,* produced by soil microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, *thyroxine,* the deficiency of which causes a disease called *goiter*. Synthetic halogen compounds, *viz.* chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of organohalogen compounds.

10.1 Classification

Haloalkanes and haloarenes may be classified as follows:

10.1.1 On the Basis of Number of Halogen Atoms

These may be classified as mono, di, or polyhalogen (tri-,tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,

C_2H_5X

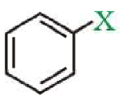
Monohaloalkane

CH_2X-CH_2X

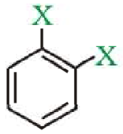
Dihaloalkane

$CH_2X-CHX-CH_2X$

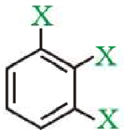
Trihaloalkane



Monohaloarene



Dihaloarene



Trihaloarene

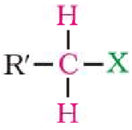
Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

10.1.2 Compounds Containing sp^3 C X Bond (X= F, Cl, Br, I)

This class includes

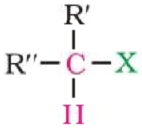
(a) *Alkyl halides or haloalkanes (R*

In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



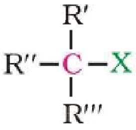
$R'-CH_2-X$

Primary (1°)



$R''-CHR'-X$

Secondary (2°)



$R''-CR'R'''-X$

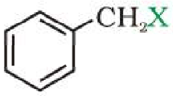
Tertiary (3°)

(b) *Allylic halides*

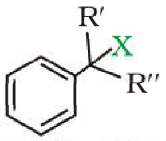
These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to carbon-carbon double bond (C=C) *i.e.* to an allylic carbon.

(c) *Benzylic halides*

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to an aromatic ring.



(1°)



$R' = CH_3$, $R'' = H$ (2°)

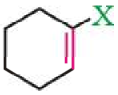
$R' = R'' = CH_3$ (3°)

10.1.3 Compounds Containing sp^2 C Bond

This class includes:

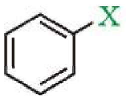
(a) *Vinylic halides*

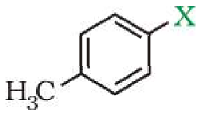
These are the compounds in which the halogen atom is bonded to an sp^2-hybridised carbon atom of a carbon-carbon double bond (C = C).



(b) *Aryl halides*

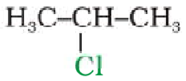
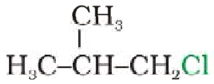
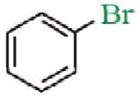
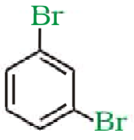
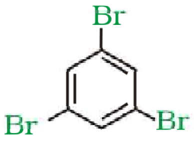
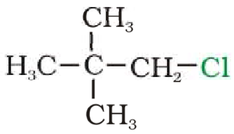
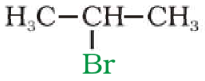
These are the compounds in which the halogen atom is bonded to the sp^2-hybridised carbon atom of an aromatic ring.



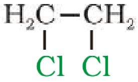


10.2 Nomenclature

Having learnt the classification of halogenated compounds, let us now learn how these are named. The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halosubstituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.

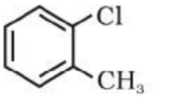
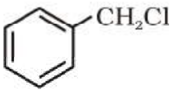
	$CH_3CH_2CH_2Br$	 $H_3C-\underset{Cl}{CH}-CH_3$	 $H_3C-\overset{CH_3}{CH}-CH_2Cl$
Common name:	n-Propyl bromide	Isopropyl chloride	Isobutyl chloride
IUPAC name:	1-Bromopropane	2-Chloropropane	1-Chloro-2-methylpropane
			
Common name:	Bromobenzene	*m*-Dibromobenzene	*sym*-Tribromobenzene
IUPAC name:	Bromobenzene	1,3-Dibromobenzene	1,3,5-Tribromobenzene
		 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Cl$	 $H_3C-\underset{Br}{CH}-CH_3$
IUPAC name:		1-Chloro-2,2-dimethylpropane	2-Bromopropane

The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo-compounds having same type of halogen atoms are further classified as geminal halides (halogen atoms are present on the same carbon atom) and vicinal halides (halogen atoms are present on the adjacent carbon atoms). In common name system, *gem*-dihalides are named as alkylidene halides and *vic*-dihalides are named as alkylene dihalides. In IUPAC system, they are named as dihaloalkanes.

	$H_3C-CHCl_2$	 $H_2C(Cl)-CH_2(Cl)$
Common name:	Ethylidene chloride (*gem*-dihalide)	Ethylene dichloride (*vic*-dihalide)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

Some common examples of halocompounds are mentioned in Table 10.1.

Table 10.1: Common and IUPAC Names of some Halides

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2=CHCl$	Vinyl chloride	Chloroethene
$CH_2=CHCH_2Br$	Allyl bromide	3-Bromopropene
	*o*-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

Example 10.1

Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Solution

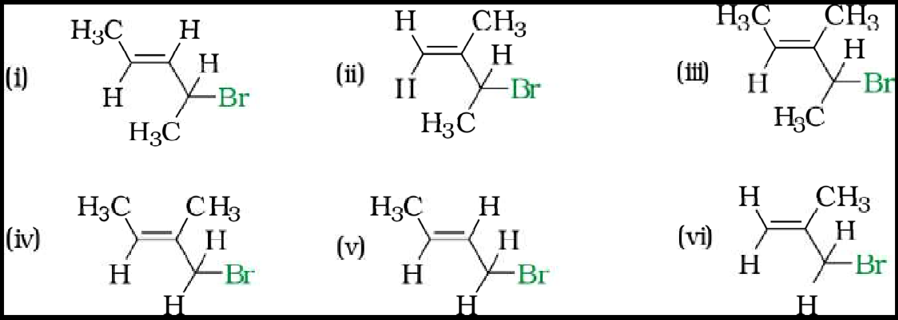
$CH_3CH_2CH_2CH_2CH_2Br$	1-Bromopentane (1°)
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane(2°)
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane (2°)
$(CH_3)_2CHCH_2CH_2Br$	1-Bromo-3-methylbutane (1°)

Br

Br

Br

Example 10.2



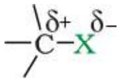
Solution

Intext Question

10.1

10.3 Nature of C-X Bond

Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



Since the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, the largest. Consequently the carbon-halogen bond length also increases from C

dipole moments are given in Table 10.2.

Table 10.2: Carbon-Halogen (C X) Bond Lengths, Bond Enthalpies and Dipole Moments

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol^{-1}	Dipole moment/Debye
CH_3 F	139	452	1.847
CH_3 Cl	178	351	1.860
CH_3 Br	193	293	1.830
CH_3 I	214	234	1.636

10.4 Methods of Preparation

10.4.1 From Alcohols

Alkyl halides are best prepared from alcohols, which are easily accessible. The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because the other two products are escapable gases. Hence the reaction gives pure alkyl halides. Phosphorus tribromide and triiodide are usually generated *in situ* (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine respectively. The preparation of alkyl chloride is carried out either by passing dry hydrogen chloride gas through a solution of alcohol or by heating a solution of alcohol in concentrated aqueous acid.

$$\text{R–OH} + \text{HCl} \xrightarrow{ZnCl_2} \text{R–Cl} + H_2O$$

$$\text{R–OH} + \text{NaBr} + H_2SO_4 \longrightarrow \text{R–Br} + NaHSO_4 + H_2O$$

$$3\text{R–OH} + PX_3 \longrightarrow 3\text{R–X} + H_3PO_3 \qquad (\text{X} = \text{Cl, Br})$$

$$\text{R–OH} + PCl_5 \longrightarrow \text{R–Cl} + POCl_3 + \text{HCl}$$

$$\text{R–OH} \xrightarrow[X_2=Br_2,I_2]{\text{red P}/X_2} \text{R–X}$$

$$\text{R–OH} + SOCl_2 \longrightarrow \text{R–Cl} + SO_2 + \text{HCl}$$

The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature. Constant boiling with HBr (48%) is used for preparing alkyl bromide. Good yields of R

with sodium or potassium iodide in 95% orthophosphoric acid. The order of reactivity of alcohols with a given haloacid is 3°>2°>1°. The above methods are not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond (Unit 11, Class XI).

10.4.2 From Hydrocarbons

(a) By free radical halogenation

Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds. Consequently, the yield of any one compound is low (Unit 13, Class XI).

