



General Chemistry 1B

ONLY STUDY GUIDE FOR CHE1502 and XHE1502

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DEPARTMENT OF CHEMISTRY

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PRETORIA

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INTRODUCTION

We take great pleasure in welcoming you as a student of the module General Chemistry 1B. This module deals with introductory principles and fundamental aspects of Organic Chemistry. We trust that you will find this module both interesting and rewarding and that you will have a successful academic semester.

Since the General Chemistry 1A module, CHE1501, is a prerequisite for the CHE1502 module, some of you may have recently studied that module. You are expected to apply the concepts and principles that you mastered in the CHE501 during the study period for the CHE1502 module.

The CHE1502 module is the introductory module for Organic Chemistry at Unisa and prepares you for further studies in Organic Chemistry at second and third levels of undergraduate studies.

Chemistry is defined as the science that deals with the composition, properties, structure of matter (substances and various elementary forms) and the changes it undergoes. Then what is *organic* chemistry all about? The most acceptable definition of organic chemistry is that it is the chemistry of compounds of carbon. Many *organic* compounds can contain hydrogen, nitrogen, oxygen, phosphorous or other elements. Organic molecules are of importance in all aspects of life. Items such as soap or detergents, plastics, cosmetics, fuel, medicines and pesticides that we use on a daily basis consist of organic compounds. By understanding how these substances are structured, chemists or chemical engineers can adapt them for various uses or even invent new substances with practical applications.

Prescribed book, study guide and structure of the module

The study material for this module consists of:

- a study guide
- a textbook
- the online platform, MasteringChemistry ©, linked to the textbook
- several tutorial letters

Textbook

The details of your textbook are as follows:

Organic Chemistry, plus MasteringChemistry®, 9th edition, Global edition, Leroy G Wade and Jan W Simek, Whitman College, August 2016, Valuepack; ISBN: 9781447963516. Publisher: Pearson.

You cannot study the CHE1502 module without the textbook and you are advised to purchase it as soon as possible (Consult Tutorial Letter 101 regarding options to access the textbook). Note that this textbook is used for first, second and third level undergraduate Organic Chemistry at Unisa.

The textbook in conjunction with MasteringChemistry® directs you to what you need to know. At the end of each chapter, there is a section called "Vocabulary" that includes the main facts and fundamental principles covered in the chapter. The textbook captures the vast number of reaction mechanisms into fundamental mechanisms that can be extended to more complicated mechanisms in "Key Mechanism" boxes. There are also *Problem-Solving Strategies* and *Solved Problems*. At the end of some chapters, you will find a "*Guide to Organic Reactions*" which describes different kinds of reactions and how the reactions covered in the chapter fit into the overall body of the book. The *Appendix 5: Summary of Organic Nomenclature* is a condensed reference of the rules for naming organic compounds.

Study guide

The study guide supports the textbook. It leads you through the study material contained in the textbook that is relevant to CHE1502. Each topic in the study guide consists of the following:

- (i) A brief description of the topics that will be studied.
- (ii) A list of the intended learning outcomes for each topic.
- (iii) A brief introduction to the topic.
- (iv) Study material.
- (v) A number of self-assessment questions appear under Activities in each section.

You should pay special attention to the key terms printed in bold. The activities provide you with practice in solving problems based on the theory covered, and serve as a guide for making notes. The questions indicated as "*problems*" can be found in the prescribed textbook. The answers to those questions can be found in one of the appendices, "*Brief Answers to Selected Problems*". The answers to the other questions in the activities are at the end of each study unit. If your answers are incorrect and you are not sure why, please ask your e-tutor or lecturer for an explanation.

Not all the information in a particular chapter in the textbook is relevant to this module. The study guide explicitly indicates which sections in the textbook fall within the scope of this module. You should read the relevant sections of each study unit before using the textbook.

MasteringChemistry®

The online platform, MasteringChemistry®, is available at: www.masteringchemistry.com. The MasteringChemistry site contains "*Dynamic Study Modules*" that allow you to study at your own pace and develop a better understanding of the fundamental concepts needed from General Chemistry 1A and in each chapter.

Each *Dynamic Study Module* contains a personalised set of questions for you to answer and enable you to understand the organic concepts quicker.

The programme also provides feedback, with an explanation of correct and incorrect answers. This feedback process is repeated until you answer a question correctly.

Purpose

The purpose of the CHE1502 module is that you, after completing this module, should be able to explain and apply chemical bonding and introductory organic chemistry principles. These principles include chemical bonding, physical properties, introduction to stereochemistry and the nature and behaviour of hydrocarbons, hydrocarbon derivatives (alkyl halides, alcohols and ethers), amines and carbonyl compounds (aldehydes, ketones, carboxylic acids, acid halides, esters and amides).

Learning outcomes

After completing this module, you should be able to:

- explain and apply the basic concepts related to molecules and ions to illustrate properties, behaviour and reactivity
- explain and apply concepts, properties and chemical reactivity related to saturated hydrocarbons
- formulate and describe the following:
 - physical and chemical properties of unsaturated hydrocarbons (alkenes and alkynes)
 - various structural and stereoisomers
 - physical and chemical properties of alcohols and ethers, alkyl halides, and amines
- describe the electronic structure and reactivity of carbonyl and carboxyl compounds

Structure of the module

The table below provides an overview of the module.

| Theme | Study unit no | Main topic | Contents |
|--|---------------|--|---|
| FUNDAMENTAL CONCEPTS IN ORGANIC CHEMISTRY | 1 | Structure and bonding | Hybridisation of carbon- sp^3 , sp^2 , sp ; bond polarity, dipole moment; bond formation and bond breakage; electron flow and homolytic and heterolytic; Lewis structures and formal charges; resonance structures and delocalisation; understanding the definition of electrophiles, nucleophiles and free radicals |
| | 2 | Acids and bases; functional groups | Intermolecular forces – London dispersion forces, van der Waals forces, dipole-dipole interaction and hydrogen bonding; polarity effects on solubility; Lewis acids and bases |
| SATURATED ORGANIC COMPOUNDS | 3 | Structure and properties of alkanes | Structure and nomenclature; physical properties; reactions; mechanism for the halogenation of alkanes; structural isomers; conformations (Newman and Sawhorse projections) |
| | 4 | The study of chemical reactions | Free radical chain reaction; mechanism in the halogenation of alkanes; reactive intermediates; free radicals and carbocations; factors that affect their stability; halogenation of higher alkanes |
| | 5 | Introduction to stereochemistry | Stereochemistry - 3-dimensional representations of simple organic molecules, chirality and R- and S-configurations |
| | 6 | Alkyl halides | Structure and nomenclature; physical properties; classification as primary, secondary or tertiary alkyl halides; selected nucleophilic substitution reactions; selected elimination reactions |
| | 7 | Saturated compounds containing oxygen and nitrogen | Alcohols: structure and nomenclature; physical properties; classification of alcohols as primary, secondary, or tertiary; stereochemistry – 3-dimensional representations of simple organic molecules, chirality and R- and S-configurations; selected reactions of alcohols: oxidation and the formation of alkyl halides, ethers and alkenes |

| | | | |
|--------------------------------------|----|---|---|
| | | | Ethers: structure and nomenclature; physical and chemical properties |
| | | | Amines: nomenclature, classification and structure; properties; reactivity / basicity |
| UNSATURATED ORGANIC COMPOUNDS | 8 | Alkenes | Structure and nomenclature; physical properties; geometric isomerism (cis/trans and E/Z configurations); reactions and mechanisms of hydrohalogenation, acid catalysed hydration and halogenation of symmetrical and unsymmetrical alkenes and the application of Markovnikov's rule; mechanism of hydrohalogenation of unsymmetrical alkenes in the presence of peroxides (anti-Markovnikov's addition); hydrogenation of alkenes. |
| | 9 | Alkynes | Structure and nomenclature; physical properties; reactions and mechanisms of hydration, halogenation and hydrohalogenation of symmetrical and unsymmetrical alkynes (Markovnikov's rule); hydrogenation of alkynes; acidity / reactivity of terminal alkynes. |
| | 10 | Carbonyl compounds and derivatives | Ketones and aldehydes: Structure and nomenclature of ketones and aldehydes; properties and reactivity of ketones and aldehydes. Carboxylic acids and derivatives Structure and nomenclature of carboxylic acids and carboxylic acid derivatives (esters and amides); properties and reactivity of carboxylic acids and carboxylic acid derivatives |

Assessment

Your first tutorial letter (Tutorial Letter 101) provides details about the assignment system. Read the entire tutorial letter carefully, in particular, the section dealing with closing dates for the submission of assignments. This tutorial letter also contains the assignment questions.

The format of the CHE1502 assignments involves multiple-choice questions, written questions AND online questions (via MasteringChemistry©).

The examination will be written at the end of each semester. The exam admission procedures are also explained in the Tutorial Letter 101.

The language of Organic Chemistry

In order to read and understand organic chemistry texts, you need to be aware that this subdiscipline of chemistry has its own peculiar vocabulary. The language is commonly graphical with specific ways of drawing structures and naming them. Normal punctuation rules do not apply when naming organic compounds in a systematic way. Furthermore, the use of arrows showing the movement of electrons and reaction mechanisms is a symbolic language used by organic chemists.

Strategies to be successful in this module:

The following STUDY PROCEDURE may be helpful during your studies of this module:

- (i) Before studying a particular topic, read the learning goals and the introduction to the topic and page through the chapter in the textbook in order to obtain an overview of the study material.
- (ii) You should always work systematically through the relevant topics of the study guide and corresponding chapters in the textbook by using rough paper and pen as often as possible. Write down formulas and structures of molecules and ions, electron flow processes, chemical reactions and reaction mechanisms.
- (iii) Take note of important terms and concepts given in boldfaced type in the textbook, and learn their definitions.

- (iv) It is important that you do not proceed to the next topic without being able to reproduce the salient parts of the previous topic in writing, without looking at the text.
- (v) Attempt the questions in each activity in each topic of the study guide. If you cannot do a particular question, revise the relevant study material and attempt the question again.

You need to have a clear understanding of the concepts before you can learn how to apply the concept to solve problems. The following online resources provide further guidance on how to successfully study organic chemistry.

A video on how to study organic chemistry:

<http://chemistry.umeche.maine.edu/CHY251/howto.html>

How to do well in organic chemistry:

<https://www.youtube.com/watch?v=YQkcNeIqdoU>

<http://www.masterorganicchemistry.com/2011/01/17/how-to-do-well-in-organic-chemistry-one-students-advice/>

How to solve organic chemistry problems:

<http://chemistry.umeche.maine.edu/CHY252/Think.html>

<https://home.cc.umanitoba.ca/~hultin/chem2220/Support/WhatHowWhy.pdf>

Sources consulted

1. **Organic chemistry**, 9th edition, Global Edition, Leroy G Wade and Jan W Simek, 2016, Pearson.
2. **Chemistry industry and the environment**, James N Lowe, 1994, Wm C Brown Publishers.
3. **Organic chemistry**, 3rd edition, International Edition, Robert C Atkins and Francis A Carey, 2002, McGraw Hill.

THEME 1

FUNDAMENTAL CONCEPTS IN ORGANIC CHEMISTRY

In this theme, we will review concepts of atomic and molecular structure and introduce new concepts that are essential for success in this module. Although you may not be assessed in all the concepts, a thorough understanding of these concepts is necessary to grasp the organic chemistry content that is covered in this module and subsequent modules.

STUDY UNIT 1

Structure and bonding

- 1.1 Introduction
- 1.2 Principles of atomic structure
- 1.3 Chemical bond formation
- 1.4 Lewis structures
- 1.5 The curved-arrow formalism
- 1.6 Resonance
- 1.7 Hybridisation and molecular shapes
- 1.8 Structural formulas
- 1.9 Isomerism
- 1.10 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- apply the various types of covalent bonding and ionic bonding to organic compounds
- draw Lewis structures and determine formal charges
- explain and apply the hybridisation and energy level diagrams in the formation of single and multiple bonds (sigma and pi bonds)
- illustrate the movement of electrons with curved arrows when showing electron delocalisation in resonance, bond-breaking and bond-making processes
- use the different structural formulas to represent organic compounds
- construct and identify constitutional isomers

1.1 Introduction

Have you ever wondered why table salt dissolves in water but not in sunflower or olive oil? Also, why inorganic compounds in general tend to have high melting points and many of their solutions in water conduct electricity, whereas organic compounds are mostly low-melting solids, liquids or gases and their water solutions do not conduct electricity?

The type of bonding that exists in these compounds plays a major role in their physical properties and behaviour. The main types of bonds that exist between atoms are ionic and covalent bonds. In **inorganic** compounds, the constituent atoms are held together by **ionic** bonds, whereas **organic** compounds in general are formed because of **covalent** bonds between atoms.

In this study unit, we will revise theoretical concepts from the General Chemistry 1A module that are vital for acquiring the objectives of this module. These include principles of atomic structure, chemical bonding and the polarity of bonds, hybridisation, the drawing of Lewis structures and the determination of formal charges. In addition, we will focus on the fundamental concepts that are essential in the understanding of the subsequent study units, such as the utilisation of curved arrows to show the movement of electrons, resonance delocalisation, the drawing and interpretation of structural formulas as well as the prediction of physical properties of organic molecules.

1.2 Principles of atomic structure (Wade et al section 1-2)

As you know, atoms consist of protons, neutrons and electrons, with the positively charged protons and neutral neutrons being located in the nucleus of the atom. The electrons are negatively charged and can be found in orbitals around the nucleus. There are four different types of orbitals, called s, p, d and f orbitals, each with a different shape.

Since organic chemistry is centred on the chemistry of the carbon atom, attention will be given to the s and p orbitals found in carbon (shapes shown below).



The orbitals are found in different **electron shells** and each successive shell is higher in energy and larger in size than the previous shell – the number of orbitals also increases as the shell becomes larger and further removed from the nucleus.

The first electron shell contains only one s-orbital. The second electron shell has one s-orbital and three p-orbitals, with the p-orbitals pointing towards the x-, y- and z- axes, respectively. Each orbital can accommodate a maximum of two electrons according to Pauli's exclusion principle. The 2p orbitals are higher in energy than 2s orbitals but the three p-orbitals have the same energy and are called degenerate orbitals. Carbon is able to form numerous compounds due to different combinations of the s- and p-orbitals that we will discuss later.

The distribution of electrons of an atom is called its **electron configuration** and electrons that are found in the outermost shell of an atom are called **valence electrons**. How do electrons fill up the orbitals? According to Hund's rule, electrons will occupy all orbitals of the same energy before pairing begins. An illustration of the electronic configurations of the first ten elements in the periodic table can be found in Table 1-1 in Wade LG and Simek JW. The table also shows the valence electrons of each atom.

1.3 Chemical bond formation (Wade et al section 1-3)

Atoms will combine with other atoms to form different bonds in order to obtain a completely filled outer shell of electrons. A filled outer electron shell is similar to the electronic configuration of a noble gas and this way of filling the outer electron shell is called the **octet rule**. Different theories have been proposed to describe how atoms combine to form molecules.

The combination of atoms is called bonding and in this process, each atom will have a filled outer shell of electrons. Atoms can form a bond via two modes:

- a) due to the electrostatic attraction between ions with opposite charges (ionic bonding)
- b) by sharing electrons (covalent bonding)

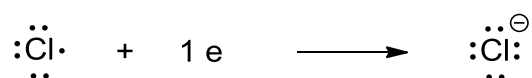
Chemical reactions (bond formation or breakage) involve the movement of valence electrons from a region of high electron density to a region of less electron density. The concept of **electronegativity**, that is, the tendency of an atom to attract a pair of bonding electrons to itself in a molecule, plays a significant role in the nature of a chemical bond and how it reacts.

1.3.1 Ionic bonding (Wade et al section 1-3A)

The elements in Group 1A (in the periodic table) each have 1s electron in its outer electron shell. These elements can **lose** the one **electron** to form a **cation**, which has a filled outer shell, for example the sodium atom:



A halogen (Group 7A element) such as a chlorine atom, on the other hand, has seven outer electrons and when it **takes up** another **electron**, the atom obtains an octet such as the formation of the **anion**:



The electrostatic attraction between the sodium cation and the chloride anion is called an **ionic bond** that is found in the ionic compound sodium chloride (NaCl), also known as table salt.

Atoms react in such a manner that the **non-metals**, which are more electronegative elements, tend to **gain electrons** to attain the noble gas configuration whereas the **metals**, which are electropositive elements, tend to **lose electrons** to obtain the noble gas configuration (octet).

1.3.2 Covalent bonding and bond polarity (Wade et al sections 1-3B and 1-6)

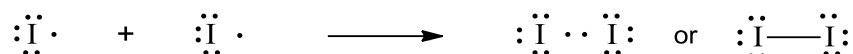
In a compound that is formed when two or more atoms combine, each bond between the two atoms is formed by the sharing of two valence electrons, with each atom providing one electron. This sharing of two electrons is called a **covalent bond**. In a covalent bond, each atom usually has a **noble gas configuration (octet)**. Normally, this type of bonding is prevalent in compounds formed by non-metals like carbon.

EXAMPLES

Two hydrogen atoms can combine to form hydrogen gas, H₂, and this bonding is illustrated as follows:



The element iodine, I₂, consists of two iodine atoms that are shown below:



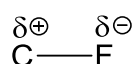
In the General Chemistry 1A module, you learnt that electronegativity is the attraction that an atom has on the bonding electrons and the electronegativity value of an atom.

Electronegativity is indicated with the symbol, χ . We will utilise this concept of electronegativity and expand its application to organic chemistry. For example, if we consider the molecules H₂ and I₂ above, the same type of atom is involved in the bond formation and therefore the bonding electrons are attracted with the same intensity by each atom. This type of bond is called a **non-polar bond**.

A covalent bond that exists between two different atoms, where the one atom attracts the bonding electrons stronger than the other atom, is quite different to a non-polar covalent bond.

The unequal sharing of the negatively charged bonding electrons by two atoms result in the bond being polarised, and this type of covalent bond is called a **polar covalent bond**. An example of a polar covalent bond is the carbon-fluorine bond.

A table with the values of the electronegativity of atoms is shown in Figure 1-8 in Wade et al. You only have to know the general trends of the electronegativity values in a group or period of the elements in Figure 1-8 in Wade et al. The electronegativity difference between C and H or between B and H is small. Therefore, a carbon-hydrogen bond or a boron-hydrogen bond is non-polar. The carbon-fluorine bond is polar due to a difference in electronegativity of 1.5 between carbon and fluorine ($X_F > X_C$). The polar C-F bond in, for example, the molecule CH_3F is represented as:



Using the symbol δ above each atom indicates that a partial charge exists above each atom, with carbon being partial positive and fluorine partial negative. Bear in mind that the above presentation is only the illustration of the C-F bond. Considering the fact that C does not have an octet and it must have four bonds attached to it, the C-F bond should be part of a molecule such as CH_3F .

In general, non-polar covalent bonds form between atoms where the difference in electronegativity is less than 0.4. Electronegativity differences of 0.4 to 1.7 between atoms result in the formation of polar covalent bonds. If the difference in electronegativity between two atoms is greater than 1.7, then such atoms will form ionic bonds. We will further discuss the polarity of bonds and molecules in study unit 2.

In section 1.5 below, we will illustrate exactly how the different covalent bonds form and break. You are encouraged to watch the video on covalent bonding via the following link: <https://www.youtube.com/watch?v=mKhTm0UUcn8>

ACTIVITY 1.1

Do Problem 1-5.

We shall discuss the specific bonding of the carbon compounds having single, double and triple bonds later in the section dealing with hybridisation.

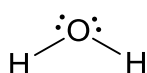
1.4 Lewis structures (Wade et al sections 1-4 and 1-5)

In the CHE1501 module, you encountered Lewis structures. Why are Lewis structures important in organic chemistry? Lewis structures help us to predict how bonds will break or how a reaction will take place. In particular, it is the way structures of molecules and ions are drawn showing the bonds and electrons *not* involved in bonding that makes this possible.

1.4.1 How to draw Lewis structures

Each respective atom has an octet in the drawing of the Lewis structure of a molecule, each valence electron of the individual atoms is indicated with a • and a pair of bonding electrons is shown as a line (—).

Let us consider the water molecule, H₂O. The oxygen atom has six valence electrons and each hydrogen atom has one valence electron. Therefore, the oxygen contributes six electrons and the two hydrogen atoms contribute two electrons to furnish eight electrons in total. When the eight electrons surround the oxygen atom, it has an octet and when each hydrogen atom shares an electron with oxygen, each hydrogen atom will have an octet. The Lewis structure of H₂O is:



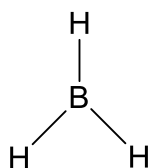
The unshared electrons in the structure above are referred to as the **lone pair** (non-bonding pair) of electrons on oxygen. Carefully study the examples containing carbon in the textbook.

The sharing of electrons between the oxygen and a hydrogen atom in the structure above is called a **single bond**. In order to obtain an octet structure, atoms sometimes form double and triple bonds. A **double bond** is formed when two pairs of electrons are being shared between two atoms and is denoted as = in the structure.

The denotation \equiv represents a **triple bond** that is formed by the sharing of three electron pairs between two atoms. Evaluate examples of the structures containing C=C and C \equiv C bonds as shown in section 1-5 in Wade et al.

The carbon atom can have a maximum of four bonds around it and hydrogen will always form only one bond.

There are exceptions to the octet rule, where atoms which are part of stable compounds have more than eight or less than eight electrons around it. Compounds containing the boron atom are frequently used in organic reactions, and in these compounds the boron atom has six electrons around it. An example is borane, BH₃, with the B atom having three outer electrons and each H atom having one valence electron. The total number of valence electrons available for bonding is thus six, which leads to the following Lewis structure.

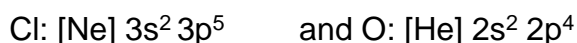


The fact that the boron atom has an empty orbital contributes to its usage in organic reactions and we will explore this further when we discuss acids and bases in study unit 2.

EXAMPLE

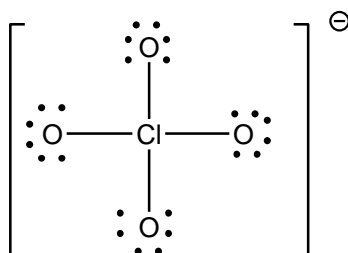
Draw the Lewis structure of the ClO₄⁻ ion.

Answer: Electronic configurations of each atom in ClO₄⁻:



The number of electrons available for bonding in ClO₄⁻ is: no of valence \bar{e} of Cl + 4 (no of valence \bar{e} of O) + 1 \bar{e} (for charge of -1) = 7 + 4(6) + 1 = 32 electrons

The Lewis structure of ClO_4^- is:



In the ClO_4^- ion, the central Cl atom forms four sigma bonds (single bonds) with each O atom and Cl contributes seven electrons *minus* the central Cl atom that has the seven electrons *plus one* electron (from the -1 charge) available for bonding with O. How these orbitals are constructed will be dealt with later.

You can watch the video on Lewis structures via the links:

<https://www.youtube.com/watch?v=1ZInzyHahvo>

<https://www.youtube.com/watch?v=8JsK6rPpi70>

ACTIVITY 1.2

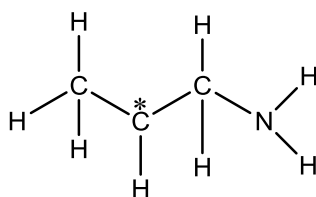
Draw the Lewis structure of a molecule with molecular formula CH_3CONH_2 .

1.4.2 Formal charges (Wade et al section 1-7)

When we write a Lewis structure, it is sometimes necessary to assign positive or negative charges to certain atoms in a molecule or ion. These charges are called **formal charges** and formal charges are determined as follows:

Formal charge, FC = Group number of atom – number of lone pair electrons – $\frac{1}{2}$ [no of bonding electrons]

Let us determine the formal charge on the carbon atom marked with * in the structure below:

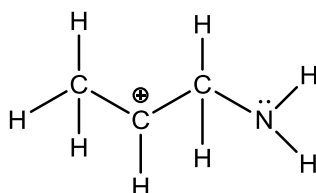


Formal charge, FC, calculation:

FC = Group number of the atom – number of lone pair electrons – $\frac{1}{2}$ [no of bonding electrons]

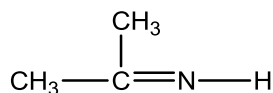
For the C atom, FC = 4 - 0 - $\frac{1}{2}$ [6] = 4 - 3 = +1
FC (C*) = +1.

The correct Lewis structure is:



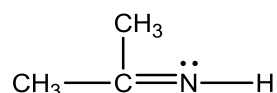
EXAMPLE

Determine the formal charge on N in the structure below:



Answer:

The redrawn structure, showing the lone pair (non-bonding) electrons is:



Formal charge, FC, = [Group number of the atom – the number of lone pair electrons – $\frac{1}{2}$ (number of bonding electrons)]

For the N atom, FC = 5 - 2 - $\frac{1}{2}$ (6) = 3 - 3 = 0

Therefore, the formal charge on nitrogen in the given structure is 0.

Study solved problem 1-1 in Wade et al. You can watch a video on formal charges via:
https://www.youtube.com/watch?v=dNPs-cr_6Bk

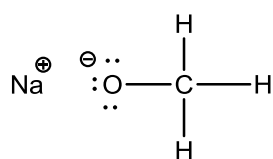
ACTIVITY 1.3

Do Problems 1-6 and 1-34.

If your answers are incorrect and you are not sure why, please ask your e-tutor or lecturer for an explanation.

1.4.3 Ionic structures (Wade et al sections 1-8)

Organic compounds may also exist as ionic compounds. This is normally the case where we have complex ions where one of the ions has atoms that are covalently bonded to each other. As an example, the compound sodium methoxide is extensively used as a reagent in organic reactions. The structure of sodium methoxide is:



There is an ionic bond between the positively charged Na and the negatively charged O. The atoms in the methoxide, OCH₃, group are connected via covalent bonds.

1.5 The curved-arrow formalism (Wade et al sections 1-6 and 2-14)

Organic chemists normally use this type of notation to show the direction of the movement of electrons during bond formation or breakage. Bond formation and bond breakage involve the movement of either one or two electrons (**note**: only electrons move). The movement of electrons is illustrated by either a half-headed curved arrow or full-headed curved arrow. Each half of the arrow represents a single electron and the curved line represents movement of the electron(s).



Half-headed curved arrow
Movement of a **single electron**



Full-headed curved arrow
Movement of **two electrons**

1.5.1 Formation and breakage of non-polar covalent bonds

In section 1.3.2 above, we discussed that a non-polar covalent bond forms between atoms of similar electronegativity. For example, when one electron from each hydrogen atom is involved in the bond formation to form a hydrogen molecule, we use a half-headed curved arrow to illustrate the movement of electrons. Elements comprising a diatomic molecule of similar atoms are held together by a covalent bond in which the bond pair electrons are equally shared between the two atoms (H_2 , N_2 , O_2 , X_2 where X is a halogen). The two atoms comprising a hydrogen molecule (H_2) or halogen molecule (X_2), for example, have equal electronegativity and therefore the bond pair electrons between them are equally shared and the entire molecule is non-polar. It is important to note that although there are only two electrons, when counting electrons belonging to each element in H_2 , the bond pair electrons form part of the total count per hydrogen atom. This simply means that the bond pair electrons belong equally to either atom, that is, each hydrogen has two electrons to itself.

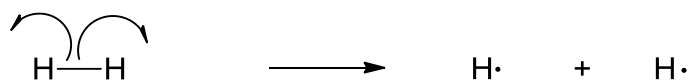
When two similar halogen atoms ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) react to form diatomic molecules (X_2), each element in the molecule has eight electrons around itself. It is important to note that although there are only two electrons in the bond, when counting electrons around each element in X_2 , the bond pair electrons form part of the total count per halogen atom, that is, eight electrons. Keep in mind that equal sharing in chemical terms does not mean dividing into equal halves, but to have equal ownership at any given time. *Remember: the bond (-) in any molecule or ion denotes two electrons.*

Examples of non-polar covalent bond formation and breakage:

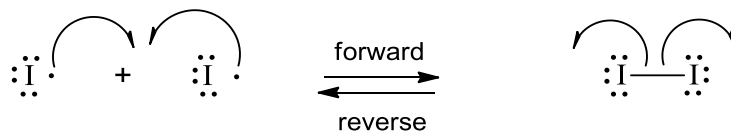
Bond formation:



Bond breakage:



The element iodine, I₂, also consists of two identical iodine atoms. The bond formation and bond breaking can be shown in one equation, because the formation is also reversible:



When either the hydrogen molecule or halogen molecule is formed, each atom has an unpaired electron that they share to form a covalent bond. We illustrate the movement of these electrons during bond formation by half-headed curved arrows moving from the unpaired electron on each atom to an area between the two atoms to form a bond.

When either hydrogen molecule or halogen molecule breaks or cleaves into two elements, each atom gains a **single electron**.

We illustrate the movement of these electrons during bond breakage by **half-headed curved arrows** moving from the middle of the bond to the respective atom (reverse reaction). This type of bond cleavage is called **homolysis** or **homolytic** bond cleavage.

1.5.2 Formation and breakage of polar covalent bonds

When two elements (non-metals) of different electronegativity react to form a bond, each atom contributes one electron to the bond pair. We use half-headed arrows that meet between the two atoms to illustrate the movement of electrons (forward reaction). When bonded together to form a molecule, the situation changes and the atom of high electronegativity pulls the bond pair electrons towards itself, rendering the less electronegative element electron poor.

The electron density becomes concentrated largely closer to the more electronegative atom, leaving the other element of less electronegativity electron poor or deficient.

As a result, the bond becomes polarised (positive and negative poles), with the atom of high electronegativity attaining a partially or slightly negative charge (represented as δ^-) and the one with less electronegativity becoming slightly or partially positive (represented as δ^+). Such a covalent bond in which the bond pair electrons are attracted towards the atom with high electronegativity is termed a polar covalent bond.

A curved arrow usually begins at an unshared pair of electrons or a covalent bond. The curved arrow moves in the direction where there is a need for electrons, for instance to an atom that is electron deficient.

Example of polar covalent bond formation:

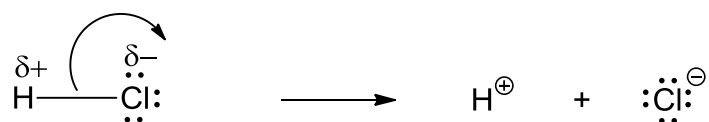


Polar covalent bonds form mostly between non-metals.

When we count electrons around each element, the bond pair electrons form part of the total count per atom. For example, in H-Cl, there are two electrons around hydrogen (these are the bond pair electrons) and eight electrons around the chlorine atom (these are the three pairs of nonbonding electrons and the bond pair electrons).

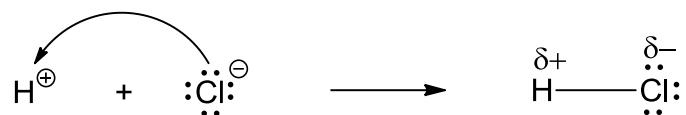
When in turn a polar covalent bond breaks, both bond pair electrons are then taken away by the atom of high electronegativity. To illustrate this type of bond cleavage, we use a full-headed curved arrow to illustrate the movement of two electrons from the middle of the bond over to the atom of high electronegativity (forward reaction). This type of bond cleavage where **both bond pair electrons** are taken away by the **more electronegative atom** is termed **heterolytic** bond cleavage or **heterolysis**.

For example:



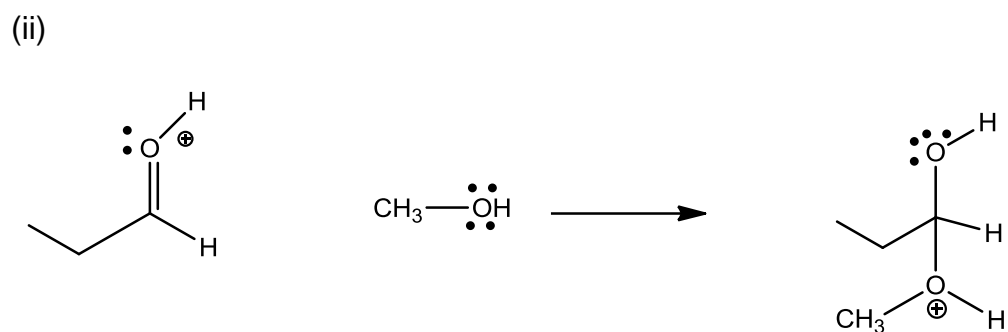
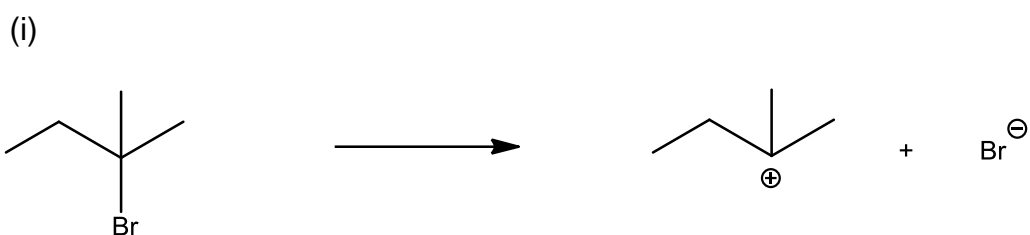
When the bond breaks, the atom of high electronegativity **gains a pair of electrons** to become a fully negatively charged ion (**anion**) and the less electronegative atom becomes fully positively charged (**cation**).

When an anion and a cation of a non-metal react, the more electron-rich ion (anion) is the one that attacks the electron-poor ion (cation) to form a polar covalent bond as shown below. The anion donates an electron pair to the cation, which is the reverse reaction of the above process.

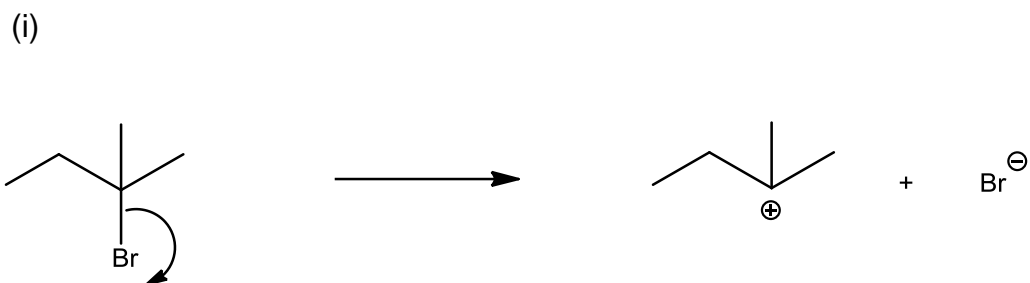


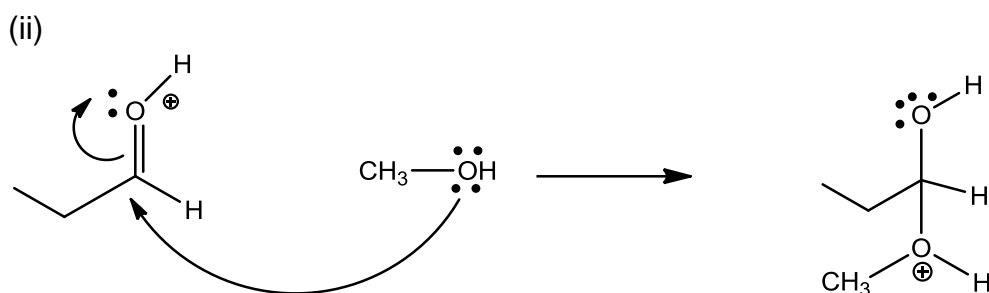
EXAMPLE

Use arrows to show how the bonds are broken or formed in the following conversions:



Answer:





Study Solved Problem 2-23 (a) and (b) in Wade et al. Watch the videos on the use of curved arrows via the links:

<https://www.youtube.com/watch?v=WaHRflsi-SU>

https://www.youtube.com/watch?v=4_EPURgVb2o

ACTIVITY 1.4

Do Problem 2-23 (d),(e) and (f).

1.6 Resonance (Wade et al 1-9)

A limitation of Lewis structures is that it tends to put electrons in a specific location. This representation does not always accurately show the bonding that exists in some molecules and ions. It is actually possible to draw two or more structures of such species where electrons are located on different locations. These structures are called **resonance structures or resonance forms**. The actual structure of such a molecule is a resonance hybrid of its resonance structures.

Guidelines for drawing resonance structures:

- 1) Do not change the connection of atoms – leave the atoms where they are.
- 2) Draw complete Lewis structures to start with, in other words, draw in all hydrogens and lone pairs of electrons.
- 3) ONLY electrons move.
- 4) The electrons in π bonds or non-bonding (unshared) pairs can freely participate in resonance.

Therefore, anions and lone pairs of electrons on, for example, nitrogen, oxygen and halogens can participate in resonance.

- 5) The total number of electrons does not change.
- 6) Obey the octet rule on any atom – do not exceed the octet rule.

[If you need to review sigma and pi bonds, read sections 11-12 and 11-3 in Wade et al and watch the following relevant video clip:

<https://www.youtube.com/watch?v=YcSPPKESpwc>]

How do electrons move in resonance structures?

Electrons can only move if the π bonds are conjugated and/ or if a charge (positive or negative) is conjugated to π bond(s).

Use the following as a guide when moving electrons:

- 1) Move π electrons toward a positive (+) charge.
- 2) Move π electrons toward π bond.
- 3) Move a non-bonding pair of electrons toward a positive (+) charge.
- 4) Move a non-bonding pair of electrons toward a π bond.
- 5) Move π electrons up onto an oxygen, nitrogen, and so forth.

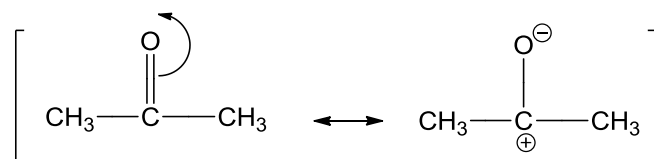
A structure is **conjugated** when the double bonds are separated by a single bond. Charged species (anions and cations) may also be conjugated. For example, when a C^+ is separated from the $C=C$ double bond by a $C-C$ single bond, we have a conjugated system.

We use the **double-headed** arrow to show the conversion between the resonance structures. Study sections 19A and 1-9 B in the textbook for more details. Pay particular attention to the information in Problem-solving Strategy in the green box and Solved Problem 1-2 and 1-21.

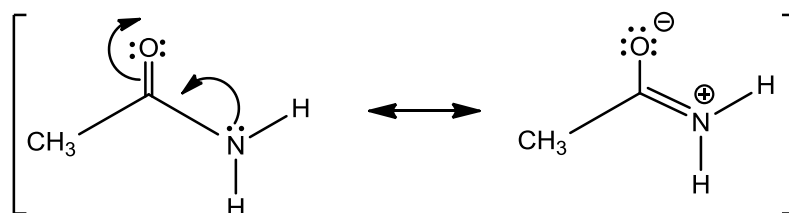
EXAMPLES

Resonance delocalisation of two different species is illustrated below:

(1)



(2)



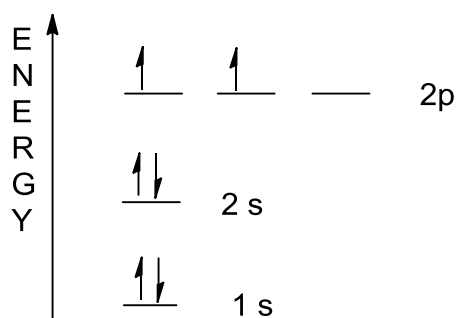
You can watch the following video clip for an additional explanation of resonance structures: <https://www.youtube.com/watch?v=6XOm3Km7r30>

ACTIVITY 1.5

Do Problem 1-41 (a) to (l).

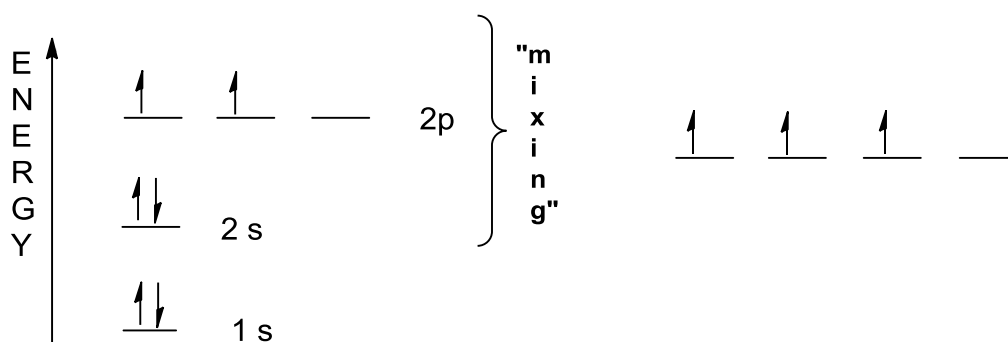
1.7 Hybridisation and molecular shapes (Wade et al sections 1-15 to 1-17)

If we consider the Lewis structure of the simplest organic compound that has one C and four H atoms, that is called methane, CH_4 . Methane has been known to be a symmetrical molecule with four identical C-H bonds, which are at equal angles from each other and the molecule has a complete tetrahedral structure in space. We know that the C atom has the electron configuration of $1s^2 2s^2 2p^2$ in its ground state, which can also be presented as follows:



According to the above presentation of the electron configuration of C, it seems that it would be impossible for C to form four equal bonds. It is thus clear that the s- and p-orbitals do not satisfactorily explain why methane is tetravalent and tetrahedral in shape. We need a presentation of the electronic structure of C where the four electrons can each overlap with an electron from hydrogen.

This is possible if the one 2s orbital and the three 2p orbitals are “mixed” to give four orbitals of equal energy with the one 2s electron “relocating” to the empty 2p orbital, as illustrated below:



The “mixing” of orbitals is called **hybridisation** and the hybridisation shown above is **sp³ hybridisation**. This process produces four orbitals. Each orbital has $\frac{1}{4}$ s character and $\frac{3}{4}$ p character and is called a sp³ hybrid orbital. This hybrid orbital is presented as follows:



Each sp³ hybrid orbital consists of the larger lobe, the “head”, having most of the electron density for bond formation, and a smaller lobe, called the “tail”.

In the CH₄ molecule, each sp³ hybrid orbital of C overlaps with a 1s atomic orbital of H to form a σ (sigma) bond. If the molecule has a tetrahedral shape, then the special orientation of the sp³ hybrid orbital is such that they are oriented at angles of 109.4° with respect to each other.

Watch the video for an additional explanation of sp³ hybridisation:

<https://www.youtube.com/watch?v=JHgTNNX01r4>

Carbon atoms are also involved in **double bond** that requires **sp² hybridisation**. The three sp² hybrid orbitals are arranged in a trigonal geometry around the sp² carbon atom.

The details of this type of hybridisation can be found in section 1-15B in Wade et al. You can also study Solved Problem 1-8 in Wade et al. You may view the video via the link: <https://www.youtube.com/watch?v=ROzkyTgscGg>

Another type of bonding that the C atom is involved in is the formation of triple bonds. **Triple bond** formation is possible when the C atom undergoes **sp hybridisation**. The orientation around the C≡C bond is linear.

Read section 1-15 A in Wade et al for more information about sp hybridisation and watch the following videos: <https://www.youtube.com/watch?v=BRHfy7envyQ>
<https://www.youtube.com/watch?v=9tEnXUuHkp4>

Study sections 1-16 and 1-17 in the textbook for more detail on the geometry of the various hybridisation and the three-dimensional drawing of structures. Study Solved Problems 1-9 to 1-13 and Problem 1-22 in Wade et al.

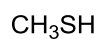
You could also watch the following video clip for additional explanation:

<https://www.youtube.com/watch?v=cPDptc0wUYI>

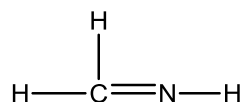
EXAMPLE

Identify the hybridisation state of carbon in each of the following species:

(a)



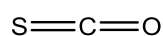
(b)



(c)



(d)

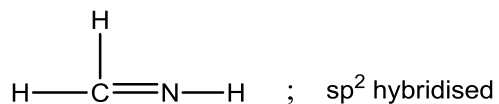


Answers:

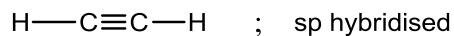
(a)



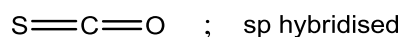
(b)



(c)

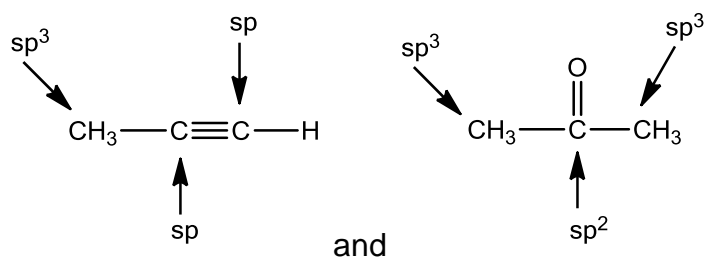


(d)



Note that you should be able to derive at the above hybridisation states. If you have difficulty, contact your e-tutor or lecturer via the **Discussion Forum** for further explanation.

We also encounter molecules containing carbon atoms with different hybridisation states, for example:



ACTIVITY 1.6

Do Problems 1-16(a), 1-17, 1-18 and 1-23 (a).

1.8 Structural formulas (Wade et al 1-10)

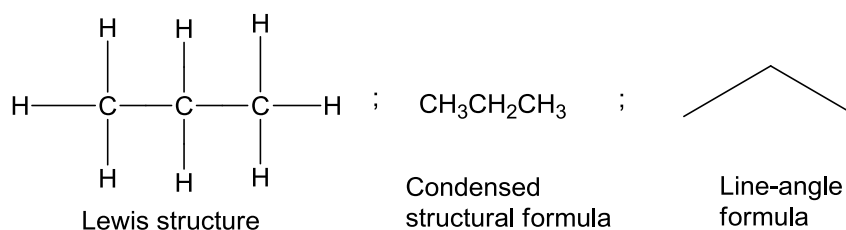
Organic chemists use various other representations of the structures of carbon-containing compounds like **Lewis structures**, **condensed structural formulas** and **line-angle formulas**. We have discussed the drawing of Lewis structures in section 1.4 above.

In **condensed structural formulas**, **no individual bonds** are drawn. The carbon atoms together with the atoms bonded to it are drawn. Non-bonding electrons are *not* shown in condensed formulas and the groups are written in the sequence of bonding. Double and triple bonds may or may not be shown.

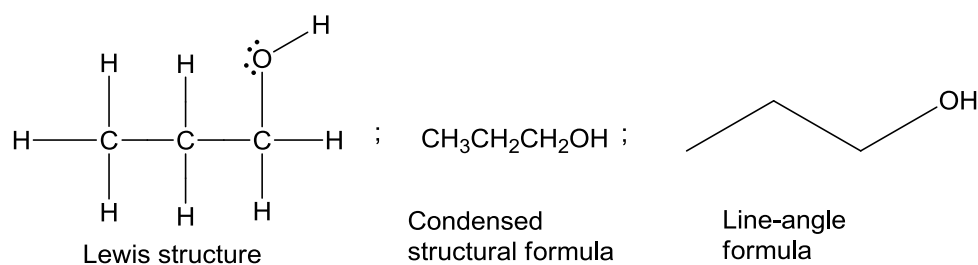
In a **line-angle formula**, also referred to as **skeletal structure**, the symbol for carbon atoms is generally *not* drawn. **Lines** represent the **bonds** with each **beginning** and **ending** of the line as well as where **two lines meet** (i.e. each tip or angle), representing a **carbon** atom. **Hydrogen** atoms are **not shown** and **elements other** than carbon and hydrogen *must be shown*. Note that around each carbon atom there are four bonds (therefore 8 electrons) to complete the noble gas configuration (octet state).

EXAMPLES

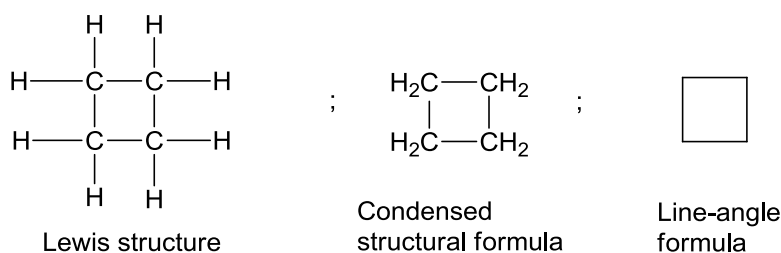
1.



2.



3.



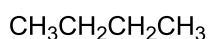
Read Wade et al and carefully study the different structural representations. Also, read section 1-11 in the textbook on molecular formulas and empirical formulas.

1.9 Isomerism (Wade et al section 1-19)

Isomers are compounds with the same molecular formula (composition) but different structural formulas. There are several types of isomers with two key classes, namely, constitutional and stereoisomers. Some of the examples of stereoisomers will be described later in study unit 5 and study unit 8.

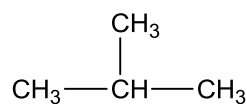
1.9.1 Constitutional/structural isomerism (Wade et al section 1-19 A)

Constitutional or structural isomers differ in the sequential arrangement of atoms or groups of atoms. Because they have different structures, structural isomers also have different names, different physical properties and in some cases different chemical properties. Butane (C_4H_{10}), for example, has two structural isomers:



Butane (n-butane)

b.p. = -0.5°C ; m.p. = -135°C

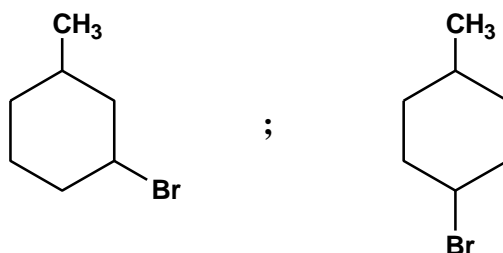


2-Methylpropane (isobutane)

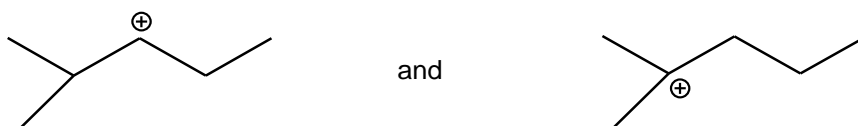
b.p = -10°C ; m.p = -145°C

EXAMPLES

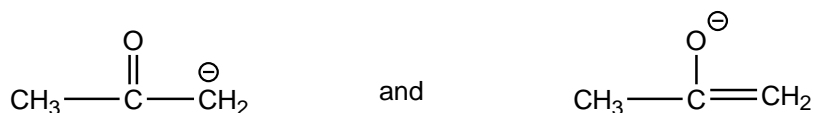
1. The two compounds below are **constitutional isomers** because they have the **same molecular formula**, but the **groups are connected at different positions on the ring**.



2. The two compounds below are **constitutional isomers** because they have the same molecular formula, but some of the **hydrogen atoms are connected at different positions**.



3. The difference in the two structures below is that the **pi-electrons are located on different carbons**. These are **not isomers** but they are **resonance structures** of the anion.



1.9.2 Stereoisomers (Wade et al section 1-19 B)

In **stereoisomers**, the atoms are connected in the same order but they are **arranged differently in space**.

Geometric isomers are the result of the different arrangement of groups within a plane formed by the double bond and are called stereoisomers. They have different physical properties, but similar chemical properties.



The above two structures are **cis- and trans isomers**. We shall discuss this in detail in study unit 8. In addition, the geometric isomerism in cycloalkanes will receive attention in study unit 3.

ACTIVITY

Do Problems 2-25 and 1-41.

1.10 Conclusion

Did you manage to complete this unit in the time you allotted to it in your study schedule? If not, you may need to adjust your pace of learning, or your schedule.

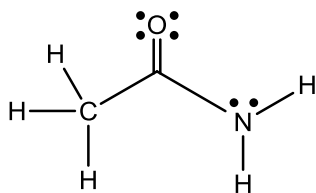
Should you need assistance with study strategies, you could find more information on the website of Unisa's Directorate Counselling and Career Development at <http://www.unisa.ac.za/default.asp?Cmd=ViewContent&ContentID=96773>.

In this study unit we reviewed the various types of covalent bonding and ionic bonding in organic compounds. We studied how to draw Lewis structures and the different types of hybridisation in the formation of single and multiple bonds. We further introduced the concept of resonance, how to draw resonance structures and the curved arrow formalism. We described the different methods of drawing structures and the different types of isomers. Please go back to the learning outcomes and make sure that you can competently perform everything listed there.

