

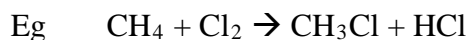
Topic 2.8

HALOALKANES

Production of haloalkanes from alkanes
Role of haloalkanes in ozone layer depletion
Nucleophilic substitution
Elimination

MANUFACTURE OF CHLOROALKANES FROM ALKANES

Chloroalkanes can be made from alkanes in a reaction known as a **free radical substitution** reaction.

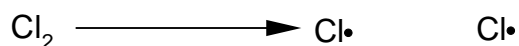


A substitution reaction is one in which one atom or group of atoms on the organic molecule is directly replaced by another. In this reaction the H atom on the alkane is replaced by a Cl atom.

Since all the carbon atoms in alkanes are attached to four other atoms, it is not possible to add another species to an alkane unless another species leaves. Thus addition reactions are not possible and alkanes can undergo substitution reactions only.

A free radical is a species which contains an unpaired electron. Free radicals are very reactive species and will bond with almost anything they come into contact with.

In this reaction the free radical which starts the reaction is a chlorine atom, formed when a chlorine molecule breaks up in the presence of ultra-violet light:



Free radicals are represented by a dot next to the atom containing an unpaired electron. They are caused by **homolytic fission** of covalent bonds.

Homolytic fission is the breaking of a covalent bond in such a way that one electron goes to each atom.

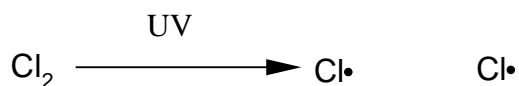
Mechanism 1: free radical substitution

Free radical substitution reactions proceed in three stages: initiation, propagation and then termination.

i) **Initiation**

Initiation is the production of free radicals by homolytic fission of a covalent bond.

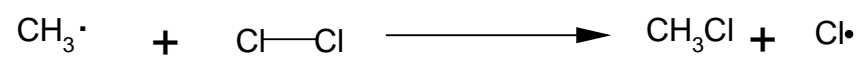
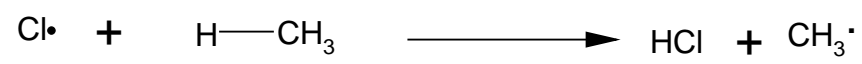
Most bonds do not undergo homolytic fission under normal conditions. Generally, UV light is required.



ii) **Propagation**

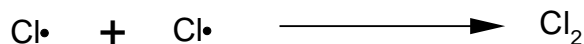
Propagation is the reaction of a free radical with a molecule to produce another free radical.

The reaction involves two propagation steps:



iii) Termination

Termination is the combination of two free radicals to form a single molecule.



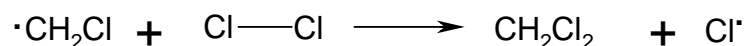
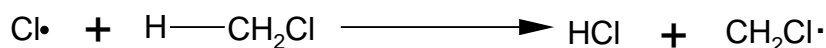
Note that the Cl radicals are recycled during the propagation steps, so the reaction only requires a very small number of Cl-Cl bonds to undergo fission for the reaction to proceed.

By-products in free radical substitution:

Chloromethane is not generally the only organic product of this reaction. Free radical reactions tend to result in a variety of different products.

i) Different propagation steps

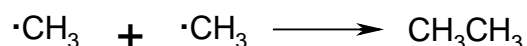
The propagation steps can continue beyond the formation of methane, and can result in the formation of dichloromethane, trichloromethane or tetrachloromethane:



These further propagation steps are likely if excess chlorine is used. If excess methane is used, then chloromethane is likely to be the major product.

ii) Different termination steps

It is also possible to get other products from alternative termination steps:



Thus when methane reacts with chlorine, a variety of products are formed including chloromethane, dichloromethane and ethane.

In order to ensure that chloromethane is the major product, it is important to use excess methane.

ROLE OF CHLOROALKANES IN OZONE LAYER DEPLETION

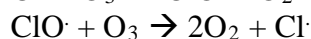
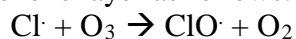
Chloroalkanes and chlorofluoroalkanes can be used as solvents. One type in particular, known as chlorofluorocarbons (CFCs), are widely used in aerosols and fridges. Chlorofluorocarbons are haloalkanes containing chlorine and fluorine atoms but not hydrogen atoms, eg CCl_2F_2 or CClF_3 . The small chlorofluorocarbons are gases and can escape into the atmosphere.

