Organic Chemistry I

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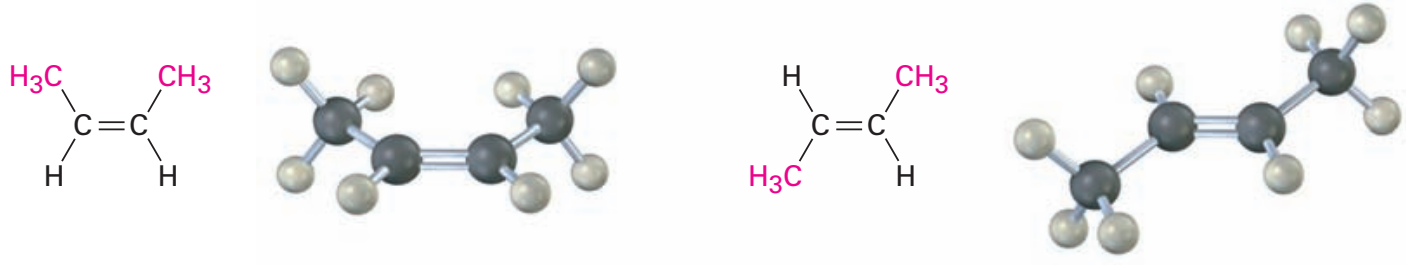
Organic Chemistry, (9th edition)

By *John McMurry*, Cengage Learning, 2016

Cis–trans isomerism in alkenes

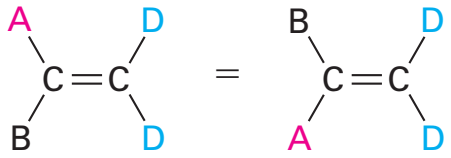
Since rotation around carbon–carbon double can't occur, a disubstituted alkene (*disubstituted* means that two substituents other than hydrogen) such as 2-butene with two possible isomers can't spontaneously interconvert; they are different, isolable compounds.

The compound with substituents on the same side of the double bond is called *cis*-2-butene, and the isomer with substituents on opposite sides is *trans*-2-butene.

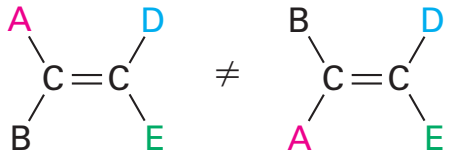


***cis*-2-Butene** ***trans*-2-Butene**

If one of the double-bond carbons is attached to two identical groups, cis–trans isomerism is not possible.



These two compounds are identical; they are not cis–trans isomers.



These two compounds are not identical; they are cis–trans isomers.

Alkene Stereochemistry and the *E,Z* Designation

The cis–trans naming system is used only for disubstituted alkenes.

For trisubstituted and tetrasubstituted double bonds, the ***E,Z* naming system** are used according to the Cahn–Ingold–Prelog sequence rules:

Rule 1

Considering each of the double-bond carbons separately, look at the two substituents attached and rank them according to the atomic number of the first atom in each. An atom with higher atomic number ranks higher than an atom with lower atomic number.

Rule 2

If a decision can't be reached by ranking the first atoms in the two substituents, look at the second, third, or fourth atoms away from the double-bond until the first difference is found.

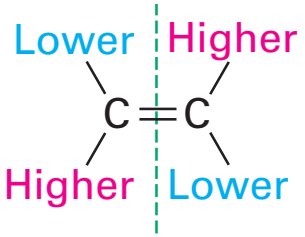
Rule 3

Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.

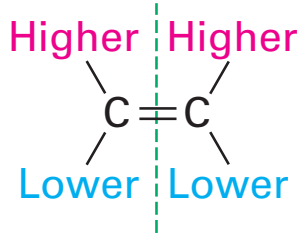
Once the two groups attached to each double-bonded carbon have been ranked as either higher or lower, look at the entire molecule.

If the higher-ranked groups on each carbon are on the same side of the double bond, the alkene is said to have ***Z* geometry**, for the German *zusammen,* meaning “together.”

If the higher-ranked groups are on opposite sides, the alkene has ***E* geometry**, for the German *entgegen,* meaning “opposite.”



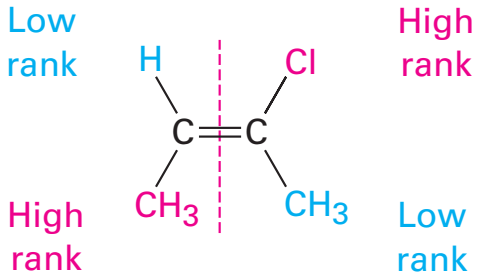
E double bond
(Higher-ranked groups
are on opposite sides.)



