

Babylon University / Pharmacy Collage

Department of Pharmaceutical Chemistry

**Monday..**

**13-16/3/2017**

## **(Lecture No. 3-4 : Alkanes )**

### Classification by structure: the family

The basis of organic chemistry, we have said, is the structural theory. We separate all organic compounds into a number of families on the basis of structure.

Having done this, we find that we have at the same time classified the compounds as to their physical and chemical properties. A particular set of properties is thus characteristic of a particular kind of structure.

### Structure of ethane

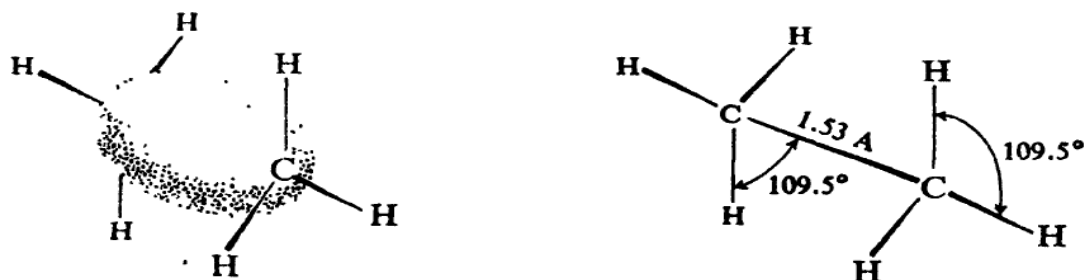
Next in size after methane is ethane,  $C_2H_6$ . If we connect the atoms of this molecule by covalent bonds, following the rule of one bond (one pair of electron), for each hydrogen and four bonds (four pairs of electrons) for each carbon, we arrive at the structure :



**Ethane**

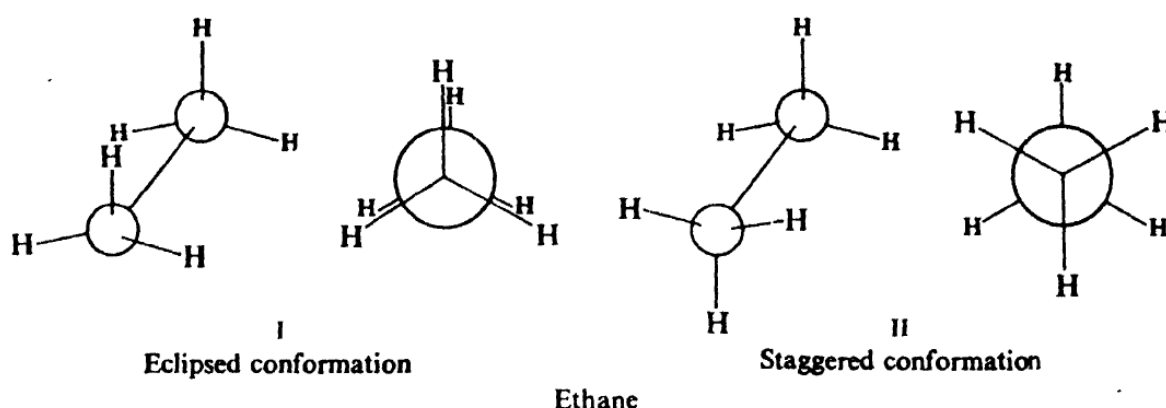
Each carbon is bonded to three hydrogens and to the other carbon. Since each carbon atom is bonded to four other atoms, its bonding orbitals ( $sp^3$  orbitals) are directed toward the corners of a tetrahedron. As in the case of methane, the carbon-hydrogen bonds result from overlap of these  $sp^3$  orbitals, with the  $s$  orbitals of the hydrogens. The carbon-carbon bond arises from overlap of two  $sp^3$  orbitals.

The carbon-hydrogen and carbon-carbon bonds have the same general electron distribution, being cylindrically symmetrical about a line joining the atomic nuclei ; because of this similarity in shape, the bonds are given the same name, a bonds (sigma bonds).



## Free rotation about the carbon-carbon single bond.

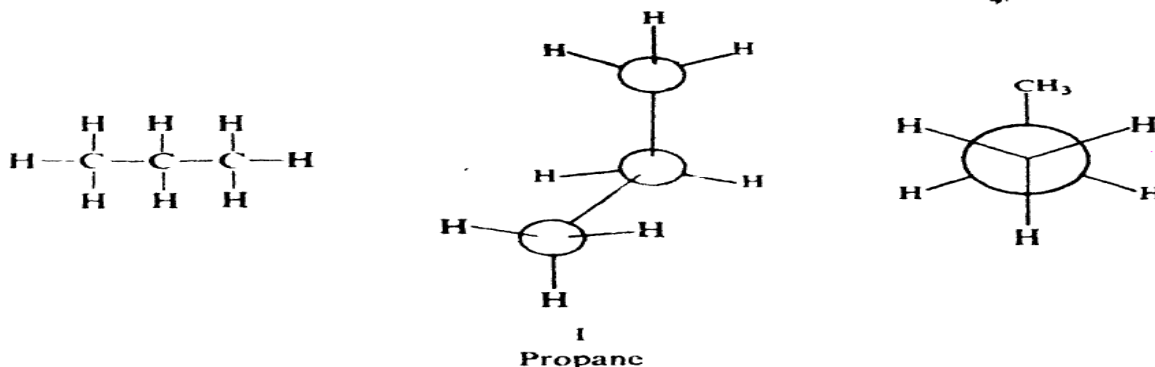
This particular set of bond angles and bond lengths still does not limit us to a single arrangement of atoms for the ethane molecule, since the relationship between the hydrogens of one carbon and the hydrogens of the other carbon is not specified.



## Propane and the butanes

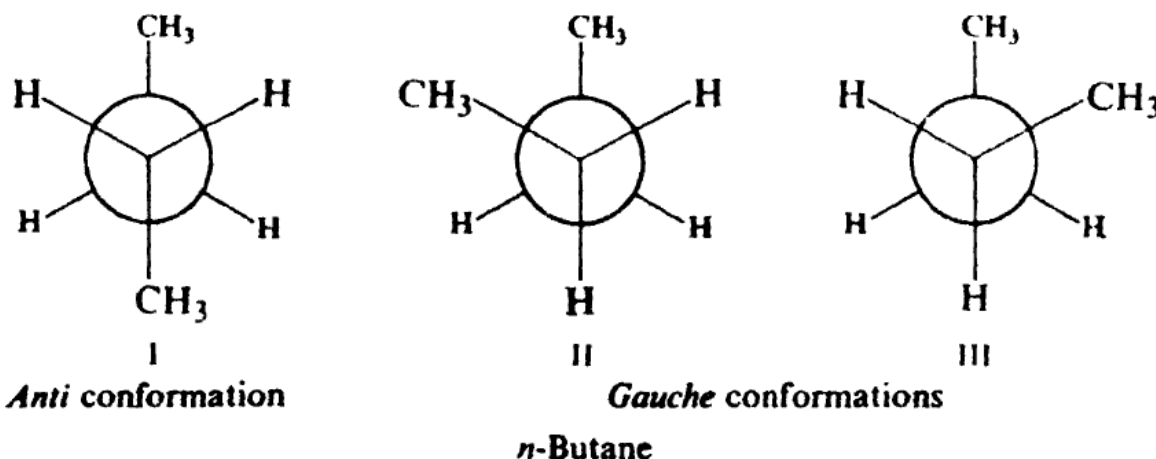
The next member of the alkane family is propane,  $C_3H_8$ . Again following the rule of one bond per hydrogen and four bonds per carbon, we arrive at structure I.

Here, rotation can occur about two carbon-carbon bonds, and again is essentially free. Although the methyl group is considerably larger than hydrogen, the rotational barrier (3.3 kcal/mole) is only a little higher than for ethane. Evidently there is still not significant crowding in the eclipsed conformation, and the rotational barrier is due chiefly to the same factor as the barrier in ethane: torsional strain.



