5.1
Alkene Nomenclature

Alkenes

Alkenes are hydrocarbons that contain a carbon-carbon double bond

also called "olefins"

characterized by molecular formula C_nH_{2n}

said to be "unsaturated"

Alkene Nomenclature

Ethene
or
Ethylene
(both are acceptable IUPAC names)

Propene

(Propylene is sometimes used but is not an acceptable IUPAC name)

Alkene Nomenclature

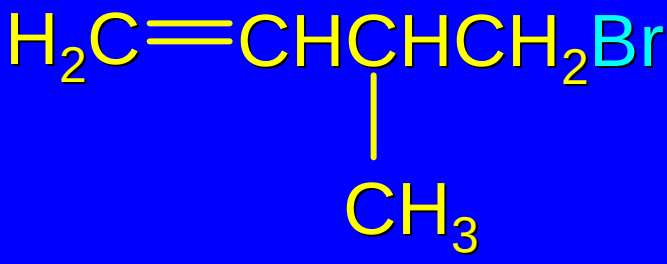
1) Find the longest continuous chain that includes the double bond.
2) Replace the -ane ending of the unbranched alkane having the same number of carbons by -ene.
3) Number the chain in the direction that gives the lowest number to the doubly bonded carbon.

Alkene Nomenclature

$H_2C{=}CHCH_2CH_3$ 1-Butene

1) Find the longest continuous chain that includes the double bond.
2) Replace the -ane ending of the unbranched alkane having the same number of carbons by -ene.
3) Number the chain in the direction that gives the lowest number to the doubly bonded carbon.

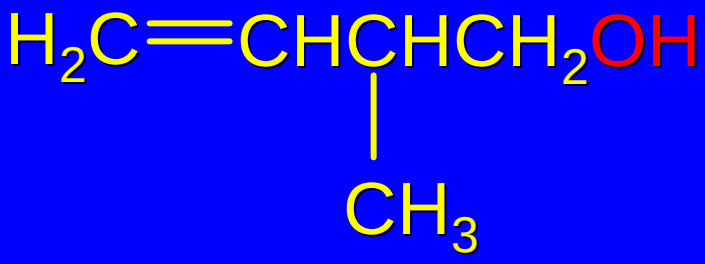
Alkene Nomenclature



4) If a substituent is present, identify its position by number. The double bond takes precedence over alkyl groups and halogens when the chain is numbered.

The compound shown above is 4-bromo-3-methyl-1-butene.

Alkene Nomenclature



4) If a substituent is present, identify its position by number. Hydroxyl groups take precedence over the double bond when the chain is numbered.

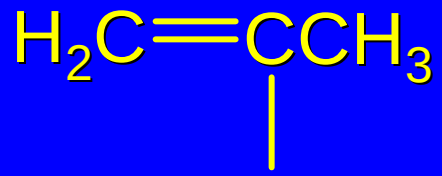
The compound shown above is 2-methyl-3-buten-1-ol.

Alkenyl Groups

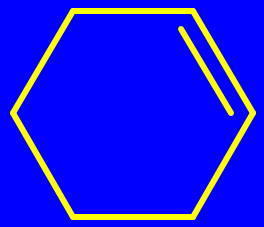
methylene $H_2C=$

vinyl $H_2C=CH-$

allyl $H_2C=CHCH_2-$

isopropenyl 

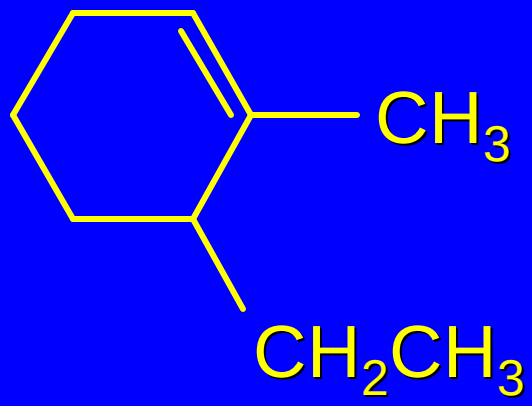
Cycloalkene Nomenclature



Cyclohexene

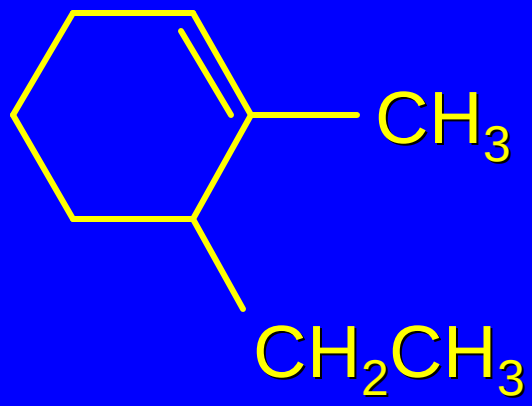
1) Replace the -ane ending of the cycloalkane having the same number of carbons by -ene.

Cycloalkene Nomenclature



1) Replace the -ane ending of the cycloalkane having the same number of carbons by -ene.
2) Number *through* the double bond in the direction that gives the lower number to the first-appearing substituent.

Cycloalkene Nomenclature



6-Ethyl-1-methylcyclohexene

1) Replace the -ane ending of the cycloalkane having the same number of carbons by -ene.
2) Number *through* the double bond in the direction that gives the lower number to the first-appearing substituent.