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

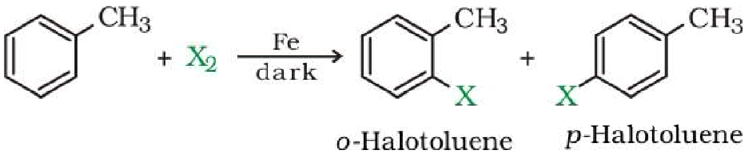
Example 10.3

[redacted]

Solution

(b) By electrophilic substitution

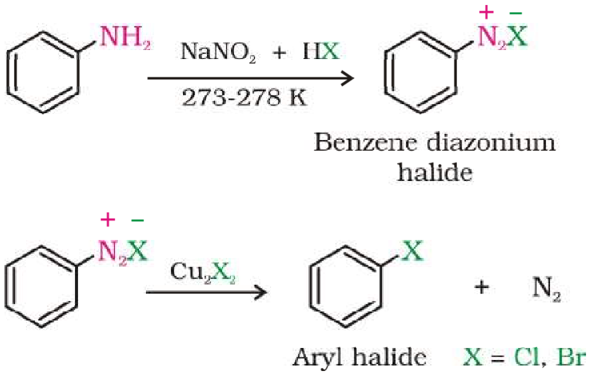
Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



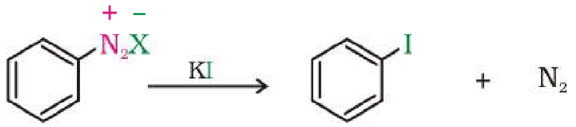
The *ortho* and *para* isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(c) Sandmeyer

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed (Unit 13, Class XII). Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by

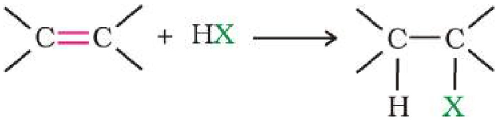


Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.



(d) From alkenes

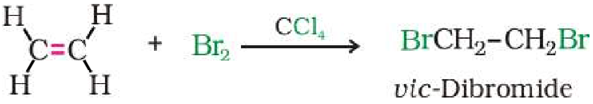
(i) *Addition of hydrogen halides*: An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.



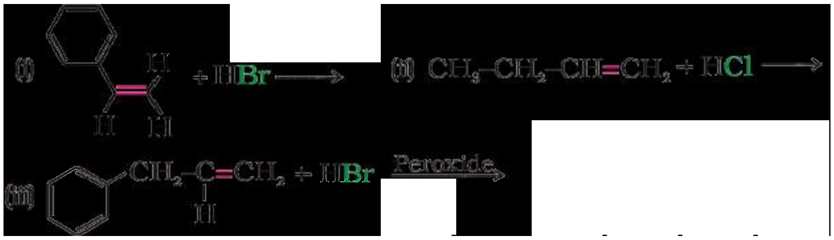
Propene yields two products, however only one predominates as per Markovnikov

$$CH_3CH=CH_2 + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(ii) *Addition of halogens:* In the laboratory, addition of bromine in CCl_4 to an alkene resulting in discharge of reddish brown colour of bromine constitutes an important method for the detection of double bond in a molecule. The addition results in the synthesis of *vic*-dibromides, which are colourless (Unit 13, Class XI).



Example 10.4 Write the products of the following reactions:



Solution

10.4.3 Halogen Exchange

Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.

$$R{-}X + NaI \longrightarrow R{-}I + NaX$$

$X = Cl, Br$

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as Swarts reaction.

$$H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$$

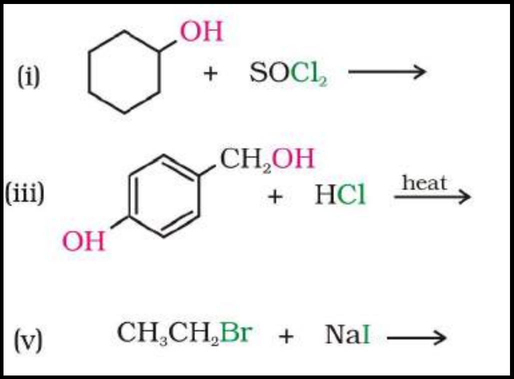
Intext Questions

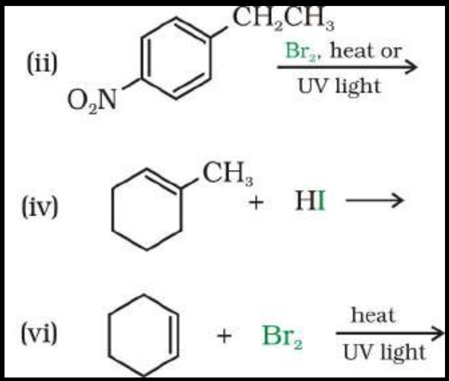
10.2

10.3

10.4

10.5





10.5 Physical Properties

Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell.

Melting and boiling points

Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids. As we have already learnt, molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

The attractions get stronger as the molecules get bigger in size and have more electrons. The pattern of variation of boiling points of different halides is depicted in Fig. 10.1. For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI> RBr> RCl> RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

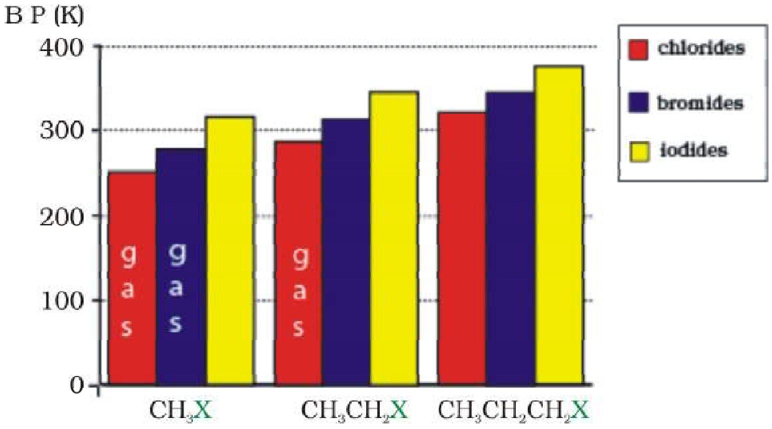
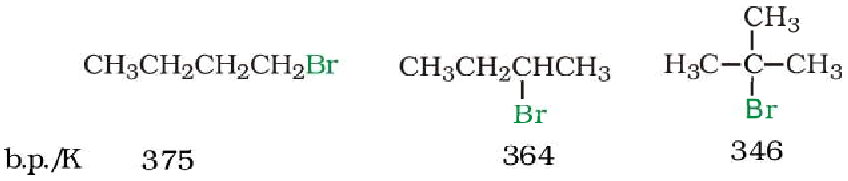


Fig. 10.1: Comparison of boiling points of some alkyl halides

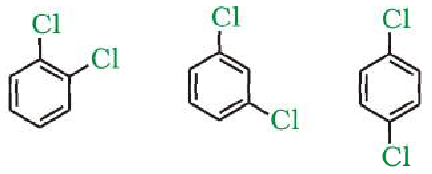
The boiling points of isomeric haloalkanes decrease with increase in branching (Unit 12, Class XI). For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.



$$CH_3CH_2CH_2CH_2Br \qquad CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \qquad H_3C-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

b.p./K	375	364	346

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the *para*-isomers are high melting as compared to their *ortho*- and *meta*-isomers. It is due to symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.



b.p / K	453	446	448
m.p/K	256	249	323

Density

Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms (Table 10.3).

Table 10.3: Density of Some Haloalkanes

Compound	Density (g/mL)	Compound	Density (g/mL)
n $_3H_7Cl$	0.89	CH_2Cl_2	1.336
n $_3H_7Br$	1.335	$CHCl_3$	1.489
n-C_3H_7I	1.747	CCl_4	1.595

Solubility

The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

Intext Question

10.6

10.6 Chemical Reactions

10.6.1 Reactions of Haloalkanes

The reactions of haloalkanes may be divided into the following categories:

(i) Nucleophilic substitution
(ii) Elimination reactions
(iii) Reaction with metals.

(i) *Nucleophilic substitution reactions*

In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

It is one of the most useful classes of organic reactions of alkyl halides in which halogen is bonded to sp^3 hybridised carbon. The products formed by the reaction of haloalkanes with some common nucleophiles are given in Table 10.4.