Usually chlorofluorocarbons are very unreactive. However in the upper atmosphere the C-Cl bonds can undergo homolytic fission if exposed to ultra-violet light:



Ozone (O_3) is a naturally occurring substance found in the upper atmosphere. It plays an important role in absorbing ultra-violet radiation from the sun and preventing it from getting to the earth's surface.

However if CFCs find their way into the upper atmosphere and the ultra-violet light breaks them down into $\text{Cl}\cdot$ radicals, these $\text{Cl}\cdot$ radicals act as catalysts in the destruction of the ozone layer as follows:



This process can repeat itself indefinitely, meaning that even small quantities of chlorine radicals can significantly destroy the ozone layer.

This process has resulted in the formation of a hole in the ozone layer.

As a result of this, chemists supported legislation to ban CFCs completely and they have been replaced in fridges and aerosols by alternative chlorine-free compounds.

The hole in the ozone layer is slowly mending itself.

REACTIONS OF HALOALKANES

The C-X bond is polar, and the carbon is δ +ve. Therefore haloalkanes can react with **nucleophiles**.

A **nucleophile** is a species with a lone pair of electrons which it can use to bond with an electropositive carbon atom on an organic molecule.

The nucleophile generally replaces the halogen atom on the molecule. Thus haloalkanes can undergo **nucleophilic substitution** reactions.

Haloalkanes can also undergo **elimination** reactions.

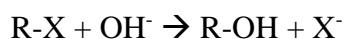
An **elimination** reaction is one in which the organic molecule loses two species from adjacent carbon atoms without replacement, resulting in the formation of a double bond between the two carbon atoms.

Mechanism 2: Nucleophilic Substitution

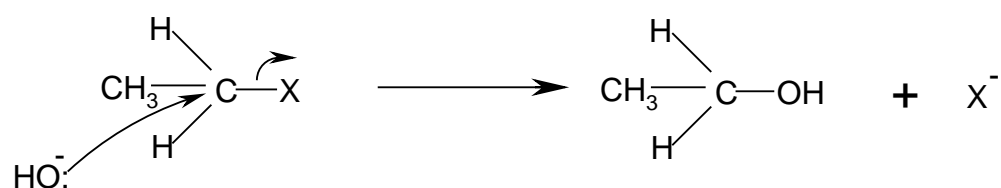
The three nucleophiles most commonly used in nucleophilic substitution of haloalkanes are hydroxide ions, OH^- , cyanide ions, CN^- and ammonia, NH_3 .

1. Reaction with hydroxide ions

Haloalkanes react with hydroxide ions when boiled under reflux with aqueous NaOH or aqueous KOH:

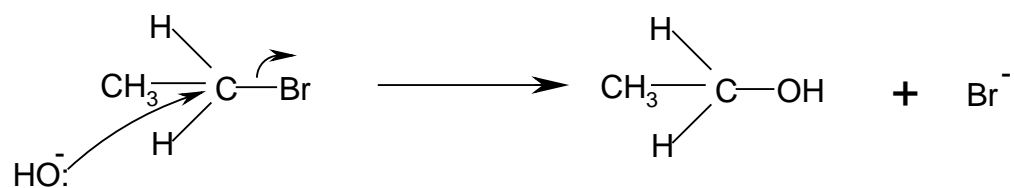


The nucleophile (ie the hydroxide ion) attacks the δ +ve carbon atom from behind, forcing the X atom to leave as the halide ion. It is a one-step mechanism:

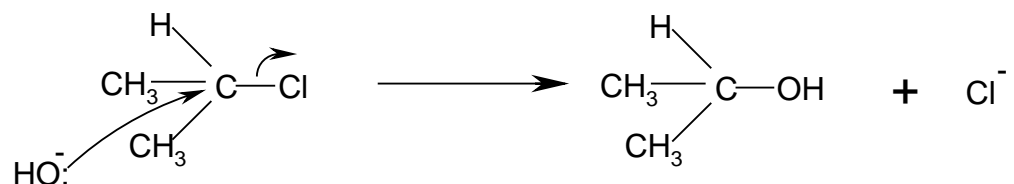


Note that the hydroxide ion is behaving as a **nucleophile** in this reaction.

