

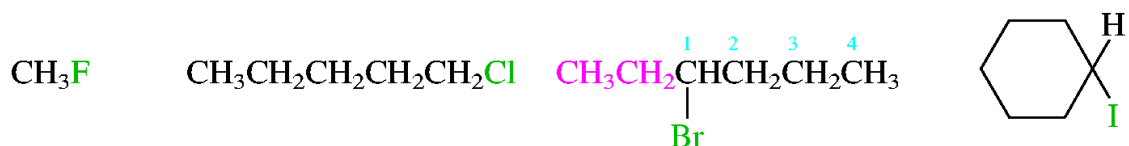
1. IUPAC NOMENCLATURE OF ALKYL HALIDES
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**TEST - Halogen derivatives of hydrocarbons**

- Give the names
- Write the structural formula
- Reactions of elimination and addition

**IUPAC NOMENCLATURE OF ALKYL HALIDES**

The IUPAC rules permit alkyl halides to be named in two different ways, called functional class nomenclature and substitutive nomenclature. In functional class nomenclature the alkyl group and the halide (fluoride, chloride, bromide, or iodide) are designated as separate words. The alkyl group is named on the basis of its longest continuous chain beginning at the carbon to which the halogen is attached.



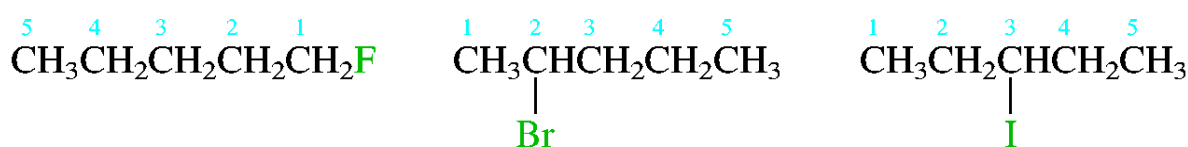
Methyl fluoride

Pentyl chloride

1-Ethylbutyl bromide

Cyclohexyl iodide

Substitutive nomenclature of alkyl halides treats the halogen as a halo--(fluoro-, chloro-, bromo-, or iodo-) substituent on an alkane chain. The carbon chain is numbered in the direction that gives the substituted carbon the lower number.

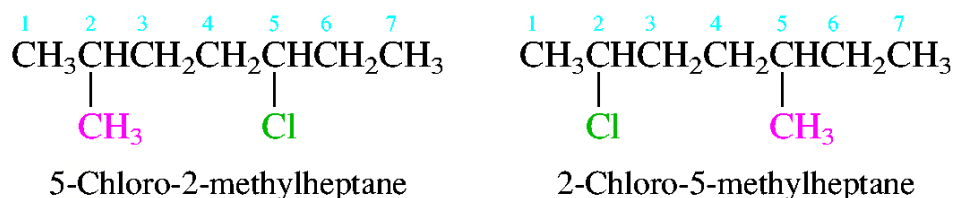


1-Fluoropentane

2-Bromopentane

3-Iodopentane

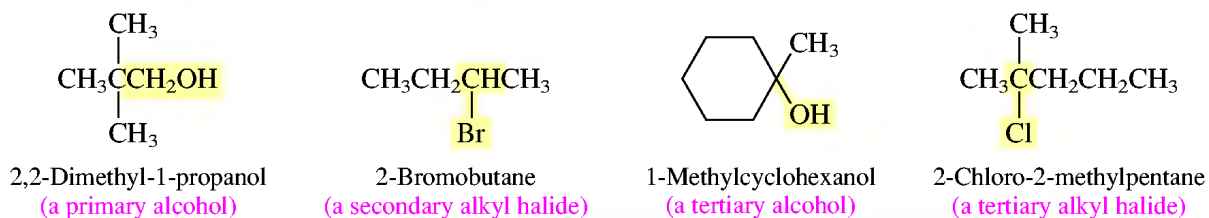
When the carbon chain bears both a halogen and an alkyl substituent, the two are considered of equal rank, and the chain is numbered so as to give the lower number to the substituent nearer the end of the chain.



