

**C10K/CHEM1902**  
**Organic Chemistry Module**  
**11 lectures**  
**Functional Group Chemistry**

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**Books**

***Solomons & Fryhle*, ORGANIC CHEMISTRY, Wiley.**

***Sykes*, A PRIMER TO MECHANISM IN ORGANIC CHEMISTRY, Longman.**

**C10K/CHEM1902**  
**Organic Chemistry Module**  
**Functional Group Chemistry**  
**Handouts**

1. Course outline, with the pertinent sections of the latest edition of the textbook (Solomons) given. Any edition of Solomons can be used; however, if you use an older edition the sections indicated for each topic in the current course outline may be different. Other organic chemistry textbooks of a level similar to that of Solomons can also be used.
2. Course objectives.

# Functional Group Chemistry

## Introduction to Functional Groups

C10J covered the structure, properties, synthesis and reactions of ALKANES, ALKENES and ALKYNES. These are all hydrocarbon compounds.

In ALKANES, the bonds are  $sp^3$ - $sp^3$  carbon-carbon bonds and  $sp^3$ -s carbon-hydrogen bonds.

ALKANES are relatively unreactive.

ALKENES and ALKYNES are much more chemically reactive than alkanes.

# Functional Group Chemistry

## Introduction to Functional Groups

The reactivity of ALKENES and ALKYNES is due to the  $C=C$  and  $C\equiv C$  bonds in these compounds.

The  $C=C$  and  $C\equiv C$  groups, which are the main sites of chemical reactivity in alkenes and alkynes, are called FUNCTIONAL GROUPS.

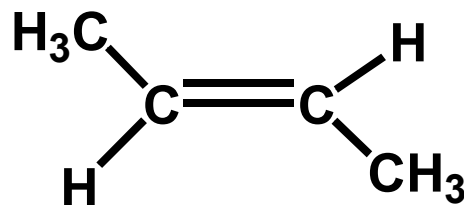
# Introduction to Functional Groups

*What is a functional group?*

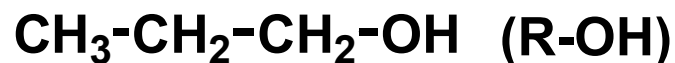
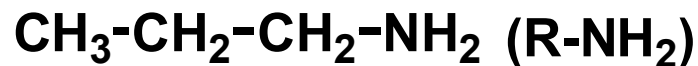
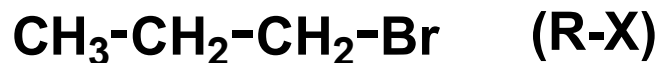
*A site of chemical reactivity in a molecule.*

Examples of functional groups:

pi bonds in alkenes;



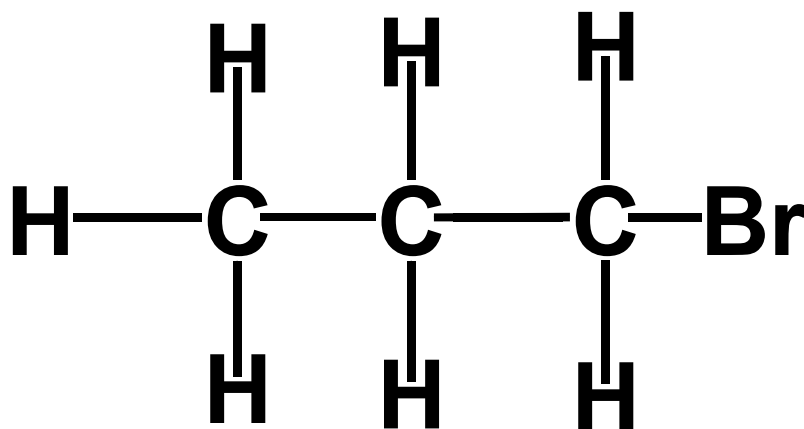
electronegative atoms in alkyl halides, amines and alcohols.