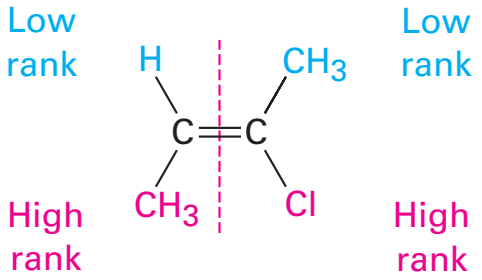
Z double bond
(Higher-ranked groups
are on the same side.)

For example 2-chloro-2-butene: chlorine has a higher atomic number than carbon, a –Cl substituent is ranked higher than a $–CH_3$ group.

Methyl is ranked higher than hydrogen, so isomer **(a)** is designated *E* because the higher-ranked groups are on opposite sides of the double bond. Isomer **(b)** has *Z* geometry because its higher-ranked groups are on opposite side of the double bond.

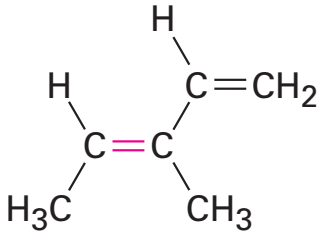


(a) (*E*)-2-Chloro-2-butene

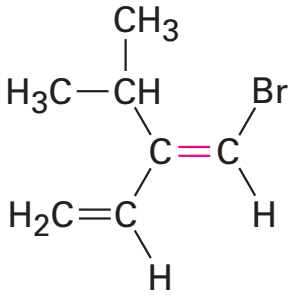


(b) (*Z*)-2-Chloro-2-butene

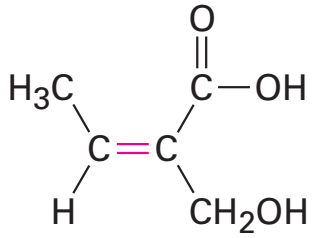
Other examples:



(*E*)-3-Methyl-1,3-pentadiene



(*E*)-1-Bromo-2-isopropyl-1,3-butadiene



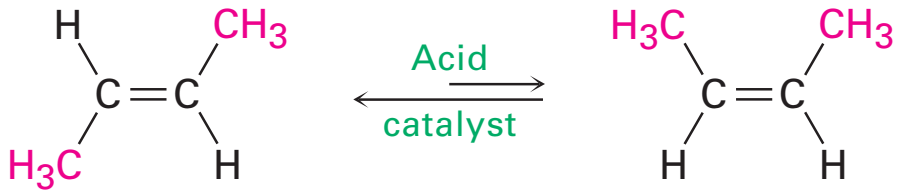
(*Z*)-2-Hydroxymethyl-2-butenoic acid

Stability of alkenes

Although the cis–trans interconversion of alkene isomers does not occur spontaneously, it can often be brought about by treating the alkene with a strong acid catalyst.

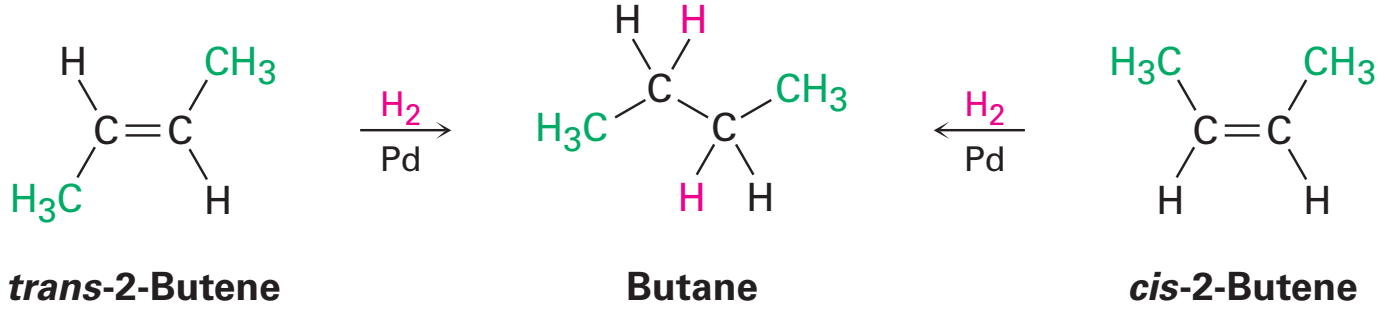
If we interconvert *cis*-2-butene with *trans*-2-butene and allow them to reach equilibrium, we find that they aren't of equal stability. The trans isomer is more stable than the cis isomer by 2.8 kJ/mol (0.66 kcal/mol) at room temperature, corresponding to a 76:24 ratio.