Substitutive names are preferred, but functional class names are sometimes more convenient or more familiar and are frequently encountered in organic chemistry.

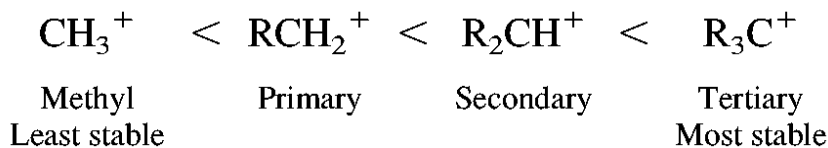
## CLASSES OF ALKYL HALIDES

Alkyl halides are classified as primary, secondary, or tertiary according to the degree of substitution of the carbon that bears the functional group. Thus, primary alcohols and primary alkyl halides are compounds of the type  $RCH_2G$  (where  $G$  is the functional group), secondary alcohols and secondary alkyl halides are compounds of the type  $R_2CHG$ , and tertiary alcohols and tertiary alkyl halides are compounds of the type  $R_3CG$ .



Many of the properties of alkyl halides are affected by whether their functional groups are attached to primary, secondary, or tertiary carbons. We will see a number of cases in which a functional group attached to a primary carbon is more reactive than one attached to a secondary or tertiary carbon, as well as other cases in which the reverse is true.

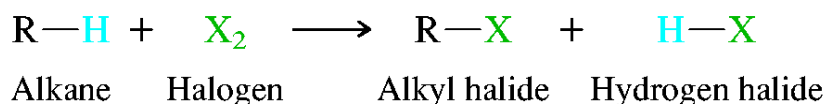
To summarize, the most important factor to consider in assessing carbocation stability is the degree of substitution at the positively charged carbon.



We will see numerous reactions that involve carbocation intermediates as we proceed through the text, so it is important to understand how their structure determines their stability.

## HALOGENATION OF ALKANES

There are a completely different method for preparing alkyl halides, one that uses alkanes as reactants. It involves substitution of a halogen atom for one of the alkane's hydrogens.



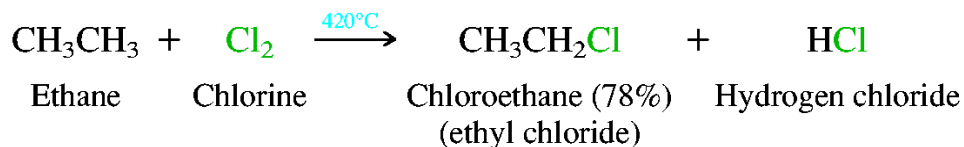
The alkane is said to undergo fluorination, chlorination, bromination, or iodination according to whether  $X_2$  is  $F_2$ ,  $Cl_2$ ,  $Br_2$ , or  $I_2$ , respectively. The general term is halogenation. Chlorination and bromination are the most widely used.

The reactivity of the halogens decreases in the order  $F_2 > Cl_2 > Br_2 > I_2$ . Fluorine is an extremely aggressive oxidizing agent, and its reaction with alkanes is strongly exothermic and difficult to control. Direct fluorination of alkanes requires special equipment and techniques, is not a reaction of general applicability, and will not be discussed further.

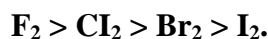
Chlorination of alkanes is less exothermic than fluorination, and bromination less exothermic than chlorination. Iodine is unique among the halogens in that its reaction with alkanes is endothermic and alkyl iodides are never prepared by iodination of alkanes.