# **CONDENSED FORMULAE**

**YOU MUST BECOME FAMILIAR WITH THE USE OF CONDENSED FORMULAE, FOR EXAMPLE:**

**CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br or CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br is**



# **ALKYL HALIDES**

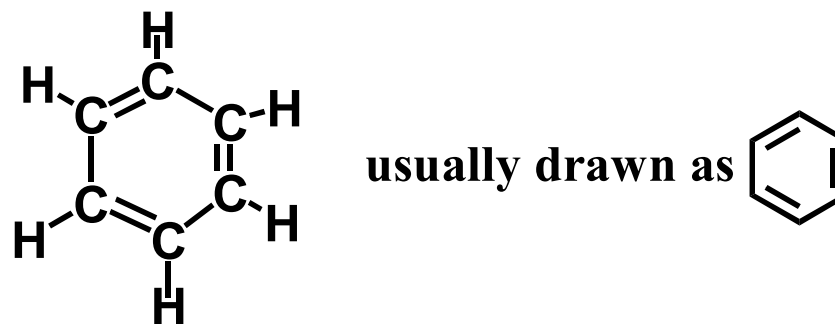
**COMPOUNDS WHICH CONTAIN ONLY CARBON, HYDROGEN AND A HALOGEN, X (F, Cl, Br, I) CAN BE ALKYL HALIDES,**



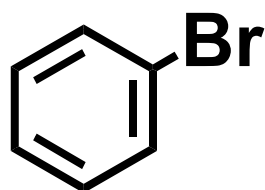
**OR ARYL HALIDES, Ar-X.**

# ARYL HALIDES (a digression)

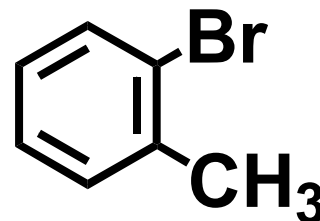
“Ar” is the generic designation for an aromatic ring, with or without substituents. Benzene is an aromatic compound.



Ar-Br could be



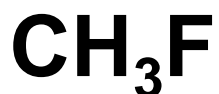
or



or any other compound with bromine attached to an aromatic ring.

# **ALKYL HALIDES** - **Nomenclature**

In the IUPAC system, an alkyl halide is named by attaching a **halo** prefix to the name of the **hydrocarbon**. All of the other standard rules of chemical nomenclature apply.



**fluoromethane**

(methyl fluoride)

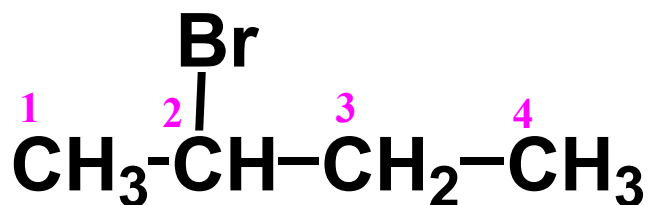


**chloroethane**

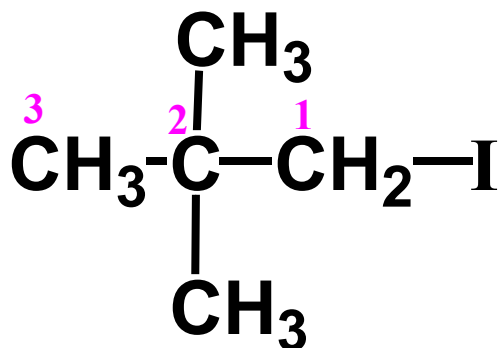
(ethyl chloride)

# ALKYL HALIDES - Nomenclature

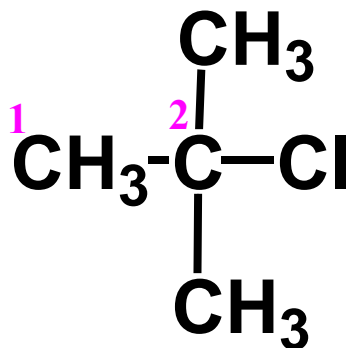
Trivially, the name of the alkyl group is given followed by the name of the halide; you are not required to know trivial names.