Cis alkenes are less stable than their trans isomers because of steric strain between the two larger substituents on the same side of the double bond.



Trans (76%) **Cis (24%)**

To find relative stabilities of alkene isomers, a *hydrogenation* reaction give the corresponding alkane when treated with H_2 gas in the presence of a catalyst such as palladium or platinum.

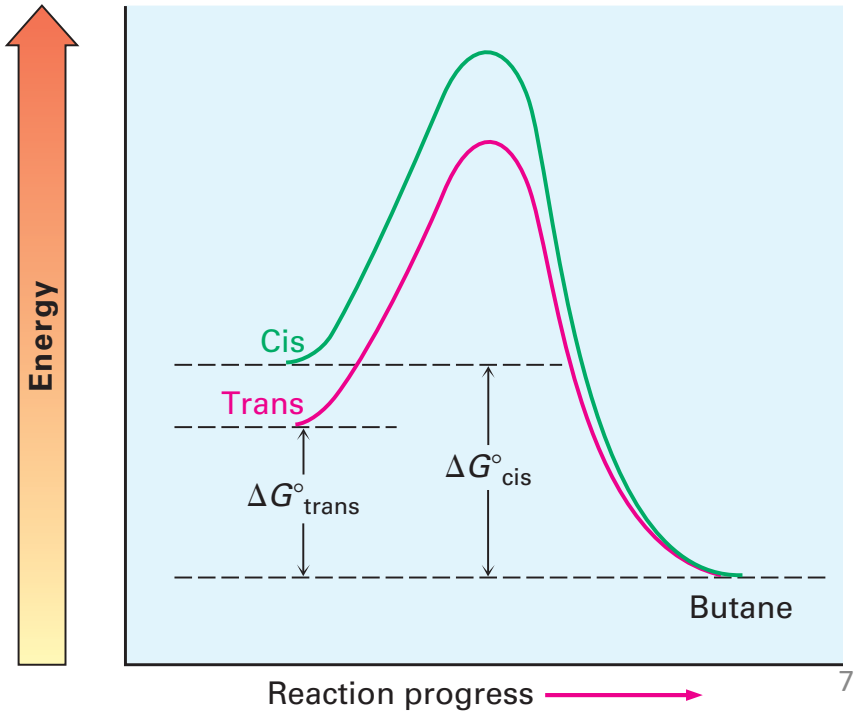


***trans*-2-Butene** **Butane** ***cis*-2-Butene**

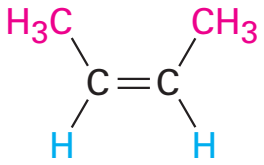
Because *cis*-2-butene is less stable than *trans*-2-butene by 2.8 kJ/mol, the energy diagram shows the cis alkene at a higher energy level.

After reaction, both curves are at the same energy level (butane).

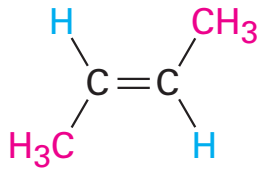
More energy is released in the hydrogenation of the cis isomer than the trans isomer because the cis isomer has more energy to begin with.



The heats of hydrogenation ($\Delta H°_{hydrog}$) is used to determine the relative stabilities of cis and trans isomers. *cis*-2-Butene has $\Delta H°$ = -119 kJ/mol (-28.3 kcal/mol), while *trans*-2-butene has $\Delta H°$ = -115 kJ/mol (-27.4 kcal/mol)—a difference of 4 kJ/mol.



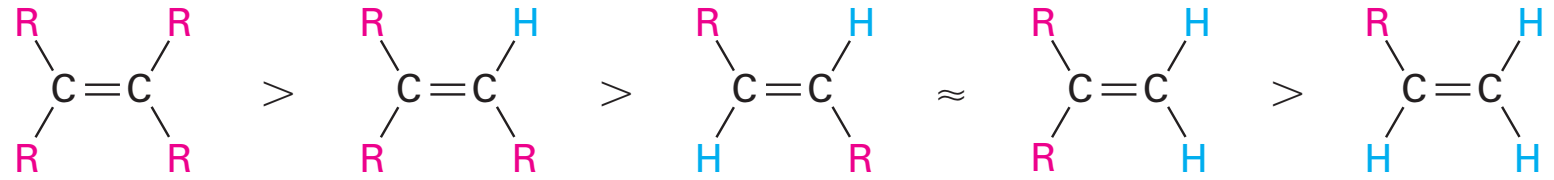
Cis isomer
$\Delta H°_{hydrog} = -120$ kJ/mol



Trans isomer
$\Delta H°_{hydrog} = -116$ kJ/mol

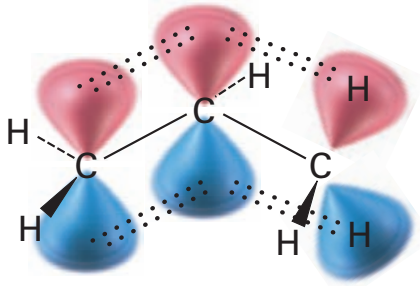
Alkenes become more stable with increasing substitution:

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted



The stability order of substituted alkenes is due to a combination of two factors. One is a stabilizing interaction between the C=C π bond and adjacent C–H σ bonds on substituents (**hyperconjugation)**.