Eg bromoethane \rightarrow ethanol

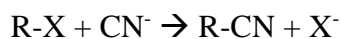


Eg 2-chloropropane \rightarrow propan-2-ol

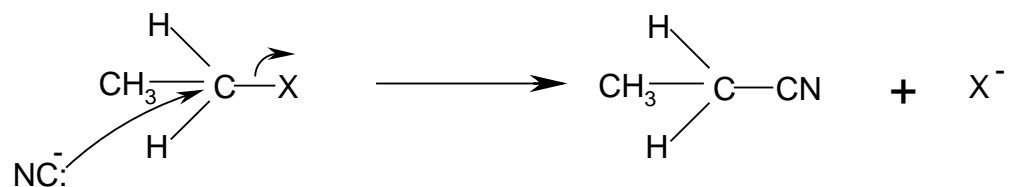


2. Reaction with cyanide ions

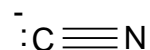
Cyanide ions are nucleophiles and react with haloalkanes by nucleophilic substitution to give nitriles. The haloalkane should be boiled under reflux with KCN in aqueous ethanol.



The mechanism is exactly the same as with the hydroxide ion.

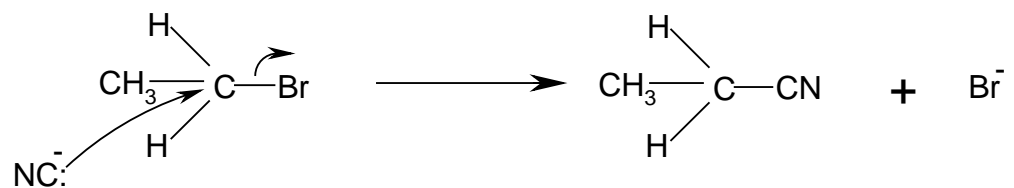


Note that the CN^- ion has the following structure:

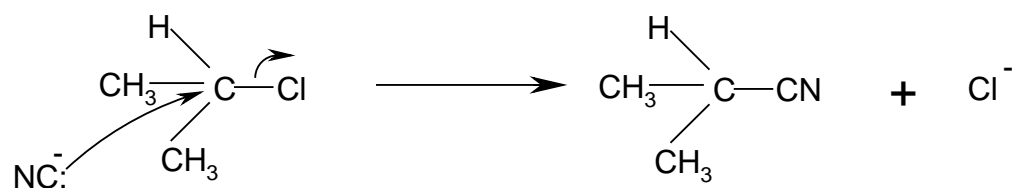


Thus the lone pair of electrons is on the carbon, not the nitrogen. It is thus the carbon which attaches itself to the organic molecule.

Eg bromoethane \rightarrow propanenitrile



Eg 2-chloropropane \rightarrow 2-methylpropanenitrile



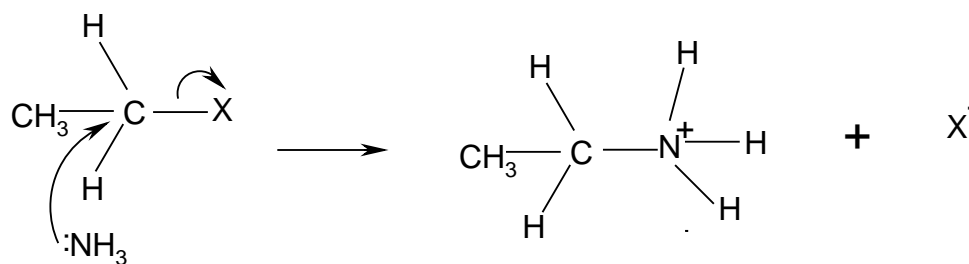
The reaction with cyanide ions is significant because it increases the number of carbon atoms on the chain, **so it provides a way of ascending the homologous series**. It is thus very useful in organic synthesis.

3. Reaction with ammonia

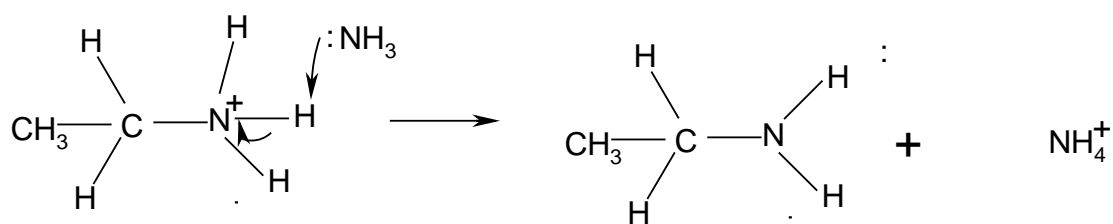
If a haloalkane is heated with ethanolic ammonia in a sealed tube, a primary amine is formed:



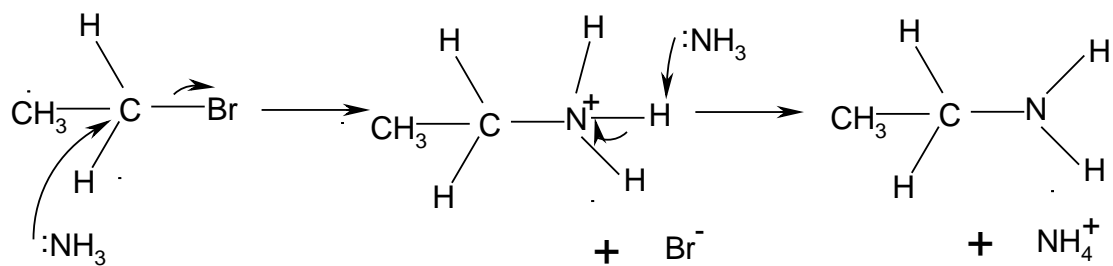
The mechanism is again nucleophilic substitution:



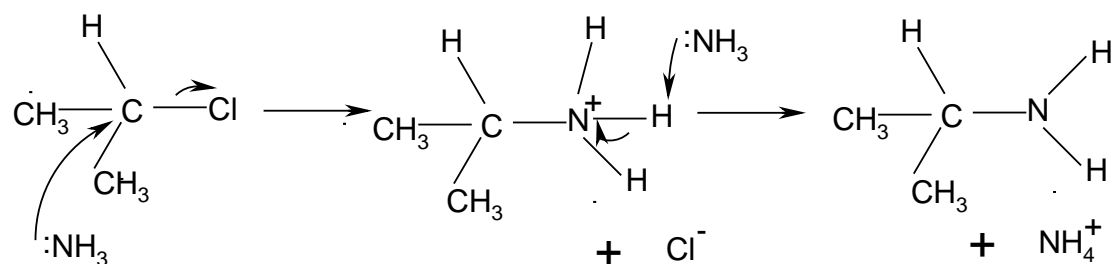
The initial substitution step forms the intermediate R-NH_3^+ ion. The H is removed by another ammonia molecule to form the amine:



Eg bromoethane \rightarrow aminoethane

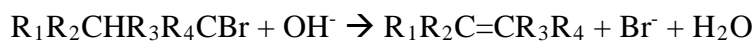


Eg 2-chloropropane \rightarrow 2-aminopropane



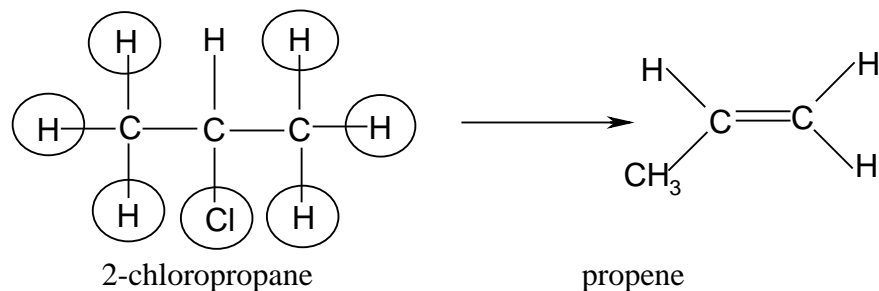
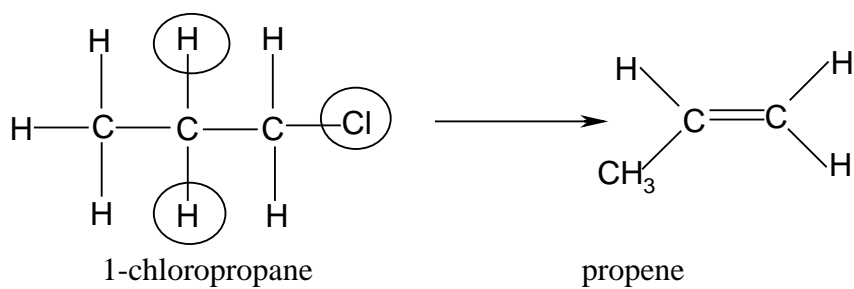
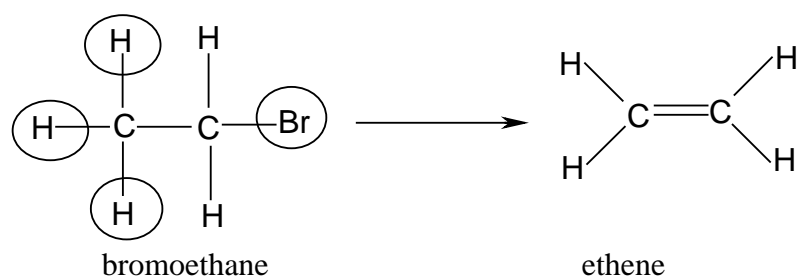
4. Elimination of hydrogen halides

