
CHAPTER

10

ALKYL HALIDES

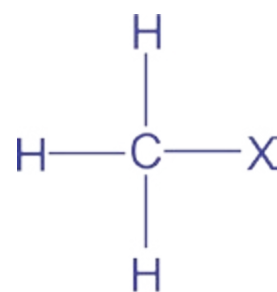
Animation 10.1: Alkyl Halides reaction
Source & Credit: chemwiki

IN THIS CHAPTER YOU WILL LEARN:

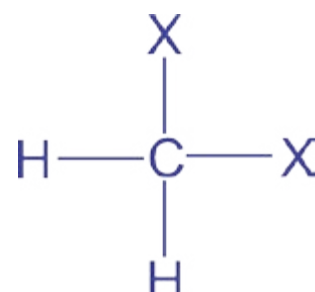
1. How to name an alkyl halide and to classify it into primary, secondary and tertiary alkyl halides.
2. Simple ways of generating alkyl halides.
3. The reason why C-X bond in chemistry is one of the most reactive type.
4. The general mechanistic details of nucleophilic substitution and elimination reactions.
5. The preparation of Grignard's reagent, the reactivity of C-Mg bond and its synthetic applications in organic chemistry.

10.1 INTRODUCTION

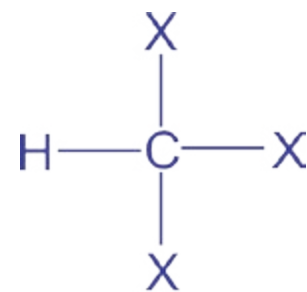
Halogen derivatives of alkanes are called haloalkanes. They may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule.



Monohaloalkane



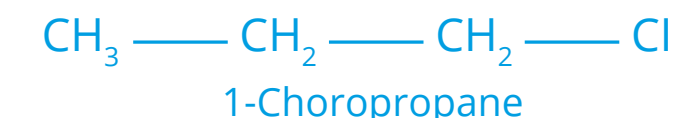
Dihaloalkane



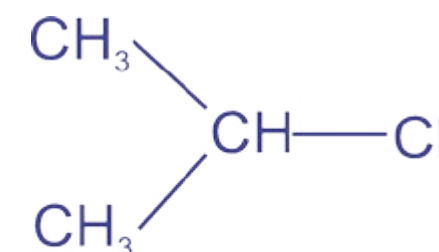
Trihaloalkane

Among these, monohaloalkanes are also called Alkyl Halides. Their general formula is $\text{R}-\text{X}$, where R may be methyl, ethyl, propyl, etc. and X represents halogen atoms (F, Cl, Br, I). Mono haloalkanes or alkyl halides are further classified into primary, secondary and tertiary alkyl halides depending upon the type of carbon atom bearing the halogen atom.

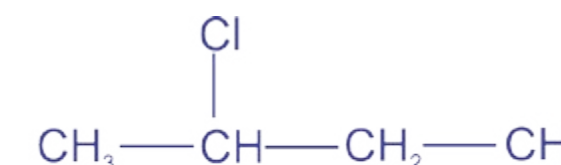
In a primary alkyl halide halogen atom is attached with a carbon which is further attached to one or no carbon atom e.g.,



Secondary alkyl halides are those in which halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly, e.g., secondary carbon atom.

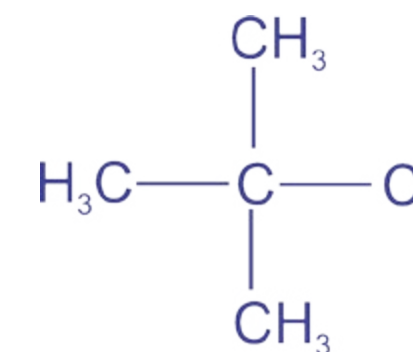


2-Chloropropane



2-Chlorobutane

In tertiary alkyl halides halogen atom is attached to a carbon which is further attached to three carbon atoms directly.

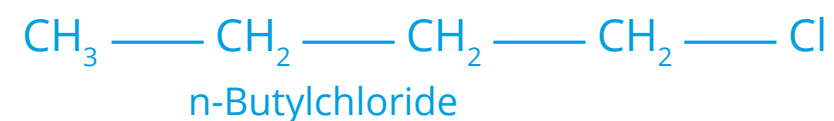
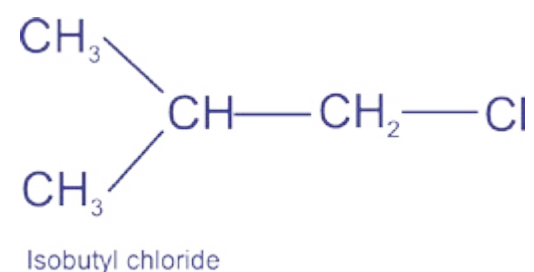
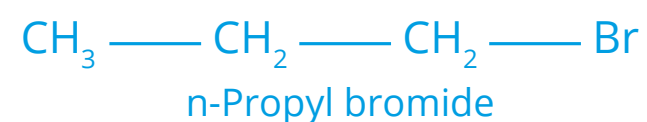
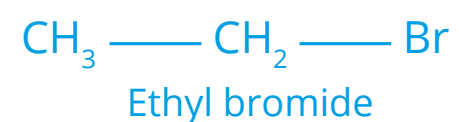
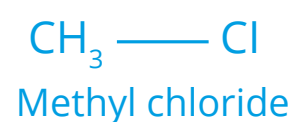


2-Chloro-2-methylpropane

10.2 NOMENCLATURE OF ALKYL HALIDES

COMMON NAMES

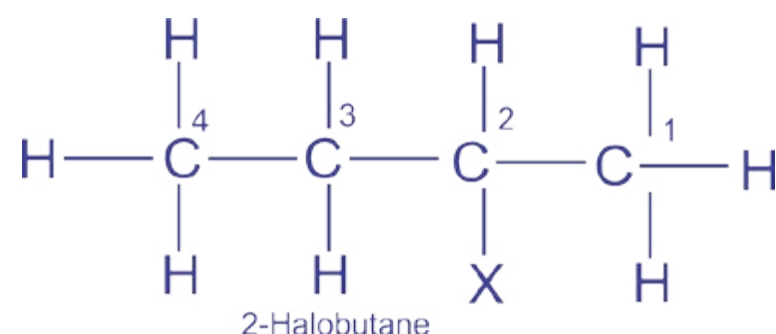
Alkyl halides (monohaloalkanes) are named according to the nature of the alkyl group to which halogen atom is attached. For example,



