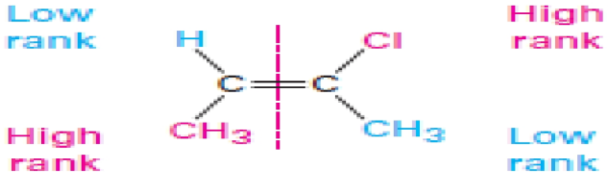
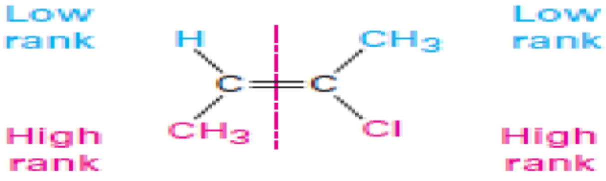
Rule 3

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." (For a simple way to remember which is which, note that the groups are on "ze zame zide" in the *Z* isomer.)

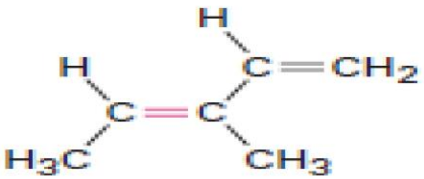


(a) (*E*)-2-Chloro-2-butene

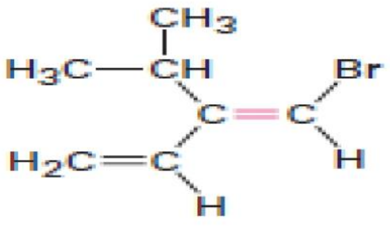


(b) (*Z*)-2-Chloro-2-butene

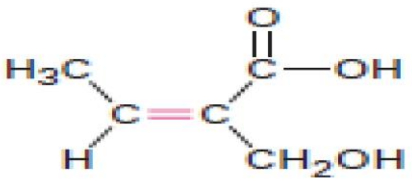
As an example, look at the following two isomers of 2-chloro-2-butene. Because chlorine has a higher atomic number than carbon, a -Cl substituent is ranked higher than a -CH_3 group. Methyl is ranked higher than hydrogen, however, so isomer **(a)** is designated *E* because the higher-ranked groups are on opposite sides of the double bond. Isomer **(b)** has *Z* geometry because its higher-ranked groups are on ze zame zide of the double bond.



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



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



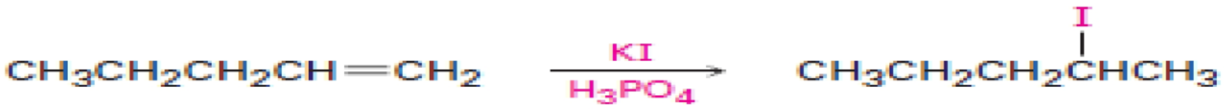
(*Z*)-2-Hydroxymethyl-2-butenoic acid

Electrophilic Addition Reactions of Alkenes

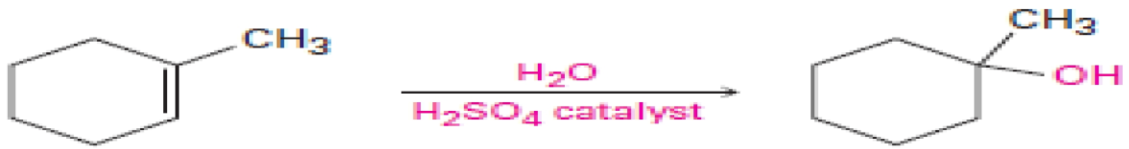
Before beginning a detailed discussion of alkene reactions, let's review briefly some conclusions. Alkenes behave as nucleophiles (Lewis bases) in polar reactions, donating a pair of electrons from their electron-rich C=C bond to an electrophile (Lewis acid). For example, reaction of 2-methylpropene with HBr yields 2-bromo- 2-methylpropane.

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 that a strong acid catalyst is needed for the addition of water.