**2-bromobutane**  
(butyl bromide)



**1-iodo-2,2-dimethylpropane**  
(neopentyl iodide)



**2-chloro-2-methylpropane**  
(*t*-butyl chloride)

# **ALKYL HALIDES - Classification**

Alkyl halides are classified as:

(a) methyl (**CH<sub>3</sub>F**);

(b) primary (1<sup>o</sup>, **CH<sub>3</sub>CH<sub>2</sub>-Cl**);

(c) secondary, 2<sup>o</sup> 
$$\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3\text{-CH-CH}_2\text{-CH}_3 \end{array}$$

(d) tertiary 3<sup>o</sup> 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{-C-Cl} \\ | \\ \text{CH}_3 \end{array}$$

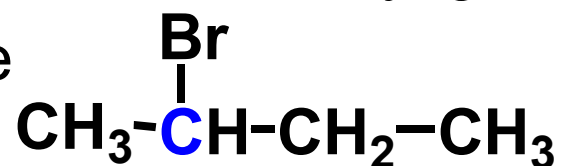
## ALKYL HALIDES - Classification

The carbon attached to the halogen is designated the **HEAD CARBON**.

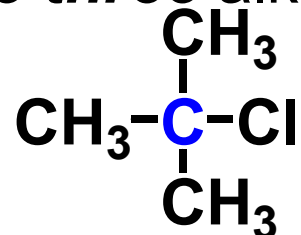
If the head carbon is attached to a *methyl* group, we have a methyl halide (e.g.  $\text{CH}_3\text{F}$ );

If the *head carbon* is attached to *one* alkyl group, the alkyl halide is primary ( $1^\circ$ ,  $\text{CH}_3\text{CH}_2\text{-Cl}$ );

If the *head carbon* is attached to *two* alkyl groups, we have a secondary ( $2^\circ$ ) alkyl halide



If the *head carbon* is attached to *three* alkyl groups, we have a tertiary  $3^\circ$  alkyl halide

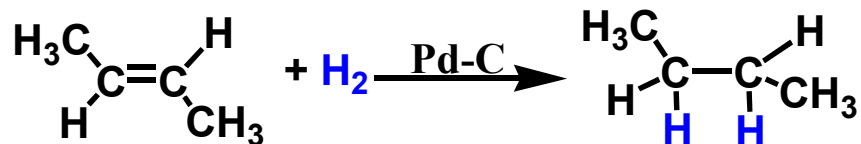


# REACTIONS OF ORGANIC COMPOUNDS

Before we discuss the *reactions of alkyl halides*, let us review what you *should* know about reactions of organic compounds.

In organic chemistry you will encounter *three types of reactions*.

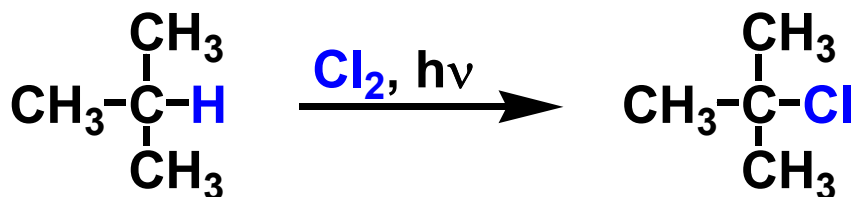
1. **ADDITION REACTIONS** in which the elements of one compound or molecule are *added* to another compound or molecule. A familiar example is the addition of H<sub>2</sub> to an alkene in the presence of a catalyst.



# REACTIONS OF ORGANIC COMPOUNDS

2. **SUBSTITUTION REACTIONS** in which an atom or group of atoms is *replaced* by a different atom or group of atoms.

In this familiar example, chlorine replaces hydrogen via a radical mechanism.