Table 10.4: Nucleophilic Substitution of Alkyl Halides (R X)

$$R-X+Nu^- \rightarrow R-Nu+X^-$$

Reagent	Nucleophile (Nu)	Substitution product R	Class of main product
NaOH (KOH)	HO	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	R′O	ROR′	Ether
NaI	I	R I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″NH	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N	R	Alkyl nitrite
$AgNO_2$	Ag O	R $_2$	Nitroalkane
R′COOAg	R′COO	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
R′ M^+	R′	RR′	Alkane

Groups like cyanides and nitrites possess two nucleophilic centres and are called *ambident nucleophiles*. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways [$^{\ominus}C\equiv N \leftrightarrow :C=N^{\ominus}$], *i.e.,* linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage [O $\ddot{N}$=O]. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

Example 10.5

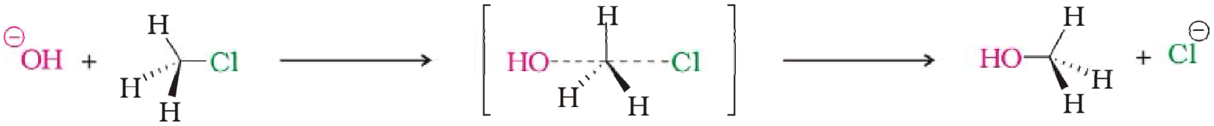
Solution

[redacted]

Mechanism: This reaction has been found to proceed by two different mechanims which are described below:

(a) *Substitution nucleophilic bimolecular (S_N2)*

The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.



[redacted]

This can be represented diagrammatically as shown in Fig. 10.2.

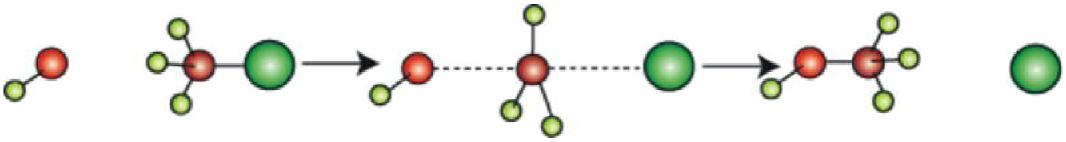


Fig. 10.2: *Red dot represents the incoming hydroxide ion and green dot represents the outgoing halide ion*

It depicts a bimolecular nucleophilic displacement (S_N2) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. As the reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away. This process is called as **inversion of configuration**. In the transition state, the carbon atom is simultaneously bonded to incoming nucleophile and the outgoing leaving

In the year 1937, Edward Davies Hughes and Sir Christopher Ingold proposed a mechanism for an S_N2 reaction.

group and such structures are unstable and cannot be isolated. This is because the carbon atom in the transition state is simultaneously bonded to five atoms and therefore is unstable.

Since this reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom have a dramatic inhibiting effect. Of the simple alkyl halides, methyl halides react most rapidly in S_N2 reactions because there are only three small hydrogen atoms. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus the order of reactivity followed is:

Hughes worked under Ingold and earned a D.Sc. degree from the University of London.

Primary halide > Secondary halide > Tertiary halide.

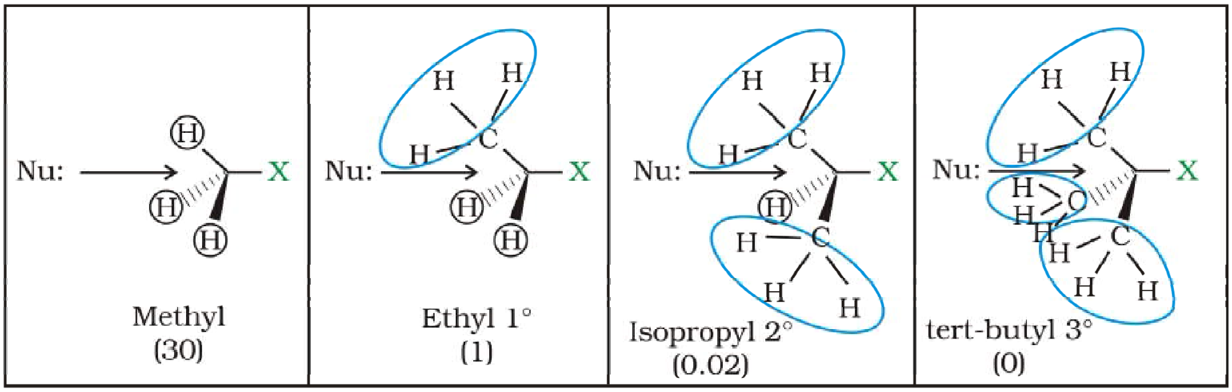


Fig.10.3: Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

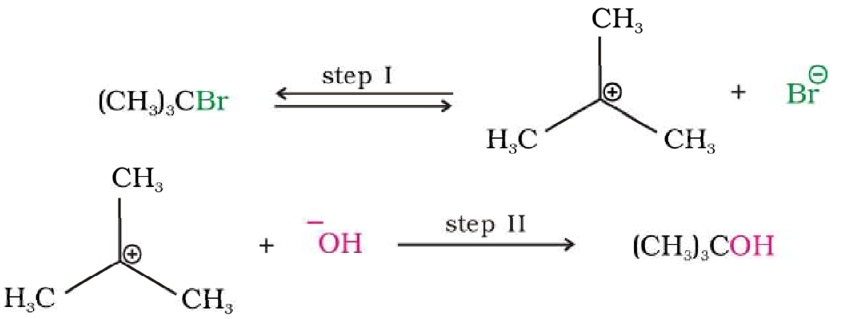
(b) *Substitution nucleophilic unimolecular (S_N1)*

S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between *tert*-butyl bromide and hydroxide ion yields *tert*-butyl alcohol and follows the first order kinetics, *i.e.,* the rate of reaction depends upon the concentration of only one reactant, which is *tert*- butyl bromide.

$$(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^{-}$$

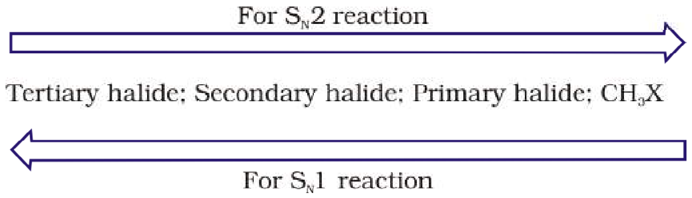
2-Bromo-2-methylpropane 2-Methylpropan-2-ol

It occurs in two steps. In step I, the polarised C
slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.

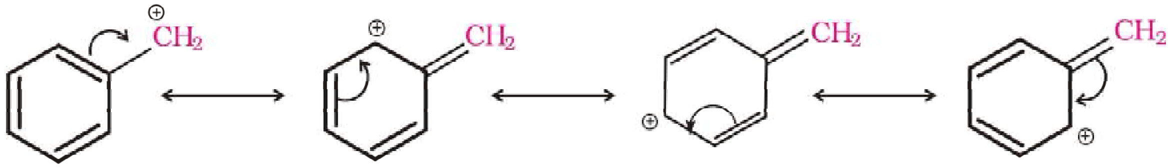


Step I is the slowest and reversible. It involves the C

energy is obtained through solvation of halide ion with the proton of protic solvent. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations. We can sum up the order of reactivity of alkyl halides towards S_N1 and S_N2 reactions as follows:



For the same reasons, allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance (Unit 12, Class XI) as shown below:

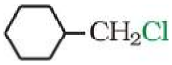


For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms R

the following pairs of halogen compounds, which would undergo $_N2$ reaction faster?

Example 10.6

Solution



It is primary halide and therefore undergoes S_N2 reaction faster.

As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Example 10.7

redict the order of reactivity of the following compounds in S_N1 and $_N2$ reactions:

(i) The four isomeric bromobutanes

(ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Solution (i) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_N1)

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_N2)

Of the two primary bromides, the carbocation intermediate derived from $(CH_3)_2CHCH_2Br$ is more stable than derived from $CH_3CH_2CH_2CH_2Br$ because of greater electron donating inductive effect of $(CH_3)_2CH$- group. Therefore, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 reactions. $CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Hence the above order is followed in S_N1. The reactivity in S_N2 reactions follows the reverse order as the steric hinderance around the electrophilic carbon increases in that order.

