

Chapter 10

Alkenes and Alkynes.

Electrophilic and Concerted Addition Reactions

from
Organic Chemistry
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Chapter Outline of the Book

I. Foundations

1. Organic Molecules and Chemical Bonding
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3. Haloalkanes, Alcohols, Ethers, and Amines
4. Stereochemistry
5. Organic Spectrometry

II. Reactions, Mechanisms, Multiple Bonds

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7. Reactions of Haloalkanes, Alcohols, and Amines. Nucleophilic Substitution
8. Alkenes and Alkynes
9. Formation of Alkenes and Alkynes. Elimination Reactions
10. Alkenes and Alkynes. Addition Reactions
11. Free Radical Addition and Substitution Reactions

III. Conjugation, Electronic Effects, Carbonyl Groups

12. Conjugated and Aromatic Molecules
13. Carbonyl Compounds. Ketones, Aldehydes, and Carboxylic Acids
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IV. Carbonyl and Pericyclic Reactions and Mechanisms

16. Carbonyl Compounds. Addition and Substitution Reactions
17. Oxidation and Reduction Reactions
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V. Bioorganic Compounds

20. Carbohydrates
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10: Alkenes and Alkynes. Electrophilic and Concerted Addition Reactions

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- Alkenes to Alcohols by Electrophilic Addition*
- Alkenes to Alcohols by Hydroboration*
- Addition of H₂ to Alkenes and Alkynes*

Preview

(To be added)

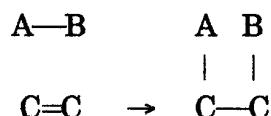
10.1 Addition Reactions

We learned about elimination reactions that form C=C and C≡C bonds in Chapter 9. In this chapter we learn about reactions in which reagents add to these multiple bonds.

General Considerations (10.1A)

We show a general equation for an addition reaction with an alkene in Figure 10.01.

Figure 10.01



This equation is the reverse of the general equation for an elimination reaction that we showed at the beginning of Chapter 9. This general equation does not show a mechanism for the addition process.

There are a number of different types of mechanisms for addition reactions, but we can group them into the four broad categories of (1) **electrophilic addition**, (2) **nucleophilic addition**, (3) **free radical addition**, and (4) **concerted addition**. *Electrophilic* and *nucleophilic* addition reactions involve intermediate ions so they are *ionic* addition reactions. In contrast, *free radical* additions, and *concerted* addition reactions, are *non-ionic* addition reactions because they do not involve the formation of intermediate ions.

Ionic Addition Reactions (10.1B)

We compare general features of nucleophilic and electrophilic addition reactions here. Later in the chapter, we follow this with a more detailed discussion of electrophilic addition reactions. We defer our more detailed discussion of nucleophilic addition reactions to later chapters.

Electrophilic Addition. Electrophilic addition reactions involve intermediate cations that arise from the reaction of a positively charged species or positively polarized reagent with a multiple bond (Figure 10.02).

Figure 10.02



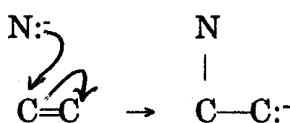
We call these positive reagents **electrophiles** because they are "electron loving". They use a pair of electrons from the multiple bond of the organic reactant to form a new C-E chemical bond. We often use the general symbol E^+ for electrophiles as we did above for its reaction with an alkene in Figure 10.02.

Electrophiles and Nucleophiles. It is important to understand the difference between *electrophiles* and *nucleophiles*. Electrophiles (E^+) are electron deficient and seek a pair of electrons from another species in order to form a chemical bond to that species. In contrast, nucleophiles ($\text{N}:^-$) or ($\text{-N}:^-$) have electron pairs, often unshared, that they use to form a bond to a species that they react with. Examples of nucleophiles that we saw in earlier chapters included halide ions ($\text{X}:^-$) and alkoxide ions ($\text{RO}:^-$).

Using this definition, we can think of the $\text{C}=\text{C}$ double bond shown in Figure 10.02 as a *nucleophile* since it supplies the bonding electron pair to the electrophile (E^+). This means that a vast number of organic reactions take place between an electrophile and a nucleophile. In order to categorize a reaction as *electrophilic* or *nucleophilic*, we look at whether the reagent (often inorganic) donates an electron pair (a nucleophile) to an organic substrate, or accepts an electron pair (an electrophile) from the organic substrate.

Nucleophilic Additions. We show a general equation for the addition of a nucleophile to a $\text{C}=\text{C}$ bond in Figure 10.03 [next page].

Figure 10.03



In contrast with electrophilic additions where a pair of π electrons of the C=C bond forms the new C-E bond, the electrons in the new C-N bond formed during nucleophilic addition (Figure 10.03) are supplied by the nucleophile N:⁻.

We will see that many nucleophilic addition reactions involve C=C bonds that are attached to C=O groups (carbonyl groups) or other *electron withdrawing groups*. Nucleophilic additions can also involve direct additions to C=O or C=N bonds. As a result, we defer our discussion of them to chapters in the text that follow our introduction of functional groups with C=O and C=N bonds.

Non-Ionic Addition Reactions (10.1C)

Addition reactions that do not involve intermediate ions include *free radical* additions and *concerted* additions. We give a general description of these reactions here, and discuss *concerted* additions in more detail later in the chapter. Our detailed discussion of *free radical* reactions is in Chapter 11.

Radical Addition. Radical addition reactions involve the addition of a reactive species with an unpaired electron (Z[.]) (a **radical** or **free radical**) to a multiple bond to give an intermediate that also has an unpaired electron as we show in the general equation for addition of a radical to an alkene in Figure 10.04.

Figure 10.04



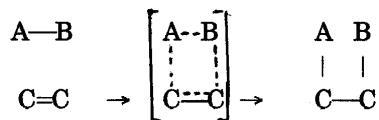
In this equation, we arbitrarily use the symbol Z[.] to represent the radical. Unlike E⁺ (for electrophiles), or N: or N:⁻ (for nucleophiles), there is no universally accepted letter designation for a radical species. In these radical addition reactions, one electron from the π bond of the C=C interacts with the unshared electron on Z to form the C-Z bond while the other electron from that π bond becomes localized on the other C.

We will see that radical addition reactions are *chain reactions*. That feature makes them

mechanistically unique from other addition reactions so we include them in Chapter 11 along with other radical reactions that are also chain reactions.

Concerted Addition. Concerted addition of reagents to multiple bonds occur in a single step without ionic or radical intermediates (Figure 10.05).

Figure 10.05



In this general representation, the center structure with the dotted bonds represents a transition state and not an intermediate. We write it in this way to show that there is simultaneous formation of both the C-A and C-B bonds at the same time that the A-B bond is breaking. We will see that the product of this concerted addition may not be the final reaction product.

Summary. Now that we have given general descriptions of the four types of addition reactions, we provide more detailed descriptions of *electrophilic* and *concerted* additions below. Remember that we will defer our discussions of *radical* additions and *nucleophilic* additions to later chapters.

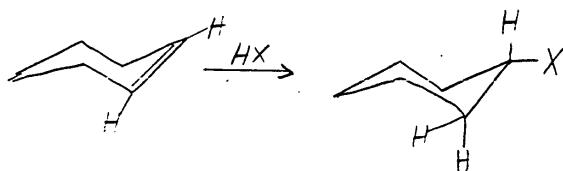
10.2 Electrophilic Addition of H-X or X₂ to Alkenes

Alkenes can be converted to haloalkanes or dihaloalkanes by electrophilic additions of hydrogen halides (H-X) or molecular halogens (X₂). Both types of reactions have cation intermediates, but we will see that the cations are dramatically different.

Addition of H-X (10.2A)

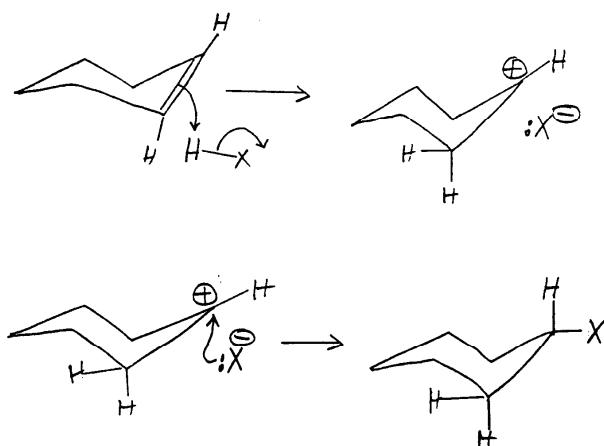
Alkenes react with HI, HBr, HCl and HF by an electrophilic addition mechanism to give the corresponding haloalkane or halocycloalkane as we show in Figure 10.06 for cyclohexene.

Figure 10.06



Intermediate Carbocations. The first step of the mechanism involves the transfer of a proton from H-X to the alkene to give a carbocation intermediate (Figure 10.07)[next page].

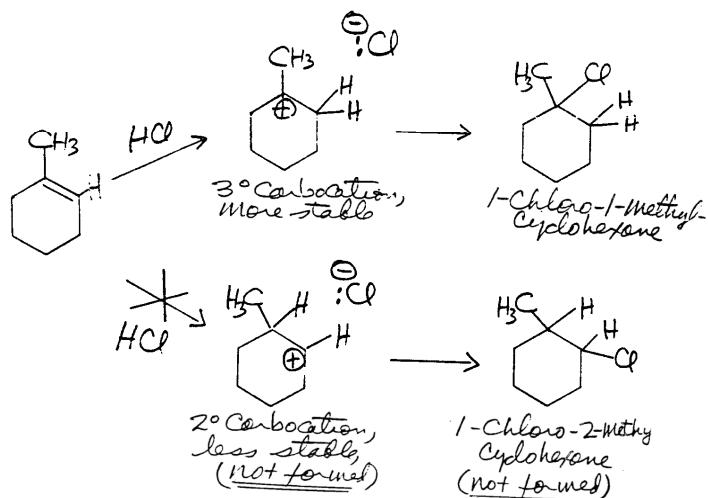
Figure 10.07



The intermediate carbocation then reacts with the halide ion X⁻ to give the final product.

When proton addition from H-X to an unsymmetrical alkene can give two different carbocations, the carbocation that is the most stable is preferentially formed. We illustrate this for addition of H-Cl to 1-methylcyclohexene in Figure 10.08.