## HALOGENATION OF HIGHER ALKANES

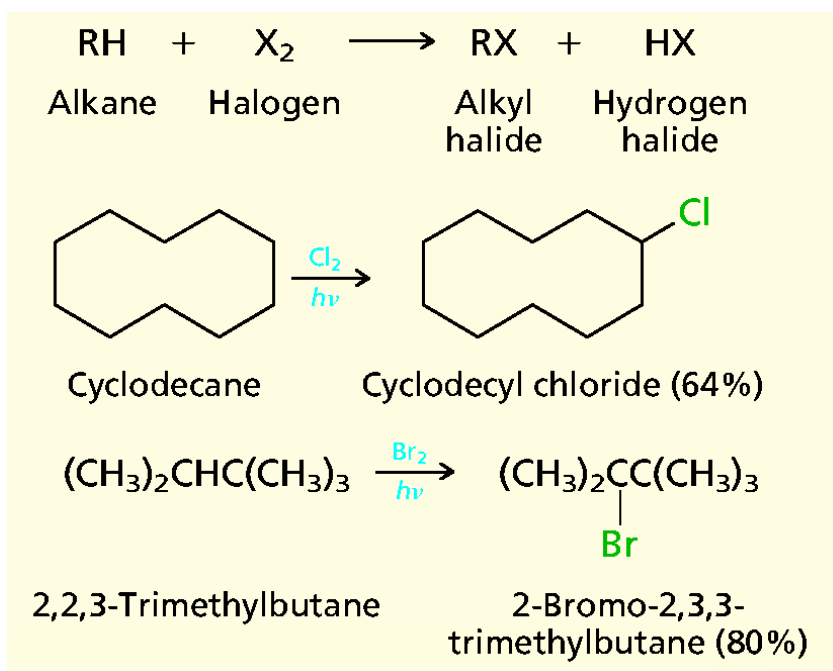
Like the chlorination of methane, chlorination of ethane is carried out on an industrial scale as a high-temperature gas-phase reaction.



*Free-radical halogenation of alkanes.* Alkanes react with halogens by substitution of a hydrogen for a hydrogen on the alkane. The reactivity of the halogens decreases in the order

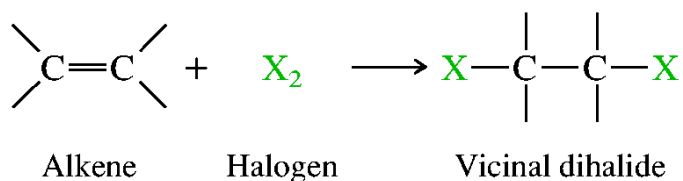


The ease of replacing a hydrogen decreases in the order tertiary > secondary > primary > methyl. Chlorination is not very selective and so is used only when all the hydrogens of the alkane are equivalent. Bromination is highly selective, replacing tertiary hydrogens much more readily than secondary or primary ones.



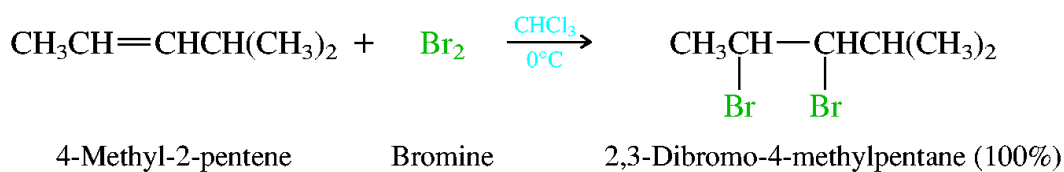
## ADDITION OF HALOGENS TO ALKENES

In contrast to the free-radical substitution observed when halogens react with alkanes, halogens normally react with alkenes by electrophilic addition.

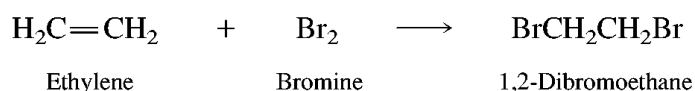


The products of these reactions are called vicinal dihalides. Two substituents, in this case the halogens, are vicinal if they are attached to adjacent carbons. The word is derived from the Latin vicinalis, which means "neighboring." The halogen is either chlorine (Cl<sub>2</sub>) or bromine (Br<sub>2</sub>),

and addition takes place rapidly at room temperature and below in a variety of solvents, including acetic acid, carbon tetrachloride, chloroform, and dichloromethane.