IUPAC Nomenclature

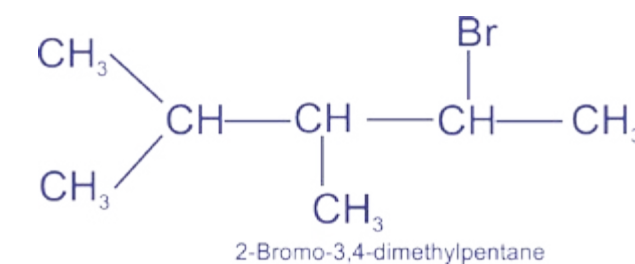
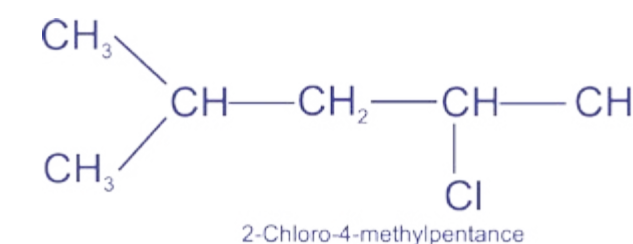
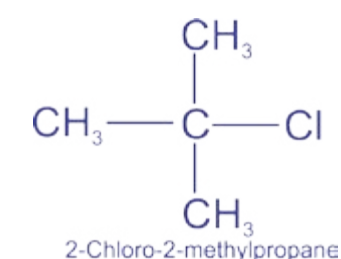
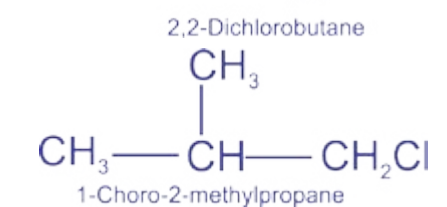
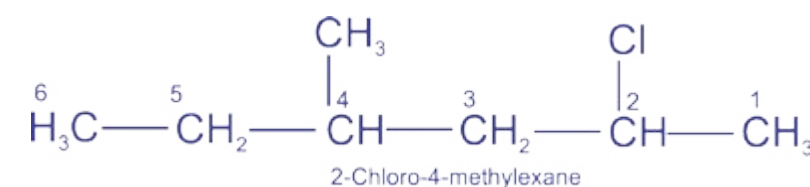
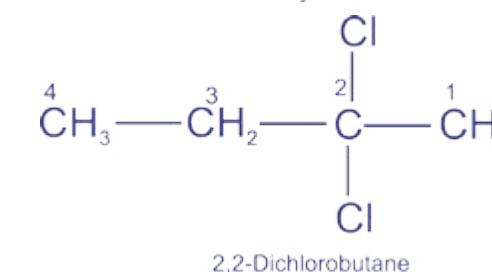
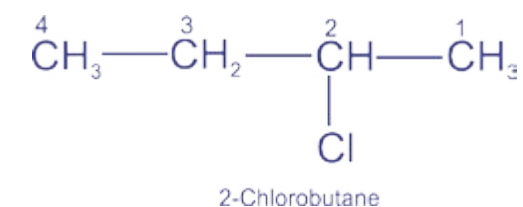
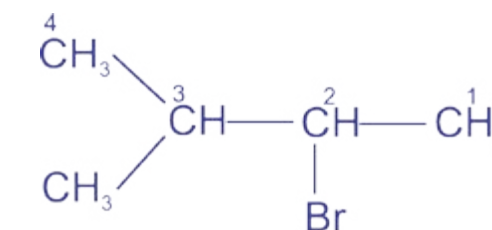
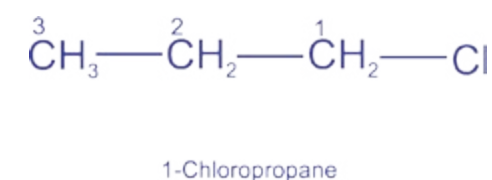
The systematic names given to alkyl halides follow the underlying rules.

1. Select the longest continuous carbon chain and consider the compound to have been derived from this structure.
2. Number the carbon atoms in the chain so that the carbon atom bearing the functional group (F, Cl, Br, I) gets the lowest possible number, e.g.,



3. If the same alkyl substituent occurs more than once on the chain, the prefix di, tri and so on are used before the name of the alkyl group.
4. The positions of the substituents are indicated by the appropriate numbers separated by commas. If the same substituent occurs twice or more on the same carbon atom the number is repeated.

Examples which follow the above mentioned rules:



10.3 METHODS OF PREPARATION OF ALKYL HALIDES

Alkyl halides can be prepared by the halogenation of alkanes and by the addition of halogen acids to alkenes. These methods have already been discussed in the previous chapters. The best method for the preparation of alkyl halides is from alcohols.

1. From Alcohols**(a)** Reaction of alcohols with halogen acids.

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of ZnCl_2 which acts as a catalyst.

**(b)** Alcohols also react with thionyl chloride in pyridine as a solvent to give alkyl chlorides. This method is especially useful since the by-products (HCl , SO_2) are gases, which escape leaving behind the pure product.**(c)** Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace —OH group by a halo group.**2.** An excellent method for the preparation of simple alkyl iodide is the treatment of alkyl chloride or alkyl bromide with sodium iodide. This method is particularly useful because alkyl iodides cannot be prepared by the direct iodination of alkanes.**10.4 REACTIVITY OF ALKYL HALIDES**

An alkyl halide molecule (R—X) consists of two parts, an alkyl group with a partial positive charge on the carbon atom attached to halogen atom and the halide atom with a partial negative charge.

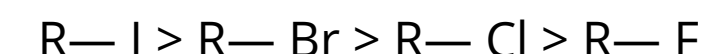
There are two main factors which govern the reactivity of R—X bond. These are:

- i) C—X Bond energy
- ii) C—X Bond polarity

Bond Energy

The following table shows the bond energies of C—X bonds in alkyl halides.

The strength of the bonds show that iodo compound (with the weakest bonds) would be the most reactive one while fluoro compound will be the least reactive i.e., the order of reactivity of alkyl halides should be

**Bond Polarity**

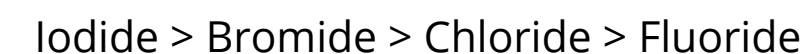
Electronegativities of halogen, carbon and hydrogen atoms present in alkyl halides are shown in the table.

The greatest electronegativity difference exists between carbon and fluorine atoms in alkyl fluorides.

If an electrophile is the attacking reagent then this difference suggests that alkyl fluorides would be the most reactive one. On the same lines, alkyl iodides should be the least reactive alkyl halides.

In the light of the above discussion it is clear that the two factors mentioned above predict different types of behaviour about the reactivity of alkyl halides.

Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of alkyl halides. So the overall order of reactivity of alkyl halides for a particular alkyl group is:



In fact the C—F bond is so strong that alkyl fluorides do not react under ordinary conditions.

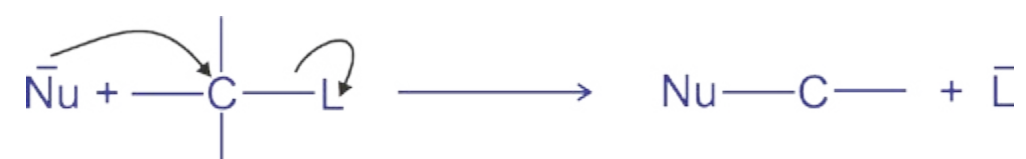
10.5 REACTIONS OF ALKYL HALIDES

The reactions of alkyl halides fall into two categories.

1. Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or S_N reactions).
2. Those which involve the removal of HX from the molecule (elimination, or E reactions).

10.5.1 Nucleophilic Substitution Reactions

Before discussing specifically the nucleophilic substitution reactions (S_N) of alkyl halides, let us look at the nucleophilic reaction in general. The overall process describing an S_N reaction is shown as follows:



In this equation the incoming group Nu is a nucleophile. Nucleophile means nucleus loving. It has an unshared electron pair available for bonding and in most cases it is basic in character. It may be negatively charged or neutral.

Examples of Nucleophiles

HO ⁻	Hydroxide ion	Cl ⁻	Chloride ion
C ₂ H ₅ O ⁻	Ethoxide ion	Br ⁻	Bromide ion
HS ⁻	Hydrogen sulphide ion	$\ddot{\text{N}}\text{H}_3$	Ammonia
SCN ⁻	Thiocyanate ion	CN ⁻	Cyanide ion
H ₂ O:	Water	I ⁻	Iodide ion
NH ₂ ⁻	Amino group		

Electrophile

It is a species which attracts electrons (electron loving). The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center. An electrophile may be neutral or positively charged.