5.12
Structure and Bonding in Alkenes

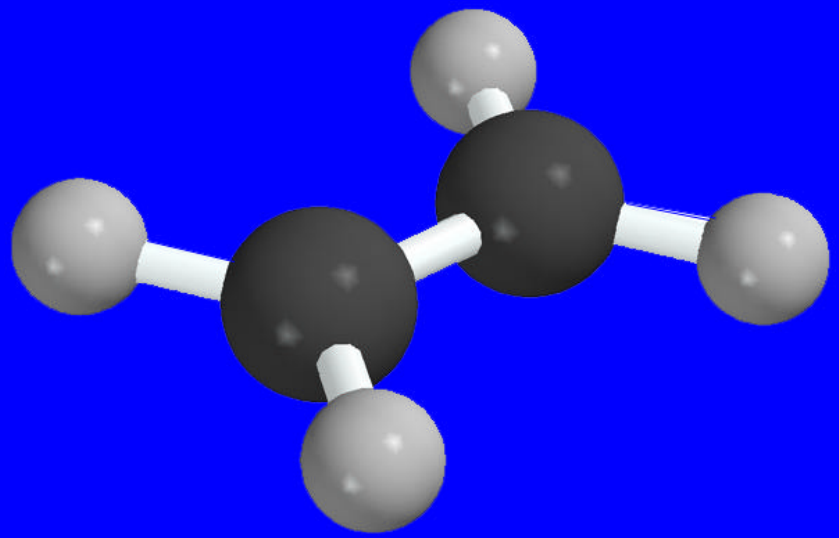
Structure of Ethylene

bond angles: H-C-H = 117°

H-C-C = 121°

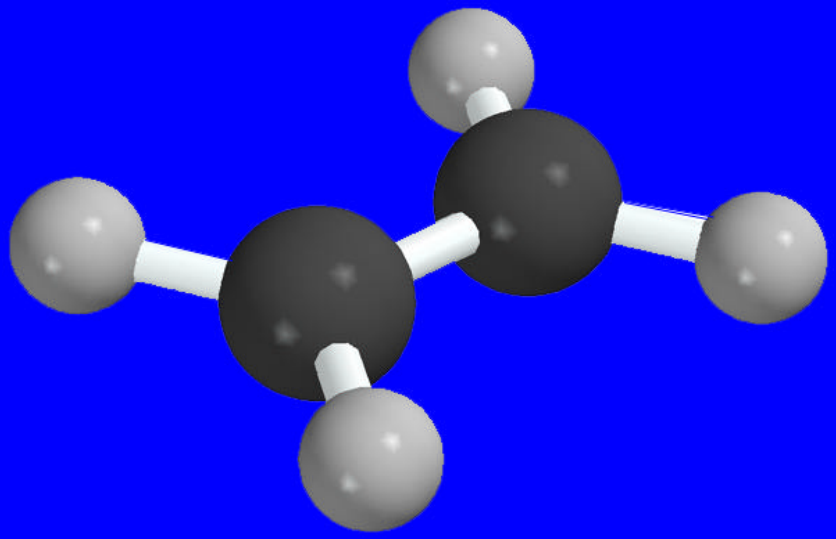
bond distances: C—H = 110 pm

C=C = 134 pm



planar

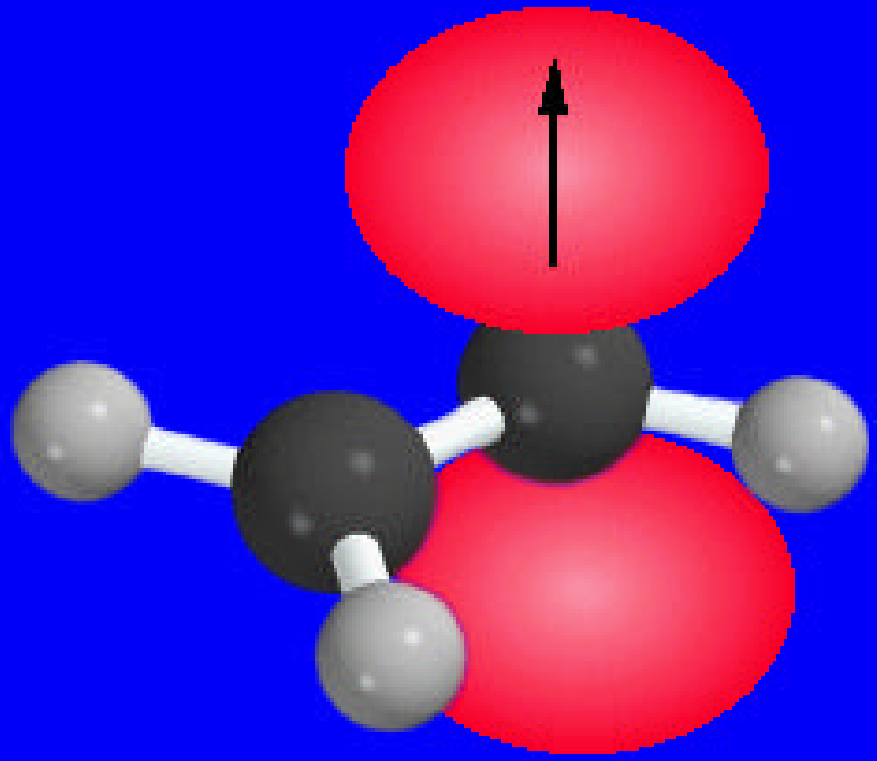
Bonding in Ethylene



Framework of σ bonds

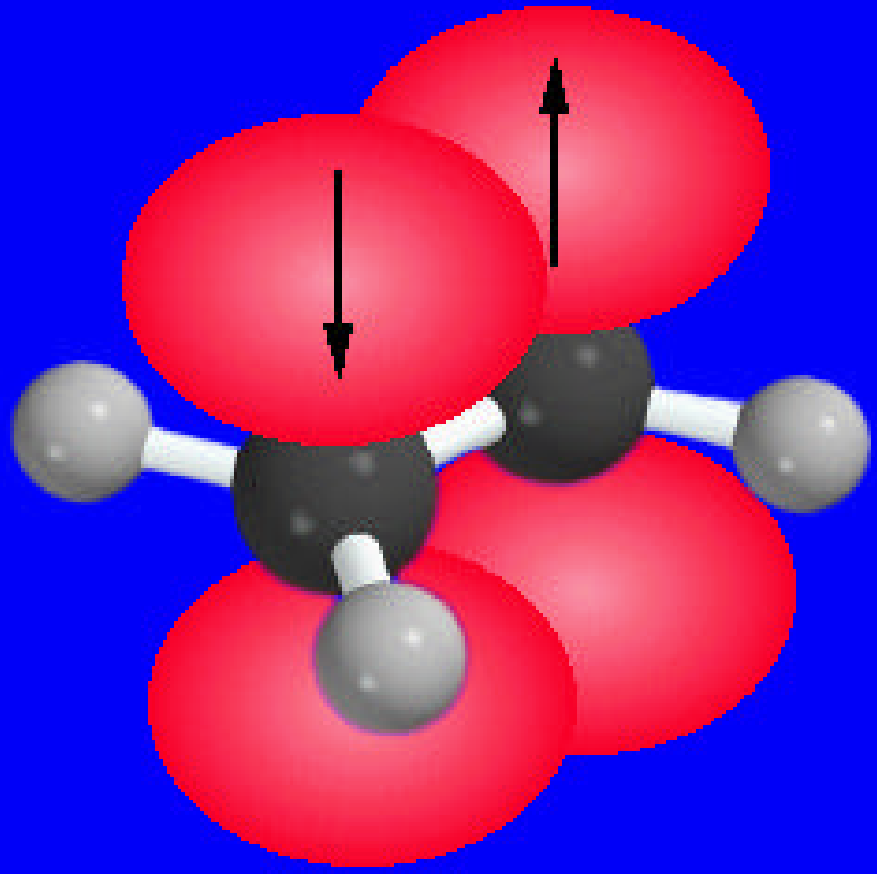
Each carbon is sp^2 hybridized