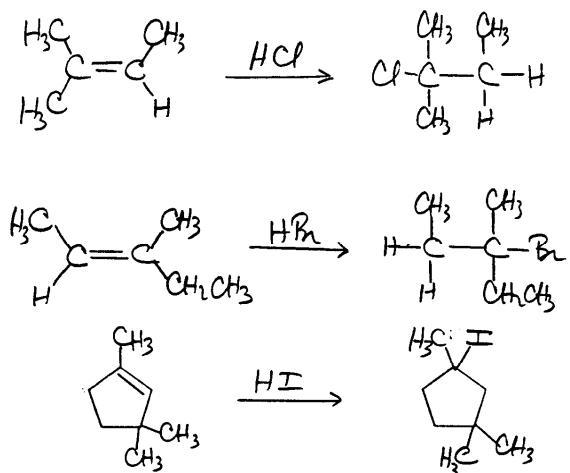
Figure 10.08



Protonation on the C-CH₃ carbon, gives a 2° carbocation that would ultimately give 1-chloro-2-methylcyclohexane. However, protonation of the other carbon of the double bond gives the more stable 3° carbocation that would then react with the chloride ion to give 1-chloro-1-methylcyclohexane.

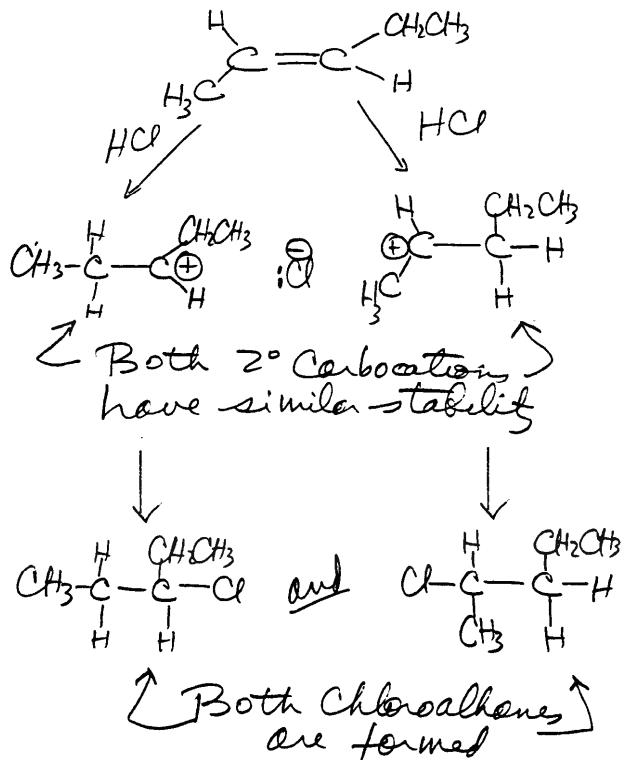
We find that the only product of this addition reaction is 1-chloro-1-methylcyclohexane that arises from the more stable 3° carbocation intermediate. We show other examples of this *regiospecificity* in H-X addition to alkenes in Figure 10.09 [next page].

Figure 10.09



When the two possible carbocations have similar stabilities, we expect both haloalkanes as reaction products (Figure 10.10).

Figure 10.10



Markovnikov's Rule. When electrophilic addition reactions of $H-X$ to alkenes were first discovered, their mechanisms were not known. However, chemists noted that the H of the $H-X$ usually bonded to the carbon of the $C=C$ that had the most H 's (the least substitution), while X bonded to the C with the fewest H 's (or the greatest substitution). We see that this occurs in the addition of $H-Cl$ to 1-methylcyclohexene that we just described. The H bonds

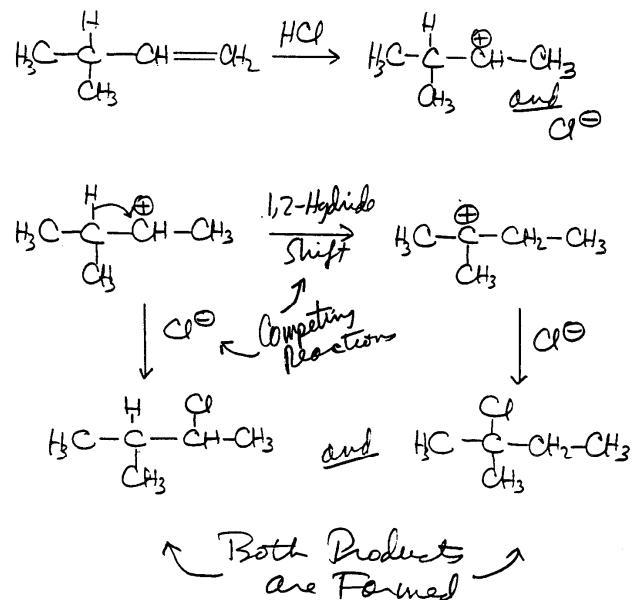
to the less substituted C while the Cl bonds to the more highly substituted carbon (Figure 10.08).

When H-X adds to an alkene in this way, organic chemists say the reaction "obeys **Makovnikov's rule**" after the Russian scientist Valdimir Markovnikov (1838-1904). Although we now know that this *regiospecificity* is a consequence of the intermediate formation of the most stable carbocation, chemists still say that these reactions "obey Markovnikov's rule". (You may also see Markovnikov spelled in slightly different ways such as Markownikoff).

Carbocation Rearrangements. The initial carbocation that forms when H-X protonates a C=C sometimes rearranges. These rearrangements are analogous to those we saw in the previous chapters on substitution and elimination. While the carbocation that initially forms is the most stable of the two possible carbocations, alkyl shifts or hydride shifts often occur if they lead to an even more stable carbocation than that first formed.

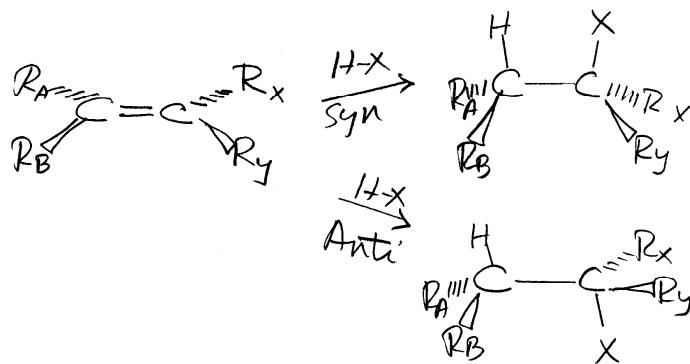
We show an example in Figure 10.11 where a rearranged haloalkane product arises as the result of a carbocation rearrangement that occurs during H-X addition to an alkene.

Figure 10.11



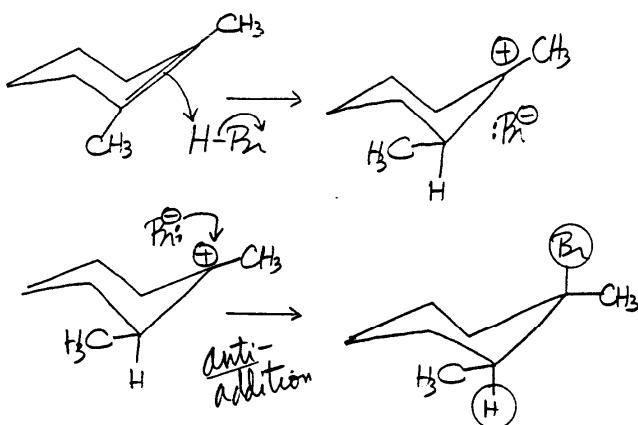
Stereochemistry. Electrophilic addition of H-X to alkenes can occur by overall *syn* addition, or *anti* addition, or a mixture of the two (Figure 10.12)[next page].

Figure 10.12



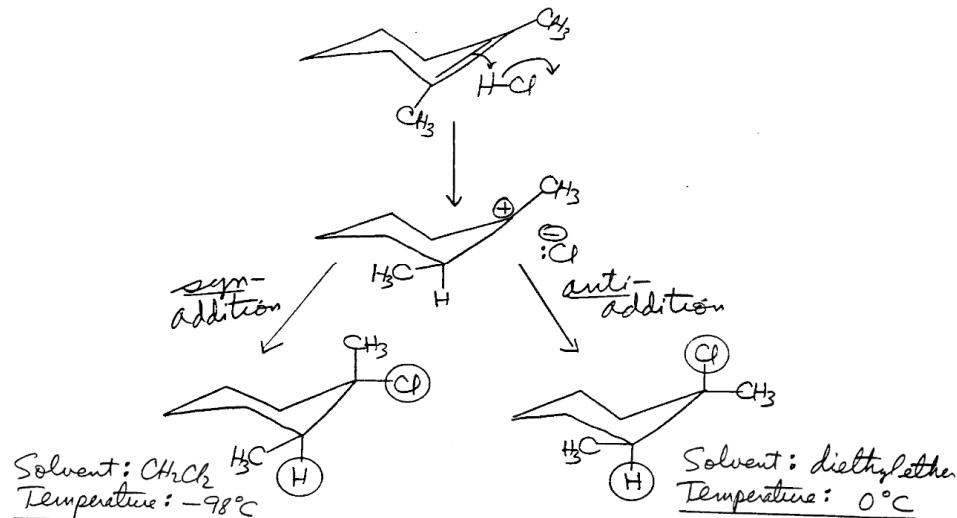
For example, addition of H-Br to 1,2-dimethylcyclohexene occurs predominantly by overall *anti* addition as we show in Figure 10.13.

Figure 10.13



In contrast, addition of H-Cl to the same compound can be *syn* or *anti* overall depending on the reaction conditions (Figure 10.14).

Figure 10.14

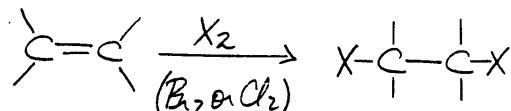


At a low temperature in the non-polar solvent CH_2Cl_2 , the Cl^- ion appears to react quickly with the C^+ on the same side of the molecule from which the proton was donated by H-Cl . In the more polar solvent diethyl ether at a higher temperature, apparently Cl^- has the opportunity to move to the other side of the C^+ ion so the more stable *anti* addition product is formed.

Electrophilic Addition of Br_2 (10.2B)

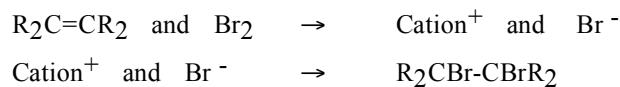
Alkenes also react with the molecular halogens such as Br_2 or Cl_2 by electrophilic addition and give dihaloalkanes as products (Figure 10.15).

Figure 10.15



Mechanism. We show the general two-step mechanism for electrophilic addition of Br_2 to an alkene in Figure 10.16.