Animation 10.3: Electrophilic addition
Source & Credit: johnwiley

Leaving Group

L is also a nucleophile. It is called leaving group because it departs with an unshared pair of electrons. If we wish a S_N reaction to proceed in the forward direction the incoming nucleophile must be stronger than the departing one. Cl⁻, Br⁻, I⁻, HSO₄⁻ are good leaving groups. Poor leaving groups are OH⁻, OR⁻ and NH₂⁻. Iodide ion is a good nucleophile as well as a good leaving group.

Substrate Molecule

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

10.5.2 Mechanism of Nucleophilic Substitution Reactions

Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

1. Nucleophilic Substitution Bimolecular (S_N2)
2. Nucleophilic Substitution Unimolecular (S_N1)

Nucleophilic substitution reactions on alkyl halides involve two main processes, the breakage of C — X bond and the formation of C — Nu bond. The mechanism of the nucleophilic substitution reactions depends upon the timing of these two processes.

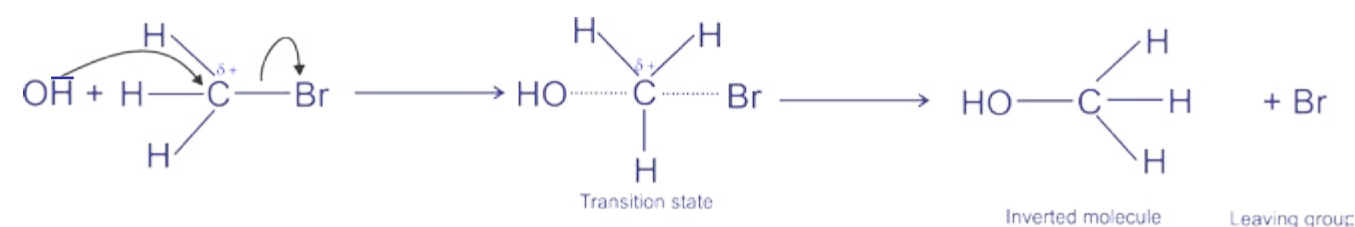
If the two processes occur simultaneously the mechanism is called S_N2 . If the bond breaks first followed by the formation of a new bond, the mechanism is called S_N1 .

Nucleophilic Substitution Bimolecular (S_N2)

This is a single step mechanism. As soon as the nucleophile starts attacking the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words the extent of bond formation is equal to the extent of bond breakage.

Another important feature of this mechanism is the direction of the attack of the attacking nucleophile. It attacks from the side which is opposite to the leaving group.

In order to give to the nucleophile enough room to attack, the substrate carbon atom changes its state of hybridization from tetrahedral sp^3 to planar sp^2 . The attack of the nucleophile, the change in the state of hybridization and the departure of the leaving group, everything occurs at the same time.



During the reaction the configuration of the alkyl halide molecule gets inverted. This is called inversion of configuration.

Molecularity of a reaction is defined as the number of molecules taking part in the rate determining step. Since in this mechanism, the reaction takes place in only one step which is also a rate determining step and two molecules are participating in this step, so it is called a bimolecular reaction.

Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon the concentrations of alkyl halide as well as the attacking nucleophile. Mathematically, the rate can be expressed as:

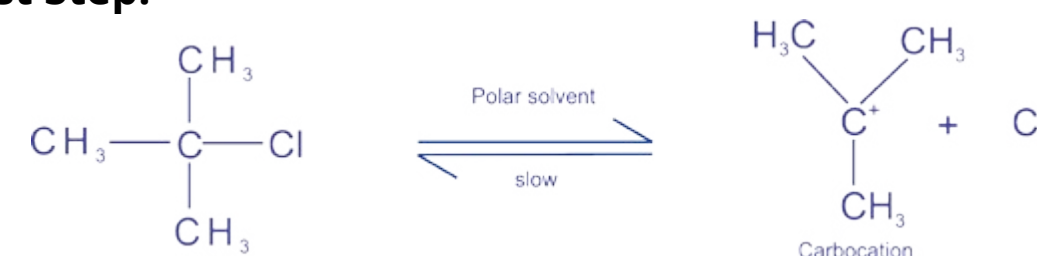
$$\text{Rate} = k [\text{Alkyl halide}]^1 [\text{Nucleophile}]^1$$

Since the exponents of the concentration terms in the above expression are unity, so the order of a typical S_N2 reaction will be $1 + 1 = 2$. Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

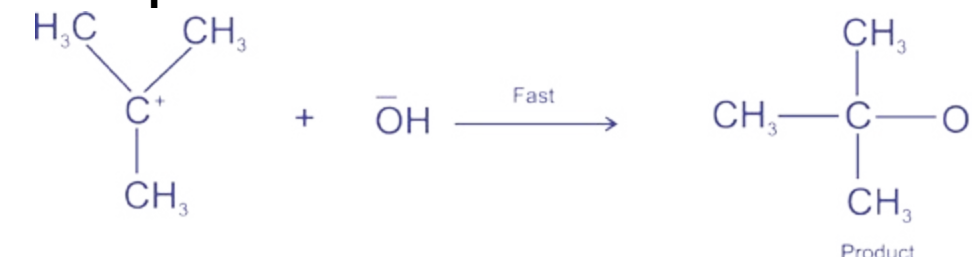
Nucleophilic Substitution Unimolecular (S_N1)

This type of mechanism involves two steps. The first step is the reversible ionization of the alkyl halide in the presence of an aqueous acetone or an aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to give the product.

First Step:

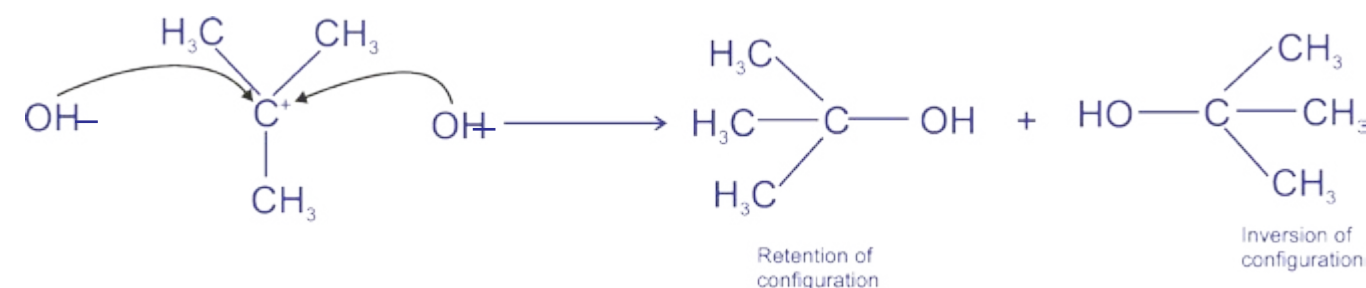


Second Step:



Since the first step involves the breakage of a covalent bond so it is a slow step as compared to the second step which involves the energetically favourable combination of ions. The first step is, therefore, called the rate-determining step. The mechanism is called unimolecular because only one molecule takes part in the rate determining step.

In S_N1 mechanism, the nucleophile attacks when the leaving group had already gone, so the question of the direction of the attack does not arise. Moreover, the intermediate carbocation is a planar specie allowing the nucleophile to attack on it from both the directions with equal ease. We, therefore, observe 50% inversion of configuration and 50% retention of configuration.



