Organic Chemistry

The Magic of Carbon

Carbon

What's special about carbon?

1. Forms 4 bonds.
2. It's bonds are stable, but not too stable.
3. It can covalently bond to numerous other elements.

Why is that important?

Suppose you want to create a language?

How would you do it, what do you need?

An alphabet – characters or letters.

Words which represent individual concepts.

Strings of words which represent more complicated ideas.

Suppose I give you only 2 letters (“a” and “b”) and limit your word length to 3 letters, how many words in your language?

aaa	bbb
aab	bba
aba	bab
baa	abb

I’ve only got 8 words! How dull!

Suppose I give you only 2 letters (“a” and “b”) and limit your word length to 3 letter chains, but each letter chain can have side chains how many words in your language?

Supose I can now have as many letter chains as possible…

I quickly have a near infinite number of words! Imagine the sentences I could write.

Simplest Organic Molecules

"Hydrocarbons" – molecules only made up of carbon and hydrogen (2 letter alphabet!)

Simplest Hydrocarbons…alkanes – all carbons are bonded to 4 other atoms!

Alkanes

- methane CH_4
- ethane $CH_3 – CH_3$
- propane $CH_3 - CH_2 – CH_3$
- butane $CH_3 - CH_2 - CH_2 – CH_3$
- pentane $CH_3 - CH_2 - CH_2 - CH_2 – CH_3$
- hexane $CH_3 - CH_2 - CH_2 - CH_2 – CH_2 – CH_3$
- heptane $CH_3 - CH_2 - CH_2 - CH_2 – CH_2 - CH_2 – CH_3$
- Octane $CH_3 -CH_2 -CH_2 -CH_2 -CH_2 –CH_2 - CH_2 – CH_3$

Alkanes – C_xH_{2x+2}

Methane – CH_4

Ethane – C_2H_6

Propane – C_3H_8

Butane – C_4H_{10}

Pentane – C_5H_{12}

Hexane – C_6H_{14}

Heptane – C_7H_{16}

Octane – C_8H_{18}

Alkanes

Alkanes are the basis for all organic molecules and organic nomenclature.

Alkanes (and organic molecules in general) begin with the longest carbon chain in the molecule

Nomenclature

There are 3 parts to organic chemistry nomenclature:

Substituents + length of longest straight C chain + ending indicating dominant functional group

The root – longest straight chain

1 C - Methyl

2 C - Ethyl

3 C - Propyl

4 C - Butyl

5 C - Pentyl

6 C - Hexyl

7 C - Heptyl

8 C – Octyl

Latin numbers take over after 5…

To name an alkane:

1. Count the longest straight chain of Carbon atoms.
2. Replace the “-yl” with an “-ane”
3. Everything else becomes a substituent.

Alkanes – C_xH_{2x+2}

Methane – CH_4

Ethane– C_2H_6

Propane – C_3H_8

Butane – C_4H_{10}

Pentane – C_5H_{12}

Hexane – C_6H_{14}

Heptane – C_7H_{16}

Octane – C_8H_{18}

Isomers

Notice that for 4 carbons or more, it is possible to arrange the backbone differently.

For example:

```
            CH3
             |
       CH3 - CH - CH3     OR   CH3 - CH2 - CH2  - CH3
```

- Different structures with the same molecular formula are called **isomers** - identical numbers and types of atoms, but stuck together differently.

Isomer nomenclature

- The systematic naming system uses the LONGEST STRAIGHT CHAIN

```
              CH3
               |
      CH3 - CH - CH3      OR   CH3 - CH2 - CH2  - CH3
```

So, the first structure would be named as a propane (2-methyl-propane) rather than a butane like the second structure. This prevents confusion.

Other substituents

Suppose I were to have a Br on my propane?

CH_3 - CH – CH_3
|
Br

Is that the only place it could go?

CH_2 – CH_2 – CH_3
|
Br

How about a 3rd one?

CH_3 – CH_2 – CH_2
|
Br

Other substituents

$CH_3 - CH - CH_3$

|

Br

$CH_2 - CH_2 - CH_3$

|

Br

3rd one is the same as the 2nd one, flipped around: it is not distinct!

$CH_3 - CH_2 - CH_2$

|

Br

How do I tell them apart?

bromo-propane

CH_3 - CH – CH_3

|

Br

bromo-propane

CH_2 – CH_2 – CH_3

|

Br

I number the carbons! (Smallest numbers possible.)

How do I tell them apart?