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



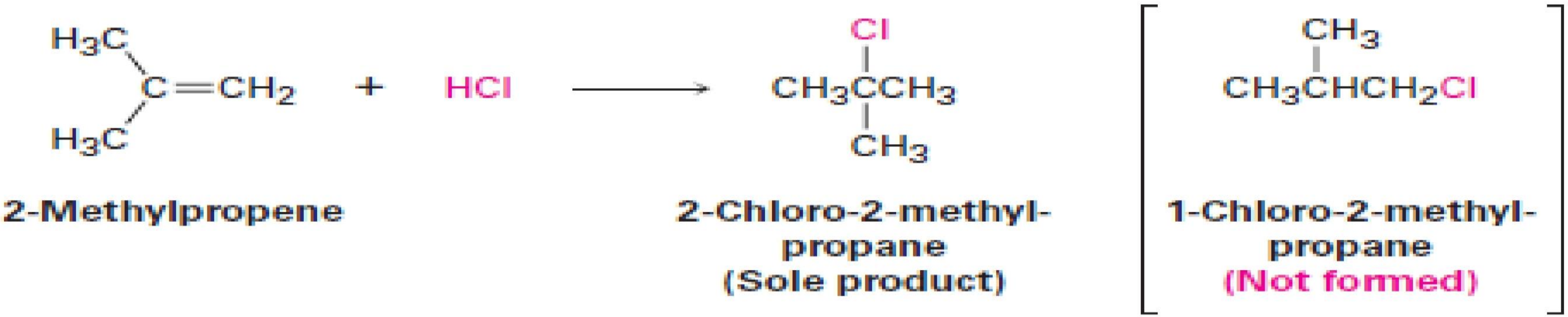
1-Pentene (HI) 2-Iodopentane



1-Methylcyclohexene → 1-Methylcyclohexanol

Orientation of Electrophilic Additions: Markovnikov's Rule

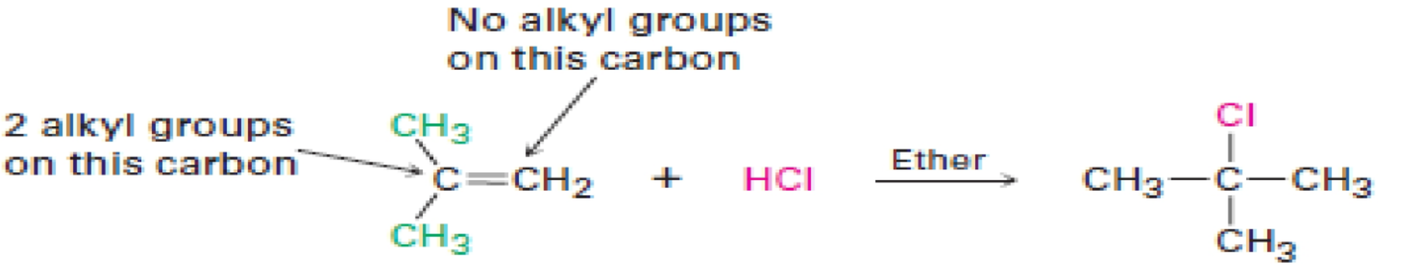
Look carefully at the electrophilic addition reactions shown in the previous section. In each case, an unsymmetrically substituted alkene gives a single addition product rather than the mixture that might be expected. For example, 2-methylpropene *might* react with HCl to give both 2-chloro-2-methylpropane and 1-chloro-2-methylpropane, but it doesn't. It gives only 2-chloro-2-methylpropane as the sole product. Similarly, it's invariably the case in biological alkene addition reactions that only a single product is formed. We say that such reactions are **regiospecific** (**ree**-jee-oh-specific) when only one of two possible orientations of an addition occurs.



