GLOBAL
EDITION

Organic Chemistry

TENTH GLOBAL EDITION

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ORGANIC CHEMISTRY

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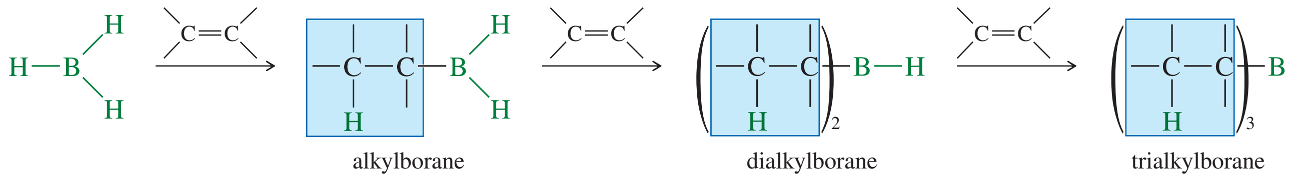
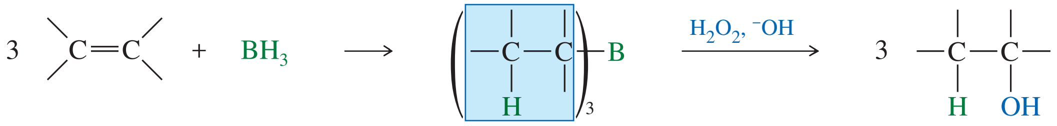
Pearson



Summary

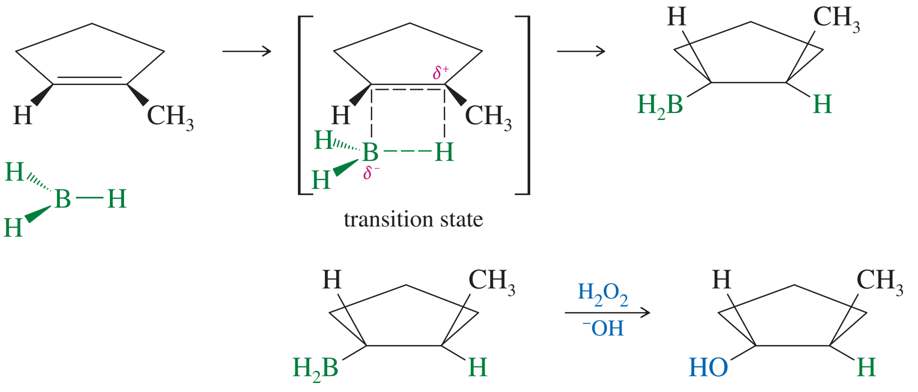


Trialkylboranes react exactly as we have discussed, and they oxidize to give anti-Markovnikov alcohols. Trialkylboranes are quite bulky, further reinforcing the preference for boron to add to the less hindered carbon atom of the double bond. Boranes are often drawn as the 1:1 monoalkylboranes to simplify their structure and emphasize the organic part of the molecule.

8-7C Stereochemistry of Hydroboration

The simultaneous addition of boron and hydrogen to the double bond (as shown in Mechanism 8-6) leads to a **syn addition:** Boron and hydrogen add across the double bond on the *same side* of the molecule. (If they added to opposite sides of the molecule, the process would be an **anti addition.**)

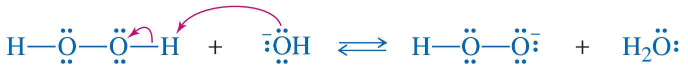
The stereochemistry of the hydroboration–oxidation of 1-methylcyclopentene is that boron and hydrogen add to the same face of the double bond (syn) to form a trialkylborane. Oxidation of the trialkylborane replaces boron with a hydroxy group in the same stereochemical position. The product is *trans*-2-methylcyclopentanol. A racemic mixture is expected because a chiral product is formed from achiral reagents.



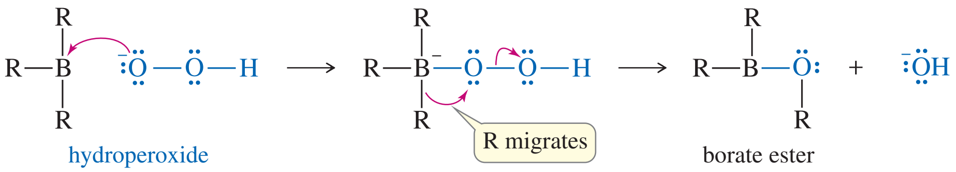
trans-2-methylcyclopentanol
(85% overall)
(racemic mixture of enantiomers)

The second step (oxidation of the borane to the alcohol) takes place with retention of configuration. Hydroperoxide ion adds to the borane, causing the alkyl group to migrate from boron to oxygen. The alkyl group migrates with retention of configuration because it moves with its electron pair and does not alter the tetrahedral structure of the migrating carbon atom. Hydrolysis of the borate ester gives the alcohol.