2-bromo-propane

CH_3 - CH – CH_3

|

Br

1-bromo-propane [NOT 3-bromo-propane)

CH_2 – CH_2 – CH_3

|

Br

What would you call this?

CH_3

|

CH_3CH_2CH

|

Cl

A. chloro-butane

B. 3-chloro-butane

C. 2-chloro-butane

D. 1-chloro-1-methyl-propane

Back to hydrocarbons!

Even without adding anything but C and H, we have an infinite number of possibilities based on all the structural isomers. And we can also change the BONDING!!!

Carbon can not only form a single covalent bond with another carbon atom, it can form a DOUBLE bond!!

$CH_3 – CH_3$ (ethane)

$CH_2 = CH_2$ (eth-?)

Hydrocarbons with one or more DOUBLE bonds are called alkenes!

$CH_2 = CH_2$ (ethene)

Alkenes ende in “-ene” instead of “-ane”

Not only does this create a whole bunch of alkenes, it also creates a whole bunch of isomers!!!

What is the structure of pentene?

A) $CH_2 = CH - CH_2 - CH_2 – CH_3$

B) $CH_3 - CH = CH - CH_2 – CH_3$

C) $CH_3 – CH_2 - CH = CH – CH_3$ (same as 2)

D) $CH_3 – CH_2 - CH_2 - CH = CH_2$ (same as 1)

E) $CH_2 = C = CH - CH_2 – CH_3$

F) $CH_2 = CH - CH = CH – CH_3$

Etc. etc. etc.

What is the structure of pentene?

A) $CH_2 = CH - CH_2 - CH_2 – CH_3$ 1-pentene

B) $CH_3 - CH = CH - CH_2 – CH_3$ 2 - pentene

C) $CH_2 = C = CH - CH_2 – CH_3$ 1,2-penta-diene

D) $CH_2 = CH - CH = CH – CH_3$ 1,3-penta-diene

Etc. etc. etc.

If you have more than 1 of something…

Use a prefix:

2 = “di”

3 = “tri”

4 = “tetra”

5 = “penta”

Etc.

CH_2Br_2

H

|

Br - C - H

|

Br

Dibromo-methane

CBr_4

Tetrabromo-methane

If two bonds are better than one, how about three?

Yes, it is true, carbon can form a TRIPLE bond.

Such molecules are called "alkynes" and are named by adding a "-yne" instead of an "-ane" to the alkane root.

And there are isomers!

$CH \equiv C - CH_2 - CH_2 - CH_3$

$CH_3 - C \equiv C - CH_2 - CH_3$

Alkane Chemistry

BORING!!!

Well, we know they burn (or oxidize)!

C_xH_{2x+2} + (3/2x+1/2) O_2 → x CO_2 + (x+1)H_2O

You can also “substitute” a halogen (X=Br, Cl, I):

$$C_xH_{2x+2} + X_2 \xrightarrow{\text{UV or heat}} C_xH_{2x+1}X + HX$$

$$CH_3CH_3 + Cl_2 \xrightarrow{\text{UV or heat}} CH_3CH_2Cl + HCl$$

Alkane Chemistry

Substitution is just a replacement reaction: remove a hydrogen, add something else

$$C_xH_{2x+2} + X_2 \xrightarrow{\text{UV or heat}} C_xH_{2x+1}X + HX$$

$$CH_3CH_3 + Cl_2 \xrightarrow{\text{UV or heat}} CH_3CH_2Cl + HCl$$

What is the major product(s) of the following reaction?

2-hexene + H-Br →

A. 1-bromo-hexane
B. 2-bromo-hexane
C. 3-bromo-hexane
D. A and B
E. B and C

Alkenes and Alkynes…

…are more interesting!

They can do pretty much everything that alkanes can do, but they also have those extra bonds!

Bonds are electrons…

So, if you have an extra bond, you have extra electrons.

It is possible for an alkene or alkyne to ADD other atoms without needing to remove anything.

A basic addition reaction:

$$CH_3\,CH = CHCH_3 + HCl \rightarrow CH_3\,CH - CHCH_3$$

$$\begin{array}{cc} | & | \\ H & Cl \end{array}$$

The key to all organic chemistry is CHARGES!

If you follow the charge, you can predict the product!