In the next study unit, we discuss various factors influencing the properties of molecules and acids, bases, and the functional groups of different classes of organic compounds are also introduced.

ANSWERS TO SELECTED ACTIVITIES

1.2



STUDY UNIT 2

Acids and bases; functional groups

- 2.1 Introduction
- 2.2 Polarity of bonds and molecules
- 2.3 Intermolecular forces
- 2.4 Polarity effects on solubilities
- 2.5 Definitions of acids and bases
- 2.6 Strengths and reactions of acids and bases
- 2.7 Lewis acids and bases
- 2.8 Functional groups
- 2.9 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- describe the polarity of molecules and bonds
- illustrate and apply intermolecular forces, particularly London dispersion forces, van der Waals and dipole-dipole interaction and hydrogen bonding
- predict different physical properties on the basis of intermolecular forces
- define and apply the different acid and base theories, electrophiles, nucleophiles and free radicals to organic molecules and reactions
- identify and describe the functional groups of the classes of organic compounds

2.1 Introduction

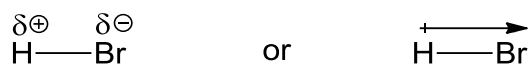
In study unit 1, we discussed the polar bond and in this study unit we will further evaluate how the polarity of bonds and the shape of the molecule influence the overall polarity of the molecule. We will introduce the concept of intermolecular forces and evaluate how these forces affect properties of molecules.

Have you ever wondered why we use vinegar in our cooking but never soap, or why sodium bicarbonate or the antacid medications relieve heartburn? In this study unit, you will get answers to these questions when we discuss the types of acids and bases and their reactions. We will further evaluate the factors that influence the relative strengths of acids and bases and introduce concepts such as nucleophiles, electrophiles and free radicals. The use of curved arrows to show the flow of electrons and various functional groups in organic chemistry will be introduced.

2.2 Polarity of bonds and molecules (Wade et al section 2-1)

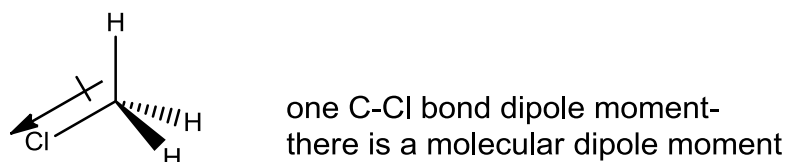
In section 1.3.2 in study unit 1, we discussed how the **electronegativity** of atoms involved in a **covalent bond** play a role in whether the bond is **polar** or **non-polar**. We will now focus on how the geometry of a molecule relates to the polarity of that molecule.

In a bond between two like atoms, for instance Br_2 , the attraction of the nucleus of the one Br atom for the bonding electrons is as strong as the attraction of the other Br atom. The electrons are found at the same distance from each Br atom. Furthermore, the bond is symmetrical, such that the centres of gravity of the positive and the negative charges correspond. In a bond between two unlike atoms, the nucleus of the one atom exerts a stronger attractive force than the nucleus of the other atom. For example, in $\text{H}-\text{Br}$, the electrons in the bond are found closer to the nucleus of the Br atom and the centres of gravity of the two atoms do not coincide. The bond is represented as:



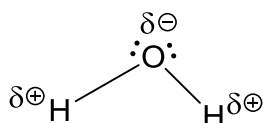
The magnitude of the opposite charges multiplied by the separation of their centres of gravity is defined as the **dipole moment** of the compound that is indicated in the latter structure above. The calculation of dipole moments is **not** part of the syllabus, but you must be able to determine whether there is a dipole moment in a molecule and the direction of the dipole moment.

If we consider the molecule CH_3Cl , we have to draw the **three-dimensional** structure of the molecule and show the dipole moment as follows:

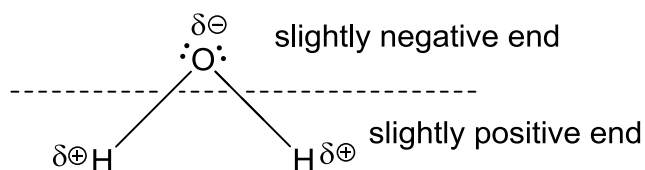


The molecular dipole moment is the same as the dipole moment of the C-Cl bond in the molecule above.

If we further evaluate the bonding in the water molecule (discussed in section 1.4.1), we know that the O—H bond is polar since $\chi_{\text{O}} > \chi_{\text{H}}$ with oxygen having a partial negative charge and hydrogen a partial positive charge.



If we assess the water molecule above, we can see that the molecule has a slightly negative end and a slightly positive end, as indicated below:



Each polar bond has a dipole moment and because of the opposing partial positive end and partial negative end existing in the molecule, water will have a net dipole, as shown below:

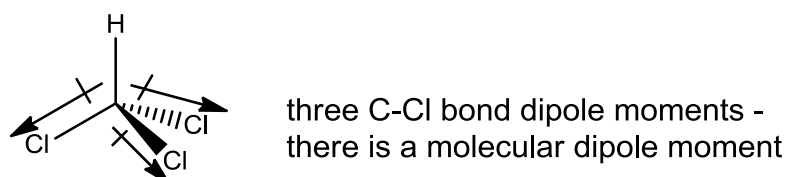


Study Solved Problem 2-1 in Wade et al.

EXAMPLES

1. Evaluate whether the $CHCl_3$ molecule has a molecular dipole moment.

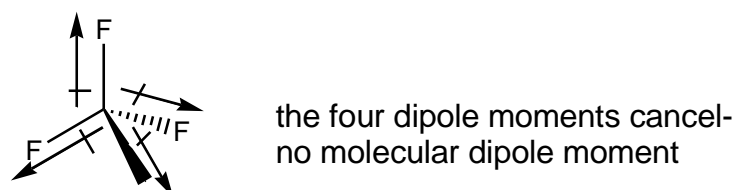
Answer:



In the above structure, the bond dipole moments do not cancel each other and hence there is a molecular dipole moment.

2. Evaluate whether the CF_4 molecule has a molecular dipole moment.

Answer:



You can watch the video clip on dipole moments of molecules via the link:

<https://www.youtube.com/watch?v=q3g3jsmCOEQ>

Study Solved Problem 2-3 in Wade et al.

ACTIVITY 2.1

Do Problems 2-2, 2-4 and 2-30.

2.3 Intermolecular forces (Wade et al section 2-2)

Intermolecular forces are **attraction forces** between one molecule and another molecule close to it. These forces hold two or more molecules together. The forces of attraction **within a molecule** that hold the atoms together in, for example, a covalent bond are known as **intramolecular forces**.

Most substances exist in one of the three states of matter, namely solid, liquid or gas, depending on the temperature and pressure. Water, for example, can exist as a solid (i.e. ice), a liquid or a gas (i.e. water vapour). The physical properties of a substance often depend on its state. In gases, the molecular motion is completely random and the forces of attraction between gas molecules are so small that each molecule moves freely and essentially independent of other gas molecules. Molecular motion is more restricted in liquids than in gases. In solids, the atoms and molecules are packed even more tightly together. The intermolecular forces are thus more significant in liquids and solids. The three **main intermolecular forces** in organic molecules are **dipole-dipole forces**, **London dispersion forces** and **hydrogen bonding**.

Dipole-dipole forces (Wade et al section 2-2 A)

This type of force exists in **polar** molecules where there is a **partial positive** and a **partial negative end** in the molecule. A dipole-dipole force is the dipole-dipole interactions that occur when the partial charges formed within one molecule are attracted to an opposite partial charge in a nearby molecule. Polar molecules align so that the positive end of one molecule interacts with the negative end of another molecule. **Dipole-dipole** interactions create attractions between molecules of a substance and are thus **intermolecular** attractions. Figure 2-3 in Wade et al gives an illustration of dipole-dipole interactions.

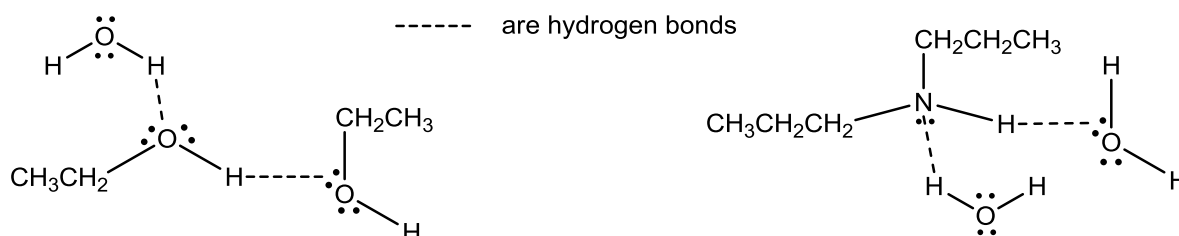
London dispersion forces (Wade et al section 2-2 B)

The **motion of electrons** in atoms or molecules can result in a **temporary uneven distribution of electrons** in the atom or molecule, thus **creating temporary dipole moments**.

The resulting attractive interaction, where one atom causes an adjacent atom to have a similar dipole, is called a **London dispersion force** or **van der Waals force**. Therefore, **London dispersion forces** can occur in molecules due to this **temporary dipole** formation as shown in Figure 2-4 in Wade et al. Every single molecule experiences this type of **intermolecular** attraction and this force is the **weakest of all** of the **intermolecular forces**. This explains why the ethane ($\text{CH}_3\text{—CH}_3$) molecule, which is non-polar, boils at a higher temperature than methane (CH_4), which is also non-polar. These molecules have no other types of attraction forces and exist in gas form at normal temperatures and pressures.

Hydrogen bonding (Wade et al section 2-2 C)

Very strong dipole-dipole attractions occur between **nonbonding pairs of electrons** on **electronegative** atoms and **hydrogens** bonded to **small strongly electronegative** atoms like O, N or F. This type of attractive force is called a **hydrogen bond**. The **hydrogen bonding** between H and O as well as between H and N is illustrated in the respective structures below:



The **hydrogen bond** is **much stronger** than **dipole- dipole interactions** between **two polar molecules**.

Study Figure 2-25 in Wade et al for an illustration of hydrogen bonding and watch the video clip on intermolecular forces via the link: https://www.youtube.com/watch?v=S8QsLUO_tgQ

ACTIVITY 2.2

Do Problem 2-31.

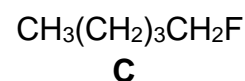
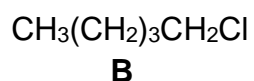
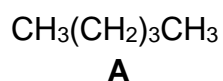
All of the above intermolecular forces play a role in the physical properties, such as melting points and boiling points, of molecules. The boiling point of a substance depends on the attraction forces between the molecules of the liquid. The weaker the attraction forces, the less energy is needed to separate the molecules to convert the liquid to the gas phase and therefore the lower the boiling point. Furthermore, a straight chain alkane will have a higher boiling point than a branched chain with the same molecular formula.

Study Solved Problem 2-2 in Wade et al.

You may view a video clip illustrating how intermolecular forces influence the boiling point of molecules via the link: <https://www.youtube.com/watch?v=08kGgrqaZXA>

EXAMPLES

1. Arrange the following compounds in order of decreasing boiling points:



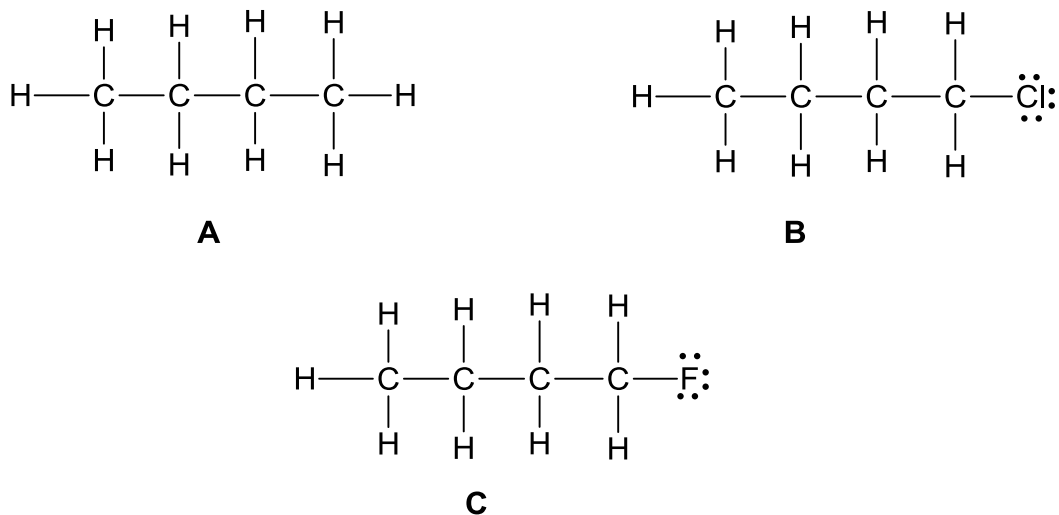
Explain your answer.

Answer:

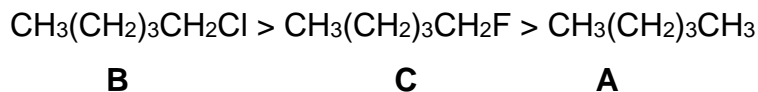
All the molecules experience London dispersion forces and these forces are the strongest intermolecular forces in compound **A**, which is an alkane. In addition to the London attraction forces in **C**, the alkyl fluoride has a higher dipole moment than the alkane. Therefore, the total attraction forces in the alkyl fluoride are greater than that in the alkane and so the alkyl fluoride, **C**, has a higher boiling point than **A**.

The Cl atom is considerably larger than the F atom that gives compound **B** a larger surface area than compound **C** and thereby giving **B** the higher boiling point than **C**.

The Lewis structures of the compounds are:



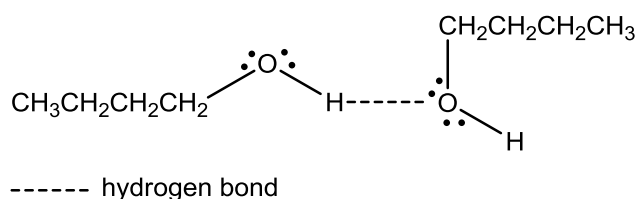
Therefore, arranging the compounds in order of decreasing boiling points, that is, from the highest to the lowest:



2. Compare the boiling points of n-butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ and butan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

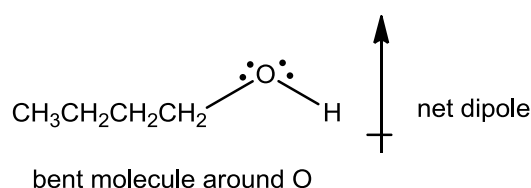
Answer:

Both the molecules can exhibit London dispersion forces. The n-butane molecule, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$, only has C-C and C-H bonds and exhibits only van der Waals/London dispersion forces. In butan-1-ol, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{OH}$, the O-H bond in two molecules can undergo hydrogen bonding as shown below:



Hydrogen bonding is a stronger type of intermolecular force than London dispersion forces.

Furthermore, the O—H bond and the C—O bonds are polar due to the electronegativity difference between O and H and electronegativity difference between O and C, respectively. The molecule has a net dipole that results in dipole-dipole interactions between the alcohol molecules.



Butan-1-ol has London dispersion forces, dipole-dipole interactions as well as hydrogen bonding between molecules and therefore has the strongest intermolecular forces existing between molecules, compared to butane. Hence, butan-1-ol has the highest boiling point.

ACTIVITY 2.3

Do Problems 2-6 (a), (b), (c) and 2-33.

2.4 Polarity effects on solubilities (Wade et al section 2-3)

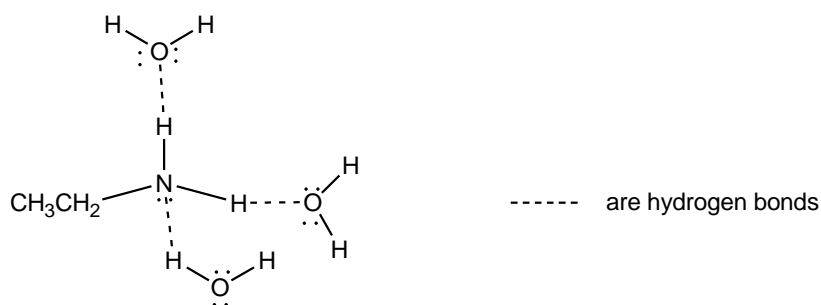
In General Chemistry 1A, you learnt that a solute dissolves in a solvent to form a solution. Intermolecular forces also play a critical role in the solubility of molecules and ions. **Polar solvents** dissolve **polar** and **ionic** substances and **non-polar solvents** dissolve **non-polar** molecules. The different intermolecular interactions that occur when the different types of solutions form are shown in Figures 2-6 to 2-9 in Wade et al.

Organic molecules cover a range of **non-polar to polar** substances and you should be able to **predict** the **solubility** of the different classes of compounds based on the **structure** and the **nature** of the **solvent**.

EXAMPLE

The compound ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, is much more soluble in water than trimethylamine, $(\text{CH}_3)_3\text{N}$. Since both compounds contain a nitrogen atom with a lone pair of electrons, one would expect the two compounds to have similar solubility in water. Why then is there a difference in solubility?

The amines can form hydrogen bonds with water. Ethylamine undergoes hydrogen bonding with water. Since there are two N—H bonds and the lone pair of electrons on nitrogen of ethylamine, three hydrogen bonds can form, as shown below:



The $(\text{CH}_3)_3\text{N}$ molecule has no N—H bonds and there can therefore be no H----O type of hydrogen bonds with water. The hydrogen bonding between trimethylamine and water is shown below:



The trimethyl amine molecule forms fewer hydrogen bonds with water compared to ethylamine. The amine that is able to form the strongest hydrogen bonds with water will be the most soluble in water. Hence, trimethyl amine has a much lower solubility than ethylamine in water.

Review Figure 2-10 in Wade et al. View the video on solubility of organic compounds via the link: https://www.youtube.com/watch?v=_mWHWJiMKXU

ACTIVITY 2.4

Do Problem 2-7 (a), (b), (c).

2.5 Definitions of acids and bases (Wade et al sections 2-4 and 2-5)

Acidity and basicity are very important concepts that are necessary for a broader understanding of various aspects of organic chemistry. Household items like vinegar and lemons contain acids, while soap and many other cleaners are bases. We need to know exactly what an acid and a base are in order to understand their reactions. With time, various definitions of acids and bases have been developed by chemists.

The first recorded definition is the **Arrhenius definition** of acids and bases, which is outlined below:

Acids are substances that dissociate in water to produce H_3O^+ ions, such as:



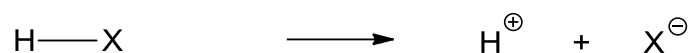
Bases are substances that dissociate in water to produce OH^- ions, for example:



This definition only accommodates bases containing a hydroxide ion.

Subsequent to the Arrhenius definition, the **Brønsted-Lowry definition** was formulated. This definition of acids and bases describes **Brønsted acids** as compounds that can **donate a proton (H^+ ion)**, and **Brønsted bases** as compounds that can **accept a proton (H^+ ion)**. **Brønsted-Lowry acids** are compounds that normally have a **H** attached to the atom of an **electronegative** element.

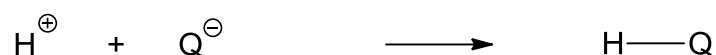
For example:



Where, H—X is the acid such as H—Cl, H—F, etc.

Brønsted-Lowry bases are compounds that normally have unshared electron pairs.

For example:

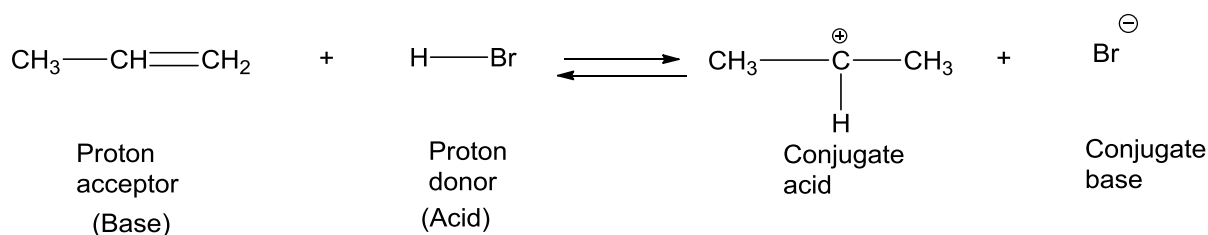


Where Q[⊖] is the base.

The **Brønsted-Lowry** definition also includes bases that do not have a hydroxide ion but can accept a proton. Furthermore, when a **base accepts a proton**, it becomes an **acidic** species that is capable of **donating** a **proton**. This species is called a **conjugate acid**. When an **acid donates a proton**, it forms a species that is capable of **accepting** a **proton** and is called a **conjugate base**.

EXAMPLE

The reaction of HBr with CH₃CH=CH₂ is an acid-base reaction and is illustrated below:



View a video on the different definitions of acids and bases via the link:

<https://www.youtube.com/watch?v=diCb6JkLIQE>

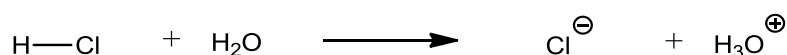
Another definition of acids and bases, called the **Lewis** definition, will be described in detail in section 2.7 below.

2.6 Strengths and reactions of acids and bases (Wade et al sections 2-5 to 2-12)

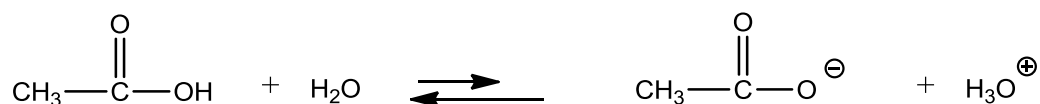
2.6.1 Strengths of acids and bases

Acids and bases are classified as either strong or weak. What makes certain acids and bases strong and others weak? The strength of acids and bases is determined by the extent to which the species ionise in water.

Hydrochloric acid is said to be a **strong acid** because it **completely dissociates** in water according to the following reaction:



Acetic acid is a **weak acid** that dissociates partially in water and the process is indicated below:



We use vinegar in our cooking because vinegar contains acetic acid, which is a weak acid and has a sour taste that enhances certain culinary dishes. Soap, on the other hand, is basic and bases tend to be taste bitter.

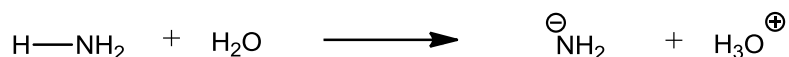
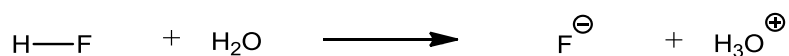
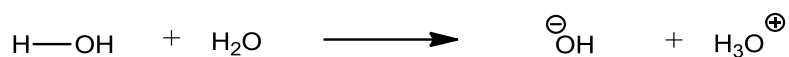
EXAMPLE

Arrange the compounds H_2O , HF and NH_3 in order of increasing acid strength.

Answer:

To compare the acid strength of compounds H_2O , HF and NH_3 , their ability to donate a proton (H^+) must be compared.

The dissociation of each of the three acids is:



When comparing the relative acidity of different molecules, it is useful to look at the relative basicity of their conjugate bases. The **stronger the acid**, the **weaker** (i.e. the more stable or less reactive) is the **conjugate base**.

In this case, we should look at the relative basicity of F^{\ominus} , OH^{\ominus} and NH_2^{\ominus} . The relative strengths of these anions can be evaluated based on the electronegativity of the charged atom in each. Since fluorine is the most electronegative, F^{\ominus} is the most stable, least reactive base in the group. This means that its conjugate acid, HF, is the strongest. The least electronegative atom is nitrogen and therefore the NH_2^{\ominus} anion is the most reactive and its conjugate acid, NH_3 , is the weakest. Therefore, the acids in order of increasing acidity are **$\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$** .

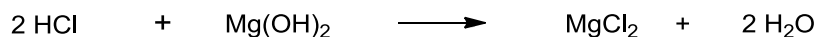
The strength of the base depends on the strength of the conjugate acid and conjugate base formed in the reaction. A **strong base** forms a **weak conjugate acid**.

2.6.2 Reactions of acids and bases

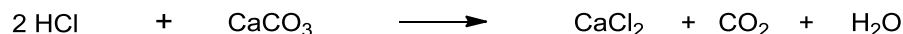
If one places an acid and a base in a flask, the resulting mixture will not display any acidic or basic properties. This is because the acid and the base neutralise each other. Antacids relieve acid indigestion and heartburn because gastric acid, which is hydrochloric acid, HCl, is neutralised by the basic components in the antacids.

We will consider two different antacids that are readily available, namely, Milk of magnesia and Maalox.

Milk of magnesia contains magnesium hydroxide and the reaction of this product in the stomach is:



Maalox contains calcium carbonate and the action of this product to relieve heartburn is as follows:



For each reaction of an acid in water, an equilibrium constant called an acid dissociation constant is available. The acid dissociation constants indicate the relative strengths of the respective acids. Similarly, a base dissociation constant is the measure of the strength of a base.

Calculations involving these dissociation constants *do not fall* within the domain of this module. You are, however, required to **compare** the **strengths** of acids and bases using **principles of bonding** and the other **properties** of the atoms and groups in the particular molecules.

Study section 2-7 that outlines how to predict the equilibrium positions of acid-base reactions and Problem 2-10 in Wade et al. Also, watch the video via the link:

<https://www.youtube.com/watch?v=m8mm.MiNGILo>

Study Problem-solving strategy: Predicting acid-base equilibrium positions in Wade et al.

ACTIVITY 2.5

Do Problem 2-11.

Solvents other than water can also be used in acid-base reactions and these solvents can be either acidic or basic, depending of the type of reaction.

If we compare acids, then the **stronger acid has a weaker conjugate base**. The **size** and **electronegativity** of the conjugate base also influence the strength of the acid.

Similarly, the nature of the conjugate acid plays a role in the strength of the base. Since a Brønsted base is a species that can accept a proton and the proton has no electrons, it is necessary for a Brønsted base to contain an electron pair, which is available for donation to the proton. The more readily a compound is able to accept a proton, the stronger the base.

If we compare the molecules NH_3 and H_2O , the atoms N and O are both in the same row on the periodic table. Oxygen is more electronegative than N and will therefore attract its lone pair of electrons more strongly than nitrogen. Nitrogen will better donate its lone pair of electrons to a proton than the oxygen atom. Therefore, the NH_3 molecule is a stronger Brønsted base than H_2O .

If we compare the bonds of hydrogen with different atoms, then acidity and polarity increase in the sequence, as follows: $-\text{C}-\text{H} < -\text{N}-\text{H} < -\text{O}-\text{H} < \text{Cl}-\text{H}$

If all other things are equal, then basicity increases in the sequence: $\text{Cl} < \text{O} < \text{N}$

We know that the **C—H** bond is essentially **non-polar**. It is evident that **the greater the electronegativity of the atom which captures the bonding electrons during the dissociation, the greater the extent (degree) of dissociation.**

Inductive effects and the **hybridisation states** of atoms also play a role in the acidity of certain molecules. If we compare the hybridisation states of compounds with the same atom attached to hydrogen, then the acidity of the compounds increase as follows: **$\text{sp}^3 < \text{sp}^2 < \text{sp}$**

These aspects will be discussed in more detail in the study units dealing with carbonyl derivatives and alkynes, respectively.

ACTIVITY 2.6

Do Problem 2-16.

When the anion (conjugate base) formed in the reaction of an acid is stabilised by resonance, the acid strength is enhanced. Similarly, resonance stabilisation of the conjugate acid of a base also increases the basicity of a substance.

Watch the video clips on factors affecting acidity via the links:

<https://www.youtube.com/watch?v=KoC-PinXWCA>

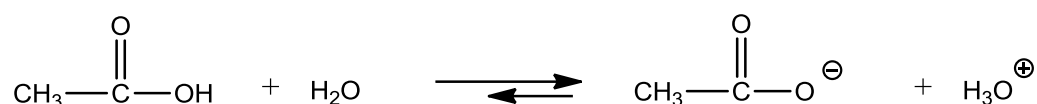
<https://www.youtube.com/watch?v=vw8urcaBOBk>

<https://www.youtube.com/watch?v=VkrOYs2LFNk>

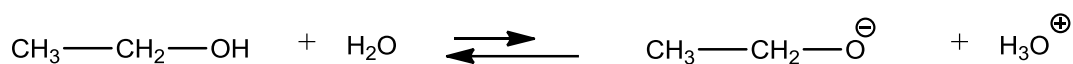
Let us compare, for example, the acid strengths of two compounds containing oxygen, CH_3COOH and $\text{CH}_3\text{CH}_2\text{OH}$.

The acid-base reaction of each compound in water:

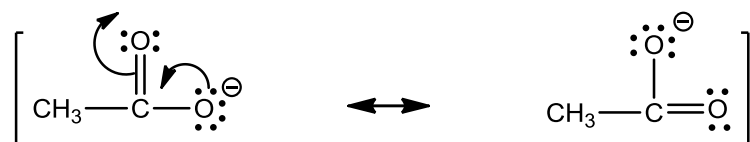
(a)



(b)



The strength of the acid depends on its ability to donate an H^+ . A strong acid will readily donate an H^+ and the forward reaction predominates. In order for that to happen, the conjugate base that forms must be stable. In the reaction (a) above, the stability of the conjugate base, that is the carboxylate ion, determines the stability of the carboxylic acid. The resonance stabilisation of the carboxylate ion is shown below:



The conjugate base formed in reaction (b) is not stabilised by resonance. Therefore, the conjugate base formed in (b) is less stable than the carboxylate ion that formed in (a). Acetic acid, CH_3COOH , is therefore a stronger acid than ethanol, $\text{CH}_3\text{CH}_2\text{OH}$.

Study Solved Problems 2-21 (a) and 2-22 (a) in Wade et al.

ACTIVITY 2.7

Do Problem 2-20.

2.7 Lewis acids and bases (Wade et al section 2-13)

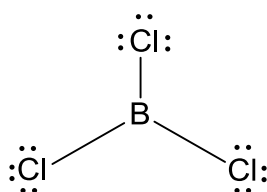
Lewis acids are compounds that can accept an electron pair and these compounds normally have a vacant atomic orbital. **A Lewis base is a compound that supplies (donates) a pair of electrons to form a bond.** The **Lewis** definition of acids and bases allows for reactions, where protons are not involved, to be considered as acids and bases.

The ability of species to accommodate the electron pair depends on many factors, including:

- the size of the atom
- the electronegativity of the atom

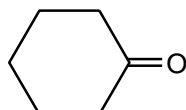
If we consider the compound, BCl_3 , is this compound a Lewis acid or a Lewis base?

The Lewis structure of BCl_3 is:



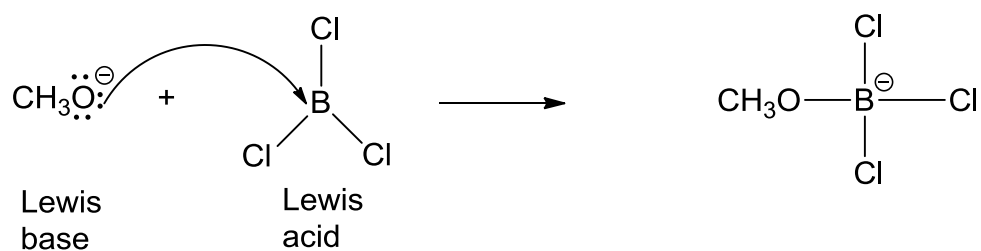
The B atom in BCl_3 does not have any lone pairs of electrons – it has an empty orbital which can **accept an electron pair**. BCl_3 is therefore a **Lewis acid**.

An example of a Lewis base is the compound below:



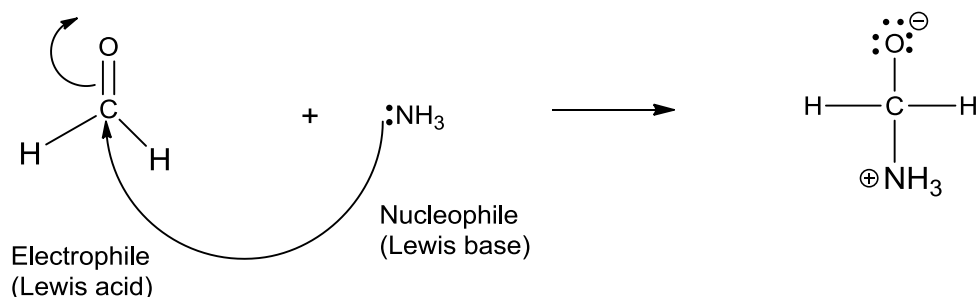
The oxygen atom has two lone pairs of electrons (draw the Lewis structure) available for donation and therefore can act as a **Lewis base**.

We use curved arrows to show how electrons move. The arrow starts at the atom or center that donates the electron pair and ends at the atom or center that accepts the electrons. A reaction where BCl_3 acts as a Lewis acid is illustrated below:



Organic chemists also refer to compounds that **accept an electron pair** in a reaction as **electrophiles** and reagents that **donate a pair of electrons** as **nucleophiles**.

In the above reaction, the CH_3O^- ion is also the **nucleophile** and the BCl_3 is the **electrophile**. Another example is:



Study Problem 2-33 in Wade et al. Watch the video on Lewis acids and bases via the links: https://www.youtube.com/watch?v=EwYzmG_19Vg
<https://www.youtube.com/watch?v=jlL333CKE9A>

ACTIVITY 2.8

Do Problem 2-40.

2.8 Functional groups (Wade et al sections 2-15 to 2-17)

Since there is such a vast range of organic compounds, we distinguish between the **different classes of organic compounds** based on **an atom or group of atoms** with a **characteristic behaviour** that is present in the molecule. That **group of atoms** is called **a functional group**. The naming of these classes of compounds will be discussed in subsequent study units.

2.8.1 Hydrocarbons (Wade et al section 2-15)

Compounds containing **carbon** and **hydrogen only** are called **hydrocarbons**. If such compounds contain **only carbon-carbon single bonds**, then the compounds are called **alkanes** or **saturated hydrocarbons**. Alkanes can have straight chain or ring structures.

If the hydrocarbon has at least one triple or a double bond, then it is called an **unsaturated hydrocarbon**. Hydrocarbons with **one carbon-carbon double bond** are called **alkenes** and the **functional group** is: **C=C**.

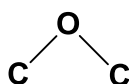
Hydrocarbons with **one carbon-carbon triple bond** are called **alkynes** and the **functional group** is: **C≡C**.

2.8.2 Organic compounds containing oxygen (Wade et al section 2-16)

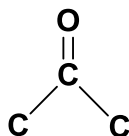
Compounds containing the **hydroxy group** as a **substituent** of the parent hydrocarbon are called **alcohols** and the **functional group** is:



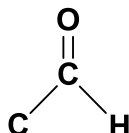
Ethers are compounds having **two alkyl groups** attached to an **oxygen** atom. The **functional group** is:



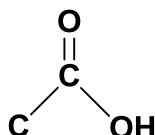
Ketones contain the **carbonyl group** in the carbon chain and the **functional group** is:



Aldehydes also have a **carbonyl group**, but the **carbonyl group** is **always** at the **one end** of the carbon chain and the functional group is:

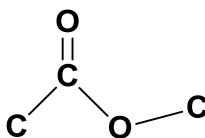


Carboxylic acids are compounds that contain the **carboxyl group** as functional group with the structure:

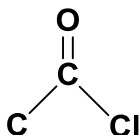


Carboxylic acid derivatives include esters, acid chlorides and amides. Carboxylic acid derivatives contain the **carbonyl group** that is **bonded** to an **oxygen atom** or **another electron-withdrawing group or atom**.

An ester has the functional group:



Acid chlorides are identified by the following functional group:

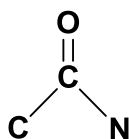


2.8.3 Organic compounds containing nitrogen (Wade et al section 2-17)

Amines are compounds where one or more hydrogens in ammonia are replaced by alkyl groups and the functional group is: **-NR₃**

Where R= H, alkyl and/or aryl

An **amide** is a carboxylic acid derivative with the following functional group at the end of the carbon chain:



Nitriles are organic compounds containing the **cyano group** as the functional group:



Watch the video on functional groups via the link:

<https://www.youtube.com/watch?v=okv2us6pVxo>

ACTIVITY 2.9

Do Problem 2-56.

2.9 Conclusion

In this study unit we reviewed fundamental concepts, including the polarity of bonds and molecules, intermolecular forces and how these forces influence the physical properties of molecules. We also studied acids and bases, including the different definitions, factors influencing their strengths and their different reactions. The functional groups of different classes of organic compounds were also introduced. Please go back to the learning outcomes and make sure that you can competently perform everything listed there. In the next study unit, we will investigate the structure and properties of alkanes.

ANSWERS TO SELECTED ACTIVITIES

2-6 (a) second compound (b) second compound (c) second compound

THEME 2

SATURATED ORGANIC COMPOUNDS

In this theme we will discuss the structure, nomenclature, properties and reactivity of selected classes of compounds containing carbon-carbon single bonds. We will focus on alkanes, introduction to stereochemistry, alkyl halides, alcohols, ethers and amines.

STUDY UNIT 3

Structure and properties of alkanes

- 3.1 Introduction
- 3.2 Molecular formulas of alkanes
- 3.3 Nomenclature of alkanes
- 3.4 Physical properties, uses and sources of alkanes
- 3.5 Reactions of alkanes
- 3.6 Structure and conformations of alkanes
- 3.7 Cycloalkanes
- 3.8 *Cis-trans* isomerism of cycloalkanes
- 3.9 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

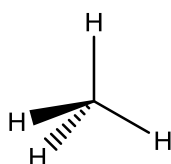
- describe the generalised structure of alkanes and cycloalkanes
- use the IUPAC rules for nomenclature correctly to construct structural formulae
- compare the physical properties of alkane molecules
- accurately construct various structural and conformational isomers and compare their relative energies and stabilities
- predict the outcome of combustion and halogenation reactions of alkanes
- identify geometric isomerism in cycloalkanes

3.1 Introduction (Wade et al section 3-1)

Petroleum and natural gas are the two of the most important alkanes. Petroleum is a liquid that consists of a complex mixture of organic compounds, of which many are alkanes and cycloalkanes. Petroleum is refined to give petrol, diesel, fuel oil and other useful substances. In this study unit we will focus on the structure and nomenclature of alkanes and cycloalkanes. The physical properties and reactions of alkanes as well as the structures and stabilities of the different conformations will receive attention. We will introduce geometric isomerism that may exist in cycloalkanes.

3.2 Molecular formulas of alkanes (Wade et al section 3-2)

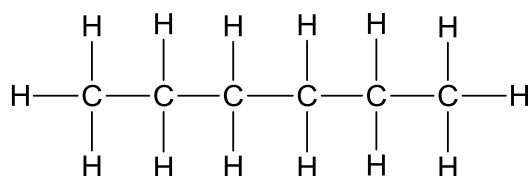
Alkanes are the simplest hydrocarbons, with a general formula of C_nH_{2n+2} . As the value of n increases, each alkane differs from another alkane by a CH_2 group. The class of compounds, the alkanes, is an example of a **homologous series**. A **homologous series** is a series of compounds whose members **differ by a repeating unit**. All the atoms in alkanes are sp^3 hybridised and the bonds are sigma (σ) bonds, which are directed to the corners of a tetrahedron as described in section 1.6 in study unit 1. The structure of the simplest alkane with one carbon atom is methane, with the structure:



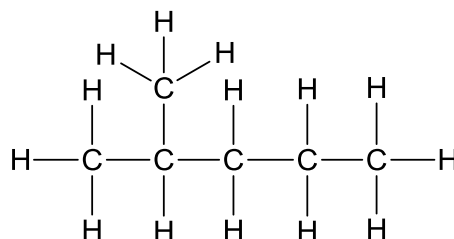
3.3 Nomenclature of alkanes (Wade et al section 3-3)

Many organic compounds are known by two or more names. Compounds can be named by a naming convention where constitutional isomers are distinguished by **trivial or common names** (like nicknames).

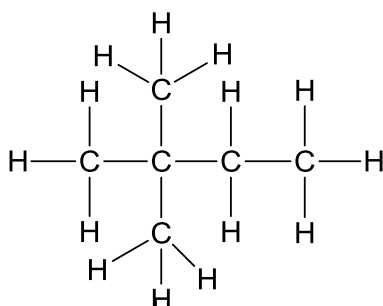
Let us consider the structural formulas of the constitutional or structural isomers of the alkane with the molecular formula of C_6H_{14} , that is, hexane.



n-Hexane



Isohexane



Neohexane

The structures above are three isomers of hexane, but hexane has a total of five isomers. Can you draw the two remaining isomers of hexane? Consult study unit 1 to review the concept of constitutional isomers.

In the common names, the prefix **normal-** or **n-** is used to indicate a straight chain and the prefix **iso-** is used to indicate a $CH_3-CH(CH_3)-$ group as part of the chain. When there is a $CH_3-C(CH_3)_2-$ group in the chain, the prefix **neo-** is used before the parent name.

3.3.1 IUPAC nomenclature

The International Union of Pure and Applied Chemistry regulates a more systematic naming system, called the **IUPAC** system. The set of rules in this system is called the **IUPAC nomenclature rules**.

The **IUPAC nomenclature rules for alkanes** can be summarised as:

- i) **Identify the longest continuous straight chain of carbon atoms.** This chain determines the parent name. Note that the longest continuous chain is not always obvious, since it is not necessarily in one direction.
Table 3-2 in Wade et al lists the parent names of the alkanes, up to twenty carbon atoms.
- ii) **Number** the longest chain from **the end closest to the first branch.**
- iii) Use the numbers obtained in (ii) to indicate the position of a substituent and name each **substituent** as an **alkyl group**. (See Figure 3-2 in Wade et al.)
- iv) If there are **two or more substituents** present, each one is assigned the **number according to its position** in the carbon chain and the groups are written in **alphabetical order**.
- v) When **two substituents** are on the **same carbon** atom, the **number** of that carbon is used **twice**.
- vi) When **two or more substituents** are **identical**, the prefixes **di-, tri- and tetra-** are used to indicate two, three and four similar groups, respectively.
The numbers for positions in the carbon chain are separated by commas.
- vii) If the first branch is the **same distance** from both ends of the chain, then **numbering** should start at the side **closest to the second branch**.
- viii) If it is possible to consider two chains of equal length for the parent name, then the **chain which has the most number of substituents** is selected as the main chain.

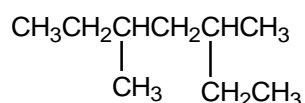
The nomenclature rules for alkanes are extremely important because the names of other classes of organic compounds are derived from the names of alkanes.

Appendix 5 in Wade et al gives a summary of the IUPAC nomenclature rules for organic compounds.

Study Solved Problems 3-1 and 3-2 in Wade et al.

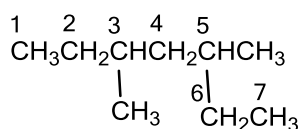
EXAMPLE

Give the IUPAC name of the following compound:



Answer: 3,5-dimethylheptane

Explanation: According to the IUPAC convention, the longest continuous carbon chain has seven carbon atoms, and a 7-carbon chain has the parent name heptane. Begin numbering at a branch to give substituents the lowest possible number:



In this case, starting from either side gives the same numbers to the substituent. There is a methyl group is correct on C-3 and another methyl group on C-5. The two methyl groups are written as 3,5-dimethyl.

Watch the relevant video at the link below:

<https://www.youtube.com/watch?v=hZpzyG9A60M>

<https://www.youtube.com/watch?v=9tEnXUuHkp4>

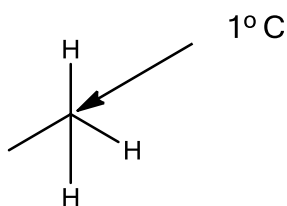
ACTIVITY 3.1

Do Problems 3-3 (a), (c); 3-4, 3-39 (a), (b), (c), and 3-41 in Wade et al.

3.3.2 Classification of alkanes

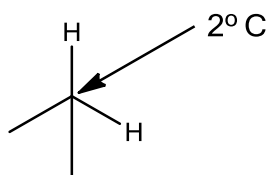
A carbon atom in the carbon chain of an alkane can also be classified based on the number of carbons bonded to it. A carbon can be classified as primary, secondary or tertiary, as illustrated below:

Primary carbon (1°) – the **C atom** has **one carbon atom** bonded to it. Example:

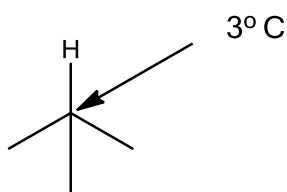


Secondary carbon (2°) – the **C atom** has **two carbon atoms** bonded to it.

Example:



Tertiary carbon (3°) – the **C atom** has **three carbon atoms** bonded to it. Example:



3.4 Physical properties, uses and sources of alkanes (Wade et al section 3-4)

The structures of compounds have a marked effect on their physical properties, such as boiling point, melting point and solubility. The structure also determines the intermolecular forces that exist between molecules. Alkanes only have carbon-carbon and carbon-hydrogen bonds. Since the electronegativity values of carbon and hydrogen are quite close, the C-H bonds are basically non-polar. An alkane molecule is therefore non-polar and these molecules interact only by weak London dispersion forces (see section 2.3 in study unit 2).

These forces determine the physical properties of alkanes, such as the relative boiling points, melting points and solubility. Alkanes are soluble in non-polar solvents and insoluble in polar solvents.

As the **size** of the alkane **increases**, the **boiling point** also **increases** and similarly, the **melting points** of alkanes that are solids **increase** with **increasing molecular mass**. Furthermore, a **straight chain** alkane will have a **higher boiling point** than its **branched chain** isomer and when there is an **increase** in the **extent of branching**, there will be a **decrease** in the **boiling point**.

ACTIVITY 3.2

Do Problem 3-10 (a) and (b), 3-42.

Alkanes are used extensively in the petrochemical industries. Read in section 3-5 in Wade et al about the uses and sources of alkanes.

3.5 Reactions of alkanes (Wade et al section 3-6 A and 3-6 C)

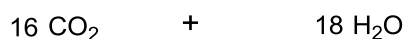
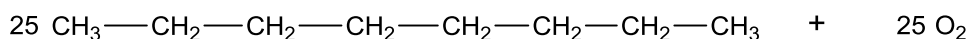
Alkanes are not very reactive and these compounds are the least reactive organic species. The important reactions of alkanes are:

3.5.1 Combustion reactions (Wade et al section 3-6A)

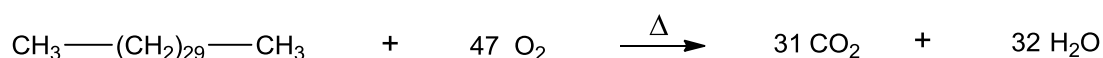
Alkanes react with **oxygen in the presence of heat** to give **carbon dioxide (CO₂) and water (H₂O)** in reactions called **combustion or oxidation reactions**. This type of reaction takes place when fuel burns to provide energy or heat. Although this reaction is extremely useful, it also has serious environmental implications through the emission of carbon dioxide gas.

EXAMPLES

1. One of the main components of gasoline is octane and when octane burns, the following reaction takes place:



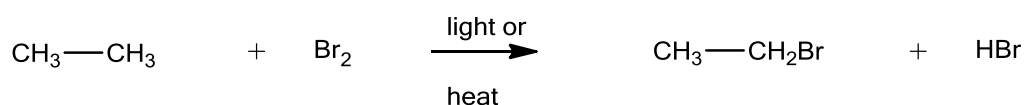
2. Candles are often used as a source of light when electricity is absent. Candles consist of paraffin wax, which is a hydrocarbon. When a candle burns, the paraffin wax undergoes a chemical reaction with oxygen to form carbon dioxide gas and water. This chemical reaction is another example of a combustion reaction. Paraffin wax is obtained from petroleum and the wax consists of a mixture of hydrocarbons.
3. These hydrocarbons contain between 20 and 40 carbon atoms and the hydrocarbon $\text{C}_{31}\text{H}_{64}$ is usually part of paraffin wax. We illustrate the combustion reaction of paraffin wax with the following chemical equation:



3.5.2 Halogenation reactions (Wade et al section 3-6 C)

Alkanes also undergo **halogenation reactions**. In this type of reaction, **alkanes react with halogens** in the **presence of ultraviolet light or heat** to produce **alkyl halides** as the **main (major) product**. This is an important type of reaction of alkanes and should be well understood.

When ethane, CH_3CH_3 , is heated (or bombarded with light) in the presence of bromine, ethyl bromide is formed as the main product, as shown below:



In study unit 4 we will discuss in detail how the halogenation reaction takes place.

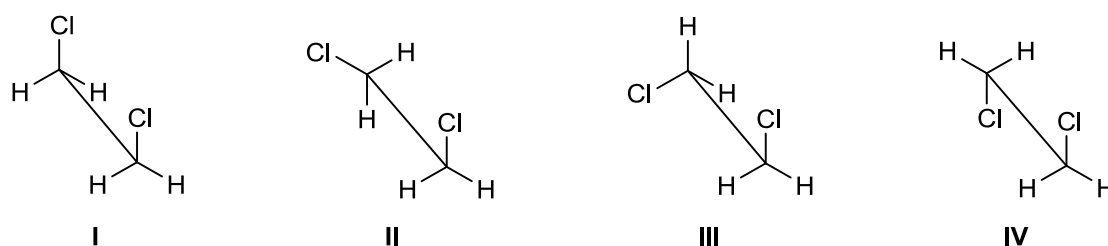
3.6 Structure and conformations of alkanes (Wade et al sections 3-7 to 3-9)

Alkanes have sp^3 hybridised carbon atoms and the carbons are connected via single bonds. Based on a range of experimental evidence, organic chemists know that **the atoms** (or groups) **rotate around carbon-carbon single bonds**. This rotation leads to different spatial arrangements of atoms or groups called **conformations**. The different conformations can be presented as Sawhorse or Newman Projections.

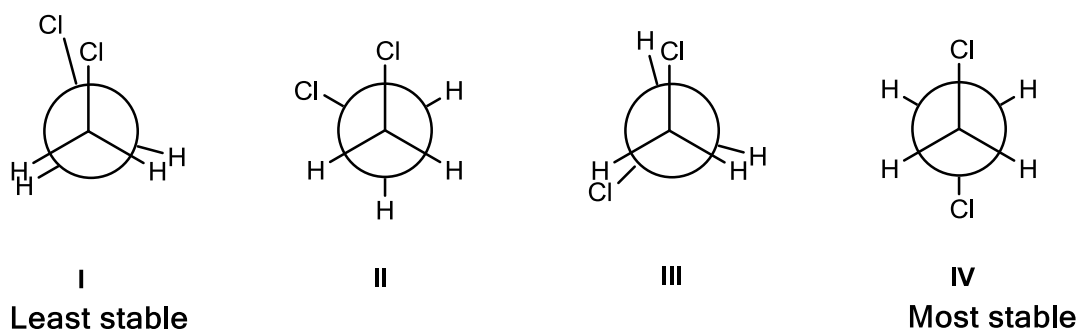
The **Sawhorse structure** is a three-dimensional representation of the relative spatial positions of all atoms or groups in a molecule. In this structure, the molecule is presented by looking down at an angle towards the C-C bond.

In **Newman Projections**, the bond between two atoms is viewed where the first carbon and its bonds are represented as 'Y', with the carbon being the midpoint in the 'Y'. The back carbon atom is represented by a circle with three lines (for bonds) pointing from it. Consider the molecule CH_2ClCH_2Cl . The different representations of the molecule are given below:

Sawhorse structures:



Newman Projections:



All the structures above represent different conformations of 1,2-dichloroethane. Each structure labelled IV is a staggered conformation, with the largest groups (Cl and Cl) being the furthest apart. This conformation has the LEAST interaction between the largest groups and is called the **anti-conformation**. The **anti-conformation** is the **most stable conformation** and therefore has the **lowest energy**.

The structure II is also a staggered conformation and the largest groups are closer to one another than in the IV. This conformation is called the **gauche conformation**. This conformation is **less stable** (of higher energy) than the anti-conformation.

In structures I and III, the bonds and groups of C-1 and C-2 are behind one another and they are called **eclipsed conformations**. The groups in the eclipsed conformations are closer to one another than in the staggered conformations. Therefore all the **eclipsed** conformations are of **higher energy** and **less stable** than the staggered conformations.