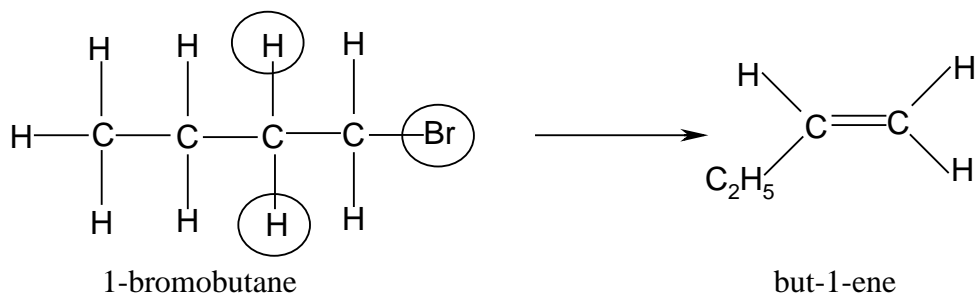
If haloalkanes are boiled with an ethanolic solution of KOH instead of with an aqueous solution, they will undergo elimination of an HX molecule to give an alkene:



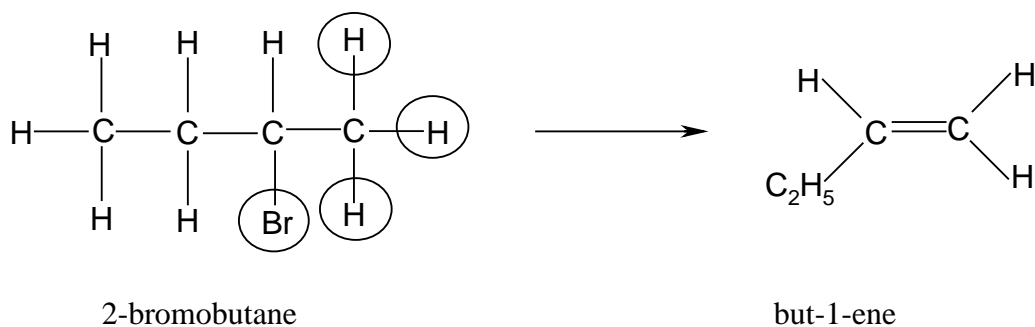
NaOH is not used since it is only sparingly soluble in ethanol. This reaction works best if distillation apparatus is used since the alkene product is volatile.

The hydrogen is always lost from a carbon atom adjacent to the carbon atom attached to the halogen (all the hydrogen atoms which could be removed have been circled). Sometimes this can result in more than one possible product:

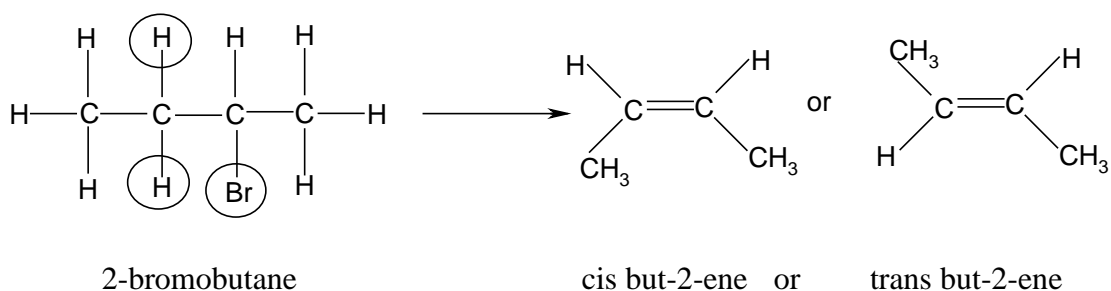




During the above elimination reactions there is only one possible product.