The basic mechanism for the addition reaction:

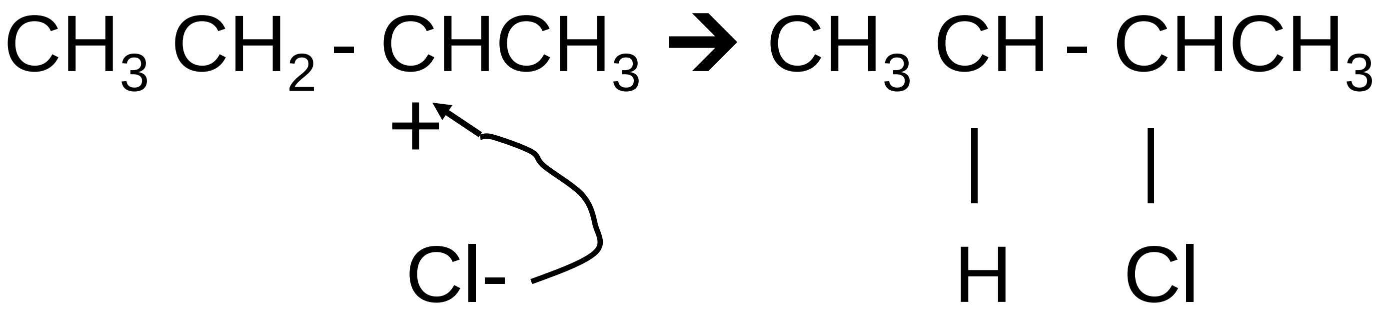
$CH_3\ CH = CHCH_3 \rightarrow CH_3\ CH_2 - CHCH_3$

+

H+

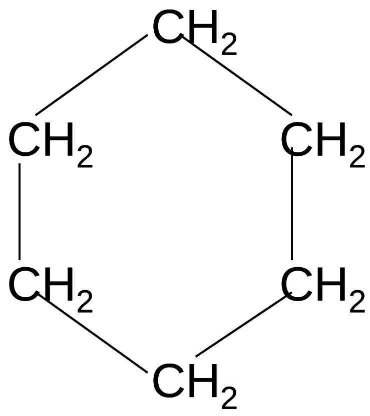
Arrows represent electrons moving in organic chemistry.

The basic mechanism for the addition reaction:



Cycloalkanes…

I've been sticking to "straight chain" hydrocarbons, but it is possible to form rings:

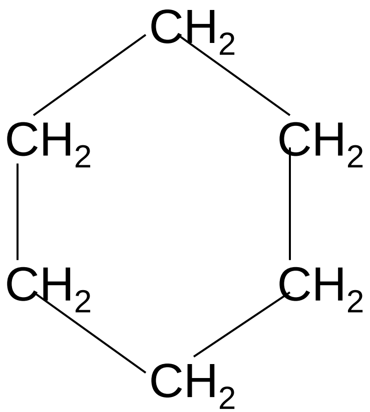


This molecule is "cyclohexane" and its molecular formula is C_6H_{12}

Cyclohexane vs. Hexane vs. Hexene

Notice that cyclohexane has the same molecular formula as hexene!

In fact, the cyclic molecules have chemistry like the alkanes, but they also have some things in common with alkenes.



Cyclohexane
C_6H_{12}

$CH_3\,CH_2\,CH_2\,CH_2\,CH_2\,CH_3$

Hexane
C_6H_{14}

$CH_3\,CH_2\,CH\ =CHCH_2\,CH_3$

Hexene
C_6H_{12}

"Saturation"

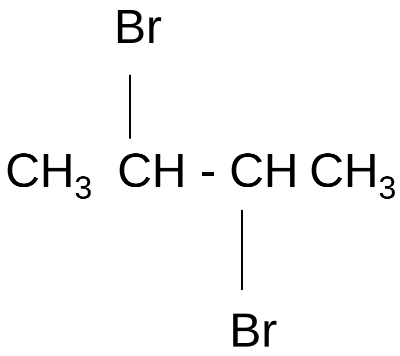
I'm sure you've heard the term "saturation" somewhere in the main stream media, probably in a commercial: "Tastes like butter but it's 100% poly-unsaturated".

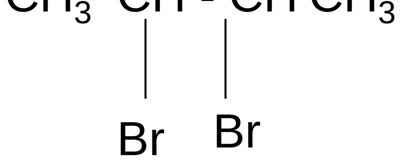
What does it mean?

Saturation refers to the number of hydrogens relative the number of carbons. Alkanes are saturated (C_xH_{2x+2}) – all the carbons are either singly bonded to another carbon or to a hydrogen. Alkenes are "unsaturated" – there's room for more hydrogens!