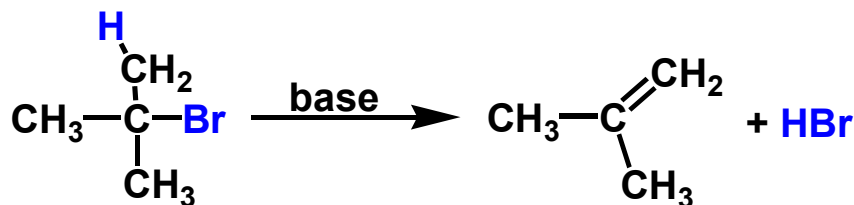
# REACTIONS OF ORGANIC COMPOUNDS

## 3. ELIMINATION REACTIONS

Elements of a simple compound are removed, or *eliminated* from the compound undergoing reaction (sometimes referred to as the *substrate*).

Small molecules expelled in elimination reactions include  $\text{H}_2\text{O}$ ,  $\text{HX}$ ,  $\text{HCN}$  and  $\text{NH}_3$ .

An elimination reaction results in the formation of a **multiple bond or a ring** in the product. An example of an elimination reaction from C10J is the elimination of  $\text{HBr}$  from 2-bromo-2-methylpropane, under the influence of base, to form 2-methylpropene.



## **REACTIONS OF ORGANIC COMPOUNDS**

The organic reactions which you will encounter in this course proceed via *either ionic or radical* mechanisms.

If a reaction goes via an ionic mechanism, the intermediates or transition states formed during the course of the reaction are either ions or very polar species.

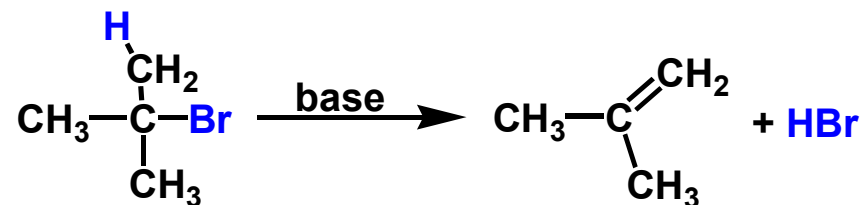
For reactions going via radical mechanisms the intermediates are free radicals, species which contain unpaired electrons.

# REACTIONS OF ALKYL HALIDES

Alkyl halides (R-X) undergo two of the three types of reactions just mentioned: **substitution** reactions and **elimination** reactions.

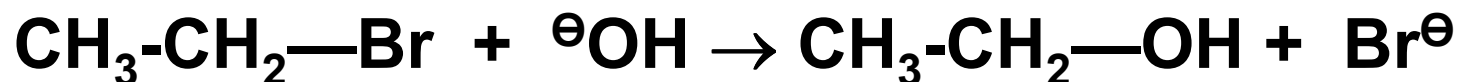
In a **substitution** reaction, the X group in R-X is **replaced** by a different group, e.g.  $\text{R-X} \rightarrow \text{R-OH} + \text{X}^\ominus$

In an **elimination** reaction, the elements of H-X are **eliminated** from R-X; the product is very often an alkene.

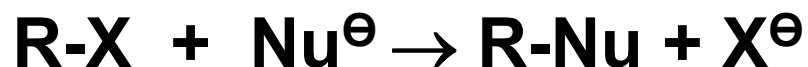




## ALKYL HALIDES – Substitution reactions



The general reaction is:



These are ionic reactions.

There are two possible ionic mechanisms for nucleophilic substitution, **S<sub>N</sub>1** and **S<sub>N</sub>2**.