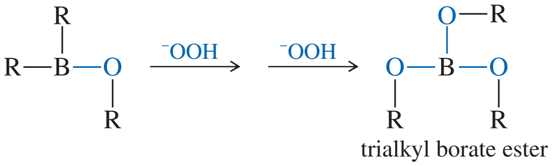
Formation of hydroperoxide ion



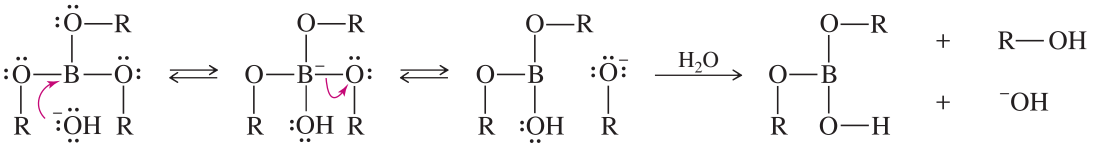
Addition of hydroperoxide and migration of the alkyl group



Twice more to oxidize the other two alkyl groups



Hydrolysis of the borate ester

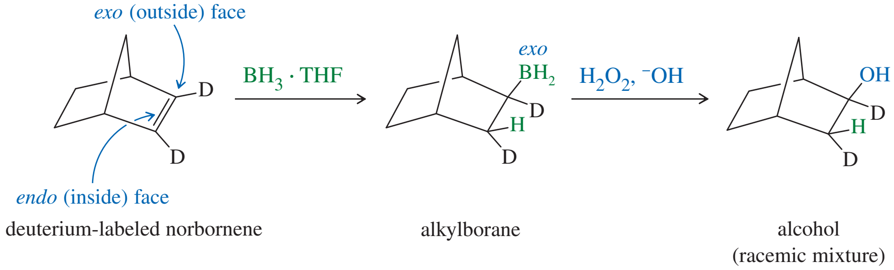


(The other two OR groups hydrolyze similarly.)

Hydroboration of alkenes is another example of a **stereospecific reaction,** in which different stereoisomers of the starting compound react to give different stereoisomers of the product. Problem 8-14 considers the different products formed by the hydroboration–oxidation of two acyclic diastereomers.

SOLVED PROBLEM 8-4

A norbornene molecule labeled with deuterium is subjected to hydroboration–oxidation. Give the structures of the intermediates and products.



SOLUTION

The syn addition of BH_3 across the double bond of norbornene takes place mostly from the more accessible outside (exo) face of the double bond. Oxidation gives a product with both the hydrogen atom and the hydroxy group in exo positions. (The less accessible inner face of the double bond is called the endo face.)

PROBLEM 8-12

In the hydroboration of 1-methylcyclopentene shown in Solved Problem 8-3, the reagents are achiral, and the products are chiral. The product is a racemic mixture of *trans*-2-methylcyclopentanol, but only one enantiomer is shown. Show how the other enantiomer is formed.

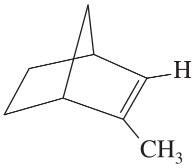
PROBLEM 8-13

Predict the major products of the following reactions. Include stereochemistry where applicable.

(a) 1-methylcycloheptene + $BH_3 \cdot THF$, then H_2O_2, OH^-

(b) *trans*-4,4-dimethylpent-2-ene + $BH_3 \cdot THF$, then H_2O_2, OH^-

(c)



+ $BH_3 \cdot$ THF, then H_2O_2, OH^-

PROBLEM 8-14

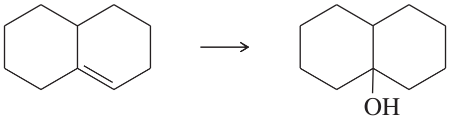
(a) When (*Z*)-3-methylhex-3-ene undergoes hydroboration–oxidation, two isomeric products are formed. Give their structures, and label each asymmetric carbon atom as (*R*) or (*S*). What is the relationship between these isomers?

(b) Repeat part (a) for (*E*)-3-methylhex-3-ene. What is the relationship between the products formed from (*Z*)-3-methylhex-3-ene and those formed from (*E*)-3-methylhex-3-ene?

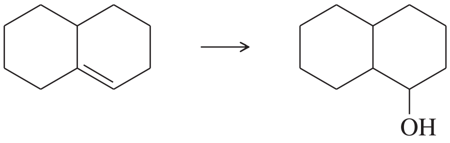
PROBLEM 8-15

Show how you would accomplish the following transformations.