Reactions involving S_N1 mechanism show first order kinetics and the rates of such reactions depend only upon the concentration of the alkyl halide. The rate equation of such reactions can be written as follows.

$$\text{Rate} = k [\text{Alkyl halide}]$$

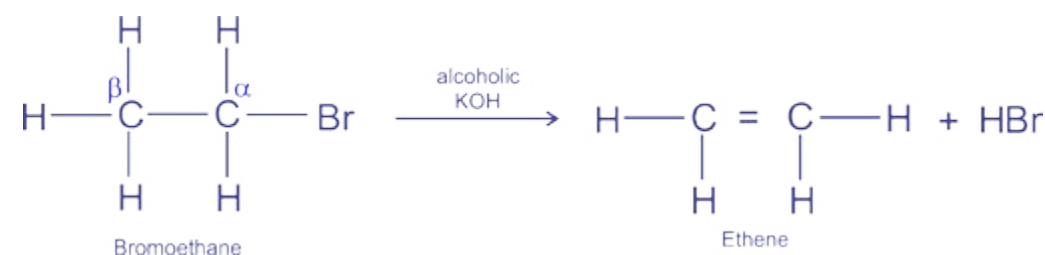
Tertiary alkyl halides when attacked by a nucleophile always follow S_N1 mechanism. Secondary alkyl halides, on the other hand, follow both S_N1 and S_N2 mechanisms.

10.5.3 β -Elimination Reactions

During nucleophilic substitution reactions, the attacking nucleophile attacks the electrophilic carbon atom of the alkyl halide. There is another site present in the alkyl halide molecule where the nucleophile can attack at the same time. Such a site is an electrophilic hydrogen atom attached to the β -carbon of the alkyl halide.

When the attack takes place on hydrogen, we get an alkene instead of a substitution product. Such a type of reactions are called elimination reactions.

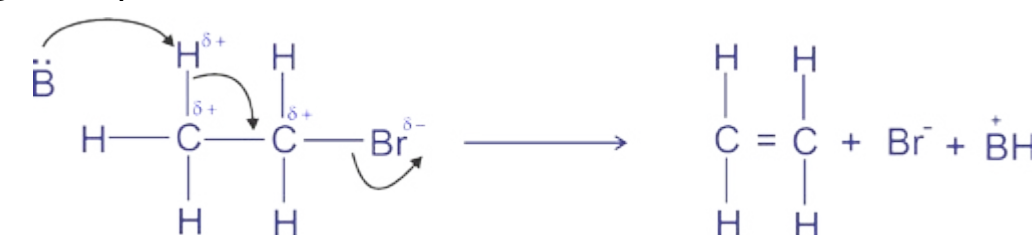
These reactions take place simultaneously with substitution reactions and often compete with them.



Like nucleophilic substitutions, the elimination reactions can also follow E2 or E1 mechanism.

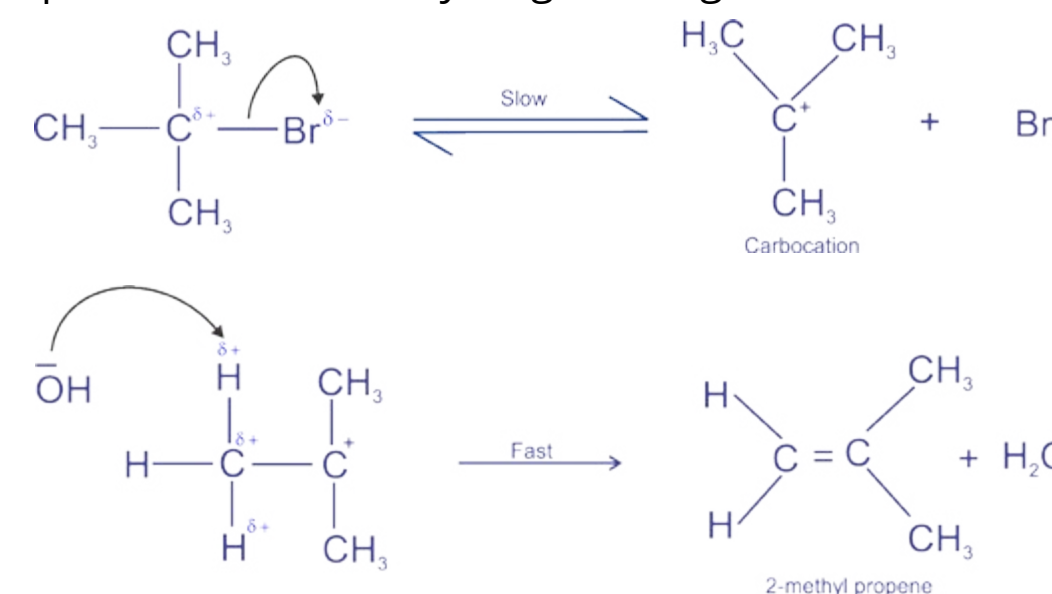
In E2 mechanism, the nucleophile attacks and the leaving group leaves at the same time with a formation of carbon carbon double bond.

The single step E2 elimination



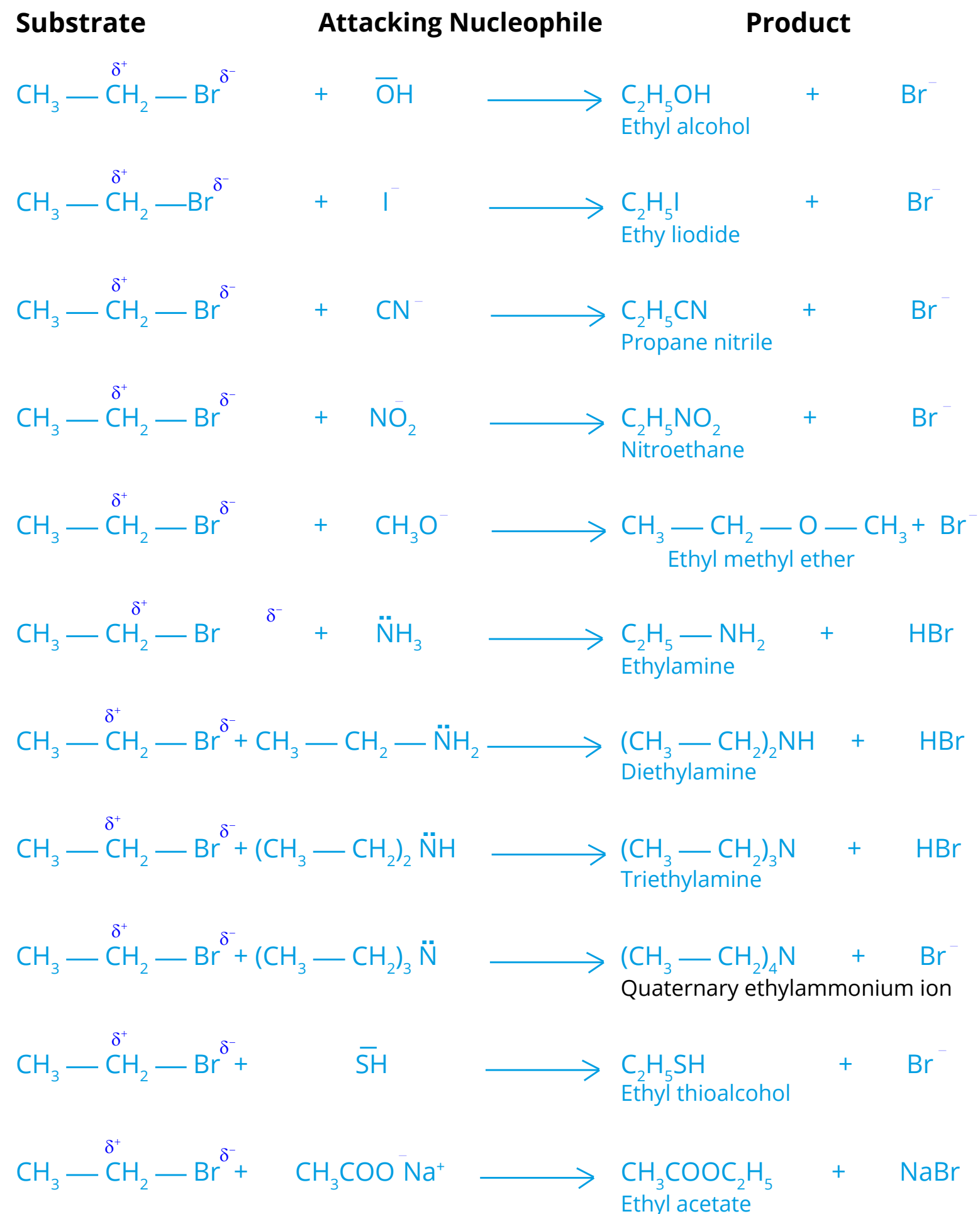
Like S_N2 reactions, the molecularity of E2 reactions is also two and these reactions show second order kinetics.