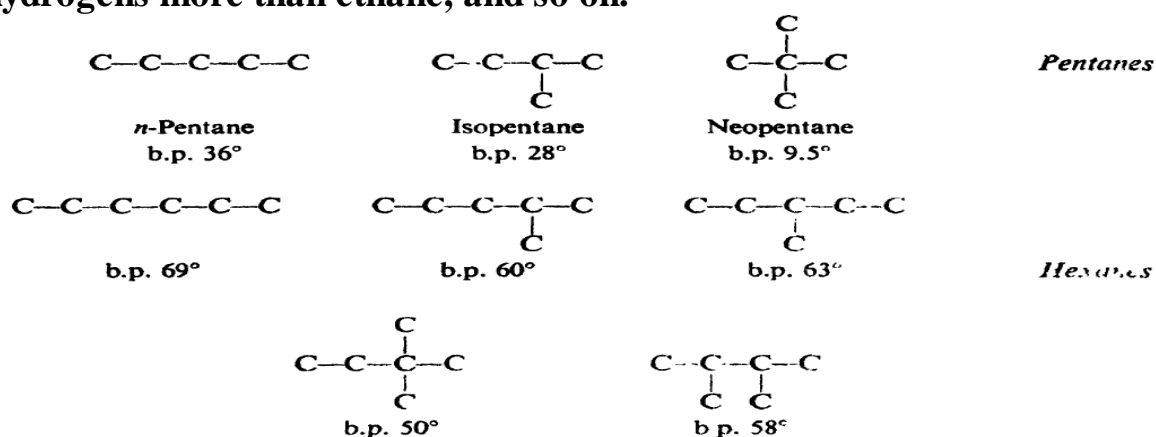
## Conformations of n-butane. Van der Waals repulsion

Let us look more closely at the n-butane molecule and the conformations in which it exists. Focusing our attention on the middle C - C bond, we see a molecule similar to ethane, but with a methyl group replacing one hydrogen on each carbon.



## Higher alkanes. The homologous series

If we examine the molecular formulas of the alkanes we have so far considered, we see that butane contains one carbon and two hydrogens more than propane, which in turn contains one carbon and two hydrogens more than ethane, and so on.



## Nomenclature

We have seen that the names methane, ethane, propane, butane, and pentane are used for alkanes containing respectively one, two, three, four, and five carbon atoms.

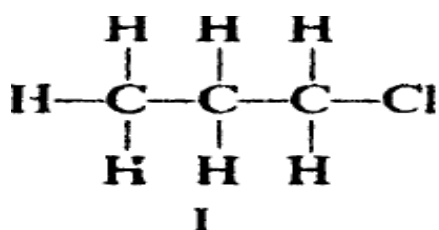
**Table 3.2 NAMES OF ALKANES**

CH <sub>4</sub>	methane	C <sub>9</sub> H <sub>20</sub>	nonane
C <sub>2</sub> H <sub>6</sub>	ethane	C <sub>10</sub> H <sub>22</sub>	decane
C <sub>3</sub> H <sub>8</sub>	propane	C <sub>11</sub> H <sub>24</sub>	undecane
C <sub>4</sub> H <sub>10</sub>	butane	C <sub>12</sub> H <sub>26</sub>	dodecane
C <sub>5</sub> H <sub>12</sub>	pentane	C <sub>14</sub> H <sub>30</sub>	tetradecane
C <sub>6</sub> H <sub>14</sub>	hexane	C <sub>16</sub> H <sub>34</sub>	hexadecane
C <sub>7</sub> H <sub>16</sub>	heptane	C <sub>18</sub> H <sub>38</sub>	octadecane
C <sub>8</sub> H <sub>18</sub>	octane	C <sub>20</sub> H <sub>42</sub>	eicosane

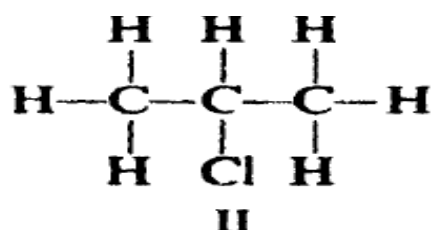
### Alkyl groups

In our study of inorganic chemistry, we found it useful to have names for certain groups of atoms that compose only part of a molecule and yet appear many times as a unit. For example, NH<sub>4</sub><sup>+</sup> is called ammonium ; NO<sub>3</sub><sup>-</sup>, nitrate ; SO<sub>3</sub><sup>-</sup>, sulfite; and so on.

In a similar way names are given to certain groups that constantly appear as structural units of organic molecules. We have seen that chloromethane, CH<sub>3</sub>Cl, is also known as methyl chloride. The CH<sub>3</sub> group is called methyl wherever it appears, CH<sub>3</sub>Br being methyl bromide, CH<sub>3</sub>I, methyl iodide, and CH<sub>3</sub>OH, methyl alcohol. In an analogous way, the C<sub>2</sub>H<sub>5</sub> group is ethyl; C<sub>3</sub>H<sub>7</sub>, propyl ; C<sub>4</sub>H<sub>9</sub>, butyl; and so on. These groups are named simply by dropping -ane from the name of the corresponding alkane and replacing it by -yl. They are known collectively as alkyl groups. The general formula for an alkyl group is C<sub>n</sub>H<sub>2n+1</sub>, since it contains one less hydrogen than the parent alkane, C<sub>n</sub>H<sub>2n+2</sub>.



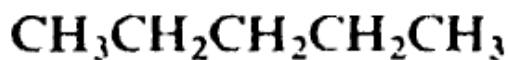
***n*-Propyl chloride**



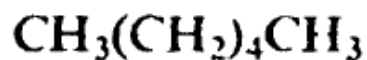
**Isopropyl chloride**

### Common names of alkanes

As we have seen, the prefixes *n*-, *iso*-, and *neo*- are adequate to differentiate the various butanes and pentanes, but beyond this point an impracticable number of prefixes would be required.



*n*-Pentane



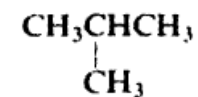
*n*-Hexane

### IUPAC names of alkanes

To devise a system of nomenclature that could be used for even the most complicated compounds, various committees and commissions representing the chemists of the world have met periodically since 1892. In its present modification, the system so devised is known as the IUPAC system (International Union of Pure and Applied Chemistry). Since this system follows much the same pattern for all families of organic compounds, we shall consider it in some detail as applied to the alkanes.

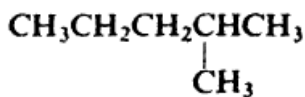
Essentially the rules of the IUPAC system are:

1. Select as the parent structure the longest continuous chain, and then consider the compound to have been derived from this structure by the replacement of hydrogen by various alkyl groups. Isobutane (I) can be considered to arise from propane by the replacement of a hydrogen atom by a methyl group, and thus may be named methylpropane .



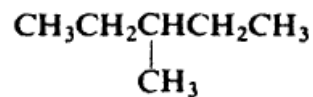
I

Methylpropane  
(Isobutane)



II

2-Methylpentane



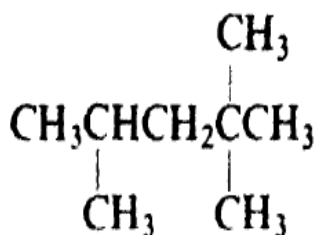
III

3-Methylpentane

2. Where necessary, as in the isomeric methylpentanes (II and III), indicate by a number the carbon to which the alkyl group is attached.