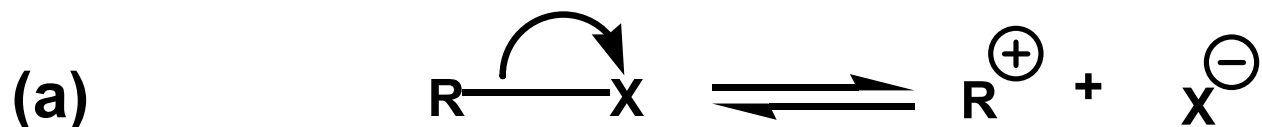
**S** – substitution; **N** – nucleophilic;

**1** – unimolecular (the rate determining, *r.d.s.*, step entails one molecule);

**2** – bimolecular (the rate determining step entails two species).

# ALKYL HALIDES

## *The unimolecular (S<sub>N</sub>1) reaction*



In the first step, R-X dissociates, forming a carbocation, R<sup>⊕</sup>, and the leaving group X<sup>⊖</sup>.

This is a slow, rate determining step (r.d.s.) and entails only one species, R-X.



In the second step the carbocation and the nucleophile combine. This occurs rapidly.

The overall reaction is  $\text{R-X} + \text{Nu}^{\ominus} \rightarrow \text{R-Nu} + \text{X}^{\ominus}$

The rate of the reaction =  $k[\text{R-X}]$

# ↪ ↪ **CURLY ARROWS** ↪ ↪

A curly, or curved double-headed arrow, in the context of a reaction mechanism, **shows movement of a pair of electrons.**

Covalent bonds consist of paired electrons, therefore curly arrows illustrate **breakage and/or formation of covalent bonds.**

Curly arrows can begin only in areas of **high electron density.**

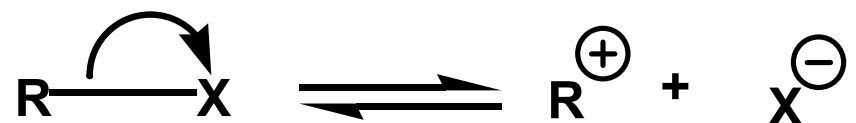
These are

- in the middle of covalent bonds  $\text{R}-\text{X} \rightleftharpoons \text{R}^{\oplus} + \text{X}^{\ominus}$
- at negative charges  $\text{R}^{\oplus} + \ominus\text{Nu} \rightarrow \text{R}-\text{Nu}$
- at lone pairs of electrons  
(examples later in the course)

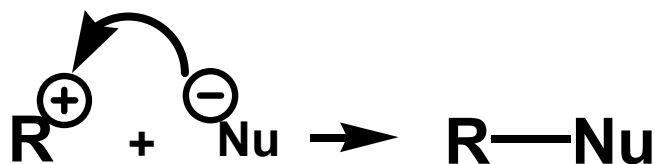
## ↪ ↪ **CURLY ARROWS** ↪ ↪

You will have seen that curly arrows can end at the following positions, with the results shown.

- at an uncharged atom or group, resulting in bond breakage and formation of a negative charge on the atom or group



- on a positively charged atom or group, resulting in bond formation and quenching of a positive charge

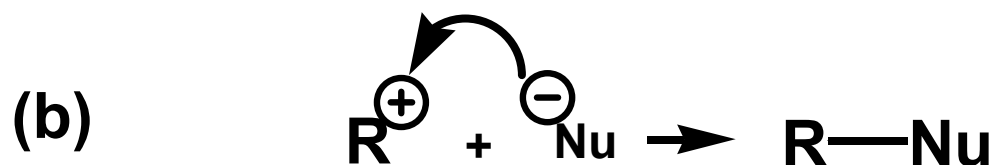


# ALKYL HALIDES

## *The unimolecular (S<sub>N</sub>1) reaction*



In the first step, R-X dissociates, forming a carbocation, R<sup>⊕</sup>, and the leaving group X<sup>⊖</sup>. This is a slow, rate determining step (r.d.s.) and entails only one species, R-X.

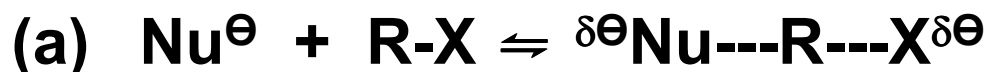


In the second step the carbocation and the nucleophile combine. This occurs rapidly.