2,3-dibromobutane

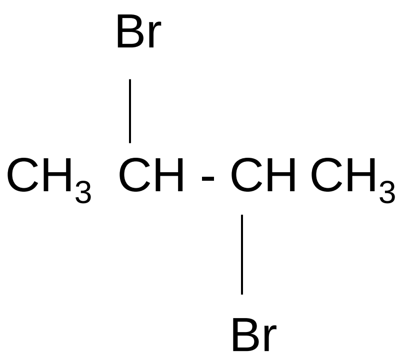
Are these molecules the same or different?

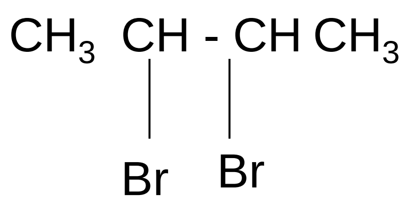




2,3-dibromobutane

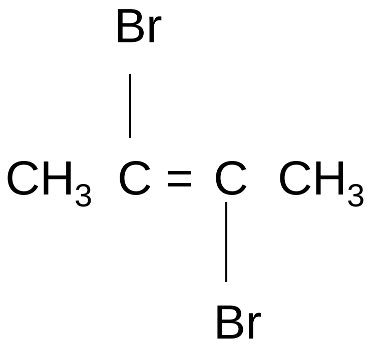
The SAME: free rotation around the bonds makes them indistinguishable!

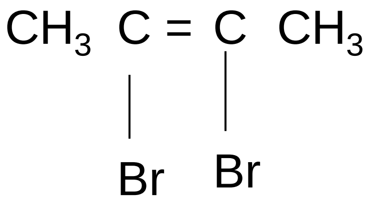




2,3-dibromo-2-butene

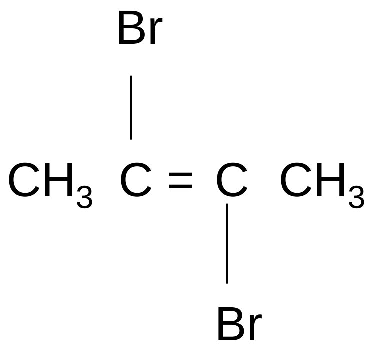
Are these molecules the same or different?



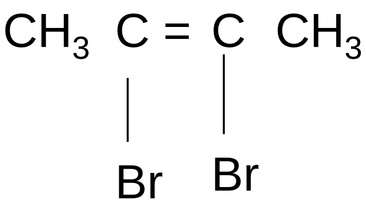


2,3-dibromo-2-butene

You can't rotate around a double bond!!! These 2 molecules are DIFFERENT – even though they have the same formula and everything is bonded to the same atoms, they are distinguishable their 3D orientation is considered.



trans-2,3-dibromo-2-butene



cis-2,3-dibromo-2-butene

Stereoisomerism

Differences in 3D orientation of atoms is a different type of isomer, called a stereoisomer.

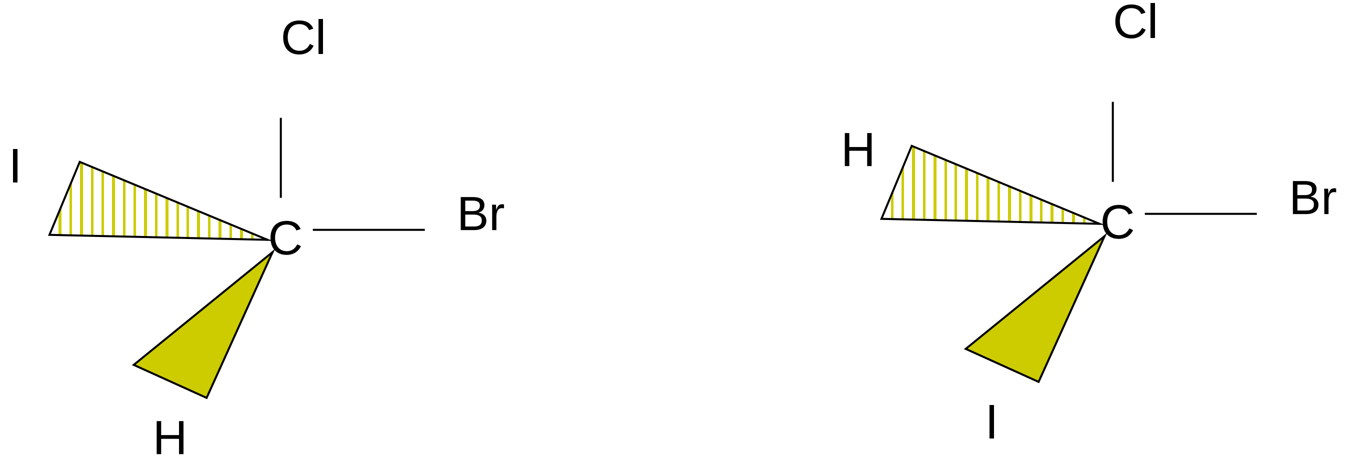
Same thing happens with cycloalkanes: the atoms can’t rotate, so if you have substituent groups, they can be oriented differently in 3D!