(a)



(b)



(c) 1-methylcycloheptanol → 2-methylcycloheptanol

PROBLEM 8-16

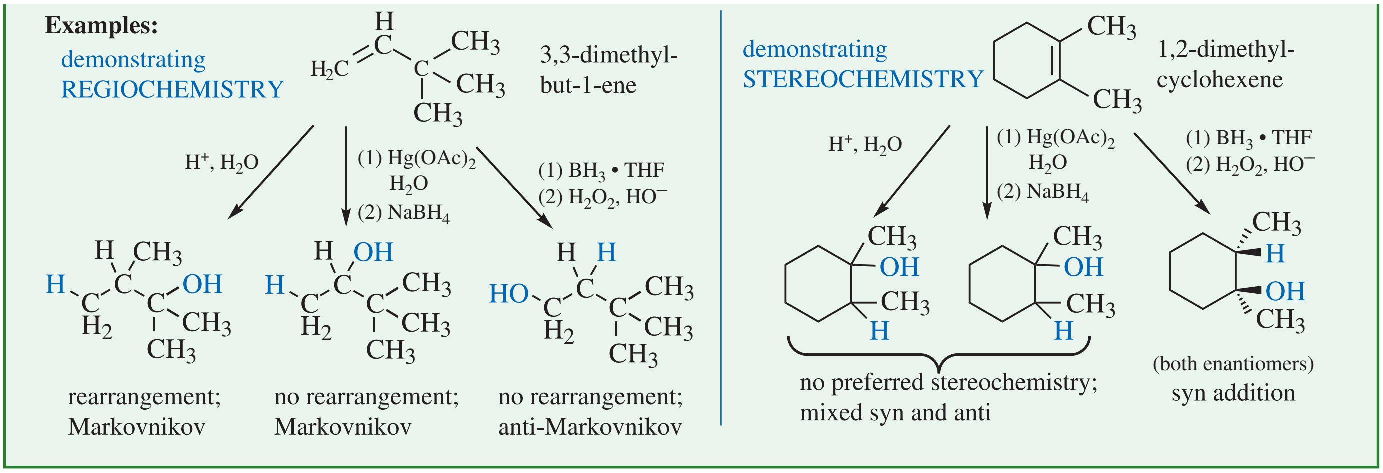
(a) When HBr adds across the double bond of 1,2-dimethylcyclopentene, the product is a mixture of the cis and trans isomers. Show why this addition is not stereospecific.

(b) When 1,2-dimethylcyclopentene undergoes hydroboration–oxidation, one diastereomer of the product predominates. Show why this addition is stereospecific, and predict the stereochemistry of the major product.

FOCUS Regiochemistry and Stereochemistry of Hydration Reactions

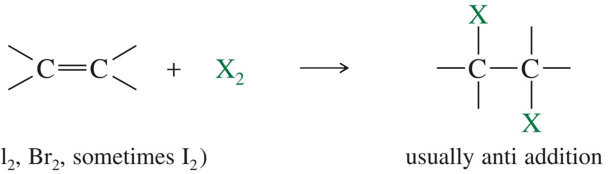
Reaction	Reagents	Orientation	Carbocation intermediate?	Rearrangement possible?	Stereochemistry of —H and —OH
Acid-catalyzed Hydration	H^+, H_2O	Markovnikov	Yes	Yes	mixed *syn* and *anti*
Oxymercuration-demercuration	(1) $Hg(OAc)_2$, H_2O (2) $NaBH_4$	Markovnikov	No	No	mixed *syn* and *anti*
Hydroboration-oxidation	(1) $BH_3 \cdot THF$ (2) H_2O_2, HO^-	anti-Markovnikov	No	No	*syn* addition only

(continued)



8-8 Addition of Halogens to Alkenes

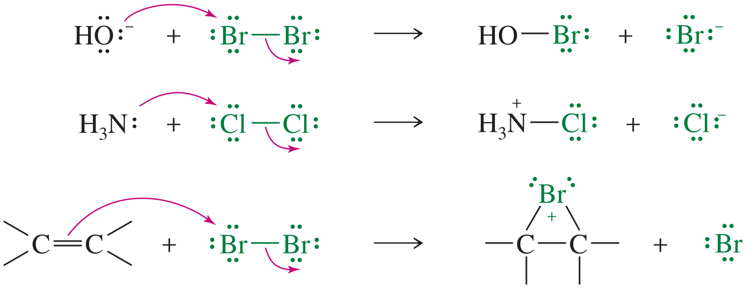
Halogens add to alkenes to form vicinal dihalides.