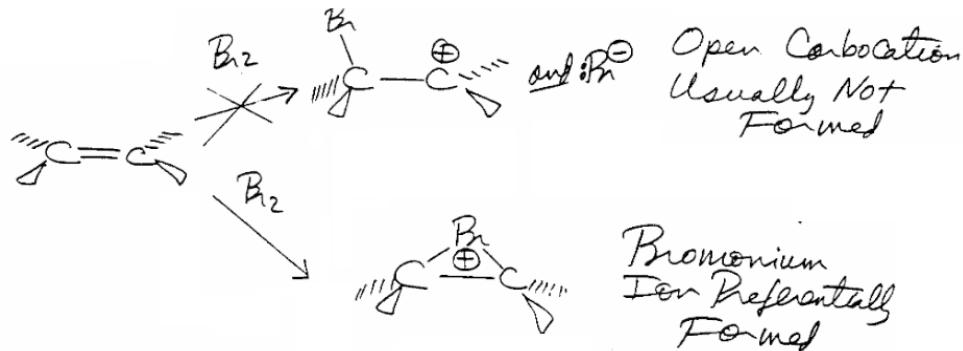
Figure 10.16



The first step involves the transfer of one Br in Br_2 to the double bond of the alkene as an electrophile. The intermediate cation then reacts with Br^- to form the dibromoalkane product.

The cation intermediate in Figure 10.16 is a cyclic ion that we call a **bromonium ion** (Figure 10.17).

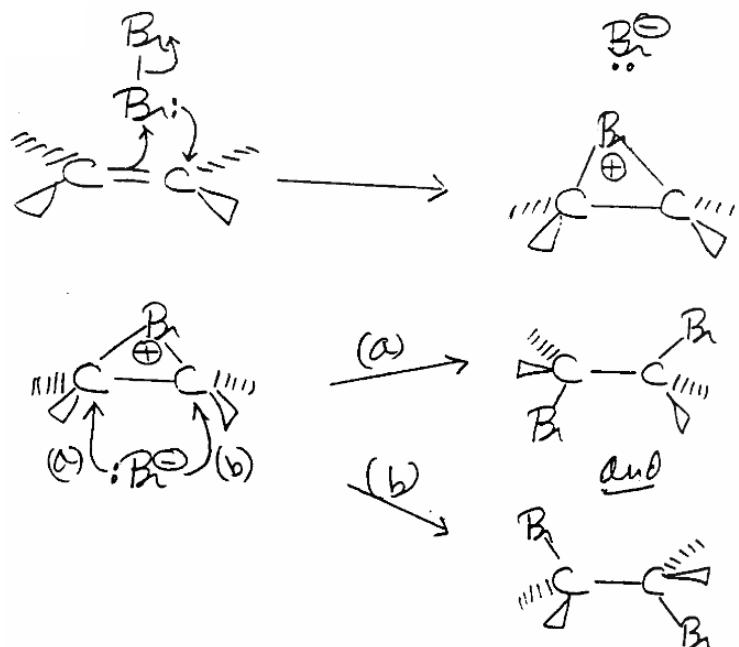
Figure 10.17



It is very different than the "open" carbocation intermediates that form during H-X addition to alkenes.

Organic chemists believe that the bromonium ion forms in a single step when Br_2 reacts with the alkene $\text{C}=\text{C}$ (Figure 10.18) and that an open carbocation ion is not an intermediate in this reaction.

Figure 10.18



Stereochemistry. The bromide ion Br^- subsequently reacts with the intermediate bromonium ion from the side opposite the Br^+ atom (Figure 10.18). This "backside" attack is analogous to the way that nucleophiles react in $\text{S}_{\text{N}}2$ reactions, and in ring-opening reactions of epoxides and protonated epoxides (Chapter 7). As a result, we describe the overall addition of Br_2 to an alkene as an *anti* addition.

Since Br is a "symmetric" reagent, the product does not tell us which C of the intermediate bromonium ion is attacked by Br^- . However, this attack most likely occurs at the most substituted C. That C is the one that we would expect to be the most favorable C⁺ if an open carbocation was formed as an intermediate.

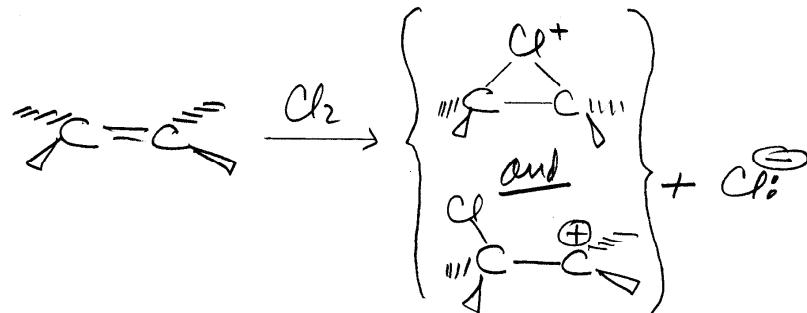
This means we can describe this addition as "obeying Markovnikov's rule". We will see support for this proposal below when we describe what happens when we react alkenes with molecular halogens in the solvent water.

Electrophilic Addition of Other Molecular Halogens (10.2C)

Cl_2 undergoes electrophilic addition to alkenes, but F_2 and I_2 are not useful reagents for dihaloalkane formation.

Cl₂ Addition. Reaction of Cl₂ with simple alkenes occurs by way of intermediate **chloronium ions**, however open carbocations are also important in chlorination reactions (Figure 10.19)

Figure 10.19



This probably reflects the lower stability of chloronium ions compared to bromonium ions. The strained 3-membered rings in cyclic halonium ions are more easily accommodated by the larger Br atom (Figure 10.20).

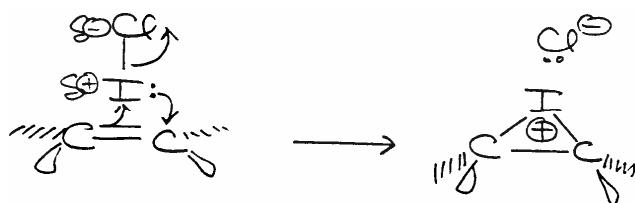
Figure 10.20



F₂ or I₂ Addition. Neither F₂ nor I₂ add efficiently to alkenes. In the case of I₂, the 1,2-diiodoalkane product is unstable and reversibly loses I₂. In contrast, 1,2-difluoroalkanes are very stable, but F₂ is so reactive that a wide range of side reactions occur in competition with its addition to the C=C.

Iodonium Ions are Possible. Although I₂ is not a useful reagent for alkene addition, iodonium ion intermediates can be formed from reactions of mixed halogens such as I-Cl with alkenes as shown in Figure 10.21.

Figure 10.21

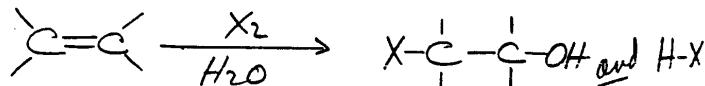


Iodonium ions should be the most stable of all of the halonium ions because of the large size of iodine. They most likely form in reactions of I₂ with alkenes even though diiodoalkanes cannot be isolated due to their instability.

Formation of Halohydrins (10.2D)

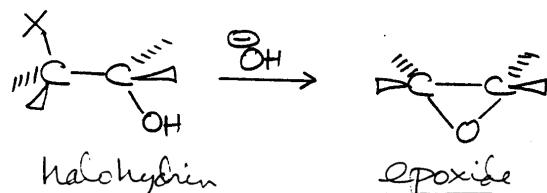
When an alkene reacts with a molecular halogen X_2 (Cl_2 , Br_2 , or I_2) in water as the solvent, the reaction product is not a dihaloalkane. Rather it is an alcohol with a halogen atom (X) on the carbon β to the OH group (Figure 10.22).

Figure 10.22



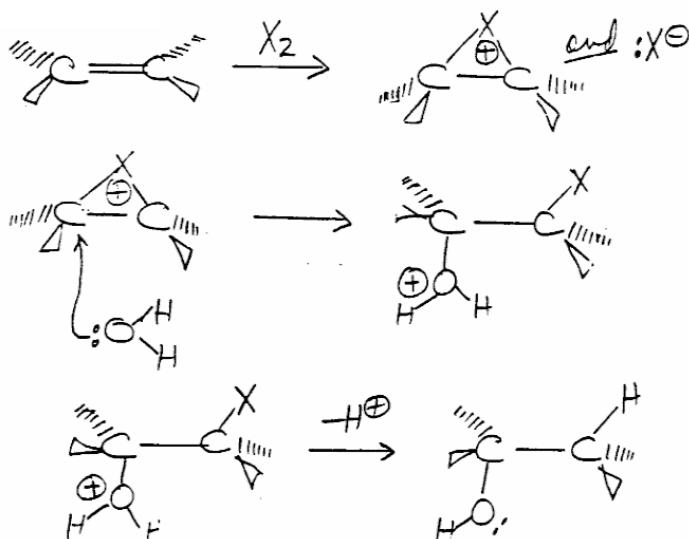
Organic chemists call this β -haloalcohol a **halohydrin**. We saw in Chapter 7 that halohydrins are important precursors for formation of cyclic ethers (epoxides) (Figure 10.23).

Figure 10.23



Mechanism. We outline the mechanism for formation of halohydrins in Figure 10.33.

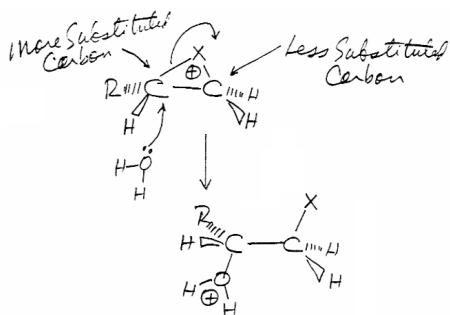
Figure 10.33



The first step forms a halonium ion intermediate as we showed earlier. However, this intermediate reacts with the solvent water to form a protonated alcohol that then loses a proton to give the halohydrin. While the halonium ion intermediate can also react with halide ion (X^-), it reacts almost exclusively with water because the concentration of water is much greater than that of the halide ion.

Orientation. Water reacts with the intermediate halonium ion at its most substituted C as we show in Figure 10.25 [next page].

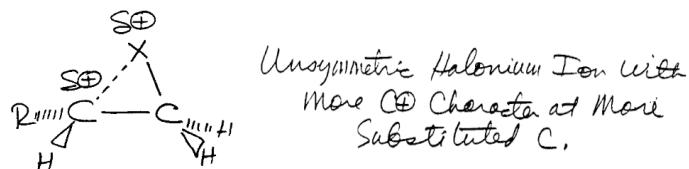
Figure 10.25



This contradicts what we would expect for S_N2 nucleophilic substitution at carbon, but it does follow Markovnikov's rule

We rationalize this regiochemistry in the reaction of the halonium ion with water by concluding that the halonium ion is unsymmetric and that it has more carbocation character at the most highly substituted C (Figure 10.26).

Figure 10.26



In this view of the reaction, we imagine that it more closely resembles an S_N1 reaction than an S_N2 displacement on the intermediate halonium ion.