The overall reaction is  $R-X + Nu^{\ominus} \rightarrow R-Nu + X^{\ominus}$

The rate of the reaction =  $k[R-X]$

## **ALKYL HALIDES: The bimolecular (S<sub>N</sub>2) reaction**



The nucleophile and the alkyl halide combine to form a pentacoordinate transition state. This is the slow rate determining step (r.d.s); it entails two species, R-X and Nu<sup>⊖</sup>. The dotted lines indicate partially formed or partially broken covalent bonds.



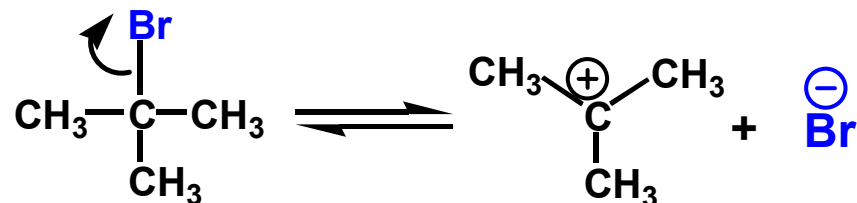
The pentacoordinate transition state dissociates to form the product, Nu-R, and the halide ion (the leaving group).

**The rate of the reaction =  $k[\text{R-X}][\text{Nu}^{\ominus}]$**

The rate is dependent of the concentration of two species; higher concentrations increase the frequency of molecular collisions.

## ALKYL HALIDES: S<sub>N</sub>1 reactions in more detail

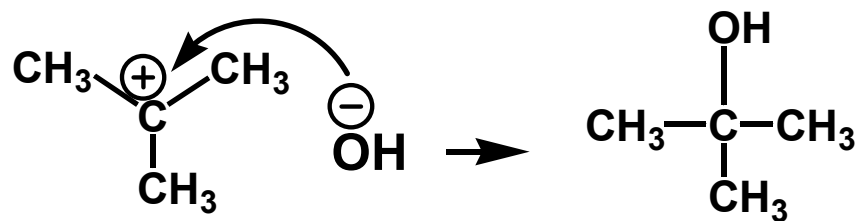
- (a) 2-bromo-2-methylpropane, a 3° alkyl halide dissociates, in a slow r.d.s. to a 3° carbocation and Br<sup>⊖</sup>.



The positively charged carbon in a carbocation is sp<sup>2</sup> hybridized and **carbocations have trigonal geometry**.

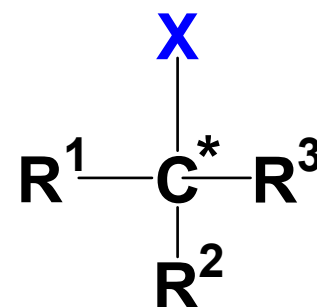
**This is a very important point.**

- (b) A nucleophile, <sup>⊖</sup>OH, adds to the carbocation to give the product, 2-methylpropanol. This is a fast process.