Bonding in Ethylene



Each carbon has a half-filled *p* orbital

Bonding in Ethylene

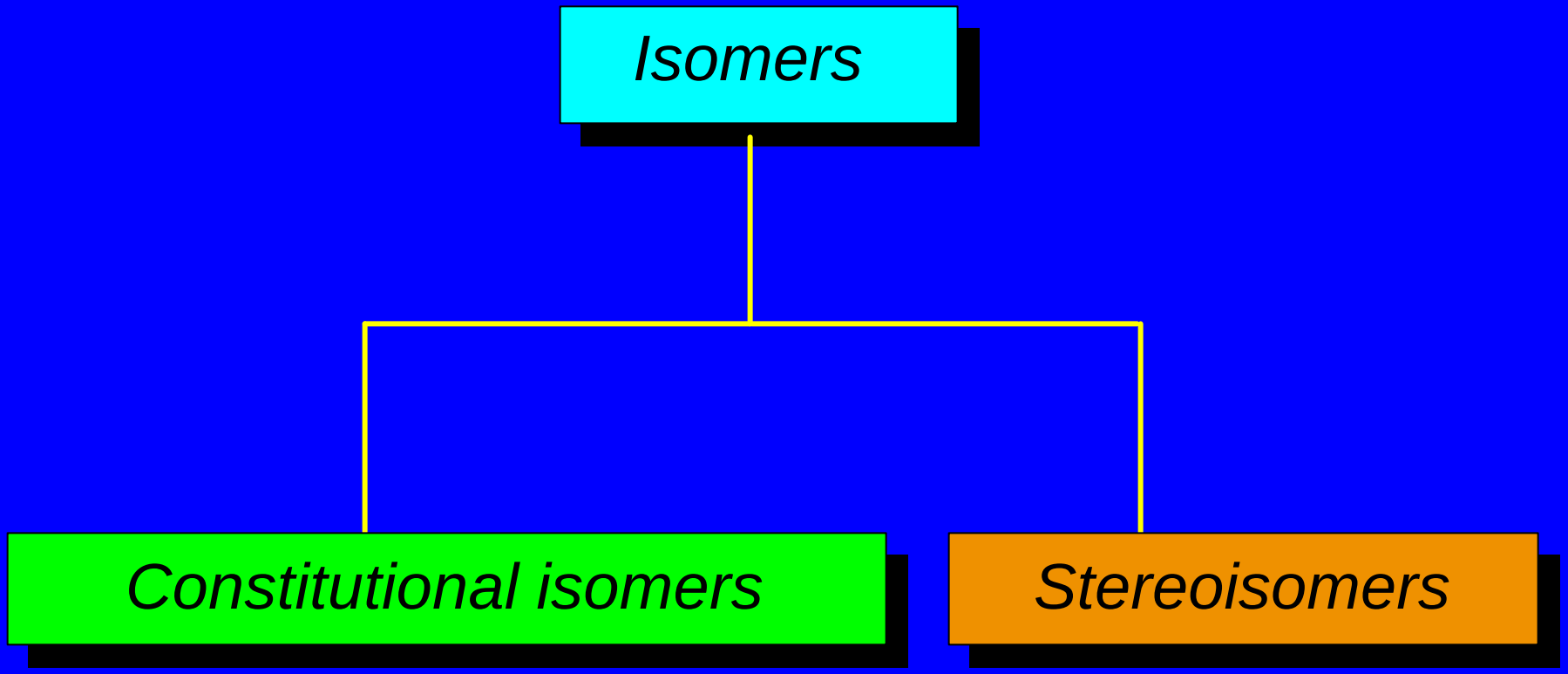


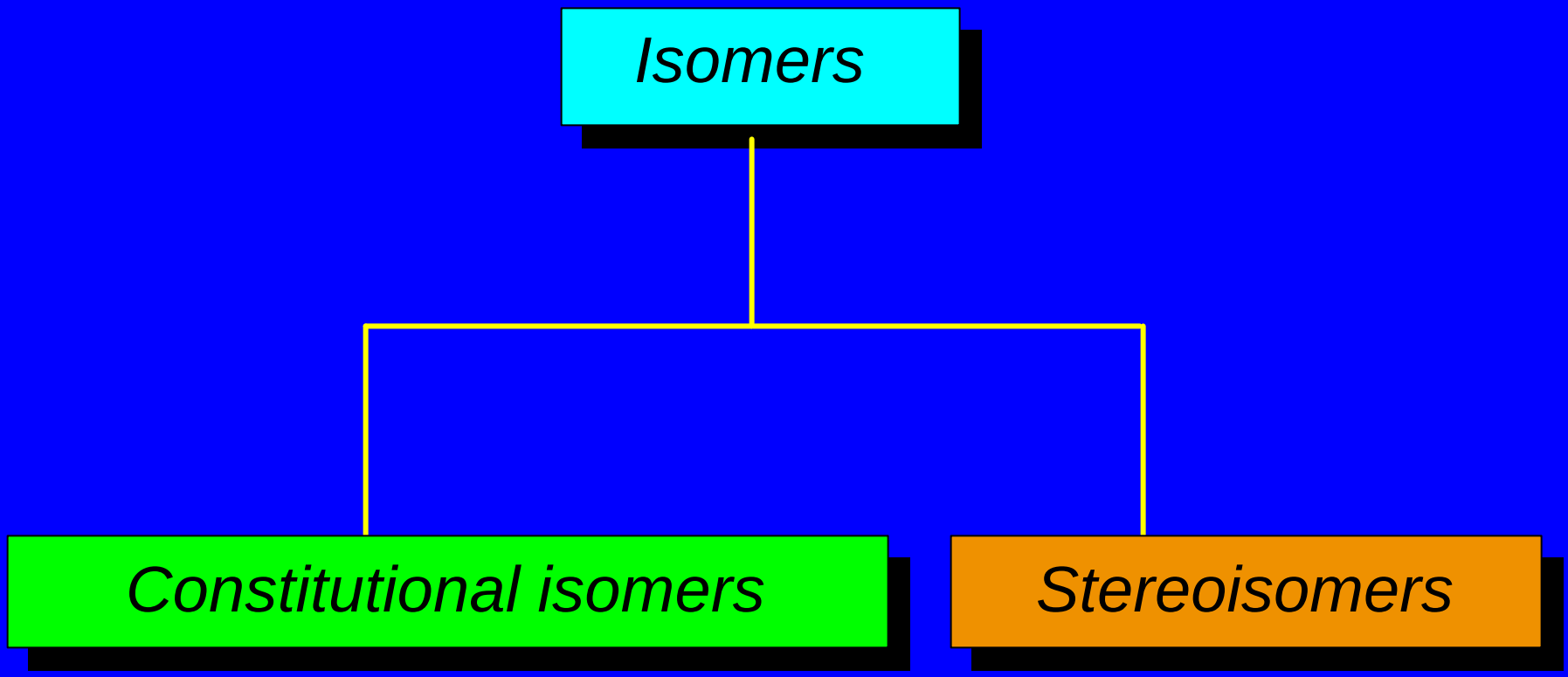
Side-by-side overlap of half-filled *p* orbitals gives a π bond

5.3
Isomerism in Alkenes

Isomers

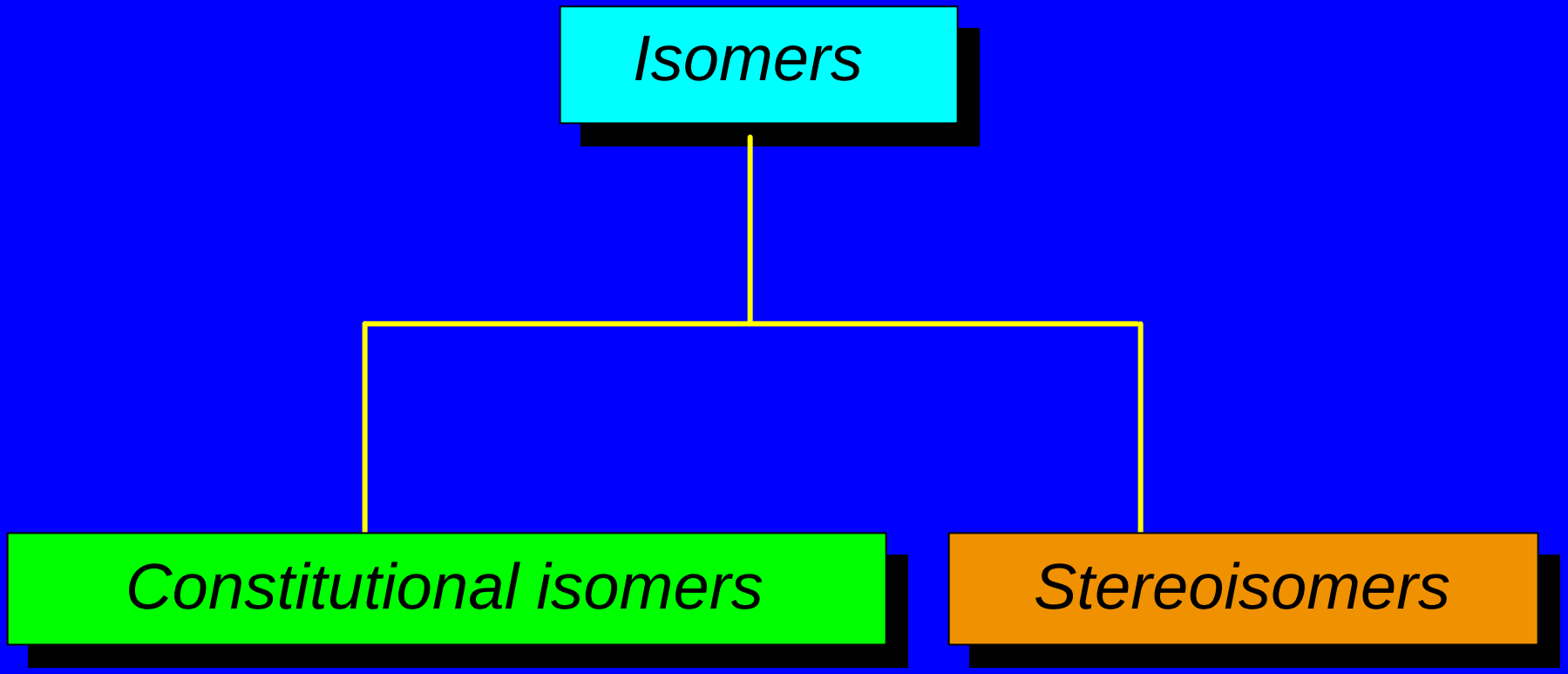
Isomers are different compounds that have the same molecular formula.


