



# Organic chemistry

Lec: 6

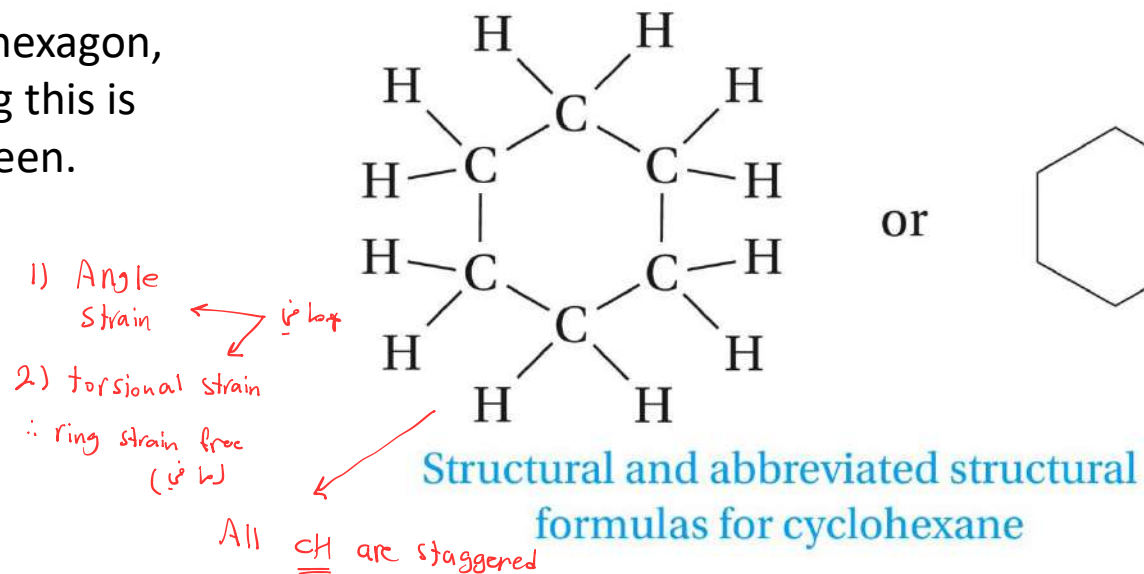
Done by: Dema Alhussine

# أكثر واحد مستقر ← cyclohexane

Cycloalkanes: cyclohexane – “chair”

- It is highly flexible and can adopt a **strain free** non-planar conformation with bond angle of 109.5°
- It is very common in nature so understanding its conformations is important.

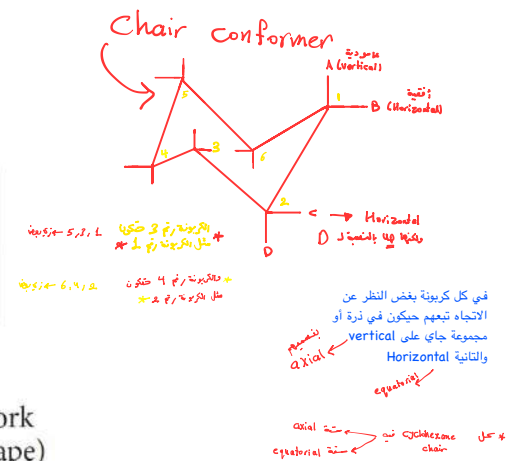
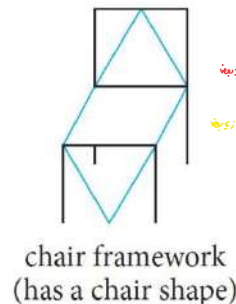
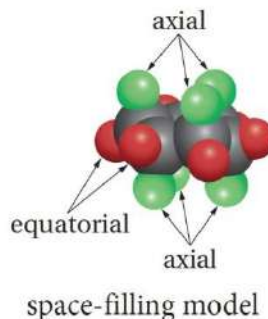
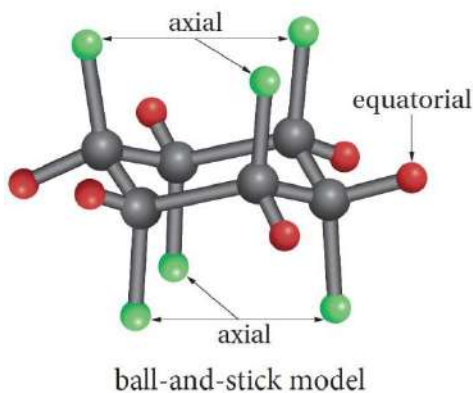
Although commonly drawn as a hexagon, implying a flat six-membered ring this is not the common conformation seen.



# Conformational Isomers (cont'd)

Cyclohexane cont'd:

The most common conformation of cyclohexane is the “chair” conformation. In this geometry the C bonds are all  $\sim 109.5^\circ$  as opposed to the  $120^\circ$  in a planar structure.