Structure I is an eclipsed conformation, which is the **least stable** of all conformations because the largest groups are closer to one another than in the other conformations. When the largest groups get very close to one another, it leads to interference between them. This interference is called **steric strain** and the **steric strain** makes the conformation **very unstable (high energy)**. This conformation is also referred to as the **totally eclipsed conformation** (the largest groups are eclipsed).

The structure III is also an eclipsed conformation, but the largest groups are not eclipsed and therefore this conformation is more stable than the first conformation.

Figure 3-7 in Wade et al gives the potential energy changes of ethane as the carbon-carbon bond rotates, and the energy changes for 1,2-dichloroethane are similar to that of ethane. Study Solved Problem 3-11 in Wade et al. In sections 3-7 C and 3-8 in Wade et al, the conformations for propane and butane respectively are illustrated and described.

Watch the relevant videos via the links:

https://www.youtube.com/watch?v=xChAkML_UbY

<https://www.youtube.com/watch?v=lkmM4CPngF0>

https://www.youtube.com/watch?v=D5NZERv_EDQ

ACTIVITY 3.3

Draw the Newman Projection formulas for the conformations of 1-bromo-2-iodoethane and identify the most stable and least stable conformation.

3.7 Cycloalkanes (Wade et al section 3-10)

Cycloalkanes are alkanes whose carbon atoms are arranged in **rings**. The structure of unsubstituted cycloalkanes is a ring formed by CH₂ groups connected to each other and there are two hydrogen atoms for every carbon atom in the ring. The general molecular formula for a cycloalkane is thus C_nH_{2n}.

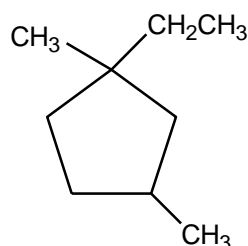
3.7.1 Nomenclature of cycloalkanes

When naming cycloalkanes, the IUPAC nomenclature rules, as stipulated in section 3.4.1 above, can be applied with the following adaptations:

- 1) Use **cycloalkane** as the **parent** name for substituted cycloalkanes and name the **alkyl** groups as **substituents**.
- 2) There is **no need to number** the substituent if there is only **ONE substituent**.
- 3) If there is **more than one substituent** on the ring, the carbons in the ring are **numbered** to give the **substituents** the **lowest possible numbers**.
- 4) If there are **two substituents** and the **numbering** could **start at any of the two substituents**, then numbering should **start** at the **alkyl** group that is **first alphabetically**.
- 5) If the **straight chain** portion has **more carbon atoms** than the **ring**, then the **cyclic** part is the **substituent**, which is named as a **cycloalkyl** group. The **parent name** is determined by the **length** of the **straight chain**.

EXAMPLE

Give the IUPAC name for the following compound:



Answer: 1-Ethyl-1,3-dimethylcyclopentane

Explanation: According to the IUPAC convention, if the longest continuous carbon chain is a ring, the prefix "cyclo" must be used. The chain contains 5 C atoms and thus the parent name is "pentane". Begin numbering at a branch to give substituents the lowest possible number, for instance at the carbon with the two substituents. Thus, on C-1 is an ethyl group indicated as 1-ethyl. There is a methyl on C-1 shown as 1-methyl and there is also a methyl group on C-3 which is indicated as 3-methyl. The two methyl groups are written as 1,3-dimethyl. List the substituents in alphabetical order.

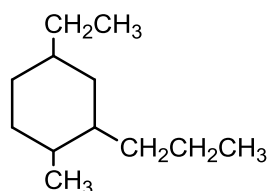
You may want to watch the video clips at the links below:

https://www.youtube.com/watch?v=YxFS_kmbtEI

<https://www.youtube.com/watch?v=OG7fXvgdydY>

ACTIVITY 3.4

(a) Give the correct IUPAC name for the molecule shown below:



(b) Do Problem 3-15.

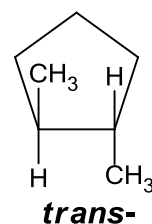
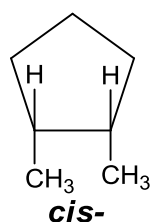
3.8 *Cis-trans* isomerism of cycloalkanes (Wade et al section 3-11)

In contrast to open chain alkanes, cycloalkanes cannot undergo rotations about the carbon-carbon single bonds. Any cycloalkane molecule has a top and bottom face and substituents can either be on the same face or on opposite faces of the ring. When the substituents are on the **same face** or **side** of the ring, they are **cis** and when the substituents are on **opposite sides** of the ring, they are **trans**. The difference between the **cis** and **trans** is the arrangement of the substituents in space and they are called **stereoisomers**. The two structures are referred to as **geometric isomers** and they are **not structural isomers**.

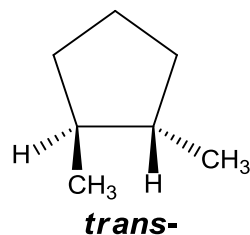
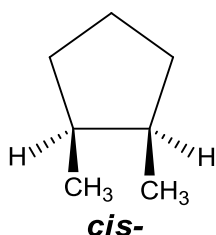
EXAMPLE

Draw the geometric isomers of 1,2-dimethylcyclopentane.

Answer:



The above isomers can also be presented as:



ACTIVITY 3.5

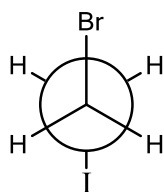
Do Problems 3-17(a), (c), 3-18 (a).

3.10 Conclusion

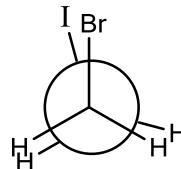
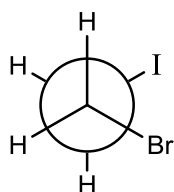
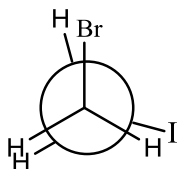
In this study unit we encountered the general structure of alkanes, the IUPAC nomenclature rules and learnt how to construct and evaluate the different conformations for alkanes. We also studied the structure, nomenclature and geometric isomerism of cycloalkanes. Furthermore, we learnt how to predict the various physical properties and the outcome of the reactions of alkanes. In the next study unit we will learn more about how chemical reactions take place.

ANSWERS TO SELECTED ACTIVITIES

3.3



Most stable



Least stable

3.4 1,3-diethyl-1-methylcyclohexane

STUDY UNIT 4

The study of chemical reactions

- 4.1 Introduction
- 4.2 Bond dissociation
- 4.3 Free-radical chain reaction mechanism in the halogenation of alkanes
- 4.4 Reactive intermediates
- 4.5 Kinetics and factors influencing the rate of the reaction
- 4.6 Halogenation of higher alkanes
- 4.7 Selectivity in halogenation
- 4.8 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- propose mechanisms and explain the steps for free-radical reactions of alkanes
- use the mechanism to predict which of several possible products is the major product
- identify free-radical intermediates and explain their properties
- identify carbocation intermediates and compare the stabilities of the different types of carbocations

4.1 Introduction (Wade et al section 4-1)

We have seen in study unit 3 that alkanes undergo halogenation and combustion reactions. How do these reactions occur and why is light or heat necessary for the halogenation of alkanes? We can write a chemical reaction indicating the conversion of the reactants to products but the equation does not tell us how the products are formed.

One of the aims of this module is to understand how and why reactions take place. If you understand the reactions of one compound in a series of similar compounds, then you can apply the knowledge to other compounds in the same series or class of compounds. This will drastically reduce the amount of memorisation. To understand a reaction it is necessary to understand the mechanism of the reaction. The reason why reaction mechanisms are included in the syllabus is to make the understanding and studying of chemical reactions easier.

What is a reaction mechanism?

A reaction mechanism is a step-by-step description of the bond-breaking and bond-making processes that take place when reactants react to form products.

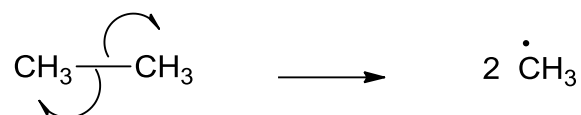
The different types of bond-breaking and bond-making processes as well as detailed reaction mechanisms are described below.

4.2 Bond dissociation (Wade et al section 4-6)

In order for a substance to be converted to another compound or compounds in a chemical reaction, bonds have to break. We will now review the bond-breaking processes described in study unit 1. A bond can break or dissociate via two possible modes, namely:

i) Homolytic bond breakage/cleavage

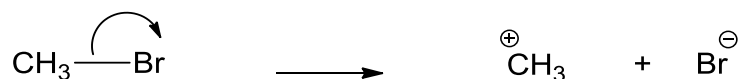
This type of **bond breaking** or **cleavage** takes place in a symmetrical way as illustrated below:



Each atom in the bond **retains a bonding electron** and the **flow of one electron** is presented by means of a **fish-hook arrow**. The species with an unpaired electron is a **radical**. This bond breaking is also called **homolysis**. **Homolysis** normally occurs in a bond between atoms with **similar electronegativity**, that is, in a **non-polar bond**.

ii) Heterolytic bond breakage/cleavage:

In this type of bond-breaking or cleavage process the **bond breaks** in an **unsymmetrical** manner as shown below:



This type of bond breakage takes place in a **polar bond** (i.e. in a bond between two atoms having different electronegativities). One of the atoms in the bond **retains both bonding electrons**. The flow of two electrons is presented by means of a **normal curved arrow**. This type of bond breaking is also called **heterolysis** and the **electrons move** in the **direction** of the **more electronegative atom**.

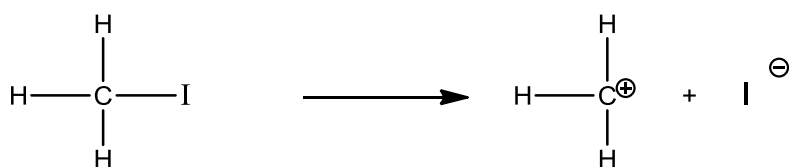
N.B Bond breakage is also referred to as **bond fission** or **bond cleavage** and **bond breaking cannot** be **interchanged with bond formation** – these are two **completely different processes**. Make sure that you review the bond-formation processes.

When bonds are formed, energy is released and energy is used when bonds break. Note that the bond-dissociation enthalpy values given in the tables in Wade et al need not be memorised.

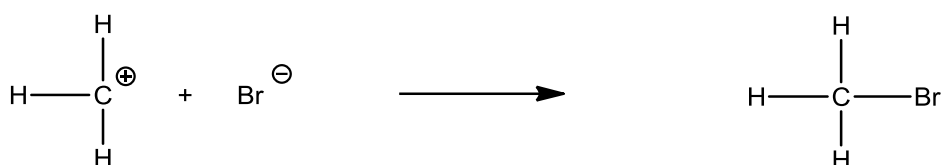
ACTIVITY 4.1

Use the appropriate curved arrows to show the bond-breaking or bond-formation process in each of the following:

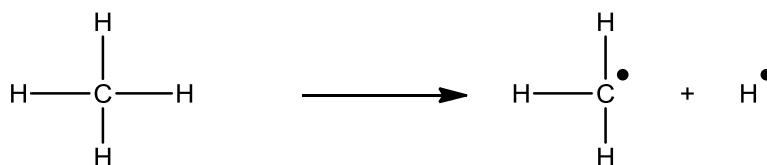
(1)



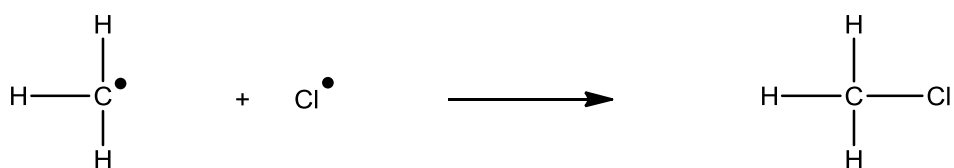
(2)



(3)

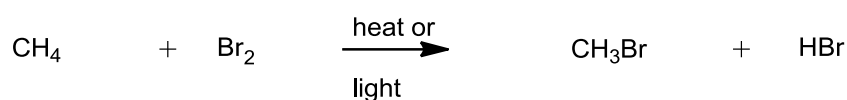


(4)



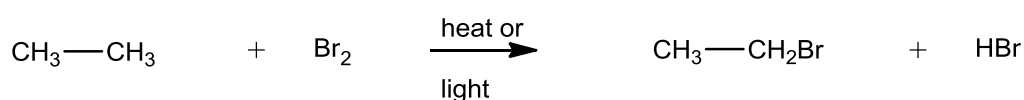
4.3 Free-radical chain reaction mechanism in the halogenation of alkanes (Wade et al sections 4-2 and 4-3)

In the **free-radical halogenation** reaction of alkanes, an **X replaces a hydrogen atom**. Of all the halogens, **chlorine and bromine are the most suitable for this type of reaction**. Hence, only the reaction with bromine (**bromination**) and the reaction with chlorine (**chlorination**) of alkanes are conducted in chemistry laboratories. For example, in the chlorination of methane (CH₄) in the presence of light or heat, **a Br replaces a hydrogen** to produce bromomethane as shown below:



The chlorination of methane is described in detail in section 4-3 (including Key Mechanism 4-1) in Wade et al.

If we consider an alkane with more than one carbon atom and the molecule has only one type of hydrogen atom, we have the ethane molecule. The reaction of ethane with bromine in the presence of light or heat is discussed below. The substitution of one of these hydrogens forms a new compound:

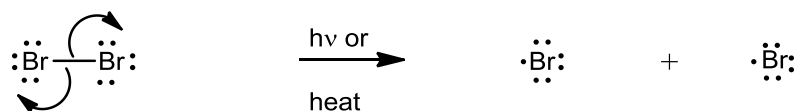


The light is in the form of ultraviolet light and the symbol **hν** is used in chemical equations to replace the word "light". The above reaction involves at least three different steps and the overall reaction is called a **chain reaction**. The first step of the reaction is called the **initiation step**, which is followed by the **propagation steps** and finally the **termination steps** take place.

The **halogenation reaction** and specifically the **bromination reaction** takes place as follows:

- **Initiation**

The irradiation bromine (**halogen**) molecule with **light or heat** leads to the homolytic cleavage of the Br-Br bond to form two **Br free radicals** or Br atoms. The step is illustrated as:

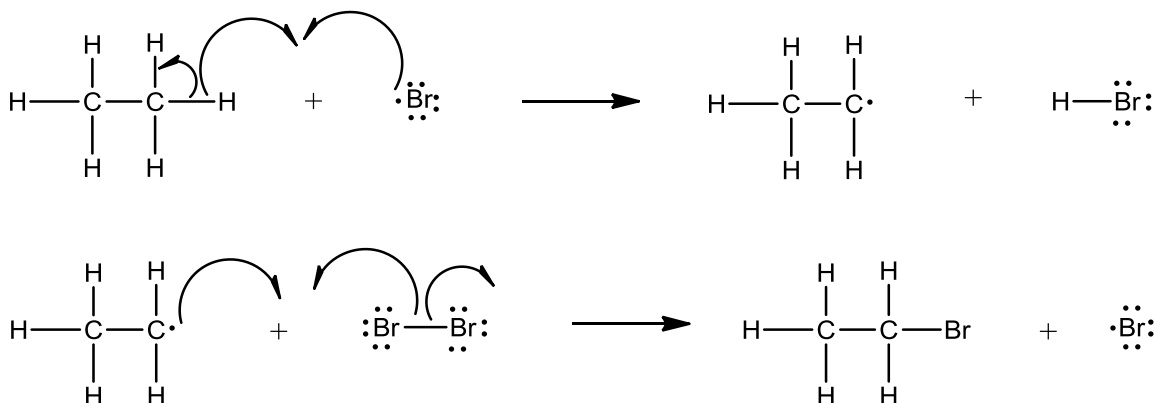


- **Propagation**

Propagation is the second phase of the reaction and there are **two** propagation steps:

- 1) The bromine radical and ethane collide. During the collision, the **bromine (halogen) free radical abstracts a hydrogen atom** from the alkane (ethane) to give a **carbon-free radical**. That is a carbon with an **unpaired electron** and in this specific example it is called an ethyl radical.
- 2) The **carbon-free radical reacts** with a **bromine (halogen) molecule** to form a **carbon-bromine (carbon-halogen) bond** and a **new bromine (halogen) free radical** is formed. Ethyl bromide or bromoethane is formed.

The steps are illustrated as:



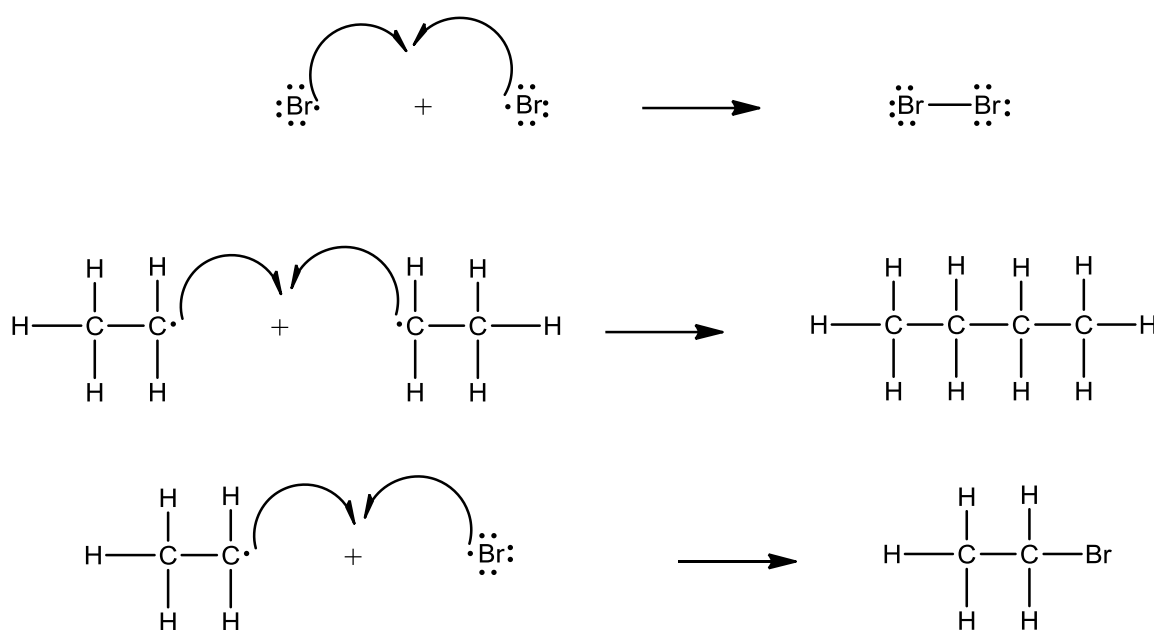
In the second step of propagation, a bromine radical is formed and reacts with another ethane molecule to produce an ethyl radical.

These two steps are repeated to produce more ethyl bromide. This type of sequential step-wise reaction in which a reactive intermediate formed in one step leads to the next step is called a **chain reaction**.

Therefore, in the **propagation steps** the **radical reacts with a stable molecule** to form **another reactive intermediate** and a **product**.

- **Termination**

Several steps can take place in which **the free radicals combine** to form **compounds without forming a new free radical, which can continue the chain reaction process**. The **chain reaction is slowed or stopped by the chain termination steps**.



These reactions above remove the radicals and cause the reaction to stop.

In the halogenation reactions above, **only one hydrogen atom is replaced** by a **halogen** and the product is called a **mono-halogenated** (mono-chlorinated or mono-brominated) product.

Study Key Mechanism 4-1 in Wade et al.

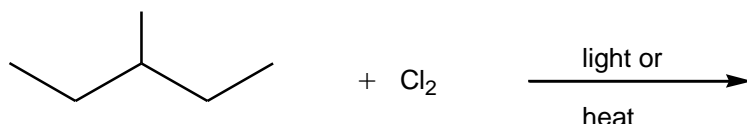
You may want to watch the relevant videos via the links:

<https://www.youtube.com/watch?v=5HgzsItWwK8>

<https://www.youtube.com/watch?v=BFCGcAPsvq4>

ACTIVITY 4.2

Give the possible mono-halogenated products that will form in the following reaction:



4.4 Reactive intermediates (Wade et al section 4-16)

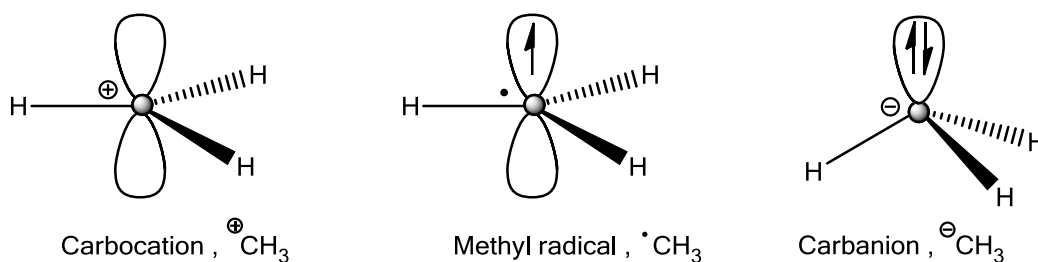
Reactive intermediates are species that are formed during a multistep reaction.

Substrates/starting materials react to form reaction intermediates (neutral or charged) that lead to the formation of products. Reaction intermediates act like a bridge between the reactants (starting materials) and the products. The stronger the bridge, the better the chances of crossing over safely to the other side.

Reaction intermediates normally lie at a minimum in the potential energy diagram of a reaction. Intermediates tend to be more stable than transition states and are generally too reactive to be isolated. A more stable intermediate is formed preferentially and leads to preferential formation of the product.

Mastering reaction mechanisms requires a thorough understanding of intermediates and their relative stabilities.

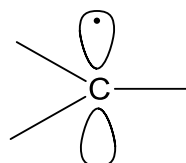
The possible reaction intermediates that may form in a chemical reaction are carbocations, carbanions and carbon radicals. Examples of these intermediates are:



At this stage, we shall focus our attention on the description of the structure of free radicals and carbocations and the factors that affect their stability.

4.4.1 Free radicals and factors that affect their stability (Wade et al section 4-16B)

A free radical is a neutral carbon species with three bonding pair electrons and a half-filled p-orbital. It runs short of a single electron to complete the octet state or noble gas configuration.

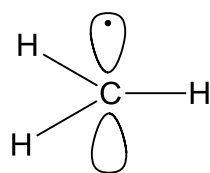


Free radicals can be classified as a methyl radical, 1° C radical, 2° C radical or 3° carbon free radical. The nature of the radical center (carbon having an unpaired electron) determines the properties of the radical. The half-filled carbon p-orbital has only one electron and is therefore electron deficient and electronwithdrawing. It pulls electron density from the neighbouring carbon atoms to become less electron poor. By so doing it reduces its energy and becomes relatively more stable.

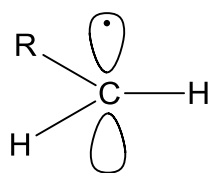
The more electron-donating alkyl groups are present around the radical carbon, the less electron poor it becomes. Thus a 3° carbon free radical is less electron poor or more electron rich than the 2° carbon free radical, which in turn is less electron poor than the 1° carbon free radical.

We say alkyl groups around a free radical carbon are **electron donating** (conversely, the free radical carbon is **electron withdrawing** because it is in need of an electron).

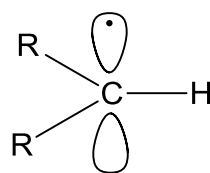
Note that a hydrogen atom is neither electron donating nor withdrawing and therefore the methyl radical is the least stable of them all.



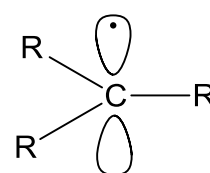
Methyl radical



Primary (1°) carbon radical



Secondary (2°) carbon radical



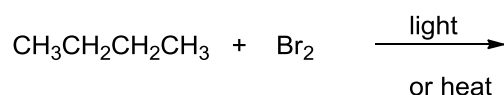
Tertiary (3°) carbon radical

In any chemical reaction involving the formation of free radicals, if both 2° and 3° free radicals can be formed, the 3° free radical will be formed preferentially to form a high proportion of the product. This is because a tertiary (3°) free radical requires less energy to form than the 2° free radical, and is more stable.

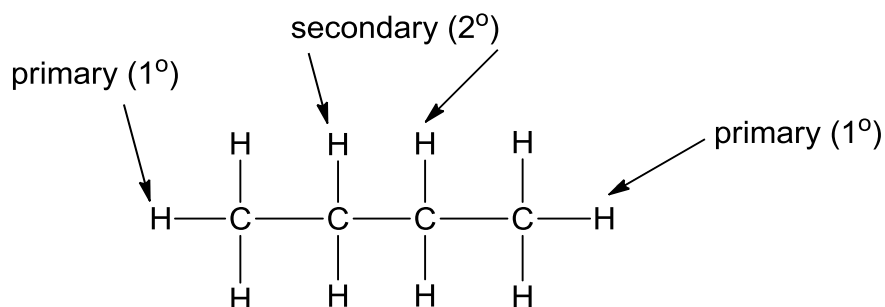
Trend in stability of carbon radicals:



Let us look at how the stability of radicals plays a role in the outcome of a halogenation reaction by determining what type of monobromination products can possibly form in the reaction below:

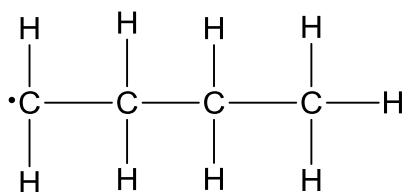


Let us draw the Lewis structure of the alkane molecule and identify the different types of hydrogens:

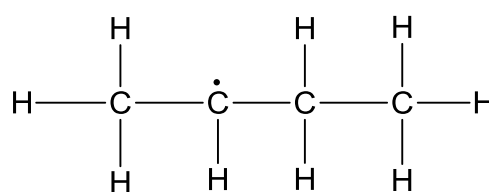


The identified primary hydrogens are in the same environment and are therefore chemically equivalent. Similarly, the secondary hydrogens are chemically equivalent because they are connected to the same atoms or groups. (If you have difficulty with this, please consult your tutor or your lecturer).

Abstraction of the distinct hydrogens gives the following two possible radicals:

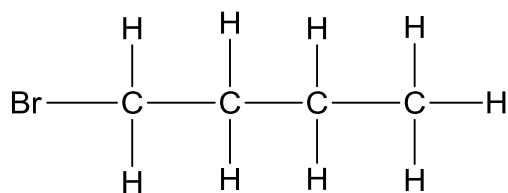


primary (1°)
radical

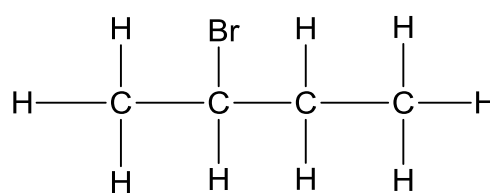


secondary (2°)
radical

Each of the above radicals can react with a bromine molecule to produce the products shown below:



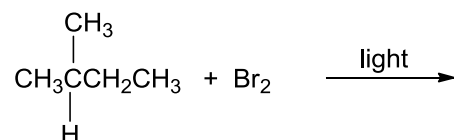
primary alkyl bromide



secondary alkyl bromide

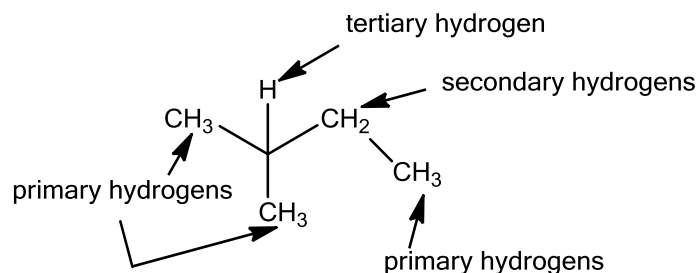
EXAMPLE

Predict the major organic product formed in the following reaction:

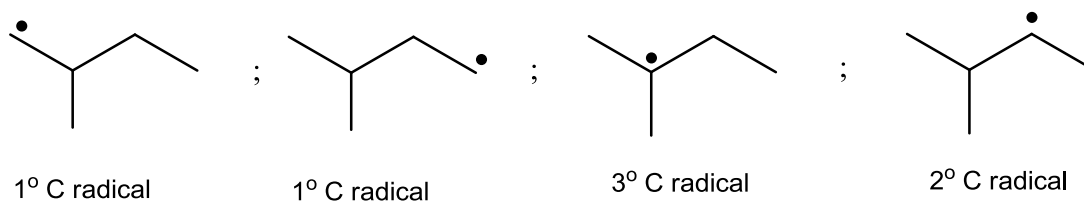


Answer:

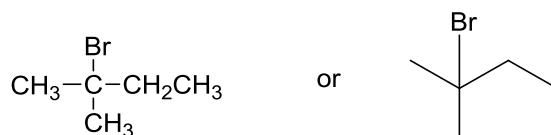
The halogenation reaction of alkanes proceeds via a radical intermediate. The possible hydrogen atoms that can be removed to form radicals are:



Possible radicals that can form in the reaction (when $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ is treated with bromine in the presence of light) are:



A secondary carbon radical is more stable than a primary carbon radical, and a tertiary carbon radical is more stable than a secondary carbon radical. The more stable radical has the lowest energy and forms more readily. Therefore, the formation of a tertiary carbon radical is always preferred over a secondary and a primary carbon radical to produce the major product. The tertiary carbon radical reacts with a bromine radical to form the major product with structure:



You may view the video of the stability of radicals via the link:

<https://www.youtube.com/watch?v=qdhLaRwYzmo>

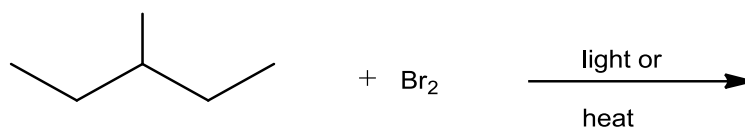
You may view the video on free-radical reaction and stability of radicals via the link:

<https://www.youtube.com/watch?v=zBVA4ibAevU>

ACTIVITY 4.3

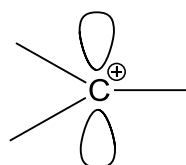
(a) Do Problems 4-4 and 4-30 in Wade et al.

- (b) Predict the structure of the major monobromination product that will form in the following reaction:



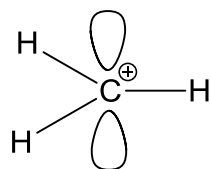
4.4.2 Carbocations and factors that affect their stability (Wade et al section 4-16A)

A carbocation is a positively charged carbon species in which the carbon atom has three bonding pairs of electrons and requires a pair of electrons to complete the noble gas (octet state) configuration in order to resemble neon. The positively charged carbon is electron poor (deficient) and will accept a pair of electrons from a nucleophile. A nucleophile is a molecule or ion that can donate a pair of electrons. The carbon bearing the positive charge is sp^2 hybridised. A carbocation center (positively charged carbon) has an empty p orbital with two lobes shaped like a figure 8 above and below the plane of the carbon framework. It is this orbital that accepts a pair of electrons from the nucleophile.

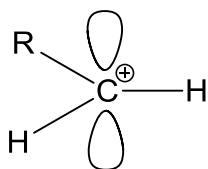


The types of carbocations include methyl carbocation (CH_3^+), 1° carbocation (RCH_2^+), 2° carbocation (R_2CH^+) and 3° carbocation (R_3C^+). The positively charged carbon is electron poor and therefore strongly electron withdrawing. It pulls electrons from the neighbouring carbon atoms to become less positive and therefore less electron poor. By so doing, it reduces its energy and becomes relatively more stable. The more electron-donating alkyl groups there are around the positively charged carbon, the less positive it becomes. A 3° carbocation is thus less positive than the 2° carbocation, which is less positive than the 1° carbocation.

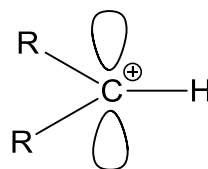
The hydrogen atom is neither electron donating nor withdrawing and therefore the methyl carbocation is the least stable. The alkyl groups are said to be electron donating by the **inductive effect**.



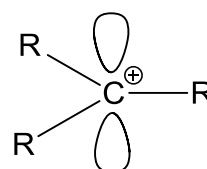
Methyl carbocation



Primary (1°) carbocation



Secondary (2°) carbocation



Tertiary (3°) carbocation

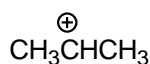
Trend in stability of carbocations: $3^\circ \text{C}^+ > 2^\circ \text{C}^+ > 1^\circ \text{C}^+ > \text{CH}_3^+$

If both 2° and 3° carbocations were to form in the same reaction, the 3° carbocation, which is more stable and requires less energy to form, will preferentially be formed. The 3° carbocation will therefore constitute a high proportion of the product.

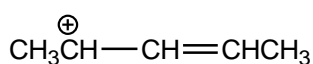
When carbocations undergo resonance delocalisation stabilisation, they tend to be more stable than carbocations that are not capable of undergoing resonance delocalisation. In the process of resonance delocalisation, the positive charge is spread over more than one atom that stabilises the carbocation.

EXAMPLE

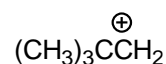
Rank the following carbocations in order of increasing stability, that is, from the least to the most stable:



A



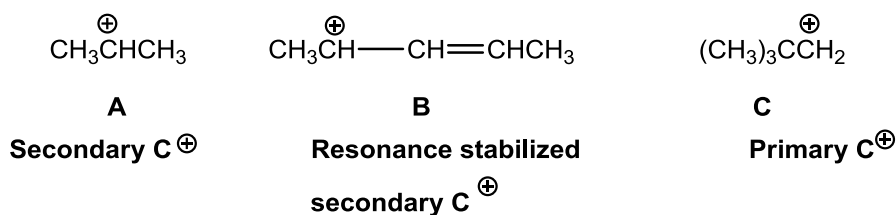
B



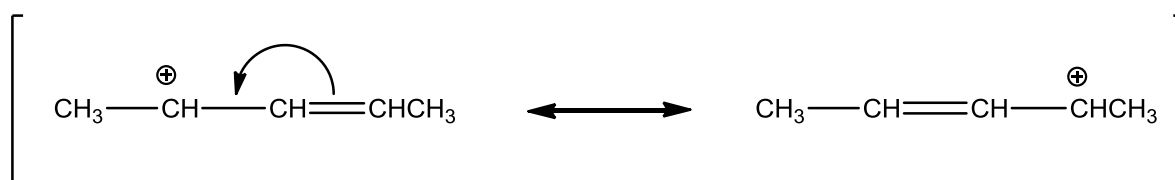
C

Answer:

The carbocations are classified as follows:



The carbocation **B** is stabilised by resonance delocalisation which is absent in the other carbocations. The resonance forms of **B** are:



The carbocation **B** is most stable and the secondary carbocation is more stable than the primary carbocation. Therefore, the trend of carbocations in order of increasing stability is $\text{C} < \text{A} < \text{B}$.

Watch the relevant videos via the links:

<https://www.youtube.com/watch?v=9aCHv67i4tM>

https://www.youtube.com/watch?v=Wz_SpSHcdg

ACTIVITY 4.4

Do Problem 4-29 (a) to (d) in Wade et al.

The other two reactive intermediates, carbanions and carbenes, and their properties (Wade et al sections 4-16C and 4-16 D) will be discussed in second and third-level chemistry modules.

4.5 Kinetics and factors influencing the rate of the reaction (Wade et al sections 4-8 to 4-11)

The **rate of a reaction is a measure of how slow or fast a particular reaction takes place. The rate of the reaction** is influenced by the **slowest step** in a sequence of reactions. The **slowest step** is called the **rate-determining step** because the **overall rate of conversion of reactant(s) to product(s) cannot occur faster than this slowest step.**

The breaking of covalent bonds requires energy. Therefore, the halogenation reactions require light energy or heat energy to take place. The heat of the reaction (energy change in a reaction) can be described as the sum of the bond dissociation energies for the products minus the sum of the bond dissociation energies for the reactants. The heat of the reaction is not dependent on the mechanism, but depends on the initial and final states of the molecules in the specific reaction. The reaction can be either exothermic or endothermic.

We have seen in section 4.4 above that tertiary radicals are more stable than secondary radicals. The bond dissociation energies of primary, secondary and tertiary hydrogens in, for example, propane have been measured experimentally.

It was found that less energy is required to remove a tertiary hydrogen compared to a secondary hydrogen. The removal of a primary hydrogen requires more energy than a secondary hydrogen. Therefore, tertiary radicals are lower in energy than secondary radicals, which are lower in energy than primary radicals.

In a reaction, the state of highest energy between reactants and products is called the **transition state**. The energy difference between the reactants and the transition state is called the **activation energy** – that is the minimum energy that reactants must have for the reaction to take place. In the halogenation reactions of alkanes, the intermediate radicals that form represent the transition state. Therefore, the transition state of a tertiary alkyl halide product forms more easily than the transition state of, for example, a secondary or primary alkyl halide. Read the sections in Wade et al to get an overall understanding of the rate and factors influencing it.

4.6 Halogenation of higher alkanes (Wade et al sections 4-13 to 4-14)

If a molecule had different types of hydrogens, the reaction could generate a mixture of products. The types of hydrogens that we refer to are primary, secondary or tertiary hydrogens. The removal of the hydrogens leads to free radicals of different stabilities. (Consult section 4.4.1 above or section 4-13B in the textbook if you need to review the stabilities of radicals.)

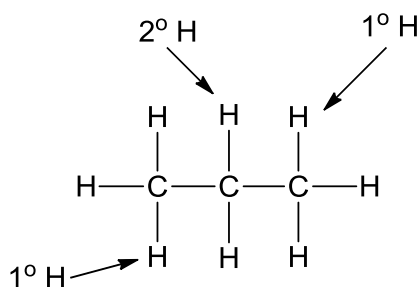
EXAMPLE

Predict the possible substitution products for the free-radical chlorination of propane.

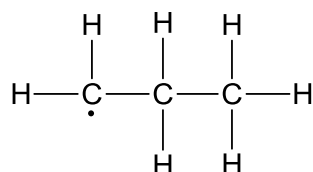
Answer:

Structural formula of propane: $\text{CH}_3\text{CH}_2\text{CH}_3$.

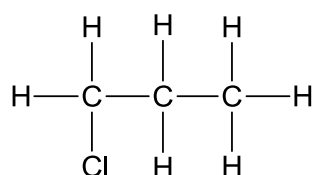
Possible hydrogens that can be abstracted:



The primary hydrogens are all identical (since the molecule is symmetrical) and removal of this hydrogen gives a primary carbon radical.

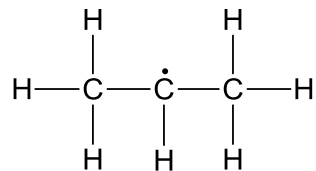


Substitution of the primary (1°) H gives:

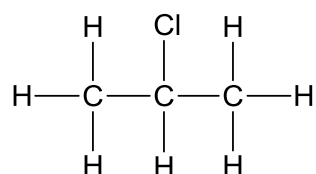


The substitution of any of these primary hydrogens will give the same product.

Substitution of the secondary (2°) H involves the removal of the secondary hydrogen to yield a secondary carbon radical:



Then the secondary carbon radical forms the secondary alkyl halide:



Study Solved Problem 4-4 and the Problem-solving Strategy in Wade et al, which outline the steps in a free-radical reaction mechanism, and the Sample Problem showing the bond-breaking and bond-formation processes in the mechanism of the reaction.

ACTIVITY 4.5

Do Problem 4-19 (a) and (c) in Wade et al.

4.7 Selectivity in halogenation (section 4-13 in Wade et al)

The chlorination of alkanes tends to give a mixture of products where the major product is not formed from the most stable radical intermediate. In fact, it is difficult to predict which species will be predominantly formed in the chlorination reaction.

Free-radical bromination alkanes and substituted alkanes, on the other hand, are very selective. The major monobrominated product is always formed from the most stable radical intermediate.

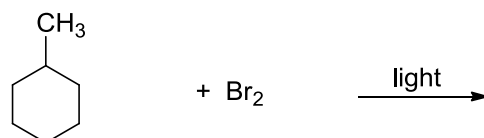
You are encouraged to view the following videos via the links:

<https://www.youtube.com/watch?v=pQy8nyWOVfQ>

<https://www.youtube.com/watch?v=3svKHJ2H2L4>

ACTIVITY 4.6

What is the major organic product formed in the following reaction?



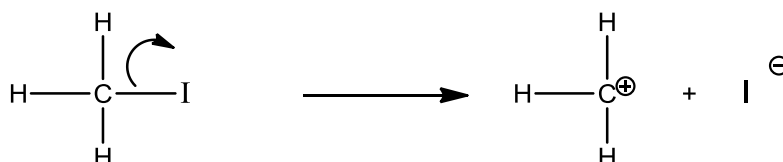
4.8 Conclusion

In this study unit, we described the different steps in free-radical chain reactions. We learnt how arrows are used when the bonds break and form in these processes. We further considered the factors that influence the stability of reactive intermediates such as carbocations and radicals and how to predict the major product of halogenation reactions. You can also access a summary of the contents of this study unit on the MasteringChemistry® site for chapter 4. In the next study unit we will explore the structure, nomenclature, properties and reactivity of alkyl halides.

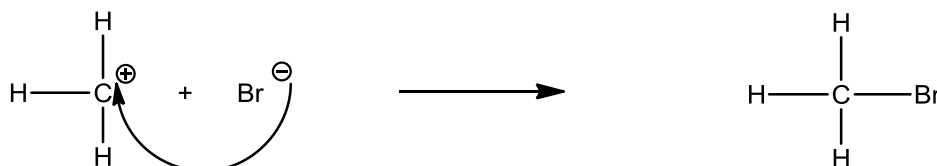
ANSWERS TO SELECTED ACTIVITIES

4.1

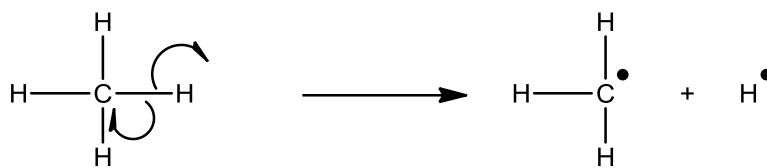
(1)



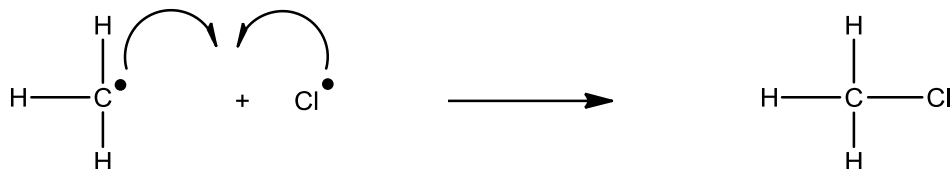
(2)



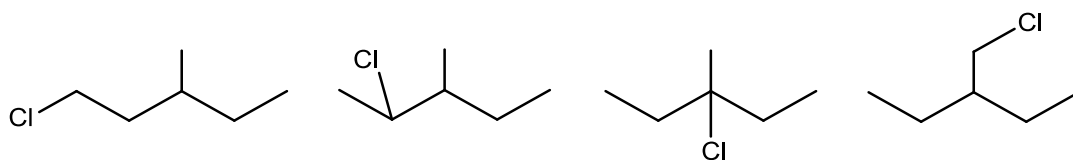
(3)



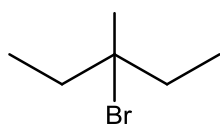
(4)



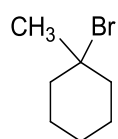
4.2



4.4



4.6



STUDY UNIT 5

Introduction to stereochemistry

- 5.1 Introduction
- 5.2 Chirality
- 5.3 (R) and (S) nomenclature of asymmetric carbon atoms
- 5.4 Diastereomers and meso compounds
- 5.5 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- identify chiral centers
- classify molecules as chiral or achiral
- identify a plane of symmetry
- draw all the stereoisomers of a given compound
- draw three-dimensional structures of chiral molecules
- assign R and S configuration to chiral molecules
- identify enantiomers, diastereomers and meso compounds

5.1 Introduction (Wade et al section 5-1)

We have seen in study unit 1 that, due to the tetrahedral arrangement of the bonds around the sp^3 hybridised atom, most organic molecules are not flat. In addition, you are familiar with the different types of isomers. This will help you to understand the description of enantiomers, chiral and achiral molecules that will receive attention in this study unit.

In this unit we will observe how the different three-dimensional arrangements of atoms in space determine their configurations. The configuration of molecules plays a major role in, for example, their biological properties.

We have already encountered the concept of stereoisomers. Stereoisomers are molecules whose atoms are connected in the same way; however, their atoms are arranged differently in space. Stereoisomers have completely different biological properties. This study unit will also introduce you to the study of the three-dimensional structure of molecules known as stereochemistry. We will also discuss the different types of stereoisomers.

5.2 Chirality (Wade et al section 5-2)

The term "**superimposable**" is one that you will encounter frequently. Consider a pair of shoes: they look alike, but no matter how you twist and turn them, you cannot place them in such a way that they coincide completely. They are said to be **non-superimposable**. However, two left-foot shoes (from two identical pairs) can be put down next to or on top of each other in such a way that they coincide completely. These shoes are said to be **superimposable**. Similarly, the structures of organic molecules can be superimposable or non-superimposable. Two chiral molecules are illustrated in figure 5.1 below.

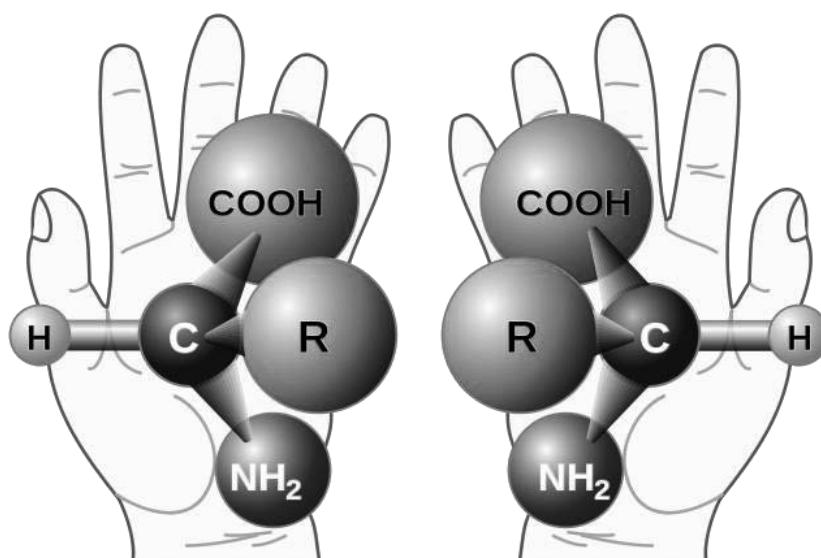


Figure 5.1: Chiral molecules

(Source: https://commons.wikimedia.org/wiki/File:Chirality_with_hands.svg)

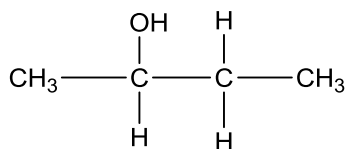
For the purposes of this module, a **chiral center** is a carbon atom with **four different groups or atoms**. A **chiral center** is also known as a stereogenic center.

Normally, a chiral center is designated as **C***. A **chiral carbon** is also referred to as an **asymmetric carbon**. Molecules having at least one **chiral center** are called **chiral molecules**. Chiral molecules are **not superimposable on their mirror images**.

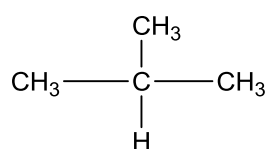
EXAMPLES

1. Identify the molecules that have a chiral center:

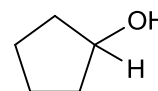
(a)



(b)

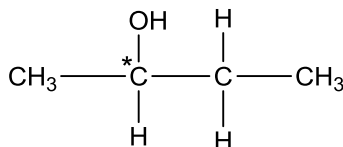


(c)



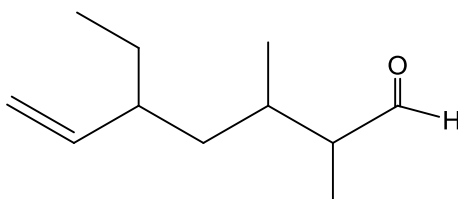
Answers:

- (a) The molecule has a chiral (asymmetric) carbon atom. It has a carbon with four different groups/atoms attached to it, that is, the carbon marked by an *(asterisk) is attached to a CH₃, H, CH₂CH₃ and OH groups.

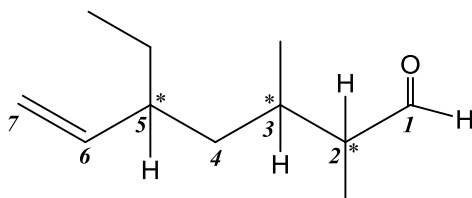


- (b) There are no carbon atoms with four different groups attached to it. Therefore, it DOES NOT have a chiral (asymmetric) carbon atom.
- (c) The carbon attached to the OH group is also attached to an H atom and two identical carbons. Hence, the molecule does not have any carbon atoms with four different groups attached to it. It therefore does not have a chiral (asymmetric) carbon atom.

2. Identify the chiral centers in the following molecule:

**Answer:**

We have to find the carbon atoms with four different atoms or groups attached to each. We can add the H to carbons that each require one H atom for an octet. The chiral centers are indicated below:



Carbon-2 is a chiral center because it has four different groups attached. There is a CH₃, an H, -(C=O)H and the entire chain starting from carbon-3 onwards to C-7. Carbon-3 is a chiral center because it has four different groups attached.

There is a CH₃, an H, -CH₂(C=O)H and the chain starting from carbon-4 to carbon-7. Carbon-5 is also a chiral center with four different groups attached. The four groups are -CH₂CH₃, an H, -CH=CH₂ and the chain starting at carbon-4 to carbon-1.

Study Solved Problem 5-1 in Wade et al for an explanation of how to identify chiral centers.

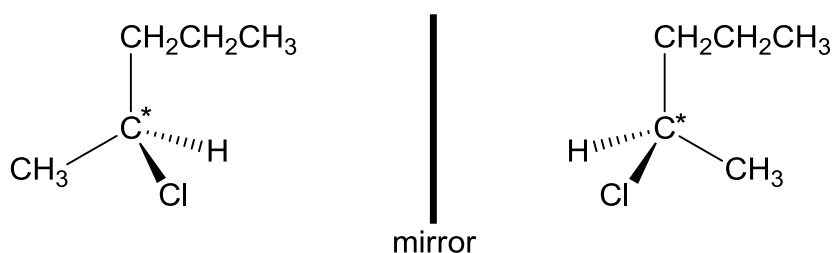
Watch the videos via the links: <https://www.youtube.com/watch?v=tk-SNvCPLCE>
<https://www.youtube.com/watch?v=yChPRfm4yvg>

ACTIVITY 5.1

Do Problem 5-2.

Study Figures 5-6 and 5-7 in the textbook for the respective illustration of mirror images of symmetric and asymmetric carbons.

Enantiomers are isomers that are **non-superimposable mirror images** of each other. Chiral molecules can exist as enantiomers, while achiral molecules cannot exist as enantiomers. See the example of 2-chloropentane below.



The second carbon is the chiral center with CH₃, Cl, CH₂CH₂CH₃ and H attached to it. The two mirror images are non-superimposable.

N.B. If necessary, read through section 5.2 several times until you have a thorough understanding of the concepts discussed in the section. Also consult your textbook for further illustrations.

Now view the videos via the links:

<https://www.youtube.com/watch?v=3WZZXPOsPNI>

<https://www.youtube.com/watch?v=yChPRfm4yvg>

<https://www.khanacademy.org/.../chirality.../v/chiral-examples-1>

<https://www.khanacademy.org/science/organic-chemistry/stereochemistry-topic/chirality-r-s-system/v/introduction-to-chirality>

ACTIVITY 5.2

Do Problems 5-3 (a), (c), (d) and (f) in Wade et al.

Planes of symmetry (Wade et al section 5-2 C)

In some molecules, it is possible to draw a line through the molecule that divides it into two equal parts. If this line splits the molecule so that the one half is the mirror image of the other half of the molecule, then this line is a **plane of symmetry** or **mirror plane of symmetry**. A **plane of symmetry** is an imaginary plane that splits a molecule in such a way that the two halves of the molecule are mirror images of each other. A chiral molecule does not have a plane of symmetry and a molecule that has a plane of symmetry is achiral.

ACTIVITY 5.3

Do Problem 5-5 (a) to (d).