(ii) $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1)

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2)

Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than obtained from $C_6H_5CH(CH_3)Br$ because it is stabilised by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in S_N1 reactions. A phenyl group is bulkier than a methyl group. Therefore, $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 reactions.

(c) *Stereochemical aspects of nucleophilic substitution reactions*

A S_N2 reaction proceeds with complete stereochemical inversion while a S_N1 reaction proceeds with racemisation.

In order to understand this concept, we need to learn some basic stereochemical principles and notations (optical activity, chirality, retention, inversion, racemisation, etc.).

William Nicol (1768-1851) developed the first prism that produced plane polarised light.

(i) *Plane polarised light and optical activity*: Certain compounds rotate the plane polarised light (produced by passing ordinary light through Nicol prism) when it is passed through their solutions. Such compounds are called optically active compounds. The angle by which the plane polarised light is rotated is measured by an instrument called polarimeter. If the compound rotates the plane polarised light to the right, i.e., clockwise direction, it is called *dextrorotatory* (Greek for right rotating) or the d-form and is indicated by placing a positive (+) sign before the degree of rotation. If the light is rotated towards left (anticlockwise direction), the compound is said to be laevo-rotatory or the l-form and a negative (
the degree of rotation. Such (+) and (
are called optical isomers and the phenomenon is termed as optical isomerism.

(ii) *Molecular asymmetry, chirality and enantiomers*: The observation of Louis Pasteur (1848) that crystals of certain compounds exist in the form of mirror images laid the foundation of modern stereochemistry. He demonstrated that aqueous solutions of both types of crystals showed optical rotation, equal in magnitude (for solution of equal concentration) but opposite in direction. He believed that this difference in optical activity was associated with the three dimensional arrangements of atoms (configurations) in two types of crystals. Dutch scientist, *J. Van* and French scientist, *C. Le Bel* in the same year (1874), independently argued that the spatial arrangement of four groups (valencies) around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, such a carbon is called asymmetric carbon or stereocentre. The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule is responsible for the optical activity in such organic compounds.

Jacobus Hendricus Van received the first Nobel Prize in Chemistry in 1901 for his work on solutions.

The symmetry and asymmetry are also observed in many day to day objects: a sphere, a cube, a cone, are all identical to their mirror images and can be superimposed. However, many objects are non superimposable on their mirror images. For example, your left and right hand look similar but if you put your left hand on your right hand, they do not coincide. The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be chiral and this property is known as chirality. While the objects, which are, superimposable on their mirror images are called achiral.

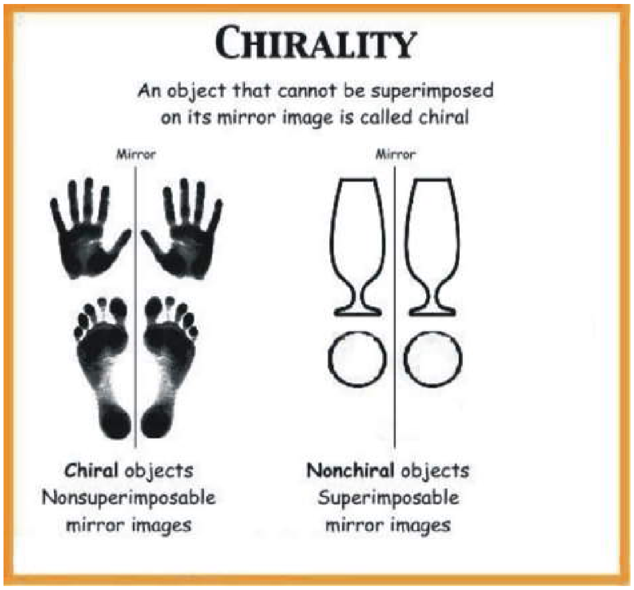
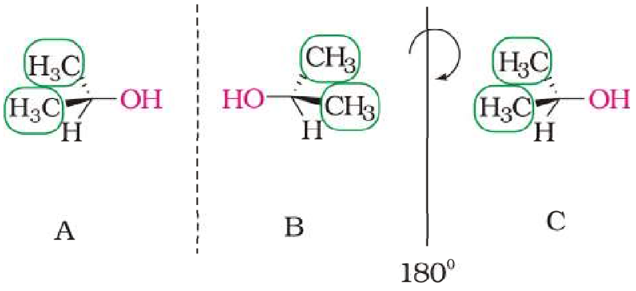


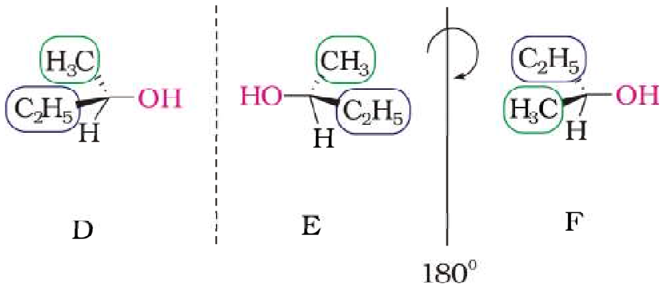
Fig 10.4: Some common examples of chiral and achiral objects

The above test of molecular chirality can be applied to organic molecules by constructing models and its mirror images or by drawing three dimensional structures and attempting to superimpose them in our minds. There are other aids, however, that can assist us in recognising chiral molecules. One such aid is the presence of a single asymmetric carbon atom. Let us consider two simple molecules propan-2-ol and butan-2-ol and their mirror images.



C obtained by rotating B by 180°
C is superimposable on its mirror image A

As you can see very clearly, propan-2-ol does not contain an asymmetric carbon, as all the four groups attached to the tetrahedral carbon are not different. Thus it is an achiral molecule.



F obtained by rotating E by 180°
F is non superimposable on its mirror image D

Butan-2-ol has four different groups attached to the tetrahedral carbon and as expected is chiral. Some common examples of chiral molecules such as 2-chlorobutane, 2, 3-dihyroxypropanal, (OHC $_2$OH), bromochloro-iodomethane (BrClCHI), 2-bromopropanoic acid (H$_3$C

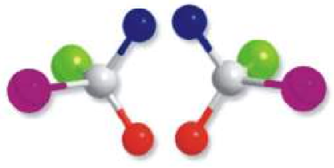


Fig. 10.5: A chiral molecule and its mirror image

The stereoisomers related to each other as non-superimposable mirror images are called enantiomers (Fig. 10.5).

Enantiomers possess identical physical properties namely, melting point, boiling point, refractive index, etc. They only differ with respect to the rotation of plane polarised light. If one of the enantiomer is *dextro rotatory,* the other will be *laevo rotatory*.

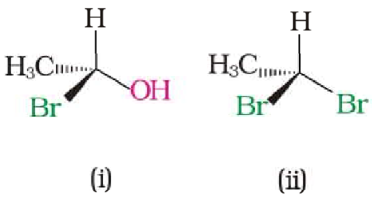
However, the sign of optical rotation is not necessarily related to the absolute configuration of the molecule.

A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification. A racemic mixture is represented by prefixing *dl* or (±) before the name, for example (±) butan-2-ol. The process of conversion of enantiomer into a racemic mixture is known as racemisation.

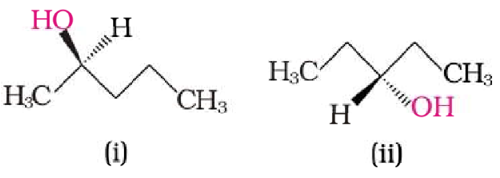
Example 10.8

Identify chiral and achiral molecules in each of the following pair of compounds. (Wedge and Dash representations according to Class XI, Fig 12.1).