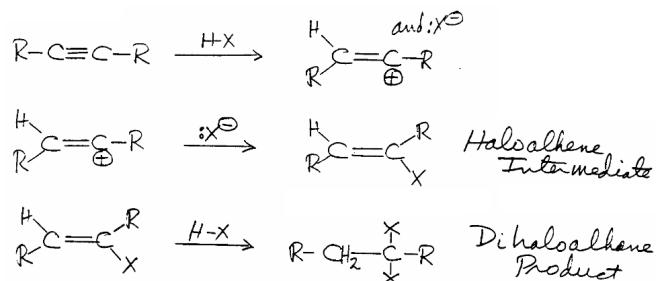
10.3 Addition of H-X and X₂ to Alkynes

Hydrogen halides and dihalogens undergo electrophilic addition to alkynes ($RC\equiv CR$) as well as alkenes ($R_2C=CR_2$).

Addition of H-X (10.3A)

Alkynes react with all four of the hydrogen halides (H-X) by electrophilic addition reactions that are analogous to those for H-X addition to *alkenes*. H-X first adds to give a haloalkene intermediate that then reacts further to give a dihaloalkane (Figure 10.27).

Figure 10.27



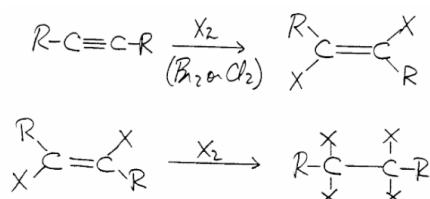
In each H-X addition step, protonation of the C≡C or C=C bond occurs on the C that leads to the most stable carbocation. The result is the overall regiochemistry that we show above.

The stereochemistry of these addition reactions is usually *anti*. We can isolate the haloalkene intermediates as reaction products if we limit the H-X concentration to one mole of H-X for each mole of starting alkyne.

Addition of X₂ (10.3B)

Alkynes also react with Br₂ or Cl₂ by electrophilic addition (Figure 10.28).

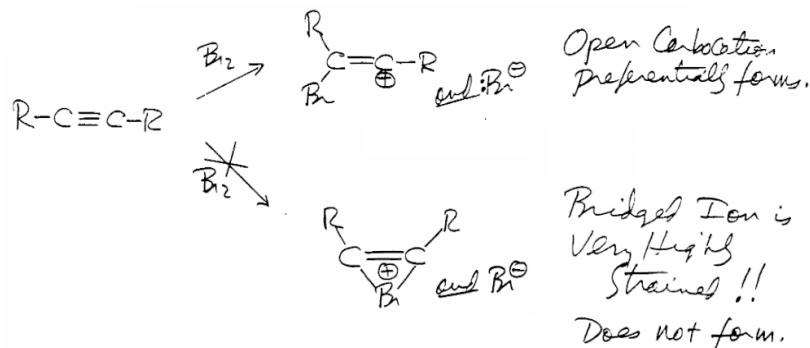
Figure 10.28



As in the case of H-X addition, these reactions involve two distinct parts. First, a dihaloalkene intermediate forms by *anti* addition, and it subsequently reacts with a second mole of Br₂ or Cl₂ to give the tetrahaloalkane.

Alkynes are usually less reactive than alkenes in electrophilic addition reactions because the π electrons are "held" more tightly in C≡C bonds than in C=C bonds. It is also more sterically difficult to form a bromonium ion from an alkyne (Figure 10.29) than from an alkene.

Figure 10.29



As a result, organic chemists believe that electrophilic addition reactions of alkynes generally involve open carbocations (Figure 10.29).

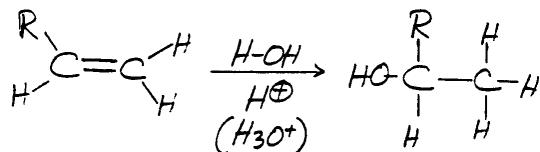
10.4 Alkenes to Alcohols by Electrophilic Addition

We can convert alkenes to alcohols by electrophilic addition reactions. We have seen one example in an earlier section, and show two more here.

Acid Catalyzed Hydration of Alkenes (10.4B)

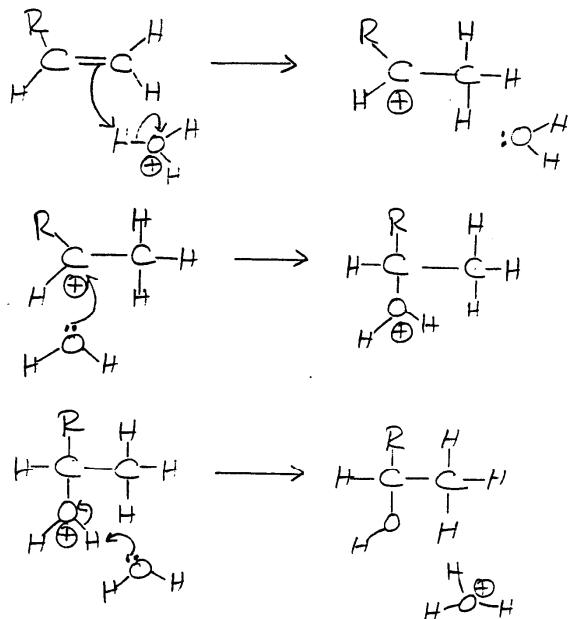
Alkenes add water in the presence of an acid catalyst to give alcohols as we show in Figure 10.30.

Figure 10.30



Mechanism. The mechanism for this reaction (Figure 10.31) involves the formation of an intermediate carbocation that is analogous to the open carbocation that forms when H-X adds to alkenes.

Figure 10.31



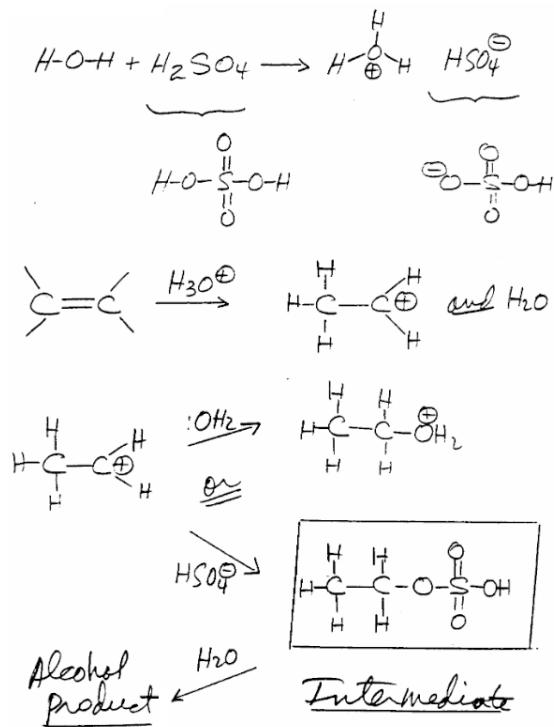
That carbocation intermediate subsequently reacts with water in a step identical to that in S_N1 reactions of substrates (R-L) that ionize in water (Chapter 7). The resultant intermediate protonated alcohol (Figure 10.31) loses a proton to give the alcohol.

The intermediate carbocation can also react with the anion of the acid catalyst (Figure 10.32)[next page]. However, with sulfuric acid (H₂SO₄) commonly used to catalyze acid hydration, the *organosulfate* intermediate is unstable and subsequently reacts further with water to give the alcohol product.

Acid catalyzed hydration of alkenes is exactly the reverse of the acid catalyzed dehydration of alcohols described in Chapter 9. These two reactions have identical mechanisms though

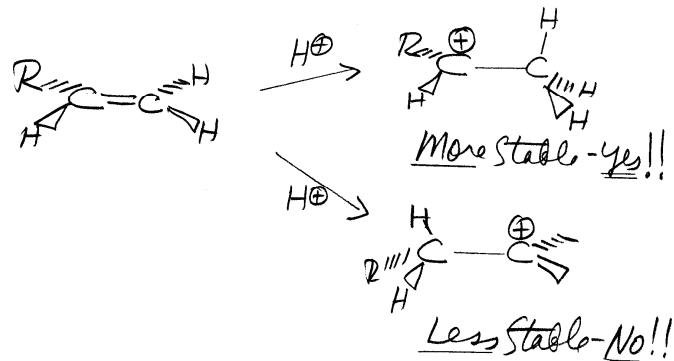
we view them from different directions depending on whether alkene is being converted to alcohol, or alcohol is being converted to alkene.

Figure 10.32



Orientation of Addition. The proton adds to the alkene so that the most stable of the two possible carbocations is formed.

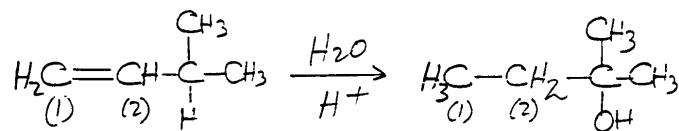
Figure 10.33



Since this generally leads to an alcohol with the OH group on the most highly substituted carbon, acid catalyzed hydrations of alkenes are *Markovnikov addition reactions*.

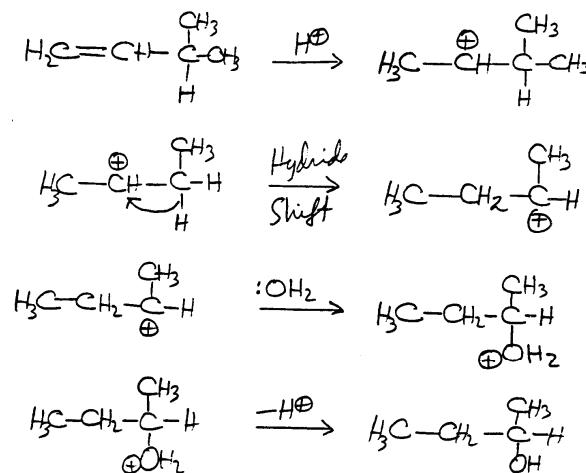
Rearranged Products. In some cases, we find rearranged alcohol products that are not the direct result of H-OH addition across the original double bond of the alkene reactant (Figure 10.34) [next page].

Figure 10.34



In this example, the rearranged alcohol arises from a rearranged carbocation (Figure 10.35).

Figure 10.35

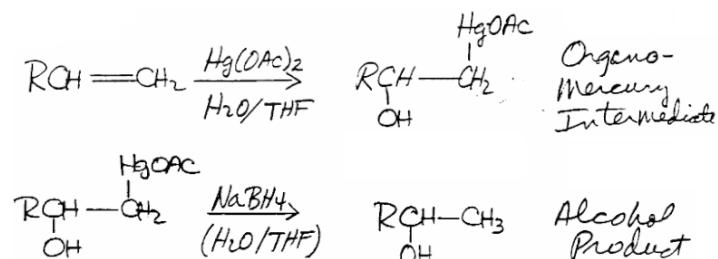


Carbocation rearrangements during acid catalyzed hydration of alkenes are analogous to those we described earlier in this chapter for electrophilic addition of H-X to alkenes, and in Chapter 9 for acid catalyzed dehydration of alcohols to give alkenes.