Mirror, mirror, on the wall!

Consider these 2 molecules; same or different?

(Remember, you are allowed to rotate them around in space)

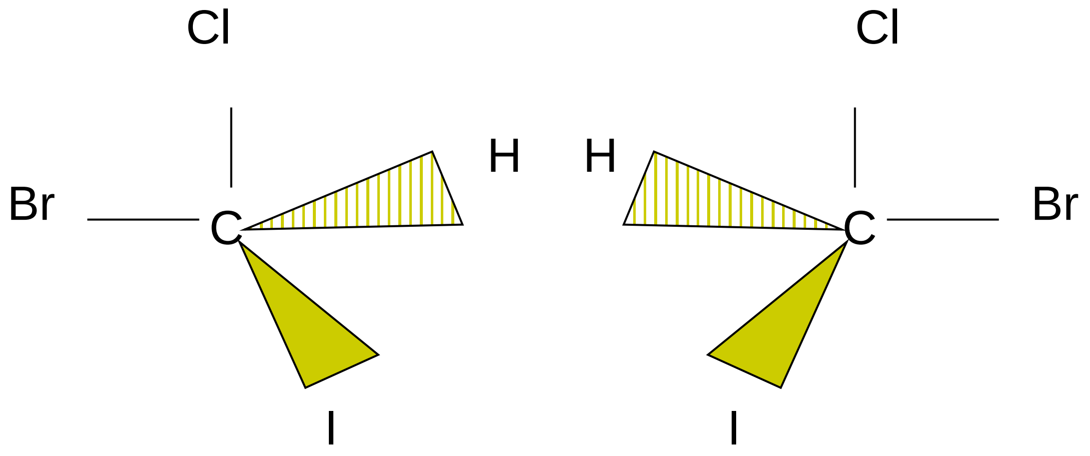
[Solid lines are in the plane of the paper, solid triangle is sticking out at you, dotted triangle is pointing back away from you.



Try this view

Consider these 2 molecules; same or different?

They are "nonsuperimposable" mirror images! (Called "enantiomers".



Does that really make a difference?

There is only one measurable difference: rotation of polarized light. If you shine a polarized light ray on the two enantiomers, one will rotate the polarization to the right, the other will rotate the polarization to the left.

Believe it or not…

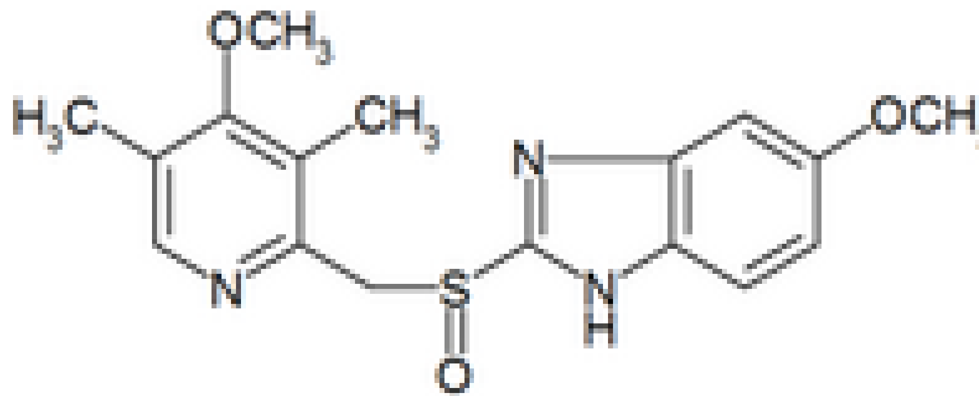
Sometimes one enantiomer will cure disease and the other will do nothing!!!