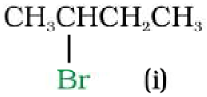
(i)



(ii)

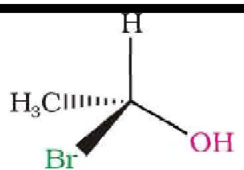


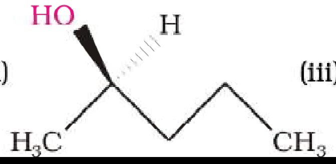
(iii)

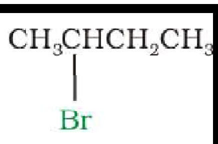


$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_2CH_3}$ (i)

$CH_3CH_2CH_2CH_2Br$ (ii)

(i) 

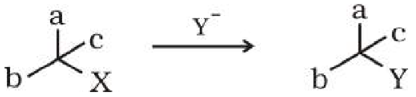
(ii) 

(iii) 

$$\underset{\displaystyle Br}{CH_3\overset{}{C}HCH_2CH_3}$$

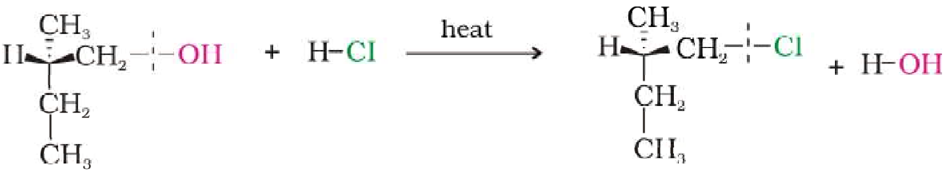
Solution

(iii) *Retention:* Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. It is also the configurational correlation when a chemical species XCabc is converted into the chemical species YCabc having the same *relative configuration*.



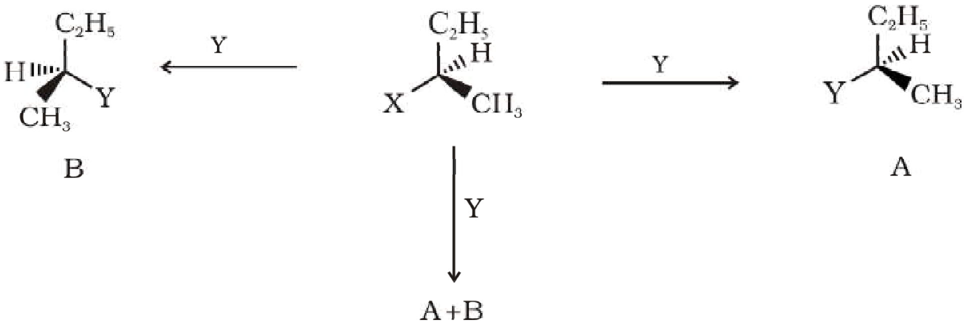
In general, if during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration of groups around the stereocentre as that of reactant. Such a reaction is said to proceed with retention of the configuration. Consider as an example, the reaction that takes place when (

is heated with concentrated hydrochloric acid.



(–)-2-Methylbutan-1-ol (+)-1-Chloro-2-methylbutane

(iv) *Inversion, retention and racemisation:* There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction;



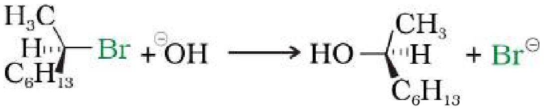
If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50:50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

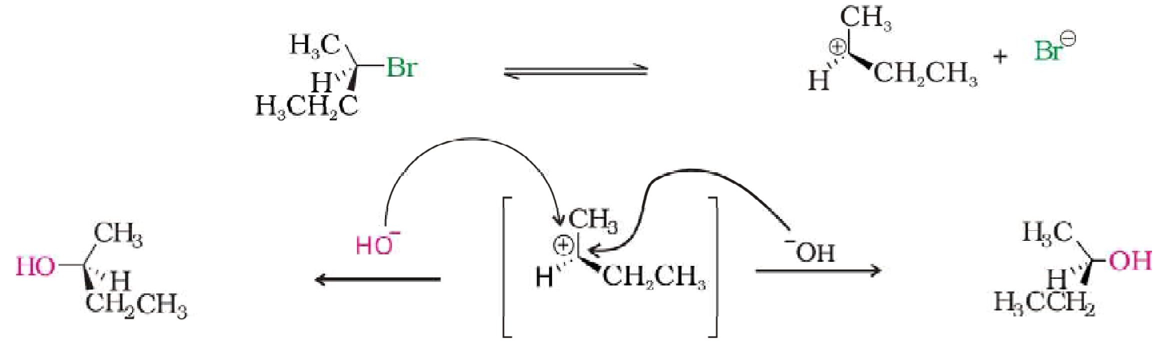
Now let us have a fresh look at S_N1 and S_N2 mechanisms by taking examples of optically active alkyl halides.

In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When
(
(+)-octan-2-ol is formed with the
opposite to what bromide had occupied.



Thus, S_N2 reactions of optically active halides are accompanied by inversion of configuration.

In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. Can you think of the reason why it happens? Actually the carbocation formed in the slow step being sp^2 hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side resulting in a mixture of products, one having the same configuration (the
as halide ion) and the other having opposite configuration (the attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butan-2-ol.

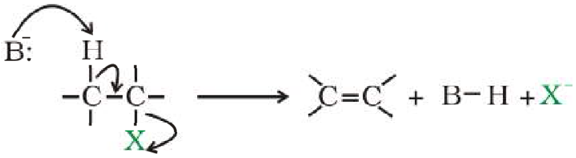


(+)-Butan-2-ol

(–)Butan-2-ol

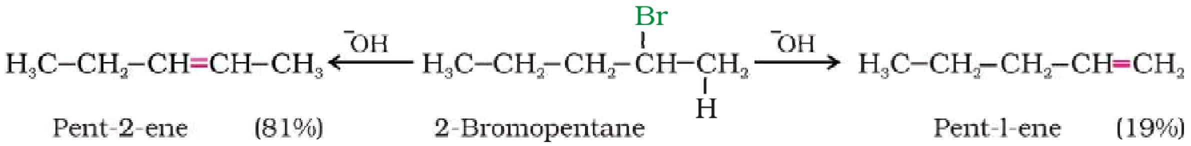
2. Elimination reactions

When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom. As a result, an alkene is formed as a product. Since β-hydrogen atom is involved in elimination, it is often called β-elimination.



B=Base ; X=Leaving group

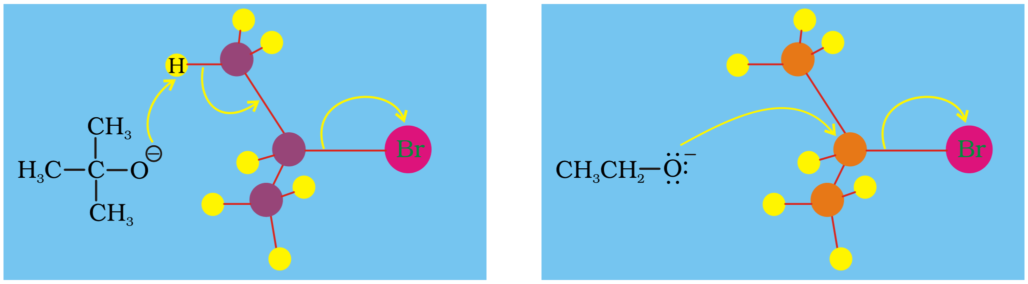
If there is possibility of formation of more than one alkene due to the availability of more than one β-hydrogen atoms, usually one alkene is formed as the major product. These form part of a pattern first observed by Russian chemist, Alexander Zaitsev (also pronounced as Saytzeff) who in 1875 formulated a rule which can be summarised as *in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms*.
pent-2-ene as the major product.



$$H_3C-CH_2-CH=CH-CH_3 \xleftarrow{^-OH} H_3C-CH_2-CH_2-\underset{H}{\overset{Br}{CH}}-CH_2 \xrightarrow{^-OH} H_3C-CH_2-CH_2-CH=CH_2$$

Pent-2-ene (81%) 2-Bromopentane Pent-1-ene (19%)

[redacted]



Elimination *vs* Substitution

3. Reaction with metals

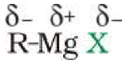
Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as organo-metallic compounds. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide, RMgX, referred as Grignard Reagents. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

Grignard reagent

Victor Grignard had a strange start in academic life for a chemist - he took a maths degree. When he eventually switched to chemistry, it was not to the mathematical province of physical chemistry but to organic chemistry. While attempting to find an efficient catalyst for the process of methylation, he noted that Zn in diethyl ether had been used for this purpose and wondered whether the Mg/ether combination might be successful. Grignard reagents were first reported in 1900 and Grignard used this work for his doctoral thesis in 1901. In 1910, Grignard obtained a professorship at the University of Nancy and in 1912, he was awarded the Nobel prize for Chemistry which he shared with Paul Sabatier who had made advances in nickel catalysed hydrogenation.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.



$$\overset{\delta-}{R}\text{-}\overset{\delta+}{Mg}\ \overset{\delta-}{X}$$

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

It is therefore necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

Wurtz reaction

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction. (Unit 13, Class XI).