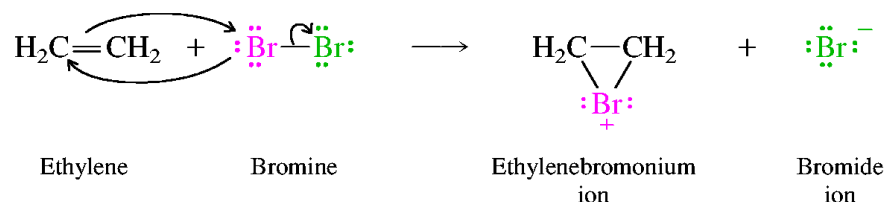


**The overall reaction:**

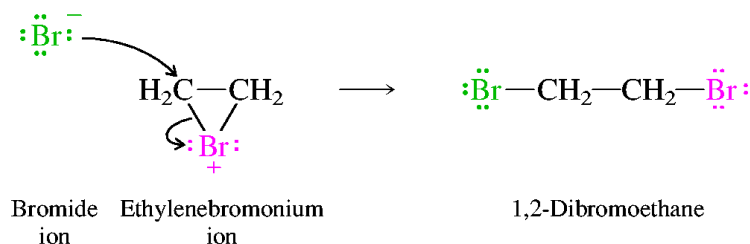


**The mechanism:**

**Step 1:** Reaction of ethylene and bromine to form a bromonium ion intermediate:



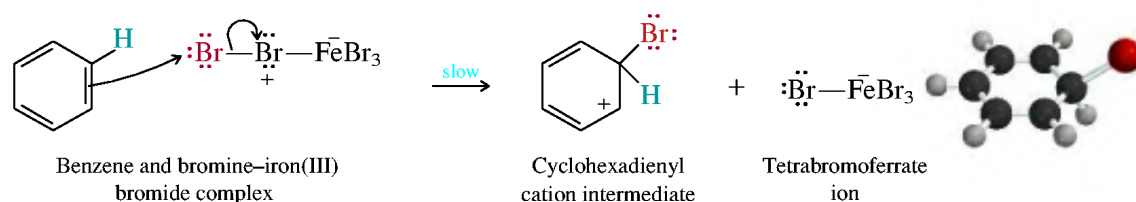
**Step 2:** Nucleophilic attack of bromide anion on the bromonium ion:



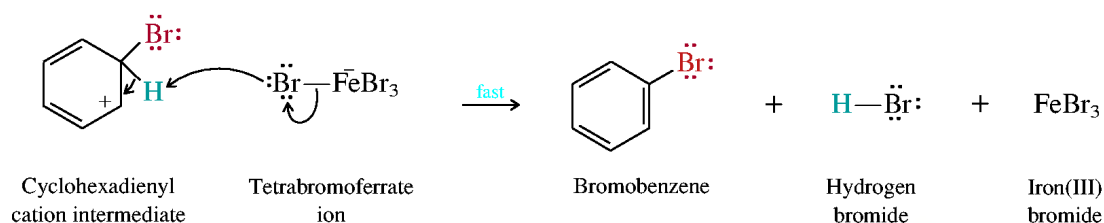
## HALOGENATION OF BENZENE

**Step 1:** The bromine-iron(III) bromide complex is the active electrophile that attacks benzene.

Two of the  $\pi$  electrons of benzene are used to form a bond to bromine and give a cyclohexadienyl cation intermediate.