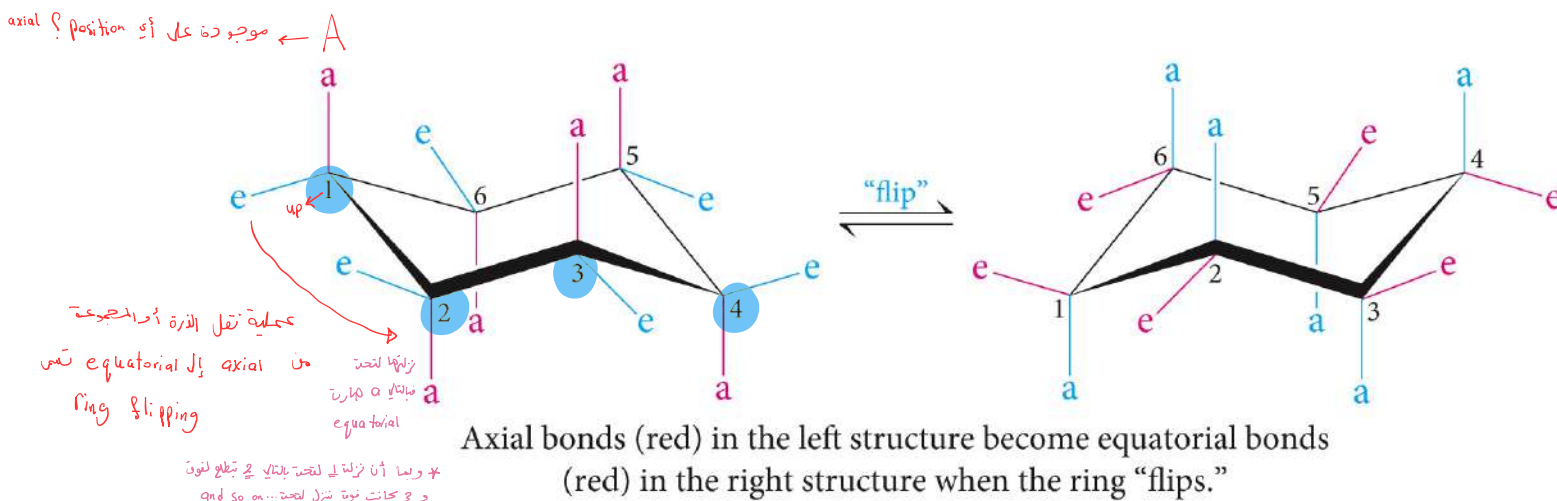


This structure creates two subsets of hydrogen atoms, those lying in the same plane as the C atoms, the equatorial H and those lying above and below that plane, the axial H atoms

Cyclohexane **interconverts** between two **chair conformers**.

Cyclohexane cont'd:

Since the C-C bonds are all single ( $\sigma$ ) bonds, it is possible to rotate about these bonds. This process is known as a **ring inversion** or a "chair-chair" **flip**. In the process of the inversion **all equatorial H become axial and axial become equatorial**.



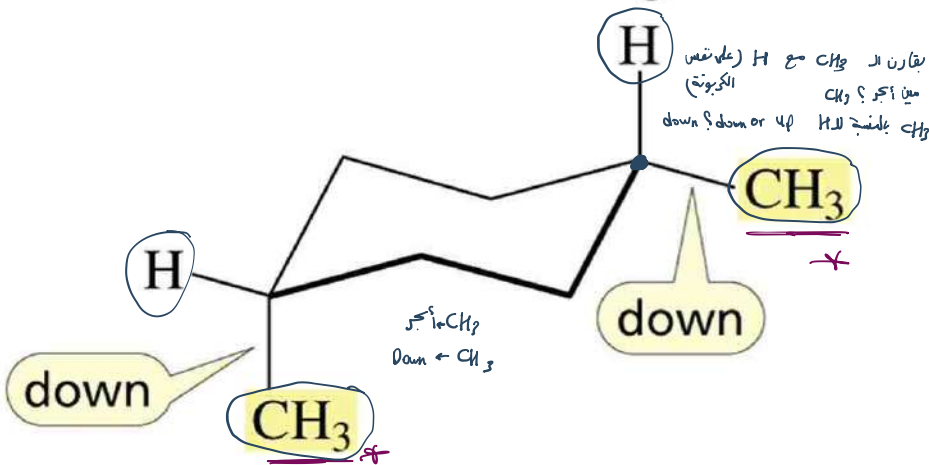
← موجود في الـ cycloAlkane بشكل عام

# Cis and Trans Isomers

رواصه سترين الي مو Chair conformer

two methyl groups are on the same side of the ring

عكشان اُصيني بينا Cis, trans



## cis-1,4-dimethylcyclohexane

← إذا كانوا الاثنين up أو الاثنين down ← جونا cis  
إذا عكس بعض ← trans

← لو عكشنا ring flipping لا cis بل trans

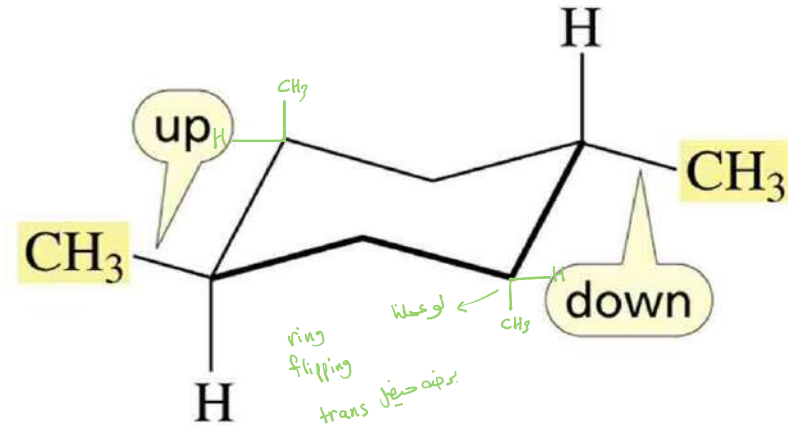
← عادي ملس شرط يكونوا

← رخصا هذا الحلال الـ energy صغير

ثابتة ← والـ stability ثابتة

(معهم)

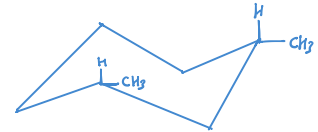
two methyl groups are on opposite sides of the ring



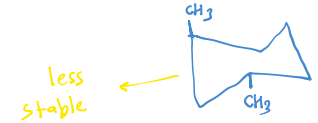
## trans-1,4-dimethylcyclohexane

← لو عكشنا ring flipping ← الـ ring flipping ← الـ ring flipping ← الـ ring flipping

less stable ← 1) ring flipping  
more stable ← 2) ring flipping  
equivalent ← 3) ring flipping