Think “lock-and-key” model of enzyme behavior. Only one enantiomer fits the lock!

Prilosec

AstraZeneca

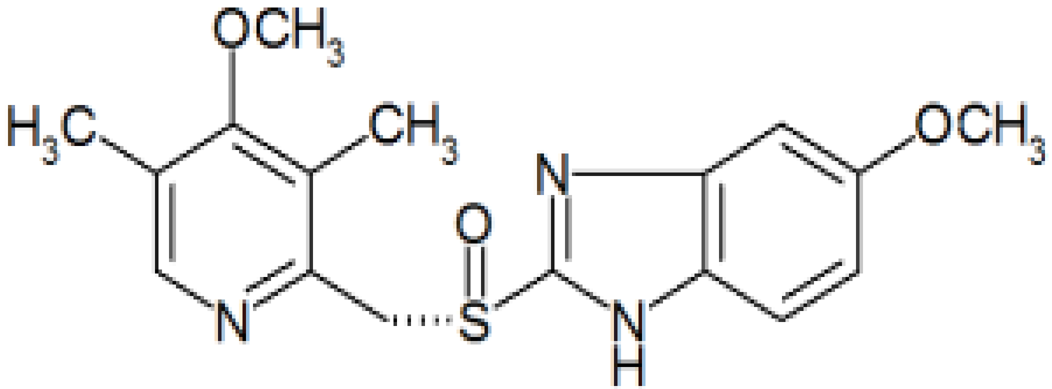
(RS)-5-methoxy-2-[[(4-methoxy-3,5-dimethyl-2-pyridinyl) methyl]sulfinyl]-1H-benzimidazole



Nexium

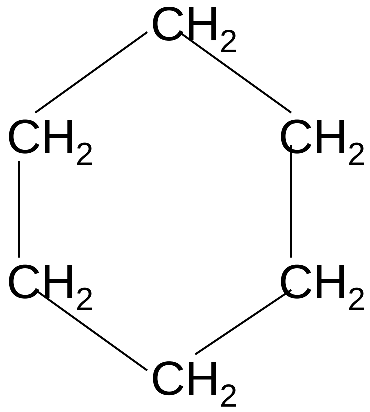
AstraZeneca

S-5-methoxy-2-[[(4-methoxy-3,5-dimethyl-2-pyridinyl) methyl]sulfinyl]-1H-benzimidazole

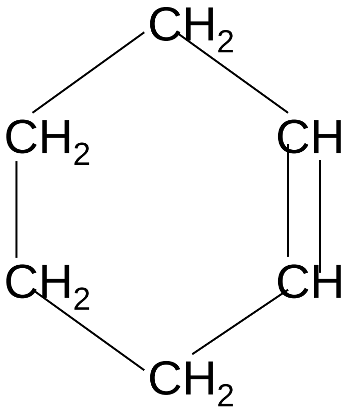


Cycloalkenes

Hey, if you can have a cyclic alkane why not a cyclic alkene?



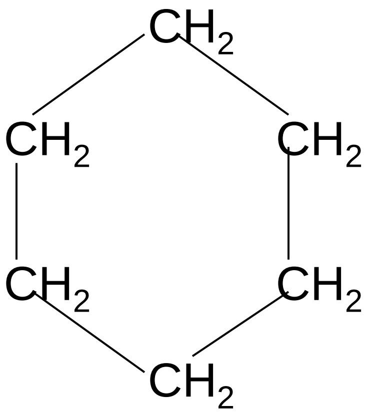
cyclohexane



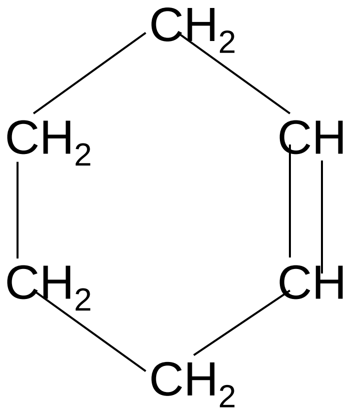
cyclohexene

Cycloalkenes

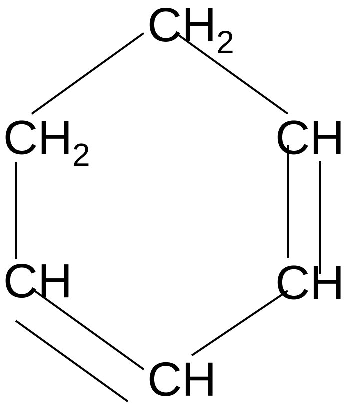
Hey, if you can have a cyclic alkane why not a cyclic alkene?