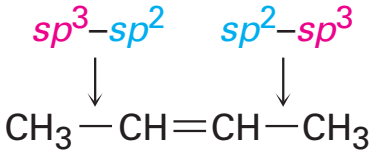
The more substituents present on the double bond, the more hyperconjugation occurs and the more stable the alkene.



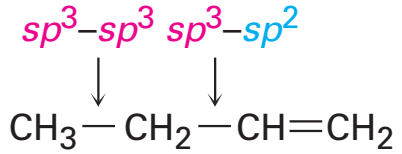
A second factor that contributes to alkene stability involves bond strengths. A bond between an sp^2 carbon and an sp^3 carbon is somewhat stronger than a bond between two sp^3 carbons.

In comparing 1-butene and 2-butene, the monosubstituted isomer has one sp^3–sp^3 bond and one sp^3–sp^2 bond, while the disubstituted isomer has two sp^3–sp^2 bonds.

More highly substituted alkenes always have a higher ratio of sp^3–sp^2 bonds to sp^3–sp^3 bonds than less highly substituted alkenes and are therefore more stable.



2-Butene
(more stable)

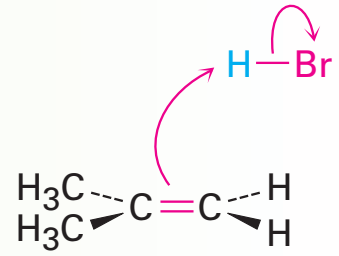


1-Butene
(less stable)

Electrophilic addition reactions of alkenes

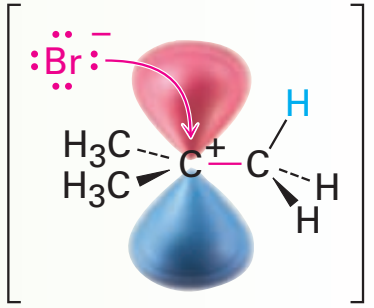
Alkenes behave as nucleophiles (Lewis bases) in polar reactions, donating a pair of electrons from their electron-rich C=C bond to an electrophile (Lewis acid).

Reaction of 2-methylpropene with HBr yields 2-bromo-2-methylpropane.



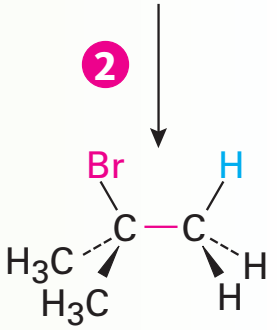
2-Methylpropene

1 A hydrogen atom on the electrophile HBr is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant *p* orbital. Simultaneously, two electrons from the H–Br bond move onto bromine, giving bromide anion.



Carbocation intermediate

2 The bromide ion donates an electron pair to the positively charged carbon atom, forming a C–Br bond and yielding the neutral addition product.