← لو عكشنا ring flipping



less stable

# Conformational Isomers (cont'd)

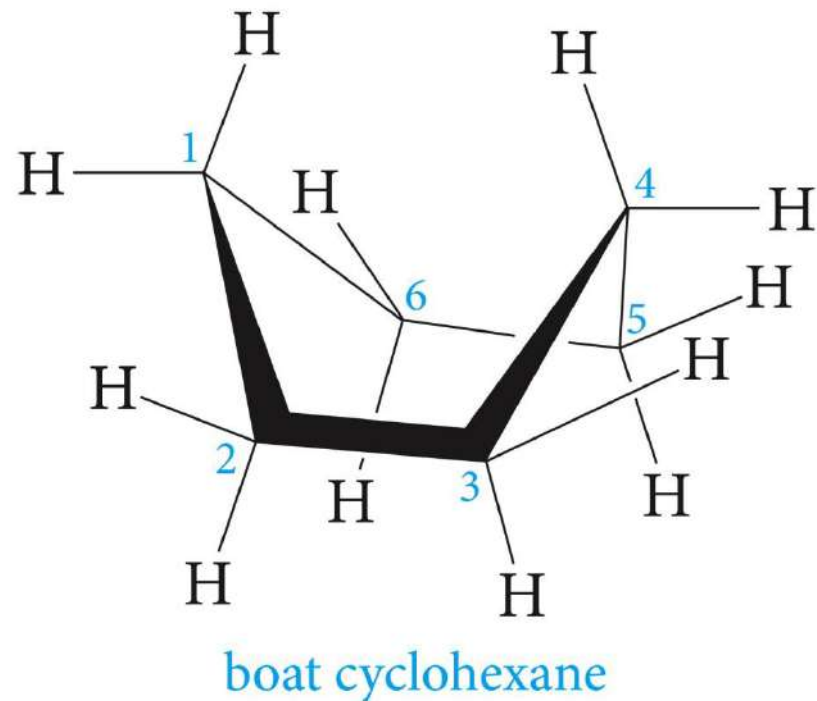
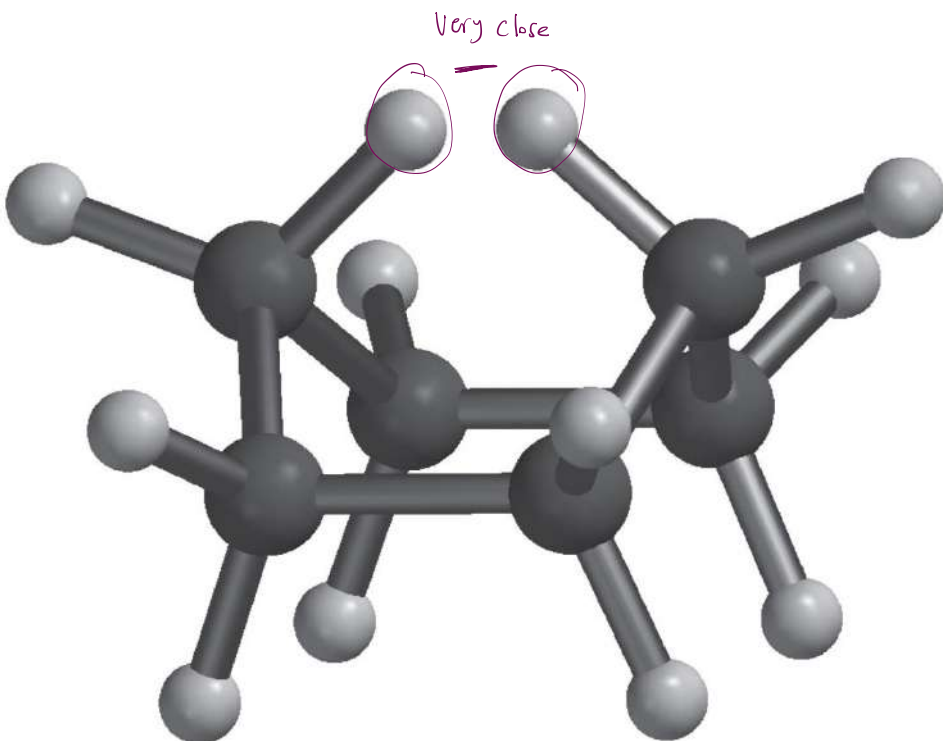
Cyclohexane cont'd:

Other conformations of cyclohexane are possible but they are **higher in energy and less stable**, i.e. the "boat" conformation

في كثير من Conformers مدروسين  
بالنتيجة للطاقة العالية لكن  
is chair conformer

← في بعضه CH  
eclipsed

إلى إنسان واحد من ال conformer  
المدروس نظريا لكن هو مش  
موجود بسبب أنه  
أعلى طاقة بطين عليه  
Boat ← باس

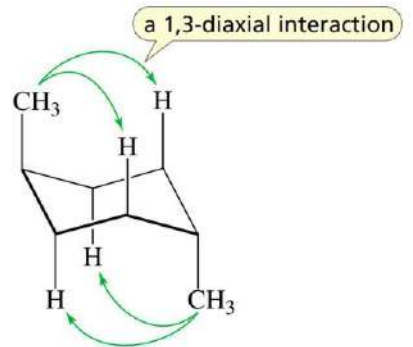
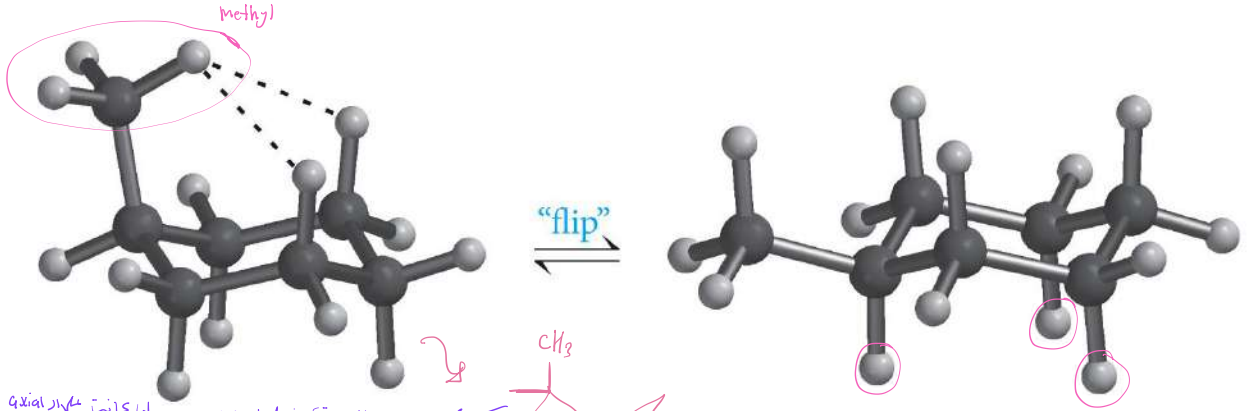


موجودہ اضافی

لکھنا ہی حال وجود مجموعہ کبیرہ

# Substituted cyclohexane: (1,3-Diaxial Interactions)

The addition of a methyl group on cyclohexane (methylcyclohexane) can have two conformations, the methyl can be axial or equatorial, i.e.