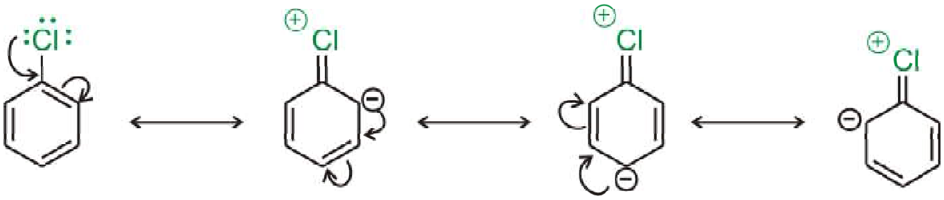
$$2RX + 2Na \longrightarrow RR + 2NaX$$

10.6.2 Reactions of Haloarenes

1. Nucleophilic substitution

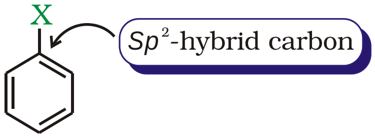
Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

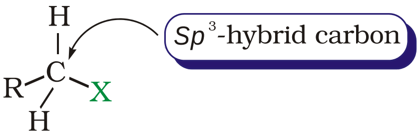
(i) *Resonance effect :* In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) *Difference in hybridisation of carbon atom in C X bond:* In haloalkane, the carbon atom attached to halogen is *sp*^{3} hybridised while in case of haloarene, the carbon atom attached to halogen is *sp*^{2}-hybridised.





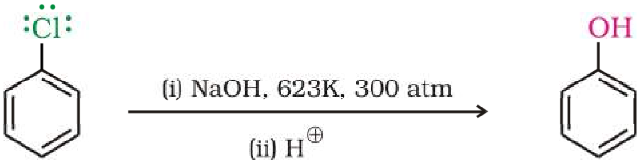
The *sp*^{2} hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C X bond more tightly than *sp*^{3}-hybridised carbon in haloalkane with less *s*-chararcter. Thus, C Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) *Instability of phenyl cation:* In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

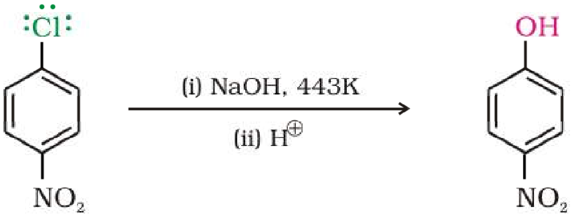
(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

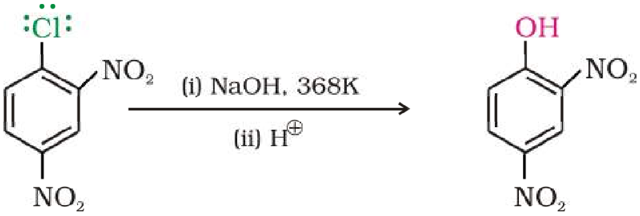
Replacement by hydroxyl group

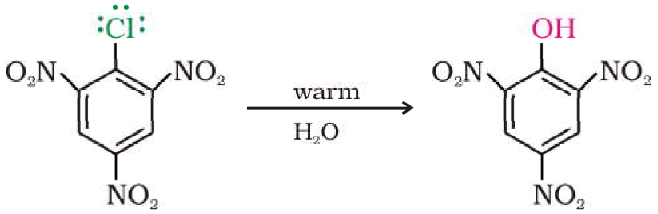
Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.



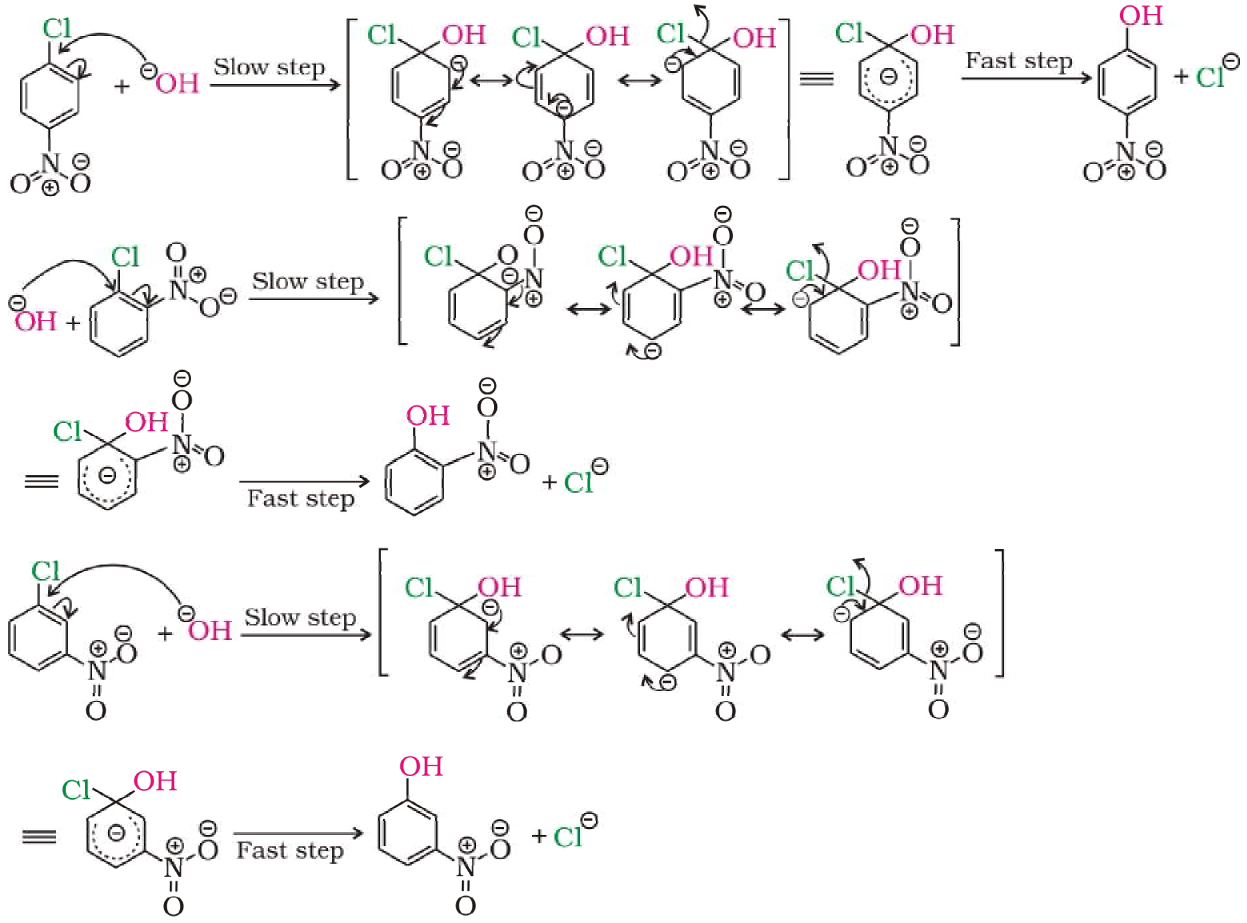
The presence of an electron withdrawing group (-NO_2) at *ortho*- and *para*-positions increases the reactivity of haloarenes.







The effect is pronounced when (-NO_2) group is introduced at *ortho*- and *para*- positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at *meta*-position. Mechanism of the reaction is as depicted:

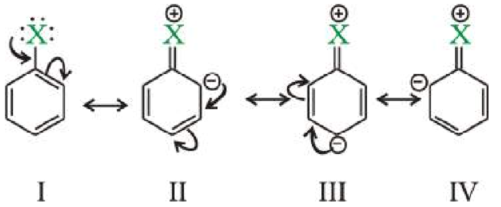


Can you think why does NO_2 group show its effect only at *ortho*- and *para*- positions and not at *meta*- position?

As shown, the presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*- positions with respect to the halogen substituent is stabilised by $_2$ group while in case of *meta*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the $_2$ group. Therefore, the presence of nitro group at *meta*- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of $_2$ group at *meta*-position.