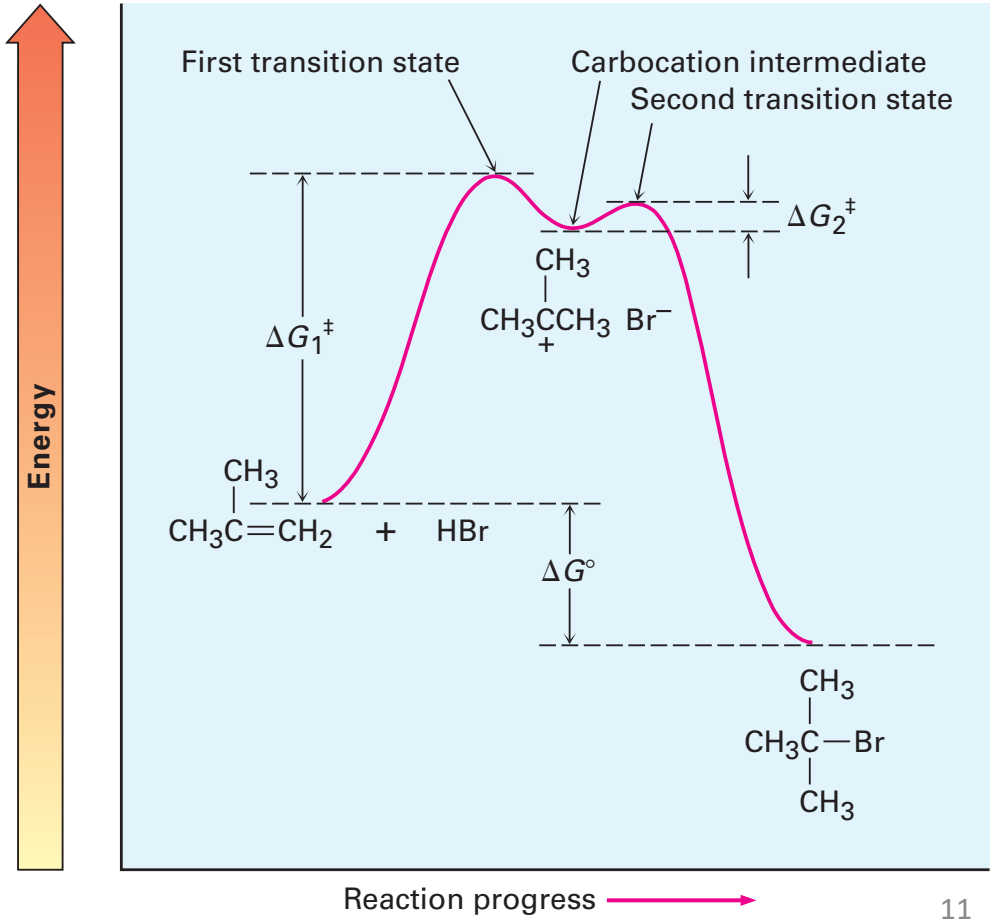
2-Bromo-2-methylpropane

An energy diagram for the overall electrophilic addition reaction has two peaks (**transition states**) separated by a valley (**carbocation intermediate**).

The energy level of the intermediate is higher than that of the starting alkene, but the reaction as a whole is exergonic (negative $\Delta G°$).

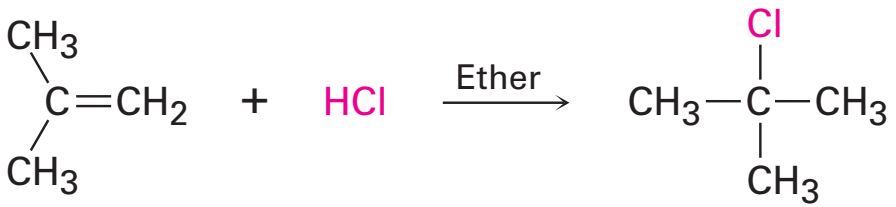
The first step, protonation of the alkene to yield the intermediate cation, is relatively slow.

But once the cation intermediate is formed, it rapidly reacts to yield the final alkyl bromide product.

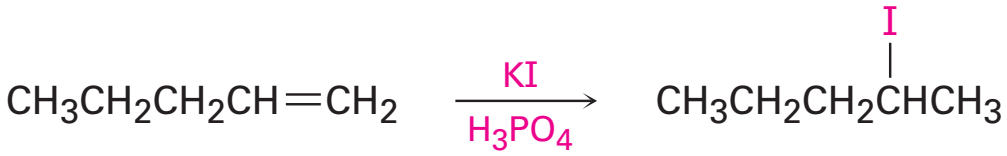


Electrophilic addition to alkenes is successful not only with HBr but with HCl, HI, and H_2O as well.

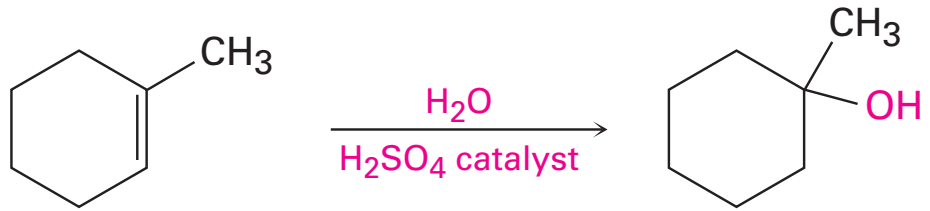
Note that HI is usually generated in the reaction mixture by treating potassium iodide with phosphoric acid, and a strong acid catalyst is needed for the addition of water.