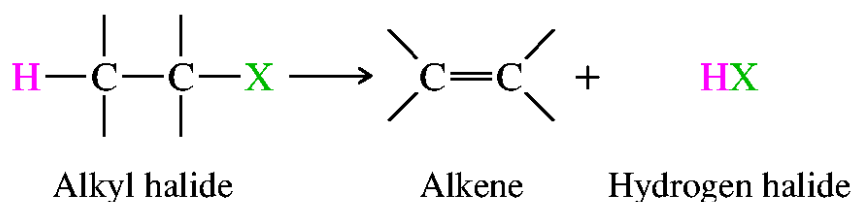


**Step 2:** Loss of a proton from the cyclohexadienyl cation yields bromobenzene.

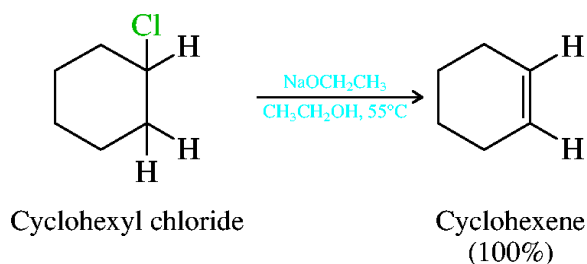
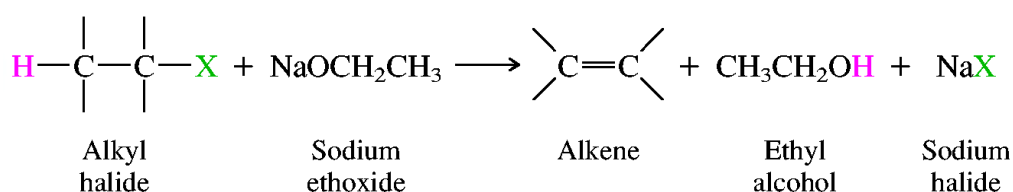


## DEHYDROHALOGENATION OF ALKYL HALIDES

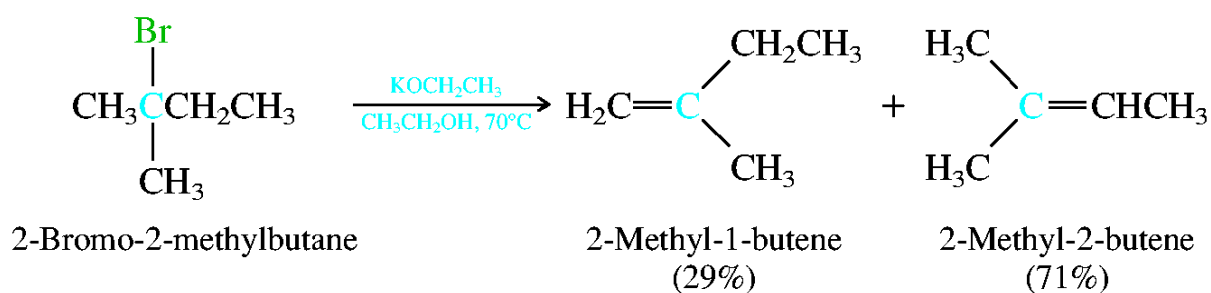
Dehydrohalogenation is the loss of a hydrogen and a halogen from an alkyl halide. It is one of the most useful methods for preparing alkenes by elimination.



When applied to the preparation of alkenes, the reaction is carried out in the presence of a strong base, such as sodium ethoxide ( $\text{NaOCH}_2\text{CH}_3$ ) in ethyl alcohol as solvent.

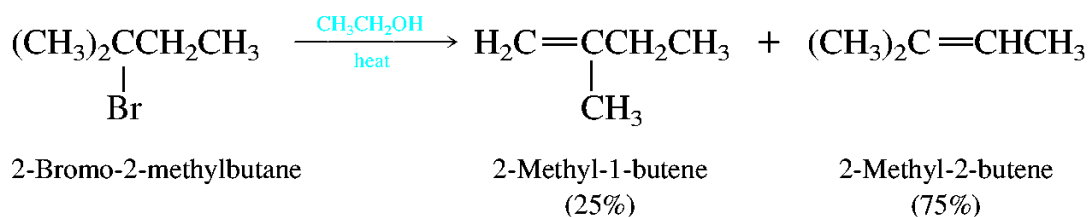


The regioselectivity of dehydrohalogenation of alkyl halides follows the Zaitsev rule: elimination predominates in the direction that leads to the more highly substituted alkene.



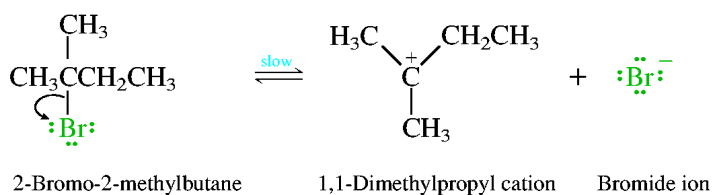
In its original form, Zaitsev's rule stated that the alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the  $\beta$  carbon having the fewest