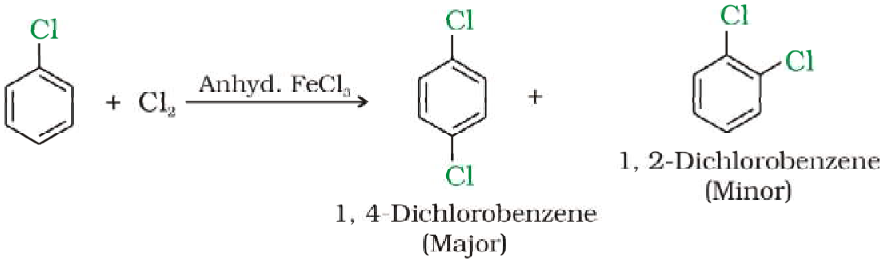
2. Electrophilic substitution reactions

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is *o, p*-directing; therefore, further substitution occurs at *ortho*- and *para*-positions with respect to the halogen atom. The *o, p*-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:

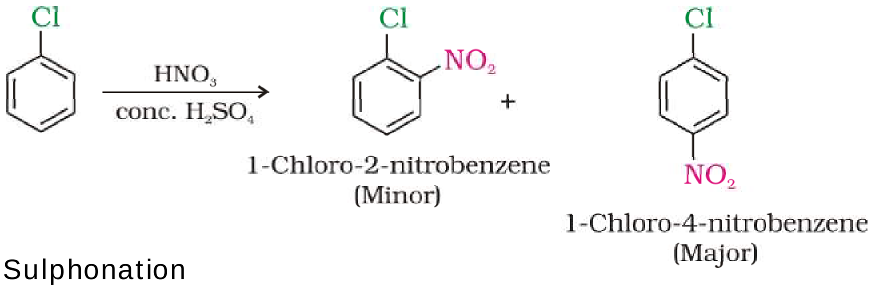


Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its
the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

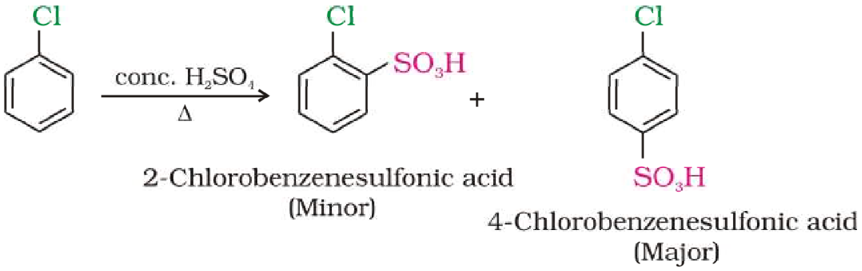
(i) Halogenation



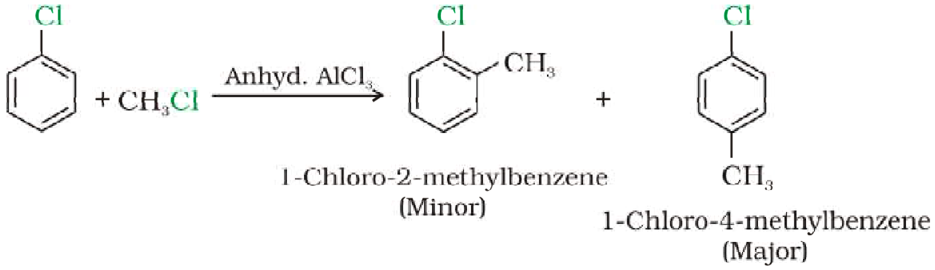
(ii) Nitration

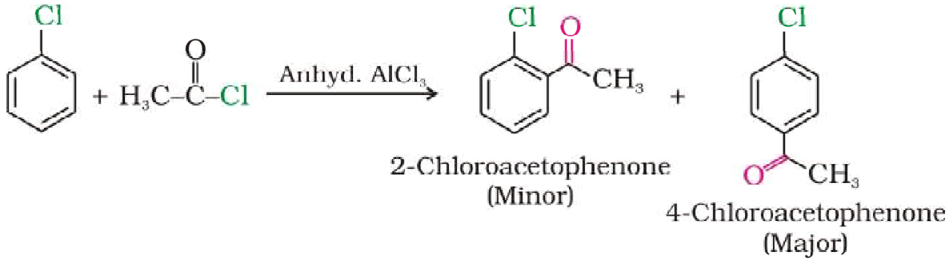


(iii) Sulphonation



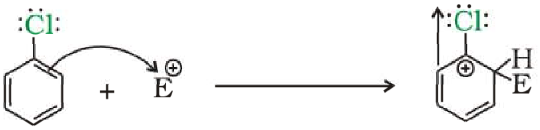
(iv) Friedel-Crafts reaction



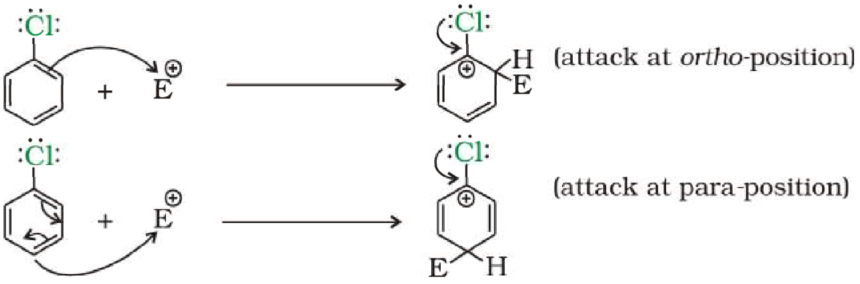


Example 10.9 Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Solution Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.



Inductive effect destabilises the intermediate carbocation



Resonance effect stabilises the intermediate carbocation

Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para*-positions and hence makes the deactivation less for *ortho*- and *para*-attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

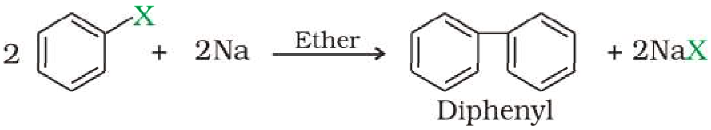
3. Reaction with metals

Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.

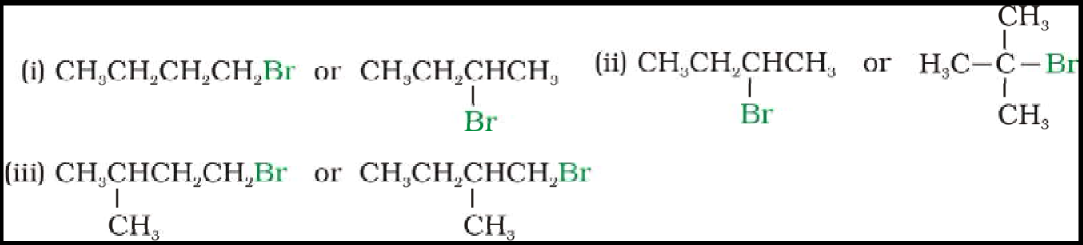
Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



Intext Questions

10.7

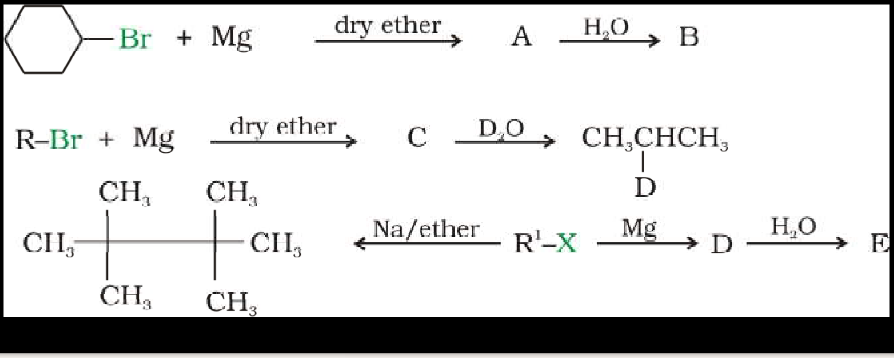


(i) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2CH(Br)CH_3$ (ii) $CH_3CH_2CH(Br)CH_3$ or $H_3C{-}C(CH_3)_2{-}Br$

(iii) $CH_3CH(CH_3)CH_2CH_2Br$ or $CH_3CH_2CH(CH_3)CH_2Br$

10.8

10.9



10.7 Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

10.7.1 Dichloromethane (Methylene chloride)

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

10.7.2 Trichloromethane (Chloroform)

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

10.7.3 Triiodomethane (Iodoform)

It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

10.7.4 Tetrachloromethane (Carbon tetrachloride)

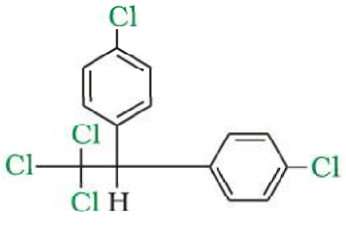
It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

10.7.5 Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. By 1974, total freon production in the world was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance (Unit 14, Class XI).