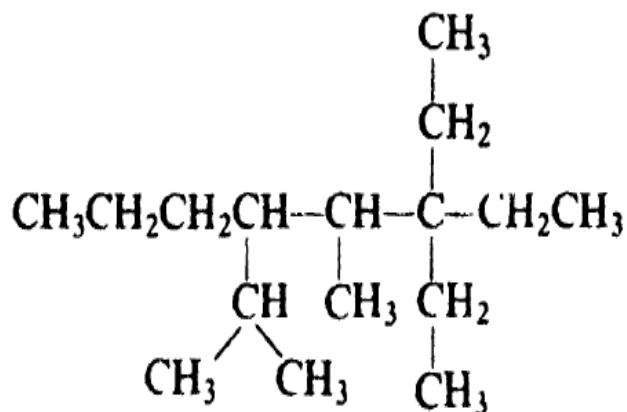
3. In numbering the parent carbon chain, start at whichever end results in the use of the lowest numbers; thus II is called 2-methylpentane rather than 4-methylpentane.

4. If the same alkyl group occurs more than once as a side chain, indicate this by the prefix di- , tri-, tetra-, etc., to show how many of these alkyl groups there are, and indicate by various numbers the positions of each group, as in 2,2,4-trimethylpentane (IV).



IV

2,2,4-Trimethylpentane



V

4-Methyl-3,3-diethyl-5-isopropyloctane

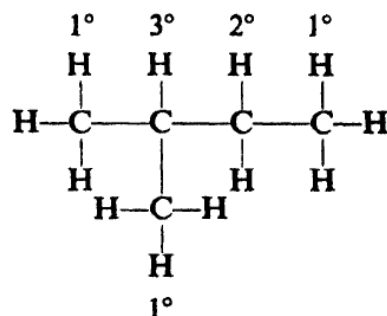
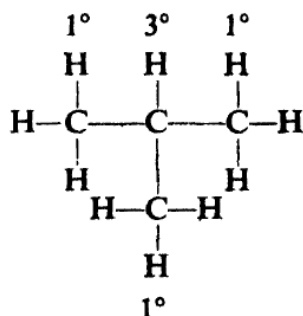
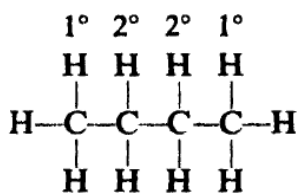
5. If there are several different alkyl groups attached to the parent chain, name them in order of increasing size or in alphabetical order; as in 4-methyl-3,3-diethyl-5-isopropyloctane (V).

There are additional rules and conventions used in naming very complicated alkanes, but the five fundamental rules mentioned here will suffice for the compounds we are likely to encounter.

### Classes of carbon atoms and hydrogen atoms

It has been found extremely useful to classify each carbon atom of an alkane with respect to the number of other carbon atoms to which it is attached.

A primary ( $1^\circ$ ) carbon atom is attached to only one other carbon atom; a secondary ( $2^\circ$ ) is attached to two others; and a tertiary ( $3^\circ$ ) to three others. For example:



Each hydrogen atom is similarly classified, being given the same designation of primary, secondary, or tertiary as the carbon atom to which it is attached. We shall make constant use of these designations in our consideration of the relative reactivities of various parts of an alkane molecule.

### Physical properties

The physical properties of the alkanes follow the pattern laid down by methane, and are consistent with the alkane structure. An alkane molecule is held together entirely by covalent bonds. These bonds either join two atoms of the same kind and hence are non-polar, or join two atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar.

### Industrial source

The principal source of alkanes is petroleum, together with the accompanying natural gas. Decay and millions of years of geological stresses have transformed the complicated organic compounds that once made up living plants or animals into a mixture of alkanes ranging in size from one carbon to 30 or 40 carbons.

### Industrial source vs. laboratory preparation

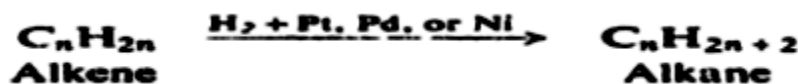
We shall generally divide the methods of obtaining a particular kind of organic compound into two categories: industrial source and laboratory preparation. We may contrast the two in the following way, although it must be realized that there are many exceptions to these generalizations. An industrial source must provide large amounts of the desired material at the lowest possible cost. A laboratory preparation may be required to produce only a few hundred grams or even a few grams; cost is usually of less importance than the time of the investigator. For many industrial purposes a mixture may be just as suitable as a pure compound; even when a single compound is required, it may be economically feasible to separate it from a mixture, particularly when the other components may also be marketed. In the laboratory a chemist nearly always wants a single pure compound. Separation of a single compound from a mixture of related substances is very time-consuming and frequently does not yield material of the required purity. Furthermore, the raw material for a particular preparation may well be the hard-won product of a previous preparation or even series of preparations, and hence he wishes to convert it as completely as possible into his desired compound.

### Preparation

Each of the smaller alkanes, from methane through pentane and isopentane, can be obtained in pure form by fractional distillation of petroleum and natural gas; neopentane does not occur naturally. Above the pentanes the number of isomers of each homolog becomes so large and the boiling point differences become so small that it is no longer feasible to isolate individual, pure compounds; these alkanes must be synthesized by one of the methods outlined below. In some of these equations, the symbol R is used to represent any alkyl group. This convenient device helps to summarize reactions that are typical of an entire family, and emphasizes the essential similarity of the various members. In writing these generalized equations, however, we must not lose sight of one important point. An equation involving RC1, to take a specific example, has meaning only in terms of a reaction that we can carry out in the laboratory using a real compound, like methyl chloride or tert-butyl chloride. Although- typical of alkyl halides, a reaction may differ widely in rate or yield depending upon the particular alkyl group actually concerned. We may use quite different experimental conditions for methyl chloride than for ten- butyl chloride; in an extreme case, a reaction that goes well for methyl chloride might go so slowly or give so many side products as to be completely useless for tert-butyl chloride.

## PREPARATION OF ALKANES

### 1. Hydrogenation of alkenes.

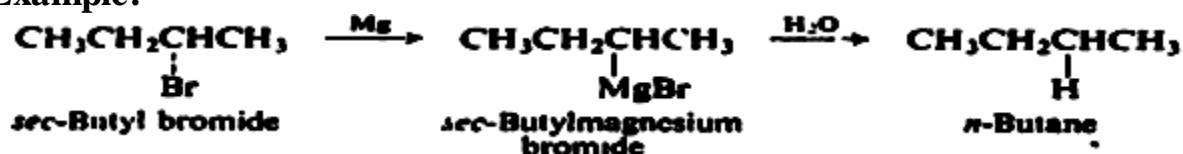


### 2. Reduction of alkyl halides

#### (a) Hydrolysis of Grignard reagent.



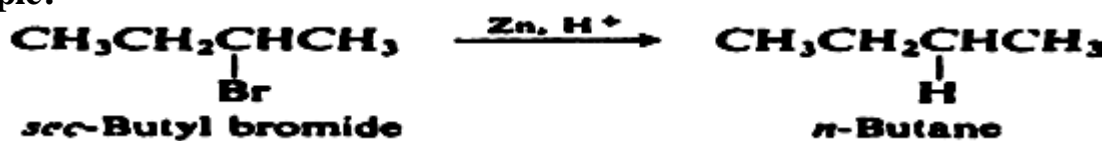
Example:



#### (b) Reduction by metal and acid.

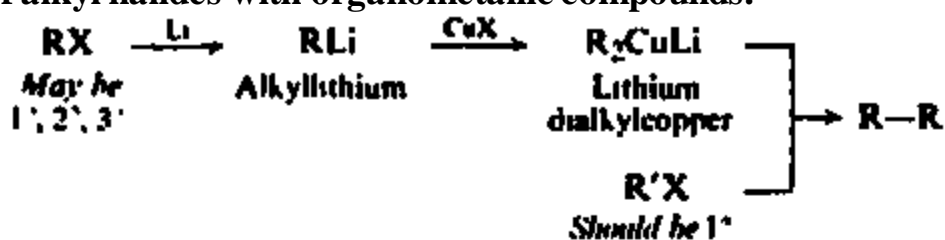


Example:

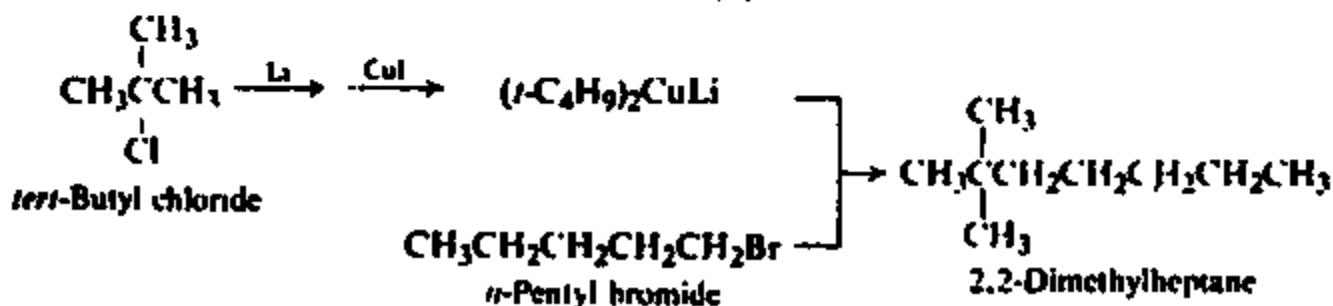
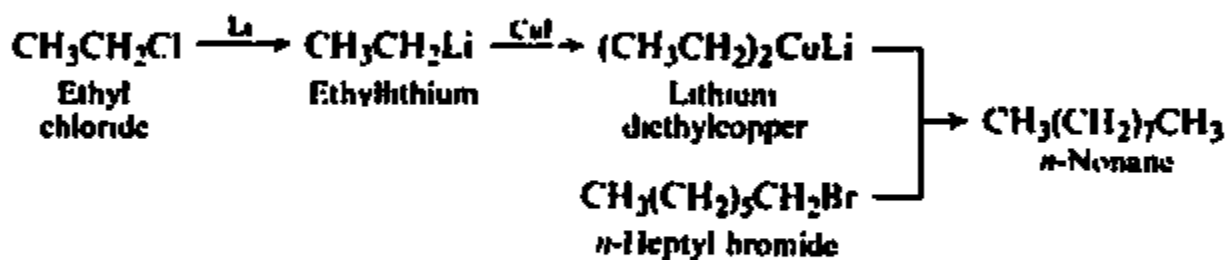




## 3. Coupling of alkyl halides with organometallic compounds.



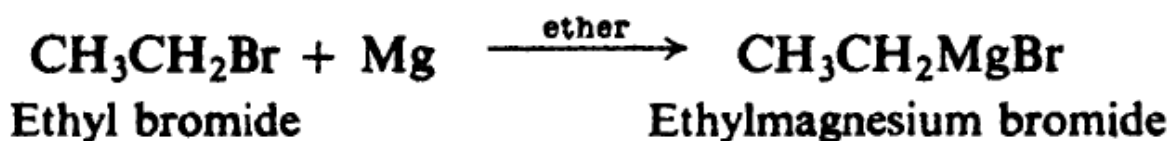
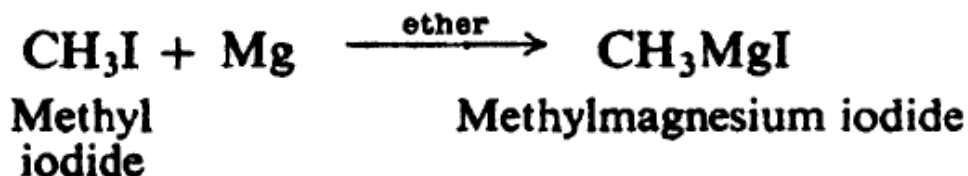
**Examples:**



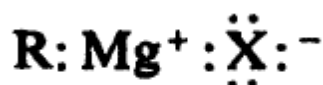
By far the most important of these methods is the hydrogenation of alkenes. When shaken under a slight pressure of hydrogen gas in the presence of a small amount of catalyst, alkenes are converted smoothly and quantitatively into alkanes of the same carbon skeleton. The method is limited only by the availability of the proper alkene. This is not a very serious limitation. Alkenes are readily prepared, chiefly from alcohols, which in turn can be readily synthesized in a wide variety of sizes and shapes. Reduction of an alkyl halide, either via the Grignard reagent or directly with metal and acid, involves simply the replacement of a halogen atom by a hydrogen atom; the carbon skeleton remains intact. This method has about the same applicability as the previous method, since, like alkenes, alkyl halides are generally prepared from alcohols. Where either method could be used, the hydrogenation of alkenes would probably be preferred because of its simplicity and higher yield. The coupling of alkyl halides with organometallic compounds is the only one of these methods in which carbon-carbon bonds are formed and a new, bigger carbon skeleton is generated.

The Grignard reagent: an organometallic compound

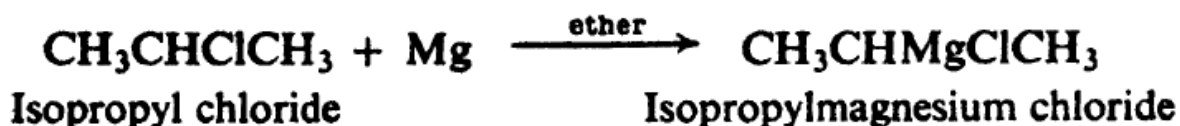
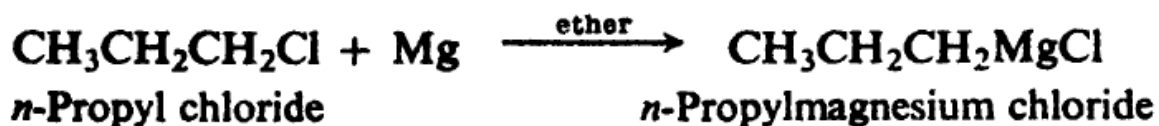
When a solution of an alkyl halide in dry ethyl ether, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, is allowed to stand over turnings of metallic magnesium, a vigorous reaction takes place: the solution turns cloudy, begins to boil, and the magnesium metal gradually disappears. The resulting solution is known as a Grignard reagent, after Victor Grignard (of the University of Lyons) who received the Nobel prize in 1912 for its discovery. It is one of the most useful and versatile reagents known to the organic chemist.



The Grignard reagent has the general formula RMgX, and the general name alkylmagnesium halide. The carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesiumhalogen bond is essentially ionic .

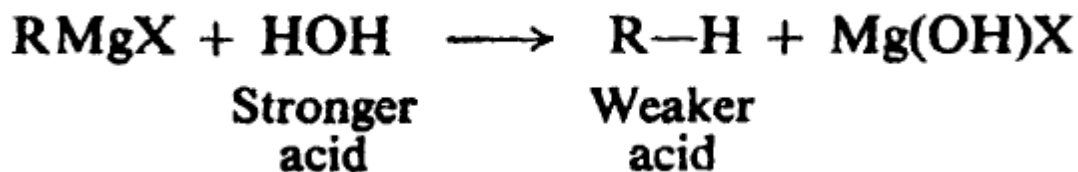


Since magnesium becomes bonded to the same carbon that previously held halogen, the alkyl group remains intact during the preparation of the reagent. Thus n-propyl chloride yields n-propylmagnesium chloride, and isopropyl chloride yields isopropylmagnesium chloride.