Oxymercuration-Demercuration (10.4C)

We can form alcohols from alkenes without rearrangement by utilizing a synthetic sequence known as **oxymercuration-demercuration** (Figure 10.36).

Figure 10.36



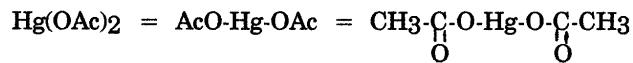
Overall Transformation. In the first step of this general sequence shown above, the Hg(II) salt, **mercuric acetate** (Hg(OAc)_2), reacts with alkene in the solvent water, to ultimately form the organomercury compound that we show as a product.

We complete the transformation by adding *sodium borohydride* (NaBH_4) to the reaction mixture where it reacts with the organomercury compound to generate the alcohol product.

As the last step, we treat the reaction mixture with aqueous acid to react with leftover sodium borohydride and bring it to a neutral pH.

Mercuric Acetate. For a general understanding of the overall reaction in Figure 10.36, we do not need to know the detailed chemical structure of mercuric acetate that we show in Figure 10.37.

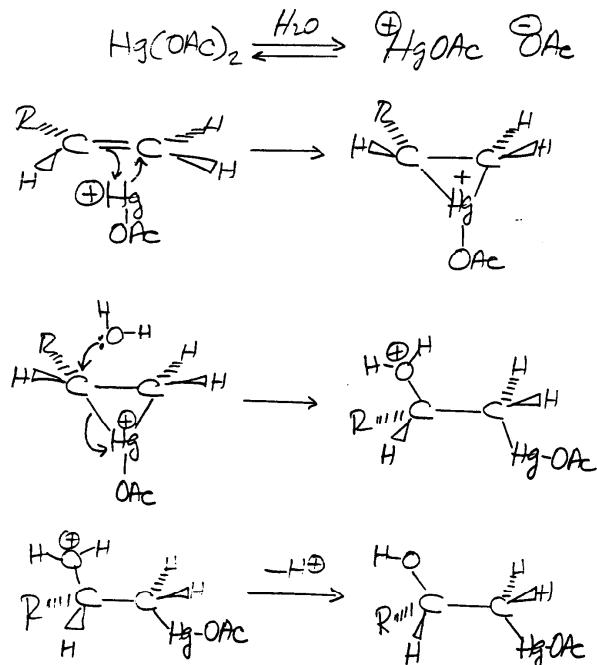
Figure 10.37



The AcO (acetate) groups contain a O-C=O functional group that we have not yet introduced.

Mechanism. Hg(OAc)_2 partially ionizes in aqueous solution and the electrophilic species ${}^+\text{HgOAc}$ adds to alkene double bonds to give an organomercury intermediate.

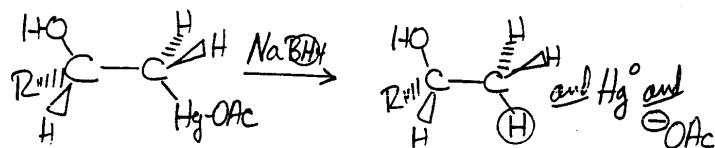
Figure 10.38



This cyclic **mercurinium ion** is analogous to *halonium* ions that we saw earlier. Its prevents carbocation rearrangements from occurring during this reaction since there are no intermediate *open carbocations*.

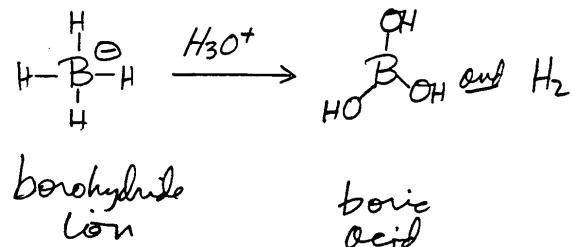
Like halonium ions, the *mercurinium* ion subsequently reacts with water at its most substituted C to form the β -hydroxy organomercury compound that is the final structure in Figure 10.38. We subsequently react it with sodium borohydride and obtain the alcohol product and elemental Hg (Figure 10.39) [next page].

Figure 10.39



We do not show the detailed mechanism for this final reaction. In that mechanism, the new C-H bond in the alcohol product forms when an H from the BH_4^- anion of sodium borohydride replaces Hg in the C-Hg bond. The aqueous hydrochloric acid that we add at the end transforms unreacted borohydride ion into H_2 and boric acid (Figure 10.40).

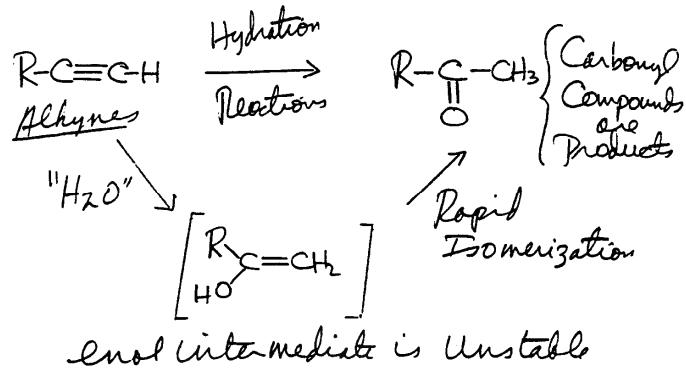
Figure 10.40



Hydration of Alkynes (10.4C)

Hydration of alkynes gives compounds that contain C=O groups (carbonyl compounds) rather than alcohols (Figure 10.41).

Figure 10.41



Alkenols (enols) are intermediates in these reactions, but they rapidly isomerize to the carbonyl compounds (Figure 10.41). We describe these reactions in more detail in a later chapter after we introduce carbonyl compounds.

10.5 Alkenes to Alcohols by Hydroboration

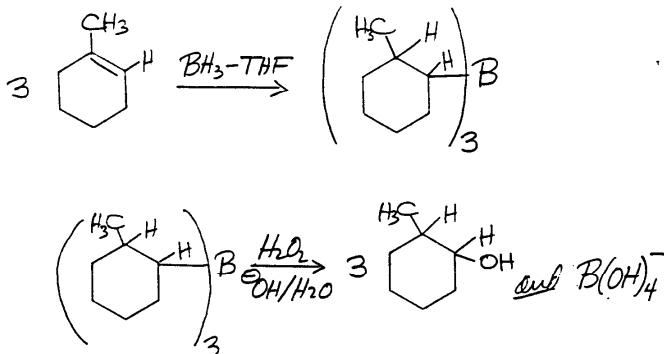
Hydroboration of alkenes is our first example of a concerted addition reaction. We will see that the product alcohols appear to have been formed by *anti-Markovnikov addition* of H_2O to alkenes.

Hydroboration of Alkenes with BH₃ (10.5A)

The simplest alkene hydroboration reagent is **borane** (**BH₃**).

Overall Reaction Sequence. We show the overall reaction sequence for conversion of 1-methylcyclohexene into 2-methylcyclohexanol in Figure 10.42.

Figure 10.42

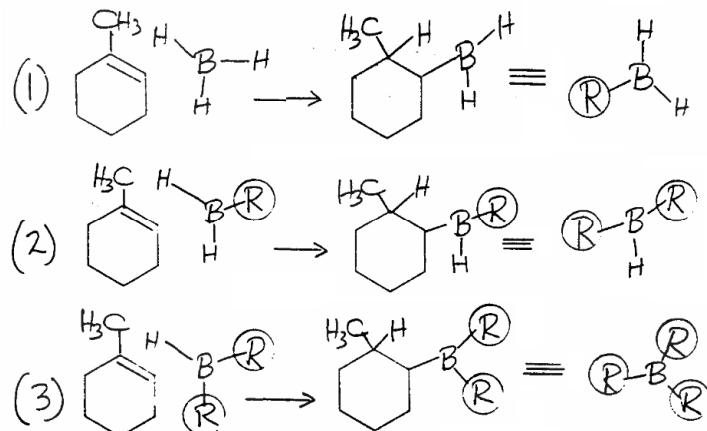


That final reaction product is what we would expect for *anti-Markovnikov* addition of H-OH to the alkene. The H is bonded to the most substituted C while the OH group ends up on the least substituted C.

This contrasts with formation of the isomeric alcohol 1-methyl-cyclohexanol from either acid catalyzed hydration or oxymercuration-demercuration of 1-methylcyclohexene. Besides this different regiochemistry, the reaction occurs without competing rearrangements.

Formation of the Organoborane Intermediate. The formation of the intermediate boron compound in Figure 10.42 occurs in three steps. Each of these involves addition of an alkene molecule across a B-H bond of **BH₃** (**borane**) so that ultimately three alkene molecules are bonded to the B atom as we show in Figure 10.43.

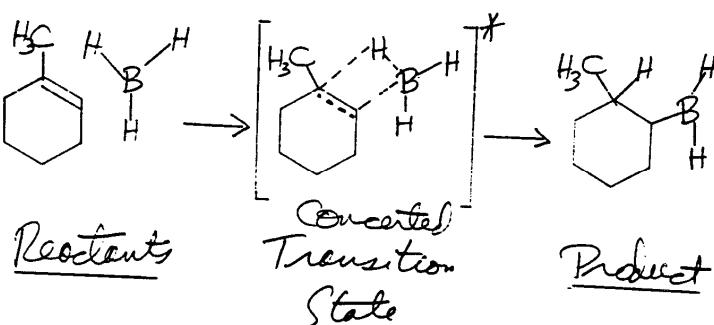
Figure 10.43



Each of these addition reactions is called **hydroboration**. We see that boron (B) bonds to the *least* substituted carbon of the alkene while H bonds to the *most* substituted C. The C-B carbon eventually becomes the C-OH carbon, so the "anti-Markovnikov" regiochemistry is determined in these hydroboration steps.

Concerted Addition Mechanism. Each of the hydroboration steps we show above is a *single step concerted reaction* without any intermediate. The C-H and C-B bonds form at the same time that the B-H bond breaks (Figure 10.44).

Figure 10.44



B bonds to the least substituted carbon primarily because this addition pathway is least sterically hindered. If B bonded to the more substituted C, the R₂B group (always larger than H) would be closer to the more sterically congested end of the double bond.

But B-H bonds are also polarized with a partial negative charge on the hydrogen and a partial positive charge on the boron (Figure 10.45).