2-Methylpropene **2-Chloro-2-methylpropane (94%)**



1-Pentene **(HI)** **2-Iodopentane**



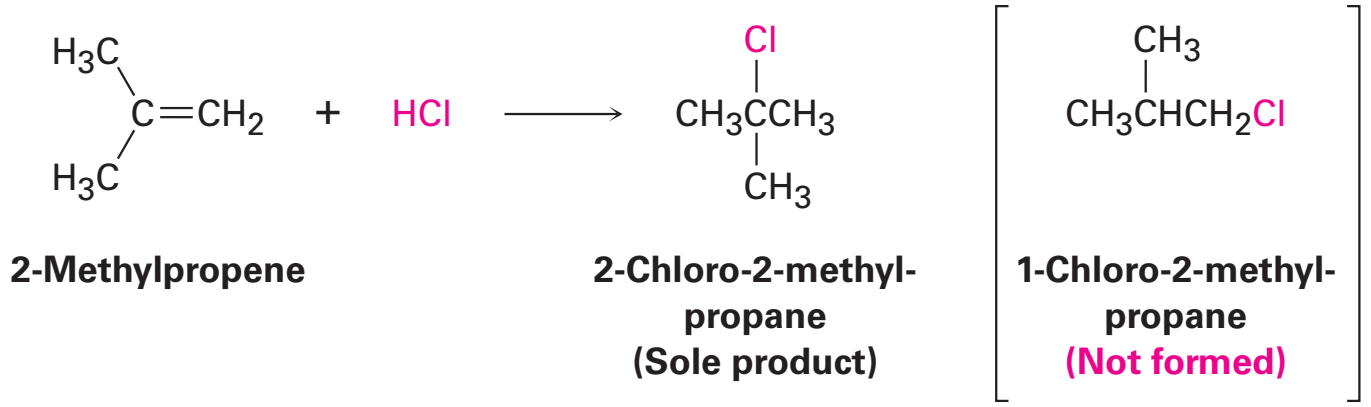
1-Methylcyclohexene **1-Methylcyclohexanol**

Orientation of electrophilic additions: Markovnikov's rule

An unsymmetrically substituted alkene gives a single addition product rather than a mixture.

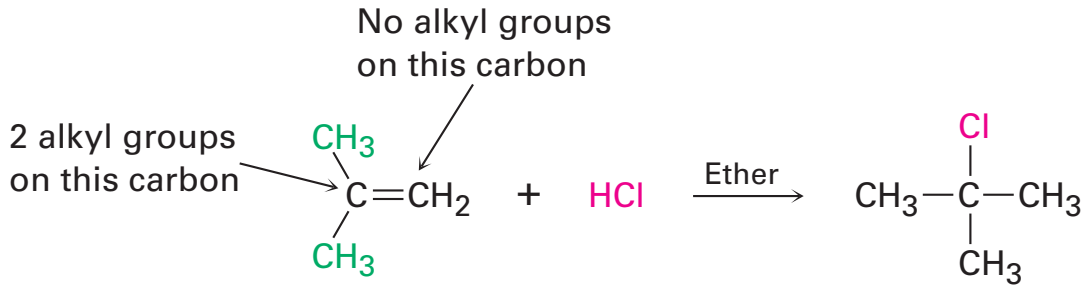
For example, 2-methylpropene *might* react with HCl to give both 2-chloro-2-methylpropane and 1-chloro-2-methylpropane, but it doesn't. It gives only 2-chloro-2-methyl- propane as the sole product.

We say that such reactions are **regiospecific** when only one of two possible orientations of an addition occurs.

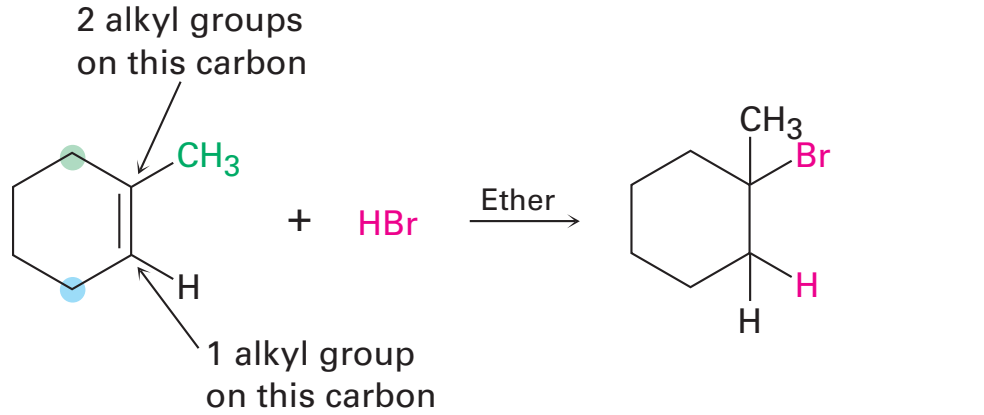


Markovnikov's rule

In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents.