5.3 (R) and (S) nomenclature of asymmetric carbon atoms (Wade et al section 5-3)

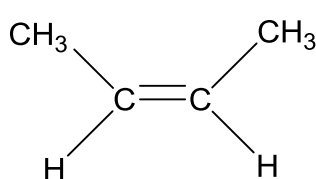
The **three-dimensional arrangement** of the four groups or atoms around the **chiral carbon** is the **only difference** that exists between **two enantiomers**. The **two different spatial arrangements** that are possible around the chiral carbon are called **the configuration** of the molecule.

We have so far used the IUPAC nomenclature system to name compounds. This system is inadequate to name two enantiomers, as they will have the same IUPAC name. The chemists RS Cahn, CK Ingold and V Prelog devised a system that could be used in conjunction with the IUPAC rules to solve this problem.

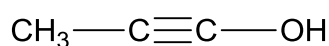
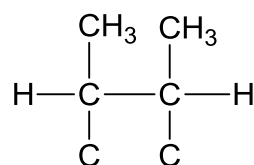
According to this system, the **Cahn-Ingold-Prelog convention**, molecules can be designated as **(R)-** or **(S)-**.

The following steps must be followed to assign R or S configurations:

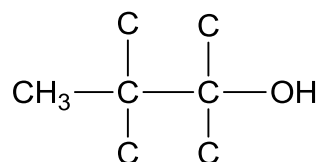
- 1) Identify the chiral center and mark it with a small asterisk (*).
- 2) **Assign priorities to each group/atom bonded to the chiral carbon.** The **highest priority group** is assigned as **group 1**, the **second highest group** is **group 2** and, proceeding in that manner, **the lowest assigned group** will be **group 4**.
- 3) The priorities are determined by looking at the first atom attached to the chiral carbon – atoms with the **highest atomic number** will have the **highest priority**. So, a hydrogen atom will always have the lowest priority.
- 4) If two groups are attached to the chiral center via the same atom, then look at the next atoms in the group and assign priorities accordingly.
- 5) Evaluate double or triple bonds as follows:



becomes



becomes

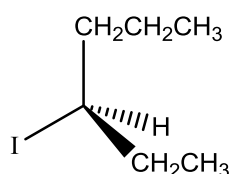


- 6) Draw the three-dimensional structure and place the fourth (lowest) priority group away from the viewer. Then assign the other priority groups.

Draw an arrow from the first priority group through the second priority group to the third priority group. If this arrow points in a clockwise direction, the chiral carbon is designated as **(R)**. When the arrow points in a **counter-clockwise direction**, the achiral carbon is called **(S)**.

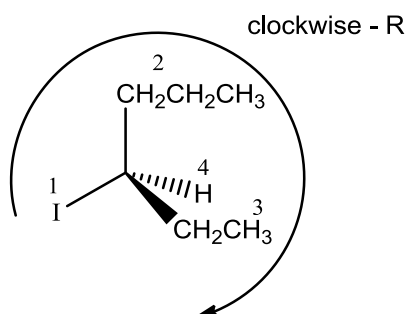
EXAMPLE

Use the Cahn-Ingold-Prelog convention to assign (R) or (S) configuration to the following compound:



Answer: According to the Cahn-Ingold-Prelog rules, assigning priorities to the groups/atoms around the chiral center:

| Group | Priority |
|---|----------|
| I | 1 |
| CH ₂ CH ₂ CH ₃ | 2 |
| CH ₂ CH ₃ | 3 |
| H | 4 |



The arrow points in a clockwise direction and therefore the molecule is **(R)**.

We include the (R) and (S) designation in the IUPAC nomenclature. The IUPAC name of the example above is **(R)-3-iodohexane**.

Study Solved Problems 5-2 and 5-3 in Wade et al, which explain how to assign the (R) and (S) designation.

View the video on how to assign configuration at the link:

<https://www.youtube.com/watch?v=kFD6hzLseVs>

<https://www.youtube.com/watch?v=Z10oC7BF4ig>

View the video on how to draw three-dimensional structures:

<https://www.youtube.com/watch?v=kXj7wbvsNDI>

ACTIVITY 5.4

Do Problems 5-2 and 5-3.

Read through the section on optical activity (Wade et al section 5-4).

5.4 Diastereomers and meso compounds (Wade et al sections 5-11 and 5-13)

Diastereomers are **stereoisomers** whose molecules are **not mirror images** of each other. *Cis-trans* isomers or molecules with more than one chiral center are **diastereomers**.

A **meso** compound is a compound whose molecules are **superimposable on their mirror images** (i.e. the molecule is **achiral**), even though they contain **two or more chiral centers**. A **meso** molecule normally has a **plane of symmetry** that divides the molecule into two parts.

For further explanation on identifying a plane of symmetry and chiral compounds, study Solved Problem 5-7 in Wade et al.

View the video which discusses all the topics in this study unit via the link:
<https://www.khanacademy.org/science/organic-chemistry/stereochemistry-topic/diastereomers-meso-compounds/v/stereoisomers-enantiomers-diastereomers-constitutional-isomers-and-meso-compounds>

ACTIVITY 5.5

1. Do Problems 5-6 and 5-22 (a), (b), (c).
 2. A skill that will help you understand the content of this study unit is the ability to visualise molecules in three dimensions. How easy or difficult do you find this? If you would like to find out more about how the internet can help you to do this, you could visit the link http://www.sciencebuddies.org/science-fair-projects/project_ideas/Chem_VisualizingMolecules.shtml.
-

5.5 Conclusion

In this study unit you were introduced to the concepts enantiomers, diastereomers and meso compounds. Make sure that you have a thorough grasp of these different types of structures and can distinguish between them. This is important because these structures help us to understand the physical and theoretical reasons behind the formation and structures of many organic molecules, and as such will form a basis for your further studies in organic chemistry. We also described the (R) and (S) designation of the three-dimensional structures of chiral molecules.

STUDY UNIT 6

Alkyl halides

- 6.1 Introduction
- 6.2 Nomenclature and classification of alkyl halides
- 6.3 Structure and physical properties of alkyl halides
- 6.4 Preparation of alkyl halides
- 6.5 Reactions of alkyl halides
- 6.6 Nucleophilic substitution reactions
- 6.7 Bimolecular substitution: S_N2 reaction
- 6.8 Unimolecular reaction: S_N1 reaction
- 6.9 Comparison of S_N2 and S_N1 reactions
- 6.10 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

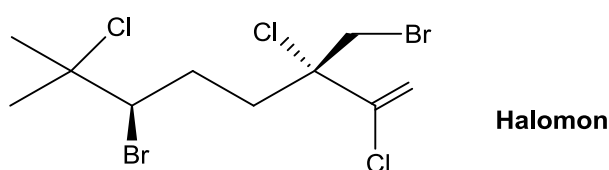
- describe the structure of alkyl halides and apply the rules for naming them
- classify alkyl halides as primary, secondary and tertiary alkyl halides
- correctly propose the mechanisms for nucleophilic substitution of alkyl halides to form alcohols and ethers and predict the products formed
- predict and show the rearrangement of carbocations in reactions

6.1 Introduction (Wade et al section 6-1 and 6-3)

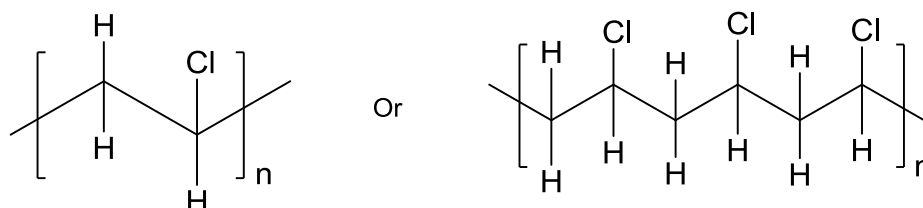
An **alkyl halide** is a saturated hydrocarbon containing a halogen atom (X= F, Cl, Br or I) as substituent of the parent hydrocarbon chain, and the functional group is: **-X**. Due to the **nature of the carbon-halogen bond**, alkyl halides are of great value in organic synthesis because many compounds can be made from them. Alkyl halides also have many uses: carbon tetrachloride, CCl_4 , for instance, is used as a fire extinguisher called Pyrene. The fluorochloro derivatives of methane and ethane, such as CFCl_3 and CF_2Cl_2 , are called freons which are used as refrigerants. Freons are suspected of contributing to the depletion of ozone. Some alkyl halides can be used as anaesthetics. Lead containing petrol has the "anti-knock" additive called tetraethyl lead. Tetraethyl lead is made by heating a lead-sodium alloy with the alkyl halide chloroethane according to the chemical reaction below:



Red algae naturally produce several related compounds, probably as a poisonous defence against fish or other marine life. One of the compounds isolated from red algae is halomon, which is an anti-tumour drug and contains bromine and chlorine atoms, as indicated in the structure below:



One of the most widely used plastics, called polyvinyl chloride (PVC), has an alkyl halide as repeating unit and has the following structural representations:



In this study unit the structure, classification and nomenclature as well as the physical properties of alkyl halides will be discussed. An organic reaction can either be a substitution, an elimination reaction or an addition reaction. Alkyl halides are capable of undergoing substitution and elimination reactions. We will explore the types, conditions and reaction mechanisms of nucleophilic substitution and elimination reactions of alkyl halides.

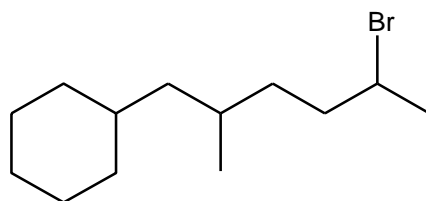
6.2 Nomenclature and classification of alkyl halides (Wade et al sections 6-2)

6.2.1 IUPAC Nomenclature

Alkyl halides are named as derivatives of the corresponding alkane. The IUPAC nomenclature rules as described in section 3.4.2 in study unit 3 must be applied. The position of the halogen atoms is shown with a number and the halogen substituent is indicated as "chloro" for Cl, "bromo" for Br, "fluoro" for F or "iodo" for the I atom.

EXAMPLES

1. Give the correct IUPAC name of the molecule shown below:



Answer:

The IUPAC name for the above molecule: **5-bromo-1-cyclohexyl-2-methylhexane**

Explanation:

According to the IUPAC convention, the longest continuous carbon chain with only C-C single bonds has 6 Cs as a straight chain or 6 Cs in a ring structure. Since the straight chain has the most substituents, it is used to determine the parent name, which is hexane.

Begin numbering at a branch to give substituents the lowest possible number – if we start from the left, the first substituent is on C-1 and if we start numbering from the right, the first substituent is on C-2. Therefore, we will start numbering from the left: on C-1 there is a ring with 6 Cs as a substituent → 1-cyclohexyl; on C-2 there is a CH₃ substituent → 2-methyl; on C-5 there is a bromine atom → 5-bromo.

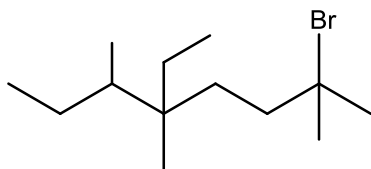
List the substituents in alphabetical order. Hence the name:

5-bromo-1-cyclohexyl-2-methylhexane

2. Draw the structure of 2-bromo-5-ethyl-2,5,6-trimethyloctane

Answer:

The structure of the molecule with the above IUPAC name is:



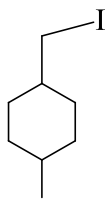
Explanation:

The parent name is octane, which means that according to the IUPAC convention, the longest continuous carbon chain contains 8 Cs. Based on the numbering, "2-bromo" means that on C-2 there is a bromine atom. The "tri" means there are three CH₃ substituents and "2,5,6-trimethyl" implies that on C-2, C-5 and C-6 there are CH₃ substituents. In conclusion, "5-ethyl" means that there is a CH₂CH₃ substituent on C-5.

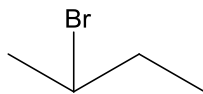
6.2.2 Classification

Alkyl halides are classified as follows:

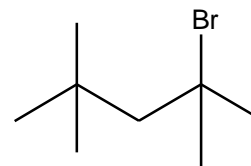
A **primary alkyl halide (1°)** has **one carbon** atom **bonded** to the **C atom** that **bears** the **halogen** atom. A **secondary alkyl halide (2°)** has **two carbon atoms** bonded to the **C atom** attached to the **halogen** atom. **Tertiary alkyl halides (3°)** have **three carbon atoms** bonded to the **C atom** attached to the **halogen** atom. Examples:



1°alkyl halide



2°alkyl halide



3°alkyl halide

You may view the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/alkyl-halide-nomenclature>

ACTIVITY 6.1

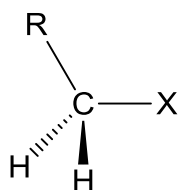
Do Problem 6-2 (a), (b) and (d)
6-3 (a), (d), (e) and (f).

Read through section 6-3 in Wade et al on the common uses of alkyl halides.

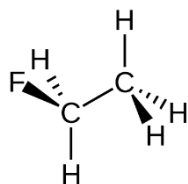
6.3 Structure and physical properties of alkyl halides (Wade et al sections 6-4 and 6-5)

6.3.1 Structure of alkyl halides (Wade et al section 6-4)

The structure of alkyl halides is **tetrahedral** because the carbon atoms linked to the halogen is sp^3 hybridised. As we observed in study units 1 and 2, the carbon-halogen bond is **polar**. A simple alkyl halide will have the following general structure:



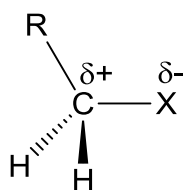
The structure of 1-fluoroethane is:



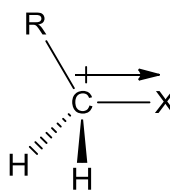
File:Fluoroethane natta.svg- From Wikimedia Commons, Public Domain

https://commons.wikimedia.org/wiki/File:Fluoroethane_natta.svg

Due to the **nature of the carbon-halogen bond**, bond dipoles will exist in alkyl halide molecules because the halogens are **more electronegative** than carbon. The **polarity** of the carbon-halogen bond depends on the type of **halogen atom (X= F, Cl, Br or I)**.



polar C-X bond



direction of dipole moment

Since the **electronegativity decreases** from top to bottom in the **group**, the C-Cl bond is **more polar** than the C-Br and the C-Br bond is **more polar** than the C-I bond.

ACTIVITY 6.2

Do Problem 6-5 (a) and (b).

6.3.2 Physical properties (Wade et al section 6-5)

In general, alkyl halides tend to be liquids or gases. Alkyl halides are soluble in organic solvents but not in water. Similar to alkanes (study unit 3), the **structures** of alkyl halides have a marked effect on their **physical properties**, such as the boiling point.

London dispersion forces are the **strongest attractive forces** in **alkyl halides**, since the **London forces** arise from the **temporary dipole moments** that are brought about in molecules by another molecule. This **attractive force** *depends* on the **molecular surface area**. A molecule with a **large surface area** will have **larger London dispersion forces** between its molecules than a molecule with a lower surface area. The **type of halogen** also affects the **boiling point** of these compounds. Because the size of the halogen increases from top to bottom in the group, **alkyl iodides** exhibit **larger dispersion forces** than the corresponding **bromides**. The **alkyl bromides** have **larger dispersion forces** between its molecules compared to the corresponding **chlorides**.

Alkyl iodides therefore **boil** at **higher temperatures** than the corresponding **bromides** and the **alkyl bromides** have **higher boiling points** than the corresponding **chlorides**. In general, **branched** compounds have **smaller surface areas** than **straight chain** molecules and therefore have **lower boiling points**.

ACTIVITY 6.3

Do Problem 6-6 (a) to (c).

6.4 Preparation of alkyl halides (Wade et al section 6-6A)

Free-radical halogenation is the most relevant method for the preparation of alkyl halides. Review the details of the reaction in study units 3 and 4. At this stage, you need not study the other methods of preparation of alkyl halides since these methods will be done at a later stage in the module.

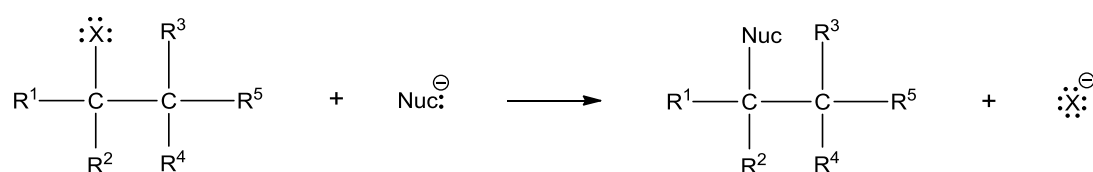
6.5 Reactions of alkyl halides (Wade et al section 6-7)

The main types of organic reactions that alkyl halides can undergo are:

- **substitution reactions**, where the **halogen** atom is **replaced** by another species

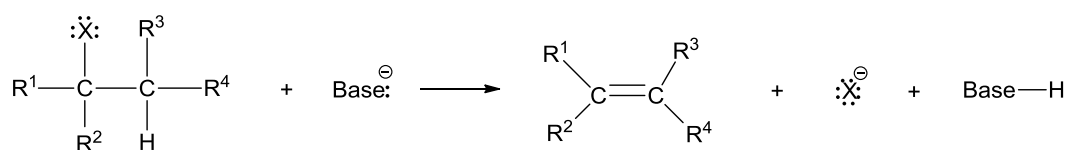
- **elimination reactions**, which involve the **removal** of an **atom / ion** or **groups of atoms** from **each of two adjacent carbon atoms** to form a **double or triple bond**

Substitution reaction takes place in reaction with nucleophiles. **Nucleophiles** are **electron-rich** molecules or ions, which provide electrons in a chemical reaction. They tend to **attract positive** or **electron-deficient** species. In a **nucleophilic substitution reaction**, the **nucleophile replaces** the **halogen** atom. A general representation of such a reaction is:



where R¹, R², R³, R⁴ and R⁵ = H or an alkyl group

Elimination reactions take place when **alkyl halides** are treated with **bases**. In an **elimination reaction**, normally a **hydrogen ion** and the **halogen leave** and a **pi bond** is **formed**. The pi bond forms between the C atoms that were attached to the halogen and that hydrogen atom. The elimination reaction of alkyl halides is illustrated as follows:



where R¹, R², R³ and R⁴ = H or an alkyl group

The different types of nucleophilic substitution reactions of alkyl halides are described in detail in sections 6.7 to 6.9 below. The elimination reactions of alkyl halides will be described in study unit 8. We will discuss the substitution and elimination reactions of other types of compounds in study unit 7.

ACTIVITY 6.4

Do Problem 6-11(a) and (b).

6.6 Nucleophilic substitution reactions (Wade et al sections 6-8, 6-11 B, 6-12 to 6-13, 6-14)

In a **nucleophilic substitution** reaction of alkyl halides, where the **nucleophile (Lewis base)** replaces the **halide ion**, the **halide ion** is called the **leaving group**.

Nucleophilic substitution reactions proceed via two reaction mechanisms, depending on the **structure** of the **alkyl halide** and/or the **nucleophile**. These mechanisms are the **S_N2 reaction mechanism** and the **S_N1 reaction mechanism**.

The "S" refers to substitution, the "N" is used because a nucleophile is involved and the "1" or "2" shows the order of the reaction.

S_N2 reactions are known as **bimolecular** nucleophilic substitution and **S_N1 reactions** as **unimolecular** nucleophilic substitution.

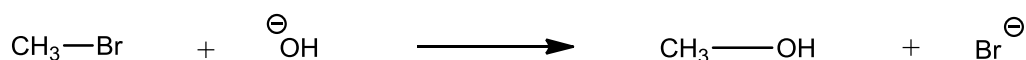
6.7 Bimolecular substitution: S_N2 reaction (Wade et al sections 6-8 and 6-9)

The **S_N2 reaction** is a **one-step process** where **both** the **alkyl halide** and the **nucleophile** are involved **simultaneously**. The rate of the reaction thus depends on both the alkyl halide and the nucleophile. The **S_N2 reaction** is a second-order reaction.

You need to understand the bimolecular nature of the reaction and the mechanism. Also, the stereochemistry of the reaction is extremely important. In a S_N2 reaction, there is **inversion of configuration (sections 6-11B and 6-12)**.

EXAMPLE

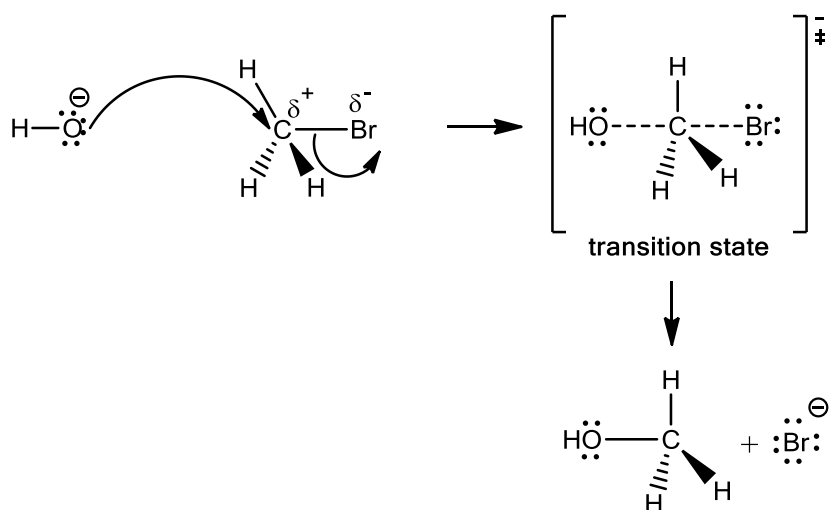
Discuss the reaction mechanism of the following reaction:



In the above nucleophilic substitution reaction, the hydroxide ion replaces the bromine atom. Because the oxygen in the hydroxide ion has a lone pair of electrons and a definite negative charge, the OH^\ominus ion is a strong nucleophile. The **strong nucleophile donates an electron pair easily** and promotes a nucleophilic substitution reaction via the **$\text{S}_\text{N}2$ reaction mechanism**. The alkyl halide is a **methyl bromide**, which can easily react in such a reaction. This reaction mechanism involves the following:

In the C-Br bond, the electronegative Br withdraws electrons from carbon, making the carbon partially positive and electrophilic. There is an attraction between the negatively charged OH^\ominus ion and the partially positive carbon. The carbon becomes partially bonded to the incoming nucleophile (OH^\ominus ion) and the departing Br at a point in the reaction called the **transition state**.

The OH^\ominus ion thus cannot become attached to the carbon on the same side where the Br is attached. The entire **mechanism** (process) is illustrated as follows:



When the **strong nucleophile attacks** the alkyl halide, the **breaking** of the **C-Br bond** takes place at the **same time** as the **formation** of the **bond** between **carbon** and the **OH^\ominus ion** (the **transition state**).

The **S_N2 reaction mechanism** is a **concerted** (single-step) process. Methyl bromide is attacked by the hydroxide ion and is called the **substrate**.

Study Key Mechanism 6-2 in Wade et al.

An **alkyl halide** can also **react** with **another halide ion** to give a **new alkyl halide** molecule – in other words, halide ions can also serve as nucleophiles in S_N2 type reactions. Iodide ions are good nucleophiles in such reactions. The summary of S_N2 reactions in section 6-9 in Wade et al shows different nucleophiles that convert alkyl halides to various other compounds via the S_N2 reaction mechanism.

You may view the video via the link: <https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/intro-to-organic-mechanisms>

ACTIVITY 6.5

Do Problem 6-14(a), (b), (d) and (e).

6.7.1 Factors influencing the S_N2 reaction mechanism (Wade et al sections 6-10 and 6-11)

Several factors influence whether a reaction will occur by the S_N2 or the S_N1 mechanism. The following factors affecting the S_N2 reaction fall within the scope of this course:

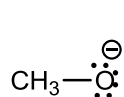
1. The type/strength of nucleophile (Wade et al section 6-10)

The nature of the nucleophile plays an important part in the S_N2 reaction. **Negatively charged** species are **strong nucleophiles** and promote nucleophilic substitution via a **S_N2** reaction mechanism. **Neutral** species are **weak nucleophiles** and **do not** participate in **S_N2** reactions. Water will react much slower than the hydroxide ion in an S_N2 reaction, because H₂O is a weaker nucleophile than the ⁻OH ion.

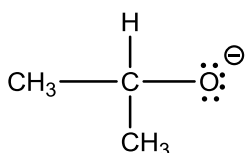
The **rate of attack** by the **nucleophile** on an **electrophilic carbon** is the **nucleophilicity** or **nucleophile strength**. In table 6-3 in Wade et al, some common nucleophiles are listed in order of increasing nucleophilicity in polar solvents like alcohols and water. This data further shows three major trends in nucleophilicity, as captured in the *Summary: trends in nucleophilicity* (Wade et al section 6-10). A **more electronegative** atom will **attract** its **electron pair more strongly** than a less electronegative atom. The more electronegative atom will thus donate its electron pair much slower than the less electronegative atom. In a particular group in the periodic table, the **nucleophilicity** of **larger** atoms is also **greater** than that of **smaller** atoms.

The electrons in the larger atom are further away from the nucleus and more loosely held than the electrons in the smaller atom. When approaching the substrate, the electrons in the larger atom can move more easily towards the partial positive charge and form a stronger bond in the transition state than a smaller atom. The larger atom is more **polarisable** and begins bonding with the carbon earlier than the smaller atom.

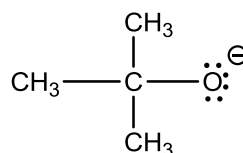
In order for the nucleophile to attack the carbon atom in an S_N2 reaction, it must move close to the carbon. It will be more difficult for a larger nucleophile to approach the carbon than for a smaller nucleophile. The larger ion will thus be a weaker nucleophile than a smaller ion due to **steric hindrance**, that is the interference of larger group(s) due to their size. For example, a methoxide (CH_3O^-) ion is a stronger nucleophile than an isobutoxide ion and the isobutoxide ion is a stronger nucleophile than a tert-butoxide ($(\text{CH}_3)_2\text{CHO}^-$) ion. As we increase the methyl groups in the nucleophile, it becomes more difficult for the nucleophile to attack the carbon atom and we decrease the nucleophilicity.



methoxide ion



iso - propoxide ion



tert - butoxide ion

You may view the video via the link: <https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/nucleophilicity-basicity-sal/v/nucleophilicity-nucleophile-strength>

The **nucleophilicity** of ions is also influenced by the **type of solvent** present in the reaction. **Protic solvents** normally have **N—H** or **O—H** bonds that can undergo **hydrogen bonding** with the **negatively charged** nucleophile. In **smaller** anions, **stronger hydrogen bonds** form with the protic solvents than in **larger** anions. **Protic solvents** thus **decrease** the **nucleophilicity** of **smaller** anions and **slow down** the **S_N2** reaction. **Aprotic solvents** (i.e. solvents without N—H or O—H bonds) **improve** the nucleophilicity of anions.

ACTIVITY 6.6

Do Problem 6-16(a) to (h).

2. The type of substrate (Wade et al section 6-11)

Not all substrates undergo S_N2 reactions at the same rate. The structure of the alkyl halide influences the rate of the reaction.

(a) The leaving group

The purpose of the leaving group in the S_N2 reaction is to polarise the C-X bond and to leave with the bonding electron pair. A **good leaving group** should thus be:

- (i) electron withdrawing
- (ii) stable after the C-X bond breaks (a weak base)
- (iii) polarisable to stabilise the transition state

Table 6-4 in Wade et al lists the weak bases that are good leaving groups.

(b) Steric effects on the substrate

Since the nucleophile must approach the carbon (attached to the leaving group) up to a distance to enable bonding, large groups near that carbon will slow down the S_N2 reaction. **Tertiary alkyl halides** have **the three large alkyl groups** (compared to H) that **sterically prevent** the **attack** by the **nucleophile on the carbon bearing the halogen** via the S_N2 reaction. Therefore, **tertiary alkyl halides** normally do **not react via the S_N2 reaction**.

Primary alkyl halides prefer the **S_N2 reaction** pathway, because primary alkyl halides do **not offer much steric hindrance** to the attack by the nucleophile as do tertiary alkyl halides. **Methyl halides** are the smallest alkyl halides and react the **fastest** via the **S_N2 reaction** pathway. **Secondary alkyl halides** can react via the **S_N2 reaction** pathway, depending on the reaction conditions and the type of nucleophile.

You may view the video via the link: <https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/sn2-mechanism-and-stereochemistry>

ACTIVITY 6.7

1. Do Problem 6-18.
 2. Do Problem 6-19 (a) to (c).
-

6.7.2 Stereochemistry of the S_N2 reaction (Wade et al section 6-12)

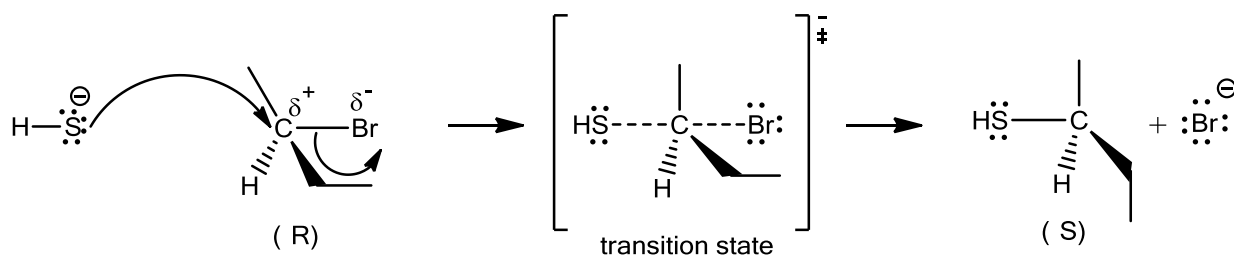
The **S_N2 reaction** involves the **attack** of the **nucleophile** from the **opposite side** of the **C-X bond**. This type of attack is known as **back-side attack** and turns the orientation of the groups attached to the tetrahedral carbon around. The **S_N2 reaction** is said to proceed with **inversion of configuration**. The S_N2 reaction is **stereospecific**. Study Mechanism 6-3 and the illustration in Figure 6-8 in Wade et al.

EXAMPLE

Propose the reaction mechanism for the reaction of (R)-2-bromobutane with NaSH.

Answer:

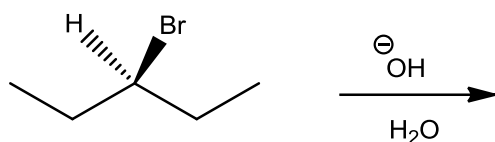
The ionic compound, NaSH, exists as Na⁺ and ⁻SH ions. The ⁻SH ion is a strong nucleophile that promotes nucleophilic substitution via a S_N2 reaction mechanism that takes place as follows:



The reaction occurs with inversion of configuration. (Review the drawing and the assignment of (R-) and (S) – configurations in study unit 5.)

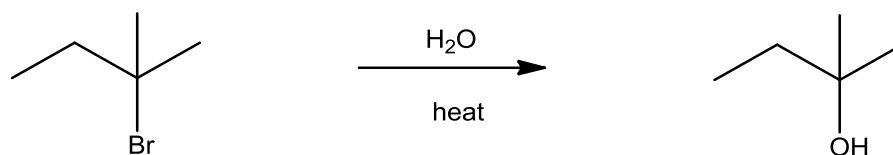
ACTIVITY 6.8

Give the product of the following nucleophilic substitution reaction:



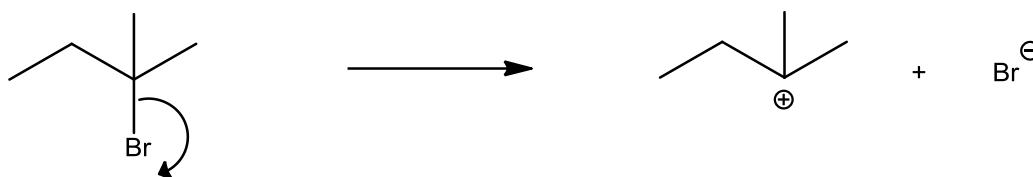
6.8 Unimolecular reaction: S_N1 reaction (Wade et al sections 6-13 and 6-13 A).

We have seen that tertiary alkyl halides do not participate in S_N2 type reactions. When a tertiary alkyl halide is heated in water, a reaction known as hydrolysis takes place, as follows:

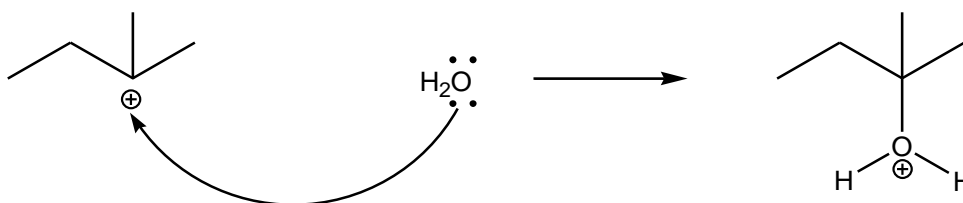


This is a nucleophilic substitution reaction. The water has lone pairs of electrons but does not have a negative charge. It is therefore less nucleophilic than, for example, a hydroxide ion. There is minimal attraction between the water and the partial positive carbon of the C-Br bond and the nucleophilic substitution reaction proceeds via the **S_N1 reaction mechanism**.

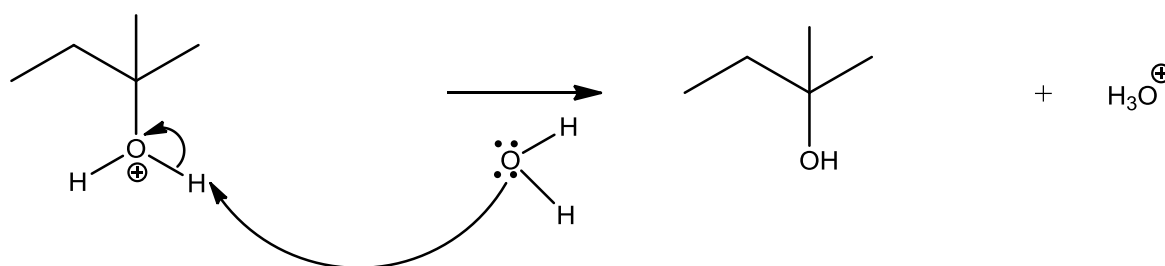
The **S_N1** reaction is a **two-step** process. In the first step, the **halide ion** departs from the **alkyl halide** molecule, leaving a **carbocation intermediate** in a slow step:



In the **second step** the **nucleophile, water**, attacks the **carbocation**:



The oxonium ion, formed above, loses a proton to form the corresponding alcohol:



The rate of the reaction is dependent on the slow step, that is, the formation of the carbocation. The **S_N1** reaction is a first-order reaction.

Study Key Mechanism 6-4 in Wade et al and you may also view the video via the link: <https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/sn2-mechanism-stereospecificity>

6.8.1 Factors influencing the S_N1 reaction mechanism (Wade et al sections 6-13 A to C)

Several factors influence the **S_N1** reaction mechanism. The nucleophile is normally the solvent, like water or alcohol. This nucleophilic substitution reaction is also a solvolysis reaction.

The **nucleophile** is **neutral** and a **weak nucleophile**, because any charged nucleophilic species tend to involve the **S_N1** reaction mechanism. The following factors affecting the S_N1 reaction fall within the scope of this course:

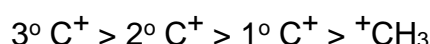
1. The type of substrate (Wade et al section 6-13A and B)

Steric factors do not play a role in S_N1 reactions.

(a) Carbocation stability (Wade et al section 6-13A)

The **S_N1 reaction** mechanism is influenced by the **stability** of the **carbocation intermediate**. Therefore, the structure of the alkyl halide determines the rate of the reaction.

The reaction that produces the **most stable carbocation** intermediate will react the **fastest** in a **S_N1 reaction**. In study unit 4, we discussed carbocations and factors that influence their stability. We recall that carbocation stability follows the following trend:



(b) The leaving group (Wade et al section 6-13B)

The leaving group in the **S_N1 reaction** is just as essential as in the S_N2 reaction. **Good leaving** groups favour the S_N1 reaction and **poor leaving groups slow down** the reaction. Table 6-4 in Wade et al which contains good leaving groups for the S_N2 reaction is also relevant for the S_N1 reaction.

ACTIVITY 6.9

Do Problem 6-23 (a) to (d).

(c) The effect of solvent (Wade et al section 6-13C)

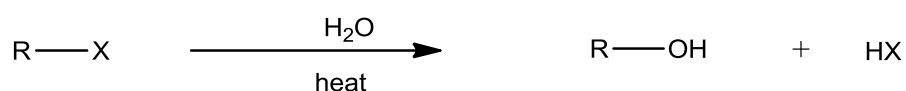
Highly polar solvents assist the **S_N1 reaction mechanism**. **Polar solvents** are able to **stabilise** the **carbocations** by solvating the ions. Solvation takes place through the interaction of the solvent's dipole moment with the carbocation.

Protic solvents are **more effective** than **aprotic solvents** due to the presence of the N-H or O-H bonds that can undergo **hydrogen bonding** with the **negatively charged halide ion**.

Alkyl halides tend to be insoluble in water, but a mixture of water and acetone is highly polar and speeds up the ionisation process.

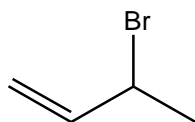
EXAMPLE

Alkyl halides may undergo nucleophilic substitution reaction according to the following reaction:

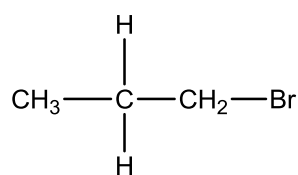


Which of the following compounds will react the fastest under these conditions?

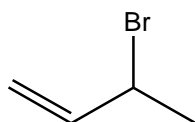
(1)



(2)



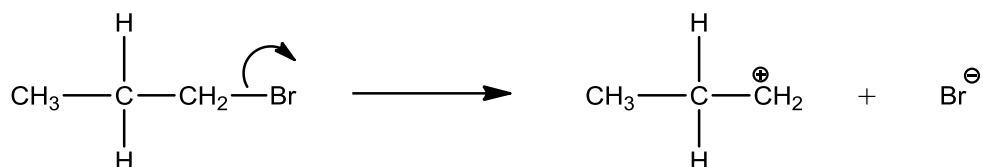
Answer: (1)



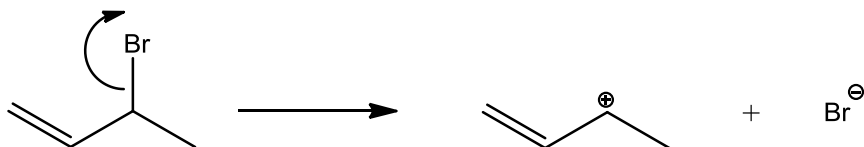
Explanation:

Under the given reaction conditions, the nucleophilic substitution reaction will proceed according to the S_N1 reaction mechanism. Thus each reaction will proceed via a carbocation intermediate.

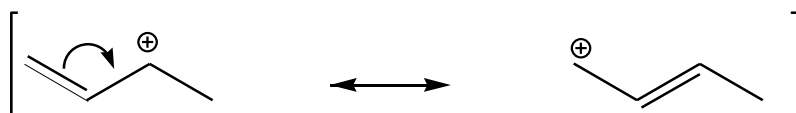
In compound (2), the Br group is the leaving group and breaking of the C-Br bond will produce a primary carbocation, which is the least stable carbocation:



In the reaction with (1), breaking of the C-Br bond will produce the secondary carbocation:



This carbocation undergoes resonance delocalisation as follows:



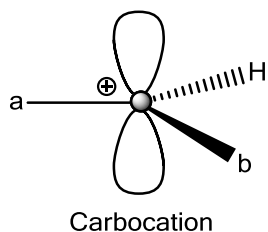
This carbocation is more stable than a regular secondary carbocation. The $\text{S}_{\text{N}}1$ reaction with (1) takes place faster, because the carbocation intermediate is more stable than the primary carbocation formed in the reaction with (2).

You may view the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/sn1-reaction-mechanism>

6.8.2 Stereochemistry of the $\text{S}_{\text{N}}1$ reaction (Wade et al section 6-14).

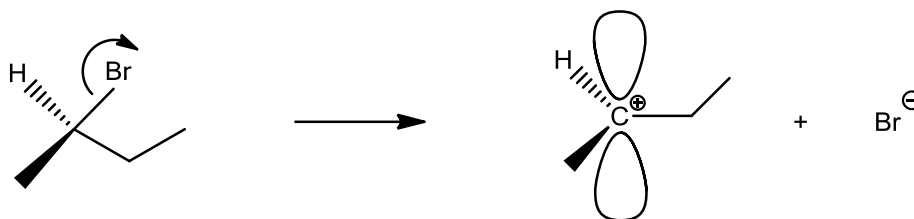
In section 6.7.2, we observed that $\text{S}_{\text{N}}2$ reactions involve inversion of configuration where the nucleophile could only attack the alkyl halide from the back-side. $\text{S}_{\text{N}}1$ reactions, on the other hand, do not have such constraints. The reaction proceeds via a **carbocation intermediate** that is **planar**. Let us consider the solvolysis reaction of a chiral alkyl halide where a carbocation is formed in the first step. This carbocation intermediate is planar and also achiral, as shown below.



The incoming nucleophile can now attack the carbocation at either the top lobe or the bottom lobe of the empty p-orbital. Two products, each having a different stereochemistry, that is enantiomers, are formed. Let us consider for example the reaction of water with (R)-2 bromobutane.

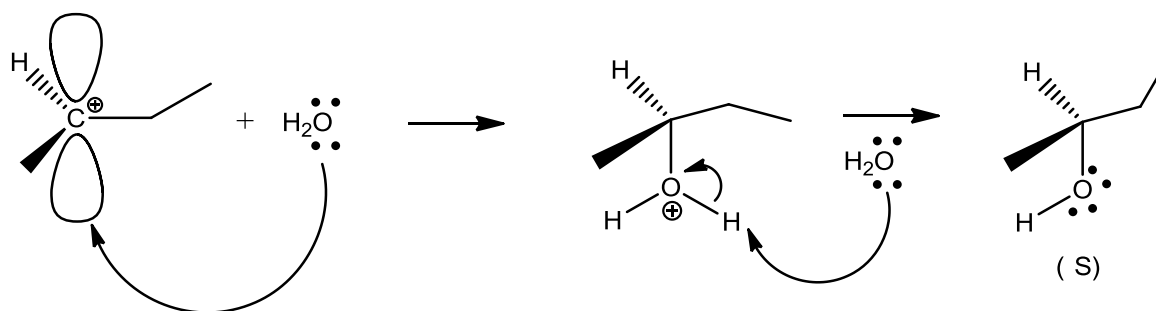
Water is a poor nucleophile that promotes nucleophilic substitution via an S_N1 reaction mechanism. The mechanism for the reaction of (R)-2-bromobutane with water involves the following steps:

Carbocation formation:



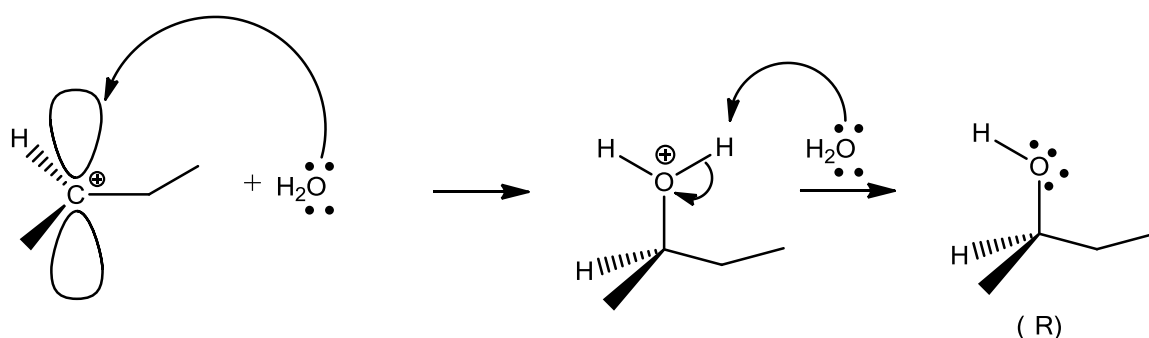
The **carbocation** is **planar** and the **nucleophile** can **attack** from **either side** of the carbocation.

The nucleophile attack from the bottom:



After the nucleophilic attack, a proton is removed from the oxonium ion by a water molecule to give the alcohol. This bottom attack involves inversion of configuration and the S-isomer is formed, namely (S)-butan-2-ol. We will discuss the nomenclature of alcohols in study unit 7. If you need to review of the Cahn-Ingold-Prelog rules for naming chiral compounds, consult study unit 5.

The nucleophile attack from the top:



The nucleophilic attack is followed by the removal of a proton from the oxonium ion by a water molecule to give the alcohol. This attack from the top gives the R-isomer, namely (R)-butan-2-ol, and retention of configuration occurs. In this reaction, a pure enantiomer is converted to a mixture of two enantiomers and racemisation occurs.

For more information, you may watch the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/sn1-reaction-stereochemistry>

6.8.3 Rearrangements in S_N1 reactions (Wade et al section 6-15)

Although the products of substitution reactions are the result of the replacement of the leaving group by the nucleophile, many reaction products are the result of some rearrangement that took place. Why and when does rearrangement take place? Rearrangement normally takes place when a carbocation intermediate is formed.

Rearrangement only takes place if it is possible to go from **one carbocation intermediate** to a **more stable carbocation intermediate**.

Rearrangements occur via **1,2-hydride shift** or **1,2-methyl shift**. The **1,2-hydride shift** in an S_N1 reaction is illustrated in Mechanism 6-6 and the **1,2-methyl shift** in Mechanism 6-7 in Wade et al.

You may watch the video on carbocation stability and rearrangement via the link:
<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/carbocation-stability-and-rearrangements-introduction>

6.9 Comparison of S_N2 and S_N1 reactions (Wade et al section 6-16)

Several factors influence whether a reaction will occur by the S_N2 or the S_N1 mechanism. The following factors fall within the scope of this course:

1. The type of substrate

Tertiary alkyl halides tend to react via the **S_N1 mechanism only** because tertiary alkyl halides form relatively **stable tertiary carbocations**. **Primary alkyl halides** prefer the **S_N2 reaction** pathway because primary alkyl halides form **primary carbocations** which are very **unstable**. **Secondary alkyl halides** can undergo either **S_N2 or S_N1 reactions**, depending on the reaction conditions and the strength of nucleophile.

2. The type of nucleophile

Neutral molecules are **poor nucleophiles** that promote nucleophilic substitution via an **S_N1 reaction mechanism**. **Negatively charged** species are **strong nucleophiles** that promote nucleophilic substitution via a **S_N2 reaction mechanism**.

3. Steric effects

Tertiary alkyl halides tend to react via the **S_N1 mechanism only** because the **presence** of the **three large alkyl groups** (compared to H) **sterically prevents the attack** by the nucleophile on the carbon bearing the halogen via the **S_N2 reaction**.

Primary alkyl halides prefer the **S_N2 reaction** pathway, because primary alkyl halides do **not offer much steric hindrance** to the attack by the nucleophile, as do tertiary alkyl halides. **Methyl halides** are the smallest alkyl halides and react the fastest via the **S_N2 reaction** pathway.

Secondary alkyl halides can react via the **S_N1 mechanism** or the **S_N2 reaction** pathway, depending on the reaction conditions and the type of nucleophile.

4. Solvent

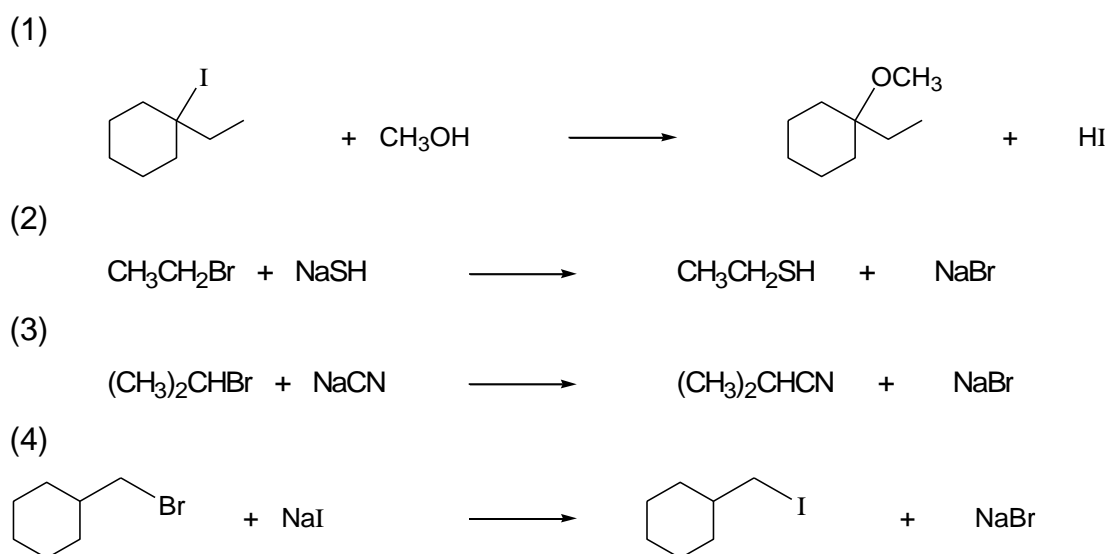
Very polar solvents are required for **S_N1** reactions to solvate the ions. **Less polar** solvents are required for **S_N2** reactions since a polar solvent will slow down the reaction.

5. Rearrangements

Carbocations can undergo **rearrangement** and therefore **S_N1** reactions can undergo rearrangement. Since there is no intermediate in an **S_N2** reaction, rearrangement is not possible.

EXAMPLE

Evaluate the following reactions and determine if it proceeds via an **S_N2** or an **S_N1** reaction mechanism.



Answer:

- (1) The reaction involves a tertiary alkyl iodide that cannot undergo S_N2 reactions easily due to steric hindrance (crowding). CH_3OH is a poor nucleophile that promotes S_N1 reactions.
- (2) The other options involve a strong nucleophile and primary or secondary alkyl halides, which all promote S_N2 reactions.

You are encouraged to view the videos via the links:

<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/sn1-sn2-tutorial/v/sn1-vs-sn2-summary>

<https://www.youtube.com/watch?v=YMKWmqK0t7g>

ACTIVITY 6.10

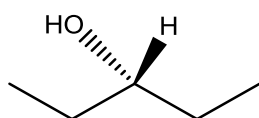
Do Problem 6-27.

6.10 Conclusion

We have discussed the structure, classification and nomenclature of alkyl halides in this study unit. We also considered the factors that influence the physical properties. You also learnt about the mechanisms and all the factors that influence the bimolecular and unimolecular nucleophilic substitution reactions of alkyl halides. We will discuss another important type of reaction of alkyl halides, namely elimination reactions, in study unit 8. We will explore the structure and properties of saturated organic compounds containing oxygen and nitrogen in the next study unit.

ANSWERS TO SELECTED ACTIVITIES

6.8



STUDY UNIT 7

Saturated compounds containing oxygen and nitrogen

7.1 Introduction

A ALCOHOLS

7.2 Structure, classification and nomenclature of alcohols

7.3 Properties of alcohols

7.4 Synthesis of alcohols: nucleophilic substitution of an alkyl halide

7.5 Reactions of alcohols

B ETHERS

7.6 Structure, physical properties and nomenclature of ethers

7.7 Preparation of ethers

7.8. Reactions of ethers

C AMINES

7.9 Classification, nomenclature and structure of amines

7.10 Physical and chemical properties

7.11 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- describe the structure of alcohols, ethers and amines and apply the rules for naming them
- classify alcohols and amines as primary, secondary and tertiary compounds
- evaluate the physical properties of alcohols, ethers and amines
- correctly describe the preparation of alcohols and ethers
- correctly propose the mechanisms for selected nucleophilic substitution reactions of alcohols and ethers
- correctly propose the mechanisms of acid catalysed elimination reactions (dehydration) of alcohols and acid cleavage reactions of ethers
- describe and compare the basicity of amines and their conjugate states

7.1 Introduction (Wade et al sections 10-1, 10-5, 14-1 and 19-1)

In the previous study unit, we focused on saturated compounds containing halogen atoms. We will now consider saturated compounds containing oxygen and nitrogen, specifically alcohols, ethers and amines. Do you know what all the drinks shown below have in common? The drinks all contain ethanol, which forms in the fermentation process when the drink is made.