Isomers
Constitutional isomers
Stereoisomers

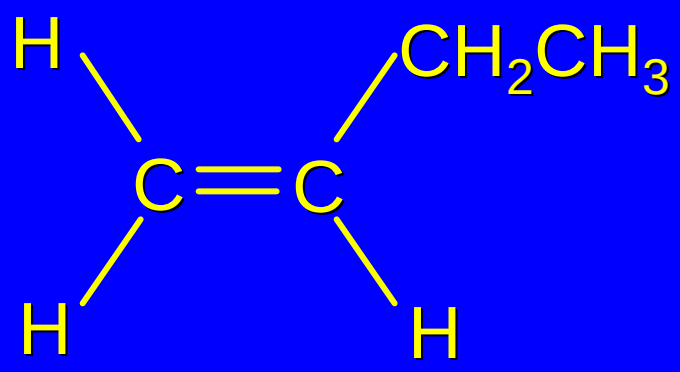


different connectivity

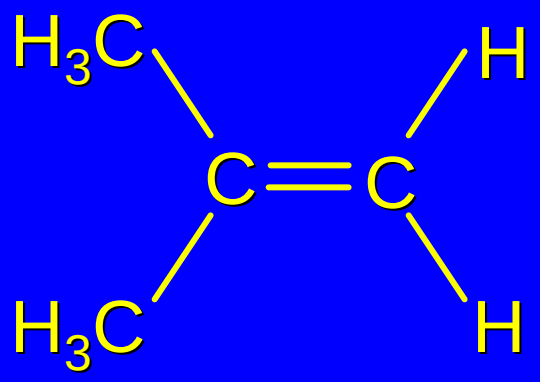
same connectivity;
different arrangement
of atoms in space



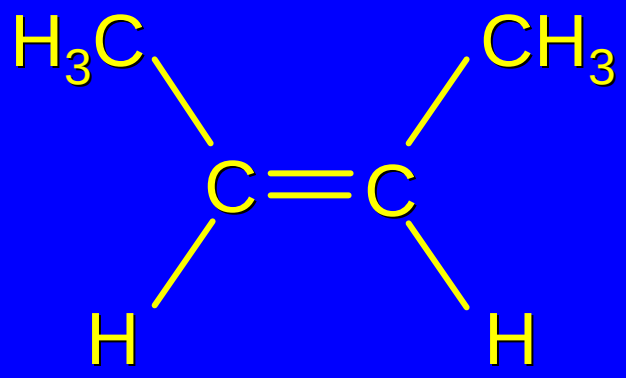
consider the isomeric alkenes of molecular formula C_4H_8