10.7.6 *p,p* -Dichlorodiphenyltrichloroethane(DDT)

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.



DDT

Summary

Alkyl/ Aryl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge, and the halogen atom bears a partial negative charge.

Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution to arenes. Fluorides and iodides are best prepared by halogen exchange method.

The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals forces of attraction. These are slightly soluble in water but completely soluble in organic solvents.

The polarity of carbon-halogen bond of alkyl halides is responsible for their nucleophilic substitution, elimination and their reaction with metal atoms to form organometallic compounds. Nucleophilic substitution reactions are categorised into S_N1 and S_N2 on the basis of their kinetic properties. Chirality has a profound role in understanding the reaction mechanisms of S_N1 and S_N2 reactions. S_N2 reactions of chiral alkyl halides are characterised by the inversion of configuration while S_N1 reactions are characterised by racemisation.

A number of polyhalogen compounds e.g., dichloromethane, chloroform, iodoform, carbon tetrachloride, freon and DDT have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving environmental hazards.

Exercises

10.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$
(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$
(iii) $CH_3CH_2C(CH_3)_2CH_2I$
(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$
(v) $CH_3CH(CH_3)CH(Br)CH_3$
(vi) $CH_3C(C_2H_5)_2CH_2Br$
(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$
(viii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$
(ix) $CH_3CH{=}CHC(Br)(CH_3)_2$
(x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$
(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$
(xii) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

10.2 Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$
(ii) $CHF_2CBrClF$
(iii) $ClCH_2C{\equiv}CCH_2Br$
(iv) $(CCl_3)_3CCl$
(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$
(vi) $(CH_3)_3CCH{=}CClC_6H_4I$-*p*

10.3 Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane
(ii) *p*-Bromochlorobenzene
(iii) 1-Chloro-4-ethylcyclohexane
(iv) 2-(2-Chlorophenyl)-1-iodooctane
(v) 2-Bromobutane
(vi) 4-tert-Butyl-3-iodoheptane
(vii) 1-Bromo-4-sec-butyl-2-methylbenzene
(viii) 1,4-Dibromobut-2-ene

10.4 Which one of the following has the highest dipole moment?

(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4

10.5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

10.6 Write the isomers of the compound having formula C_4H_9Br.

10.7 Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.

10.8 What are ambident nucleophiles? Explain with an example.

10.9 Which compound in each of the following pairs will react faster in S_N2 reaction with OH?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

10.10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane
(iii) 2,2,3-Trimethyl-3-bromopentane.

10.11 How will you bring about the following conversions?

(i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

10.12 Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
(ii) alkyl halides, though polar, are immiscible with water?
(iii) Grignard reagents should be prepared under anhydrous conditions?

10.13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

10.14 Write the structure of the major organic product in each of the following reactions:

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$

(viii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

10.15 Write the mechanism of the following reaction:

$nBuBr + KCN \xrightarrow{EtOH\text{-}H_2O} nBuCN$

10.16 Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

10.17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH.

10.18 *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.

10.19 How the following conversions can be carried out?

(i) Propene to propan-1-ol
(ii) Ethanol to but-1-yne
(iii) 1-Bromopropane to 2-bromopropane
(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to chlorobenzene
(ix) 2-Chlorobutane to 3, 4-dimethylhexane
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(xi) Ethyl chloride to propanoic acid
(xii) But-1-ene to n-butyliodide
(xiii) 2-Chloropropane to 1-propanol
(xiv) Isopropyl alcohol to iodoform
(xv) Chlorobenzene to *p*-nitrophenol
(xvi) 2-Bromopropane to 1-bromopropane
(xvii) Chloroethane to butane
(xviii) Benzene to diphenyl
(xix) *tert*-Butyl bromide to isobutyl bromide
(xx) Aniline to phenylisocyanide

10.20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

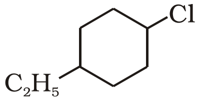
10.21 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

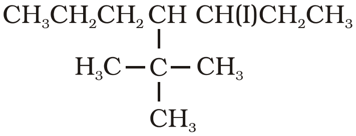
10.22 What happens when

(i) n-butyl chloride is treated with alcoholic KOH,
(ii) bromobenzene is treated with Mg in the presence of dry ether,
(iii) chlorobenzene is subjected to hydrolysis,
(iv) ethyl chloride is treated with aqueous KOH,
(v) methyl bromide is treated with sodium in the presence of dry ether,
(vi) methyl chloride is treated with KCN?

Answers to Some Intext Questions

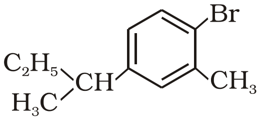
10.1 (i) $CH_3CH_2CH(CH_3)CHClCH_3$

(ii) 

(iii) 

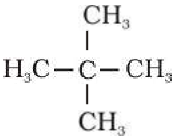
$$\mathrm{CH_3CH_2CH_2\underset{\displaystyle H_3C-\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3}{\underset{|}{CH}}\,CH(I)CH_2CH_3}$$

(iv) $BrCH_2CH = CHCH_2Br$

(v) 

10.2 (i) H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding acid, HI which is then oxidised by it to I_2.

10.3 (i) $ClCH_2CH_2CH_2Cl$ (ii) $ClCH_2CHClCH_3$ (iii) $Cl_2CHCH_2CH_3$ (iv) $CH_3CCl_2CH_3$

10.4 (i) 

$$\mathrm{H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-CH_3}$$

All the hydrogen atoms are equivalent and replacement of any hydrogen will give the same product.

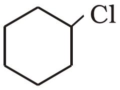
(ii) $C^aH_3C^bH_2C^cH_2C^bH_2C^aH_3$

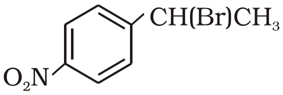
The equivalent hydrogens are grouped as a, b and c. The replacement of equivalent hydrogens will give the same product.

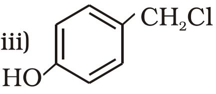
(iii) 

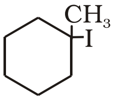
$$\mathrm{C^aH_3\underset{\underset{\displaystyle CH_3{}^a}{|}}{C^bH}C^cH_2C^dH_3}$$

Similarly the equivalent hydrogens are grouped as a, b, c and d. Thus, four isomeric products are possible.

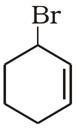
10.5 (i) 

(ii) 

(iii) 

(iv) 

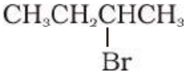
(v) CH_3CH_2l

(vi) 

10.6 (i) Chloromethane, Bromomethane, Dibromomethane, Bromoform. Boiling point increases with increase in molecular mass.

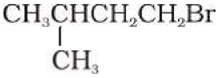
(ii) Isopropylchloride, 1-Chloropropane, 1-Chlorobutane. Isopropylchloride being branched has lower b.p. than 1-Chloropropane.

10.7 (i) $CH_3CH_2CH_2CH_2Br$ Being primary halide, there won hindrance.

(ii) 

$$\mathrm{CH_3CH_2\underset{\underset{\displaystyle Br}{|}}{CH}CH_3}$$

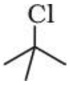
Secondary halide reacts faster than tertiary halide.

(iii) 

$$\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CH_2Br}$$

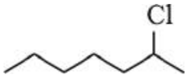
The presence of methyl group closer to the halide group will increase the steric hindrance and decrease the rate.

10.8 (i)



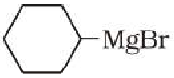
Tertiary halide reacts faster than secondary halide because of the greater stability of tert-carbocation.

(ii)

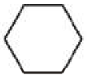


Because of greater stability of secondary carbocation than primary.

10.9 A =

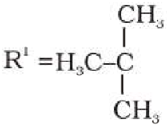


B =

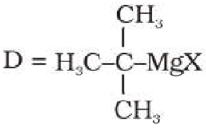


C = RMgBr R =

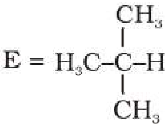
$\text{CH}_3\underset{|}{\text{C}}\text{HCH}_3$



$R^1 = H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}$



$D = H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-MgX$



$E = H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-H$