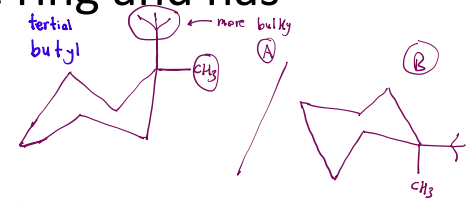


this chair conformer has four 1,3-diaxial interactions

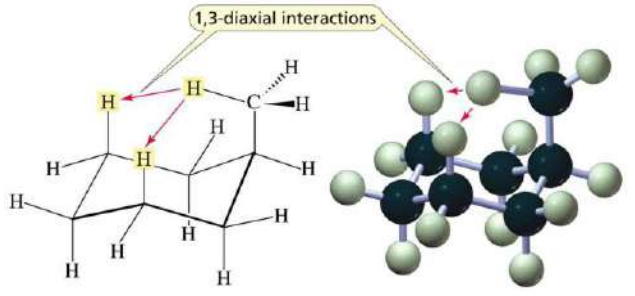
axial ← لی گانتی گھرا axial  
 5% ← گانت نسبتہا بی الی  
 methyl axial  
 5% ← تیکو نا علی ال  
 equatorial  
 95% ← تیکو نا علی ال  
 equatorial  
 95% ← گانت نسبتہا

methyl equatorial  
 95% ← گانت نسبتہا  
 ال bulky group گانت  
 ال stability

The equatorial is preferred as there is significantly less steric interactions than when in the axial position. This will be true for any group on a cyclohexane ring and has implications for the chemical reactivity of the compound.



میں ایسی استعمار مرکب A / وگہ مرکب B جو ما عملیہ ring flipping الجواب B



Note: The larger the substituent, the more the equatorial-substituted conformer is favored.

# Geometric Isomers (*Cis-trans* isomerism)

يختلفوا عن بعض قول من ارجاه  
المجموعه على الكيره

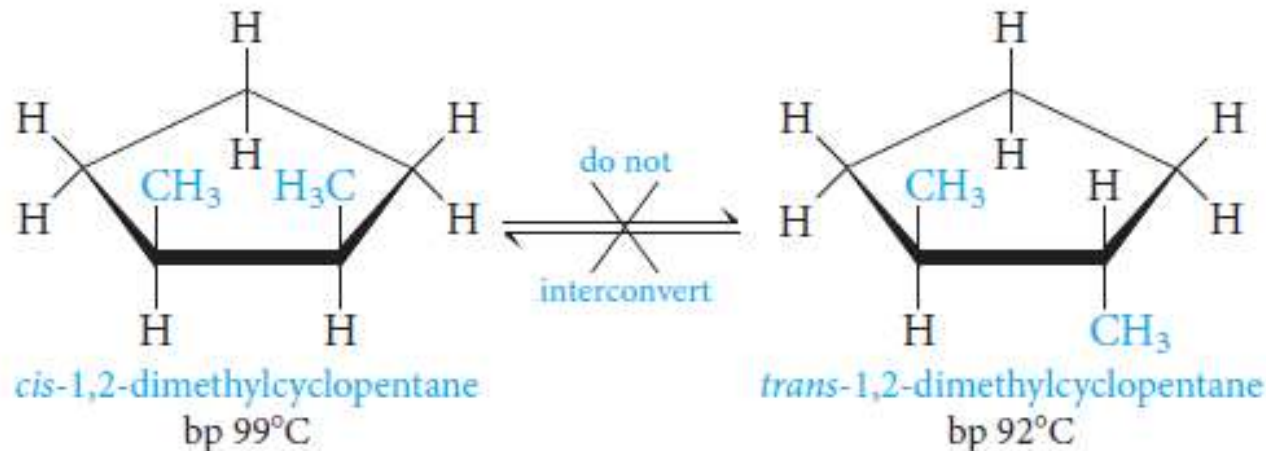
*Geometric isomers* (or **configurational** isomers, a subset of stereoisomers) are molecules which have the same chemical formula, the atoms are bonded in the same order, but located in different positions in space. Unlike conformational isomers, where the atoms are located in different location in space due to rotation about C-C single ( $\sigma$ ) bonds, geometric isomers are not related by rotation about  $\sigma$  bonds. This situation arises with cyclic structures.