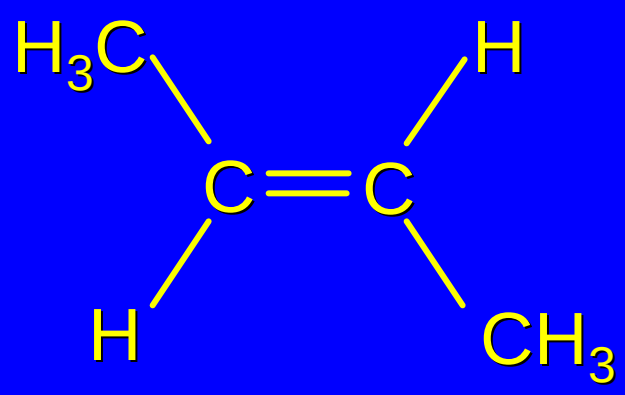
1-Butene



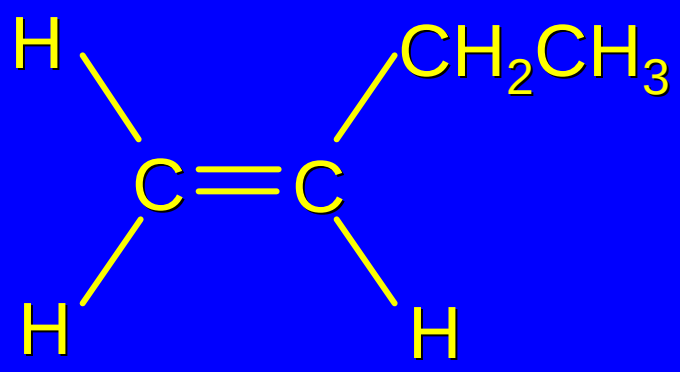
2-Methylpropene



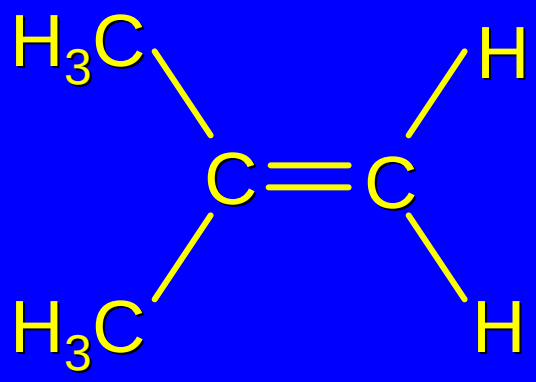
cis-2-Butene



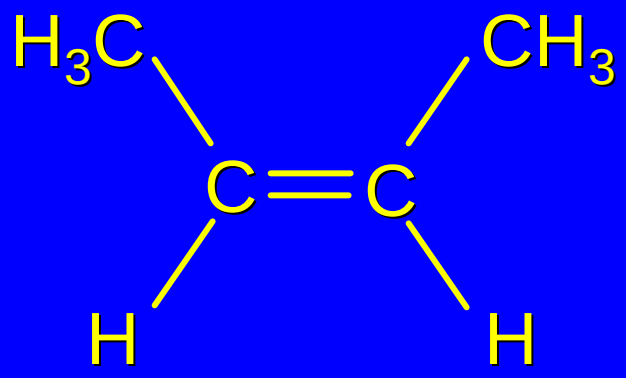
trans-2-Butene



1-Butene

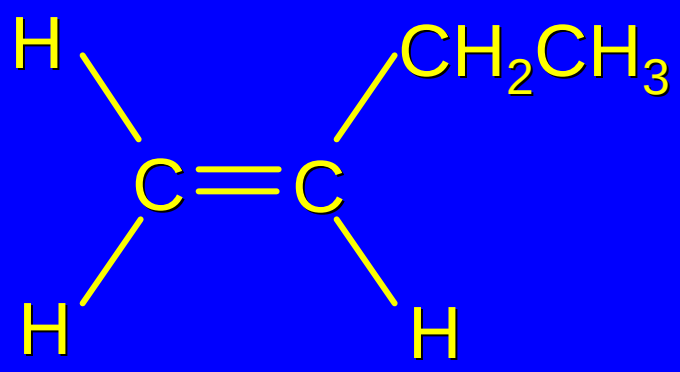


2-Methylpropene

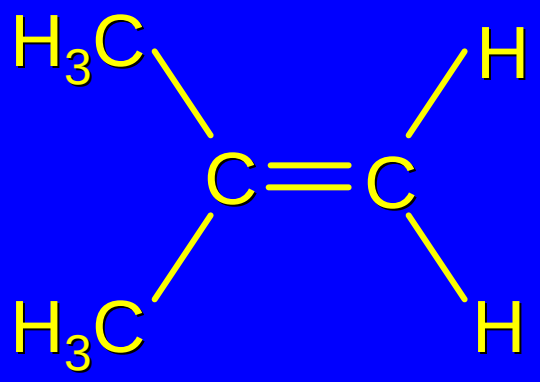


cis-2-Butene

Constitutional isomers

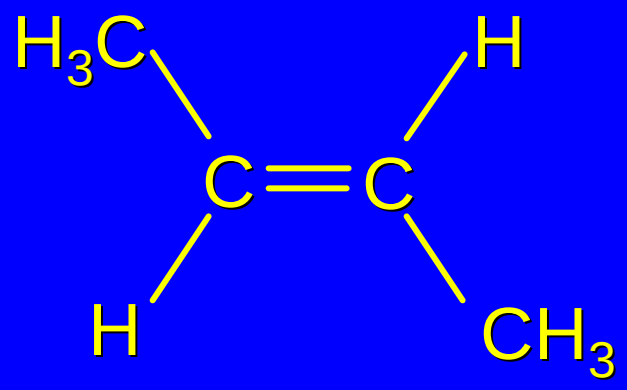


1-Butene



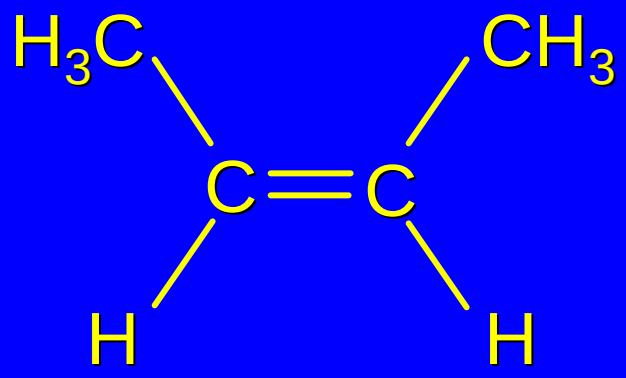
2-Methylpropene

Constitutional isomers