Figure 10.45

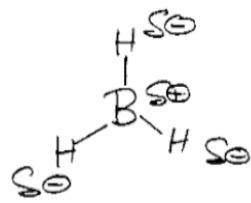
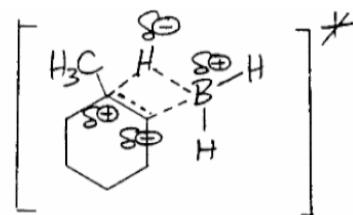


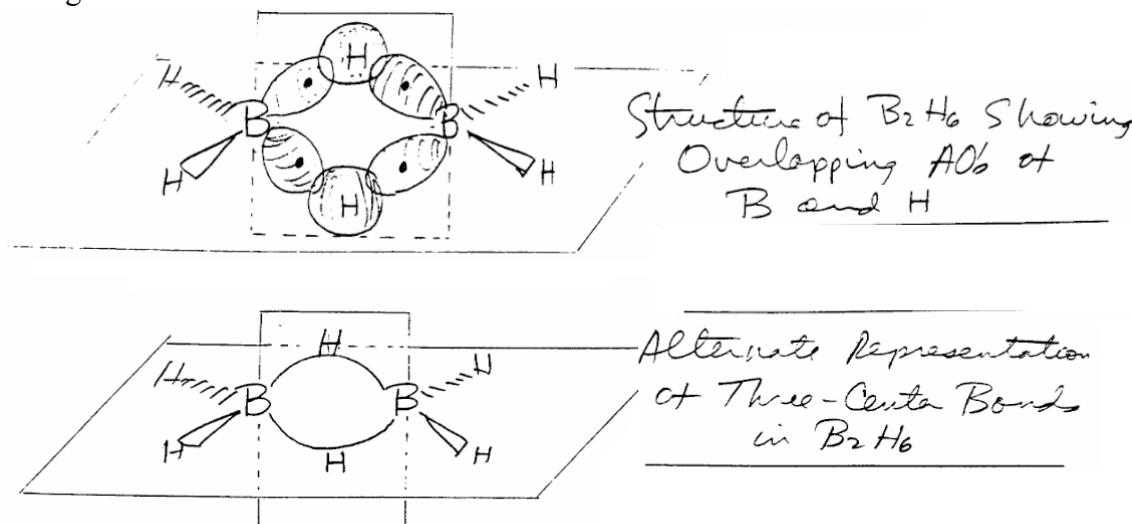
Figure 10.46



As a result, we can also rationalize that B adds to the least substituted carbon of the C=C because this places *carbocation character* on the more highly substituted carbon of the C=C (Figure 10.46).

The BH₃ Reagent. BH₃ is not a stable molecule. It usually exists as **diborane (B₂H₆)** that is a dimer of BH₃ with the unusual structure that we show in Figure 10.47 [next page]. There is no B-B bond in this dimer. The two BH₃ species are held together by "hydrogen atom bridges" between the two B atoms.

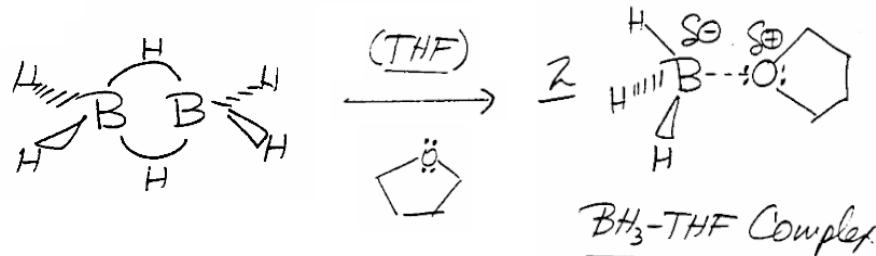
Figure 10.47



Chemists call these "BHB bridged bonds" **three-center bonds** and we represent them with the curved lines in the figure above. We use these curved lines because each BHB *three-center bond* contains just two electrons rather than four electrons that would be implied by a representation such as B-H-B.

We prepare the *borane reagent* used in the hydroboration reaction of 1-methylcyclohexene (Figure 10.44) by dissolving gaseous *diborane* in the solvent *tetrahydrofuran* (*THF*). *THF* is a cyclic ether (Chapter 3) that breaks the diborane dimer into BH_3 -*THF* complexes (Figure 10.48).

Figure 10.48

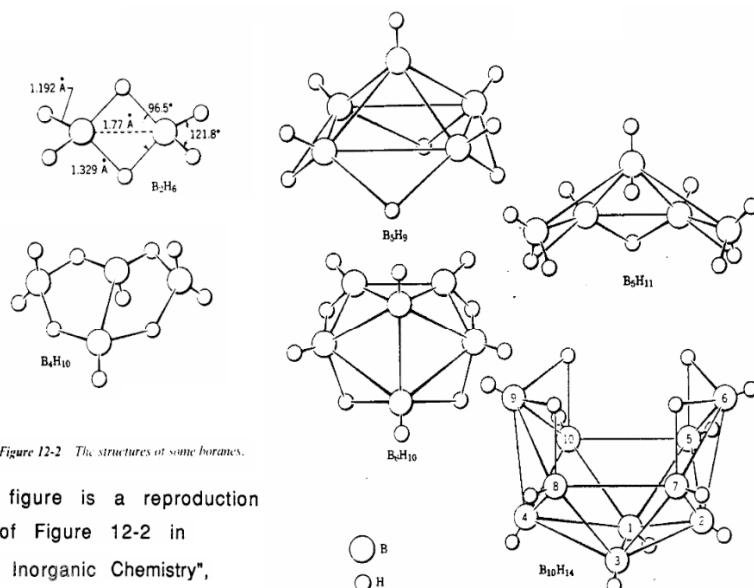


THF solutions of diborane are commercially available, but are relatively unstable and sensitive to moisture.

Other Boranes. Diborane is the lowest molecular mass example of a vast array of very interesting molecules generally referred to as boranes or boron hydrides. Some examples of these higher mass boranes are shown along with diborane in Figure 10.49 [next page].

These molecules are held together by (1) "real" covalent B-B bonds, (2) the bridged three center BHB bonds illustrated in Figure 10.47, and (3) other multi-center bonds involving B.

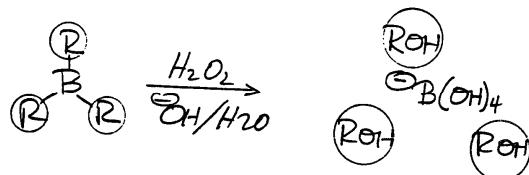
Figure 10.49

*Figure 12-2 The structures of some boranes.*

This figure is a reproduction
of Figure 12-2 in
"Basic Inorganic Chemistry",
by F. A. Cotton and G. Wilkinson,
John Wiley & Sons, Inc., N. Y., N. Y., 1976

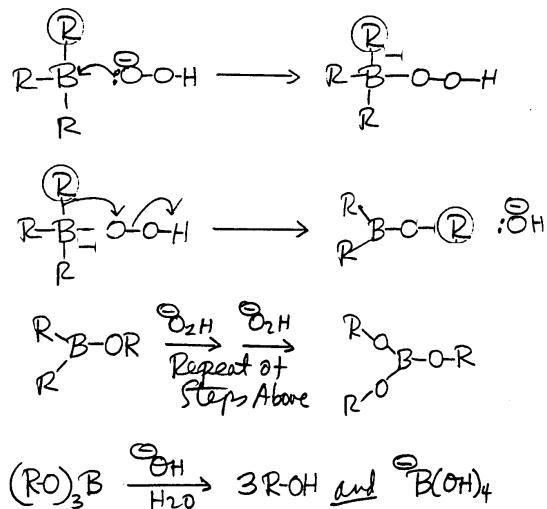
Conversion of R₃B to the Alcohol (R-OH). The trialkylborane (R₃B) intermediate (e.g. the product of the first reaction in Figure 10.42) gives an alcohol product after reaction with an aqueous solution of sodium hydroxide and hydrogen peroxide (Figures 10.50 and 10.42).

Figure 10.50



In this reaction, a hydroperoxide ion (H-O-O⁻) first adds to the B of R₃B (Figure 10.51).

Figure 10.51



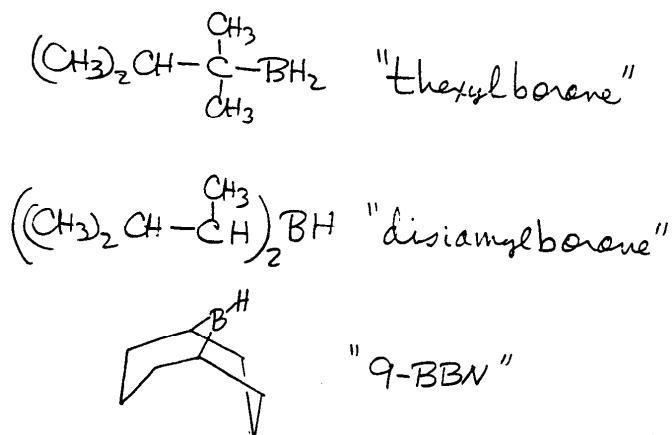
An R group then migrates from B to O with the loss of :OH . The migration of the R group occurs with retention of configuration at the carbon that was originally attached to boron in the trialkylborane. After all three R groups have migrated from B to O, the resulting trialkylborate hydrolyzes to give three molecules of alcohol and one molecule of boric acid.

Hydroboration with RBH_2 and R_2BH Reagents (10.5B)

BH_3 primarily adds to alkenes so that the least substituted (anti-Markovnikov) alcohols form. However, relatively simple alkenes sometimes give product mixtures that include the more substituted alcohol with Markovnikov regiochemistry.

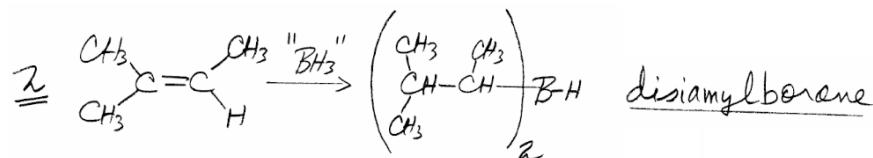
To avoid this, organic chemists use alkyl substituted boron hydride reagents that are more sterically bulky such as those described below. We describe 3 of these sterically bulky boron hydrides below (see Figure 10.52).

Figure 10.52



Disiamylborane. When BH_3 reacts with the bulky alkene 2-methyl-2-butene, the reaction stops after two of the B-H bonds react (Figure 10.53)

Figure 10.53

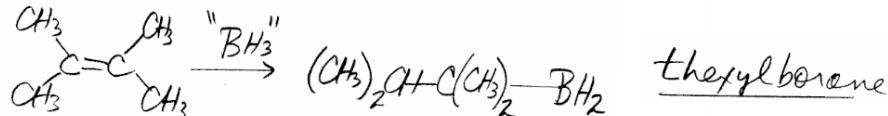


The resulting boron hydride has the general structure $\text{R}_2\text{B}-\text{H}$ and is named **disiamylborane**.