## The reaction:

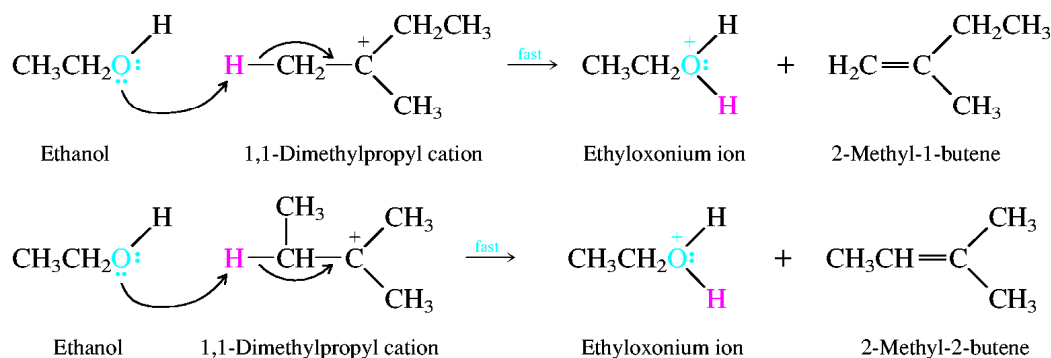


## The mechanism:

**Step (1):** Alkyl halide dissociates by heterolytic cleavage of carbon–halogen bond. (Ionization step)

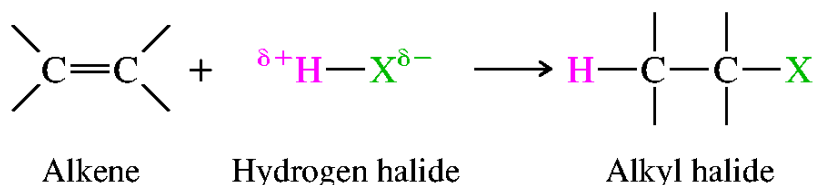


**Step (2):** Ethanol acts as a base to remove a proton from the carbocation to give the alkene products. (Deprotonation step)

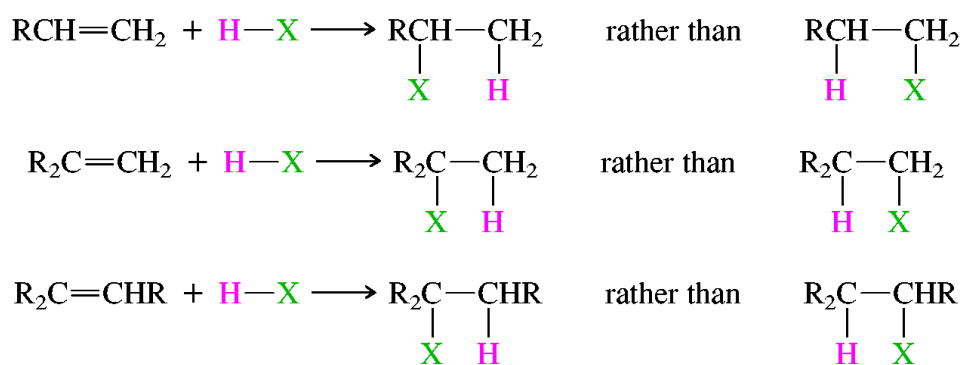


## ELECTROPHILIC ADDITION OF HYDROGEN HALIDES TO ALKENES: MARKOVNIKOV'S RULE

In many addition reactions the attacking reagent, unlike  $\text{H}_2$ , is a polar molecule. Hydrogen halides are among the simplest examples of polar substances that add to alkenes.



In principle a hydrogen halide can add to an unsymmetrical alkene (an alkene in which the two carbons of the double bond are not equivalently substituted) in either of two directions. In practice, addition is so highly **regioselective** as to be considered regiospecific.



In 1870, Vladimir Markovnikov, a colleague of Alexander Zaitsev at the University of Kazan, noticed a pattern in the hydrogen halide addition to alkenes and organized his observations into a simple statement. **Markovnikov's rule states that when an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogens, and the halogen adds to the carbon having fewer hydrogens.** The preceding general equations illustrate regioselective addition according to Markovnikov's rule, and the equations that follow provide some examples.