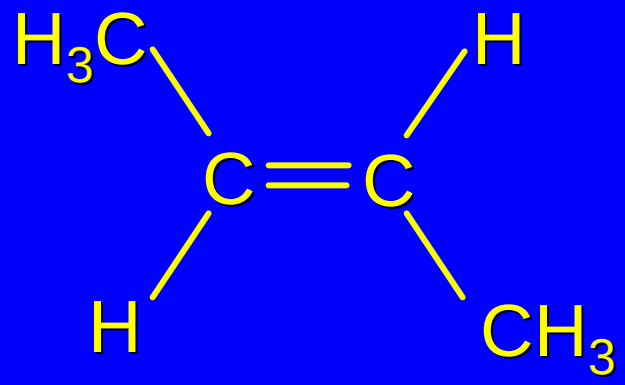


trans-2-Butene

Stereoisomers

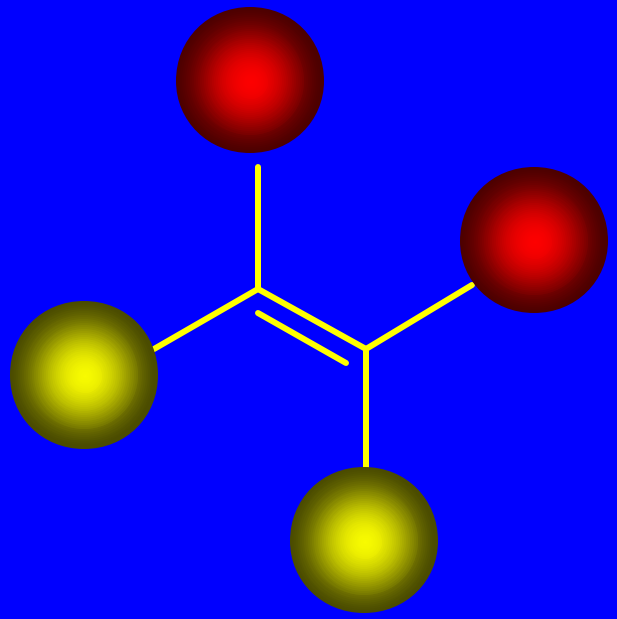


cis-2-Butene

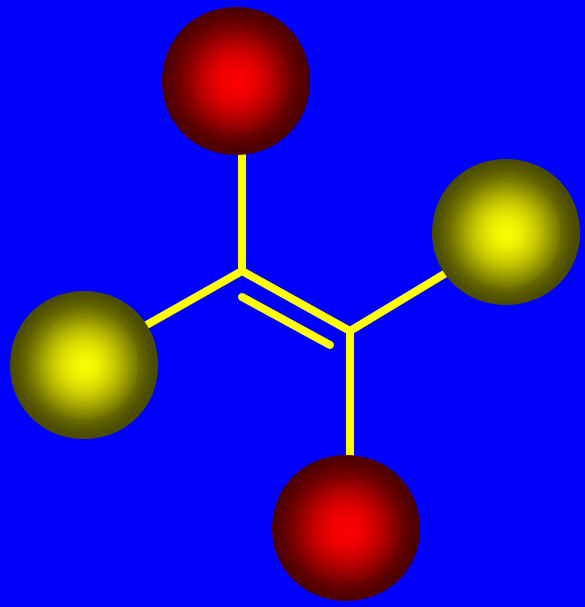


trans-2-Butene

Stereochemical Notation



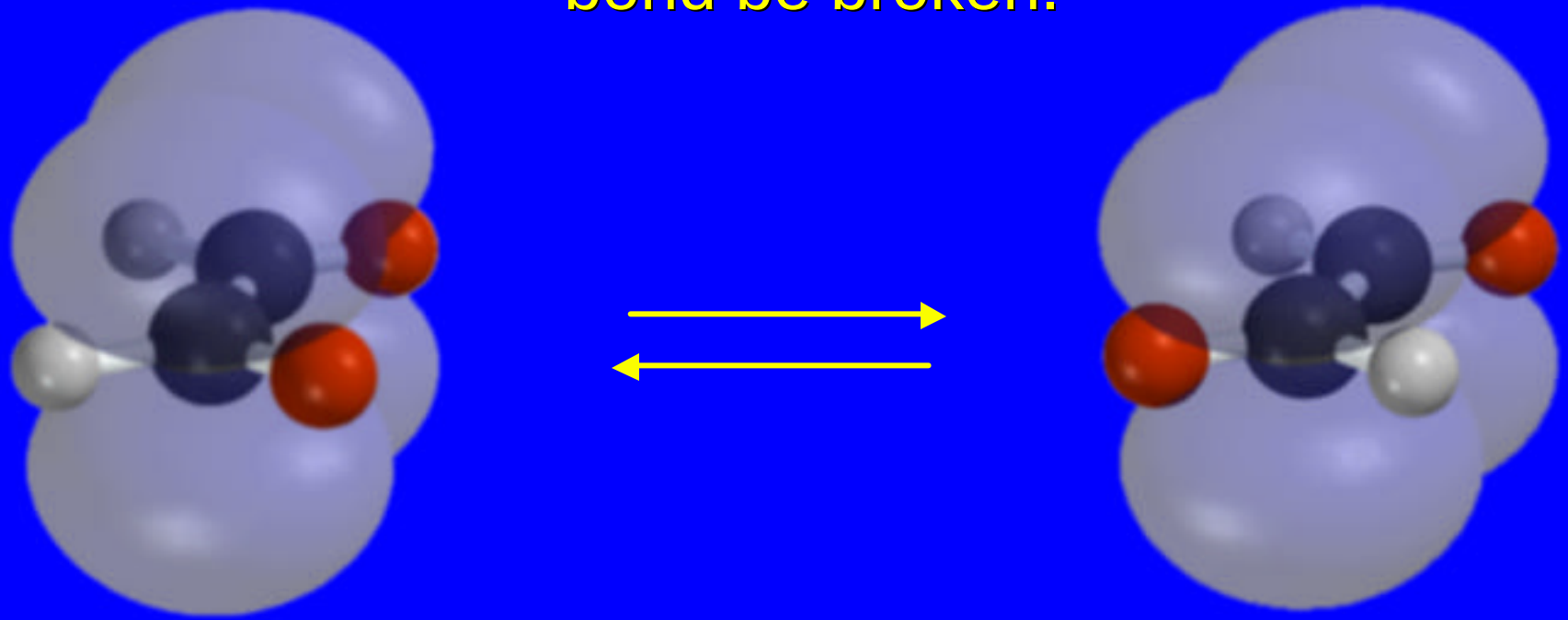
cis (identical or analogous substitutents on same side)



trans (identical or analogous substituents on opposite sides)

Figure 5.2

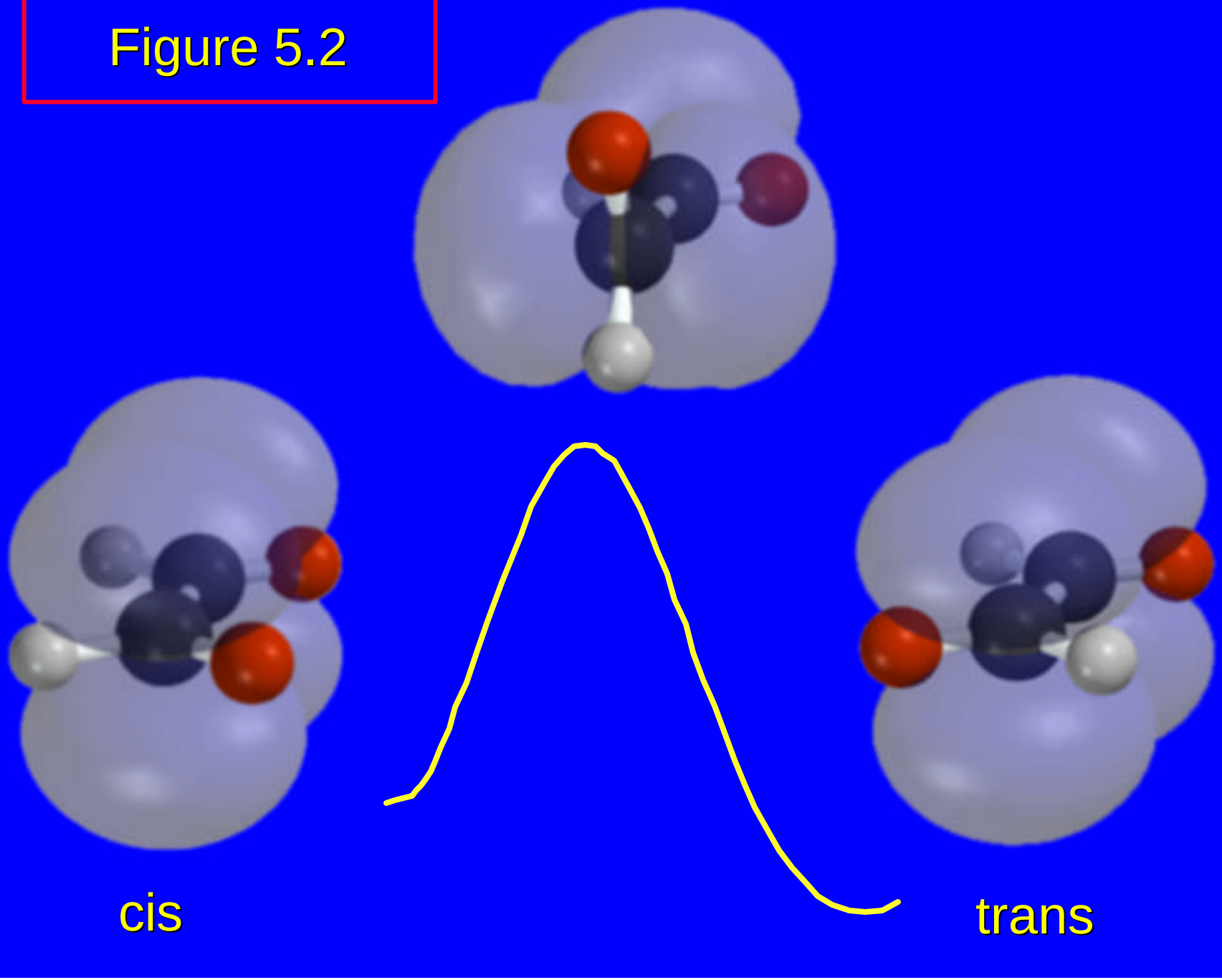
Interconversion of stereoisomeric alkenes does not normally occur. Requires that π component of double bond be broken.