Author: [TrafficJan82](#) Public domain

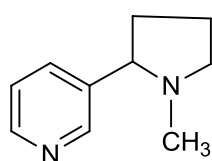
https://commons.wikimedia.org/wiki/File:Common_alcoholic_beverages.jpg

Figure 7.1 Common alcoholic beverages

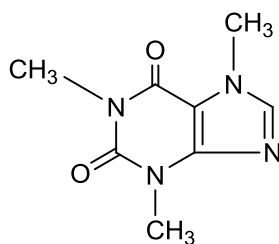
Ethanol is an example of the class of compounds known as **alcohols**, which contain one or more **-OH** groups (**hydroxy groups**) as functional group. Ethanol is extensively used as a solvent and as a starting material for other chemical reactions. Alcohol occurs in nature and is of biological and industrial importance. Another alcohol, ethylene glycol, is used as a coolant in car engines and to make textile fibres. The alcohol glycerol (also known as glycerin) is formed as a by-product during the manufacturing of soap. Glycerol is used to make protective coating for appliances, to manufacture dynamite and as a moisturiser in cosmetics.

Ethers are compounds that also contain oxygen and have **two alkyl and/or aryl groups attached to an oxygen atom**. Ethers are highly flammable and when mixed with air, they form highly explosive mixtures. Ethers are not as widely used as alcohols and are relatively stable to be used in organic reactions.

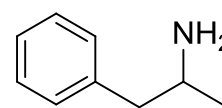
Amines, on the other hand, contain **nitrogen**. Amines are derivatives of a widely used chemical called ammonia, NH_3 , which may have one, two or three alkyl groups replaced for the hydrogens in ammonia. Many amines found in nature have potent physiological actions. Amines isolated from plants include nicotine found in tobacco and caffeine found in tea and coffee. Another amine, amphetamine, is a stimulant used as a performance enhancer for athletes as well as to improve cognitive functions.



Nicotine



Caffeine



Amphetamine

Figure 7.2

In this unit, we will discuss the structure, nomenclature and properties of alcohols, ethers and amines. The synthesis and selective reactions of alcohols and ethers will also receive attention.

A. ALCOHOLS

7.2 Structure, classification and nomenclature of alcohols (Wade et al sections 10-2 and 10-3)

7.2.1 Structure of alcohols (Wade et al section 10-2)

The structure of alcohols is similar to water, with one of the hydrogens replaced by an alkyl group. The oxygen atoms in alcohols have two non-bonding pairs of electrons and are electronegative.

7.2.2 Classification of alcohols (Wade et al section 10-2)

Similar to the alkyl halides, alcohols are classified as primary, secondary, tertiary or phenol. For example, a **primary (1°) alcohol** is a molecule with the OH group attached to a primary carbon, and a **secondary (2°) alcohol** has the OH group attached to a secondary carbon atom. In a **tertiary (3°) alcohol**, the OH group is attached to the tertiary carbon, and when the OH group is attached to an aromatic group, the alcohol is called a phenol. Specific examples are shown in Figure 7.3 below:

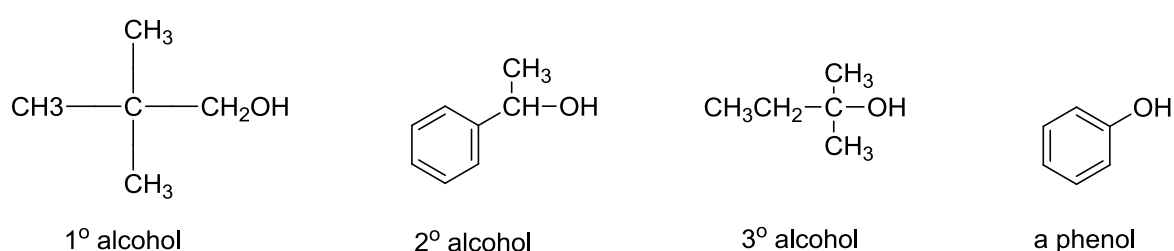


Figure 7.3

7.2.3 Nomenclature of alcohols (Wade et al section 10-3)

The IUPAC nomenclature rules as outlined in section 3.4.2 in study unit 3 are applicable, with the following adaptations:

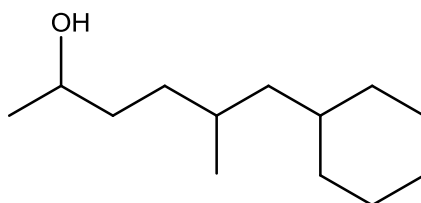
1. The "e" at the end of the name is replaced by an "ol".
2. The position of the OH group in the carbon chain is assigned by numbering the carbon chain in such a way that the **OH group has the lowest possible number**.
3. Two or more alcohol groups are indicated as **diol**, **triol**, and so forth, with the positions of the OH groups shown by the appropriate numbers.

Carefully study Solved Problem 10-1 in Wade et al.

EXAMPLES

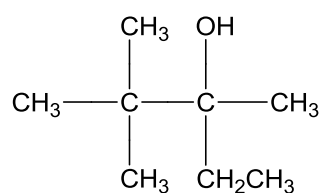
1. Draw the structure of 6-cyclohexyl-5-methylhexan-2-ol

Answer:



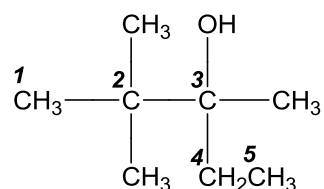
Explanation: According to the IUPAC convention, the longest continuous carbon chain with the most branches is called "hexan", that is, it has 6 carbon atoms. The "2-ol" means that the longest chain is an alcohol and contains an OH group on C-2, the second carbon in the chain. The substituents are indicated as "6-cyclohexyl", in other words, there is a ring containing 6 Cs on C-6, and "5-methyl" means that there is a methyl on C-5.

2. Provide the correct IUPAC name for the following compound:



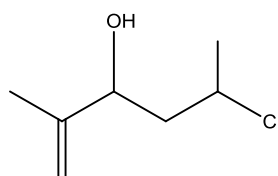
Answer: 2,2,3-Trimethylpentan-3-ol

Explanation: This compound has an OH group and is an alcohol. According to the IUPAC convention, the longest continuous carbon chain is numbered from the end that will give the OH substituent the lowest possible number:



The longest chain that contains the OH group has 5 Cs and the parent name is pentane. Starting the numbering from the left, the OH is on C-3, and starting from the right, the OH is on C-3. Numbering will start from the left-hand side because then all the other groups will have the lowest possible numbers. With the OH on C-3, we change the ending "e" to "ol" and thus 3-ol. On C-2 there are two CH₃ groups and on C-3 there is another CH₃ group. For three CH₃ groups, use the prefix "tri" and write the groups as "2,2,3-trimethyl".

3. Provide the correct IUPAC name for the following compound:



Answer: The IUPAC name is **5-chloro-2-methyl-1-hexen-3-ol**.

Explanation: According to the IUPAC convention, the longest continuous carbon chain containing the C=C bond has 6 Cs → hexane, but since there is a C=C bond and an OH group in the chain → change the ending from "ane" to "enol". Begin numbering at the end of the C-chain to give the OH the lowest number. Then the OH group is on C-3 → 3-ol and C=C on C-1 → 1-en. The substituents are at C-2, a CH₃ group → 2-methyl and at C-5, a Cl atom → 5-chloro; name substituents in alphabetical order.

You may view the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides/alcohol-nomenclature-properties/v/alcohol-nomenclature>

ACTIVITY 7.1

Do Problem 10-1(a) to (e), 10-4(a) to (d).

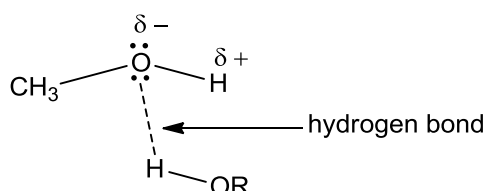
7.3 Properties of alcohols (Wade et al sections 10-4 and 10-6)

The presence of the oxygen atom plays a pivotal role in the characteristic properties of alcohols.

7.3.1 Physical properties of alcohols (Wade et al section 10-4)

We know that oxygen is more electronegative than carbon and hydrogen and that there is more electron density around the O atom. In the OH group, the oxygen has a partial negative charge and the hydrogen atom has a partial positive charge. The **O-H bond** is therefore **polar** and the consequence of this polarisation is an alcohol molecule with a permanent dipole. **Dipole-dipole interactions** thus exist, which play a role in the physical properties of alcohols.

Hydrogen bonds exist between the positively polarised H atom (of the OH group) of one alcohol molecule and the negatively polarised oxygen atom of another alcohol molecule.

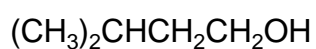


This **hydrogen bonding** causes alcohols to have higher melting and boiling points than alkanes and alkenes of similar molecular weights. The density and boiling points of alcohols increase with an increase in size/molecular weight.

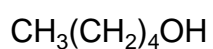
The solubility of alcohols in water decreases with an increase in molecular weight. Alcohols are more soluble in water compared to the hydrocarbons because alcohols can form hydrogen bonds with water.

EXAMPLE

Rank the following compounds in order of increasing boiling point:



A



B



C

Explain your answer.

Answer: Hydrogen bonding is the major intermolecular attractive force between alcohol molecules. When branching in the chain is increased, the boiling point decreases. **B** has no branching and has the highest boiling point. **C** has the most branching and has the lowest boiling point. The order of increasing boiling point is:



C

A

B

You may view the video on the physical properties of alcohols via the link:

<https://www.khanacademy.org/test-prep/mcat/chemical-processes/alcohols-and-phenols/v/properties-of-alcohols>

ACTIVITY 7.2

Do Problem 10-5 (a), (c), (d).

7.3.2 Acidity of alcohols (Wade et al section 10-6)

Alcohols are weakly acidic and the OH hydrogen can be removed by a strong base like sodium or potassium metal.

As the size of the alkyl group increases, the solvation of the alkoxide ion decreases and therefore alcohols with larger molecular weights are less acidic than smaller alcohols.

Sodium hydride and potassium hydride react better to form alkoxides than the metals. Electron delocalisation in the alkoxide also increases the acidity of the alcohol.

ACTIVITY 7.3

Do Problem 10-9 and 10-10.

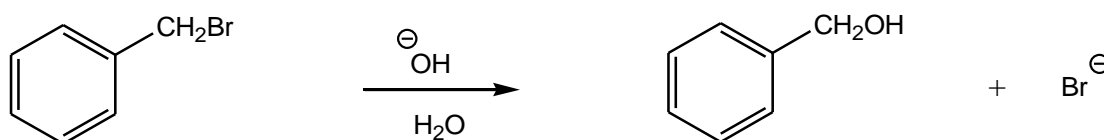
7.4 Synthesis of alcohols: nucleophilic substitution of an alkyl halide (Wade et al section 10-7)

The liver has the function of removing toxins from our bodies. The liver repeatedly hydroxylates (introduces hydroxy groups) unwanted compounds until they become water soluble, so that they can be excreted in urine or the bile. Thus, chemical reactions to prepare alcohols occur in the human body and are also conducted in the chemistry laboratory. In this section, we will focus on how organic chemists convert other compounds to alcohols.

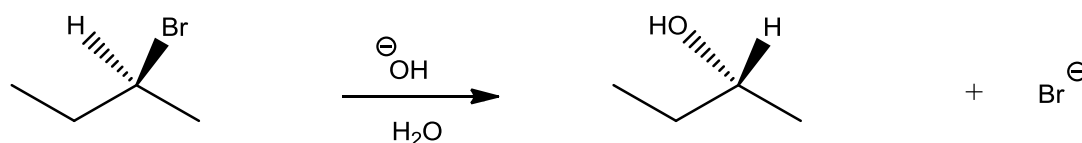
We now review the reaction of alkyl halides with either hydroxide ions or water molecules to produce alcohols as described in sections 6.7 and 6.8 in study unit 6.

For example, let us compare the rates of the following reactions:

(a)



(b)



(c)

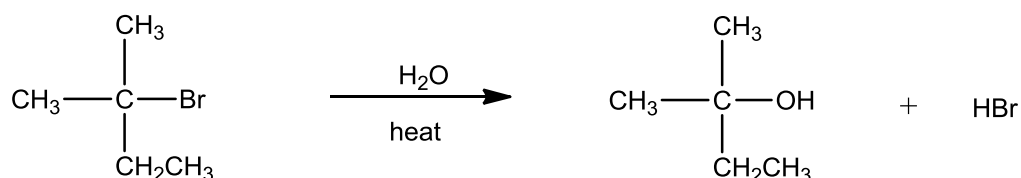


The hydroxide ion is a strong nucleophile and all the reactions proceed via an $\text{S}_{\text{N}}2$ reaction mechanism. In (a) the alkyl halide is a primary alkyl halide and the alkyl halide in (c) is also primary. Compared to the alkyl halide in (c), the alkyl halide in (a) has a larger group attached to the C where the nucleophile, OH^\ominus , must attack.

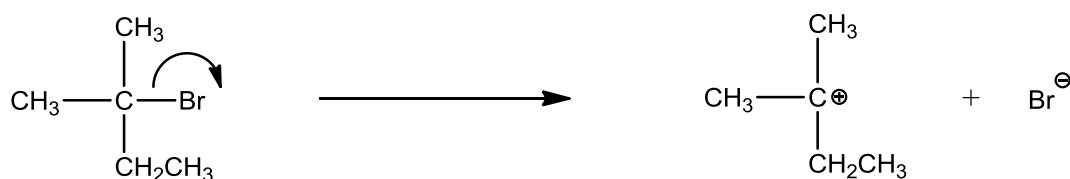
The $\text{S}_{\text{N}}2$ reaction in (a) will therefore take place at a slower rate than the reaction in (c). The alkyl halide in (b) is a secondary alkyl bromide that can undergo $\text{S}_{\text{N}}2$ reaction.

However, the reaction of primary alkyl halides is always faster than the reaction of secondary alkyl halides under similar reaction conditions. Therefore reaction (b) takes place the slowest and reaction (c) the fastest.

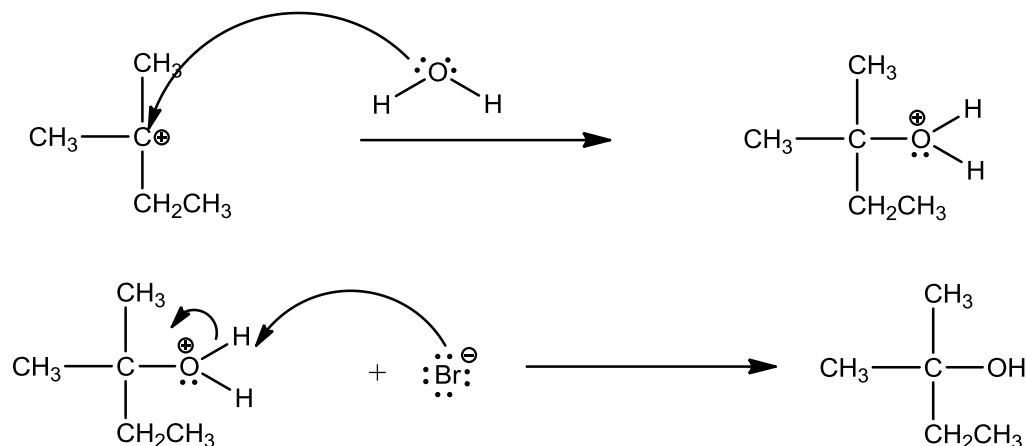
An example of the $\text{S}_{\text{N}}1$ reaction is:



Under the given reaction conditions, the nucleophilic substitution reaction proceeds according to the $\text{S}_{\text{N}}1$ reaction mechanism because H_2O is a poor nucleophile. Thus, each reaction will proceed via a carbocation intermediate. The reaction that produces the most stable carbocation will react fast under these conditions. The reaction forms a stable tertiary carbocation intermediate in the first step of the reaction mechanism:



The final alcohol product is formed by the nucleophilic attack of H₂O on the carbocation. The second and third steps of mechanism for product formation are as follows:



Alcohols can also be prepared from the acid-catalysed hydration, oxymercuration-demercuration and hydroboration-oxidation reactions of alkenes. We will discuss these reactions in study unit 8.

ACTIVITY 7.4

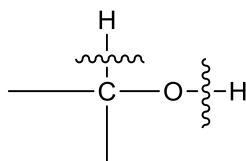
Do Problem 6-34 (a) to (f).

7.5 Reactions of alcohols (Wade et al chapter 11)

In this section, we will focus on how organic chemists convert alcohols to other compounds.

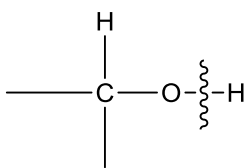
The reactions of alcohols involve the breaking of bonds. The possibilities are:

- (i) The **breaking** of the **O-H** bond and the **adjacent C-H** bond:



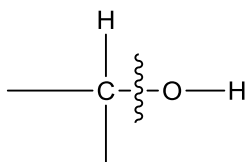
This type of bond breaking takes place in **oxidation reactions** as described in section 7.5.1 below.

(ii) The **breaking** of the **O-H** bond:



This type of bond breaking leads to the formation of **alkoxide ions**. We will consider the formation of alkoxide ions in the preparation of ethers in section 7.7.2 below.

(iii) The **breaking** of the **C-OH** bond:



This type of bond breaking takes place in **nucleophilic substitution** and **elimination** reactions, which will be discussed in sections 7.5.2 and 7.5.3, respectively.

Alcohols as nucleophiles and electrophiles

Depending on which bond is being broken, an alcohol can act as an electrophile or a nucleophile. Alcohols behave as weak nucleophiles in reactions with strong electrophiles. An alcohol acts as a strong nucleophile when it is converted to an alkoxide ion. Alcohols are weak electrophiles because the OH group is a poor leaving group. An alcohol can however become strongly electrophilic when the OH group is protonated. Protonation converts the poor leaving group into a good leaving group.

Alcohols undergo substitution and elimination reactions as discussed in Wade et al sections 11-5, 11-7, 11-10A and 11-10B.

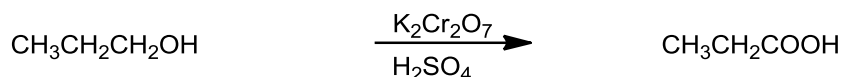
N.B. Leave out the section on tosylates in the textbook.

7.5.1 Oxidation of alcohols (Wade et al sections 11-1 and 11-2)

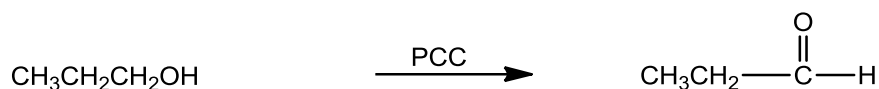
In the **oxidation** of an alcohol, the type of product formed depends on the **nature** of the **oxidising agent** and the **classification** of the **alcohol**. **Pyridinium chlorochromate (PCC)** can **oxidise primary alcohols** to **aldehydes**. When **stronger oxidising agents** are used, **primary alcohols** are **oxidised** to **carboxylic acids**. Reagents like potassium dichromate, $K_2Cr_2O_7$, or sodium dichromate, $Na_2Cr_2O_7$, in the presence of sulphuric acid; or potassium permanganate, $KMnO_4$, in the presence of hydroxide ions make this conversion possible. **Secondary alcohols** can be **oxidised** to form **ketones** when **$KMnO_4$** is used as oxidant. **Tertiary alcohols cannot** be oxidised.

EXAMPLES

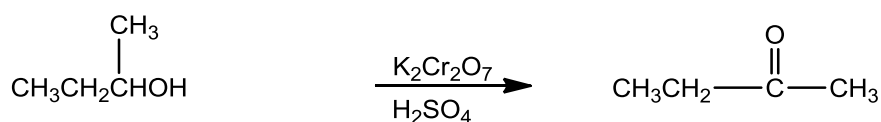
(1)



(2)



(3)



You may view the video via the link: <https://www.khanacademy.org/test-prep/mcat/chemical-processes/alcohols-and-phenols/v/oxidation-of-alcohols>

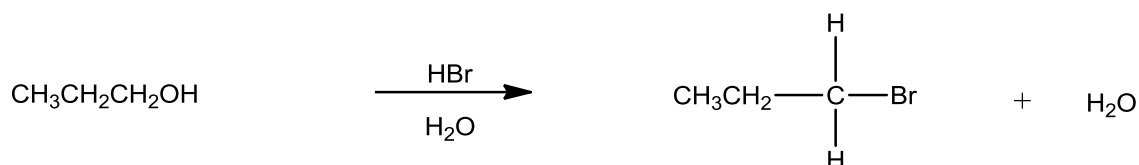
ACTIVITY 7.5

Do Problem 11-1.

7.5.2 Reaction with hydrohalic acids (Wade et al section 11-7)

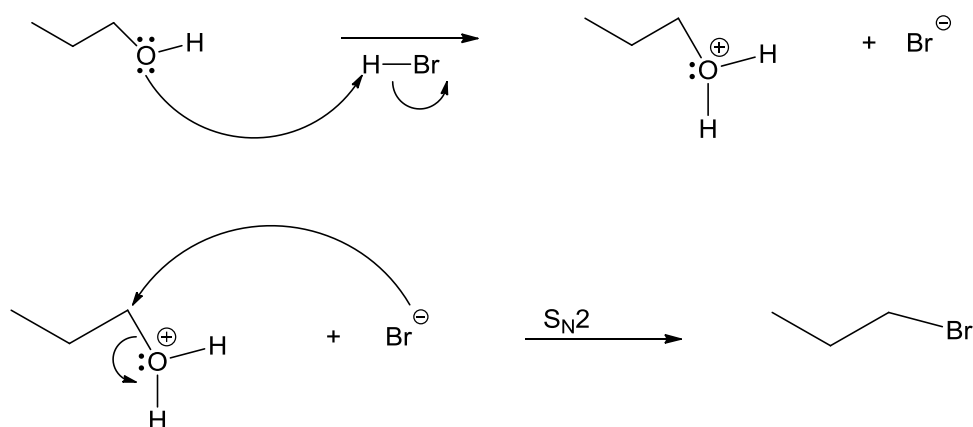
In order for alcohols to undergo substitution reactions, the OH groups must be replaced by a nucleophile. The **OH group** is a **poor leaving group** and must be **converted to a good leaving group**. In the **presence of acid**, the **O atom of OH** becomes **protonated** to form the oxonium ion that is a **good leaving group**. The group is then replaced by the halide ion, either via S_N1 or via S_N2 , depending on the nature of the original alcohol.

In the reaction of an alcohol with hydrohalic acid, HX, the protonated hydroxy group is substituted by the halide ion. Consider the reaction below:

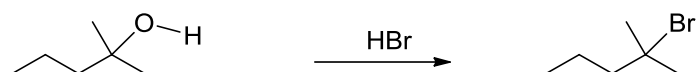


The alcohol in the reaction is a primary alcohol, which after protonation undergoes loss of water and simultaneous attack by the bromide ion to give the alkyl halide.

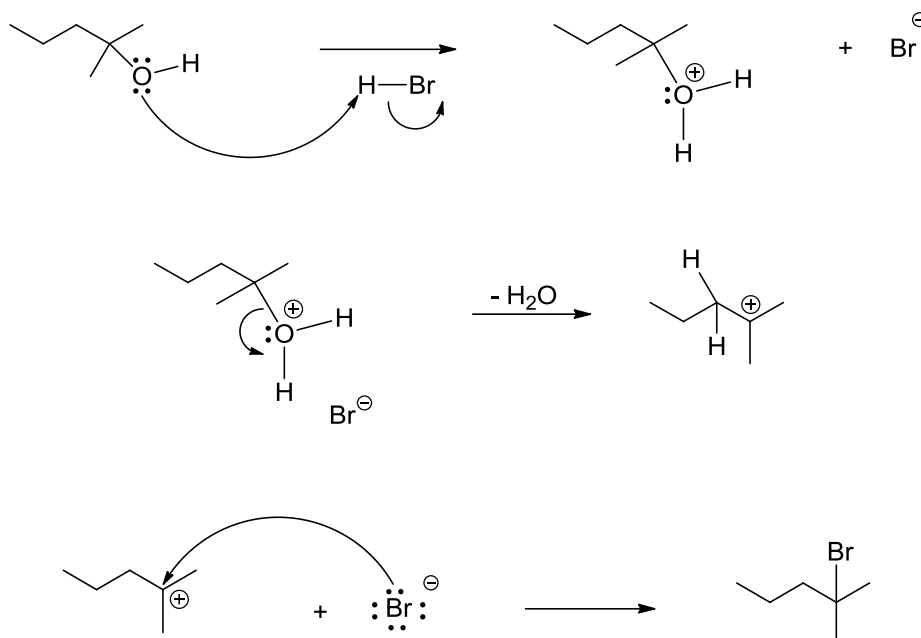
The complete mechanism of the reaction is:



The reaction of the primary alcohol proceeds via the S_N2 reaction mechanism because a primary carbocation is unstable, which prevents the S_N1 reaction from taking place. The reaction below is an example of an S_N1 reaction.



The complete mechanism of the reaction is:



Loss of water gives a carbocation and the reaction produces a stable tertiary carbocation, which promotes the S_N1 reaction mechanism.

Study Solved Problem 11-1 and 11-2 as well as Mechanism 11-1 and 11-2 in Wade et al.

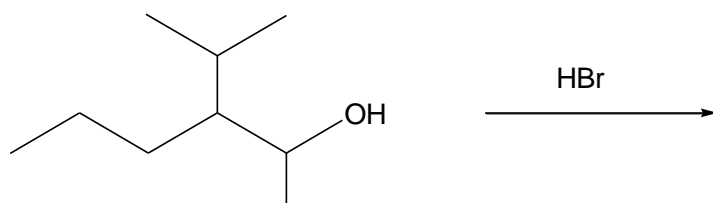
Also, watch the video on the reactions of alcohols via the link:

[https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides#reactions-alcohols-tutorial](https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides/reactions-alcohols-tutorial)

The limitations on the reaction of hydrohalic acids with alcohols are discussed in section 11-7C in Wade et al.

ACTIVITY 7.6

Give the product formed in the following reaction:



7.5.3 Elimination reactions (Wade et al section 11-10 A)

Alcohols undergo **dehydration** (loss of water) in the **presence of a strong acid**. When alcohols are heated with sulphuric acid or phosphoric acid, they form alkenes (compounds containing C=C bonds). We say that **dehydration** reactions of **alcohols** are **acid catalysed**. As indicated in section 7.5.2 above, the O atom becomes protonated to form the oxonium ion in the presence of acid. The mechanism of the dehydration reaction involves the following steps:

- i. **protonation of O** atom to form the $-\text{OH}_2^+$ group
- ii. **loss of water** gives a **carbocation**
- iii. **loss of H⁺** to give an alkene

A dehydration reaction will take place if the reaction produces a **stable carbocation**.

N.B. This reaction will **not take place if the acid is absent**. Primary alcohols do not undergo dehydration easily.

The general mechanism of this reaction is outlined in Mechanism 11-4 in Wade et al. Also, study Solved Problem 7-5 in Wade et al.

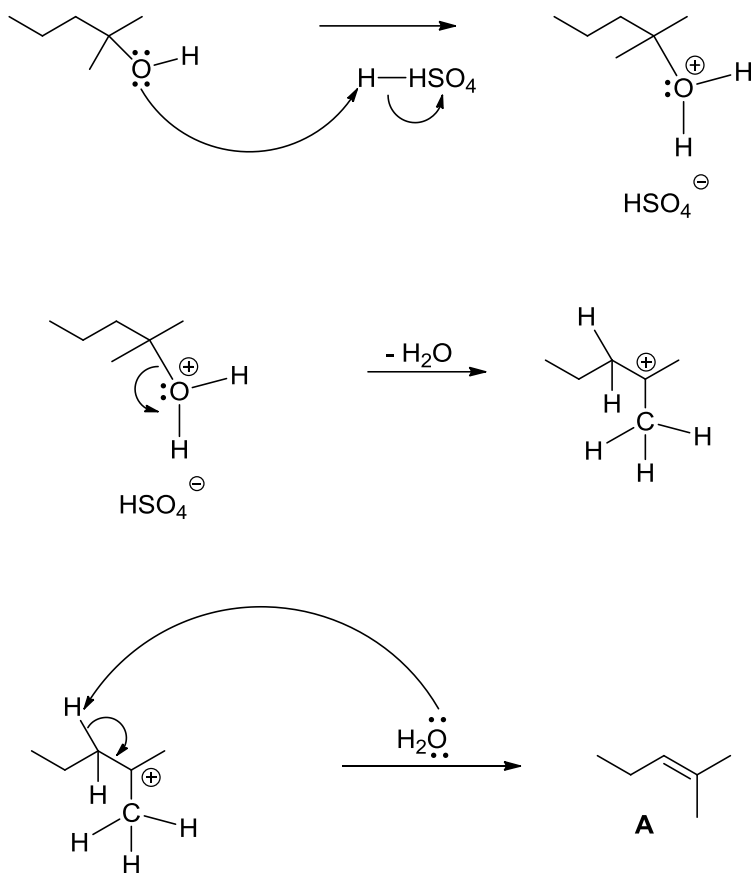
Alcohols normally undergo dehydration via the E1 reaction mechanism since it proceeds via a carbocation intermediate.

EXAMPLE

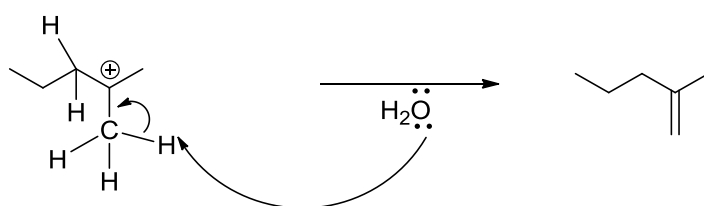
Propose the mechanism for the formation of the major organic product formed in the following dehydration reaction:



Answer: The complete mechanism of the reaction is:



The following is also possible:

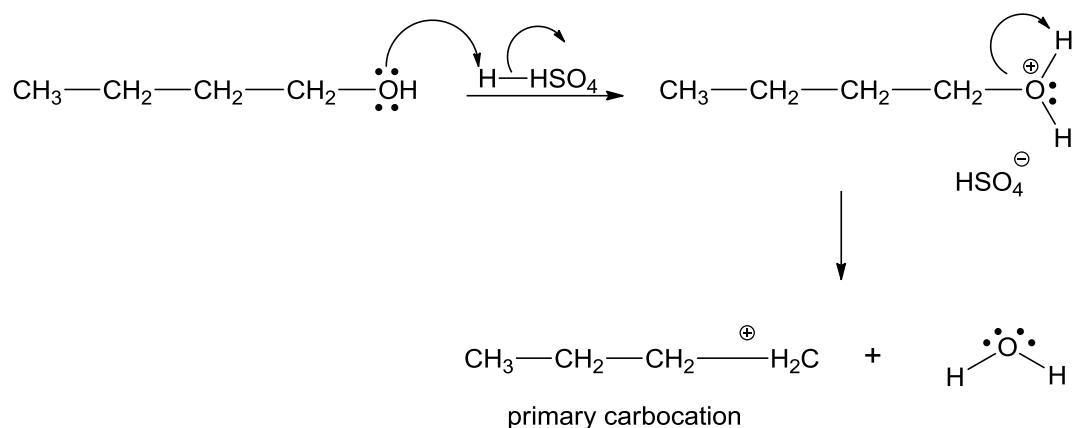


According to **Zaitsev's rule**, the product with the **most substituted double bond** will predominate. Therefore, the product labelled **A** is the **major product**.

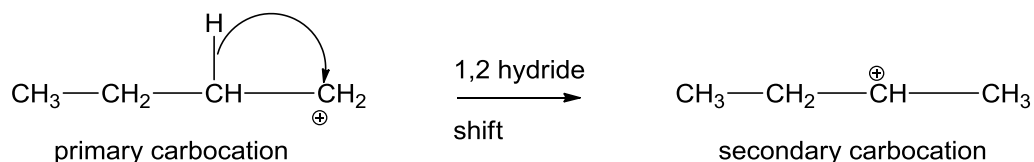
The carbocation can also undergo rearrangement to form a more stable carbocation.

The E-1 type elimination mechanism proceeds with or without rearrangement. Rearrangement involves a hydride or methyl shift in the carbocation intermediate. For example, the dehydration reaction of 1-butanol with concentrated sulfuric acid at 140°C forms mainly trans-2-butene.

In the reaction, protonation of the OH group gives an oxonium ion. The loss of water results in a carbocation intermediate. The compound that forms the more stable carbocation intermediate will undergo dehydration at the fastest rate. The first step of the reaction is:

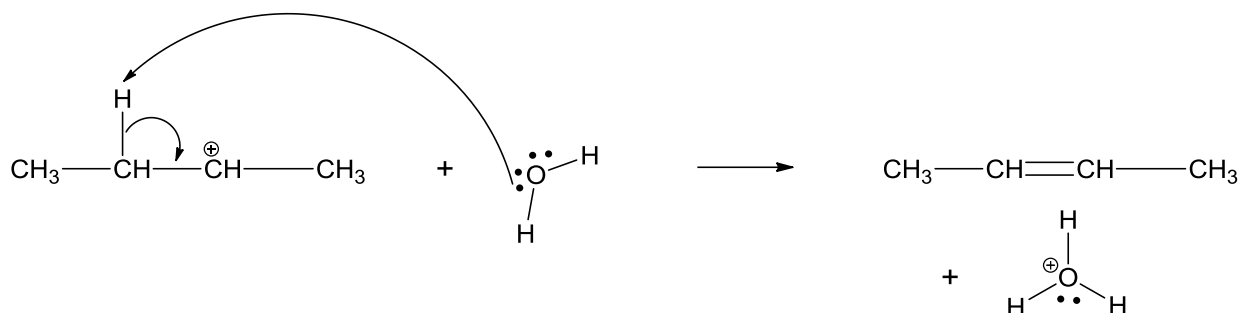


Carbocation rearrangement to form a more stable secondary carbocation takes place as follows:



Carbocation stability: 3° C⁺ > 2° C⁺ > 1° C⁺ > ⁺CH₃

In the next step, the abstraction of an H atom from an α -carbon (carbon attached to the C^+) takes place. The secondary carbocation has two different α -carbons with H atoms attached to it. The abstraction of the H on the secondary α -carbon takes place to give the more substituted alkene as the product:



Abstraction of the H on the other α -carbon (primary C) will lead to the formation of the alkene $CH_3CH_2CH=CH_2$, which is the least substituted alkene. According to Zaitsev's rule, the product with the most substituted double bond (C=C containing the most alkyl groups) will predominate.

Study Solved Problem 11-3 and the PROBLEM-SOLVING STRATEGY in the green box in Wade et al.

You may view the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/e1-e2-tutorial/v/e1-elimination-regioselectivity>

ACTIVITY 7.7

Do Problem 11-22.

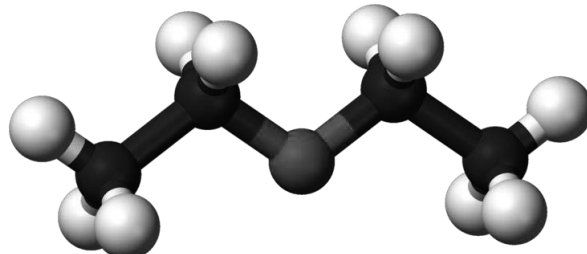
B. ETHERS

7.6 Structure, physical properties and nomenclature of ethers (Wade et al sections 14-2A to 14-2C, 14-3A and 14-3B)

7.6.1 Structure and physical properties of ethers (Wade et al sections 14-2A to 14-2C)

Structure

The presence of the electronegative oxygen and the shape of an ether molecule play an important role in the properties of ethers. Ethers may be symmetrical (alkyl groups are the same) or unsymmetrical (alkyl groups are different). The oxygen atom in ethers is sp^3 hybridised, which contributes to ethers having bent structures. A representation of the arrangement of the atoms in diethyl ether (Et_2O) is given in figure 7.4 below.



Author: Benjah-bmm27 public domain

<https://commons.wikimedia.org/wiki/File:Diethyl-ether-3D-balls.png>

Figure 7.4

Physical properties

The presence of the electronegative oxygen and the shape of an ether molecule play an important role in the properties of ethers. Ethers are polar molecules with a molecular dipole, which is the result of the polar O-C bonds. Weak dipole-dipole interactions thus exist between molecules of ethers, but ethers tend to have low boiling points.

The polarity of ether is less than that of alcohols due to the absence of the OH group. The lone pair of electrons on oxygen can form weak hydrogen bonds with molecules containing an O-H group. See the illustration in figure 14-2 in Wade et al.

ACTIVITY 7.8

Rank the following compounds in the order of increasing solubility in water: propane, dimethyl ether and ethanol.

7.6.2 Nomenclature of ethers (Wade et al sections 14-3A and 14-3B)

Read in section 14-3A in the textbook about the common names of ethers that are widely used.

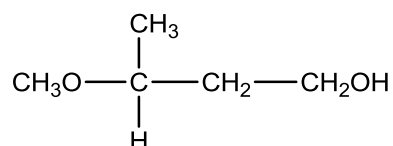
According to the IUPAC nomenclature rules, the **more complex alkyl group is the parent or root name** and the **remaining part** of the molecule is an **alkoxy group**. The systematic nomenclature rules as described in section 3.4.2 in study unit 3 apply.

EXAMPLES

1. Give the IUPAC name for $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$.

Answer: methoxypropane

2. Provide the correct IUPAC name for the following compound:



Answer: The correct IUPAC name for the compound shown above is:

3-methoxybutan-1-ol

Explanation: This compound has an OH group and an OCH₃ group – this is an alcohol and the OCH₃ group is a substituent. According to the IUPAC convention, the longest continuous carbon chain that contains the OH group has 4 Cs → butane. Begin numbering at the end that will give the OH substituent the lowest possible number; the OH is thus on C-1, change the ending "e" to "o" → 1-ol; the OCH₃ group is on C-3 → 3-methoxy. Write the name in alphabetical order.

Watch the video on ether nomenclature via the link:

<https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides/nomenclature-properties-ethers/v/ether-nomenclature>

ACTIVITY 7.9

Do Problems 14-4.

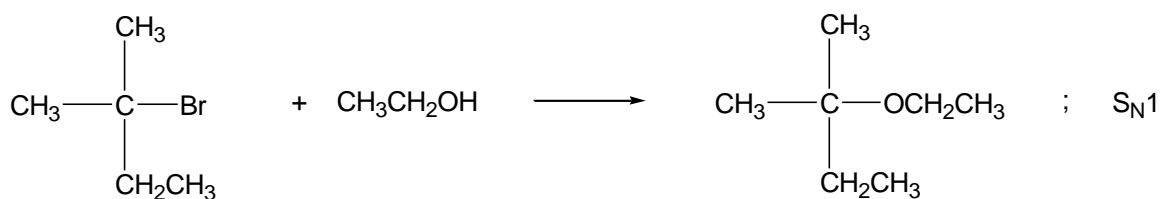
7.7 Preparation of ethers (Wade et al sections 11-14, 14-5)

Ethers can be prepared by the nucleophilic substitution reactions of alkyl halides with alcohols or the nucleophilic substitution reactions of alkyl halides with alkoxide ions.

7.7.1 Preparation of ethers (Wade et al sections 11-14 and 14-5 and a review of sections 11-10B and 14-7).

The description of the synthesis of ethers from the bimolecular condensation of alcohols can be found in section 7.5.2.2 above.

Ethers can also be prepared by the reaction of alkyl halides with alcohols, as discussed in study unit 6 (the unimolecular reaction: the S_N1 reaction).



The alkyl halide is a tertiary alkyl bromide that will produce a stable carbocation intermediate. Therefore, the S_N1 reaction will occur.

Ethers can also be prepared by the bimolecular dehydration of alcohols, as described in sections 11-10B and 14-7 in Wade et al.

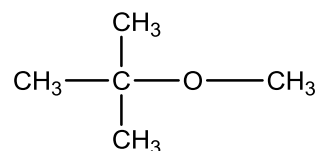
7.7.2 Preparation of ethers: Williamson ether synthesis (Wade et al sections 11-14 and 14-5)

The method to prepare ethers using the reaction of an alkoxide with an alkyl halide is called the **Williamson ether synthesis**. This reaction proceeds through the S_N2 reaction mechanism. The use of a methyl or primary alkyl halide in a reaction with an alkoxide is a very favourable way to prepare ethers.

Study Solved Problem 14-1 and Key Mechanism 11-6.

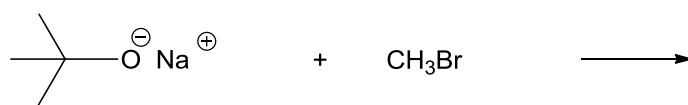
EXAMPLE

What is the most appropriate method to prepare the following compound?



Answer:

The reaction of an alkoxide with an alkyl halide proceed is an S_N2 reaction and the most appropriate method is:



You may view the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides/synthesis-cleavage-ethers/v/williamson-ether-synthesis>

ACTIVITY 7.10

Do Problems 11-33, 14-9.

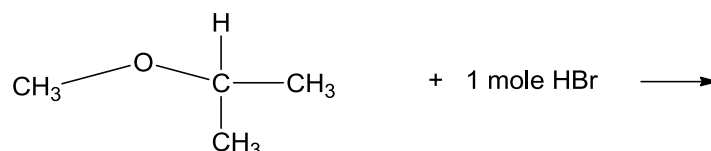
7.8 Reactions of ethers (Wade et al section 14-8)

Ethers do not react with bases. Ethers undergo cleavage reaction in the presence of strong acids like HBr and HI. The type of product depends on the ratio of the reagents and the structure of the ether. In the presence of excess acid, the ether cleavage reaction produces two alkyl halide molecules. When equimolar quantities of the ether and acid are used, an alcohol and an alkyl halide are formed.

Study Mechanism 14-1 in Wade et al.

EXAMPLE

Consider the following reaction:

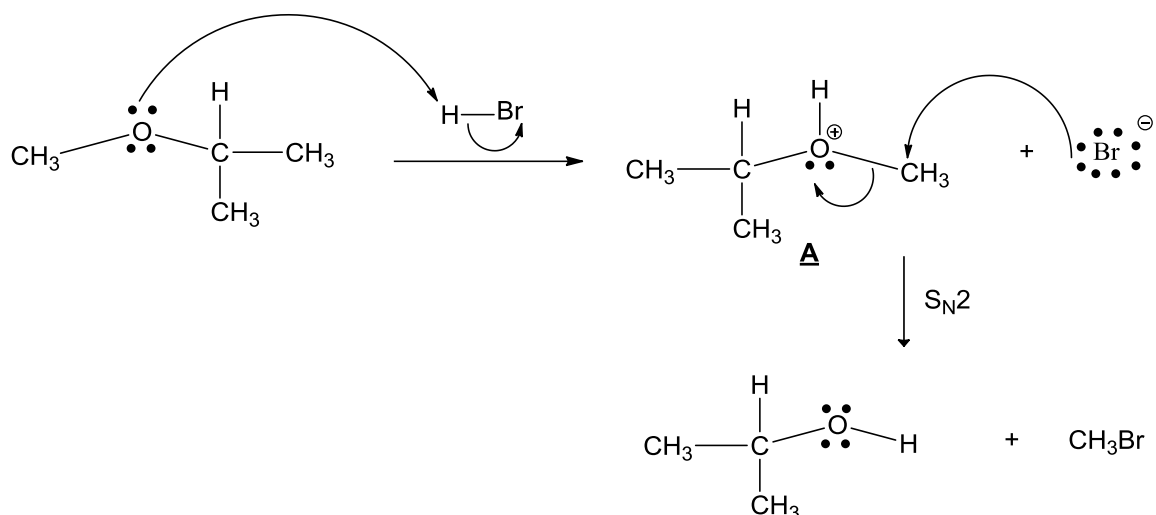


Give a detailed mechanism for the reaction.

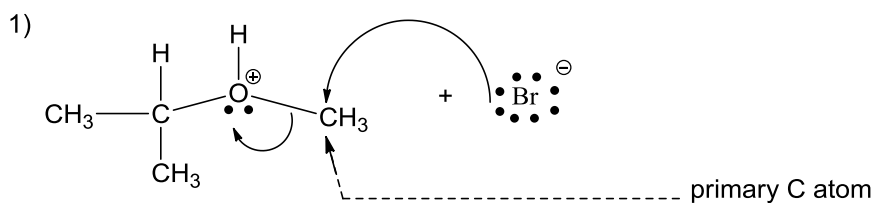
Answer:

The above reaction is an example of a cleavage reaction of the ether with HBr.

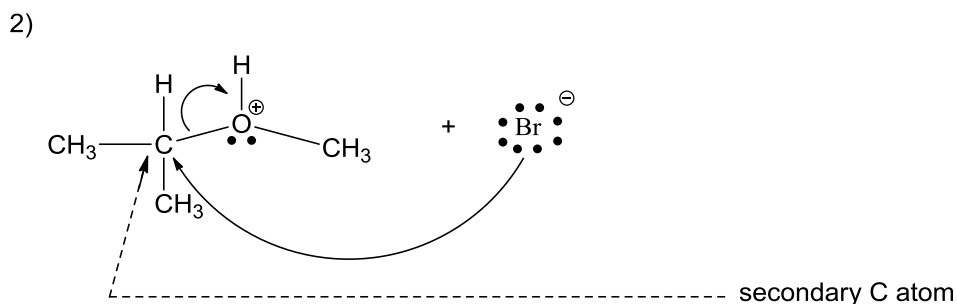
The reaction proceeds as follows:



In the first step, the oxygen atom becomes protonated by the H-Br (the H- Br bond breaks in the process) to form an oxonium ion, **A**. The bromide ion (Br^-) then acts as a strong nucleophile and reacts via $\text{S}_{\text{N}}2$ reaction with **A** to form an alcohol and an alkyl halide. If we consider the positively charged O in A, then there are two possibilities for the Br^- ion to attack, namely:



OR



Since the **primary carbon is less hindered** compared to the **secondary carbon for attack by the Cl^- ion, the $\text{S}_{\text{N}}2$ process in process 1) is preferred** and will lead to the formation of the products in the reaction.

You may view the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides/synthesis-cleavage-ethers/v/acidic-cleavage-of-ethers>

ACTIVITY 7.11

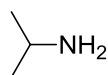
Do Problem 4-15.

C. AMINES

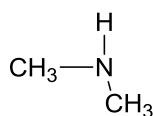
7.9 Classification, nomenclature and structure of amines (Wade et al sections 19-2 and 19-3)

7.9.1 Classification of amines (Wade et al section 19-2)

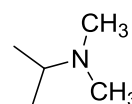
Amines are classified as alkyl or aryl derivatives of NH_3 . Replacing **one H** with an alkyl or aryl group gives a **primary (1°)** amine, and replacing **two Hs** with alkyl or aryl group gives a **secondary (2°)** amine, whereas replacing **three Hs** with alkyl or aryl group results in a **tertiary (3°)** amine, as illustrated below:



1° / primary amine



2° / secondary amine



3° / tertiary amine

When four alkyl or aryl groups are attached to the nitrogen, the nitrogen has a positive charge and the species is called a quaternary ammonium salt, for example, tetramethyl ammonium chloride is $(\text{CH}_3)_4\text{N}^+ \text{Cl}^-$.

ACTIVITY 7.12

Classify the amines in 19-3 (a) and (b).

7.9.2 Nomenclature of amines (Wade et al sections 19-2 and 19-3)

The common names of amines are derived from the names of the alkyl groups bonded to the nitrogen atom and the suffix "**amine**". As per normal naming convention, two, three or four identical groups are indicated as di-, tri- and tetra-, respectively. Methyl amine is the common name for CH_3NH_2 and $(\text{CH}_3)_3\text{N}$ is called trimethyl amine.

When naming amines according to IUPAC nomenclature, the ending "e" in the alkane name is replaced by "amine". The longest continuous carbon chain containing the amino group is the parent or root name. Number the carbon chain from the end that will give the amine the lowest possible number. Include the number of the amino group in the chain.

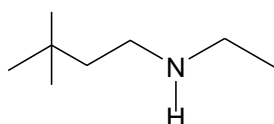
EXAMPLES

1. Give the IUPAC name of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$.

Answer: Propanamine

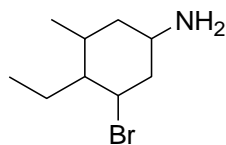
2. Give the structure of N-ethyl-3,3-dimethyl-1-butanamine.

Answer:



Explanation: According to the IUPAC convention, "but" means that the longest continuous carbon chain has 4 Cs. "N-ethyl" means that there is a 2C chain (not part of the main chain) attached to N. Since numbering begins at a branch to give the substituents the lowest possible number, the "3,3-dimethyl" indicates that there are two methyl groups on C-3 and 1-butanamine implies that an NH_2 group is on C-1.

3. Give the IUPAC name for the following compound:



Answer: 1-amino-3-bromo-4-ethyl-5-methylcyclohexane

Explanation: According to the IUPAC convention, the longest continuous carbon chain is a ring with 6 Cs → cyclohexane. Begin numbering at a branch to give the substituents the lowest possible numbers; C-1 has an NH₂-group → 1-amino and C-3 have a Br group → 3-bromo. C-4 has an ethyl group → 4-ethyl and C-5 have a methyl group → 5-methyl. Name the substituents in alphabetical order.

Watch the videos for more information via the link:

<https://www.khanacademy.org/science/organic-chemistry/amines-topic/naming-amines/v/amine-naming-introduction>

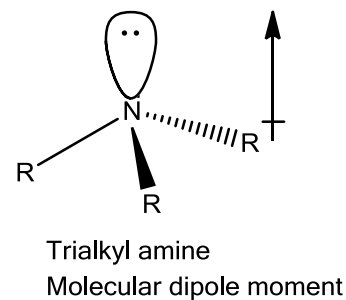
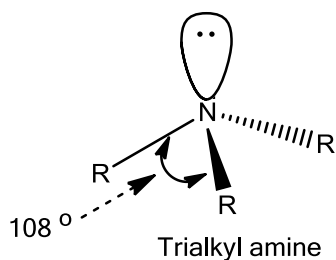
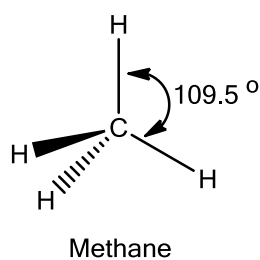
<https://www.youtube.com/watch?v=STlamn93rds>

ACTIVITY 7-13

Do Problems 19-3 (a), (b), 19-32 (a), (b), and (f), (h).

7.9.3 Structure of amines (Wade et al section 19-3)

The nitrogen atom in amines is sp³ hybridised with the lone pair of electrons occupying a sp³ hybrid orbital. Unlike methane, with the typical tetrahedral sp³ bond angle of 109.5 °, the bond angles in amine derivatives are smaller. The bulky lone pair of electrons tend to compress the H-N-R bond angles, as shown below:



Furthermore, the lone pair of electrons and the fact that nitrogen is more electronegative than hydrogen and carbon contribute to amines having **molecular dipole moments**.

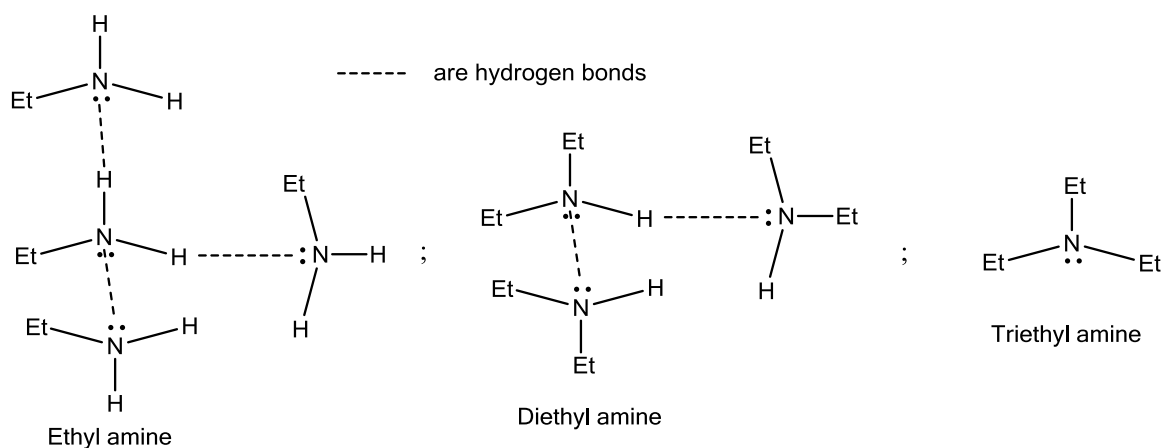
The chirality of amines does not fall within the scope of this module.