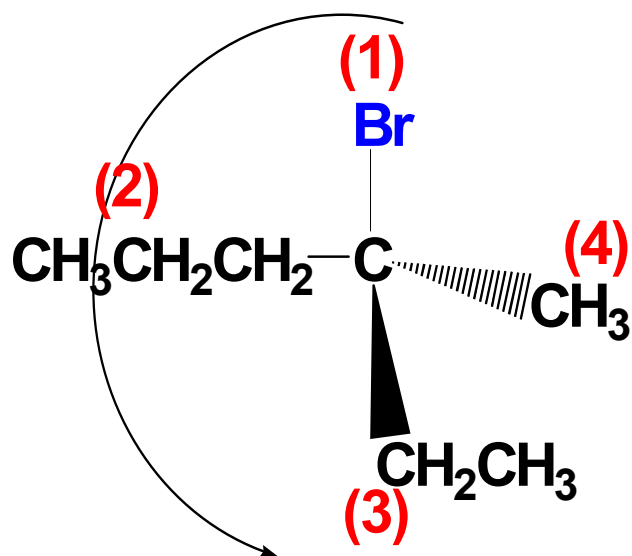


# The Stereochemistry of $S_N1$ Reactions

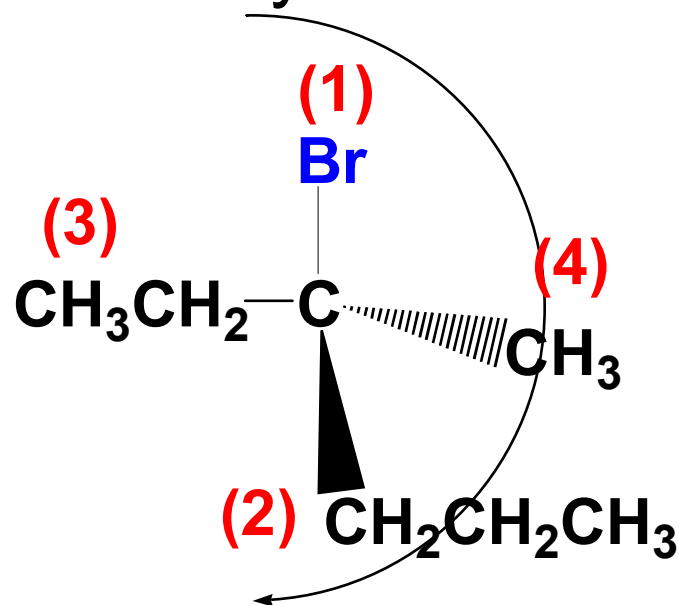
A 3° alkyl halide with *three different alkyl groups* attached to the head carbon is chiral.



There are two enantiomers of such a compound, e.g. 3-bromo-3-methylhexane.

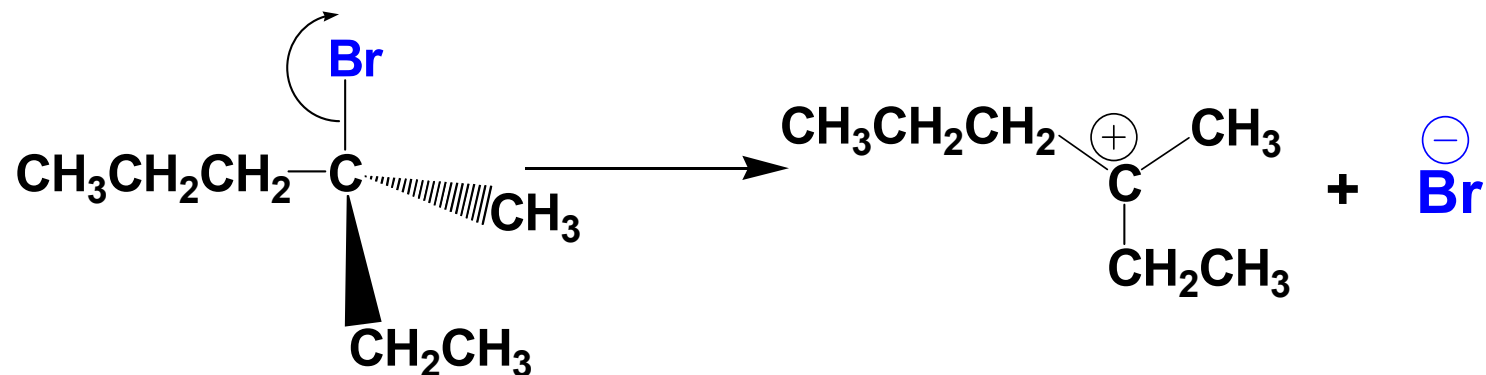


(S)-enantiomer



(R)-enantiomer

# The Stereochemistry of $S_N1$ Reactions



*(S)*-enantiomer