cyclohexane

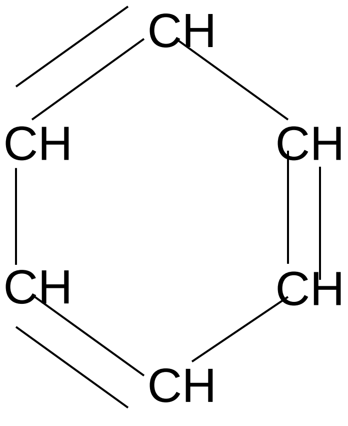


cyclohexene



1,3-cyclohexadiene

1,3,5-cyclohexatriene?

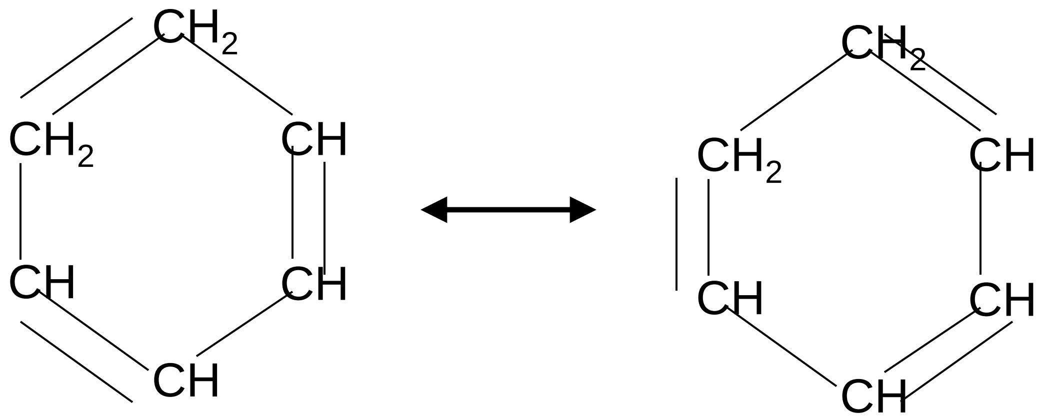


Aromatic compounds

Actually, the 3 alternating double bonds give the molecule an added stability. To see why, we'd really need to take a look at the 3D geometry of the bonds:

1. The 2nd bond is perpendicular to the ring.
2. The ring lies flat.
3. Remember our old friend resonance?

The real structure is the “average” of the resonance structures: A perfectly flat ring with the electrons completely delocalized around the ring.



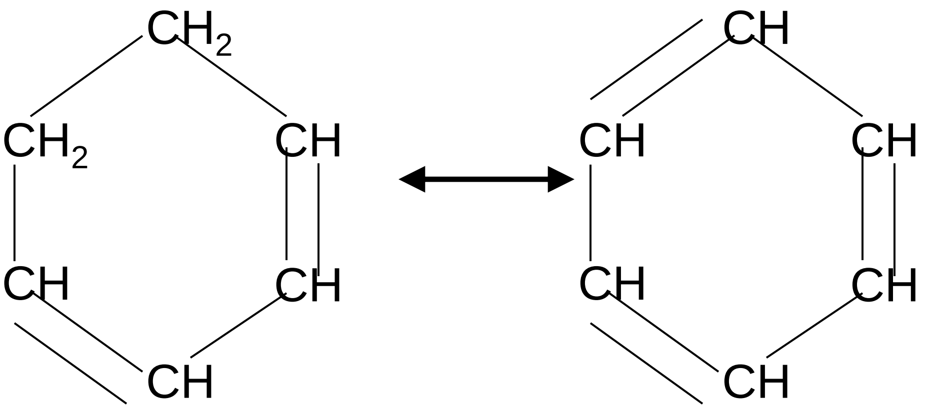
Benzene

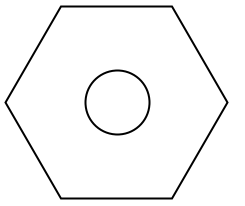
Aromatic rings

Benzene is an aromatic ring. As such, it is kind of a "functional group" unto itself. The double bonds are so delocalized and superstrong, that they are NOT capable of addition reactions.