cis

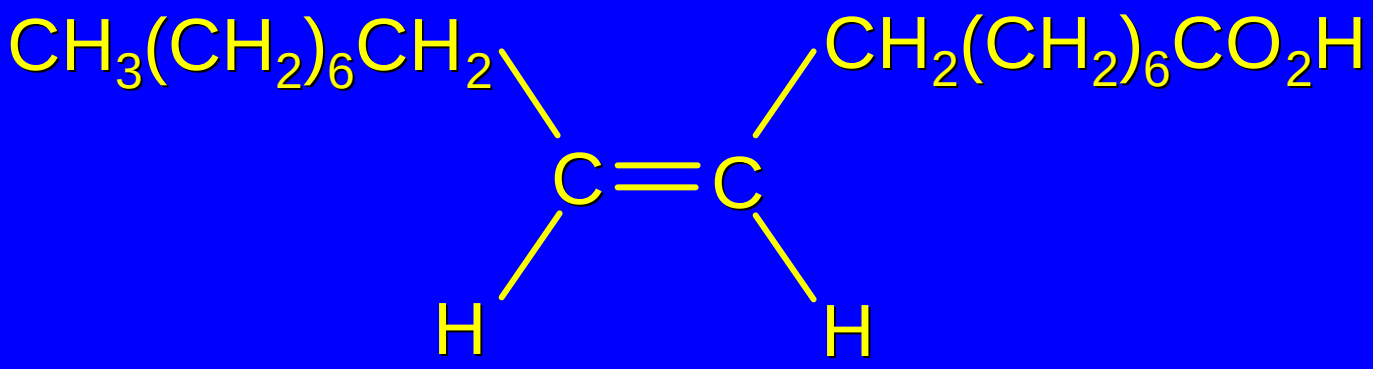
trans

Figure 5.2



5.4
Naming Steroisomeric Alkenes by the E-Z Notational System

Stereochemical Notation

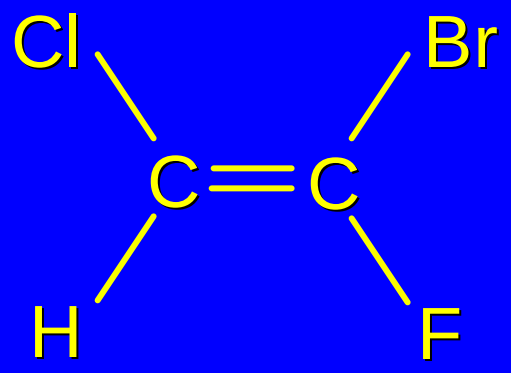


Oleic acid

cis and trans are useful when substituents are identical or analogous (oleic acid has a cis double bond)

cis and trans are ambiguous when analogies are not obvious

Example



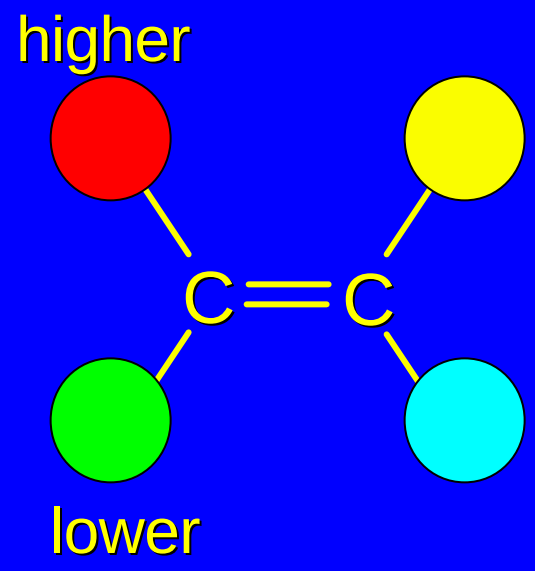
What is needed:

1) systematic body of rules for ranking substituents
2) new set of stereochemical symbols other than cis and trans

The E-Z Notational System

E : higher ranked substituents on opposite sides

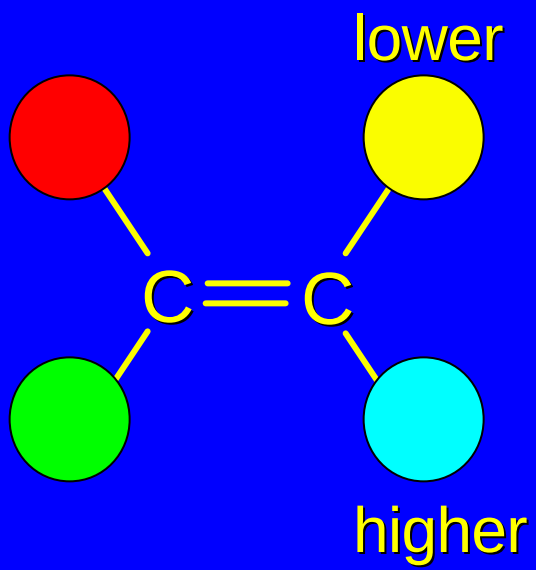
Z : higher ranked substituents on same side



The E-Z Notational System

E : higher ranked substituents on opposite sides

Z : higher ranked substituents on same side



The E-Z Notational System

E : higher ranked substituents on opposite sides

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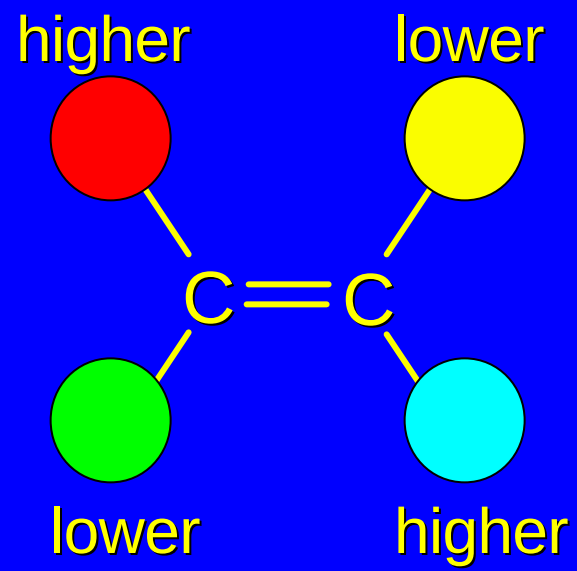
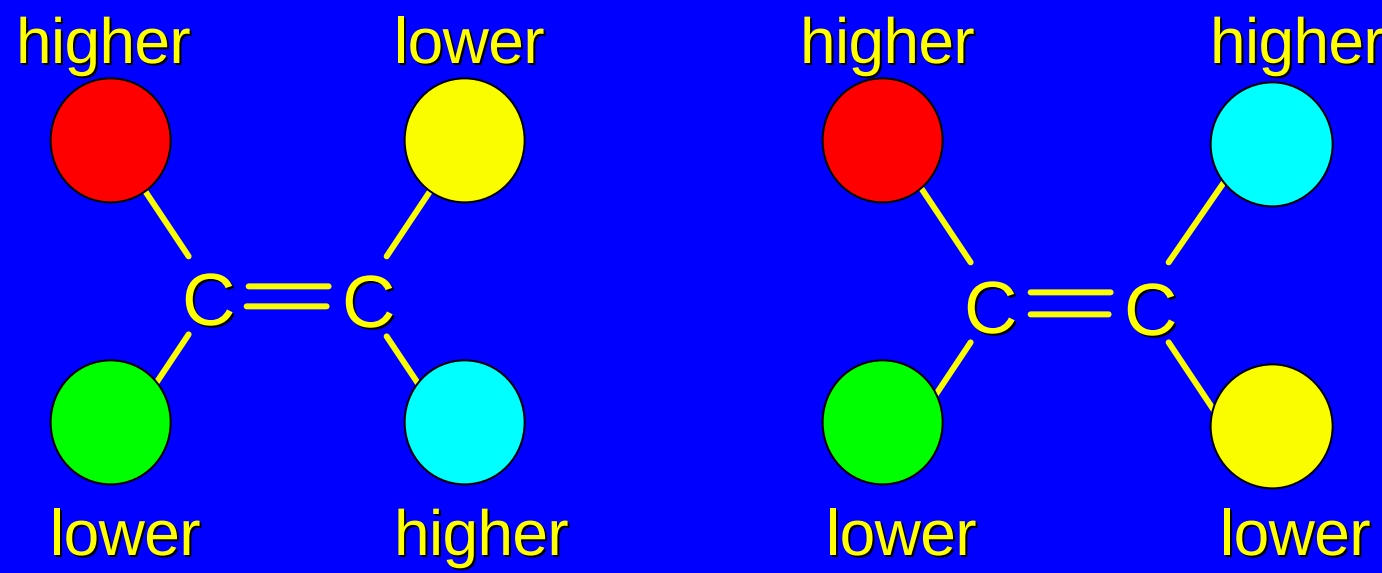