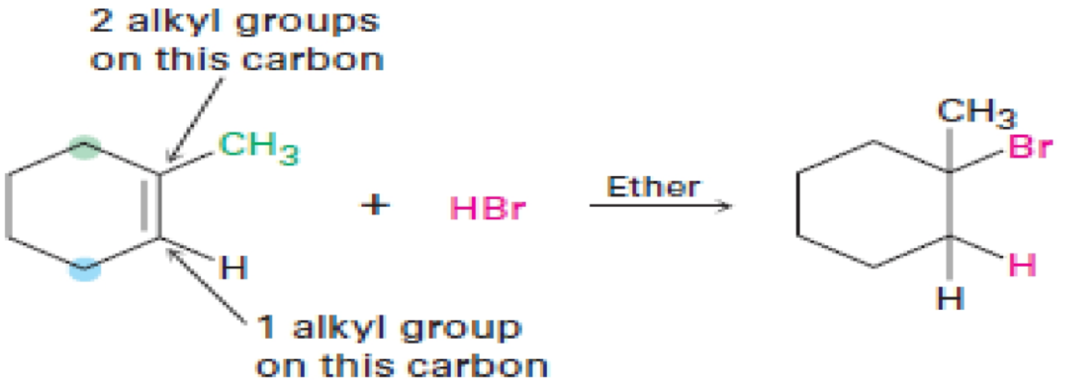
After looking at the results of many such reactions, the Russian chemist Vladimir Markovnikov proposed in 1869 what has become known as **Markovnikov's rule**.

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.

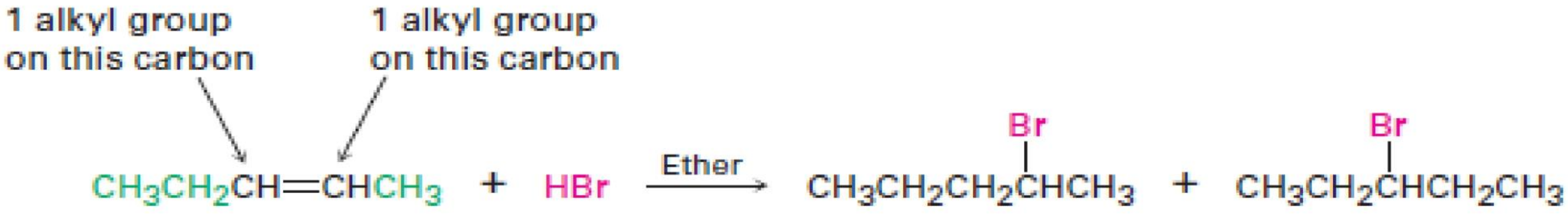


2-Methylpropene   2-Chloro-2-methylpropane



1-Methylcyclohexene   1-Bromo-1-methylcyclohexane

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



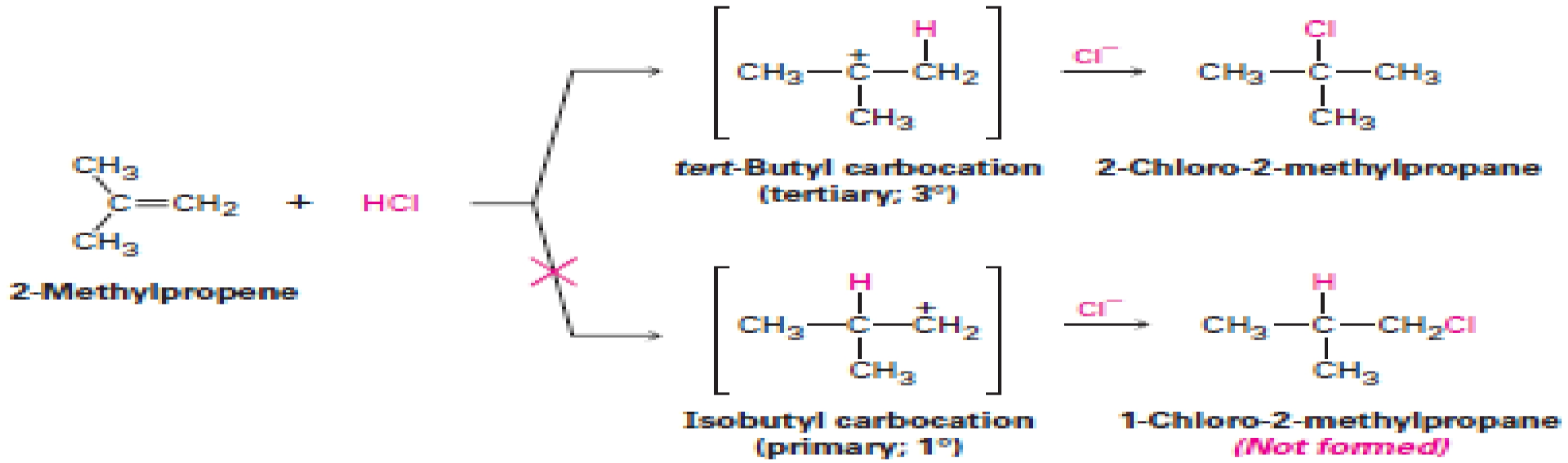
$$CH_3CH_2CH{=}CHCH_3 + HBr \xrightarrow{\text{Ether}} CH_3CH_2CH_2\overset{\overset{\displaystyle Br}{|}}{C}HCH_3 + CH_3CH_2\overset{\overset{\displaystyle Br}{|}}{C}HCH_2CH_3$$