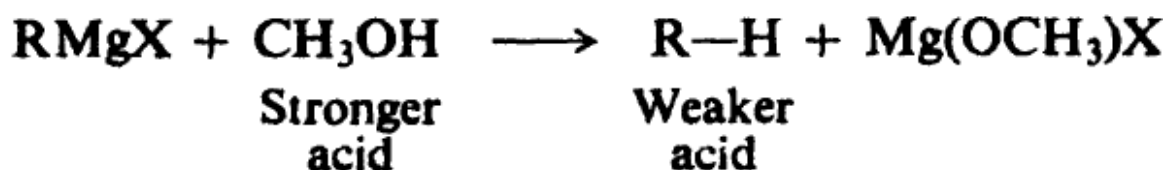
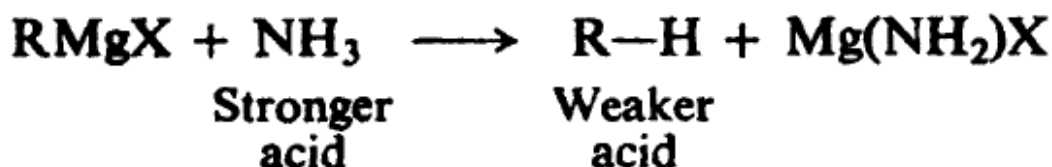


The reaction with water to form an alkane is typical of the behavior of the Grignard reagent and many of the more reactive organometallic compounds toward acids. In view of the marked carbanion character of the alkyl group, we may consider the Grignard reagent to be the magnesium salt, RMgX, of the extremely weak acid, R H. The reaction is simply the

displacement of the weaker acid, R H, from its salt by the stronger acid, HOH.



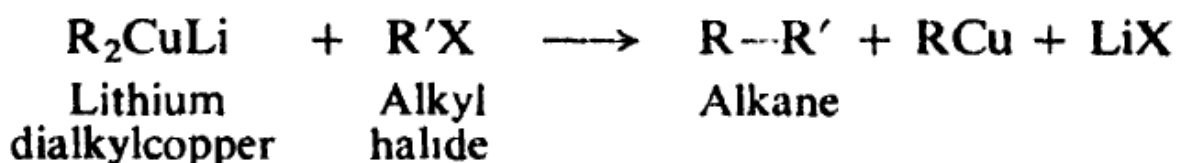
An alkane is such a weak acid that it is displaced from the Grignard reagent by compounds that we might ordinarily consider to be very weak acids themselves, or possibly not acids at all. Any compound containing hydrogen attached to oxygen or nitrogen is tremendously more acidic than an alkane, and therefore can decompose the Grignard reagent: for example, ammonia or methyl alcohol.



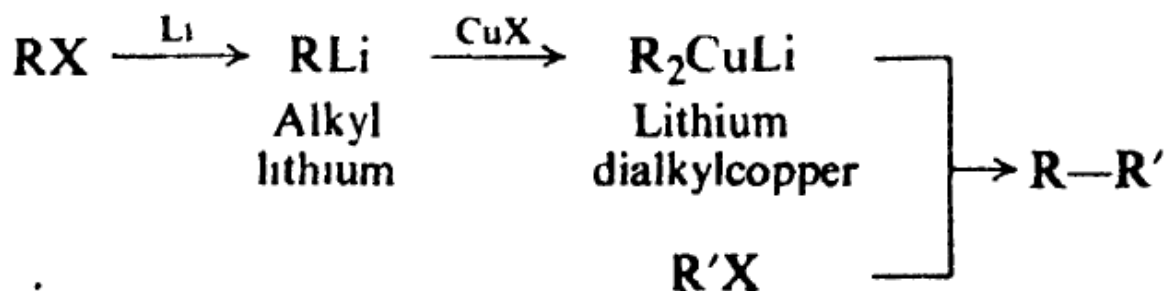
### Coupling of alkyl halides with organometallic compounds

To make an alkane of higher carbon number than the starting material requires formation of carbon-carbon bonds, most directly by the coupling together of two alkyl groups.

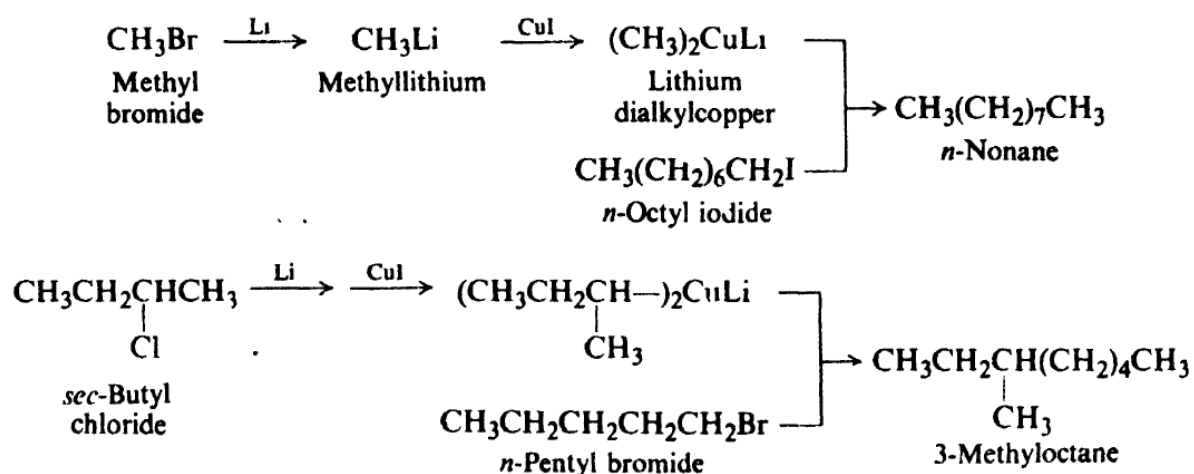
Coupling takes place in the reaction between a lithium dialkylcopper,  $\text{R}_2\text{CuLi}$ , and an alkyl halide,  $\text{R}'\text{X}$ . ( $\text{R}'$  stands for an alkyl group that may be the same as, or different from,  $\text{R}$ .)



An alkyllithium,  $\text{RLi}$ , is prepared from an alkyl halide,  $\text{RX}$ , in much the same way as a Grignard reagent. To it is added cuprous halide,  $\text{CuX}$ , and then, finally, the second alkyl halide,  $\text{R}'\text{X}$ . Ultimately, the alkane is synthesized from the two alkyl halides,  $\text{RX}$  and  $\text{R}'\text{X}$ .



For good yields, R'X should be a primary halide; the alkyl group R in the organometallic may be primary, secondary, or tertiary. For example:



The choice of organometallic reagent is crucial. Grignard reagents or organolithium compounds, for example, couple with only a few unusually reactive organic halides.

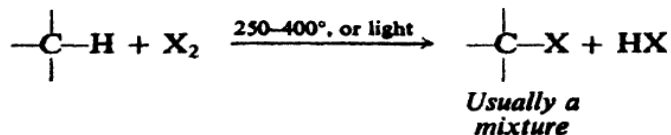
## Reactions

The alkanes are sometimes referred to by the old-fashioned name of paraffins. This name (Latin: parum affinis, not enough affinity) was given to describe what appeared to be the low reactivity of these hydrocarbons. Much of the chemistry of alkanes involves free-radical chain reactions, which take place under vigorous conditions and usually yield mixtures of products. A reactive particle typically an atom or free radical is needed to begin the attack on an alkane molecule. It is the generation of this reactive particle that requires the vigorous conditions: the dissociation of a halogen molecule into atoms, for example, or even (as in pyrolysis) dissociation of the alkane molecule itself. In its attack, the reactive particle abstracts hydrogen from the alkane; the alkane itself is thus converted into a reactive particle which continues the reaction sequence, that is, carries on the chain. But an alkane molecule contains many hydrogen atoms and the particular product eventually obtained depends upon which of these hydrogen atoms is abstracted. Although an attacking particle may show a certain selectivity, it can abstract a hydrogen

from any part of the molecule, and thus bring about the formation of many isomeric products.