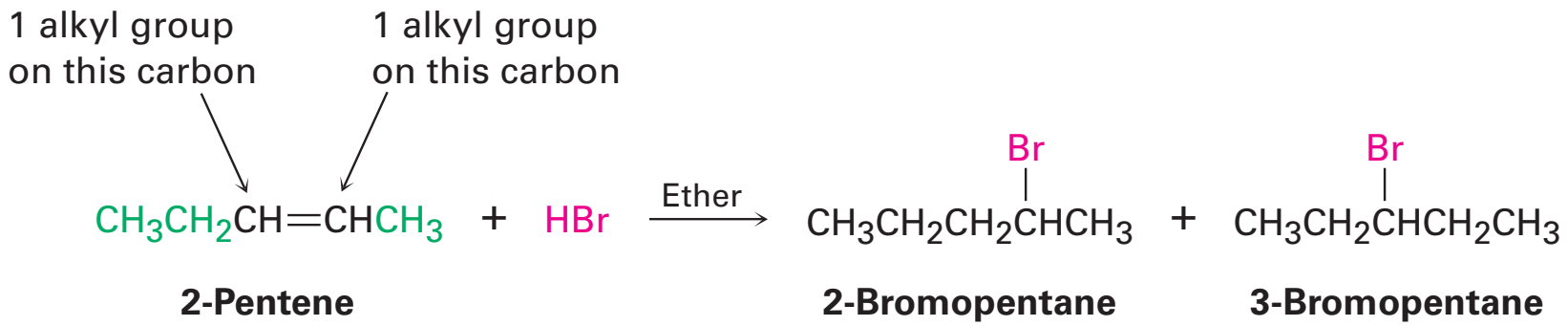


2-Methylpropene **2-Chloro-2-methylpropane**



1-Methylcyclohexene **1-Bromo-1-methylcyclohexane**

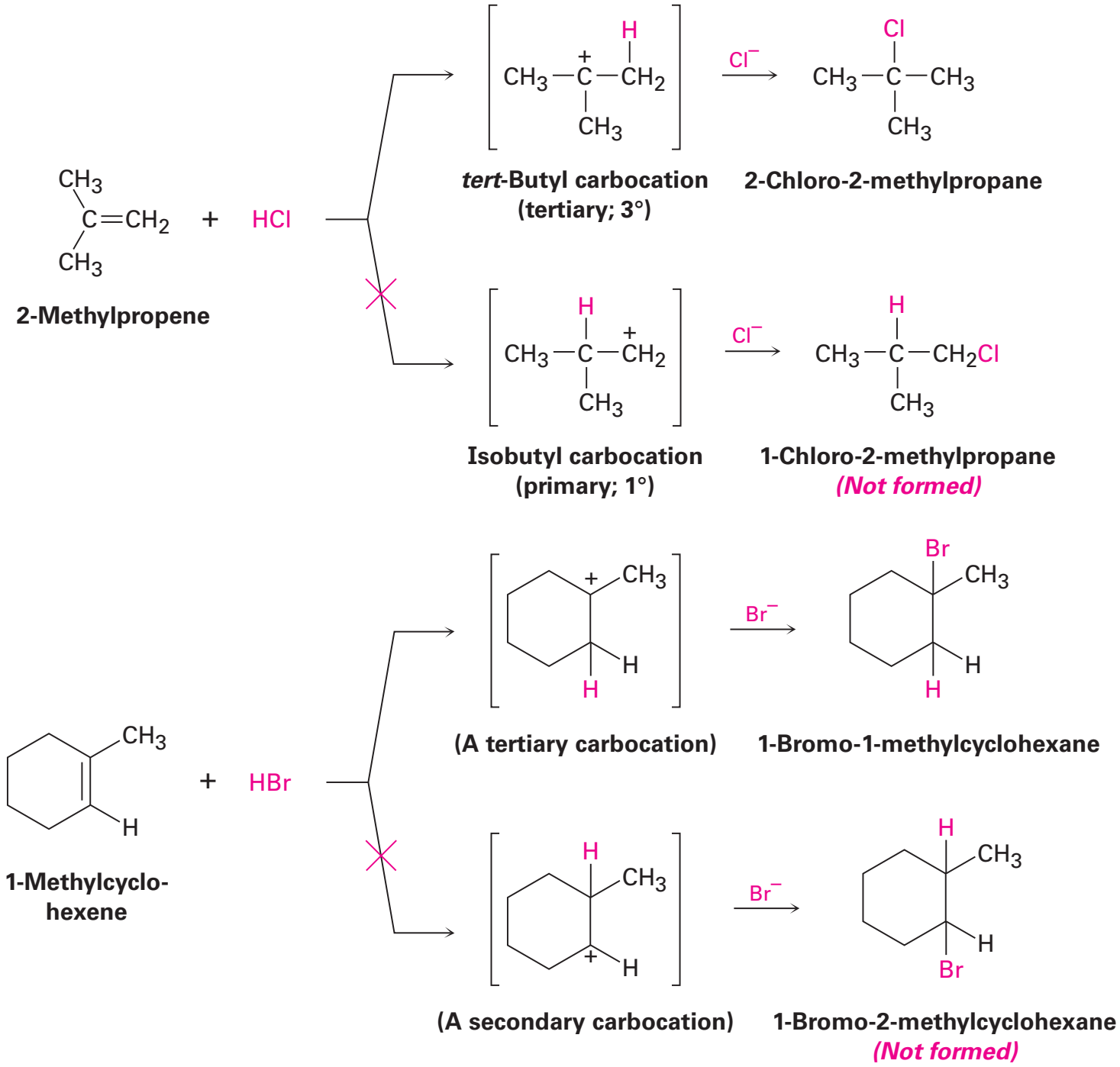
When both double-bonded carbon atoms have the same degree of substitution, a mixture of addition products results.