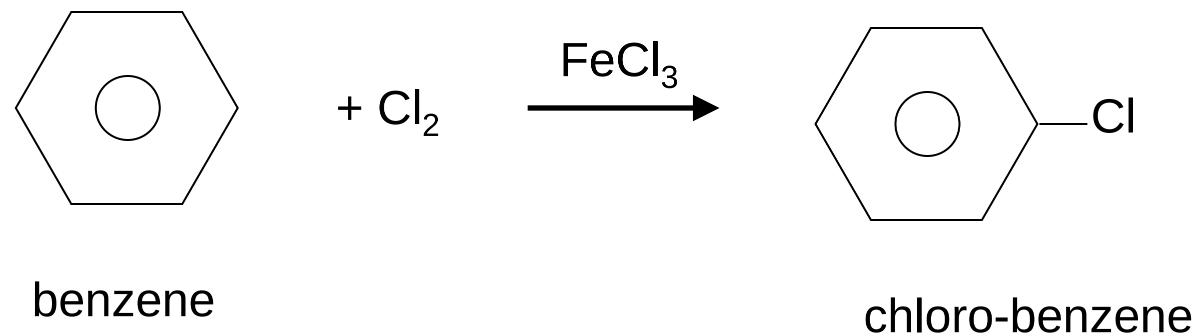
Benzene chemistry happens on the outside of the ring, not inside it.

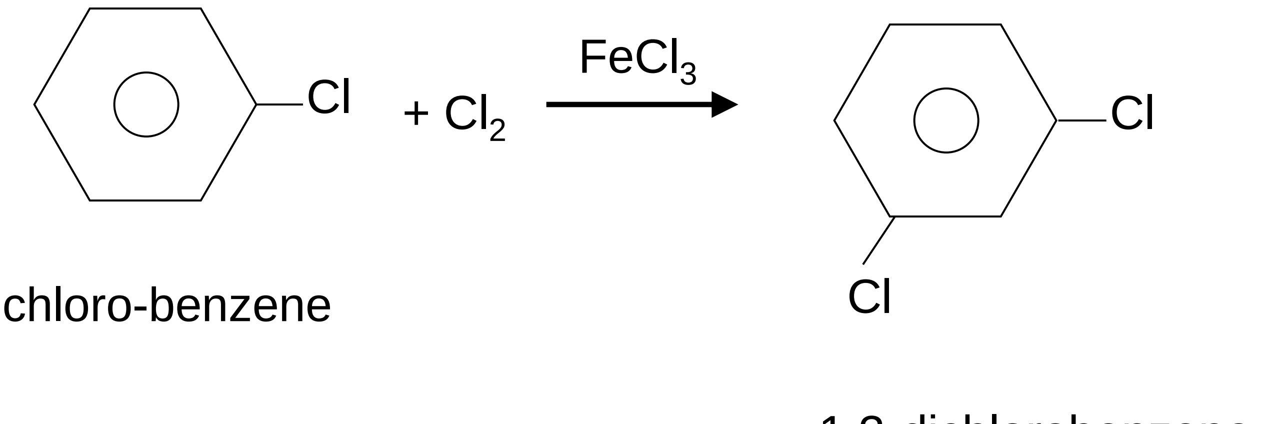
Because it is a single unit, it is often represented as a hexagon (for the carbons) with a circle in the middle (for the delocalized double bonds).





- Reactions of benzene are ring substitution





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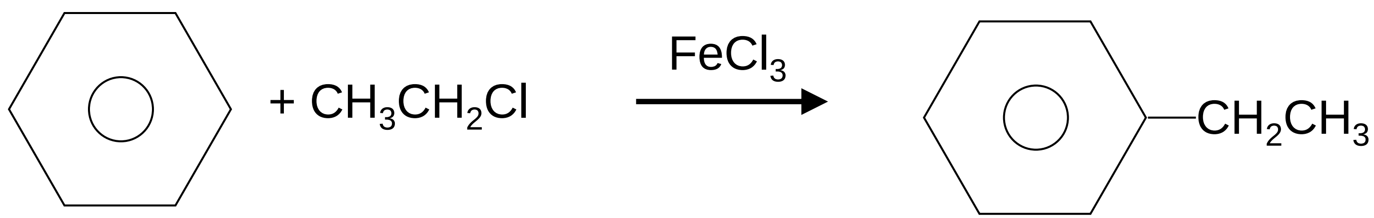

benzene

ethyl-benzene

Other functional groups:

Alcohols (-OH)

Amines (-NH_2)

Aldehydes and Ketones (C=O)

Carboxylic Acids and Esters