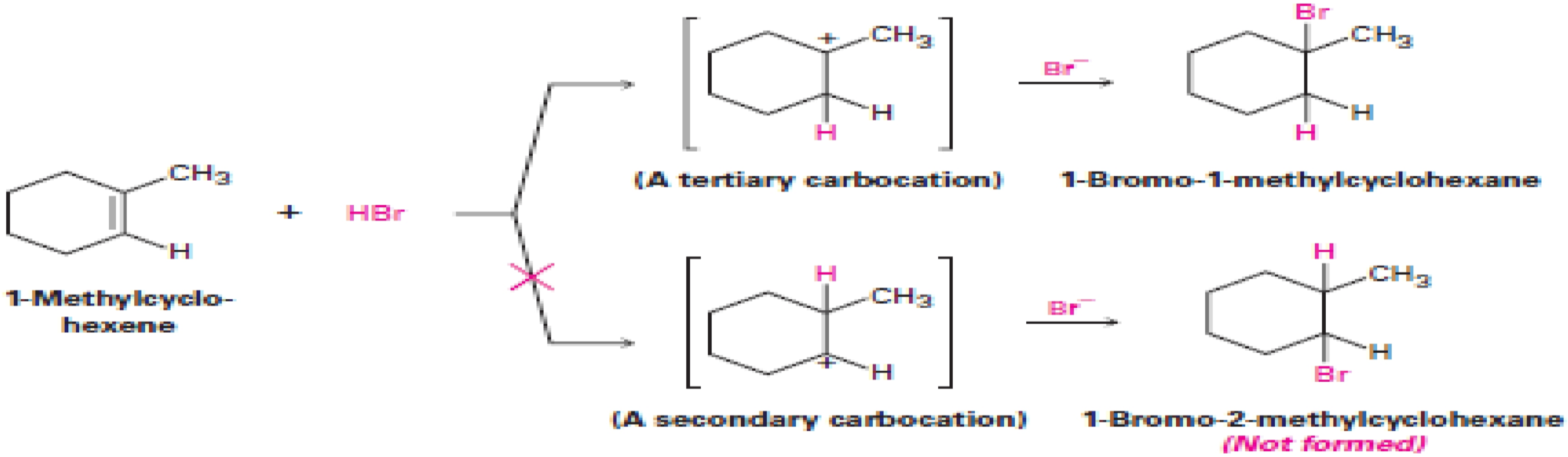
2-Pentene 2-Bromopentane 3-Bromopentane

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. For example, addition of HI to 2-methylpropene yields the intermediate *tertiary* carbocation rather than the alternative primary carbocation, and addition to 1-methylcyclohexene yields a tertiary cation rather than a secondary one.


2-Methylpropene
HCl
tert-Butyl carbocation (tertiary; 3°)
Cl⁻
2-Chloro-2-methylpropane
Isobutyl carbocation (primary; 1°)
Cl⁻
1-Chloro-2-methylpropane
(Not formed)


1-Methylcyclohexene
HBr
(A tertiary carbocation)
Br⁻
1-Bromo-1-methylcyclohexane
(A secondary carbocation)
Br⁻
1-Bromo-2-methylcyclohexane
(Not formed)

Carbocation Structure and Stability

To understand why Markovnikov's rule works, we need to learn more about the structure and stability of carbocations and about the general nature of reactions and transition states. The first point to explore involves structure. A great deal of experimental evidence has shown that carbocations are planar. The trivalent carbon is *sp*2-hybridized, and the three substituents are oriented toward the corners of an equilateral triangle, as indicated in **Figure 7-9**.