Because carbocations are involved as intermediates in these electrophilic addition reactions, Markovnikov's rule can be restated in the following way:

Markovnikov's rule (restated)

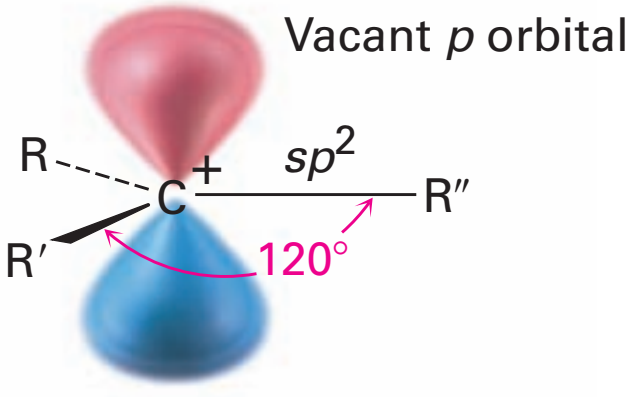
In the addition of HX to an alkene, the more highly substituted carbocation is formed as the intermediate rather than the less highly substituted one.


2-Methylpropene
HCl
tert-Butyl carbocation
(tertiary; 3°)
2-Chloro-2-methylpropane
Isobutyl carbocation
(primary; 1°)
1-Chloro-2-methylpropane
(Not formed)
1-Methylcyclo-
hexene
HBr
(A tertiary carbocation)
1-Bromo-1-methylcyclohexane
(A secondary carbocation)
1-Bromo-2-methylcyclohexane
(Not formed)

Carbocation Structure and Stability

Carbocations are planar. The trivalent carbon is sp^2-hybridized, and the three substituents are oriented toward the corners of an equilateral triangle.

Because there are only six valence electrons on carbon and all six are used in the three σ bonds, the p orbital extending above and below the plane is unoccupied.



Thermodynamic measurements show that the stability of carbocations increases with increasing substitution: tertiary > secondary > primary > methyl

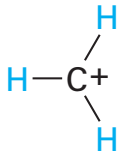
Methyl **Primary (1°)** **Secondary (2°)** **Tertiary (3°)**

Stability

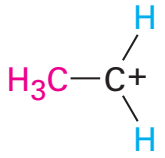
Carbocations Stability: Reason?

1. Inductive effects: electrons from a relatively larger and more polarizable alkyl group (sp^3) can shift toward a neighboring positive charge (sp^2) more easily than the electron from a hydrogen (sp^2 hybrid is more electronegative than sp^3 hybrid).

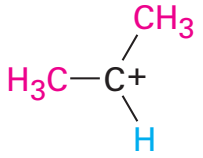
more alkyl groups → more electron density shifts → more inductive stabilization



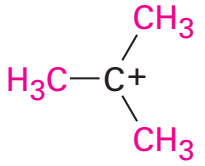
Methyl:
No alkyl groups
donating electrons



Primary:
One alkyl group
donating electrons



Secondary:
Two alkyl groups
donating electrons



Tertiary:
Three alkyl groups
donating electrons

2. Hyperconjugation: the stabilizing interaction between a *p* orbital and properly oriented C–H σ bonds on neighboring carbons that are roughly parallel to the *p* orbital.

more alkyl groups → more possibilities of hyperconjugation → more carbocation stability