## REACTIONS OF ALKANES

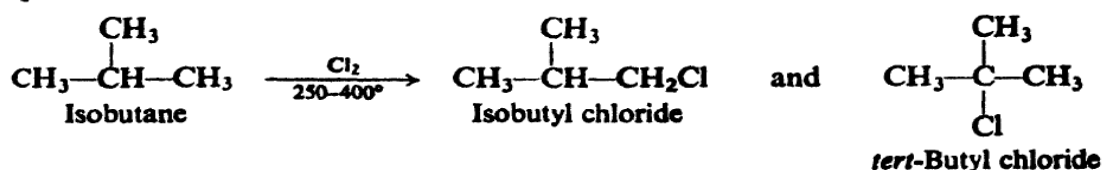
### 1. Halogenation. Discussed in Secs. 3.19–3.22.



**Reactivity**



*Example:*



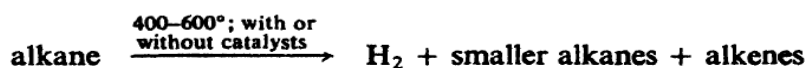
### 2. Combustion. Discussed in Sec. 3.30.



*Example:*

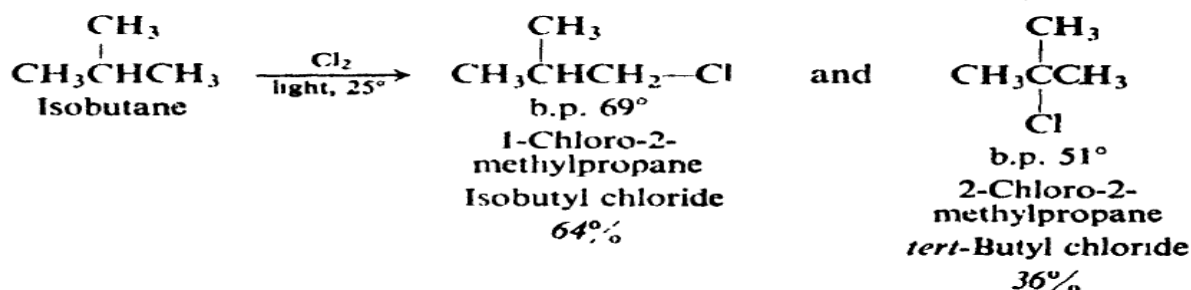
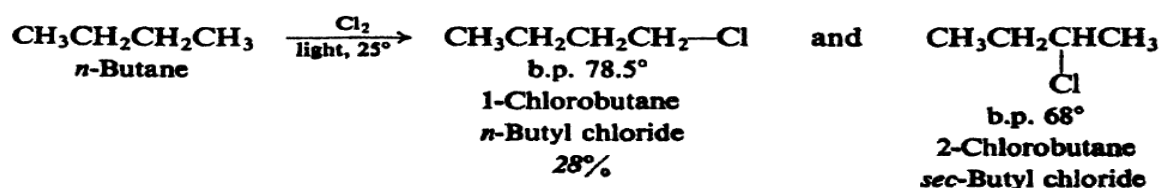
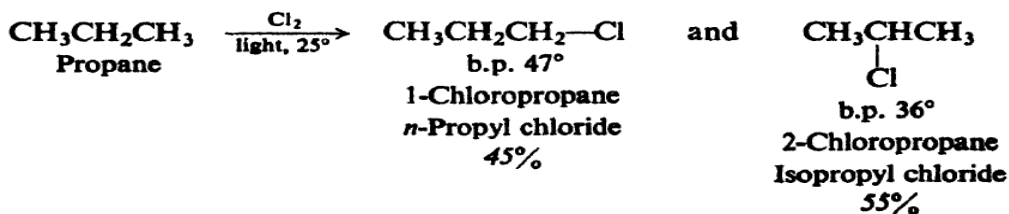
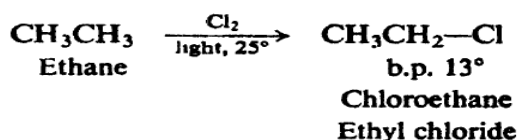


### 3. Pyrolysis (cracking). Discussed in Sec. 3.31.

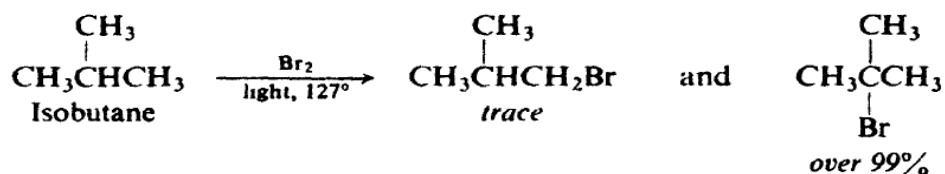
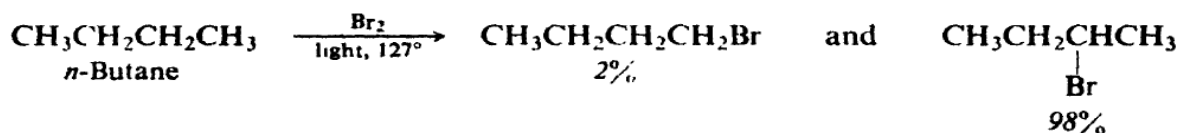
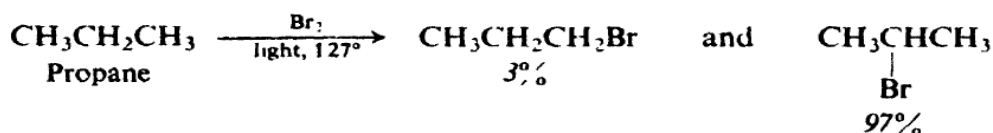
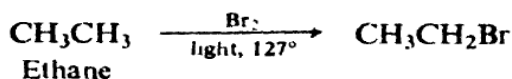


## Halogenation

As we might expect, halogenation of the higher alkanes is essentially the same as the halogenation of methane. It can be complicated, however, by the formation of mixtures of isomers.

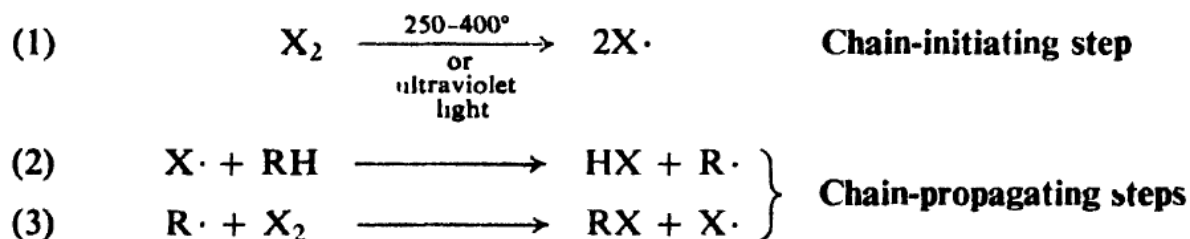


Bromination gives the corresponding bromides but in different proportions:



## Mechanism of halogenation

Halogenation of alkanes proceeds by the same mechanism as halogenation of methane:



then (2), (3), (2), (3), etc., until finally a chain is terminated  
 A halogen atom abstracts hydrogen from the alkane (RH) to form an alkyl radical (R·). The radical in turn abstracts a halogen atom from a halogen molecule to yield the alkyl halide (RX).

Which alkyl halide is obtained depends upon which alkyl radical is formed.