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.

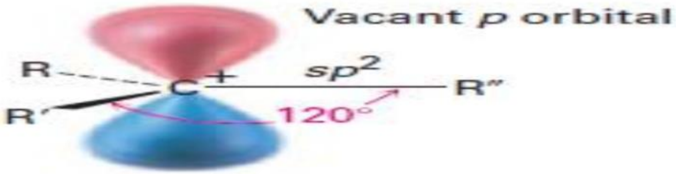
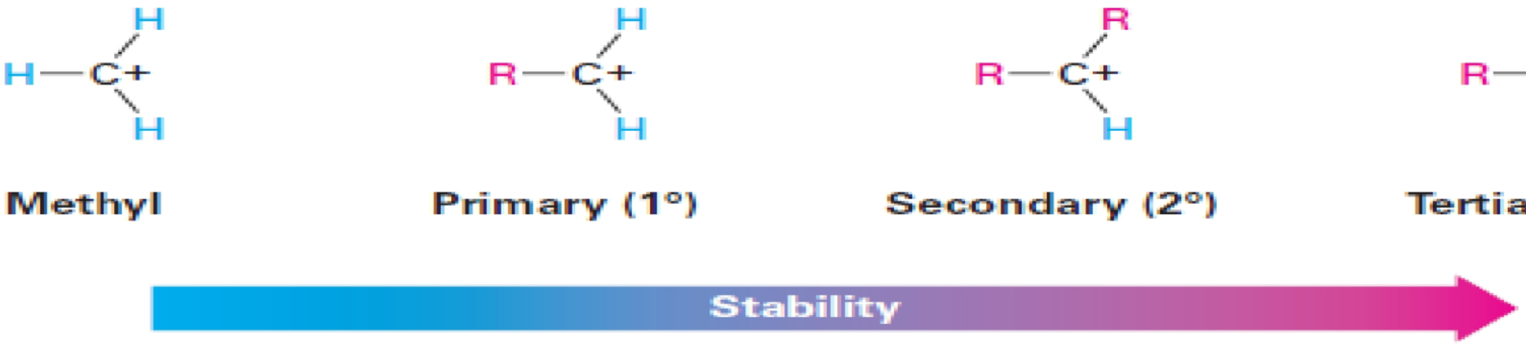
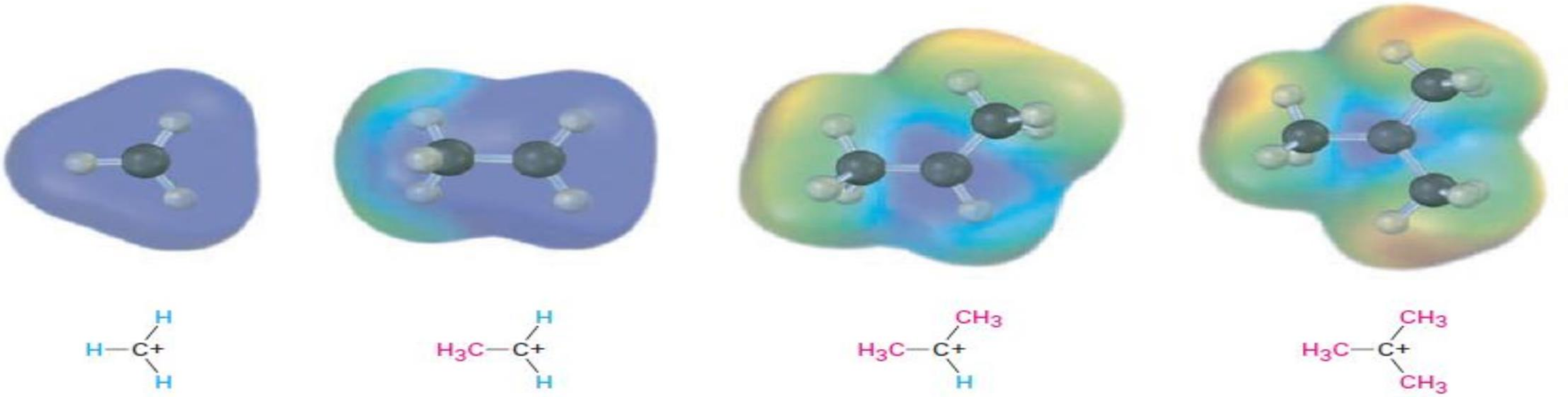


Figure 7-9 The structure of a carbocation. The trivalent carbon is *sp*2-hybridized and has a vacant *p* orbital perpendicular to the plane of the carbon and three attached groups.