An example of this is 1,2-dimethylcyclopentane

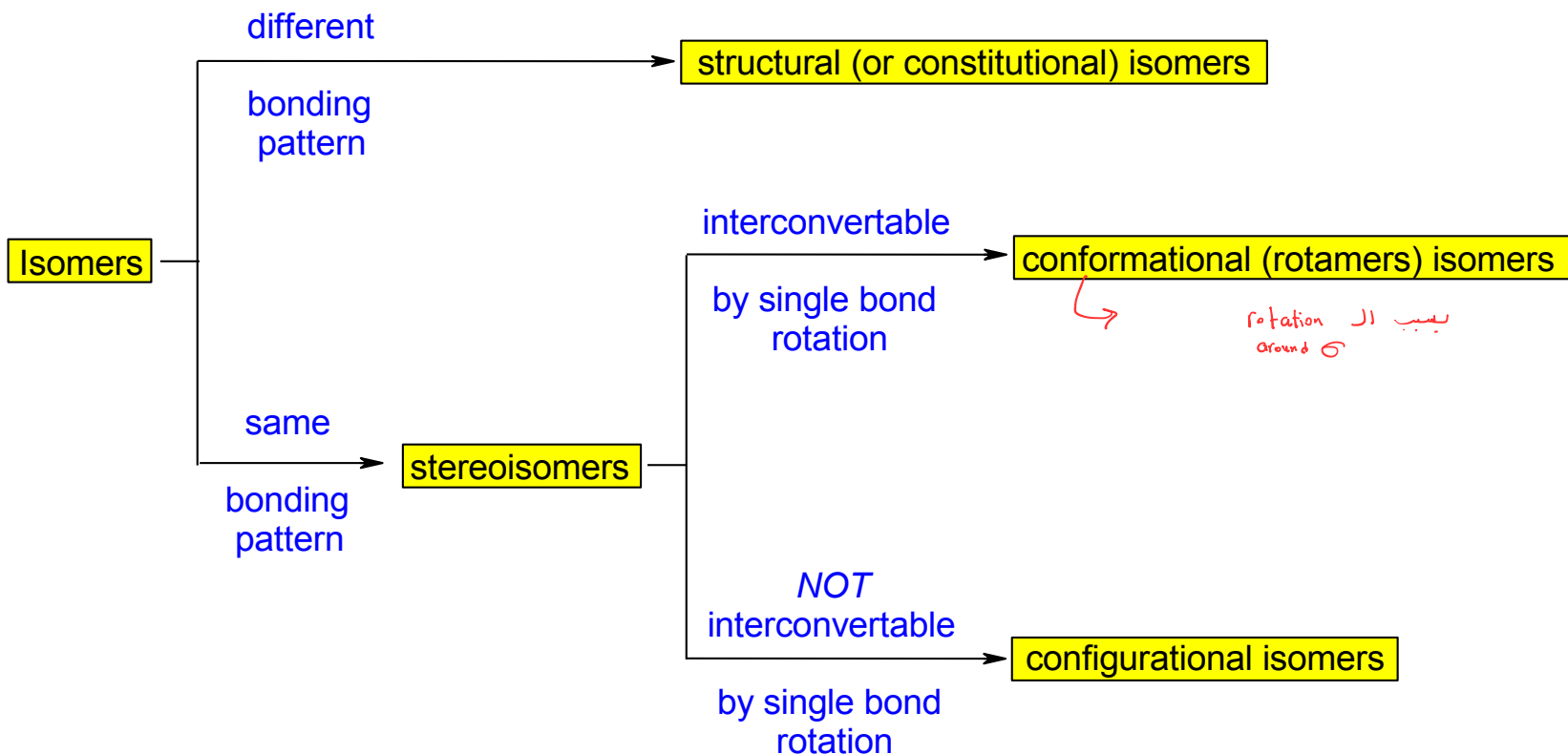
Physical properties  
cis, trans  
- also

These structures can not interconvert without breaking a C-C bond.



- The two methyl groups may be on the same side of the ring plane (*cis*)
- or they may be on the opposite sides (*trans*)
- Cis–trans isomers differ from one another only in the way that the atoms or groups are positioned in space. Yet this difference is sufficient to give them different physical and chemical properties
- *Cis–trans* isomers can be separated from each other and kept separate

# Summary of Isomers (to date)



# Chemical Reactions of Alkanes

لم یحتر inert (ما یتفاعل بشکل کلی)

In general, because of their strong non-polar covalent bonds alkanes are fairly inert. They do not react with most common acids, bases, oxidizing or reducing reagents. They means they do make good solvents for extraction, recrystallization or as a reaction solvent. They do however have two substances they react with; molecular oxygen and halogens.

# Oxidation Reactions

All chemical processes are redox (oxidation / reduction) reactions. Formally oxidation is the loss of electrons (increase in oxidation state) and reduction the gain of electrons (decrease in oxidation state). The two processes are coupled since whatever gains the electrons must gain them from somewhere and whatever loses the electrons must lose them to somewhere.

# Oxidation Reactions (cont'd)

For the C atom, oxidation involves increasing the number of C-O (or other atoms more EN than C) bonds and/or decreasing the number of C-H bonds.

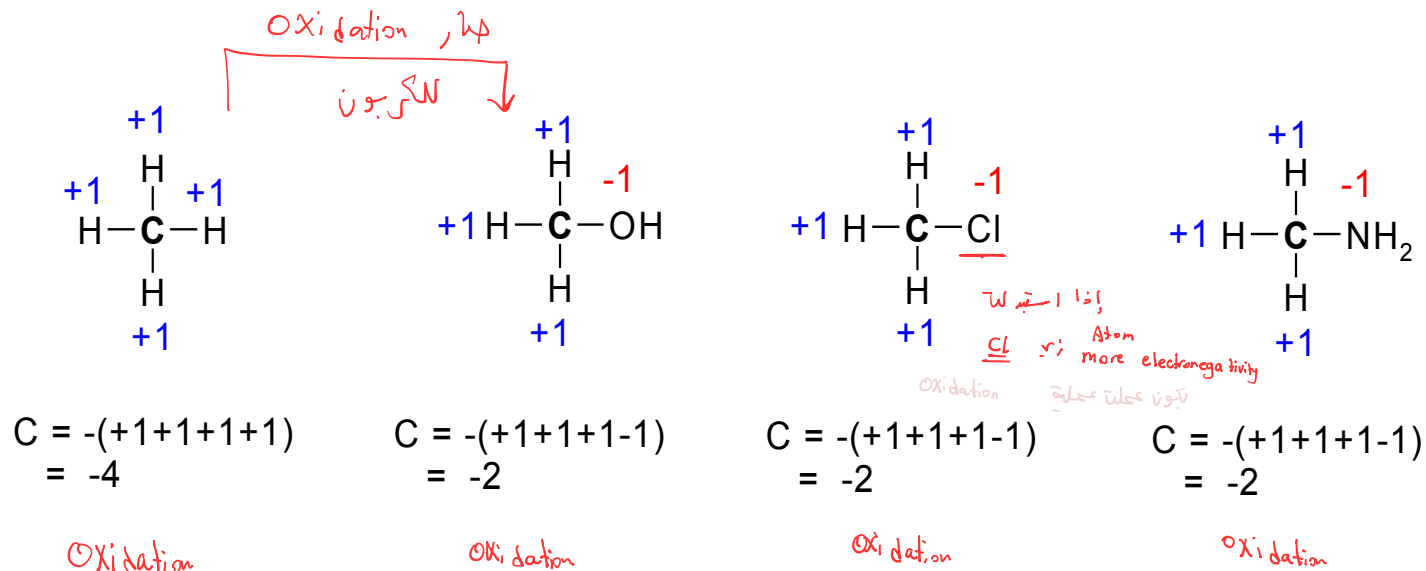
Reduction will be the opposite, a decrease in the number of C-O bonds or increase in the number of C-H bonds.