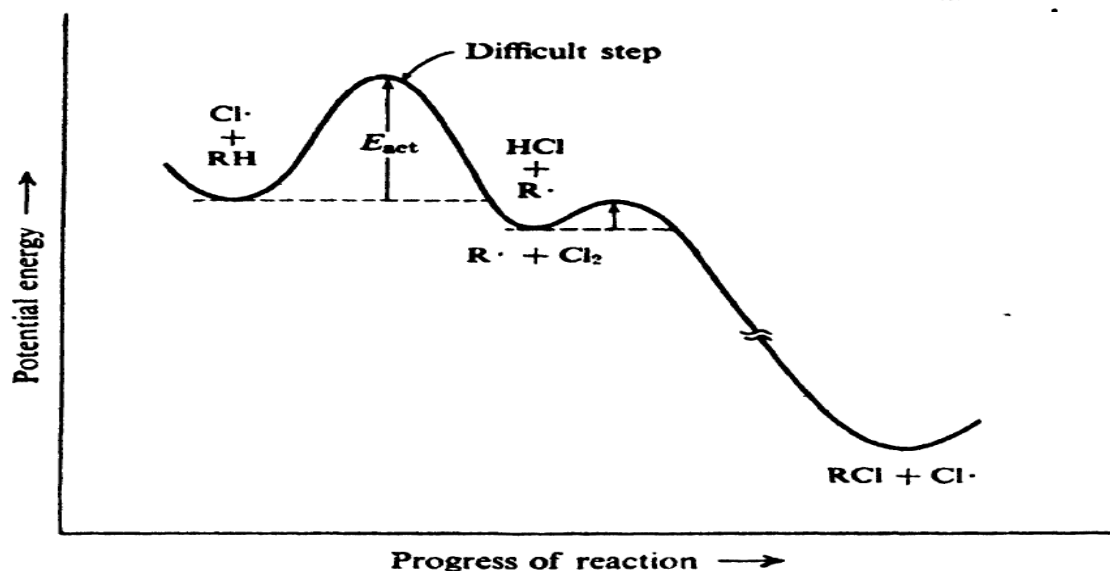
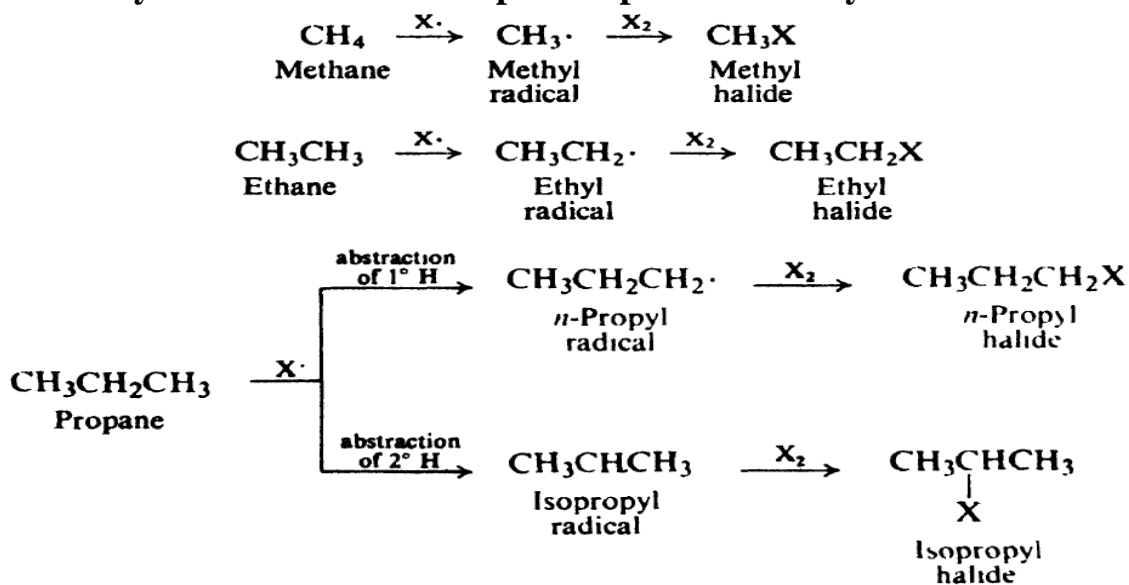
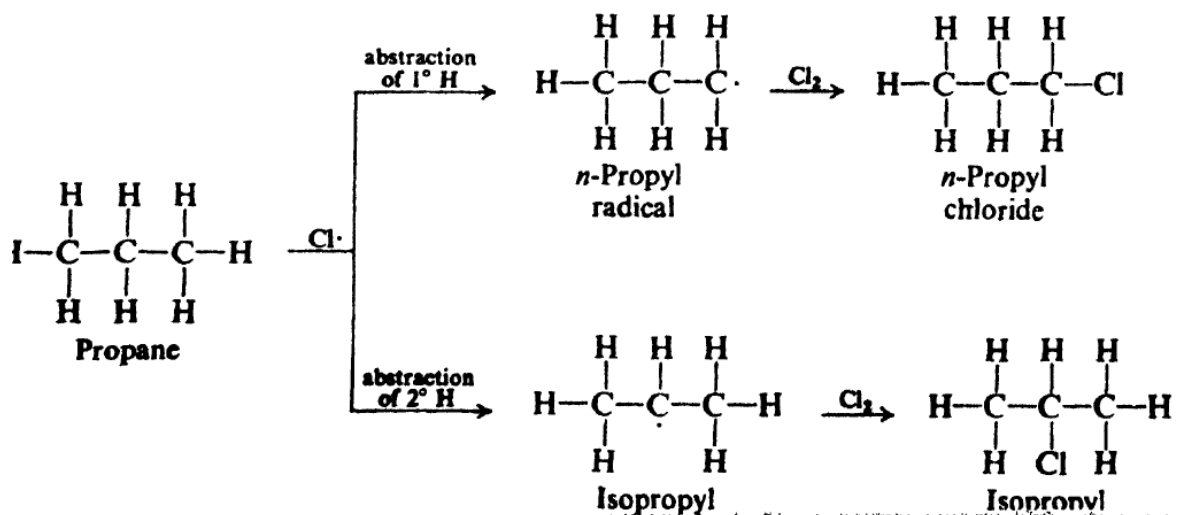


Figure :: Potential energy changes during progress of reaction: chlorination of an alkane. Formation of radical is rate-controlling step.

### Orientation of halogenation

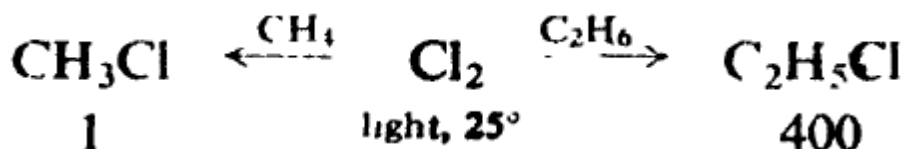
With this background let us turn to the problem of orientation; that is, let us examine the factors that determine where in a

molecule reaction is most likely to occur. As an example let us take chlorination of propane. The relative amounts of n-propyl chloride and isopropyl chloride obtained depend upon the relative rates at which n-propyl radicals and isopropyl radicals are formed. If, say, isopropyl radicals are formed faster, then isopropyl chloride will be formed faster, and will make up a larger fraction of the product. As we can see, n-propyl radicals are formed by abstraction of primary hydrogens, and isopropyl radicals by abstraction of secondary hydrogens.



### Relative reactivities of alkanes toward halogenation

The best way to measure the relative reactivities of different compounds toward the same reagent is by the method of competition, since this permits an exact quantitative comparison under identical reaction conditions. For example, if equimolar amounts of methane and ethane are allowed to react with a small amount of chlorine, about 400 times as much ethyl chloride as methyl chloride is obtained, showing that ethane is 400 times as reactive as methane. When allowance is made for the relative numbers of hydrogens in the two kinds of molecules, we see that each hydrogen of ethane is as reactive as each hydrogen of methane.