The second point to explore involves carbocation stability. 2-Methylpropene might react with H^+ to form a carbocation having three alkyl substituents (a tertiary ion, 3°), or it might react to form a carbocation having one alkyl substituent (a primary ion, 1°). Since the tertiary alkyl chloride, 2-chloro-2-methylpropane, is the only product observed, formation of the tertiary cation is evidently favored over formation of the primary cation. Thermodynamic measurements show that, indeed, the stability of carbocations increases with increasing substitution so that the stability order is **tertiary > secondary > primary > methyl**.



Why are more highly substituted carbocations more stable than less highly substituted ones? There are at least two reasons. Part of the answer has to do with inductive effects, and part has to do with hyperconjugation. Inductive effects, in connection with polar covalent bonds, result from the shifting of electrons in an σ bond in response to the electronegativity of nearby atoms. In the present instance, electrons from a relatively larger and more polarizable alkyl group can shift toward a neighboring positive charge more easily than the electron from hydrogen. Thus, the more alkyl groups attached to the positively charged carbon, the more electron density shifts toward the charge and the more inductive stabilization of the cation occurs **(Figure 7-11)**.



Methyl: No alkyl groups donating electrons

Primary: One alkyl group donating electrons

Secondary: Two alkyl groups donating electrons

Tertiary: Three alkyl groups donating electrons

Figure 7-11 A comparison of inductive stabilization for methyl, primary, secondary, and tertiary carbocations. The more alkyl groups that are bonded to the positively charged carbon, the more electron density shifts toward the charge, making the charged carbon less electron poor (blue in electrostatic potential maps).

Hyperconjugation, in connection with the stabilities of substituted alkenes, is 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. The more alkyl groups there are on the carbocation, the more possibilities there are for hyperconjugation and the more stable the carbocation. **Figure 7-12** shows the molecular orbital for the ethyl carbocation, $CH_3CH_2^+$, and indicates the difference between the C-H bond perpendicular to the cation *p* orbital and the two C-H bonds more parallel to the cation *p* orbital. Only these roughly parallel C-H bonds are oriented properly to take part in hyperconjugation.

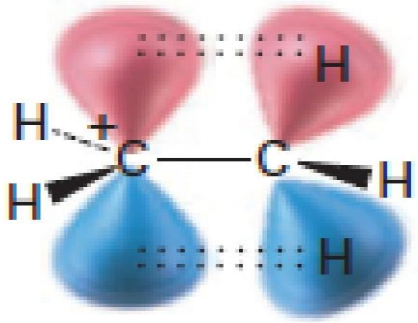
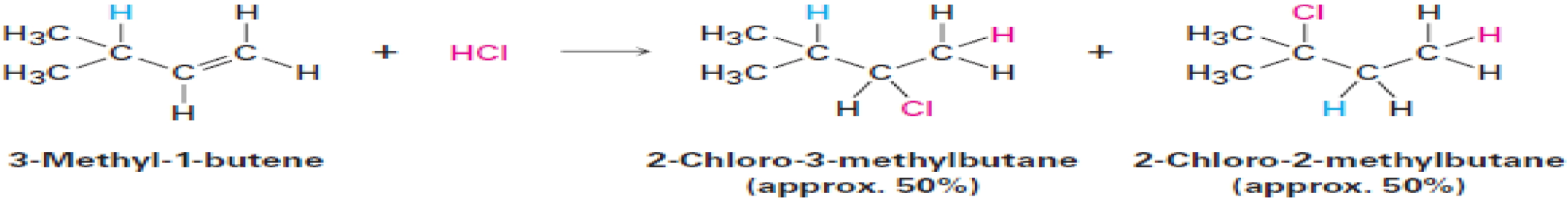


Figure 7-12 Stabilization of the ethyl carbocation, $CH_3CH_2^+$, through hyperconjugation. Interaction of neighboring C-H *s* bonds with the vacant *p* orbital stabilizes the cation and lowers its energy. The molecular orbital shows that only the two C-H bonds more parallel to the cation *p* orbital are oriented properly. The C-H bond perpendicular to the cation *p* orbital cannot take part.