7.10 Physical and chemical properties (Wade et al sections 19-4 and 19-5)

The molecular dipole moments of amine molecules make these compounds very **polar**. The ability to form **hydrogen bonds** strongly affects the physical properties of amines.

7.10.1 Physical properties of amines (Wade et al section 19-4)

An amine molecule containing an **N-H bond** can participate in **hydrogen bonding** with another amine molecule. This **intermolecular hydrogen bonding** results in primary amines having **higher boiling points** than secondary amines and tertiary amines of comparable molecular weights, with the tertiary amine having the lowest boiling point. Hydrogen bond formation is **absent** in **tertiary amines** because there is **no N-H bond** and the extent of hydrogen bonding is the highest in primary amines, as shown below:



It is also possible to compare the boiling points of amines with other organic molecules of similar molecular weight by evaluating the extent of hydrogen bonding for each compound.

The solubility of amines in water and alcohols is also influenced by hydrogen bonding.

EXAMPLES

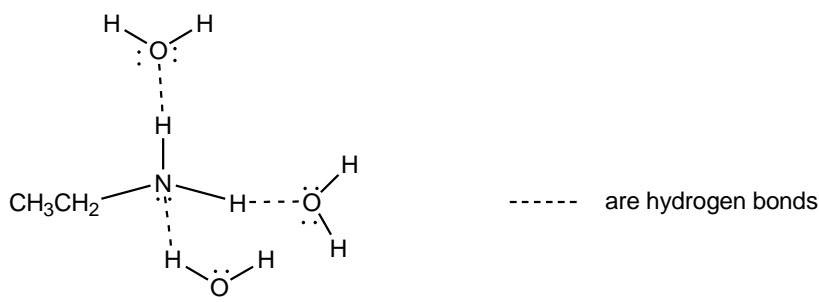
1. Compare the boiling points of propan-1-ol and 1-propanamine.

Answer: Propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, contains an O-H bond and 1-propanamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, contains two N-H bonds. Because N is less electronegative than O, the O-H bond is more polar than the N-H bond. Both molecules can undergo hydrogen bonds but the hydrogen bonds that form between an H and the lone pair of electrons on N is weaker than the hydrogen bonds formed between the H and the lone pair of electrons on O. The intermolecular attractions between propan-1-ol molecules are stronger than the intermolecular hydrogen bonding in 1-propanamine. Therefore, propan-1-ol has a higher boiling point than 1-propanamine.

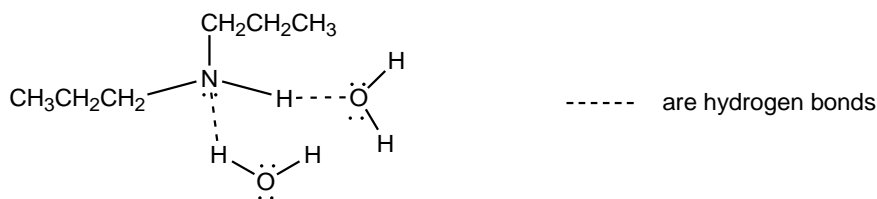
2. Which of the compounds ethylamine and diethyl amine is the most soluble in water? Explain your answer.

Answer: Amines are soluble in alcohols and some amines are relatively soluble in water because amines can form hydrogen bonds with these solvents. The amine that is able to form the strongest hydrogen bonds with water will be the most soluble in water.

Ethylamine undergoes hydrogen bonding with water as follows:



There is only one N-H bond in diethyl amine $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$ molecule; the molecule forms hydrogen bonds with water as follows:



The extent of hydrogen bonding between a $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$ molecule and water (two hydrogen bonds) is less than the hydrogen bonding between an ethylamine molecule and water (three hydrogen bonds). Therefore, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$ is less soluble in water and ethylamine is most soluble in water.

Watch the relevant videos via the link:

https://www.youtube.com/watch?v=y6A_VCFoApM

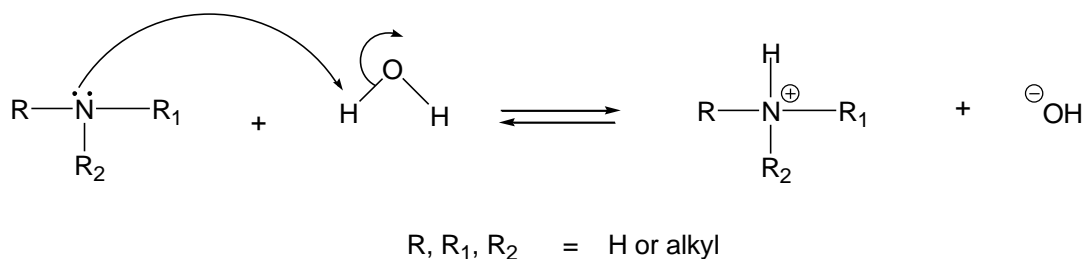
<https://www.youtube.com/watch?v=nvJHBQZoOBw>

ACTIVITY 7.14

Consider the compounds propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$), 1-propanamine ($\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$) and dimethyl amine ($(\text{CH}_3)_2\text{NH}$). Identify the compound that is most soluble in water. Explain your answer.

7.10.2 Basicity of amines (Wade et al sections 19-5 and 19-6)

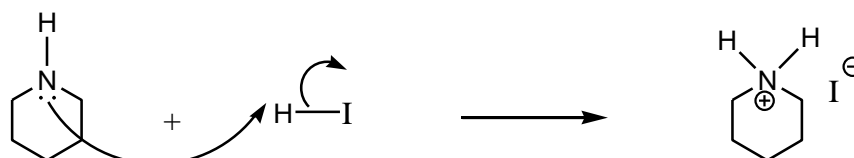
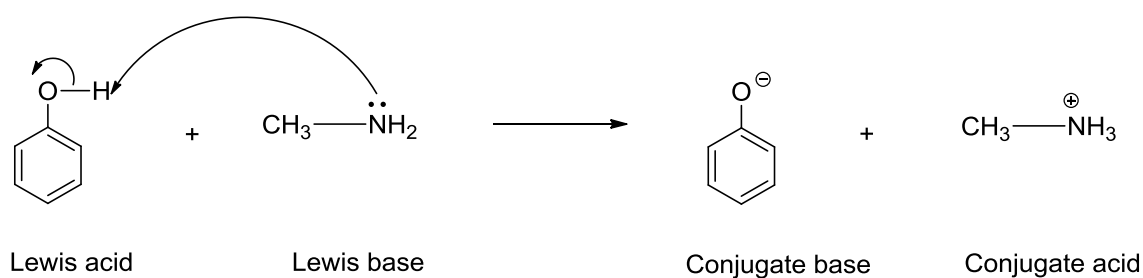
The basicity of an amine is measured in terms of the ability of the N atom to donate its pair of electrons in the general reaction:



The basicity of amines is influenced by the amount of substitution by alkyl groups, resonance effects and hybridisation, as described in Wade et al.

Amines are Lewis bases and react readily with acids. When a Lewis base donates a pair of electrons to a Lewis acid, the conjugate acid and conjugate base pairs formed must be weak for the reaction to take place.

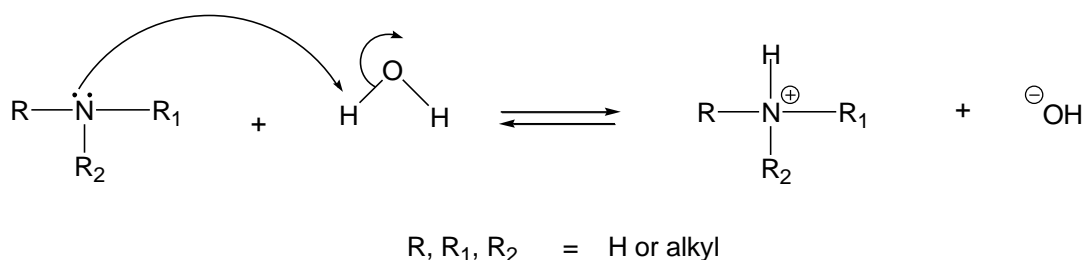
Examples of acid-base reactions:



EXAMPLE

Arrange NH_3 , $\text{CH}_3\text{CH}_2\text{NH}_2$, $(\text{CH}_3\text{CH}_2)_2\text{NH}$ in order of increasing basicity (weakest first).

Answer: The basicity of an amine is measured in terms of the ability of the N atom to donate a pair of electrons in the general reaction:



If we compare the bases above, $\text{CH}_3\text{CH}_2\text{NH}_2$ has one ethyl group; $(\text{CH}_3\text{CH}_2)_2\text{NH}$ has one more ethyl group, that is, 2 ethyl groups; and NH_3 has no ethyl group, only 3 H atoms attached to the N atom. An alkyl group is electron donating towards cations and an ethyl group will stabilise the positive charge on N. When we increase the number of electron-donating groups, we therefore increase the basicity.

The order of increasing basicity is **$\text{NH}_3 < \text{CH}_3\text{CH}_2\text{NH}_2 < (\text{CH}_3\text{CH}_2)_2\text{NH}$** .

Watch the videos for more clarification via the links:

<https://www.youtube.com/watch?v=tJPR4jRNhgc>

<https://www.youtube.com/watch?v=1gf6b7Fylo>

ACTIVITY 7-15

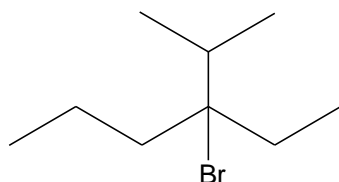
Do Problem 19-6 (a), (b).

7.11 Conclusion

In this study unit we discussed the nomenclature, physical and chemical properties of alcohols, ethers and amines. We also described the preparation and selected reactions of ethers. The oxidation, nucleophilic substitution and dehydration reactions of alcohols received considerable attention. This unit concludes the theme on saturated compounds and the next study unit will introduce you to the unsaturated compounds.

ANSWERS TO SELECTED ACTIVITIES

7.6



7.8 Propane < dimethyl ether < ethanol.

7.14 Propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)

THEME 3

UNSATURATED ORGANIC COMPOUNDS

In Theme 2, we focused on compounds containing carbon-carbon single bonds and in this theme we will concentrate on unsaturated compounds. Unsaturated compounds have multiple bonds and specifically alkenes (containing carbon-carbon double bonds), alkynes (having carbon-carbon triple bonds) and different carbonyl- containing (carbon-oxygen double bond) compounds will receive attention.

STUDY UNIT 8

Alkenes

- 8.1 Introduction
- 8.2 Structure and nomenclature
- 8.3 Geometric isomerism in alkenes
- 8.4 Physical properties and stability of alkenes
- 8.5 Formation of alkenes by dehydrohalogenation of alkyl halides
- 8.6 Unimolecular elimination: The E1 reaction
- 8.7 Bimolecular elimination: The E2 reaction
- 8.8 Alkene synthesis by dehydration of alcohols
- 8.9 Reactivity of the carbon-carbon double bond
- 8.10 Electrophilic addition to alkenes
- 8.11 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- describe the general structure of alkenes
- accurately use the IUPAC rules for nomenclature to construct structural formulae, and *vice versa*
- correctly propose the mechanisms of addition reactions of symmetrical and unsymmetrical alkenes and apply Markovnikov's rule to hydrogenation, hydrohalogenation, hydration and halogenation reactions
- correctly propose the mechanism of hydrohalogenation of alkenes in the presence of peroxides and light

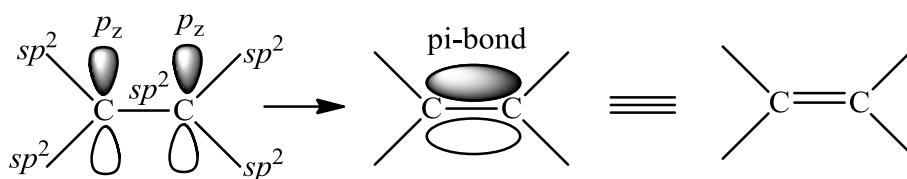
8.1 Introduction (Wade et al sections 7-1 and 7-6)

Alkenes are compounds that contain the **carbon-carbon double bond** with the **functional group, C=C**. Alkenes are much more reactive than alkanes. Alkenes react with a wide range of reagents due to the presence of the double bond. In this study unit, we will study the structure, naming, preparation and reactions of alkenes. This involves two major types of reaction, namely addition and elimination, where elimination is the formation of pi bonds and addition involves the reaction of pi bonds.

8.2 Structure and nomenclature (Wade et al sections 7-2, 7-4 to 7-5)

8.2.1 Orbital description of the carbon-carbon double bond (Wade et al section 7-2)

The **carbon-carbon double bond** consists of a **sigma bond** formed by the **overlap** of **two sp^2 -hybridised orbitals** of adjacent carbon atoms. The **pi (π) bond** is formed by the **overlap** of **two atomic (unhybridised) 2p orbitals**.



Each carbon atom in the carbon-carbon double bond is sp^2 hybridised.

The **geometry is trigonal planar** with the bond angles being **120°** , that is, each carbon atom and the atoms directly attached to them are on the **same plane**.

8.2.2 Nomenclature of alkenes (Wade and Simek section 7-4)

The **IUPAC** nomenclature rules, as outlined in section 3.4.2 in study unit 3, are applicable, with the following adaptations:

1. The ending "ane" in the name is replaced by an "**ene**".
2. The **longest carbon chain** containing the **double bond** is the parent name.
3. Numbering the carbon chain starts at the end **closest** to the **C=C group (C=C has the lowest possible number)**.
4. Assign the position of the C=C group in the carbon chain by allocating the lower number of the two C=C atoms.
5. Assign the number "1" to the C=C in cycloalkenes.
6. Two or more C=C groups are indicated as **diene**, **triene**, and so forth, with the positions of the C=C groups shown by the appropriate numbers.

View the video on the naming of alkenes at the link:

<https://www.youtube.com/watch?v=dsQIK6in-XM>

ACTIVITY 8.1

Do Problems 7-5 (a) to (f) and 7-43.

Common names like ethylene and propylene are routinely used for ethene and propene, respectively.

8.3 Geometric isomerism in alkenes (Wade et al section 7-5)

We have seen that rotation about the sigma bond in alkanes produces molecules with different spatial arrangements of the constituent atoms, in other words, different conformations can be written as described in section 3.6 in study unit 3. We also described the geometric isomerism in cycloalkanes in section 3.9 of that unit.

Rotation about the pi bond would cause the overlap of adjacent p-orbitals to decrease and will finally result in the breaking of the bond. The double bond is therefore more rigid compared to the single bond. Due to this inflexibility, **different spatial arrangements** will produce **different isomers**. **Two** types of **spatial arrangement** of atoms around the C=C bond are possible and the structures are **geometric isomers**.

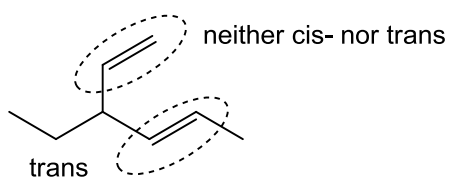
When similar groups are **on the same side of the C=C bond**, the isomer is called ***cis*-isomer** and where these groups are **on opposite sides of C=C**, the isomer is referred to as the ***trans*-isomer**.



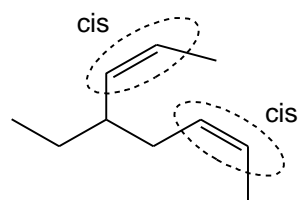
When one of the carbons in the C=C bond has the same atoms or groups attached to it, then the molecule does not have *cis* or *trans* isomers. Alkenes can easily be classified as *cis* or *trans* when the same atoms or groups of similar nature are bonded to the C=C bond.

EXAMPLES:

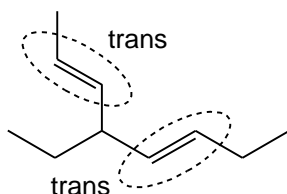
(1)



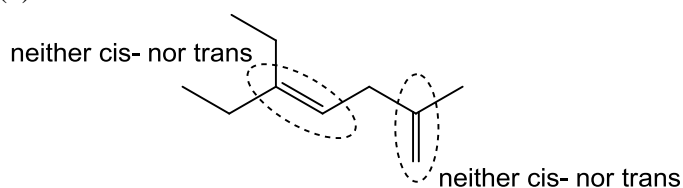
(2)



(3)

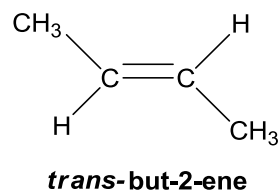
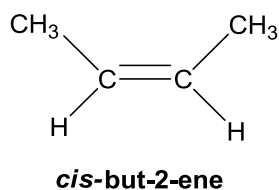


(4)



8.3.1 Nomenclature of cis-trans isomers (Wade et al section 7-5)

The **orientation of the groups** (methyl groups) with respect to another must be indicated as ***cis*-** or ***trans*-** in the name. If we consider the but-2-ene molecule, then it is possible to have the following two geometric isomers of the molecule:

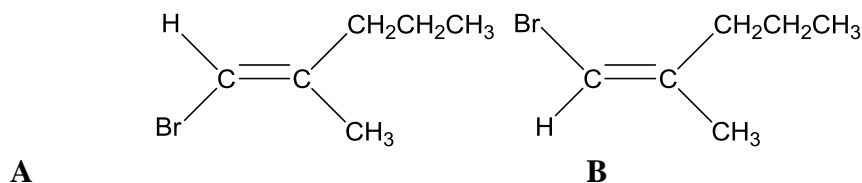


The *cis* isomer is the structure with the methyl groups on the same side of the C=C bond. When the methyl groups are on opposite sides of the C=C bond, we have the *trans* isomer.

8.3.2 E-Z nomenclature (Wade et al section 7-5B)

What happens if there is no clear distinction between the two groups? We use a different convention to assign to the different geometric isomers.

Consider for example the following two structures:



There is a clear distinction in how the groups are arranged around the C=C in the two structures.

The **E-Z** nomenclature is used when the **groups** attached to the **C=C** are **different**.

How to determine the E- or Z- isomer:

- Consider **each carbon** that is part of the **C=C**.
- **Assign priority order** to the **groups** attached to **each carbon** of the C=C similar to the Cahn-Ingold-Prelog rules used when assigning (R-) and (S-) configurations to chiral centers in study unit 5.
- We therefore **assign priority** in terms of **atomic number** of **atom attached** to **C=C**, with the **first priority** to the **larger atomic number** atom.

- Should the **two atoms directly** bonded to each carbon of the C-C double bond be **similar, move further until a point of difference** is obtained, for example, if methyl (CH₃) and ethyl (CH₃CH₂) groups are attached by **C**. The difference between the two is that the methyl group has H, which is smaller than the second C of the ethyl group, thus CH₃CH₂ > CH₃.
- For **multiple bonded groups** (double or triple), **each atom** of the multiple bond is **multiplied** according to the **multiplicity of the bond** (**2 for double** and **3 for triple bond**), for example, a C=O is evaluated as (2xO+ 2xC).
- If the **two first priority groups** are on the **same side** of the **C=C** bond, then the structure is the **Z-isomer**.
- If the **two first priority groups** are on **opposite sides** of the **C=C** bond, then the structure is the **E-isomer**.

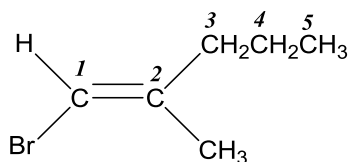
In our example:

On C-1: -H and -Br; **Br has higher priority.**

On C-4: -CH₂CH₂CH₃ and -CH₃; **-CH₂CH₂CH₃ has higher priority.**



In **A**: The two priority groups are **on the opposite side of the C=C double bond**, therefore this is an **E-isomer**. In **B**: The two priority groups are **on the same side of the C=C double bond**, therefore this is a **Z-isomer**.



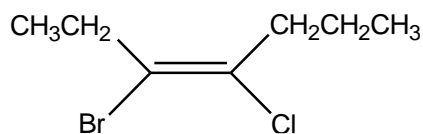
The IUPAC name for the alkene is 1-bromo-2-methylpent-1-ene. Therefore **A** is **(E)-bromo-2-methylpent-1-ene** and **B** is **(Z)-1-bromo-2-methylpent-1-ene**.

You are encouraged to watch the relevant video via the link:

<https://www.youtube.com/watch?v=CGPyTUrSF2E>

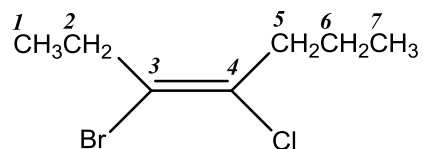
EXAMPLE

What is the IUPAC name of the following compound?



Answer: (4) (Z)-3-bromo-4-chlorohept-3-ene

Explanation: According to the IUPAC convention, the longest continuous carbon chain has 7 Cs → heptane, but there is a C=C bond in the chain → change the ending from **ane** to **ene**. Begin numbering at the C-chain end to give the C=C the lowest number → 3-ene.



The substituents are on C-3 a Br atom → 3-bromo and on C-4 a Cl group → 4-chloro. Name the substituents in alphabetical order.

The Z-E nomenclature must be used when the groups attached to the C=C are different. The (Z) or (E) notation of the molecule must therefore be determined.

Assign priority order to the groups attached to the each carbon of the C=C in terms of atomic number of the atom attached to C=C:

On C-3: -CH₂CH₃ and -Br and; **Br has higher priority.**

On C-4: -CH₂CH₂CH₃ and -Cl and; **Cl has higher priority.**

The two priority groups are **on the same side of the C=C double bond**, therefore this is a **Z-isomer**.

ACTIVITY 8.2

Do Problems 7-6 and 7-7.

8.4 Physical properties and stability of alkenes (Wade et al sections 7-7 and 7-8 to 7-8C, 7-8F)

8.4.1 Physical properties (Wade et al section 7-7)

The physical properties of alkenes tend to be similar to that of equivalent alkanes.

Boiling points

The boiling points of alkenes increase with increase in molecular weight. Similar to the trend in alkanes, the boiling points of alkenes decrease when the branching becomes more.

Polarity of alkenes

The solubility of alkenes is also similar to that of alkanes and, in general, these compounds are soluble in non-polar solvents. Alkenes and alkanes are **non-polar** molecules, with the polarity of alkenes being slightly more than that of alkanes.

Alkyl groups tend to donate a small amount of electron density towards the C=C bond.

This creates a small partial negative charge on the C=C bond and a small partial positive charge on the alkyl group, resulting in a **small dipole moment** on some alkene molecules. ***Trans* alkenes do not have a molecular dipole moment** (dipole moments cancel each other), whereas ***cis* alkenes have molecular dipole moments**. When the C=C bond is at the end of the chain, the molecule has a molecular dipole moment. **Dipole-dipole interactions** exist between molecules having a **molecular dipole moment**. The intermolecular forces between ***cis* alkenes** are **greater** than the intermolecular forces between ***trans* alkenes**. Therefore, the boiling points and densities of ***cis* alkenes** are slightly higher than the corresponding ***trans* isomer**.

ACTIVITY 8.3

Do Problem 7-11.

8.4.2 Stability of alkenes (Wade et al sections 7-8 to 7-8C and 7-8F)

In some elimination reactions, it is possible to obtain more than one product. When that occurs, how do we know which product will predominantly form? We have to determine which **product forms the fastest**. The energy of alkenes is often compared by measuring the heat of hydrogenation. **Hydrogenation** is the **addition of hydrogen**. The reaction requires a catalyst, and the reaction is called catalytic hydrogenation. Hydrogenation reactions are exothermic and the heat released in a hydrogenation reaction is known as the heat of hydrogenation.

Consider the following reactions:



Since the two reactions form the same product, the energy of the product is the same for each reaction. The two reactions have different heats of hydrogenation; therefore, the two reactants must have different energies.

This means that for the reaction with the least negative ΔH value (-112 kJ mol^{-1}), the energy difference between the reactant and the product is smaller than that of the reaction with the greater ΔH value (-129 kJ mol^{-1}).

Therefore, alkene **A** is higher in energy than alkene **C**. **The more stable a compound is, the lower the energy.** Hence, alkene **A** is **more stable** than alkene **C**.

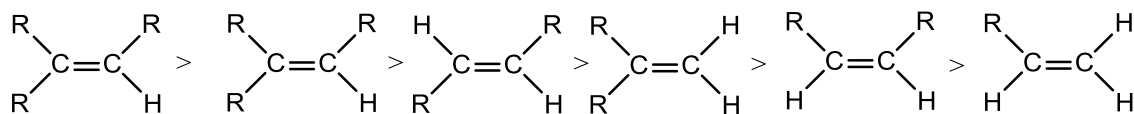
Experimental studies have shown that:

The more alkyl groups that are bonded to the sp^2 carbon atoms of the alkene, the more stable the alkene.

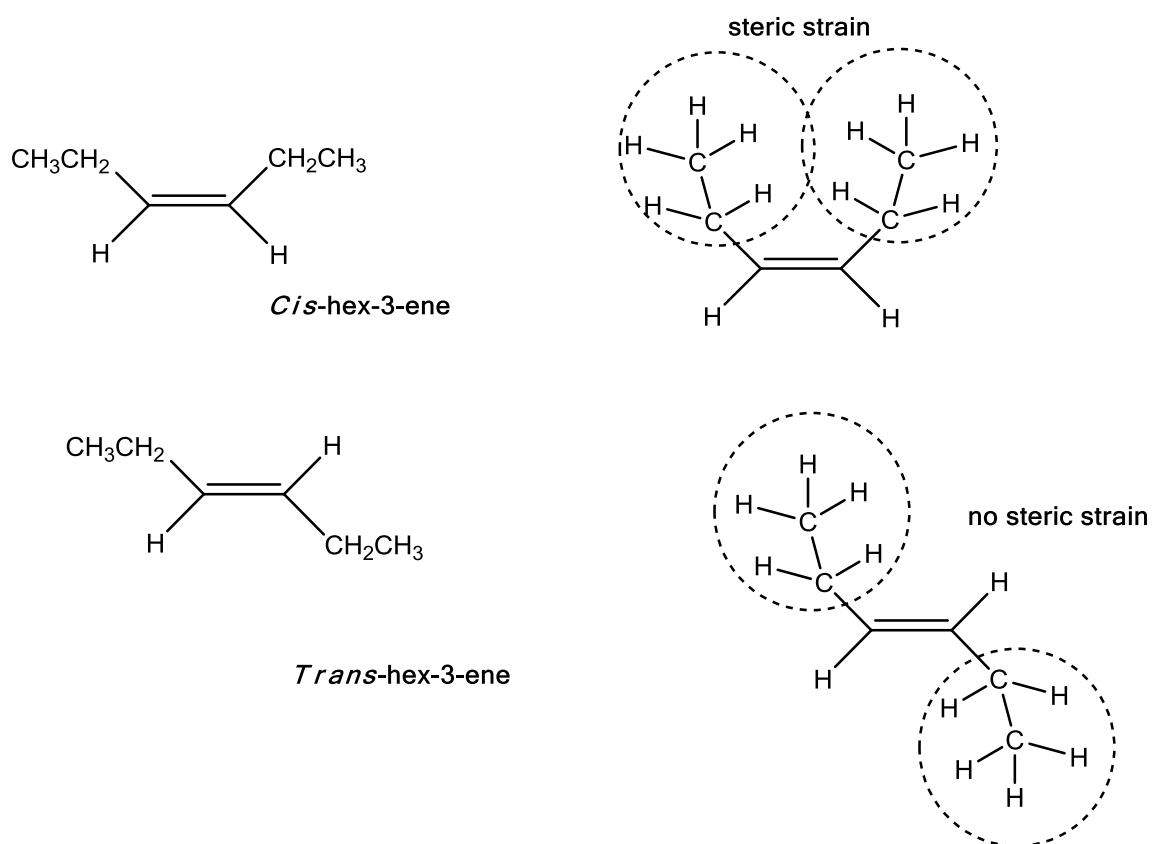
Or

The fewer hydrogen atoms that are bonded to the sp^2 carbon atoms of the alkene, the more stable the alkene.

The relative stabilities of alkenes:



Through the measurement of the heats of hydrogenation, the relative stabilities of cis-trans isomers have been assessed. This leads to the general trend that **trans isomers** are **more stable** than **cis isomers**. For example, consider the geometric isomers of hex-3-ene:



Steric strain in a molecule is caused when the electron clouds of substituents interfere with each other.

Zaitzev's rule states that in an elimination reaction, the most substituted alkene is predominantly formed.

View the relevant video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/naming-alkenes-jay/v/alkene-intro-and-stability>

<https://www.youtube.com/watch?v=RgbQya8HXBM>

Double bonds that are **separated** from one another by **one single bond** are called **conjugated double bonds**. **Isolated double bonds** are **separated** from one another by **two or more single bonds**. **Delocalisation** of the **pi electrons** in the double bonds of **conjugated** systems occurs, which makes the conjugated double bonds **more stable** than isolated double bonds.

ACTIVITY 8.4

Do Problem 7-12.

A SYNTHESIS OF ALKENES

8.5 Formation of alkenes by dehydrohalogenation of alkyl halides (Wade et al section 7-9)

Basic reagents may react with alkyl halides to form alkenes via elimination reactions. An **elimination reaction** involves the **removal** of **atoms or groups** from **each** of **two adjacent carbon** atoms to **form** a **double** or **triple bond**.

Similar to nucleophilic substitution reactions, an elimination reaction may be a unimolecular (E1) process or a bimolecular (E2) process, depending on the reagents and reaction conditions. In section 8.6 below, we will discuss the E1 process in detail and section 8.7 covers the E2 reaction.

8.6 Unimolecular elimination: The E1 reaction (Wade et al section 7-10)

A **unimolecular elimination reaction** occurs via **two steps** and the process is referred to as **E1** reactions. The steps in an **E1 reaction** are:

- 1) **breaking** of the **polar C-X bond** to form a **carbocation intermediate**
- 2) **loss** of a **H⁺** to form an **alkene**

The E1 reaction usually occurs when a weak base like water or an alcohol is used. Study the Key Mechanism 7-1 in Wade et al.

ACTIVITY 8.5

For an interactive example of the E1 reaction mechanism and a quiz, visit the website: <http://www.chem.ox.ac.uk/vrchemistry/iom/E1/default.htm#>

8.6.1 Competition between the E1 and S_N1 reactions (Wade et al section 7-10A)

When a carbocation is formed in the reaction, substitution as well as elimination can take place. In most cases, the reaction of an alkyl halide with water or alcohol gives both the substitution (S_N1) and elimination (E1) products.

Both reactions proceed via a carbocation intermediate, and alkyl halides that form stable carbocations facilitate these reactions. Study section 7.10B in Wade et al for a description of the orbitals participating in the E1 reaction and the energetics of the reaction.

8.6.2 Rearrangements in E1 reactions (Wade et al section 7-10C)

Similar to the S_N1 type reactions, the E1 reaction carbocation intermediate can undergo rearrangement. Rearrangement only occurs in reactions where a carbocation intermediate can undergo a hydride or methyl shift to form a more stable carbocation. See the example involving rearrangement in section 8.10.4. Study Mechanism 7-2 and Solved Problem 7-3 in Wade et al for more details.

ACTIVITY 8.6

Do Problem 7-21.

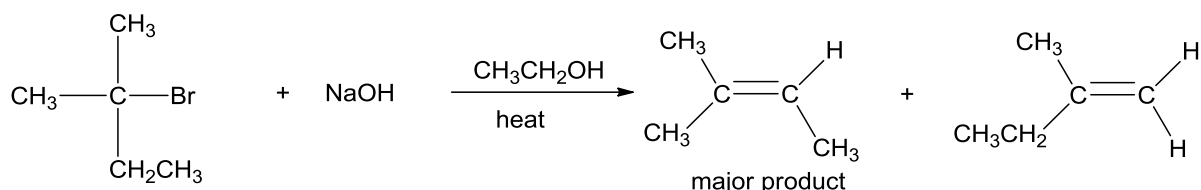
A table containing a summary of carbocation reactions can be found at the end of section 7-10C in the textbook.

8.6.3 Positional orientation of elimination: Zaitsev's rule (Wade et al section 7-11)

In **elimination reactions** where it is possible to **form more than one product**, the **most highly substituted alkene**, according to Zaitsev's rule, is the **major product**.

Study Solved Problem 7-4 in Wade et al.

An example of the formation of a mixture of products:



ACTIVITY 8.7

Do Problem 7-22.

8.7 Bimolecular elimination: The E2 reaction (Wade et al section 7-12)

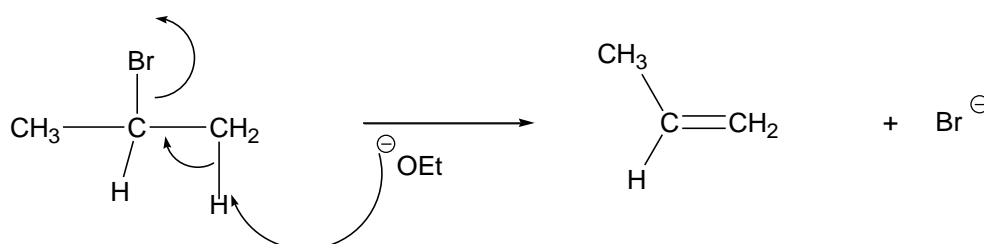
An **E2** elimination reaction occurs via **one step**. The **E2 reaction** involves the **breaking of the polar C-X bond** and the **simultaneous removal** of an **H⁺** to form an **alkene**. This reaction is a concerted reaction. The **E2** reaction is a **bimolecular** elimination reaction. This reaction takes place in the presence of a strong base. Study the Key Mechanism 7-3 in Wade et al.

If there is more than one possible proton that can be abstracted by the base, then Zaitsev's rule must be applied to determine which product will predominantly form.

EXAMPLE

Propose the mechanism of the reaction of 2-bromopropane with sodium ethoxide.

Answer:



The ethoxide ion is a strong base, and in the reaction with the secondary alkyl bromide, E2 elimination occurs.

ACTIVITY 8.8

Do Problem 7-23.

8.7.1 Reactivity of the substrates in the E2 reaction

The E2 reaction does not involve the formation of an intermediate, but the one-step reaction may involve a transition state. A more substituted alkene is more stable than a less substituted alkene. The elimination of a more substituted alkyl halide will give the more substituted alkene, which is stable. In an elimination reaction, a secondary alkyl halide will thus produce a less substituted alkene compared to a tertiary alkyl halide. Tertiary substrates thus are more reactive than secondary alkyl halides and secondary alkyl halides are more reactive than primary substrates.

8.7.2 Mixtures of products in the E2 reaction

The E2 reaction involves the removal of an H on a carbon adjacent to the carbon attached to the halogen. If the C-X group has different adjacent C-H groups, then more than one product can form. Zaitsev's rule applies to reactions that produce a mixture of alkene products.

The examples in Wade et al illustrate the formation of the products.

8.7.3 Bulky bases in E2 reactions (Wade et al section 7-13)

The elimination reaction involving a bulky strong base does not follow Zaitzev's rule. A base like the *tert*-butoxide ion, $^-\text{OC}(\text{CH}_3)_3$, is very big and will abstract the least hindered proton more easily than a proton surrounded by more alkyl groups. An E2 reaction with this base gives the less substituted alkene as the major product.

ACTIVITY 8.9

Do Problem 7-15.

8.7.4 Stereochemistry of E2 (Wade et al section 7-14A)

Similar to the SN2 reaction, the E2 reaction involves certain stereochemical requirements. The E2 reaction needs the coplanar arrangement of the orbitals. The hydrogen and the halogen must be anti to each other with their orbitals aligned for the E2 reaction to take place. This arrangement, with the H and X to be eliminated, is known as the anti-coplanar orientation. When the H and X to be eliminated have a syn-coplanar orientation, the E2 reaction does not occur due to steric hindrance. Figure 7 in the textbook illustrates the orbital arrangement of the E2 reaction. Study Mechanism 7-4 in the textbook.

8.7.5 Comparison of E1 and E2 elimination mechanisms (Wade et al section 7-16)

There are clear distinctions between the E1 and E2 reactions, and certain factors allow us to predict what type is mechanism an elimination reaction will follow. These factors are:

(i) **Type of base**

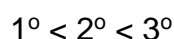
The E2 reaction requires a strong base, while E1 reactions can take place in the presence of a weak base.

(ii) **Type of solvent**

The slow step of the E1 reaction involves the formation of a carbocation. Good polar solvents are required to solvate these cations. The E2 reaction does not require polar solvent.

(iii) **Type of substrate**

The E2 reaction occurs with methyl, primary, secondary and tertiary substrates. The E1 reaction, however, needs a substrate that can form a stable carbocation intermediate. **Both E1 and E2** have followed this trend with respect to reactivity:



(iv) **Orientation of elimination**

In most E1 and E2 reactions with the possibility of forming more than one product, the most stable alkene product predominantly forms. The reactions follow Zaitsev's rule, except when a bulky base is used in an E2 reaction. Due to steric hindrance, the bulky base will abstract the least hindered proton. Then the least stable alkene product forms.

(v) **Stereochemistry**

No specific geometry for the formation of the carbocation intermediate is required for the E1 reaction. The halogen and hydrogen to be eliminated in the E2 reaction must be co-planar. Usually, the anti-coplanar arrangement in the transition state is preferred.

(vi) **Rearrangements**

Since carbocations undergo rearrangement, rearrangements only occur in reactions that proceed via a carbocation intermediate. Therefore, E1 has rearrangements and E2 has no rearrangement.

A table containing a summary of elimination reactions is available at the end of section 7-16 in the textbook.

ACTIVITY 8.10

Do Problem 7-5.

8.7.6 Competition between substitution and elimination reactions (Wade et al section 7-17)

Elimination and nucleophilic substitution reactions are competitive reactions. It is not always possible for us to predict one sole mechanism or one sole product. We can, however, apply some general principles to help us predict the outcome of a reaction.

(i) Bimolecular substitution versus bimolecular elimination (strong base or nucleophile) (Wade et al section 7-17A)

A **strong base or nucleophile** ALWAYS promotes the **E2 and S_N2** reactions. However, a **tertiary alkyl halide** undergoes the **E2** elimination with a strong base or nucleophile. A tertiary alkyl halide will NEVER undergo the S_N2 reaction. A **secondary alkyl halide** will ALWAYS undergo **E2 and S_N2** reactions with a strong base or nucleophile. A **primary alkyl halide** will ALWAYS undergo **E2 and S_N2** reactions with a weak base or nucleophile.

A **bulky strong base** favours the **E2** reaction. **Good nucleophiles** that are also **weak bases**, like **iodide and bromide** ions, favour the **S_N2** reaction. High temperatures tend to favour elimination.

(ii) Unimolecular substitution versus unimolecular elimination (weak base or nucleophile) (Wade et al section 7-17B)

A **weak base or nucleophile** ALWAYS promotes the **E1 and S_N1** reactions. The fastest reaction is either the E1 elimination or the S_N1 substitution reaction.

A **tertiary alkyl halide** will ALWAYS undergo **E1 and S_N1** reactions with a weak base or nucleophile, but NEVER S_N2 reactions. A **secondary alkyl halide** will ALWAYS undergo **E1 and S_N1** reactions with a weak base or nucleophile, but NEVER S_N2 reactions. High temperatures also favour elimination reactions.

A table containing a summary of elimination reactions is available at the end of section 7-17B in the textbook.

Study Solved Problem 7-6 in Wade et al and pay particular attention to the information in "Problem-solving Strategy", Predicting Substitutions and Eliminations, in the green box after the Solved Problem 7-6 in the textbook.

ACTIVITY 8.11

Do Problem 7-51.

8.8 Alkene synthesis by dehydration of alcohols (Wade et al section 7-18)

The dehydration reaction of alcohols was discussed in section 7.5.3 in study unit 7. Study Key Mechanism 7-5 and Solved Problem 7-7 in Wade et al.

Watch the videos on dehydration of alcohols via the links:

<https://www.youtube.com/watch?v=etznYI-fsoY>

<https://www.youtube.com/watch?v=3Ts4CGISq9w>

The key points of the reactions in Section A is summarised in PROBLEM-SOLVING STRATEGY Proposing Reaction Mechanisms at the end of chapter 7 in Wade et al.

ACTIVITY 8.12

Do Problem 7-37 (a), (b), (c).

B REACTIONS OF ALKENES (Wade et al chapter 8)

8.9 Reactivity of the carbon-carbon double bond (Wade et al section 8-1)

Alkenes contain pi electrons, which are more available for donation than the electrons in a sigma bond. Therefore, pi electrons act as nucleophiles and react with electrophiles like a proton or a carbocation.

Alkenes undergo electrophilic addition reactions. **Addition reactions** involve the **breaking** of the **pi bond** and **replacing** it with **two single bonds**.

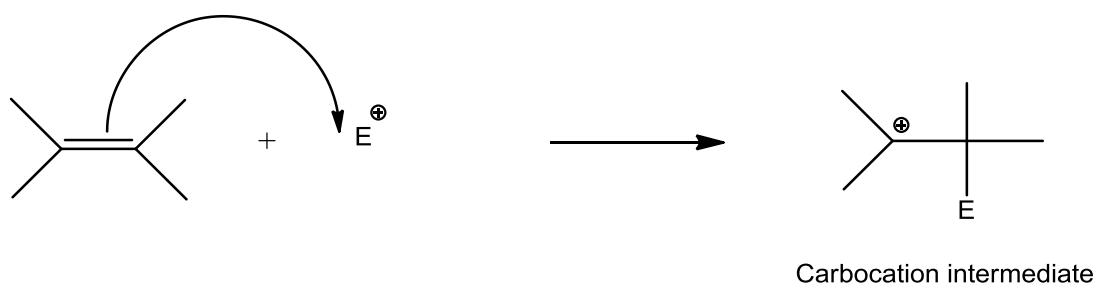
8.10 Electrophilic addition to alkenes (Wade et al section 8-2)

In any electrophilic addition reaction to an alkene, the pi bond electrons are always the ones that attack the electron-poor species (electrophile). Since the pi electrons are equally shared by both carbon atoms of the double, any of the carbon atoms of the double can use the pi bond electrons independently to attach the electrophile.

The mechanism of an addition reaction involves:

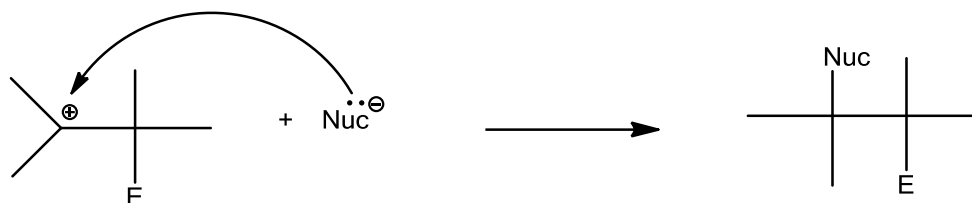
STEP 1

When the pi electrons react with the electrophile, the pi bond is broken and a new sigma bond forms with the electrophile. A positively charged (carbocation) intermediate is formed.



STEP 2

A nucleophile attacks the positively charged (carbocation) intermediate and a new sigma bond forms.



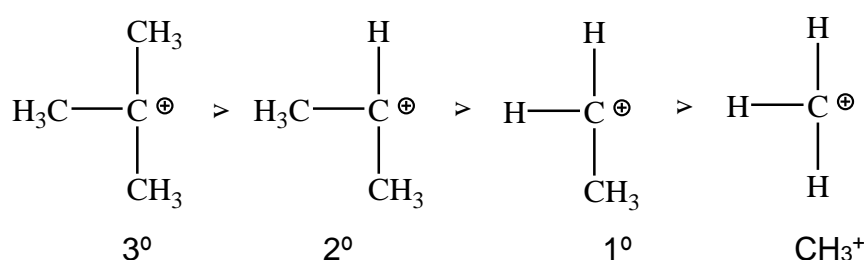
The structure of the alkene directs the outcome of the reaction. An alkene is classified as either symmetrical or unsymmetrical, based on the **plane of symmetry**, which bisects the double bond.

If one cuts through the middle of a double and the two halves are **similar** or **equivalent**, then the molecule is **symmetrical**. For **unsymmetrical** alkenes, the two halves are unequal and therefore **different**.

For **unsymmetrical alkenes**, the preferred addition will depend on the **stability** of the **carbocation** formed in the first step. The relatively **more stable carbocation** is formed preferentially, which **reacts faster** to form the product in a relatively large amount. Thus, if a mixture of products form, both carbocations have to be included in the mechanism and their relative stabilities compared. The product that **predominantly forms** is the **major product** of the reaction. If only one product forms, this implies that only the most stable carbocation is produced to form the only product.

Study Key Mechanism 8-1 in Wade et al.

We have already encountered the stability of carbocations with the following trend:



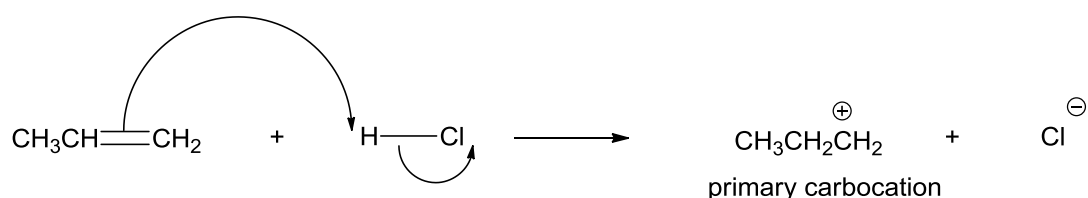
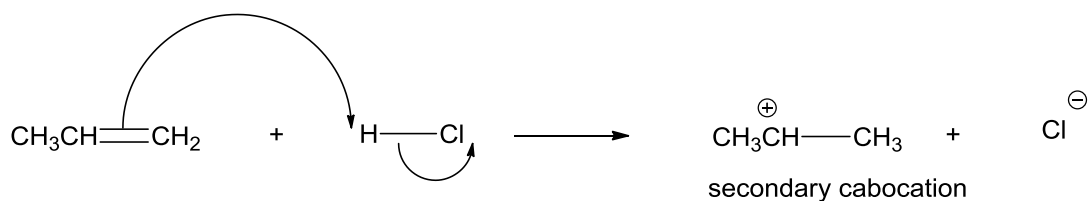
Trend in stability of carbocations: $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

In the sections below, we will discuss the reaction of alkenes with hydrogen halides, water, halogens, borane, hydrogen, and so forth.

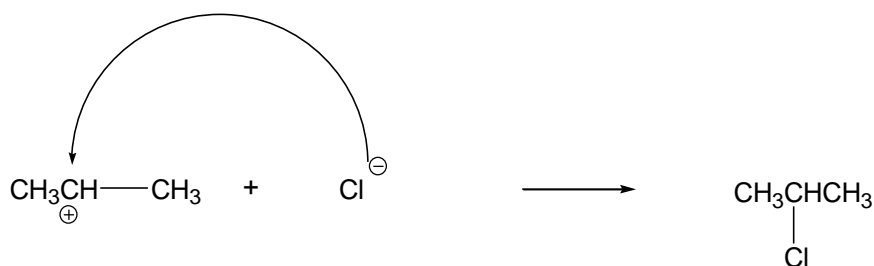
8.10.1 Addition of hydrogen halides to alkenes (Wade et al section 8-3)

The reaction of alkenes with hydrogen halides produce alkyl halides as products. The first and most important step of the reaction involves the addition of a proton to the C=C bond.

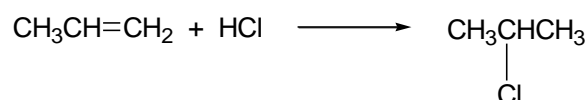
Let us consider the reaction of HCl with $\text{CH}_3\text{CH}=\text{CH}_2$. The reaction with HCl first proceeds via the electrophilic addition of H^+ to give two possible carbocation intermediates:



The more stable intermediate is formed in the mechanism of the reaction. The secondary carbocation is more stable and of lower energy than the primary carbocation. The secondary carbocation therefore forms faster than the primary carbocation. The secondary carbocation will mainly react with the nucleophile to form the product.



The reaction produces a major product:



Study Key Mechanism 8-2 in Wade et al.

In an electrophilic addition to a carbon-carbon double bond, the most stable carbocation is formed as an intermediate.

8.10.2 Orientation of addition: Markovnikov's rule (Wade et al section 8-3A)

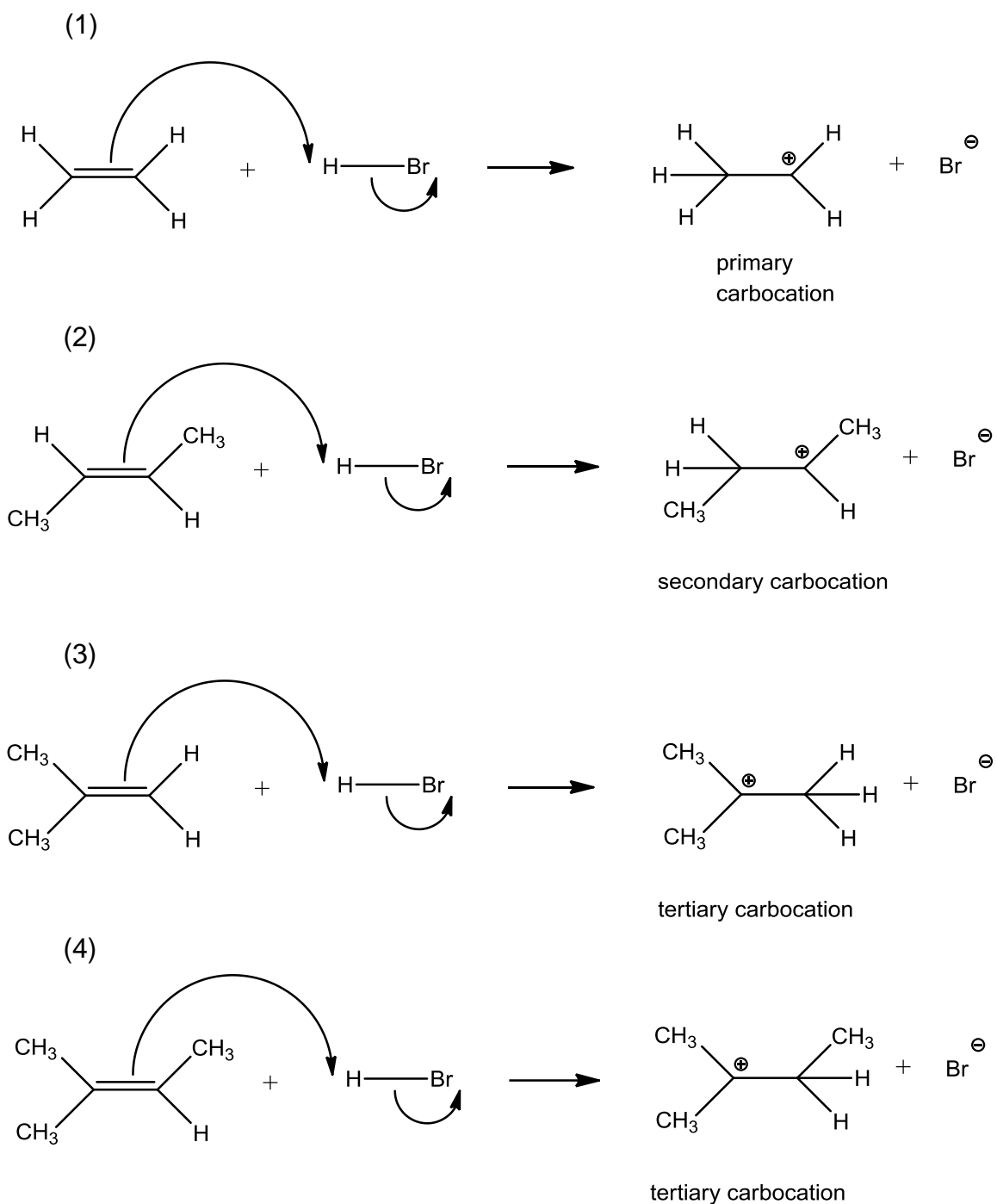
Vladimir Markovnikov, after studying the addition of a variety of acids (HY) to unsymmetrical alkenes, formulated the **Markovnikov Rule**, which states:

In the addition of a proton acid to a carbon-carbon double bond, the proton attaches itself to the carbon atom containing the greatest number of hydrogens.

Rephrasing this rule:

In any electrophilic addition to the carbon-carbon double bond of an unsymmetrical alkene, the electrophilic hydrogen (proton) attaches to the carbon of the double bond with the most hydrogen atoms to form a more stable carbocation that results in the formation of a major or sole product.