Oxygen  
content  
↑  
hydrogen  
content

# Oxidation Reactions (cont'd)

To determine the oxidation state:

- each bond to a C atom counts: 0
- each bond to a H atom counts +1
- Each (single) bond to a more EN atom count -1, i.e.





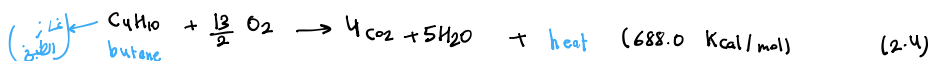
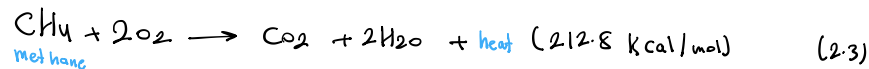
# Oxidation Reactions (cont'd)

Heat and ← عملية احتراق  
Combustion

عملية الاحتراق الهيدروكربونية

The most important use of alkanes is as a fuel. The light weight ones are gases and intermediate weight liquids which makes them handy for storage and transportation. Natural gas is composed primarily of methane with varying amounts of ethane, propane and butanes. It is commonly used to heat homes. The liquid hydrocarbons are used as gasoline, kerosene and jet fuels.

← الهيدروكربون يحتاج إلى أكسجين  
← يمتصنا ← Heat, H<sub>2</sub>O, CO<sub>2</sub>





# Oxidation Reactions (cont'd)

The energy of the hydrocarbon is released when combusted or burned. This is an oxidation process and requires atmospheric oxygen. The final oxidation product (assuming sufficient oxygen) is carbon dioxide. If insufficient oxygen is present then partial oxidation products such as carbon monoxide, formaldehyde or formic acid may be formed.

# Halogenation of Alkanes

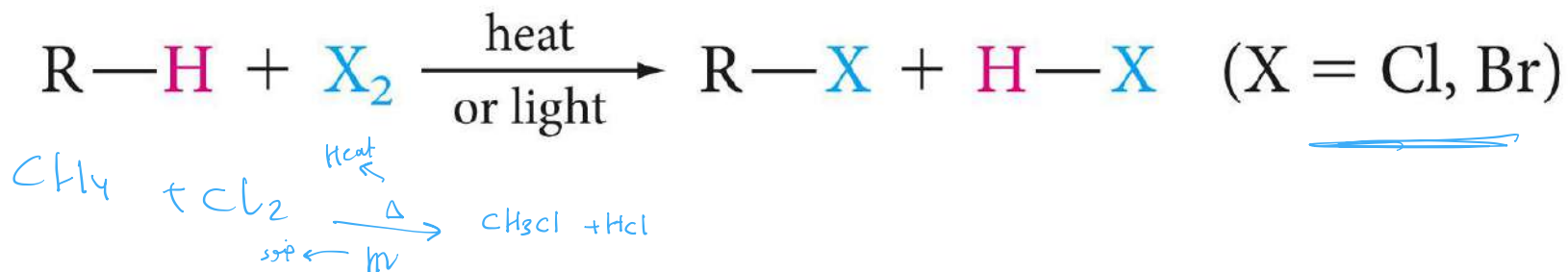


Besides combustion, the only other useful chemical reaction that alkanes undergo is halogenation.

This is a free radical process in which heat or light is used to break a halide-halide bond forming two halide free radicals.

# Halogenation of Alkanes (cont'd)

This type of reaction is a *substitution reaction* where a halide atom is substituted for a H atom in the alkane.

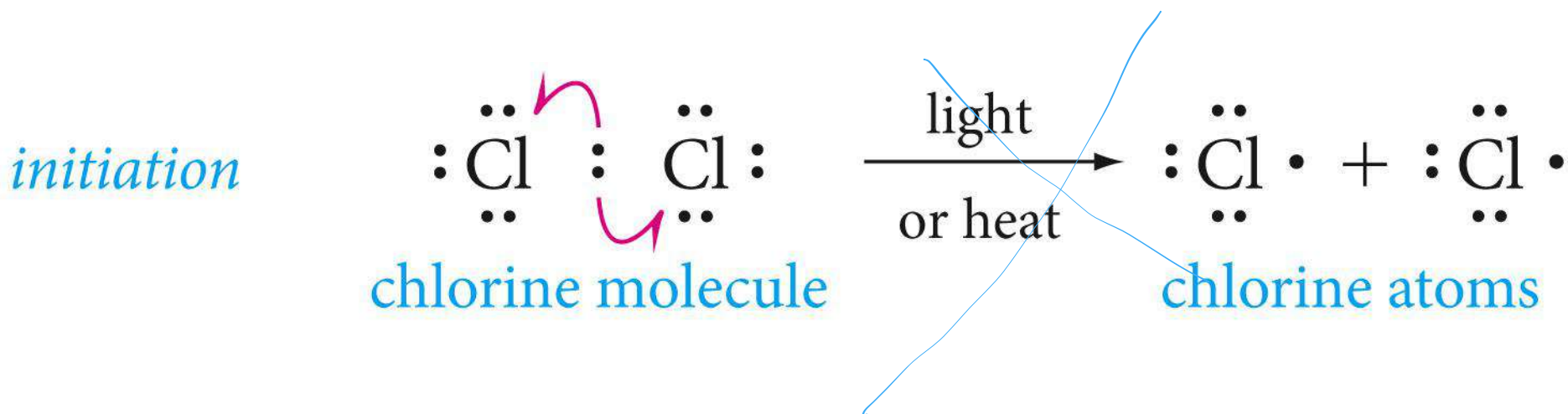


The two common halides used are chlorine and bromine.