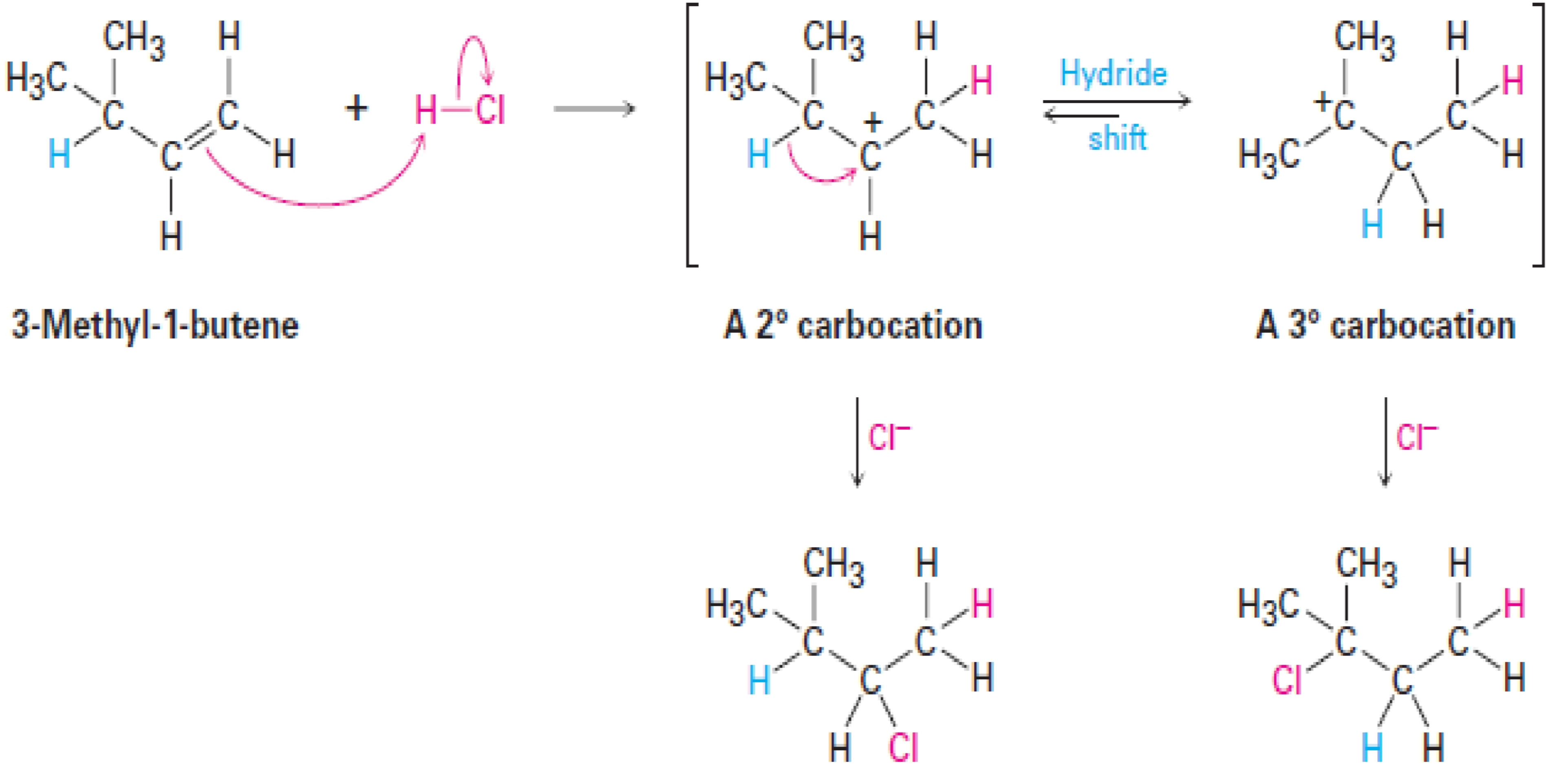
Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements

One of the best pieces of evidence supporting the carbocation mechanism for the electrophilic addition reaction was discovered by F. C. Whitmore of Pennsylvania State University, who found that structural rearrangements often occur during the reaction of HX with an alkene.