Let us look at examples where the most stable carbocation is formed, where applicable:



Reactions (1) and (2) above involve **symmetrical alkenes** and **only one carbocation** can form. The **most stable carbocation** is formed in reactions (3) and (4) involving **unsymmetrical alkenes**.

Watch the video on the mechanism of the addition reactions via the link:
<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkene-reactions/v/introduction-to-reaction-mechanisms>

ACTIVITY 8.13

Do Problem 8-1.

8.10.3 Free-radical addition of HBr: Anti-Markovnikov's Rule (Wade et al section 8-3B)

In the presence of peroxide (ROOR' ; $\text{R}, \text{R}' = \text{H}$ or alkyl) and light, hydrohalogenation of alkenes gives an alkyl halide product. In this reaction, a hydrogen atom attaches to the carbon of the double bond that previously had the least number of hydrogen atoms (anti-Markovnikov). This observation implies that this reaction involves a different mechanism to that of the hydrohalogenation of alkenes without peroxide.

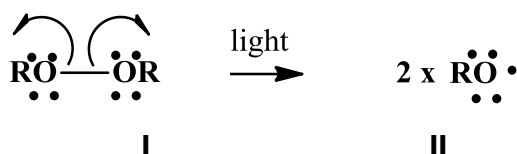
In the **presence of peroxide** and light, the mechanism involves **free radicals** and **not** carbocations. The **more stable free radical** is the one that preferentially forms the product.

Generalised mechanism of hydrohalogenation of alkenes in the presence of peroxide:

Step 1 Chain initiation step

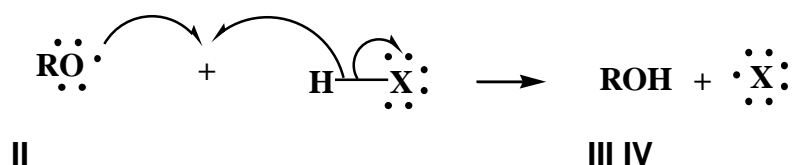
In the presence of light, the peroxide (I) undergoes homolytic bond cleavage to generate the hydroxy (if $\text{R} = \text{H}$) or alkoxy ($\text{R} = \text{alkyl}$) radicals (II).

(i)



The homolytic bond cleavage of the peroxide forms free radicals. This reaction is initiated by light.

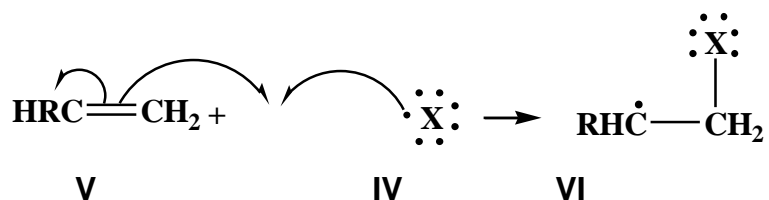
- (ii) The radical (II) generated above abstracts a hydrogen atom from HX to form water or an alcohol (III) and a halogen atom (IV).



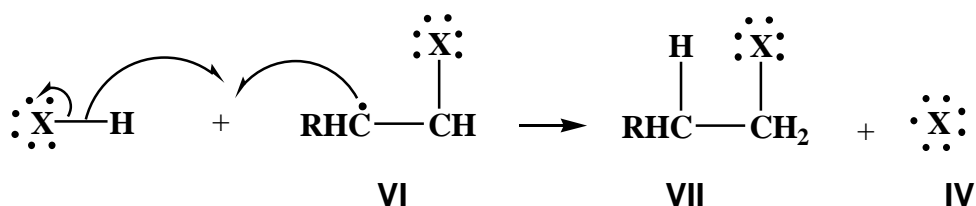
Step 2 Propagation steps

The halogen radical or atom (IV) released above pairs its spin with one of the pi electrons from the C-C double bond of an alkene (V) to form a bond. The other pi electron is taken by the second carbon of the double bond to generate a more stable free radical (intermediate VI). For unsymmetrical alkenes, formation of a more stable free radical is preferred (*recall factors that affect the stability of free radicals*).

(i)



(ii)

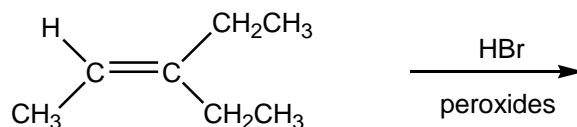


The halogenated free radical (VI) abstracts a hydrogen atom from excess H-X to form an alkyl halide (VII) releasing a halogen atom (IV). In the product (VII), the hydrogen atom is attached to the carbon of the double bond with the least number of hydrogen atoms (anti-Markovnikov fashion).

Study Mechanism 8-3 in Wade et al.

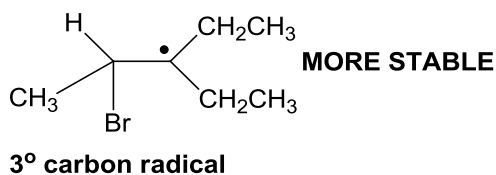
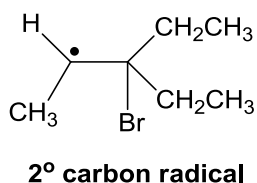
EXAMPLE

Give the major organic product formed in the following reaction:



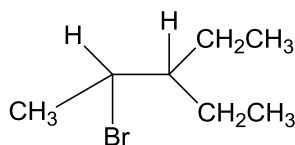
Answer:

Alkenes react with hydrogen halides in the presence of peroxides to give alkyl halides via an anti-Markovnikov addition method. The alkene can form two possible alkyl radicals:



Stability of carbon radicals: $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

The more stable radical intermediate is mostly formed in the reaction and gives the major product:



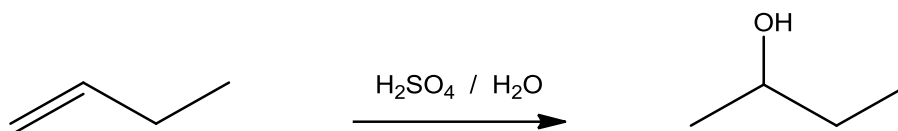
Study Solved Problem 8-1 in Wade et al.

ACTIVITY 8.14

Do Problem 8-3.

8.10.4 Addition of water: Acid-catalysed hydration of alkenes (Wade et al section 8-4)

In the presence of catalytic amounts of acid, water adds to alkenes to yield alcohols. An example is a hydration reaction:

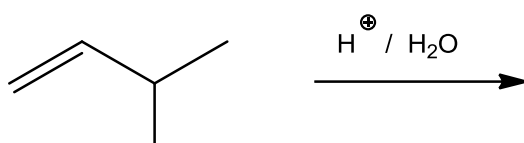


The mechanism of the reaction is similar to that of H-X addition above where a proton (H^+) is attacked by the pi bond electrons of the alkene to generate a carbocation. The proton can bond to either carbon of the double bond. However, the formation of the more stable carbocation directs the reaction. The water molecule attacks the carbocation (oxygen has a lone pair of electrons and is therefore nucleophilic). This attack leads to the formation of a protonated alcohol (ROH_2^+). The latter then loses a proton (H^+) to produce a neutral alcohol. Note that the catalyst kick-starts the reaction, speeds it up and at the end of the reaction it is being regenerated.

Study Mechanism 8-4 in Wade et al.

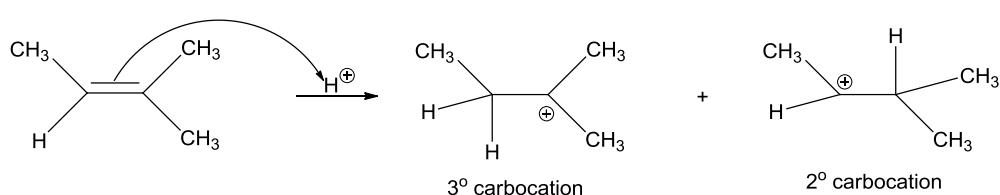
EXAMPLE

Propose a mechanism for the formation of the alcohol produced by the following reaction:

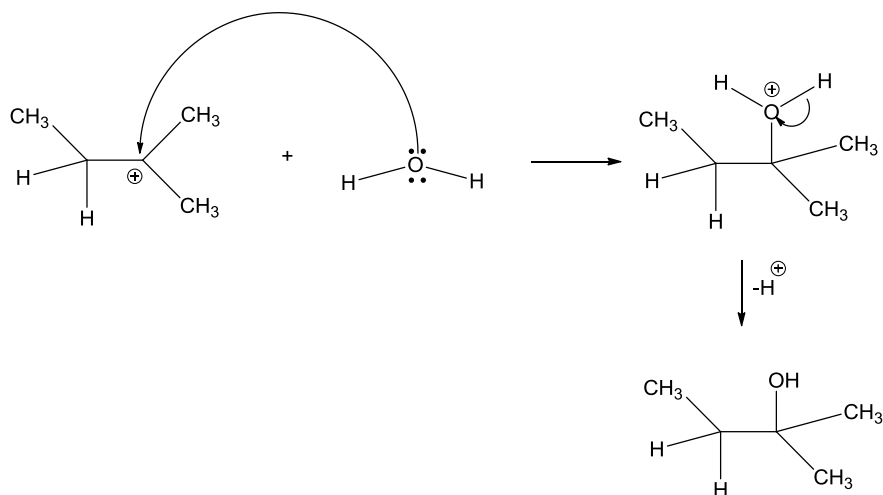


Answer:

The first step in the acid-catalysed hydration of the compound, 2-methyl-2-butene is:

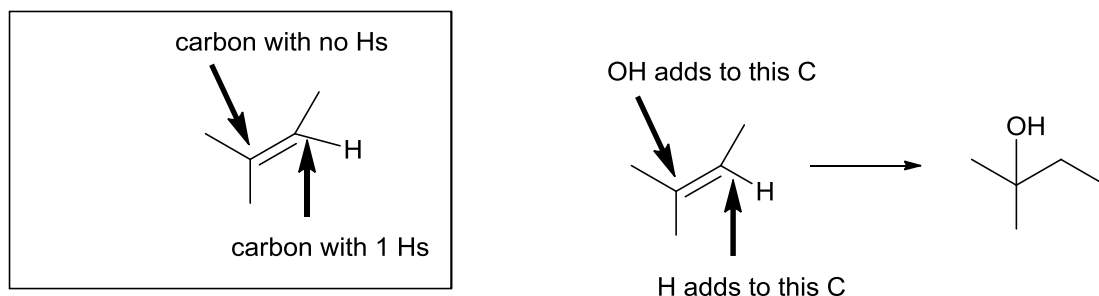


The most stable carbocation is the tertiary carbocation, which is lower in energy than the secondary carbocation, and is predominantly formed. The reaction of the tertiary carbocation will give the predominant/major product. The nucleophilic water molecule attacks the electrophilic carbocation, that is, the lone pair of electrons on O are donated to the C⁺ to form a bond.



NB. This reaction will not take place if the acid is absent.

SUMMARY: Markovnikov addition:

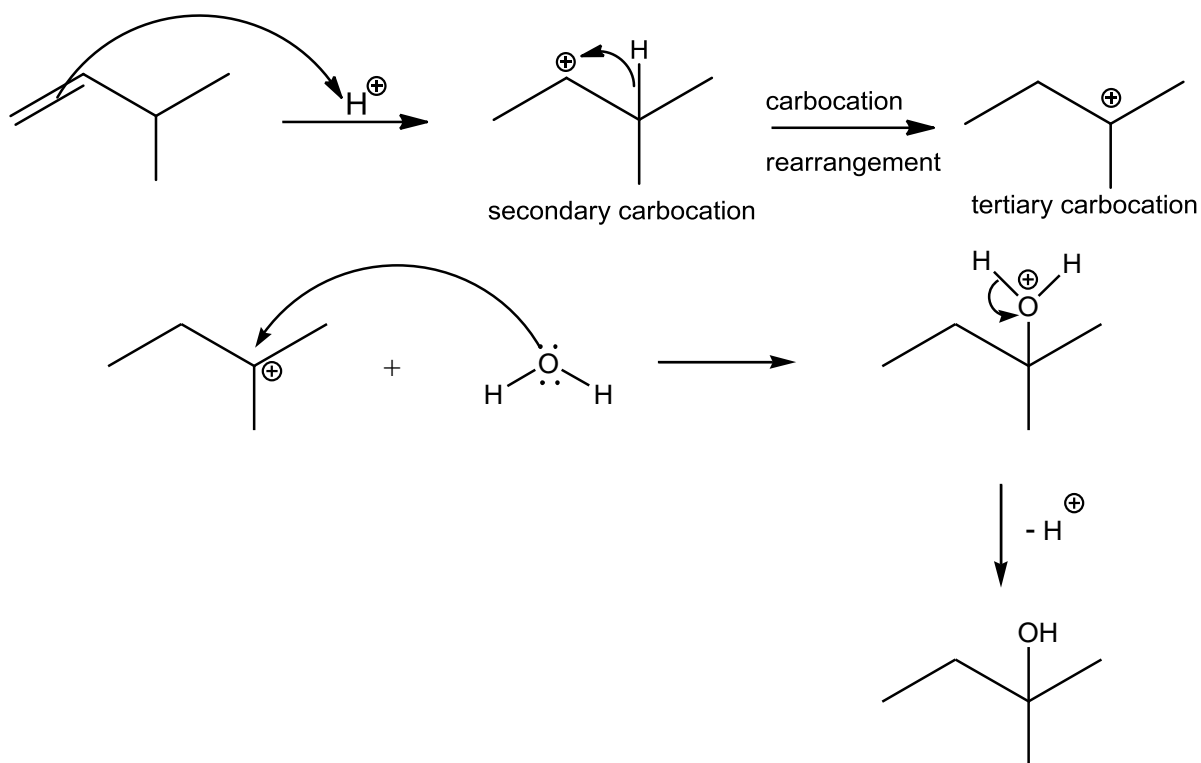


In the addition reactions of alkenes, which involve the formation of carbocation intermediates, rearrangements may sometimes occur

EXAMPLE

Give the mechanism for the conversion of 3-methylbut-1-ene to 2-methylbutan-2-ol.

The reaction proceeds via the following steps:



Watch the relevant video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkene-reactions-tutorial/v/hydration>

ACTIVITY 8.15

Do Problem 8-6.

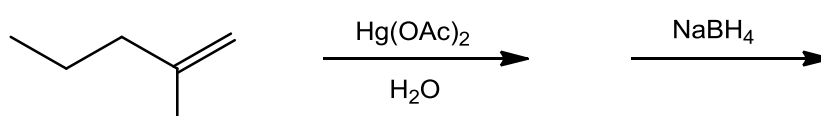
We also notice that the hydration of an alkene is the opposite reaction to the dehydration of an alkene. Reaction conditions therefore have to be carefully controlled to force the formation of the alcohol or to obtain the alkene.

Alkenes can also be converted to alcohols by oxymercuration-demercuration and hydroboration of alkenes.

8.10.5 Hydration by oxymercuration-demercuration (Wade and Simek section 8-5)

Not all alkene molecules can be converted to alcohols via the acid-catalysed hydration reaction. A more useful method for the conversion of alkenes to alcohols is oxymercuration-demercuration. This method takes place under milder reaction conditions and proceeds with Markovnikov orientation.

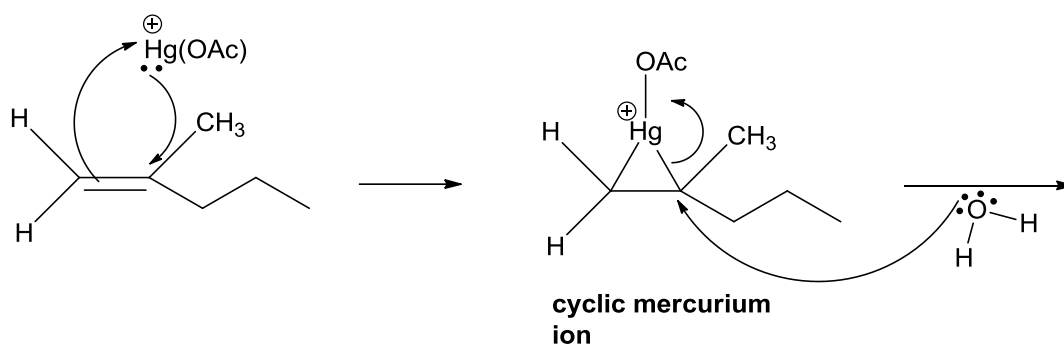
Let us consider the following reaction:

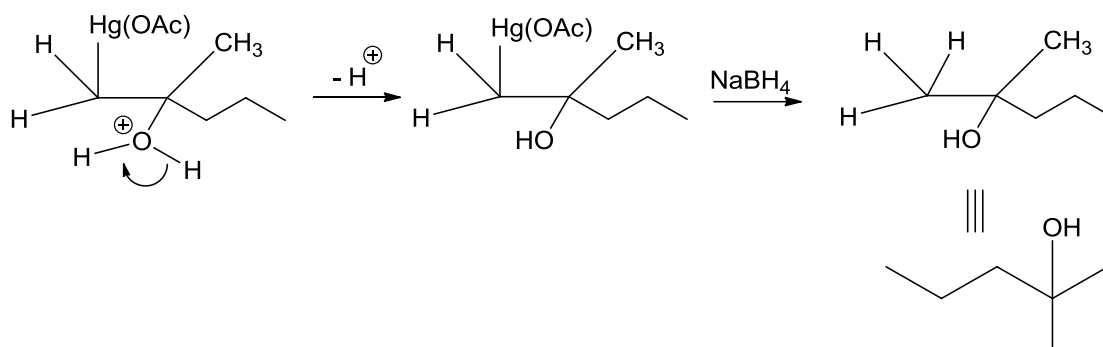


This is an example of a hydration reaction of alkenes via an oxymercuration-demercuration process. In the reaction mechanism, mercuric acetate is believed to dissociate a little to give a positively charged mercuric species, $^+\text{Hg(OAc)}$, and the acetate ion (^-OAc).

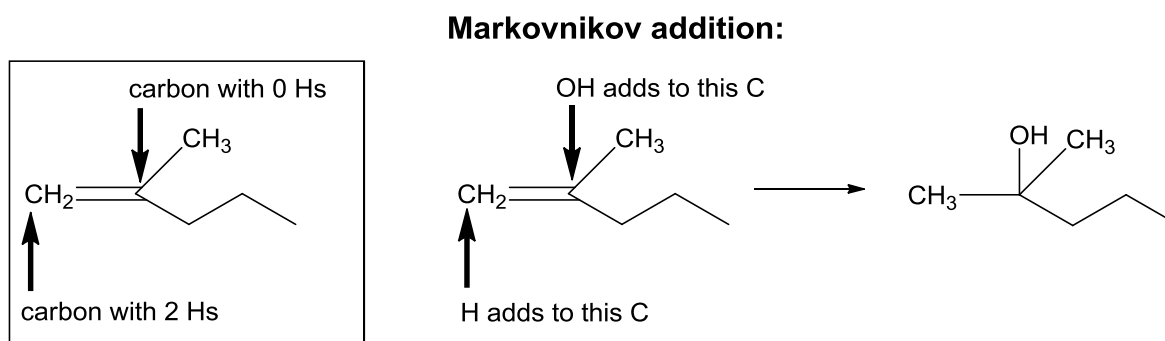


The electrophile attacks the pi bond to form a cyclic mercurium ion. The nucleophilic attack by water results in a ring opening of the mercurium ion. In the last step, demercuration takes place and is replaced by H.





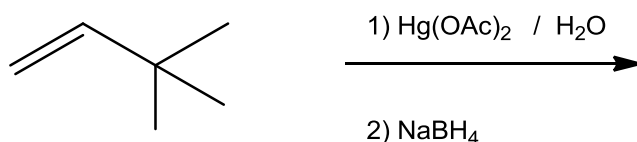
The hydration reaction proceeds via the Markovnikov addition method. The H adds to the C with the most number of H atoms and the OH adds to the C of the C=C with the most number of C atoms attached to it, as summarised below:



Study Mechanism 8-5 in Wade et al.

ACTIVITY 8.16

Predict the structure of the major product formed in the following reaction:



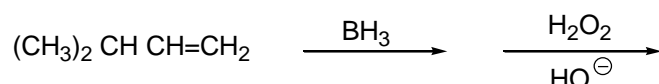
Watch the appropriate videos via the links:

<https://www.youtube.com/watch?v=lvLlewBCPl0>

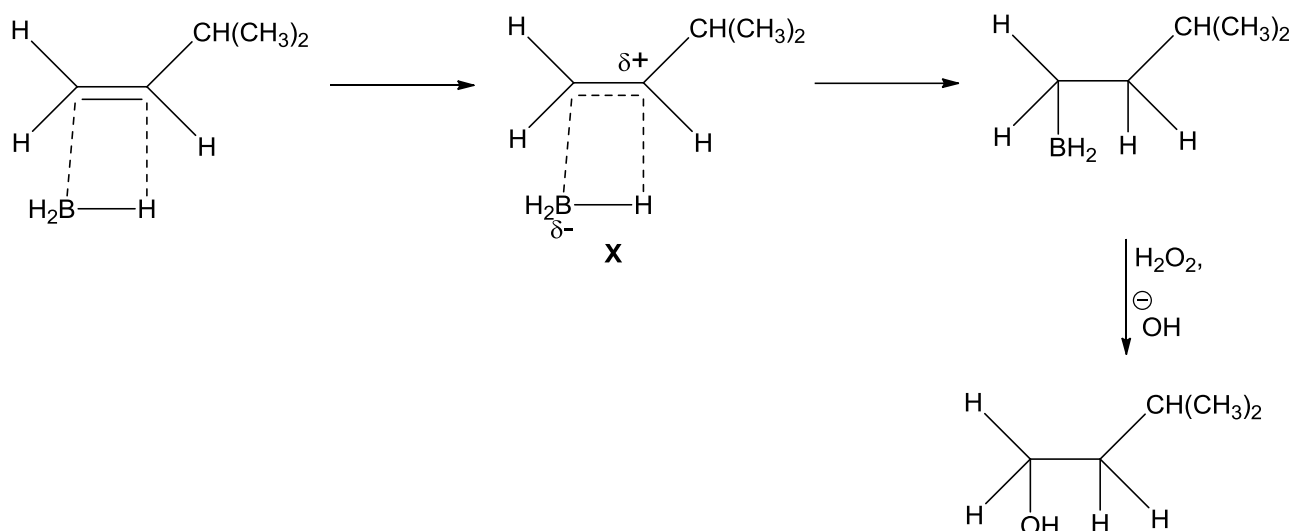
<https://www.youtube.com/watch?v=b7Qj-QZR9Ck>

8.10.6 Hydroboration of alkenes (Wade et al section 8-7)

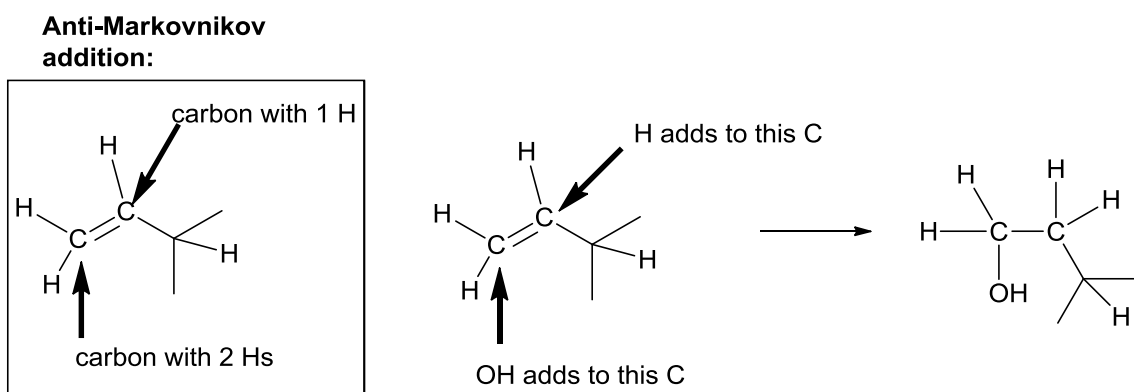
Alkenes can also be converted to alcohols, where the reaction involves **anti-Markovnikov addition**. This can be achieved with **hydroboration-oxidation**, which involves treatment with diborane (B_2H_6) or BH_3 .THF reagent followed by the removal of the boron atom by oxidation with sodium hydroxide and hydrogen peroxide in water. If we consider the reaction:



The reaction involves the addition of water to the alkene in an anti-Markovnikov manner as shown below. BH_3 is a strong Lewis acid with the B atom having an empty orbital and adds to the $C=C$ in the following manner:



A summary of the above reaction:



Study Mechanism 8-6 and Solved Problem 8-3 in Wade et al.

Watch the relevant video via the link:

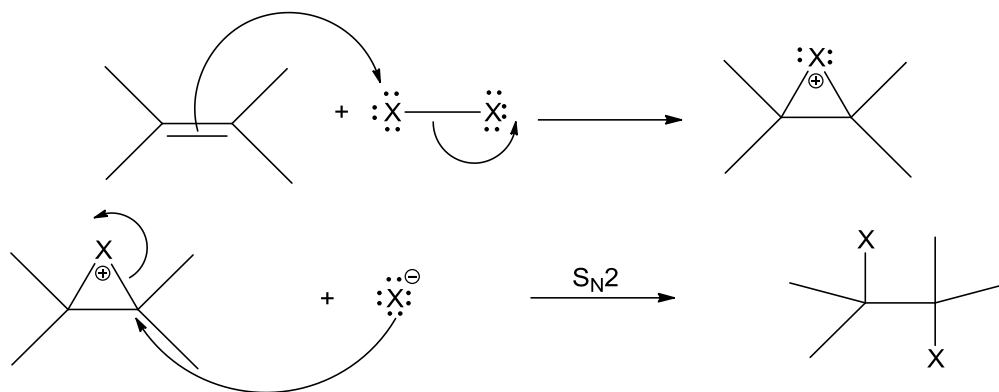
<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkene-reactions-tutorial/v/hydroboration-oxidation-mechanism>

ACTIVITY 8.17

Do Problems 8-10 and 8-13.

8.10.7 Addition of halogens to alkenes (Wade et al section 8-8)

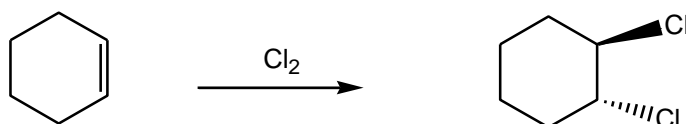
Alkenes undergo addition reactions with halogens (X_2) like bromine (Br_2) or chlorine (Cl_2). One of the halogen atoms acts as an electrophile, breaking the $X-X$ bond. This leads to the formation of a halide ion and a positively charged intermediate. The positively charged intermediate has a bridged structure and is known as a **halonium ion**. The halide ion then acts as a nucleophile and attacks the halonium ion in a S_N2 mode. The bromide ion forms a bond from the side of the molecule opposite to the halogen bridge.



Study Mechanism 8-7 in Wade et al.

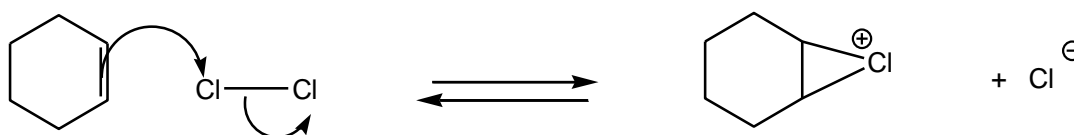
Stereochemistry of halogen addition (Wade et al section 8-8B)

The **addition of the halogens** is **stereospecific** and the halogens add in an **anti**-manner. An example of anti-addition is the reaction of cyclohexene with chlorine:

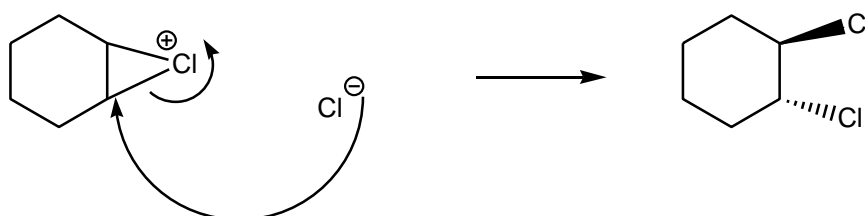


The mechanism for the reaction is:

The formation of a chloronium ion (general halonium ion)



The chloride ion attacks the chloronium ion in a $\text{S}_{\text{N}}2$ type reaction (the Cl^- ion attacks from the back), causing the two chlorine atoms to be attached on opposite sides of the ring. *Trans*-1,2-dichlorocyclohexane is formed as the main product:



You are encouraged to watch the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkene-reactions-tutorial/v/halogenation>

ACTIVITY 8.18

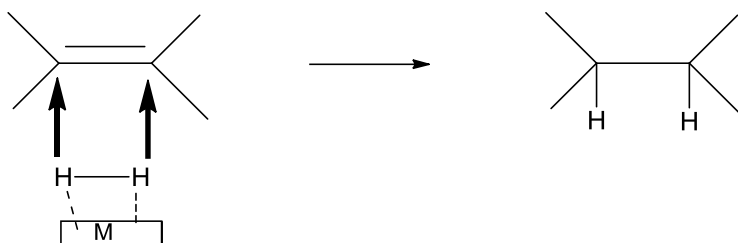
Do Problem 8-49 in Wade et al.

8.10.8 Catalytic hydrogenation of alkenes (Wade et al section 8-10)

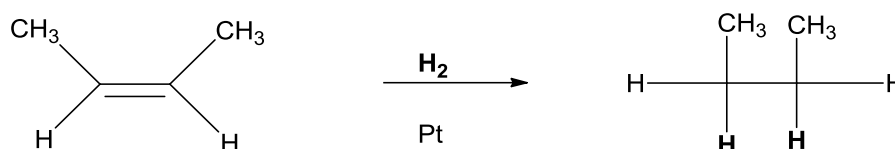
Alkenes react with molecular **hydrogen**, H_2 , in the presence of a transition metal **catalyst** (Pt, Pd and Ni) to form **alkanes**. Hydrogenation (also known as reduction) involves addition of hydrogen atoms from a hydrogen molecule to the alkene double bond.

The reaction occurs on the surface of a metal catalyst (Pd, Ni or Pt). The nonpolar hydrogen molecule is adsorbed onto the metal surface and becomes polarised.

The mechanism of hydrogenation of the carbon-carbon pi bond occurs in one step in a concerted fashion. The hydrogen atoms are added on the same face/side of the C-C double bond.



For example:



Both hydrogens add to the same face of the C=C bond and the mode of addition is called **syn addition**.

Study Mechanism 8-7 in Wade et al. You are encouraged to watch the video on hydrogenation via the following link:

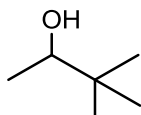
<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkene-reactions-tutorial/v/hydrogenation>

8.11 Conclusion

In this study unit, we described the structure, nomenclature, physical properties and stabilities of alkenes. We further focused on the different methods to prepare alkenes from alkyl halides. We concentrated on the mechanisms of addition reactions of symmetrical and unsymmetrical alkenes and applied Markovnikov's rule to hydrogenation, hydrohalogenation, hydration and halogenation reactions. We further described the hydrohalogenation of alkenes in the presence of peroxides and light. In the next study unit, we will discuss the structure, nomenclature, physical and chemical properties of alkynes.

ANSWERS TO SELECTED ACTIVITIES

8.16



STUDY UNIT 9

Alkynes

- 9.1 Introduction
- 9.2 Nomenclature
- 9.3 Alkyne structure and properties
- 9.4 Acidity of alkynes: formation of acetylide ions
- 9.5 Synthesis of alkynes
- 9.6 Addition reactions of alkynes
- 9.7 Interconversion of alkynes, alkenes and alkanes
- 9.8 Conclusion

LEARNING OUTCOMES

At the end of this study unit, you should be able to:

- describe the general structure of alkynes
- accurately use the IUPAC rules for nomenclature to construct structural formulae, and *vice versa*
- predict product formation and propose the mechanisms for the formation of alkenes
- correctly propose the mechanisms of the hydrohalogenation, hydration and halogenation reactions of symmetrical and unsymmetrical alkynes and apply Markovnikov's rule
- correctly propose the mechanism of hydrohalogenation of alkynes in the presence of peroxides
- develop strategies for the inter-conversion of alkynes, alkenes and alkynes using various reagents

9.1 Introduction (Wade et al sections 9-1 and 9-4)

In study unit 8 we discussed alkenes that contain the carbon-carbon double bond. This study unit focuses on alkynes. Alkynes are hydrocarbons containing a carbon-carbon triple bond, in other words, the functional group is $\text{C}\equiv\text{C}$. The simplest alkynes, namely acetylene ($\text{H}-\text{C}\equiv\text{C}-\text{H}$) and methylacetylene ($\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$), are widely used in the welding industry. Derivatives of estrogen that contain a $-\text{C}\equiv\text{CH}$ group are extremely useful as contraceptives and for treating menstrual and menopausal problems in females. In this study unit, we will describe the structure, nomenclature, preparation and reactions of alkyne.

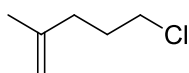
9.2 Nomenclature (Wade et al section 9-2)

The **IUPAC** nomenclature rules, as outlined in section 3.4.2 in study unit 3, are applicable with the following adaptations:

1. The ending “ane” in the name is replaced by an “yne”.
2. The **longest carbon chain** containing the **triple bond** is the parent name.
3. The numbering of the carbon chain starts at the end **closest to the $\text{C}\equiv\text{C}$ group ($\text{C}\equiv\text{C}$ has the lowest possible number)**.
4. Assign the position of the $\text{C}\equiv\text{C}$ group in the carbon chain by allocating the lower number of the two $\text{C}\equiv\text{C}$ atoms.
5. Two or more $\text{C}\equiv\text{C}$ groups are indicated as **diyne**, **triyne**, and so forth, with the positions of the $\text{C}\equiv\text{C}$ groups shown by the appropriate numbers.
6. If both double and triple bonds are present, indicate each bond with a number where it appears in the carbon chain. Double bonds precede triple bonds in the IUPAC name, in other words, the ending is “enyne”. Number the chain from the end nearest a multiple bond, regardless of its nature.

EXAMPLES

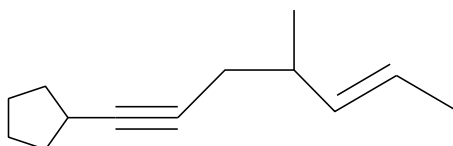
1. Give the IUPAC name of the following compound:



Answer: The IUPAC name is **5-chloro-2-methyl-1-pentene**.

Explanation: According to the IUPAC convention, the longest continuous carbon chain containing the C=C bond has 5 Cs → pentane, but since there is a C=C bond in the chain → change the ending from “ane” to “ene”. Begin numbering at the end of the C-chain to give the C=C the lowest number → 1-ene. The substituents are at C-2 a CH₃ group → 2-methyl and at C-5 a Cl atom → 5-chloro. Name substituents in alphabetical order.

2. What is the IUPAC name of the following compound?



Answer: **(E)-1-cyclopentyl-4-methylhept-5-en-1-yne**

Explanation: According to the IUPAC convention, the longest continuous carbon chain has 7 Cs → heptane, but there is a C=C bond (“ene”) and a carbon-carbon triple bond (“yne”) in the chain → change the ending from “ane” to “enyne”. Numbering starts from the end nearest to the first multiple bond. Start numbering from the left with the triple bond at C-1 and C=C at C- 5 and the ending is “-5-en-1-yne”. The substituent on C-1 is a ring with 5 Cs → 1-cyclopentyl, and there is a methyl on C-4 → 4-methyl. Name substituents in alphabetical order to give 1-cyclopentyl-4-methylhept-5-en-1-yne. We assign the E-Z notation according to the guidelines described in section 8.3.2 in study unit 8.

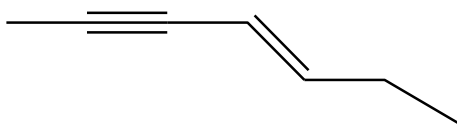
View the relevant video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/naming-preparation-alkynes/v/alkyne-nomenclature>

ACTIVITY 9.1

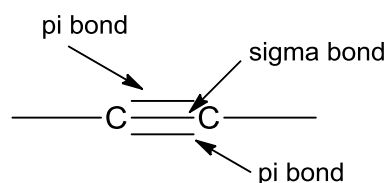
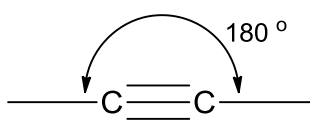
(a) Give the structure of 6-bromo-5-ethyl-2-methyloct-3-yne.

(b) Give the IUPAC name for the following structure:



9.3 Alkyne structure and properties (Wade et al sections 9-3 and 9-5)

The **carbon-carbon triple bond** is composed of **one σ** bond and **two π** bonds. The **carbon** that forms part of a triple bond is **sp hybridised**. Each carbon that is part of the $C\equiv C$ bond has **two sp** hybrid orbital and **two unhybridised 2p** orbitals. A σ bond between the two Cs is formed by the overlap of two sp hybrid orbitals and a π bond is formed by the overlap of two 2p orbitals, above and below the plane of the two nuclei. Therefore, 2 π bonds are formed between the two Cs. The unhybridised p_y and p_z orbitals overlap sideways to form two pi bonds. The geometry around the triple bond is linear, with bond angle of 180° .

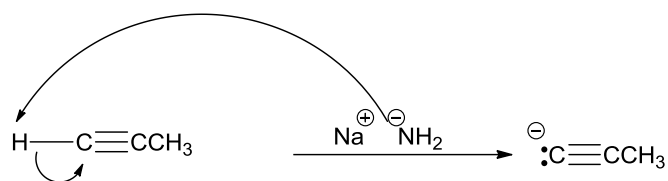


The triple bond is made up of one sigma bond (**middle**) and two pi bonds, one above and the other below the sigma bond. Alkynes are also sources of pi electrons (nucleophiles) and can donate in sequence one pair of pi electrons to change from triple to double and another pair to a single bond state, respectively.

9.4 Acidity of alkynes: formation of acetylide ions (Wade et al section 9-6)

The acidity of a C-H bond in hydrocarbons varies according to the hybridisation state of the C. When the s character of the orbital increases, the acidity also increases. An sp hybrid orbital has half s-character and half p character, an sp² hybrid orbital has one-third s-character and an sp³ hybrid orbital has one-fourth s-character. Therefore, the sp hybrid orbital has the highest s-character and is thus the strongest acid of the hydrocarbons, followed by a sp² hybrid orbital. An sp³ hybrid orbital has the least s character and has the weakest acidity. Alkynes are therefore stronger acids than alkenes, with alkanes having the least acidity of the hydrocarbons.

Prop-1-yne has an acidic H and reacts with sodium amide as follows:



An internal alkyne does not have a $\equiv\text{C}-\text{H}$ bond and is therefore not acidic. For example,
 $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ does not have an acidic H atom
but-2-yne

ACTIVITY 9.2

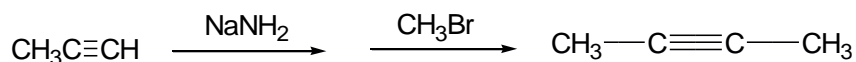
Do Problem 9-5.

9.5 Synthesis of alkynes (Wade et al sections 9-7 and 9-8)

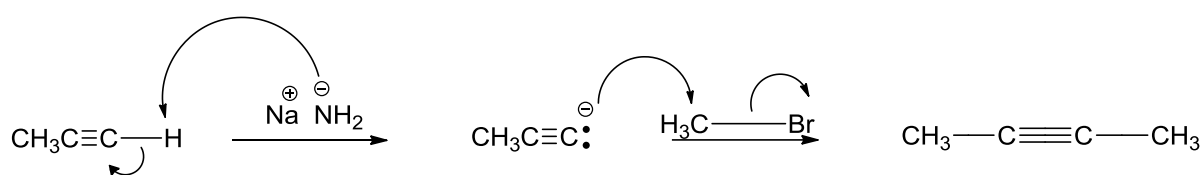
We will describe two methods to prepare alkynes, namely by the reaction of an acetylide ion with alkyl halides and through the double dehydrohalogenation of alkyl dihalides.

9.5.1 Synthesis of alkynes from acetylide ions (Wade et al section 9-7A)

A terminal alkyne reacts with a very strong base like sodium amide to form an acetylide ion. The acetylide ion reacts with an alkyl halide via an S_N2 reaction mechanism to give a new alkyne. Consider, for example, the following reaction:



The mechanism of the above reaction takes place as follows:



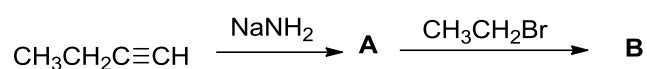
Study Solved Problem 9-1 in Wade et al.

Watch the relevant video via the link:

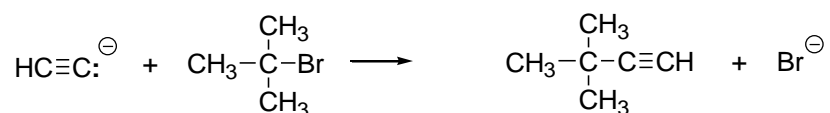
<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/naming-preparation-alkynes/v/alkyne-acidity-and-alkylation>

ACTIVITY 9.3

- (a) Do Problem 9-7.
- (b) Provide the structures of **A** and **B** in the reaction sequence below.



- (c) Explain in detail whether or not the following reaction will take place.



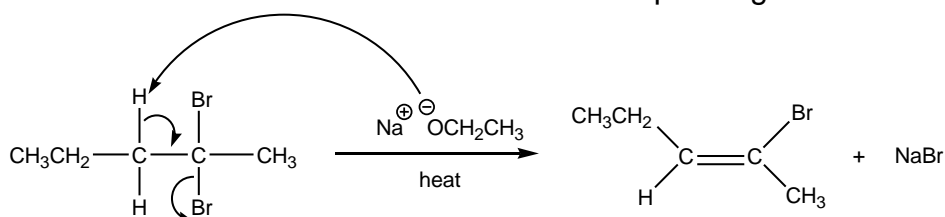
9.5.2 Synthesis of alkynes by elimination reactions (Wade et al section 9-8)

Dehydrohalogenation of geminal or vicinal dihalides

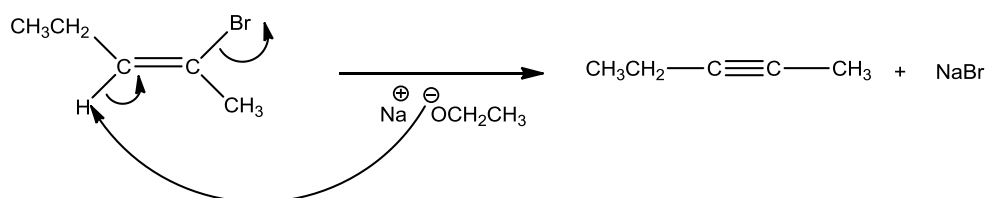
Alkynes can be prepared from vicinal dihalides (the halogens atoms are on adjacent carbon atoms) or from geminal dihalides (both halogens are in the same carbon atom). The reaction to form alkynes involves the double dehydrohalogenation, using a strong base like sodium amide, NaNH_2 , or alcoholic KOH at very high temperatures.

This is a two-step process, where the dihalide is converted in the first step to a haloalkene. In the second step, the haloalkene is converted to the alkyne. Let us consider, for example, the reaction where 2,2-dibromopentane is heated in the presence of sodium ethoxide. 2-Dibromopentane is an example of a geminal dihalide.

First, the E2 elimination of 1 mole HBr to form the corresponding alkene:



Subsequent elimination of another HBr molecule to produce the alkyne:



ACTIVITY 9.4

Do Problem 9-10.

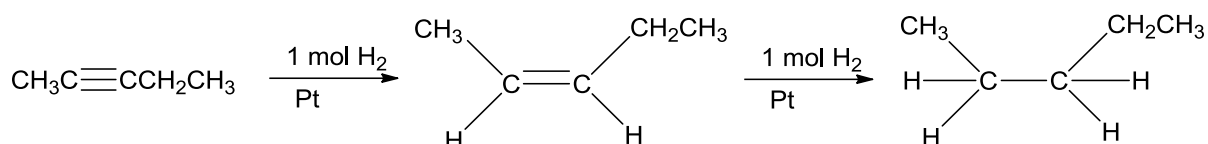
9.6 Addition reactions of alkynes (Wade et al section 9-9)

Similar to alkenes, alkynes have pi bonds capable of acting as nucleophiles. Alkynes therefore also undergo electrophilic addition. The same type of electrophilic reagents that add to alkenes also add to alkynes to give alkene products.

The reactivity of alkynes and the proportion and type of the addition products formed depend on the structure of the alkyne molecule.

9.6.1 Catalytic hydrogenation to alkenes and alkanes (Wade et al section 9-9A)

Alkynes also undergo hydrogenation in the presence of catalysts such as nickel, palladium and platinum. The type of product that forms, depends on the amount or proportion of the hydrogen molecule used. **One mole** equivalent of **hydrogen** reduces an alkyne to an **alkene** and the **second** equivalent of **H₂** completely reduces the resulting alkene to an **alkane**. For example:

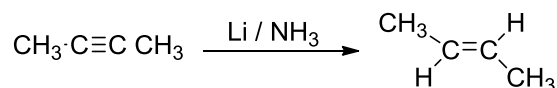


9.6.2 Partial catalytic hydrogenation to cis-alkenes (Wade et al section 9-9B)

When hydrogenation takes place in the presence of Lindlar's catalyst, the product is an alkene and no alkane is formed. In the presence of **Lindlar's catalyst**, the **hydrogen atoms add** to the **same side** of the **carbon-carbon triple bond** to give the **cis alkene**. For example, the reaction of 2-butyne with H₂/Lindlar's catalyst gives *cis* but-2-ene as product.

9.6.3 Metal-ammonia reduction to *trans* alkenes (Wade et al section 9-9C)

The **metal-ammonia reductions** of **alkynes** involve reagents such as Li / NH₃. This reaction involves **two hydrogens adding** to the **C≡C bond** in such a way that **each H** is on **opposite sides** of the resulting **C=C bond**, that is, a ***trans* alkene** forms. The product will have the two Hs on opposite sides of the C=C. For example:



View the video on the reduction of alkynes via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkyne-reactions/v/reduction-of-alkynes>

ACTIVITY 9.5

Do Problem 9-12 (a) to (d).

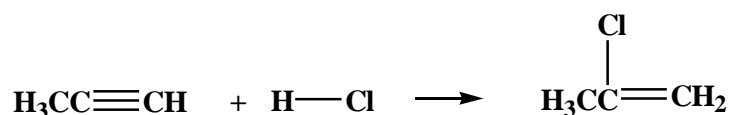
9.6.4 Addition of halogens (Wade et al section 9-9D)

Halogenation of alkynes takes place with a **halogen** atom **adding** to **each carbon** of the **C≡C bond**. Unlike the halogenation of alkenes, the addition of halogens to alkynes may take place in a **syn or anti** manner. Often, **mixtures of cis and trans dihaloalkenes** are produced. When **equimolar** quantities of the **alkyne** and **halogen** are used, **dihaloalkenes** are formed.

When the **halogen** is in **excess**, the dihaloalkene undergoes further addition of the halogen to give a **tetrahalide**. Study the examples given in Wade et al.

9.6.5 Addition of hydrogen halides (Wade et al section 9-9E)

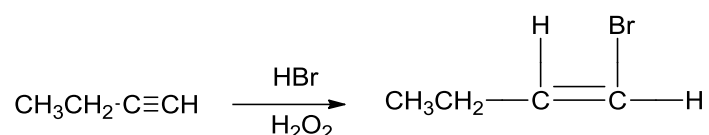
The **addition** of **hydrogen halides** proceeds with **Markovnikov** orientation to give an alkenyl halide. When there is excess hydrogen halide, the alkenyl halide can react form a geminal dihalide. The reaction proceeds via a carbocation intermediate. Consider the reaction of prop-1-yne with hydrochloric acid:



Study the different examples and the mechanism given in Wade et al.

Alkynes react similar to alkenes when peroxides are added to the reaction mixture, with the addition occurring in an anti-Markovnikov manner.

For example:



Watch the video on hydrohalogenation via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes>

ACTIVITY 9.6

Do Problem 9-18 (a) to (f).

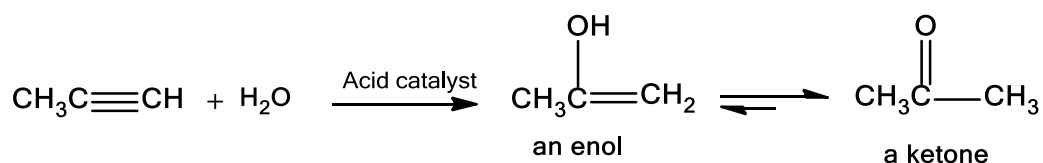
9.6.6 Hydration of alkynes to ketones and aldehydes (Wade et al section 9-9F)

We would expect that, similar to alkenes, the hydration of alkynes would give alcohols. The alcohols formed in the reaction of alkynes are quite different where the hydroxy group is attached to a C=C bond.

This type of alcohol is known as an **enol** (*ene + ol*) and enols rapidly convert to their isomeric forms called **ketones** or **aldehydes**. This interconversion is called **keto-enol tautomerism**.

Acid-catalysed hydration

Alkynes also undergo acid-catalysed hydration following Markovnikov's rule, with H attached to carbon bearing more hydrogens. The initial product of the reaction is an **enol**. The enol immediately rearranges to a **ketone** by *keto-enol tautomerism*.



The only change between the keto form (structure on the left) and the enol form (structure on the right) is the location of the H atom and the pi-electrons. All the other groups or atoms remain the same.

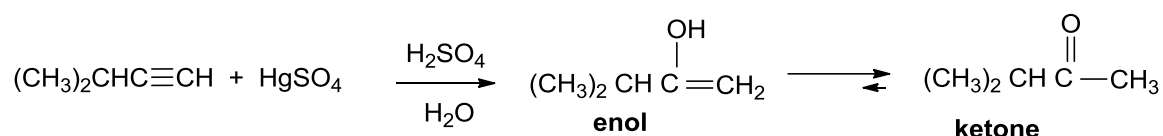
Watch the relevant video via the link:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkyne-reactions/v/hydration-of-alkynes>

Mercuric ion-catalysed hydration (Wade et al section 9-9F)

Another method of **adding water** to the **C≡C** bond is via the acid-catalysed reaction in the presence of **mercuric ion as catalyst**. The reaction produces an **enol** which immediately converts to the corresponding **ketone (keto-enol tautomerism)**.

Mercuric ion hydration takes place with **Markovnikov** orientation. For example:

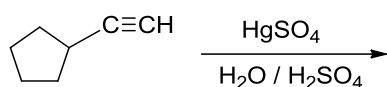


Study the complete mechanism of the reaction in section 9-9F and Mechanism 9-2 Acid-Catalysed Keto-enol Tautomerism in Wade et al.

ACTIVITY 9.7

(a) Do Problem 9-21.