# Halogenation of Alkanes (cont'd)

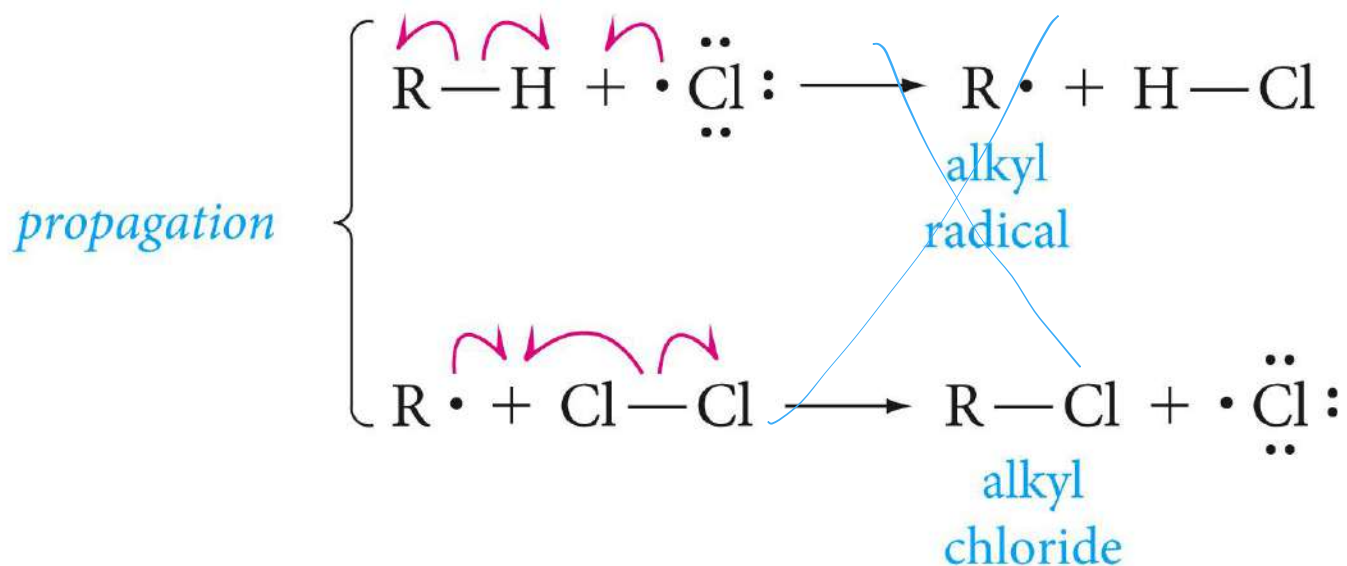
The process involves three steps:

- 1. initiation:** this is where the free radical is formed: note we generate 2 free radical atoms in this process.



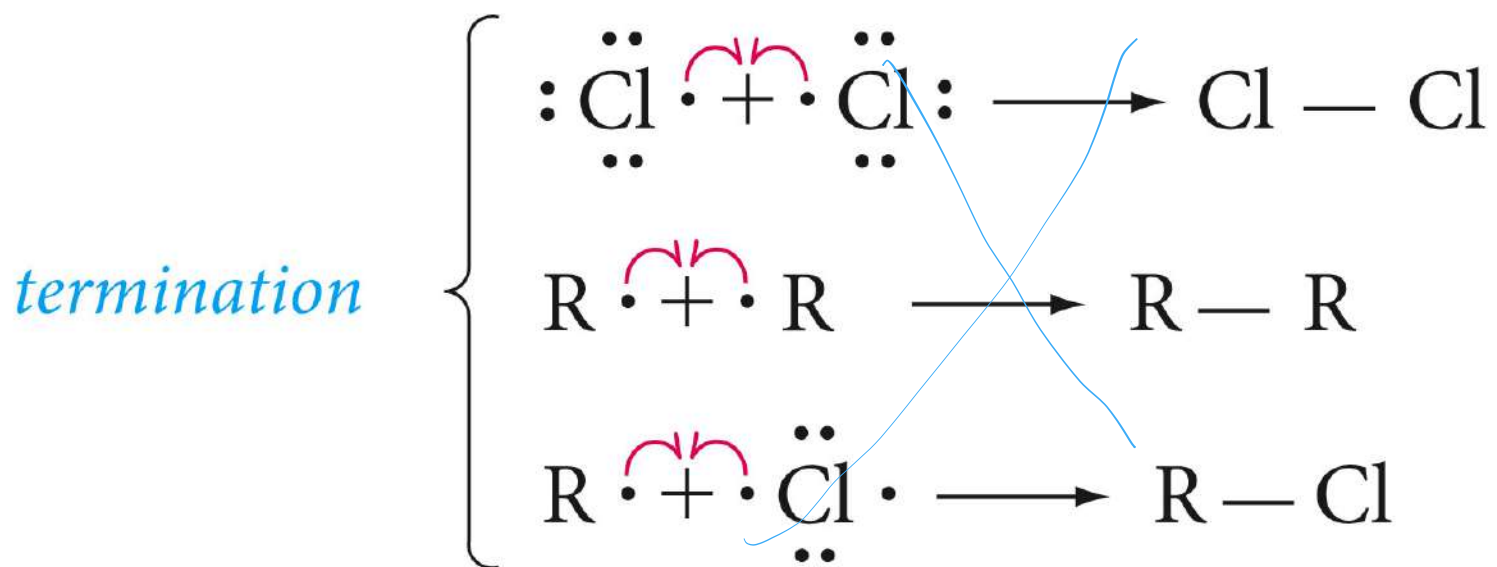
# Halogenation of Alkanes (cont'd)

2. **Propagation**: this is where the halide free radical reacts with the hydrocarbon, extracting a H atom, generating an intermediate C radical, and then adding a halide atom. This process can repeat many times depending on the amount of halide radical available.