In E1 mechanism, like S_N1 mechanism, the first step is the slow ionization of the substrate to give a carbocation. In the second step, the nucleophile attacks on hydrogen to give an alkene as a product



E2 mechanism is a bimolecular mechanism and the rates of those reactions which follow this mechanism depend upon the concentrations of the alkyl halide as well as the attacking nucleophile or a base. E1 mechanism, on the other hand, is a unimolecular mechanism and the rates of those reactions which follow this mechanism depend only upon the concentration of the alkyl halide molecule. Primary alkyl halides generally follow E2 mechanism whereas tertiary alkyl halides follow E1 mechanism.

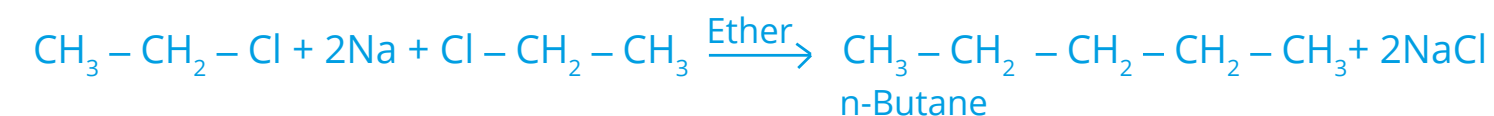
Examples of S_N reactions are given below. These reactions show the usefulness of alkyl halides as synthetic reagents.



Other reactions shown by alkyl halides are as follows:

1. Wurtz Synthesis

Alkyl halides react with sodium in ether solvent to give alkanes. The reaction is particularly useful for the preparation of symmetrical alkanes.



2. Reduction of Alkyl Halides

Alkyl halides can be reduced with zinc in the presence of an aqueous acid such as HCl or CH_3COOH .



3. Reaction with Sodium Lead Alloy (Na_4Pb)

Methyl chloride and ethyl chloride react with sodium lead alloy giving tetramethyl lead and tetraethyl lead, respectively. These compounds are important anti-knock agents and are used in gasoline.

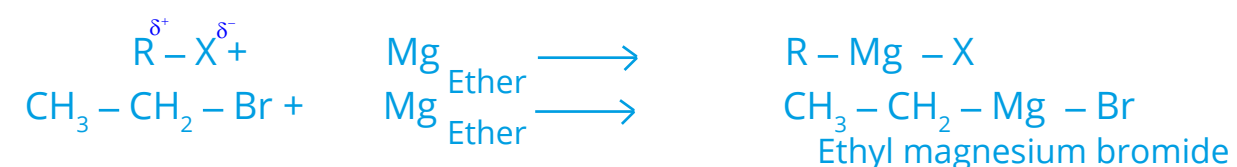


10.6 GRIGNARD REAGENT

Grignard reagents RMgX are derivatives of alkyl halides belonging to class of organo-metallic compounds. Grignard reagent was first prepared by Victor Grignard in 1900. These reagents are so important in organic synthesis that almost all the classes of organic compounds can be prepared from them. Due to their importance and applications Victor Grignard was awarded Nobel prize in chemistry.

Preparation:

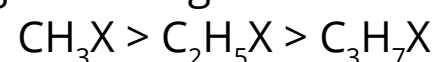
Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of dry ether (alcohol free, moisture free).



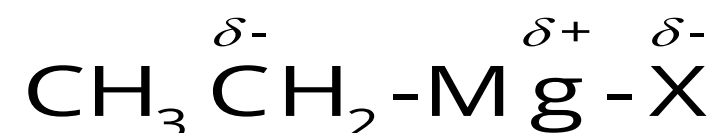
It is important that all the reactants must be absolutely dry and pure because Grignard reagents are so reactive that they may react with moisture or any impurity present. Reactivity of alkyl halides with magnesium is in the following order:

Alkyl iodide > Alkyl bromide > Alkyl chloride

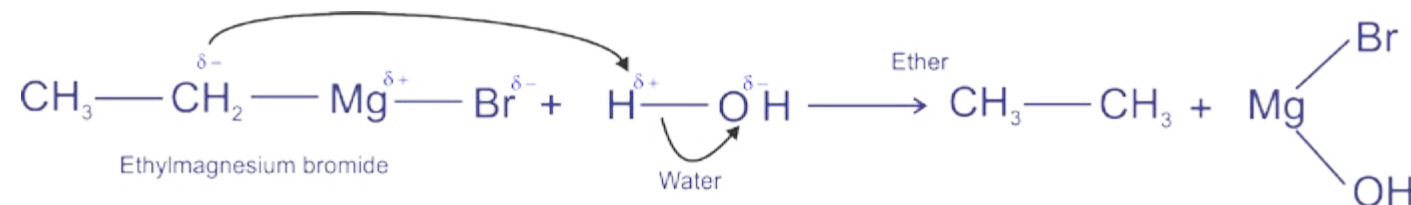
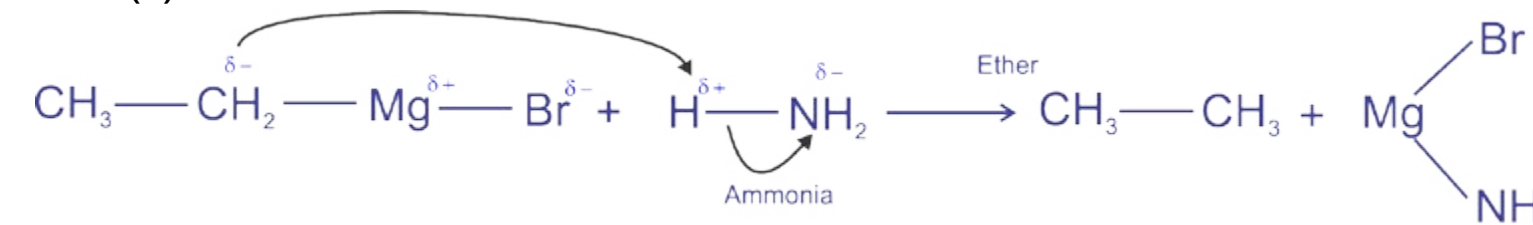
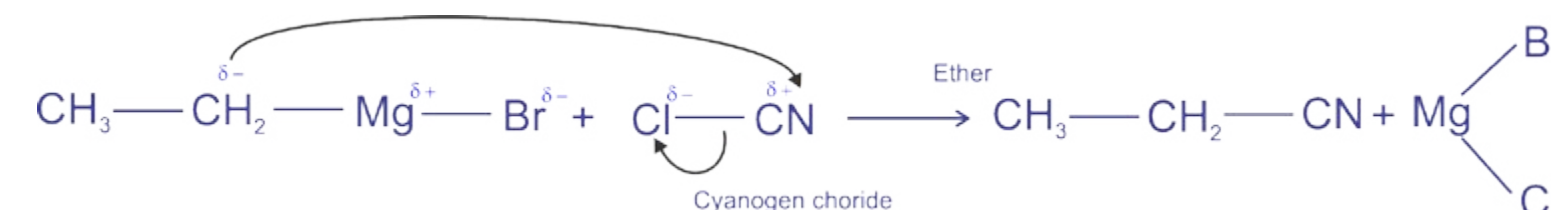
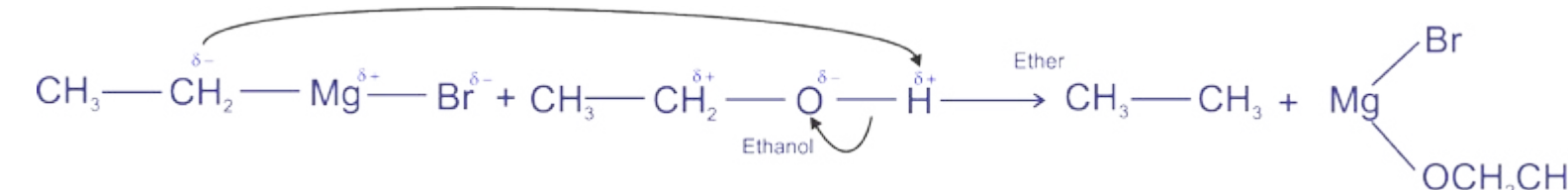
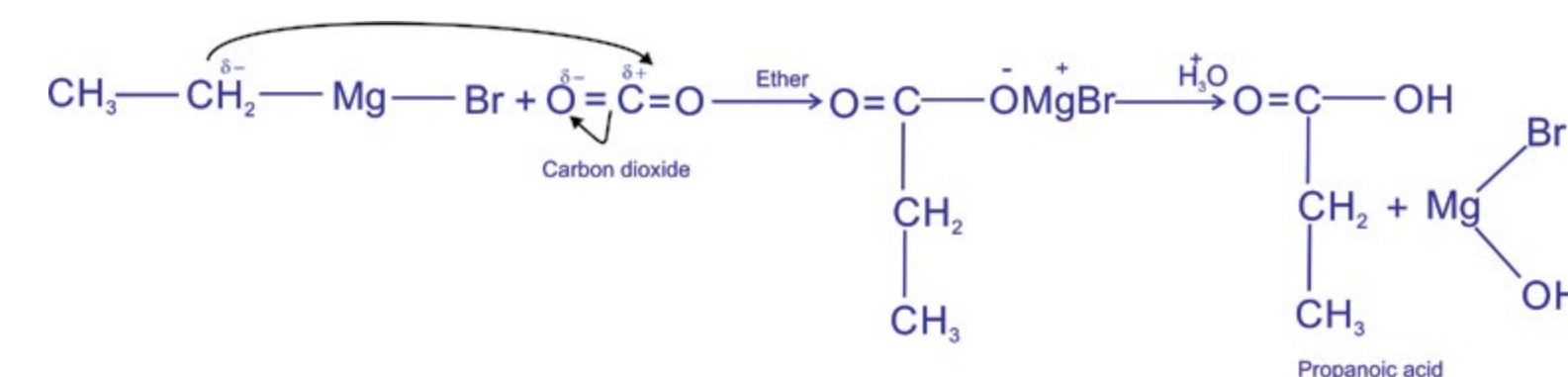
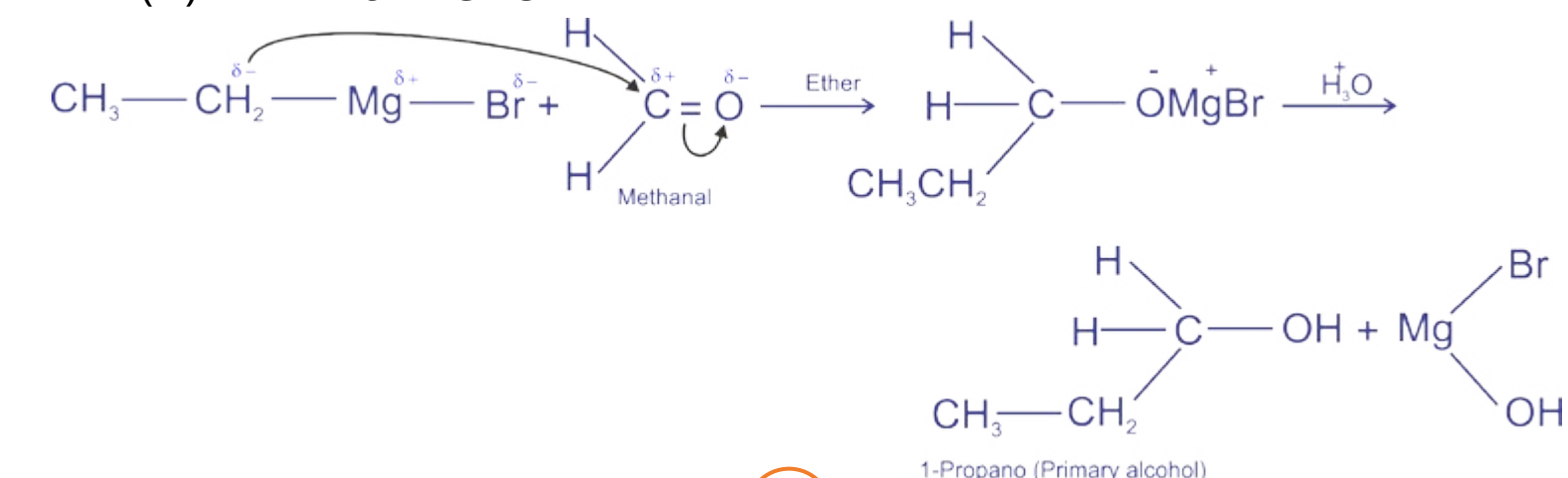
And for a given halogen the order of reactivity is as follows:

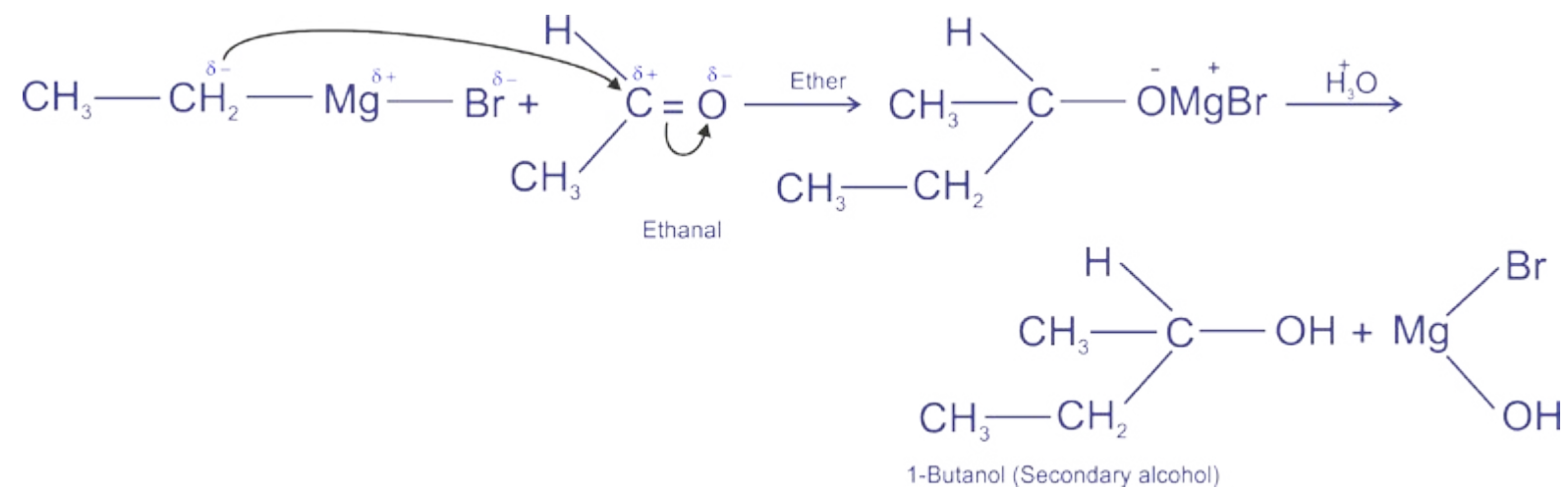
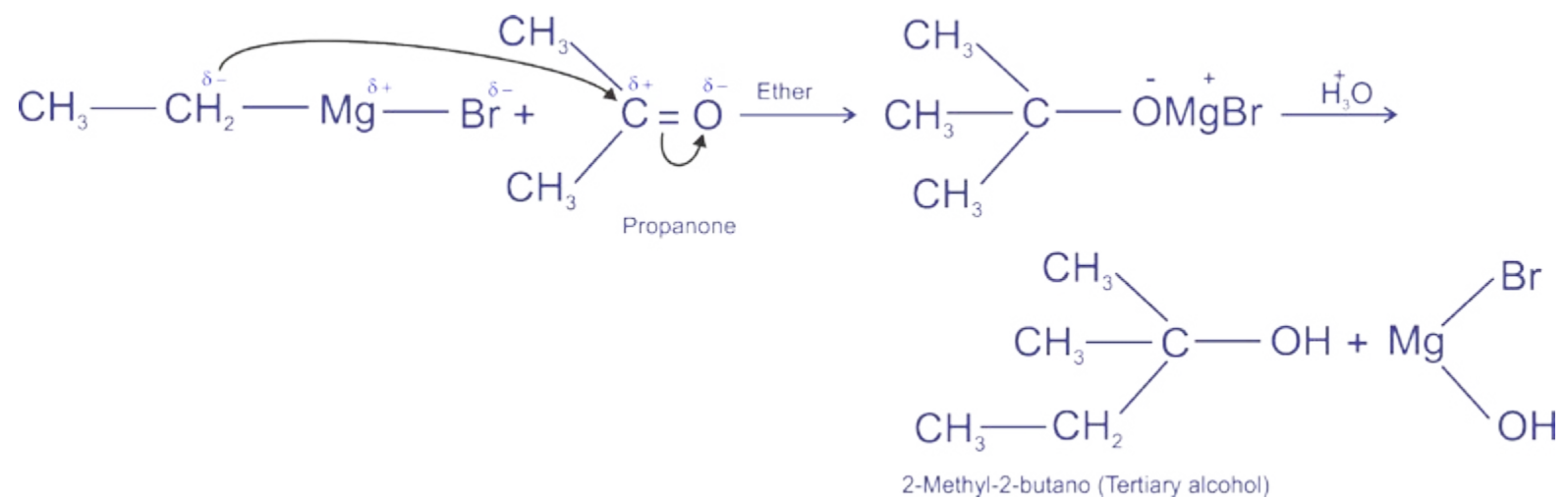
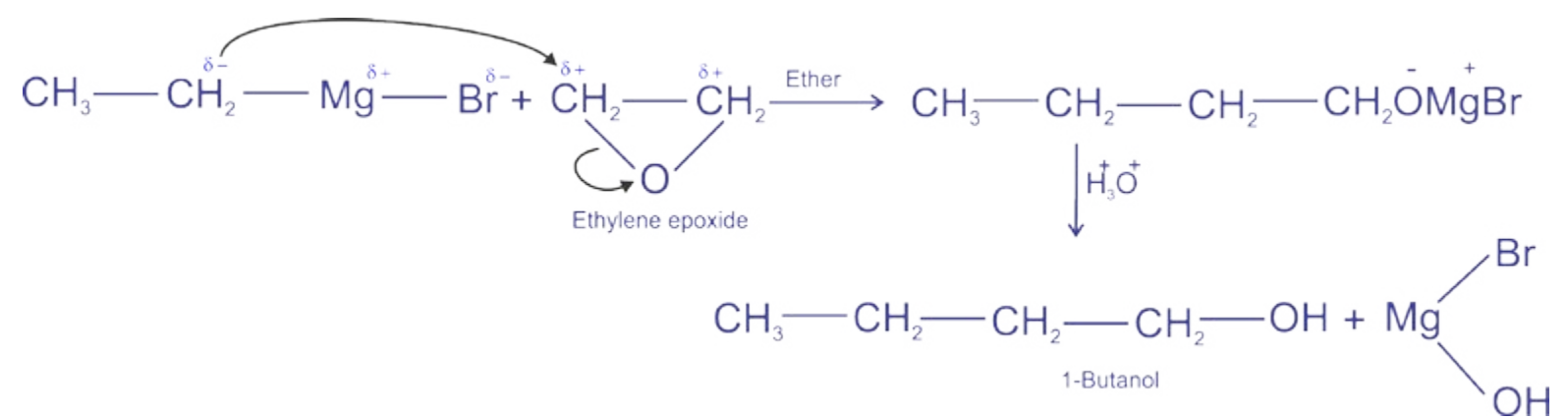
**Structure and Reactivity**

Grignard reagents are much more reactive than most of the organic compounds. The reactivity is due to the nature of C - Mg bond which is highly polar.



Magnesium is more electropositive than carbon and the C-Mg bond though covalent is highly polar, giving alkyl carbon the partial negative charge. This negative charge is an unusual character which makes the alkyl groups highly reactive towards electrophile centres. Mostly reactions shown by Grignard reagent are exothermic.

Reactions**(i) With Water****(ii) With ammonia****(iii) With cyanogen chloride****(iv) With alcohols****(v) With CO₂****(vi) With HCHO**

(vii) **With CH_3CHO** (viii) **With CH_3COCH_3** (ix) **With Epoxide**

Simulation 10.3: Interactive Periodic Table
Source & Credit: learnerstv

KEY POINTS

1. Monohalo derivatives of alkanes are called alkyl halides.
2. The general formula of alkyl halides is $C_nH_{2n+1}X$.
3. The best method for the preparation of alkyl halides is by the reactions of alcohols with inorganic halides like $SOCl_2$, PX_3 and PX_5 .
4. Alkyl halides are a very reactive class of organic compounds. They undergo nucleophilic substitution reactions and elimination reactions in the presence of a nucleophile or a base.
5. Nucleophilic substitution reactions can take place in two distinct ways. A one step mechanism is called S_N2 while a two step mechanism is called S_N1 . S_N1 reactions show first order kinetics whereas S_N2 reactions show 2nd order kinetics.
6. Nucleophilic substitution reactions take place simultaneously with elimination reactions and often compete with them.
7. Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction. Like nucleophilic substitution, (3-elimination reaction also takes place in two distinct ways E2 and E1.
8. Grignard reagent can be prepared by adding alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
9. Grignard reagent has a reactive nucleophilic carbon atom which can react with electrophilic centres to give the products in high yields.
10. Primary, secondary and tertiary alcohols can be best prepared by reacting Grignard reagent with formaldehyde, any other aldehydes and ketones, respectively.