### Ease of abstraction of hydrogen atoms. Energy of activation

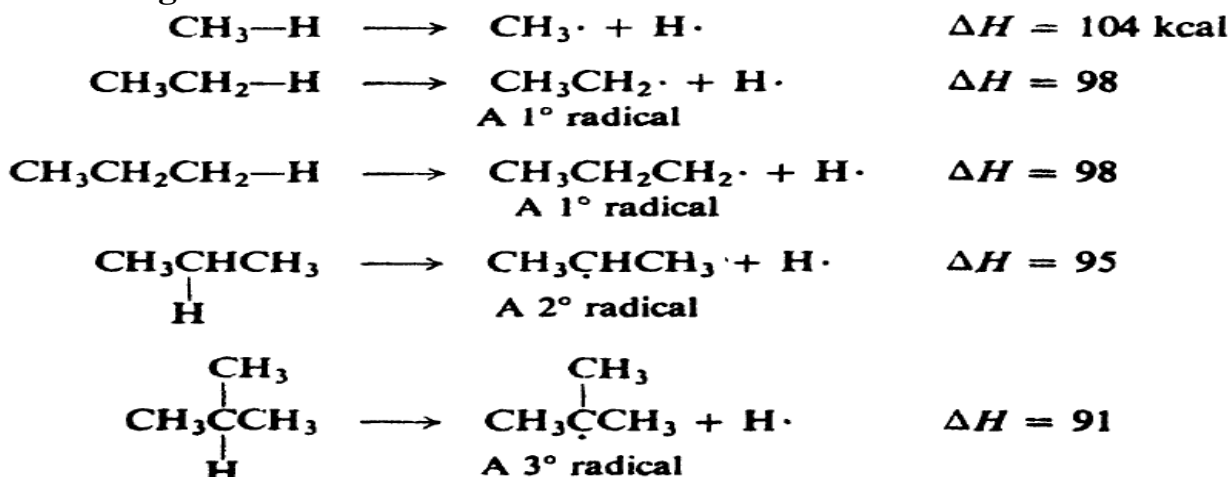


At this stage we can summarize the effect of structure on halogenation of alkanes in the following way. The controlling step in halogenation is abstraction of hydrogen by a halogen atom :



### Stability of free radicals

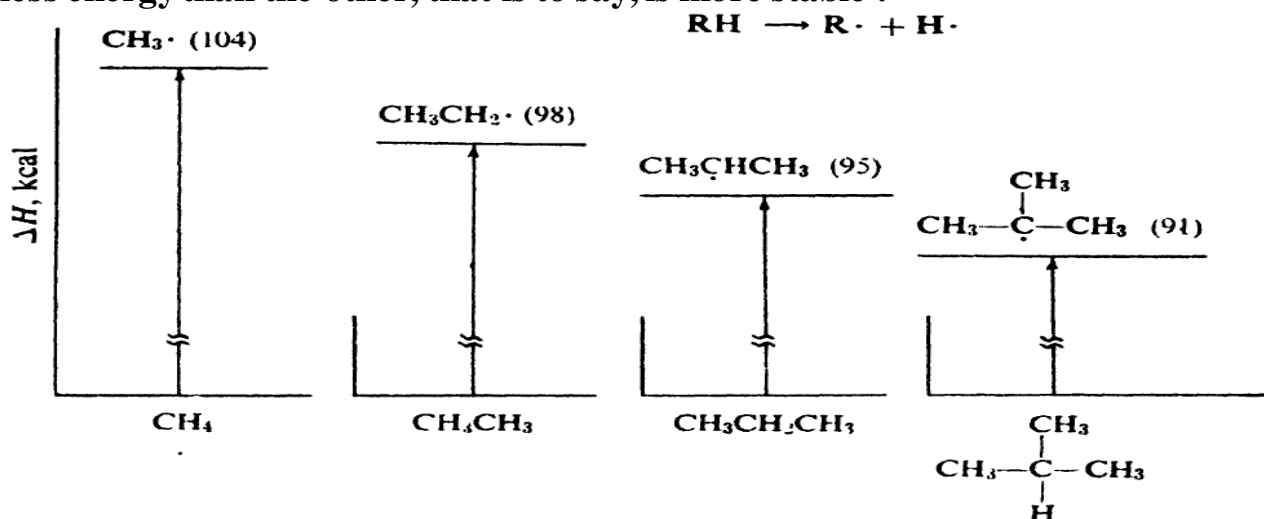
We find the dissociation energies of the bonds that hold hydrogen atoms to a number of groups. These values are the  $\Delta H$ 's of the following reactions:



By definition, bond dissociation energy is the amount of energy that must be supplied to convert a mole of alkane into radicals and hydrogen atoms. As we can see, the amount of energy needed to form the various classes of radicals decreases in the order :  $\text{CH}_3\cdot > 1^\circ > 2^\circ > 3^\circ$ .



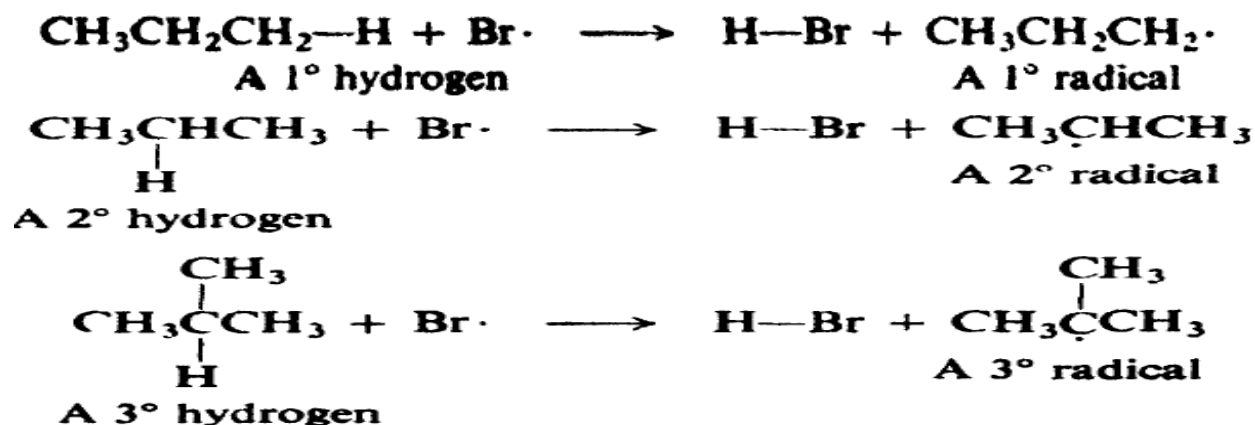
If less energy is needed to form one radical than another, it can only mean that, relative to the alkane from which it is formed, the one radical contains less energy than the other, that is to say, is more stable .



Relative stabilities of free radicals. (Plots aligned with each other for easy comparison.)

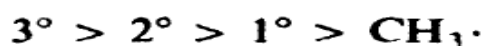
### Ease of formation of free radicals

Let us return to the halogenation of alkanes. Orientation and reactivity, are governed by the relative ease with which the different classes of hydrogen, atoms are abstracted. Just by definition, the hydrogen being abstracted and the radical being formed belong to the same class. Abstraction of a primary hydrogen yields a primary radical, abstraction of a secondary hydrogen yields a secondary radical, and so on. For example:



If the ease of abstraction of hydrogen atoms follows the sequence  $3^\circ > 2^\circ > 1^\circ > \text{CH}_4$ , then the ease of formation of free radicals must follow the same sequence:

**Ease of formation  
of free radicals**



In listing free radicals in order of their ease of formation, we find that we have at the same time listed them in order of their stability. The more stable the free radical, the more easily it is formed.

### Transition state for halogenation

Is it reasonable that the more stable radical should be formed more easily? We have already seen that the differences in reactivity toward halogen atoms are due chiefly to differences in  $E_{\text{act}}$ : the more stable the radical, then, the lower the  $E_{\text{act}}$  for its formation. This, in turn, means that the more stable the radical, the more stable the transition state leading to its formation both stabilities being measured, as they must be, against the same standard, the reactants.