For example, reaction of HCl with 3-methyl-1-butene yields a substantial amount of 2-chloro-2-methylbutane in addition to the "expected" product, 2-chloro-3-methylbutane.



If the reaction takes place in a single step, it would be difficult to account for rearrangement, but if the reaction takes place in several steps, rearrangement is more easily explained. Whitmore suggested that it is a carbocation intermediate that undergoes rearrangement. The secondary carbocation intermediate formed by protonation of 3-methyl-1-butene rearranges to a more stable tertiary carbocation by a **hydride shift**—the shift of a hydrogen atom and its electron pair (a hydride ion, **:**H-) between neighboring carbons.



3-Methyl-1-butene

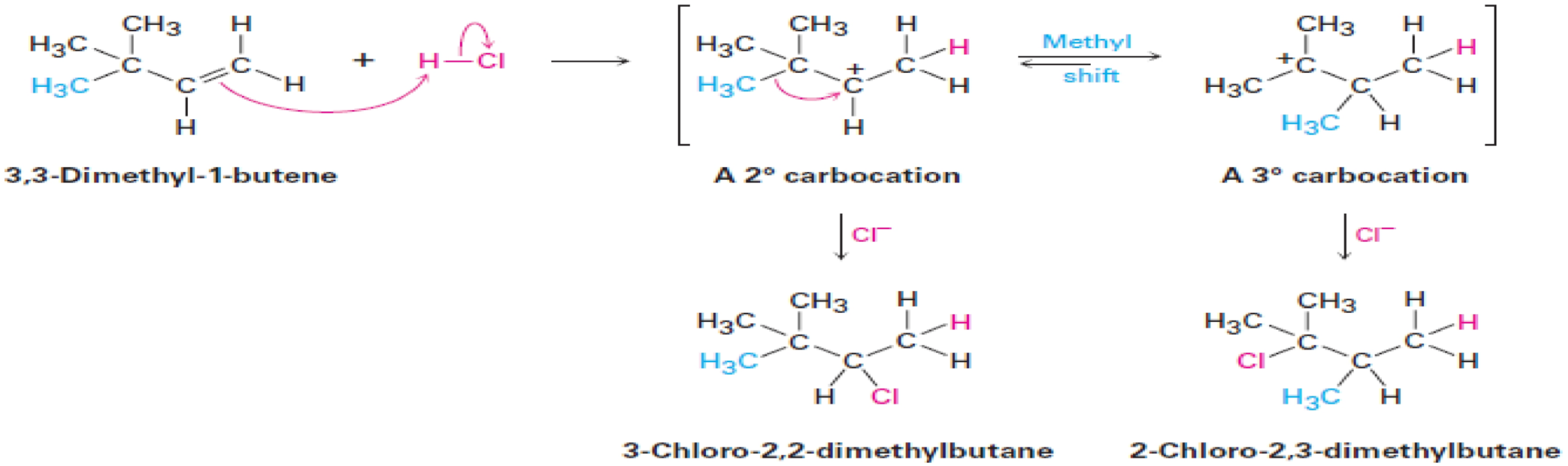
A 2° carbocation

A 3° carbocation

2-Chloro-3-methylbutane

2-Chloro-2-methylbutane

Carbocation rearrangements can also occur by the shift of an alkyl group with its electron pair. For example, reaction of 3,3-dimethyl-1-butene with HCl leads to an equal mixture of unrearranged 3-chloro-2,2-dimethylbutane and rearranged 2-chloro-2,3-dimethylbutane. In this instance, a secondary carbocation rearranges to a more stable tertiary carbocation by the shift of a methyl group.



Note the similarities between the two carbocation rearrangements: in both cases, a group (:H- or :CH_3-) moves to an adjacent positively charged carbon, taking its bonding electron pair with it. Also in both cases, a less stable carbocation rearranges to a more stable ion.