EXERCISE

Q.1. Fill in the blanks.

- i) In tertiary alkyl halides the halogen atom is attached to a carbon which is further attached to _____ carbon atoms directly.
- ii) The best method for the preparation of alkyl halides is the reaction of _____ with inorganic reagents.

- iii) An alkyl group with a partial positive charge on the carbon atom is called _____ centre.
- iv) The mechanism is called _____ if it involves one molecule in the rate determining step.
- v) Molecularity of a reaction is defined as the number of molecules taking part in the _____.
- vi) The molecularity of E2 reactions is always two and the reactions show _____ order kinetics.
- vii) Wurtz synthesis is useful for the preparation of _____ alkanes.
- viii) Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of _____.

Q.2. Indicate True or False.

- i) In secondary alkyl halides, the halogen atom is attached to a carbon which is further attached to two carbon atoms directly.
- ii) Alcohols react with thionyl chloride in ether as solvent to give alkyl halides.
- iii) Order of reactivity of alkyl halides for a particular alkyl group is: Iodide > Bromide > Chloride > Fluoride
- iv) In S_N2 reactions the attacking nucleophile always attacks from the side in which the leaving group is attached.
- v) Methyl magnesium iodide on hydrolysis yields ethyl alcohol.
- vi) Primary, secondary and tertiary amines react with Grignard reagents in the same way.
- vii) The reactions of secondary alkyl halides may follow both S_N1 and S_N2 mechanisms.
- viii) S_N1 mechanism is a one stage process involving a simultaneous bond breakage and bond formation.
- ix) In β -elimination reactions, the two atoms or groups attached to two adjacent carbon atoms are lost under the influence of an electrophile.
- x) The reactivity order of alkyl halides is determined by the strength of carbon-halogen bond.

Q. 3. Multiple choice questions. Encircle the correct answer.

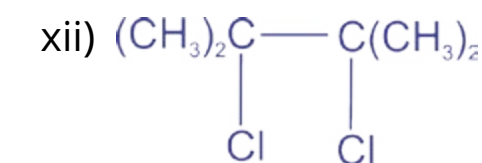
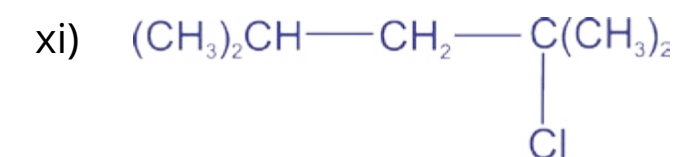
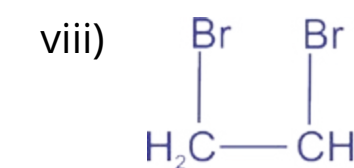
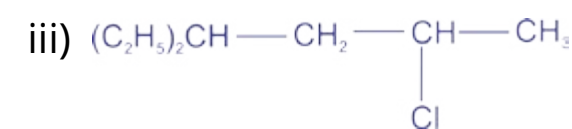
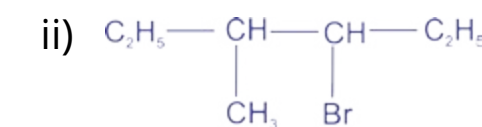
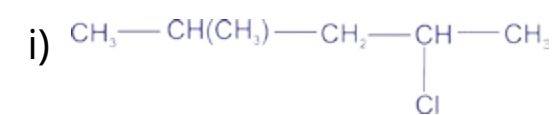
- i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms.
 (a) Two (b) Three (c) One (d) Four
- ii) The reactivity order of alkyl halides for a particular alkyl group is:
 (a) Fluoride > Chloride > Bromide > Iodide
 (b) Chloride > Bromide > Fluoride > Iodide
 (c) Iodide > Bromide > Chloride > Fluoride
 (d) Bromide > Iodide > Chloride > Fluoride
- iii) When CO_2 is made to react with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is:
 (a) Propane (b) Propanoic acid (c) Propanal (d) Propanol
- iv) Grignard reagent is reactive due to:
 (a) the presence of halogen atom (b) the presence of Mg atom
 (c) the polarity of C -Mg bond (d) none of the above
- v) $\text{S}_\text{N}2$ reactions can be best carried out with:
 (a) Primary alkyl halides (b) Secondary alkyl halides
 (c) Tertiary alkyl halides (d) All the three
- vi) Elimination bimolecular reactions involve:
 (a) first order kinetics (b) second order kinetics
 (c) third order kinetics (d) zero order kinetics
- vii) For which mechanisms, the first step involved is the same.
 (a) E1 and E2 (b) E2 and $\text{S}_\text{N}2$ (c) $\text{S}_\text{N}1$ and E2 (d) E1 and $\text{S}_\text{N}1$
- viii) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:
 (a) they have an electrophilic carbon
 (b) they have an electrophilic carbon and a good leaving group
 (c) they have an electrophilic carbon and a bad leaving group
 (d) they have a nucleophilic carbon and a good leaving group

- ix) The rate of E1 reaction depends upon:
 (a) the concentration of substrate
 (b) the concentration of nucleophile
 (c) the concentration of substrate as well as nucleophile
 (d) None of the above
- x) Which one of the following is not a nucleophile :
 (a) H_2O (b) H_2S (c) BF_3 (d) NH_3

Q.4. Define alkyl halide. Which is the best method of preparing alkyl halides?

Q.5. Write down a method for the preparation of ethyl magnesium bromide in the laboratory?

Q.6. Give IUPAC names to the following compounds.



Q.7. Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$. Classify each as primary, secondary or tertiary chloride. Give their names according to IUPAC system.

Q.8. Using ethyl bromide as a starting material how would you prepare the following compounds. Give also the inorganic reagents and conditions necessary to carry out these reactions:

- | | |
|-------------------|--------------------|
| (a) n-Butane | (b) Ethyl alcohol |
| (c) Ethyl cyanide | (d) Ethane |
| (e) Ethene | (f) Propanoic acid |
| (g) Propane | |

Q.9. Write a detailed note on the mechanism of nucleophilic substitution reactions.

Q.10. What do you understand by the term β -elimination reaction. Explain briefly the two possible mechanisms of β -elimination reactions.

Q.11. What products are formed when the following compounds are treated with ethyl magnesium bromide, followed by hydrolysis in the presence of an acid,

- | | | |
|------------------|--------------------|-------------|
| i) $HCHO$ | ii) CH_3CHO | iii) CO_2 |
| iv) $(CH_3)_2CO$ | v) CH_3-CH_2-CHO | vi) $ClCN$ |

Q. 12. How will you carry out the following conversions.

- | | | |
|----------------------|-------------------|--------------------------|
| i) CH_4 | $\longrightarrow$ | CH_3CH_2COOH |
| ii) CH_3-CH_3 | $\longrightarrow$ | $(CH_3-CH_2)_4N^+ Br^-$ |
| iii) $CH_2=CH_2$ | $\longrightarrow$ | $CH_3-CH_2-CH_2-CH_2-OH$ |
| iv) $CH_3CH_2CH_2Cl$ | $\longrightarrow$ | $CH_3-CH=CH_2$ |
| v) CH_3COOH | $\longrightarrow$ | CH_3CH_2COOH |