Since its R groups are sterically bulky, it reacts with other alkenes so that B bonds almost exclusively to its least substituted C. The *1,2-dimethylpropyl* groups in *disiamylborane* are commonly called **isoamyl** groups, so its name is derived from its common name **diisoamylborane**.

Thehexylborane. Similarly, hydroboration of the even more highly substituted alkene 2,3-dimethylbutene leads to the formation of a monoalkylborane (R-BH_2) named **thehexylborane** (Figure 10.54).

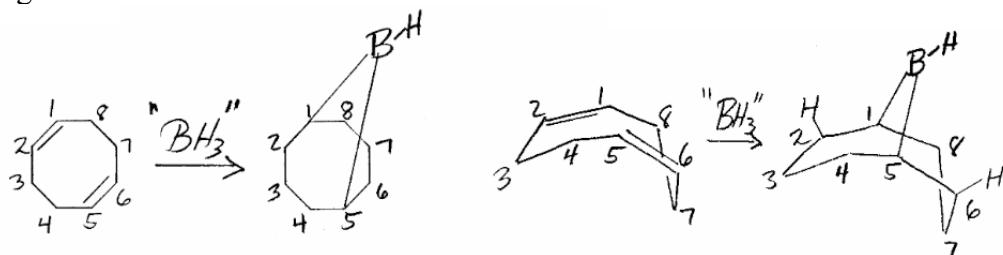
Figure 10.54



Thehexylborane, like *disiamyborane*, is a very selective reagent that gives almost exclusively addition of B to the least substituted C of alkenes. Its name comes from contracting *tert*-hexyl or *t*-hexyl (the common name of its R group) to *thehexyl*.

9-BBN. The third example of a selective hydroboration reagent is 9-BBN that forms by hydroboration of 1,5-cyclooctadiene using borane (Figure 10.55).

Figure 10.55



9-BBN is an acronym for 9-borabicyclo[3.3.1]nonane that is the systematic name of this unusual boron hydride.

Regioselectivity. We show a comparison of the regioselectivity of two of these sterically bulky boron hydrides with that of diborane in Table 10.1

Table 10.1. Hydroboration with Diborane, Disiamylborane, and 9-BBN*.

<u>Alkene</u>	Relative % Yield**					
	<u>Diborane</u>		<u>Disiamylborane</u>		<u>9-BBN</u>	
	C _a	C _b	C _a	C _b	C _a	C _b
cis-Et-C _a H=C _b H-i-Pr	56	43	87	3	90	3
cis-Me-C _a H=C _b H-i-Pr	57	43	97	3	>99	<1
Bu-C _a H=C _b H ₂	94	6	99	1	>99	<1

*From M. B. Smith, "Organic Synthesis", McGraw-Hill, 1994, p. 513

**Relative % of product with H added to the designated C

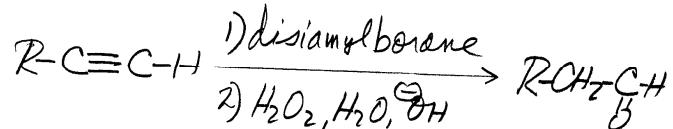
You can see that they dramatically improve regiochemical selectivity in the first two cases where BH_3 from diborane shows little selectivity.

Hydroboration of Alkynes (10.5C)

Alkynes react with boron hydrides, but the final reaction products are not alcohols. Like hydration of alkynes (10.4C), hydroboration of alkynes is an important route to carbonyl compounds.

We describe these reactions in more detail later in the text, but preview a general example here to show an important feature of the reaction (Figure 10.56).

Figure 10.56

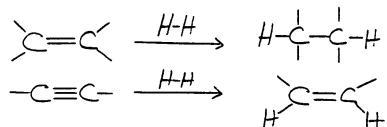


The C=O group ends up on the terminal carbon of the alkyne which is very different regiochemistry than that observed for alkyne hydration (Figure 10.41).

10.6 Addition of H₂ to Alkenes and Alkynes

We have described a variety of reactions that put C=C and C≡C bonds in molecules. This section describes reactions, many concerted, where we remove them by adding an H to each C of C=C or C≡C bonds

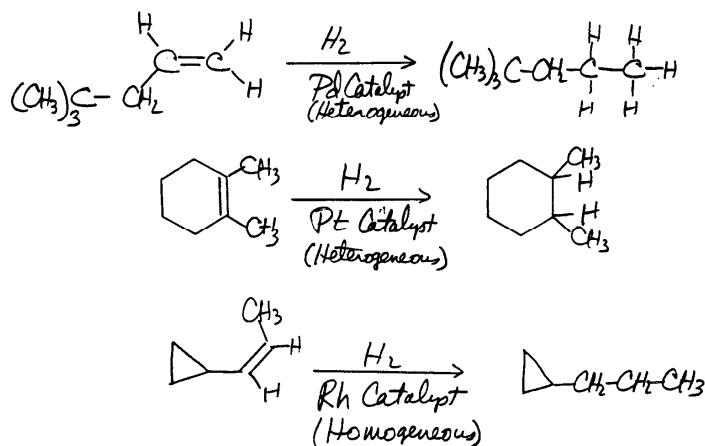
Figure 10.57



Catalytic Hydrogenation of Alkenes (10.6A)

Carbon-carbon double bonds (C=C) add an H at each carbon by reaction with molecular hydrogen (H₂) in the presence of a catalyst. We call this type of addition reaction **catalytic hydrogenation** and show some examples in Figure 10.58.

Figure 10.58



Organic chemists group the catalysts used in these reactions into two categories.

Heterogeneous catalysts are *insoluble* in the reaction solvent, while **homogeneous catalysts** are *soluble*.

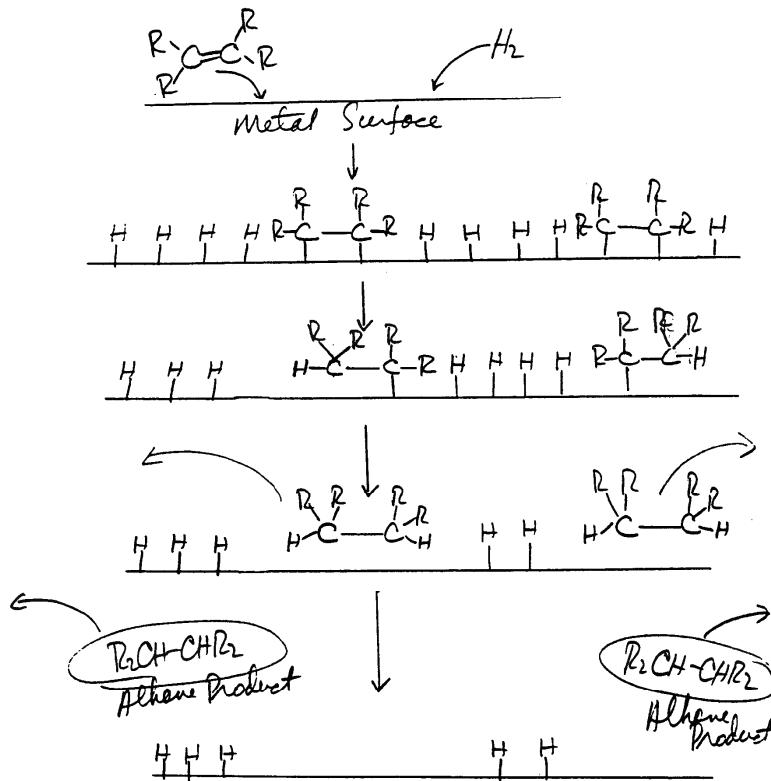
Heterogeneous Catalysts. Chemists have used *heterogeneous hydrogenation catalysts* (Table 10.2) for many years. While they are easy to remove from the reaction mixture because they are insoluble, they are easily contaminated ("poisoned") causing them to lose their activity.

Table 10.2. Some Common Heterogeneous Catalysts

Metal	Description
Ni (nickel)	Raney Nickel: a 50/50 Ni/Al alloy treated with NaOH to remove Al
Pd (palladium)	Pd(C), Pd(BaSO₄), Pd(CaCO₃): catalysts of 5-10% Pd metal dispersed on the solid compound in parentheses Lindlar Catalyst: Pd metal dispersed on CaCO ₃ treated with an aqueous lead salt which deposits PbO
Pt (platinum)	Pt₂O or Adams Catalyst: solid Pt ₂ O

Heterogeneous Catalysis Mechanisms. Heterogeneous catalysts absorb both the alkene and H₂ on their surface (Figure 10.59).

Figure 10.59



The interaction of the catalyst (M) with the alkene causes the π bond of the C=C to break and each of the carbons to become σ bonded to the metal surface (M-C-C-M).

When H₂ bonds to the catalyst surface, the H-H bond breaks and two M-H bonds are formed. These M-H hydrogen atoms are sequentially transferred to each of the M-C carbons leading to the formation of the C-H bonds (Figure 10.59). Using these heterogeneous catalysts, addition of H₂ occurs by overall syn addition to the alkene.

Homogeneous Catalysts. Homogeneous catalysts (Table 10.3) are more recent additions to the collection of reagents available for organic synthesis. They are easier to use in the hydrogenation reaction, but more difficult to remove at the end of the reaction than heterogeneous catalysts.

Table 10.3. Some Homogeneous Hydrogenation Catalysts

Metal	Description
Rh (ruthenium)	$\text{RhCl}(\text{PPh}_3)_3$ also known as Wilkinson's Catalyst
Ir (iridium)	$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ also known as Vaska's Catalyst

Structures of Homogeneous Catalysts. We illustrate the structure of the homogeneous catalyst RhCl(PPh₃)₃ that is commonly called **Wilkinson's catalyst** in Figure 10.60.