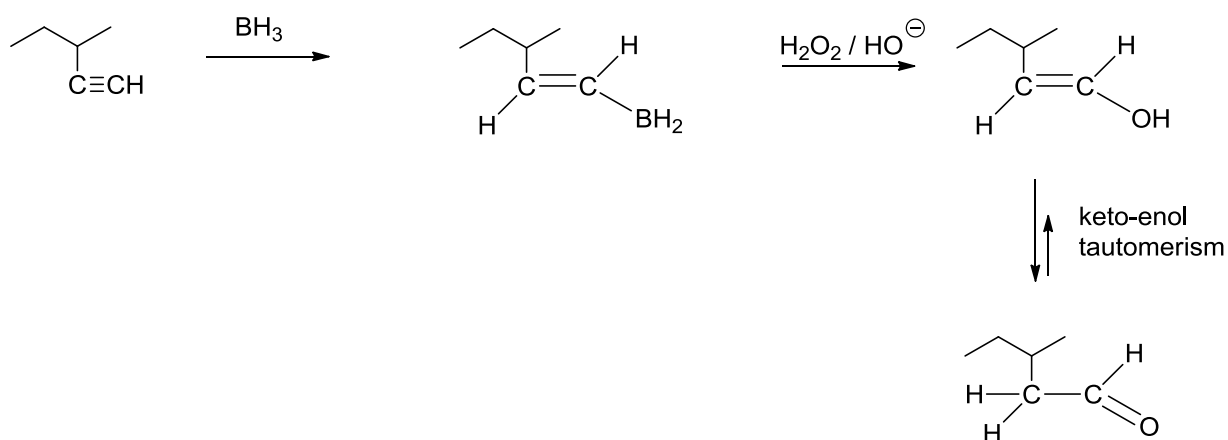
(b) Give the product formed in the following reaction:



Hydroboration

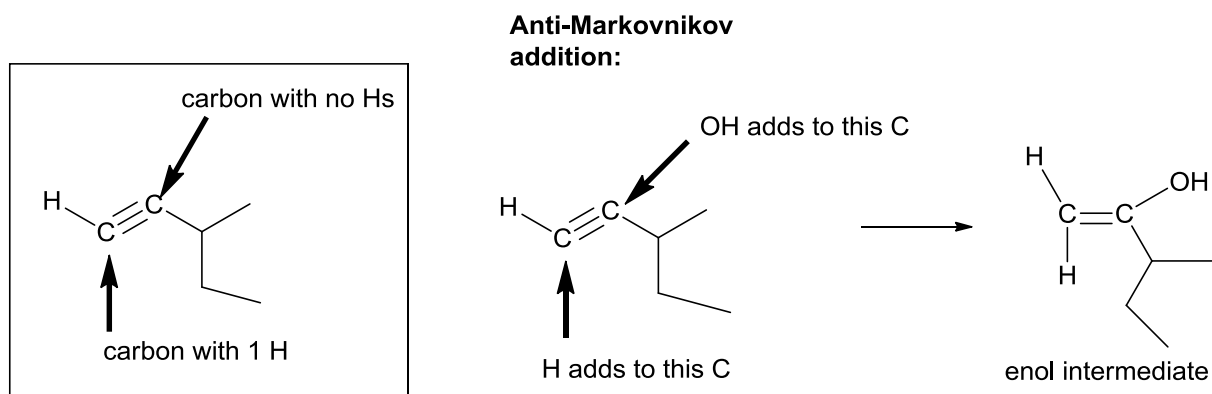
This reaction involves the addition of water to the alkyne in the presence of BH₃. BH₃ is a strong Lewis acid with the B atom having an empty orbital and is therefore electrophilic.

The **H** and **OH** add to the **C≡C** in an **anti-Markovnikov** manner followed by "enol-keto" interconversion to give an aldehyde. Consider the following reaction scheme:



The keto-enol tautomerism gives an aldehyde as the final product.

This is a hydration (the addition of water) reaction. H_2O adds to the $\text{C}\equiv\text{C}$ as follows:



Carefully study Mechanism 9-3 Base-Catalysed Keto-enol Tautomerism. Watch the videos on hydroboration via the links:

<https://www.khanacademy.org/science/organic-chemistry/alkenes-alkynes/alkyne-reactions/v/hydroboration-oxidation-of-alkynes>

[https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/Map%3A_Organic_Chemistry_\(Smith\)/Chapter_11%3A_Alkynes/11.10%3A_Hydroboration%20and%20Oxidation](https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/Map%3A_Organic_Chemistry_(Smith)/Chapter_11%3A_Alkynes/11.10%3A_Hydroboration%20and%20Oxidation)

View the video on oxymercuration and hydroboration of alkynes via the link:

<http://www.masterorganicchemistry.com/2013/05/14/hydroboration-and-oxymercuration-of-alkynes/>

For details about all the alkyne reactions, watch the video:

https://www.youtube.com/watch?v=LUjUOc69w_0

ACTIVITY 9.8

Do Problem 9-20.

9.7 Interconversion of alkynes, alkenes and alkanes

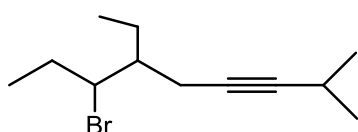
Alkenes, alkanes and alkynes can be interconverted using various reagents and reaction conditions. You are expected to use your knowledge of reaction mechanisms and reactivity to interconvert alkanes, alkenes and alkynes.

9.8 Conclusion

In this study unit we described the structure and nomenclature of alkynes. We further applied Markovnikov's rule in relation to carbocation stability to the mechanisms of hydrohalogenation, hydration, and halogenations of symmetrical and unsymmetrical alkynes. The hydrogenation of alkynes also received attention and we considered the anti-Markovnikov addition of hydrohalic acids in the presence of peroxides. In the next study unit, we will focus on the structure and reactivity of compounds containing a carbon-oxygen double bond.

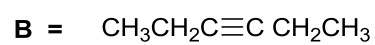
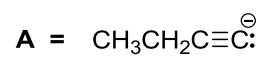
ANSWERS TO SELECTED ACTIVITIES

9.1 (a)



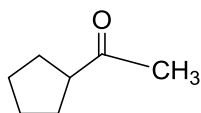
(b) Hept-4-en-2-yne

9.3 (a)



(b) The reaction above does not take place at all. The acetylide ion reacts with an alkyl halide via an $\text{S}_{\text{N}}2$ reaction mechanism. The alkyl bromide is a tertiary alkyl halide which, due to crowding at the tertiary C atom, cannot undergo $\text{S}_{\text{N}}2$ reaction to give the product as shown.

9.7 (b)



STUDY UNIT 10

Carbonyl compounds and their derivatives

A ALDEHYDES AND KETONES

- 10.1 Introduction
- 10.2 Structure and nomenclature of ketones and aldehydes
- 10.3 Properties and reactivity of the carbonyl group

B CARBOXYLIC ACIDS

- 10.4 Structure and nomenclature of carboxylic acids
- 10.5 Physical properties
- 10.6 Acidity and reaction of carboxylic acids with base

C CARBOXYLIC ACID DERIVATIVES

- 10.7 Structure of carboxylic acid derivatives
- 10.8 Nomenclature of carboxylic acid derivatives
- 10.9 Physical properties and reactivity
- 10.10 Conclusion

LEARNING OUTCOMES

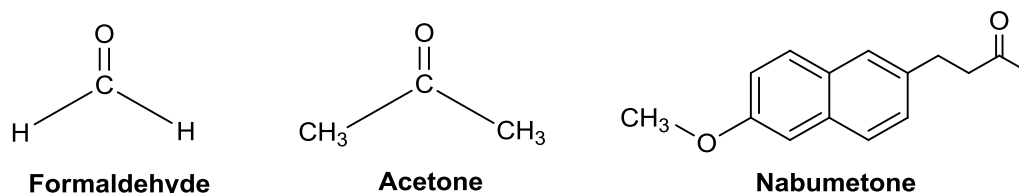
At the end of this study unit, you should be able to:

- describe the generalised structures of aldehydes, ketones and the different carboxyl compounds
- compare the physical properties and chemical reactivity of aldehydes, ketones and the different carboxyl compounds
- correctly apply the IUPAC rules for naming aldehydes, ketones and the different carboxyl compounds
- describe and compare the acidity of carboxylic acids and their conjugate bases

10.1 Introduction (Wade et al sections 18-1 and 18-6)

In study unit 8, we discussed alkenes that contain the carbon-carbon double bond as functional group. In this study unit we introduce the various classes of compounds containing a **carbon-oxygen double bond (C=O)**, called the **carbonyl group**. This includes aldehydes and ketones, carboxylic acids and carboxylic acid derivatives.

Ketones and aldehydes are extremely useful compounds in industrial, medical and pharmaceutical sectors. For example, formalin, a solution of formaldehyde in water, is used to preserve biological samples. Formaldehyde is also used in drug testing and photography. Acetone is extensively used as a solvent and Nabumetone is an anti-inflammatory drug.



Carboxylic acids and its derivatives are widely found in nature, with esters contributing to the sweet smell of fruits and the amide functional group being a fundamental part of the structure of proteins. Many of the carbonyl compounds are of importance in material manufacturing, pharmaceutical, food and cosmetic industries. A considerable amount of carbonyl containing compounds is being used as preservatives; a few examples are shown in Figure 10.1 below:

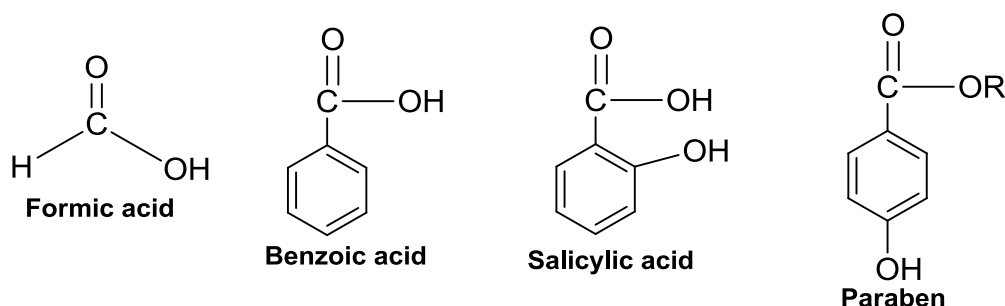


Figure 10.1 Structures of some food and cosmetic preservatives

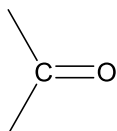
In this study unit, we will discuss the structure, nomenclature and properties of carbonyl-containing compounds, namely, aldehydes and ketones, carboxylic acids and carboxylic acid derivatives (esters, amides, acid halides, acid anhydrides and cyanides).

A. ALDEHYDES AND KETONES

In section A of this study unit, we will describe the structure and bonding of the carbonyl group. We will also focus on the IUPAC nomenclature rules for ketones and aldehydes and compare the properties and reactivity of these compounds.

10.2 Structure and nomenclature of ketones and aldehydes (Wade et al sections 18-1, 18-3 and 18-6)

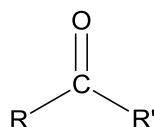
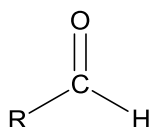
We now introduce a new class of compounds, called ketones and aldehydes, which are the simplest carbonyl-containing compounds. The **carbonyl group** is the **functional group** of aldehydes and ketones.



The distinction between an aldehyde and a ketone is:

- The **carbonyl** group is attached to **one or two hydrogen atoms** in an **aldehyde**.
- In a **ketone**, **two carbon atoms** are attached to the **carbonyl** group.

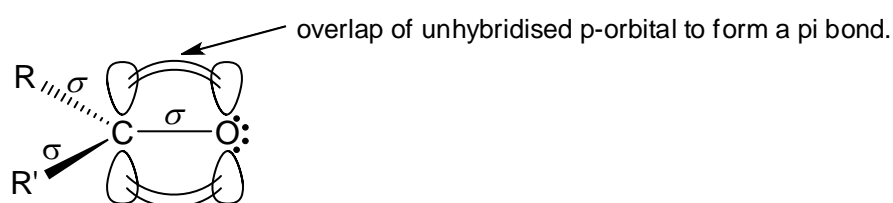
Aldehydes: ketones:



where R = H, alkyl or aryl group where R, R' = alkyl or aryl groups

10.2.1 The structure of the carbonyl group (Wade et al section 18-2)

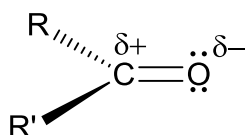
The carbon and oxygen atoms of the double bond are **sp²** hybridised, with carbon bonded by single bonds to oxygen and two other atoms. The three single bonds formed through the overlap of sp² orbitals are the sigma bonds. Each of the remaining **unhybridised 2p** orbitals on **carbon** and **oxygen** contains a **single electron** and has a lobe above and below the sigma bond. These two parallel orbitals overlap sideways to form a **weak pi (π) bond**. There are also **two lone pairs** of electrons on the **oxygen**, and each pair occupies an **sp²** hybrid orbital.



The carbonyl group geometry is **planar (flat)** with bond angles of 120°:

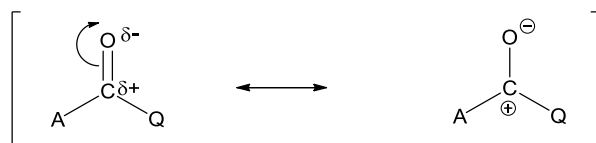


The electrons of the pi (π) bond are weakly held and are concentrated largely around oxygen atoms, because oxygen is more electronegative than carbon. The C=O is **polarised** with a **partial positive** charge on **C** and a **partial negative** charge on **O**.



The **C=O** bond is **shorter** and **stronger** than a **C—O** single bond. However, the **C=O** bond is **more reactive** than a **C—O** bond due to the weak pi (π) bond.

Since the carbonyl group is flat, it is accessible to other reagents. The carbonyl group exists as the following resonance forms:



NB. The actual structure of the carbonyl group is the resonance hybrid of the above two structures.

10.2.2 Nomenclature of ketones and aldehydes (Wade et al section 18-3)

The common names and IUPAC names are generally used for ketones and aldehydes.

IUPAC nomenclature of ketones:

The IUPAC names for ketones involve changing the ending "e" of the corresponding alkane to "one". The IUPAC nomenclature rules, as described in section 3.4.2 in study unit 3, must be applied. The position of the carbonyl group is shown with a **number** that reflects the **position** of the **carbonyl group** in the carbon chain. The numbering of the carbon chain **starts** at the **end closest** to the **carbonyl group**.

The carbonyl group is assigned the number "1" in cyclic ketones. Furthermore, the **carbonyl group** is given **priority** over **C=C** and **C≡C** groups.

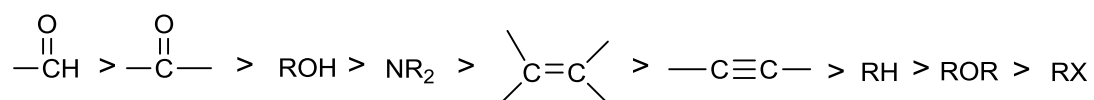
IUPAC nomenclature of aldehydes:

The IUPAC names of aldehydes involve replacing the "e" in the corresponding alkane name to "al". The aldehyde functional group is always **at the end of the chain** and the numbering **starts** at the **C=O** of the aldehyde. Therefore, it is **unnecessary** to indicate the **number** of the aldehyde functional group in the name. When the **aldehyde** group is attached to a **ring**, the suffix **carbaldehyde** is used.

Aldehydes have a **higher priority** than ketones in nomenclature. When a **ketone** and an **aldehyde** functional group are present in **one molecule**, then the **ketone** group is named as "**oxo**".

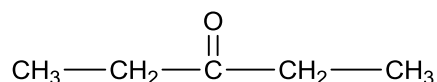
Aldehydes can also be termed "**oxo**" if it is in the same molecule with, for example, a carboxylic acid group (in section B we shall discuss the nomenclature of carboxylic acids).

When deciding on the parent name of compounds containing more than one functional group (covered up to this point in the guide), use the following priority order:



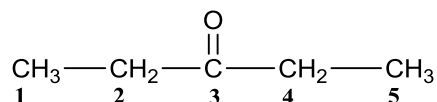
EXAMPLES

1. Let us determine the IUPAC name of the compound shown below:



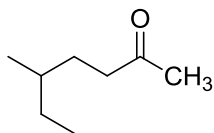
Answer: The IUPAC name is **pentan-3-one**.

Explanation: We number the chain from the end closest to the C=O (either end is the same):



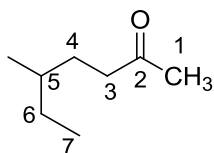
The compound has the longest continuous chain of 5 carbons, hence pentane. The carbonyl group is at C-3 and the ending "e" must change to "-3-one".

2. Provide the correct IUPAC name for the following compound:



Answer: The IUPAC name of the compound is **5-methylheptan-2-one**.

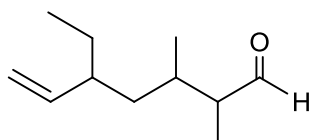
Explanation: Number the longest carbon chain from the end closest to the C=O group:



The longest continuous carbon chain has 7 Cs → heptane. The ketone functional group (C=O) is at C-2; so the ending "e" changes to "one" and the parent name is heptan-2-one. At C-5 there is a methyl group which is indicated as 5-methyl.

3. Draw the structure of **5-ethyl-2,3-dimethylhept-6-enal**.

Answer:

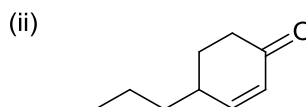
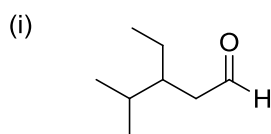


Common names

In many instances, common names are used to refer to ketones and aldehydes instead of the systematic IUPAC names. In general, the common names for ketones consist of the names of the two alkyl groups followed by "ketone". There are certain common names that do not follow this convention. For example, acetone is used instead of dimethyl ketone (common name) or propan-2-one (IUPAC name). Acetophenone is the common name for 1-phenylethan-1-one and benzaldehyde is used instead of 1-phenylmethanal.

ACTIVITY 10.1

- (a) Give the correct structure of 2,5-dimethylhexan-3-one.
 (b) Give the IUPAC name for the following structure:



- (c) Do Problem 18-1 in Wade et al.
-

10.3 Properties and reactivity of the carbonyl group (Wade et al sections 18-4 and 18-11)

The properties and reactivity of ketones and aldehydes are due to the **polarity** of the carbonyl group.

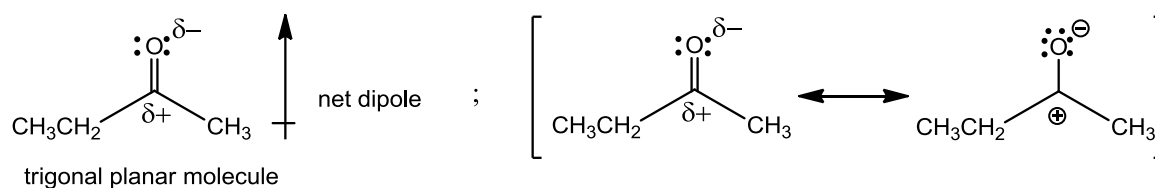
10.3.1 Physical properties of ketones and aldehydes (Wade et al section 18-4)

Boiling point

The **polar nature** of the **carbonyl group** causes these compounds to interact via **dipole-dipole interactions**. Therefore, **ketones and aldehydes** have **higher boiling points** than corresponding **hydrocarbons** and **ethers**. Since there are **no O—H** or **N—H** bonds in **aldehydes** and **ketones**, these compounds **cannot form hydrogen bonds** with **each other**. Therefore, their **boiling points** are **lower** than those of **alcohols** (see study unit 7).

EXAMPLE

2-Butanone molecules exhibit dipole-dipole interaction. 2-Butanone has a C=O bond that has a large dipole moment due to the unequal sharing of the bonding electrons by C and O, which is shown by the resonance structures below. This results in strong dipole-dipole interactions between the 2-butanone molecules.



Pentane, CH₃CH₂CH₂CH₂CH₃, has only non-polar bonds with no dipole-dipole interactions. The attraction between pentane molecules is thus much weaker than that in 2-butanone. Therefore, 2-butanone has a higher boiling point than pentane.

Solubility

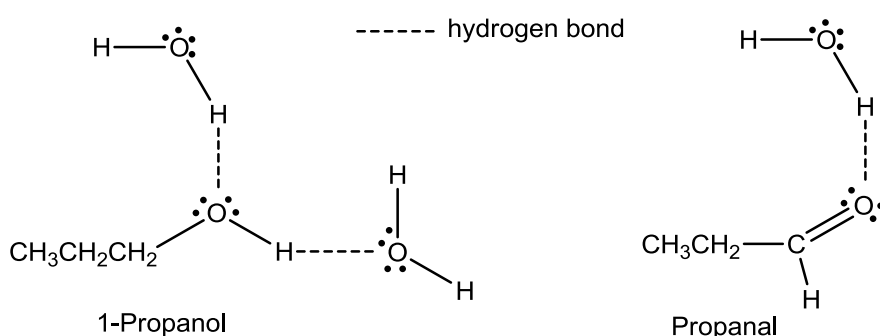
Low molecular weight ketones and aldehydes (up to four carbon atoms) are soluble in water. Due to the presence of the **electronegative oxygen** with **lone pairs of electrons**, **aldehydes** and **ketones** can form **hydrogen bonds** with compounds containing an **O—H** or **N—H** bond. They are thus soluble in, for example, alcohols.

EXAMPLE

Rank the compounds 1-propanol, 1-butene and propanal in order of increasing solubility in water. Explain your answer.

Answer:

The solubility of a compound in water depends on the extent of hydrogen bonding formed by a molecule of the compound and water. Propanal and 1-propanol can form hydrogen bonds with water. As seen below, 1-propanol forms more hydrogen bonds with water than propanal and therefore 1-propanol is more soluble in water.



1-Butene does not have any electronegative atoms that can undergo hydrogen bonding with water and it is therefore insoluble in water. Therefore, in terms of increasing solubility in water: **1-butene < propanal < 1-propanol**.

You are advised to watch the video via the link:

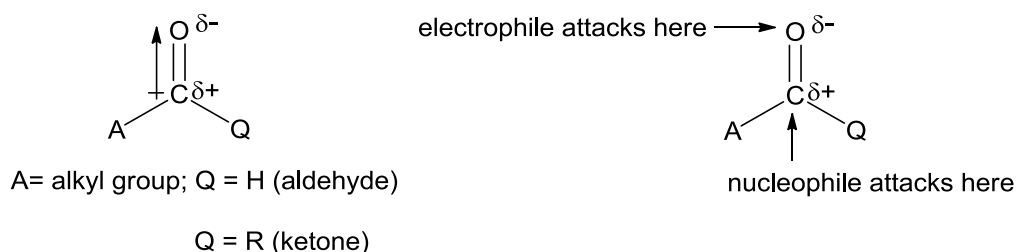
<https://www.khanacademy.org/science/organic-chemistry/aldehydes-ketones/nomenclature-aldehyde-ketone/v/physical-properties-of-aldehydes-and-ketones>

ACTIVITY 10.2

Evaluate the following statement: n-Hexane is more soluble in water than 2-butanone.

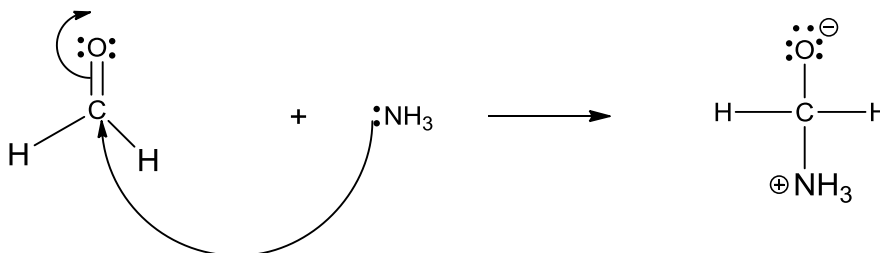
10.3.2 Reactivity of the carbonyl group (Wade et al section 18-11)

The presence of the carbonyl group makes ketones and aldehydes prone to **addition reactions** due to the pi bond. The **positively polarised carbon** atom of a carbonyl group acts as an **electrophile** by **accepting electrons** during a reaction. Since a Lewis acid can **accept an electron pair** from a base, the **positively polarised carbon** atom of a carbonyl group acts as a **Lewis acid**. A **nucleophile attacks** the **partially positive carbon** atom of the carbonyl group. Similarly, atom **electrophiles** will react at the **negatively polarised oxygen**.

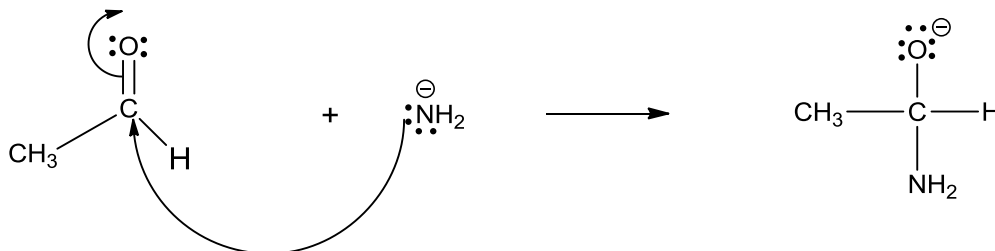


Examples of these processes are:

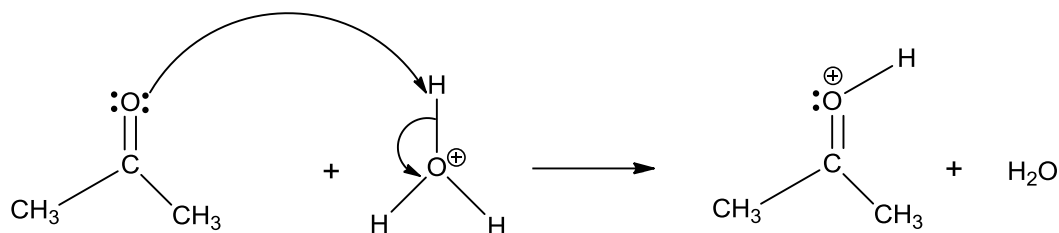
Reaction with a neutral nucleophile:



Reaction with a negatively charged nucleophile:



Reaction with acid:



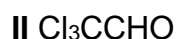
Aldehydes have one electron-releasing alkyl group and this group partially reduces the positive charge at their carbonyl carbon. Ketones have two electron-releasing alkyl groups and these groups reduce the partial positive charge on the carbonyl carbon to a greater extent than the one group in aldehydes. Therefore, ketones are more stable than aldehydes but less reactive towards nucleophiles.

Remember that reactivity at the carbonyl carbon is influenced by the size of the surrounding atoms (steric hindrance) and electronic factors (inductive and/or resonance effect) of the surrounding substituents. Electron-donating groups reduce the electrophilicity of the carbon, whereas electron-withdrawing groups make the carbon more electron poor and therefore more electrophilic for attack by nucleophiles.

When the carbonyl group of a neutral ketone is protonated, the resulting species has a positive charge. The compound becomes more electrophilic and is activated toward nucleophilic attack. Study **step 1 for basic** conditions and **steps 1 and 2 under acidic** conditions in Key Mechanism 18-1 in Wade et al.

EXAMPLE

Rank the following compounds in order of their increasing tendency to undergo nucleophilic addition reaction (i.e., start with the compound that reacts the slowest with a nucleophile):



Explain your answer.

Answer:

Ketones are less reactive than aldehydes because of steric crowding around the carbonyl carbon (C=O). In compound **I**, the ketone is the least reactive. An increase in the positive nature of the carbonyl carbon (C=O) will result in an increase in the reactivity to react with a nucleophile. Compound **III** has an electron-donating ethyl group, which makes the carbonyl carbon less electropositive. Compound **II** has a CCl₃ group, which contains strong electron-withdrawing Cl atoms that make the carbonyl carbon very electron poor. Compound **IV** will therefore be more reactive than compound **III**. The order of increasing tendency to undergo nucleophilic addition reaction is **I < III < II**.

You are encouraged to watch the video via the link:

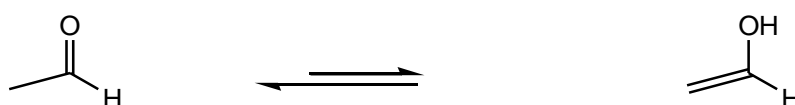
<https://www.khanacademy.org/science/organic-chemistry/aldehydes-ketones/nomenclature-aldehyde-ketone/v/reactivity-of-aldehydes-and-ketones>

ACTIVITY 10.3

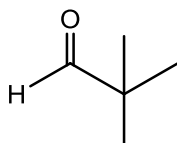
- Draw the resonance structures of propanone in the ground state, indicating bond polarity with partial or full charges.
 - Use curved arrows to show how propanone reacts with a mineral acid catalyst (H⁺) and draw the resonance structures of the protonated propanone.
 - Which of the resonance states (ground or protonated) is more electrophilic (i.e. more reactive)?
-

Keto-enol tautomerism (Wade et al 22-2A)

We introduced keto-enol tautomerism in section 9.6.6 in study unit 9. A ketone or aldehyde can undergo keto-enol tautomerism if the carbon atom adjacent to the carbonyl group has at least one H atom attached to it. In the compound below, there are three Hs attached to the adjacent C (the α-carbon). Hence, it will exhibit keto-enol tautomerism.



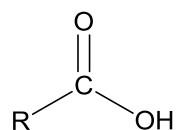
In the compound below, there are *no* Hs attached to the adjacent C (the α -carbon) and it will *not* exhibit keto-enol tautomerism.



B CARBOXYLIC ACIDS

10.4 Structure and nomenclature of carboxylic acids (Wade et al sections 20-1 and 20-2)

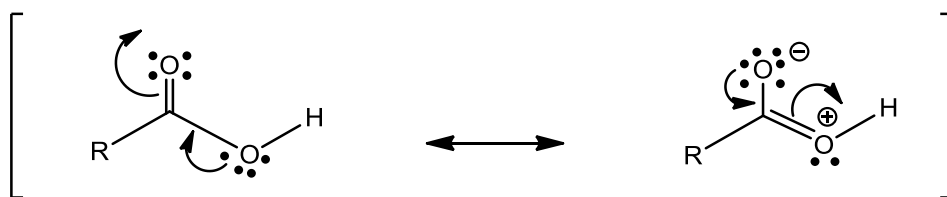
Carboxylic acids are characterised by a hydroxy group (OH) attached to the carbon of the carbonyl group, called the **carboxyl** functional group.



10.4.1 Structure of carboxylic acids (Wade et al section 20-3)

The hybridisation state of the carbonyl group is the same as described for ketones and aldehydes. The carboxyl group is stabilised by resonance delocalisation. When the carbonyl oxygen pulls the pi electrons towards itself, it renders the carbonyl carbon electron deficient and positive.

Oxygen of the hydroxy group donates a pair of electrons to carbon to form a double bond. This interaction renders the hydroxy oxygen positive. It fulfils octet state or noble gas configuration, even though it bears a positive charge. Note that the positive charge is equally (50:50) distributed on the carbonyl carbon and oxygen. The carboxyl group can be described as planar, and resonance delocalisation takes place as follows:



10.4.2 Nomenclature of carboxylic acids (Wade et al section 20-2)

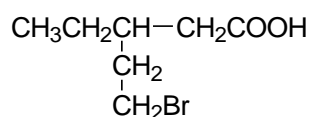
The **carboxylic** group takes **priority over the other functional groups** and is **always** the **parent** functional group. The ending "**e**" in the corresponding alkane is changed to "**oic acid**". The carboxylic acid functional group is **always** at the **end** of the carbon **chain** and its number is *not* indicated in the name.

When **two carboxyl** groups are present in a molecule, is it called a dicarboxylic acid and the suffix "**dioic acid**" is used.

The common names of carboxylic acids and dicarboxylic acids are also widely used. These are described in detail in Wade et al sections 20-2A and 20-2C, respectively.

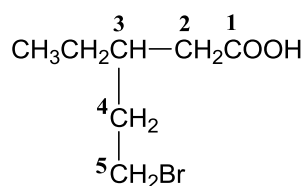
EXAMPLES

(1) Give the correct IUPAC name of the following compound:



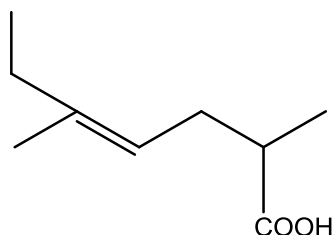
Answer: 5-Bromo-3-ethylpentanoic acid

Explanation: Start numbering from the carboxylic acid functional group and consider the chain that contains the most substituents:



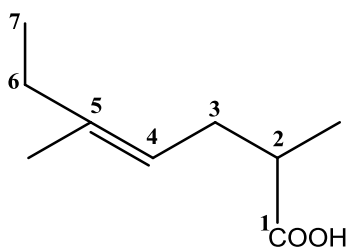
According to the IUPAC convention, the longest continuous carbon chain that contains the most substituents, including the carboxyl group, has 5 Cs → pentane. The compound has a carboxyl group, COOH, at the end of the chain, so the ending "e" changes to "oic acid". On C-3 there is an ethyl group → 3-ethyl and on C-5 there is a Br group → 5-bromo. The substituents must be named in alphabetical order.

(2) Name the following compound according to the IUPAC rules.



Answer: (Z)- 2,5-dimethylhept-4-enoic acid

Explanation: According to the IUPAC convention, start numbering the longest carbon chain from the carboxylic acid functional group and consider the chain that contains the most substituents:



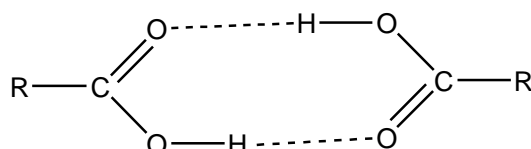
The longest continuous carbon chain has 7 Cs → heptane. The compound has a carboxyl group, COOH, at the end of the chain, so the ending "e" changes to "oic acid". There is a C=C bond in the chain at C-4 → change the "an" to "en" → hept-4-enoic acid. At C-2 and C-5 there are methyl groups → 2,5-dimethyl. Note that since the C=C has a specific arrangement, we should further describe it as E-/ Z- (review the rules for assigning the E-/Z- notation in study unit 9).

ACTIVITY 10.4

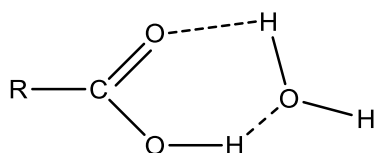
Do Problem 20-2 (a), (b), (d), and (f).

10.5 Physical properties (Wade et al section 20-3)

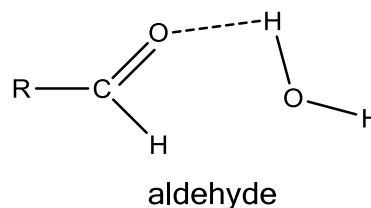
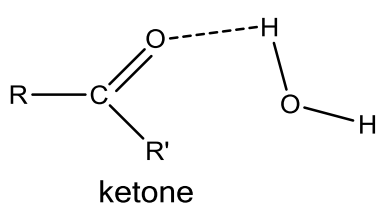
The O—H bond in carboxylic acids is polarised and can easily form strong hydrogen bonds. Carboxylic acids boil at much higher temperatures than ketones or alcohols of similar molecular weights because they form stable hydrogen-bonded dimers. The dimer formation due to hydrogen bonding between two acid molecules:



The presence of the intermolecular hydrogen bonding also contributes to the high melting points of the carboxylic acids and the high solubility in water. Carboxylic acids are **more soluble** in **water** compared to ketones or aldehydes of similar molecular weights, because they form **stable hydrogen bonds** with **water**. Carboxylic acids tend to be **more soluble** in **water** due to **hydrogen-bond formation between the acid** molecules with **water** molecules:



Ketones and aldehydes undergo hydrogen bonding as follows:



Watch the video via the link: <https://www.khanacademy.org/science/organic-chemistry/carboxylic-acids-derivatives>

ACTIVITY 10.5

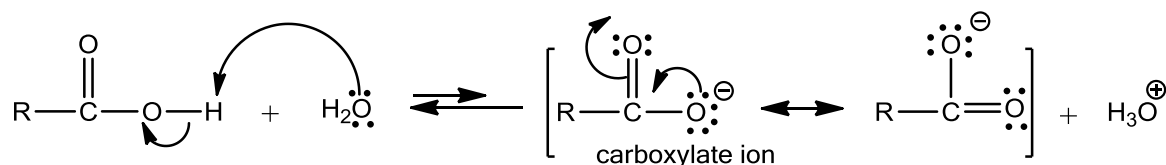
Compare the solubility of propanoic acid with butan-1-ol in water. Explain your answer.

10.6 Acidity and reaction of carboxylic acids with base (Wade et al section 20-4)

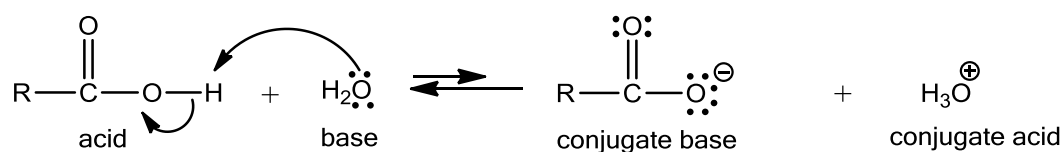
The acidity of carboxylic acids influences their behaviour. In study unit 2, we discussed the various factors that play a role in the acidity of molecules.

Acidity of carboxylic acids

We determine the acidity by evaluating how the acid dissociates in water when it donates a proton. Carboxylic acids may dissociate in water as follows:

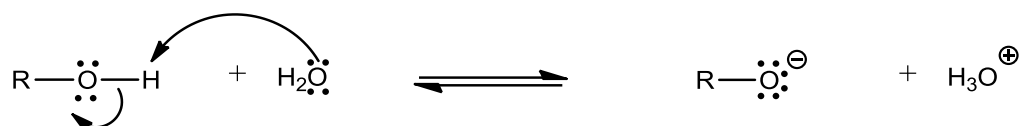


The hydroxy hydrogen is strongly acidic for abstraction by a base to form a carboxylate ion (RCO_2^-). The carboxylate ion is resonance stabilised, with the negative charge distributed equally on the two oxygen atoms. The more resonance structures a charged species can form, the more stable the species. Also, the more stable the conjugate base, the more acidic is the parent acid. The strength of the acid depends on its ability to donate an H^+ . A strong acid will readily donate an H^+ and the forward reaction predominates. In order for that to happen, the conjugate base that forms must be stable. The reaction of the acid with water involves the species as follows:



In the reaction above, the stability of the conjugate base, that is, the carboxylate ion, determines the stability of the carboxylic acid.

The more stable the carboxylate ion that forms, the more acidic the acid. Alcohols dissociate in water to form an alkoxide ion as the conjugate base. This conjugate base is not stabilised by resonance, as shown below:



Carboxylic acids are thus more acidic than alcohols.

10.6.1 Substituent effects on acidity (Wade et al section 20-4B)

If an electron-withdrawing group is attached to the α -carbon of the carboxylic acid, the electron-withdrawing group **withdraws electron density** from the negatively charged **carboxylate ion** by the **inductive effect**. In addition to the delocalisation of the negative charge, this withdrawal of electron density stabilises the carboxylate ion. This substituted carboxylate ion is thus more stabilised than the carboxylate ion from an unsubstituted carboxylic acid and the substituted acid will be the stronger one. Electronegative atoms or groups withdraw electron density from the carboxylate ion and increase the acidity. Similarly, electron-donating groups on the α -carbon of the carboxylic acid destabilise the carboxylate ion, resulting in a weaker acid.

If one increases the number of electron-withdrawing groups on the acid, we increase the acidity. The electron-withdrawing inductive effect of electronegative groups and atoms is transmitted through the sigma bonds. The inductive effect decreases as we increase the number of bonds between the carboxylate ion and the substituent. This means that the stabilising effect of the electron-withdrawing group decreases as the group is further away from the carboxylate ion and the acid becomes weaker.

Consult the Problem-Solving Hint in Wade et al.

EXAMPLES

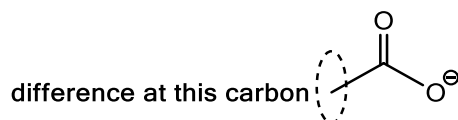
1. Is $\text{CH}_3\text{CH}_2\text{COOH}$ a stronger acid than ClCH_2COOH ?

Answer: We have to compare the stability of the carboxylate ions formed for each acid.

The corresponding carboxylate ions for the given acids are:



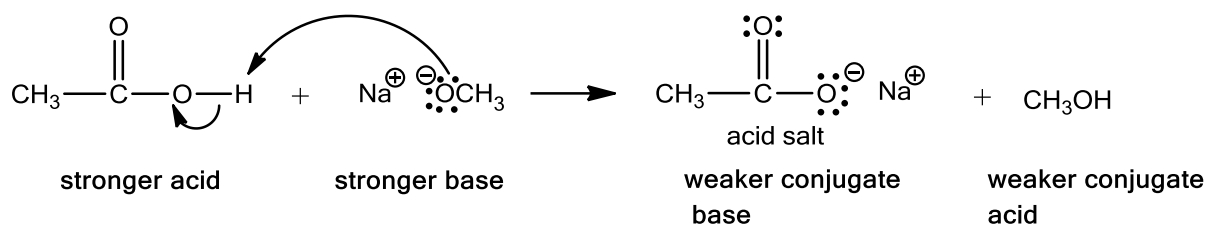
Each carboxylate ion has a substituent attached to it and the substituent that stabilises the negatively charged carboxylate ion, improves the dissociation of the acid and results in a stronger acid. We now have to compare the stability of the carboxylate ions formed in each acid. The difference between the carboxylate ions is at the C attached to the carboxylate group:



We have to consider the electron donation or withdrawal of groups through the sigma bond at that carbon. The carboxylate ion, **2**, has a Cl atom on the C atom adjacent to the COO^- group. The electronegative Cl atom withdraws electron density from the carboxylate ion, thereby stabilising the carboxylate ion and increasing the strength of the acid. In structure **1**, there is a CH_3 group on the C atom adjacent to the COO^- group. The methyl group does not withdraw electron density from the carboxylate ion and has the least stabilising effect on the carboxylate. Therefore $\text{CH}_3\text{CH}_2\text{COOH}$ is a weaker acid than ClCH_2COOH .

2. Compare the acidities of ClCH_2COOH and Cl_2CHCOOH .

Both acids form carboxylate ions that are resonance stabilised. The carboxylate ions formed by the given acids in water are:



The salts of carboxylic acids are more soluble in water than their corresponding acids. Acids such as mineral acids that are stronger than carboxylic acids can convert the salt to the acid.

Watch the relevant video via the link:

https://www.youtube.com/watch?v=4KfheXm7DIU&list=PLqOZ6FD_RQ7nqVjmYjBSZOkjIn_K31ATj

ACTIVITY 10.6

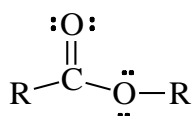
- (a) Rank the following acids in order of increasing acidity:
- (i) $\text{CH}_3\text{CH}_2\text{COOH}$ (ii) $\text{CH}_3\text{OCH}_2\text{COOH}$ (iii) $\text{NO}_2\text{CH}_2\text{COOH}$
- (b) Do Problem 20-3.
-

C CARBOXYLIC ACID DERIVATIVES

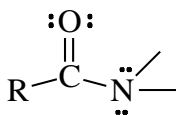
10.7 Structure of carboxylic acid derivatives (Wade et al sections 21-1 and 21-2)

Carboxylic acid derivatives are compounds having an acyl group $\text{R}(\text{C}=\text{O})$ attached to an oxygen, nitrogen or halogen atom. Carboxylic acid derivatives are compounds where the hydroxy group of carboxylic acids is replaced by another group. These compounds can be transformed into carboxylic acids by simple hydrolysis.

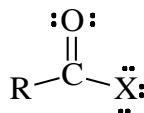
Carboxylic acid derivatives are characterised by a polar carbonyl group attached to an alkoxy group (OR) in esters, an amino group (NH_2 , NHR , NR_2) in amides, a halogen ($\text{X} = \text{Cl}$ or Br) in acid halides or a carboxyl group in acid anhydrides. These compounds have the general structures:



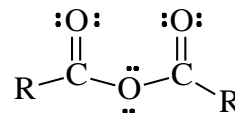
esters



amides



acid halides



acid anhydrides

Except for acid halides, the other acid derivatives are less reactive than aldehydes and ketones. Draw all the resonance structures of the acid derivatives and compare the number of possible resonance hybrids with those of aldehydes and ketones. Note that the **more resonance structures** are possible, the **greater the stability** of these carbonyl derivatives.

10.8 Nomenclature of carboxylic acid derivatives (Wade et al section 21-2)

Esters: The **IUPAC** name of an ester consists of two words, with the **first word** of the name being the stem name of the **alkyl** group **attached** to **oxygen**. The **second word** in the name is the name of the **parent acid**, where the ending "**ic acid**" is replaced by "**ate**".

Amides: **IUPAC** nomenclature rules for an amide are the same as that of acids, where the ending "**oic acid**" is replaced by "**amide**".

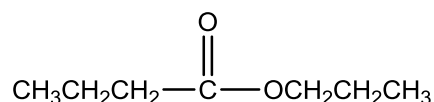
Acid halides: The **IUPAC** name for acid halides is based on the name of the corresponding acid, with the ending "**ic acid**" being replaced by "**yl chloride**" for acid chlorides and "**yl bromide**" for acid bromides.

Acid anhydrides: The **IUPAC** nomenclature rules for an amide is the same as that of acids, with the word "**acid**" being changed to "**anhydride**".

EXAMPLES

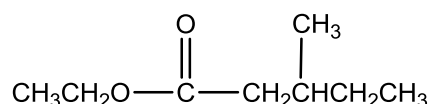
1. Provide the correct structure of propyl butanoate.

Answer:



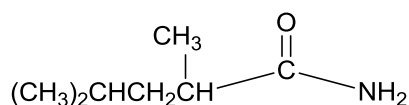
2. Draw the structure of ethyl 3-methylpentanoate.

Answer:



Explanation: The ending "oate" says this is an ester and has a $-(\text{C}=\text{O})$ OR group with $\text{C}=\text{O}$ designated as C-1. The name "pentan" means that the longest carbon chain, which includes the $\text{C}=\text{O}$, has 4 Cs and the rest of the chain has C-C single bonds. The $\text{C}=\text{O}$ is C-1 and "3-methyl" means that there is a CH_3 group on C-3. The "ethyl" indicates that this is an ethyl ester, that is, the OR group is OCH_2CH_3 .

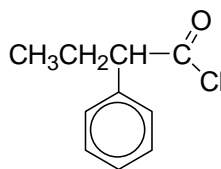
3. Give the IUPAC name for the following compound:



Answer: 2,4-dimethylpentanamide

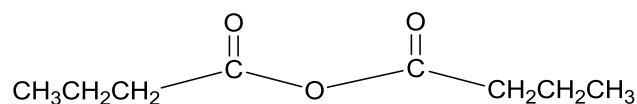
4. Draw the structure of 2-phenylbutanoyl chloride.

Answer:



Explanation: The "butanoyl" means that the longest C chain, which includes the $\text{C}=\text{O}$, has 4 carbons and "chloride" has the $\text{Cl}-\text{C}=\text{O}$ group. "2-Phenyl" means that on C-2 there is a Ph substituent and the numbering starts at the $\text{C}=\text{O}$ carbon atom.

5. Give the IUPAC name for the following compound:



Answer: **Butanoic anhydride**

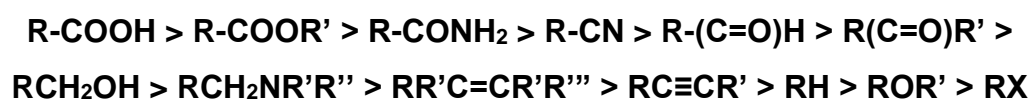
Explanation: The longest carbon chain containing the C=O has 4 Cs and hence the parent name is "butanoic". We simply add anhydride at the end.

ACTIVITY 10.7

Do Problem 21-1.

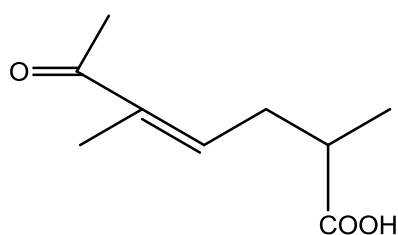
10.8.1 Nomenclature of multifunctional compounds (Wade et al section 21-2F)

When choosing the parent or root name of a compound that contains more than one functional group, we use the following priorities:



EXAMPLE

Provide the IUPAC name for the following compound:



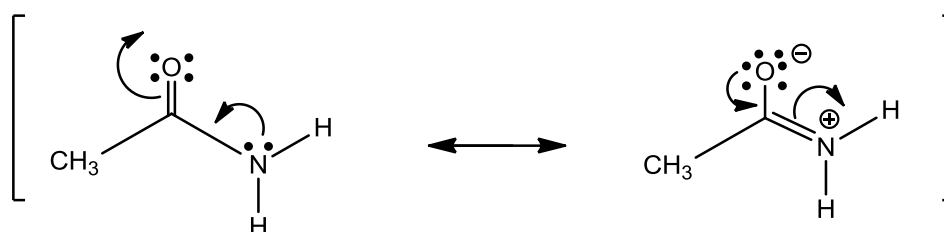
Since the carboxylic acid group has priority over the ketone functional group, the ketone carbonyl group becomes a substituent with the name "oxo". In example 2 in section 10.4.2 we determined the name of the compound without the C=O. We simply include the "oxo" which is on C-6 as "6-oxo". The name is (Z) **2,5-dimethyl-6-oxohept-4-enoic acid**.

10.9 Physical properties and reactivity (Wade et al sections 21-3 and 21-5A)

The same factors that influence the physical properties of all the other classes of compounds also play a role in carboxylic acid derivatives. These factors are **polarity** and the ability to form **hydrogen bonds**. Groups that contain the N—H bond can undergo hydrogen bonding. Therefore, the boiling points of amides containing at least one N—H bond will be higher than the boiling points of the other carboxylic acid derivatives. Since dipolar attractions exist in tertiary amides, their boiling points are also relatively high. Wade et al describes the solubility of the carboxylic acid derivatives in section 21-3B.

Reactivity

Amides are less basic than amines because the carbonyl group withdraws electrons by resonance, as follows:



In the reaction of an amide with a strong acid, protonation takes place at the oxygen instead of the nitrogen atom because, in the resonance structure, the O has a partial negative charge and N a partial positive charge. Electrons on O are therefore available for donation to the proton.

If we compare amides to esters, the **nitrogen** is **less electronegative** than **oxygen** and **donates** an **electron pair more readily** than **oxygen**. **Resonance stabilisation** occurs more in amides than in esters. This makes amides more stable and less reactive than esters. This resonance delocalisation also makes the carbonyl carbon in amides unreactive towards a nucleophilic attack. The other carbonyl groups are more susceptible towards attack by a nucleophile similar to ketones and aldehydes. You only need to know the electronic effects in the reaction with a nucleophile or electrophile.

Study Key Mechanism 21-1 Step 1 in Wade et al.

You are encouraged to watch the video via the link:

<https://www.khanacademy.org/science/organic-chemistry/carboxylic-acids-derivatives/formation-carboxylic-acid-derivatives-sal/v/relative-stability-of-amides-esters-anhydrides-and-acyl-chlorides>

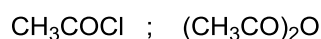
ACTIVITY 10.8

(a) Which of the following are strongly hydrogen bonded in the liquid phase?

- (1) acid chlorides (2) tertiary amides
(3) nitriles (4) secondary amides

Explain your answer.

(b) Compare the reactivity of the following compounds to nucleophilic attack and explain your answer:



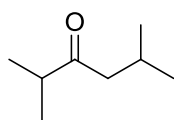
10.10 Conclusion

In this study unit, we described the electronic structure and nomenclature of ketones and aldehydes, carboxylic acids, esters, acid halides, amides and anhydrides. We further focused on their physical properties and chemical reactivity.

The acidity of carboxylic acids and their conjugate bases and keto-enol tautomerism received attention.

ANSWERS TO SELECTED ACTIVITIES

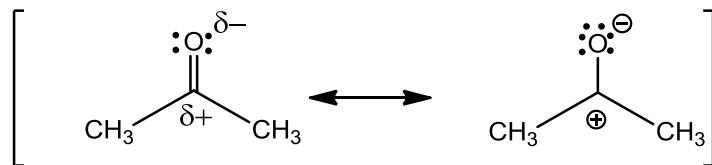
10.1 (a)



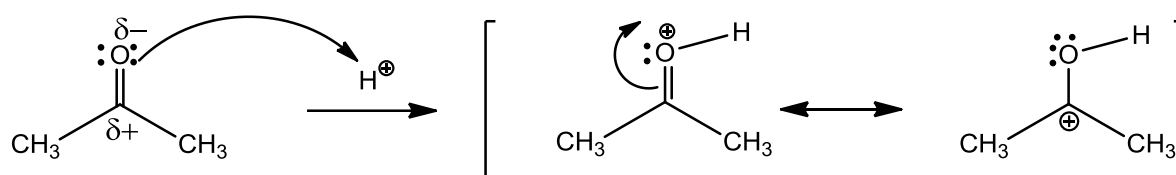
(b) (i) 3-ethyl-4-methylpentanal (ii) 4-propylcyclohex-2-enone

10.2 *n*-Hexane is less soluble in water than 2-butanone

10.3 (a)



(b)



(c) The protonated state is more electrophilic.

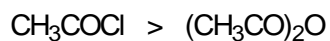
10.5 Propanoic acid is more soluble than butan-1-ol in water.

10.6 (a) (ii) < (i) < (iii)

10.7 21-1 (c) methyl 2-phenylpropanoate (e) *N*-benzyl ethanamide
(h) 2,2-dichloroethanoyl chloride

10.8 (a) (4) secondary amides

(b)



END OF STUDY GUIDE