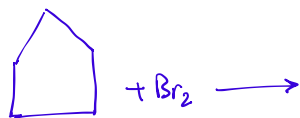
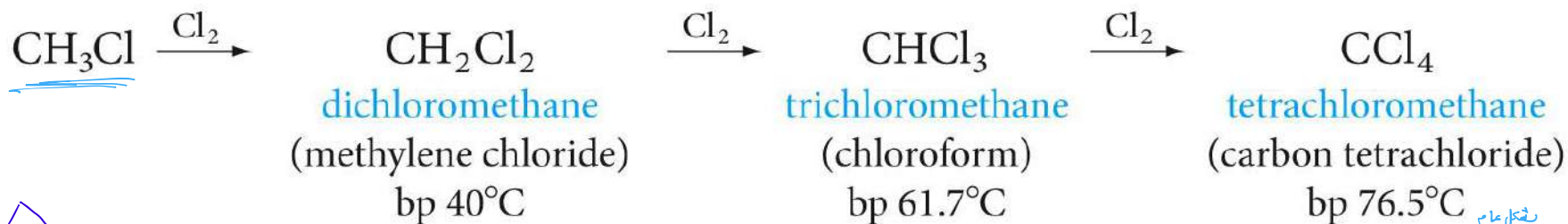
# Halogenation of Alkanes (cont'd)

3. **Termination**: this is the final step where the remaining free radicals are consumed. It can involve the halide radical reacting with another halide radical, a carbon radical or two carbon radicals combining.



# Halogenation of Alkanes (cont'd)

A single alkane molecule can undergo several substitution steps depending on the concentration of the halide radical, i.e.



excess product ممكن يطلع ؟ واحد

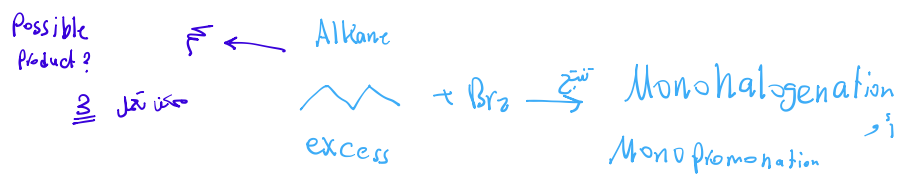
بسته ما يطلع Br<sub>2</sub> من قبله

Bromo cyclopentane

يعتبر على ال reactivity لل Alkane وعلى ال intermediate  
وعلى اتمور؛ حتى لا يبي ما يونا تدخل بالتناهي

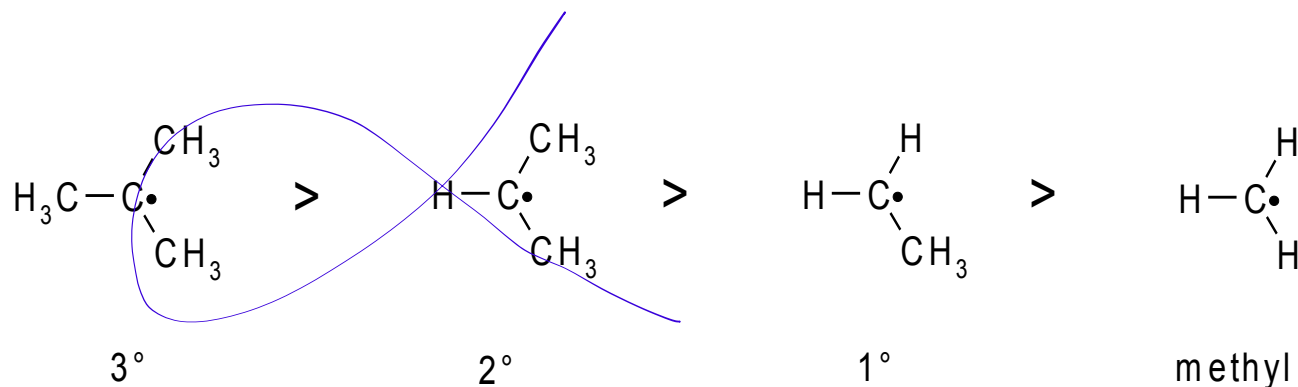
As a matter of fact, unless the concentration of chlorine is kept quite low there will be a mixture of these produces.

Multi halogenation  
 mixture of these produces  
 خليط ويتطلي



# Halogenation of Alkanes (cont'd)

What about longer chain hydrocarbons? All of the H atoms in a hydrocarbon are susceptible to substitution, but not equally. The process involves the formation of a carbon radical as an intermediate. Not all carbon radicals are created equal. As a matter of fact there is a predictable trend in their stability:



bond dissociation energies	kJ/mol	380	397	410	435
	kcal/mol	91	95	98	104



# Halogenation of Alkanes (cont'd)

In addition the halide free radicals are different. Bromine radicals are less reactive than chlorine radicals. This means that Br· tend to be more selective in its reactions and prefers to react with weaker C-H bonds. As a results the halides have different reactivities to each other and to different types of C-Hs, i.e.

Reactivity factors $R_i$		
	Br	Cl
1°	1	1
2°	82	3.9
3°	1640	5.2

$$\%P_i = \frac{100 * nH_i * R_i}{\sum_i nH_i * R_i}$$

$\%P_i$  = %yield of product  $i$

$nH_i$  = number of H of type  $i$

$R_i$  = reactivity factor for type  $i$

$\sum_i$  = sum of all types

# Halogenation of Alkanes (cont'd)

With this information we can now determine the product distributions. For example for propane, there are two 2° H and 6 1° H, so for chlorination:

$$\%1^\circ = 100 \times (6 \times 1) / (6 \times 1 + 2 \times 3.9) = 600 / 13.8 = 43.5\%$$

$$\%2^\circ = 100 \times (2 \times 3.9) / (6 \times 1 + 2 \times 3.9) = 780 / 13.8 = 56.5\%$$

Or for bromination:

$$\%1^\circ = 100 \times (6 \times 1) / (6 \times 1 + 2 \times 82) = 600 / 170 = 3.53\%$$

$$\%2^\circ = 100 \times (2 \times 82) / (6 \times 1 + 2 \times 82) = 16400 / 170 = 96.47\%$$

# Halogenation of Alkanes (cont'd)

The bottom line is fairly simple here.

If you want a 3° halide use bromine since it is 1640 times more likely than a 1°, and 20 times more likely than a 2°.

If you want a 2°, if no 3° present use bromine, other wise use chlorine.

If you want a 1° use chlorine and accept the fact you will have a mixture of products.