Figure 10.60

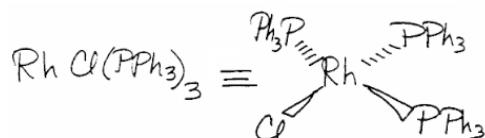
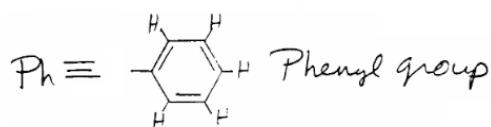


Figure 10.61

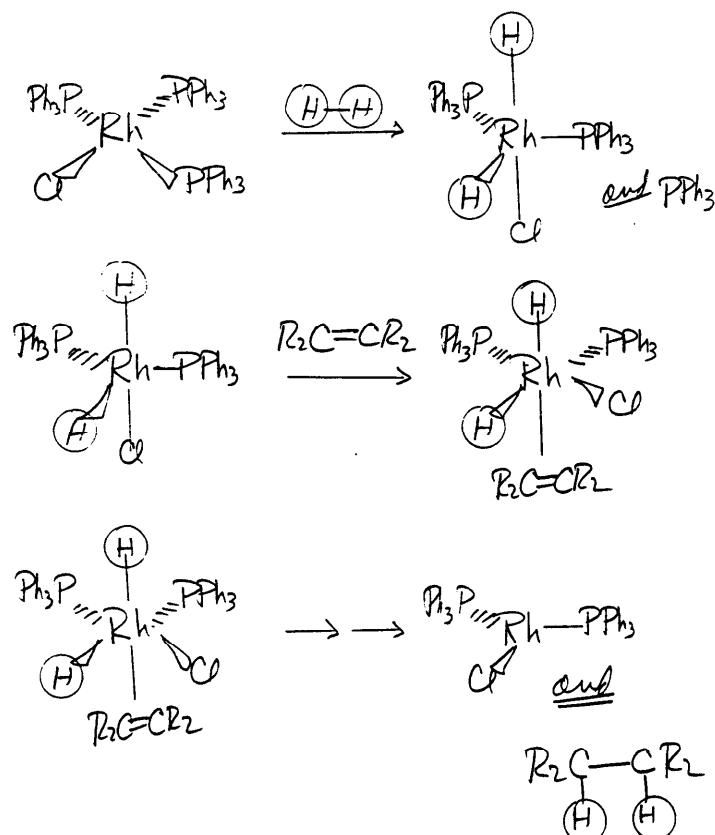


The first P in PPh₃ is the atomic symbol for phosphorous while Ph stands for a **phenyl group** that has the structure we show in Figure 10.61. This six membered *phenyl* ring has this unusual name because it has special properties that we describe in a later chapter.

For this discussion of *homogeneous hydrogenation catalysts*, we do not need to know the detailed structure of the PPh₃ (triphenylphosphine) groups attached to Rh. The structure of IrCl(CO)(PPh₃)₂ is analogous to that of RhCl(PPh₃)₃ except that one PPh₃ group has been replaced by a CO group.

Homogeneous Catalysis Mechanisms. Homogeneous catalysts simultaneously bond both the alkene and H₂ (Figure 10.62)[next page].

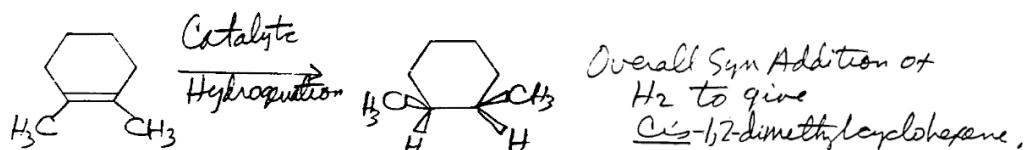
Figure 10.62



In the resultant complex, reaction occurs between the alkene and H_2 to give the alkane product that is released from the catalyst.

We illustrate this here for homogeneous hydrogenation of an alkene using **Wilkinson's catalyst**. As with heterogeneous catalysts, H_2 adds by overall syn addition to the alkene.

Figure 10.63

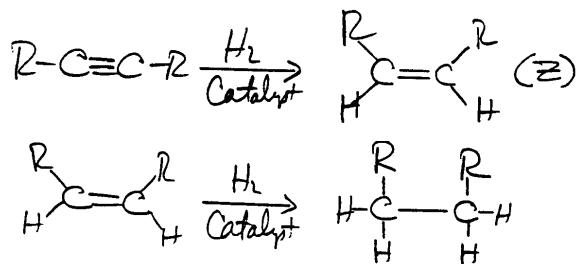


Hydrogenation of Alkynes (10.6B)

Hydrogenation of *alkynes* gives *alkenes* that often undergo further hydrogenation to give *alkanes*.

Catalytic hydrogenation. We can hydrogenate alkynes using the heterogeneous or homogeneous catalysts that we just described for alkene hydrogenation. By a stepwise mechanism, the *alkyne* first gives an *alkene* that frequently hydrogenates further in the reaction mixture to give an *alkane* as we show in Figure 10.64 [next page].

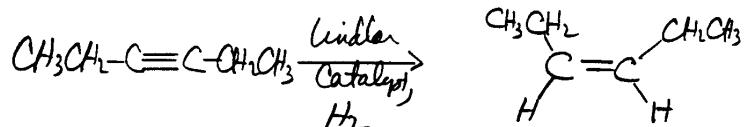
Figure 10.64



The stereochemistry of the hydrogenation reaction of the alkyne occurs with *syn* addition of H_2 to yield the (Z) -alkene.

Lindlar Catalyst. We can stop the hydrogenation of an alkyne after formation of the intermediate alkene with some catalysts. An example is the **Lindlar catalyst** (Table 10.2) that is based on Pd metal (Figure 10.65).

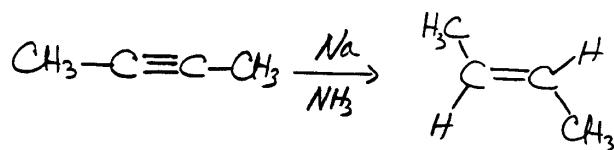
Figure 10.65



The Lindlar catalyst is a deactivated palladium catalyst that we describe as $Pd-CaCO_3-PbO$. It is prepared by precipitating $PdCl_2$ on $CaCO_3$ and then reacting that with lead tetraacetate.

Sodium Metal in NH_3 . We can also selectively transform an alkyne into an alkene by reaction of the alkyne with sodium (Na) metal in liquid ammonia as we illustrate in Figure 10.66.

Figure 10.66

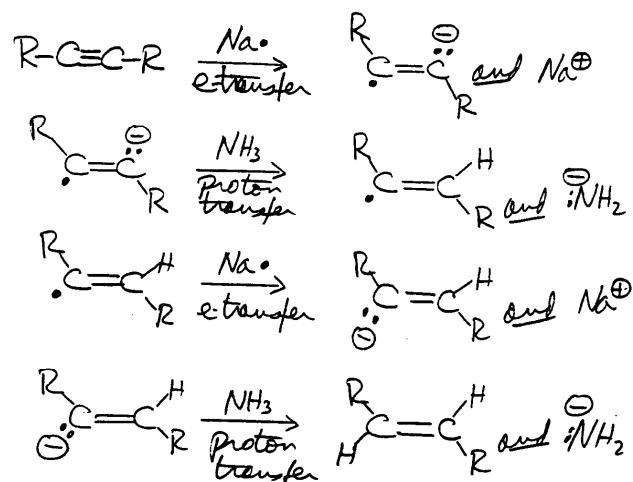


This is not a catalytic hydrogenation reaction. An important feature of this reaction is that its stereochemistry is *anti* rather than *syn* (Figure 10.66). We outline its detailed mechanism in Figure 10.67[next page]. You can see that it involves a series of electron and proton transfer steps that ultimately transform the alkyne into the alkene product.

H_2 Addition Reactions are Reduction Reactions (10.6C)

All of the hydrogenation reactions that transform *alkynes* to *alkenes*, and *alkenes* to *alkanes*, are **reduction reactions** as well as *addition reactions*. This is because **oxidation numbers** (see below) assigned to the C's of $C=C$ and $C\equiv C$ decrease during hydrogenation. However,

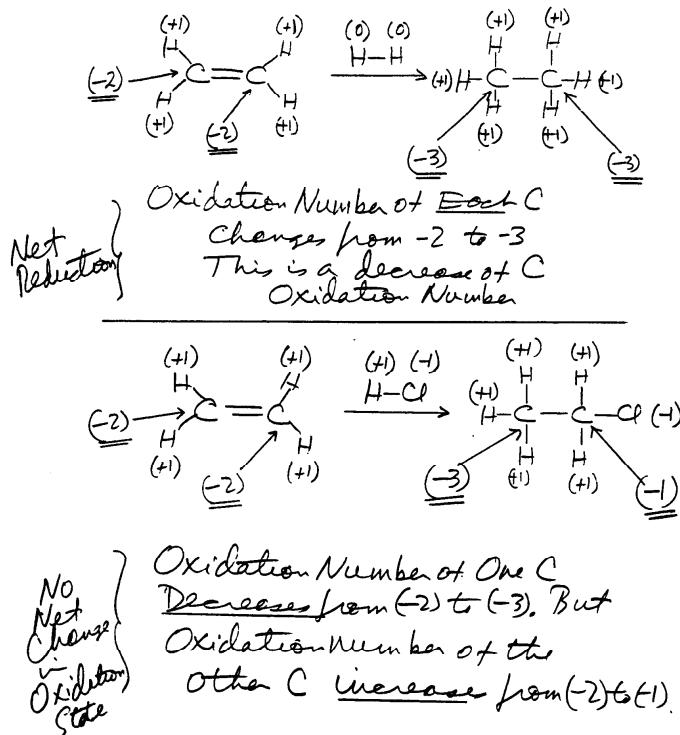
Figure 10.67



other addition reactions that we have seen in this chapter, such as H-X or H-OH addition to multiple bonds, are neither reduction or oxidation reactions. We present a detailed discussion of *oxidation* and *reduction* of organic compounds, and of oxidation numbers, in our later chapter on Oxidation and Reduction. The following section previews some of that material.

Oxidation Numbers. In order to show that hydrogenation of alkenes and alkynes is reduction, while H-X addition is not, let's compare the changes in C oxidation numbers that occur when H₂ or H-Cl are added to ethene (H₂C=CH₂) (Figure 10.68).

Figure 10.68



We use the standard oxidation number assignments for atoms as described in general chemistry texts. As a result: (1) the oxidation number of H is +1 when it is bonded to C or a more electronegative atom such as Cl, (2) the oxidation number of any atom in its elemental state is 0 (zero) as in the case of the H's in H₂, and (3) the sum of the oxidation numbers of all atoms in a molecule must equal the net electrical charge on the molecule. You can see that the resultant changes in oxidation number of C in each of these two reactions (Figure 10.68) show that H₂ addition is *reduction* while H-Cl addition is neither reduction or oxidation

Other Addition Reactions. There are a variety of other addition reactions involving carbon-carbon multiple bonds besides those in this chapter. We have already mentioned that free radical addition reactions are in the next chapter, while nucleophilic addition reactions are in chapters that follow our introduction of compounds with C=O groups.

We include C=C oxidation reactions that lead to carbon-carbon bond cleavage, as well as to diols of the structure HO-C-C-OH, in our chapter on Oxidation and Reduction reactions. Finally, the very large class of mostly concerted reactions, referred to as cyclization reactions because they lead to ring formation, are described in a separate chapter devoted to cyclization reactions.

Review

(To be added)