Entgegen

The E-Z Notational System

E : higher ranked substituents on opposite sides

Z : higher ranked substituents on same side

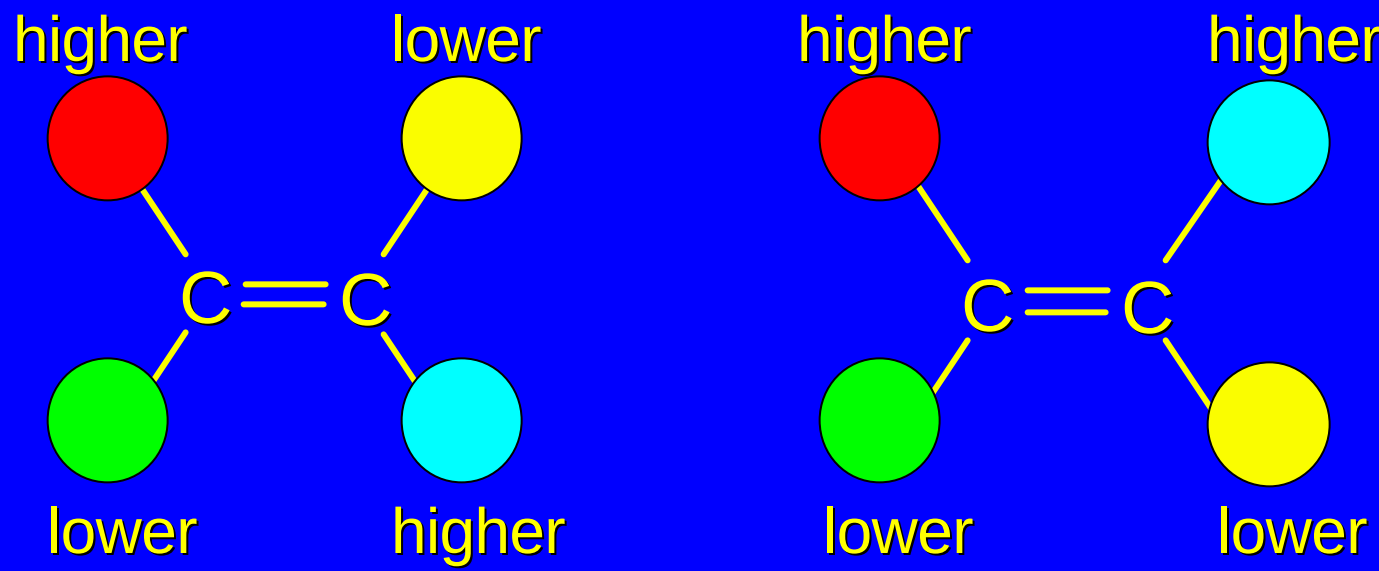


Entgegen *Zusammen*

The E-Z Notational System

Question: How are substituents ranked?

Answer: They are ranked in order of decreasing atomic number.



Entgegen *Zusammen*

The Cahn-Ingold-Prelog (CIP) System

The system that we use was devised by

R. S. Cahn
Sir Christopher Ingold
Vladimir Prelog

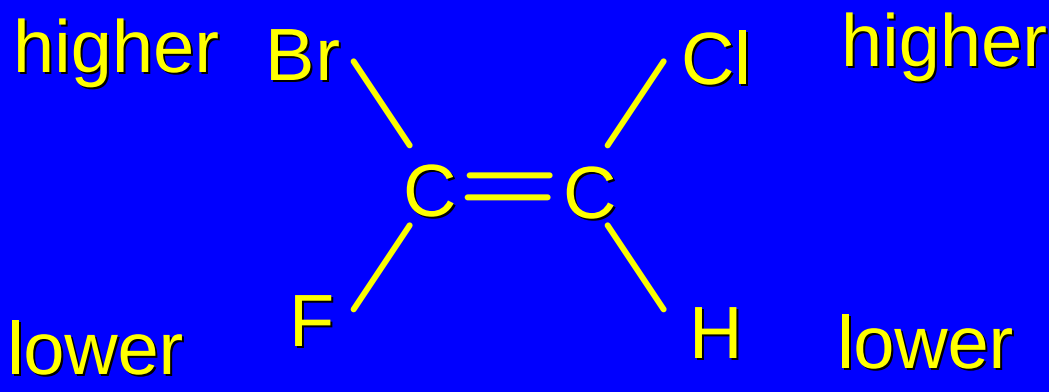
Their rules for ranking groups were devised in connection with a different kind of stereochemistry—one that we will discuss in Chapter 7—but have been adapted to alkene stereochemistry.

Table 5.1 CIP Rules

(1) Higher atomic number outranks lower atomic number

Br > F

Cl > H



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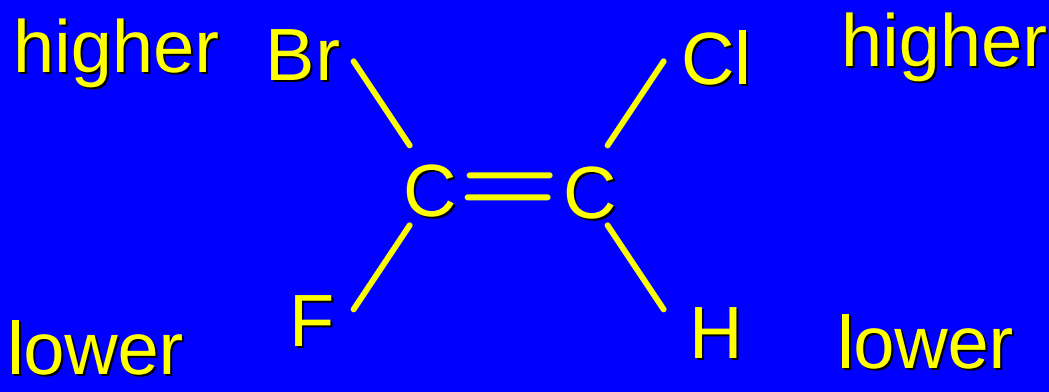

(*Z*)-1-Bromo-2-chloro-1-fluoroethene

Table 5.1 CIP Rules

(2) When two atoms are identical, compare the atoms attached to them on the basis of their atomic numbers. Precedence is established at the first point of difference.

—CH_2CH_3 outranks —CH_3

—C(C,H,H) —C(H,H,H)

Table 5.1 CIP Rules

(3) Work outward from the point of attachment, comparing all the atoms attached to a particular atom before proceeding further along the chain.

—CH(CH$_3$)$_2$ outranks —CH$_2$CH$_2$OH

—C(C,C,H) —C(C,H,H)

Table 5.1 CIP Rules

(4) Evaluate substituents one by one.
Don't add atomic numbers within groups.

—CH_2OH outranks —$C(CH_3)_3$

—C(O,H,H) —C(C,C,C)

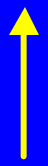

Table 5.1 CIP Rules

(5) An atom that is multiply bonded to another atom is considered to be replicated as a substituent on that atom.

—CH=O outranks —CH_2OH

—C(O,O,H) —C(O,H,H)

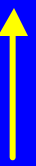

Table 5.1 CIP Rules

A table of commonly encountered substituents ranked according to precedence is given on the inside back cover of the text.