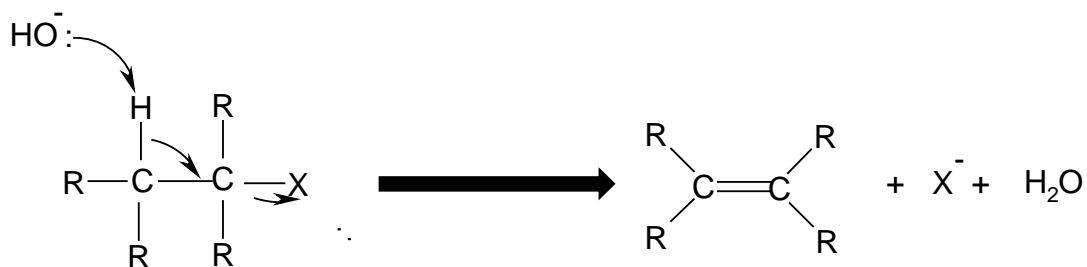


In this reaction, losing an H atom on the other side of the Br atom results in two different products:



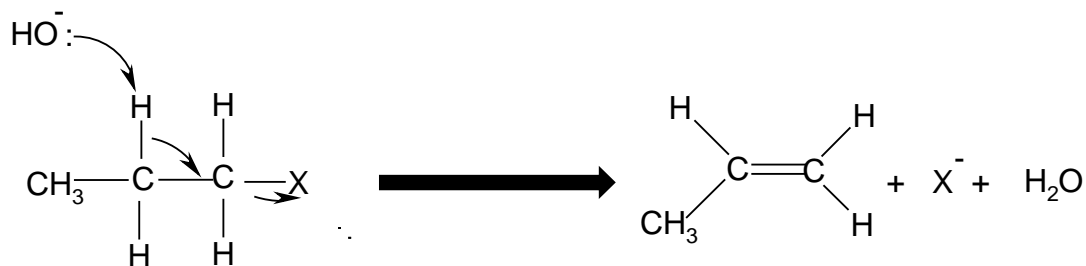
Mechanism 3: elimination

The mechanism of this reaction involves the hydroxide ion attacking a hydrogen atom on the haloalkane:



Note that the hydroxide ion is behaving as a **base**, not a nucleophile

Eg 1-chloropropane \rightarrow propene



RATES OF REACTION OF HALOGENOALKANES

The rate of substitution or elimination of haloalkanes depends on the ease with which the C-X bond can be broken. This depends on the strength of the C-X bond, which in turn depends on the length of the bond.

Since the C-F bond is very short, it is very strong and difficult to break. Thus fluoroalkanes react very slowly.

The C-Cl bond is longer and weaker than the C-F bond, and the C-X bonds become progressively longer and weaker on descending the group. Thus the C-I bond is the longest, weakest and easiest to break and thus iodoalkanes react the most quickly.

Thus rates of reactions decrease in the order:

Iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

As the halogen atom becomes larger, the C-X bond becomes longer, weaker and easier to break and the corresponding halogenoalkanes react more quickly.

1. Summary of reactions of haloalkanes

Haloalkane \rightarrow alcohol

Reagent: NaOH(aq) or KOH(aq)

Conditions: warm under reflux

Equation: $R-X + OH^- \rightarrow R-OH + X^-$

Mechanism: nucleophilic substitution

Role of hydroxide ion: nucleophile

Haloalkane \rightarrow nitrile

Reagent: KCN in aqueous ethanol

Conditions: boil under reflux

Equation: $R-X + CN^- \rightarrow R-CN + X^-$

Mechanism: nucleophilic substitution

Haloalkane \rightarrow Amine

Reagent: ammonia in ethanol in a sealed tube

Conditions: heat

Equation: $R-X + 2NH_3 \rightarrow R-NH_2 + NH_4X$

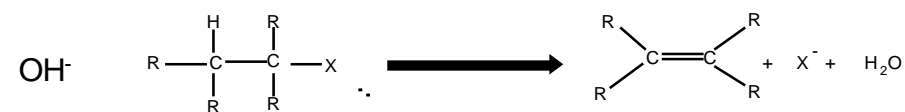
Mechanism: nucleophilic substitution

Haloalkane \rightarrow alkene

Reagent: KOH in ethanol

Conditions: heat

Equation:



Mechanism: elimination

Role of hydroxide ion: base