8-8A Mechanism of Halogen Addition

A halogen molecule (Br_2, Cl_2, or I_2) is electrophilic; a nucleophile can react with a halogen, displacing a halide ion:

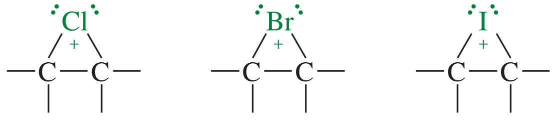
In this example, the nucleophile attacks the electrophilic nucleus of one bromine atom, and the other bromine serves as the leaving group, departing as bromide ion. Many reactions fit this general pattern; for example:



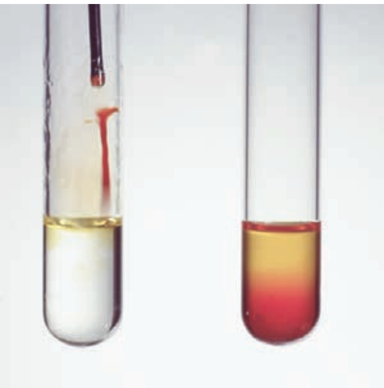
bromonium ion

In the last reaction, the pi electrons of an alkene attack the bromine molecule, expelling bromide ion. A **bromonium ion** results, containing a three-membered ring with a positive charge on the bromine atom. This bromonium ion is similar in structure to the mercurinium ion discussed in Section 8-5. Similar reactions with other halogens form other **halonium ions,** including *chloronium ions* and *iodonium ions*.

Examples



chloronium ion bromonium ion iodonium ion



When a solution of bromine (red-brown) is added to cyclohexene, the bromine color quickly disappears because bromine adds across the double bond. When bromine is added to cyclohexane (at right), the color persists because no reaction occurs.

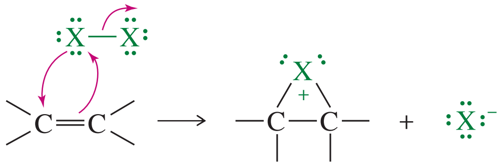
Unlike a normal carbocation, all the atoms in a halonium ion have filled octets. The three-membered ring has considerable ring strain, however, which, combined with a positive charge on an electronegative halogen atom, makes the halonium ion strongly electrophilic. Attack by a nucleophile, such as a halide ion, opens the halonium ion to give a stable product.

Chlorine and bromine commonly add to alkenes by the halonium ion mechanism. Iodination is used less frequently because diiodide products decompose easily. Any solvents used must be inert to the halogens; methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) are the most frequent choices.

The addition of bromine has been used as a simple chemical test for the presence of olefinic double bonds. A solution of bromine in carbon tetrachloride is a clear, deep red color. When this red solution is added to an alkene, the red bromine color disappears (we say it is "decolorized"), and the solution becomes clear and colorless. (Although there are other functional groups that decolorize bromine, few do it as quickly as alkenes.)

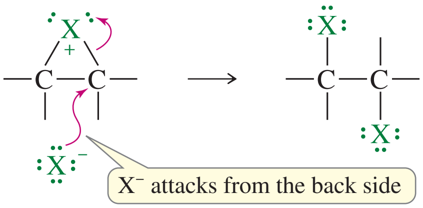
MECHANISM 8-7 Addition of Halogens to Alkenes

Step 1: Electrophilic attack forms a halonium ion.



halonium ion

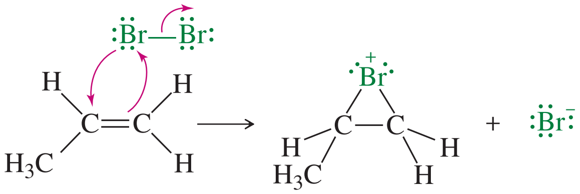
Step 2: The halide ion opens the halonium ion.



X⁻ attacks from the back side

EXAMPLE: Addition of Br_2 to propene.

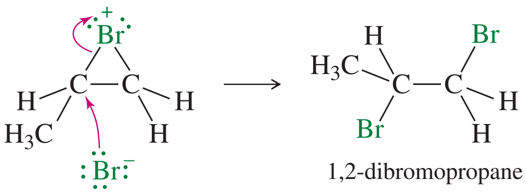
Step 1: Electrophilic attack forms a bromonium ion.



propene

bromonium ion

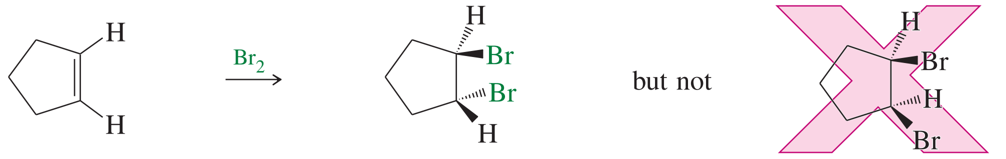
Step 2: Bromide ion opens the bromonium ion.



1,2-dibromopropane

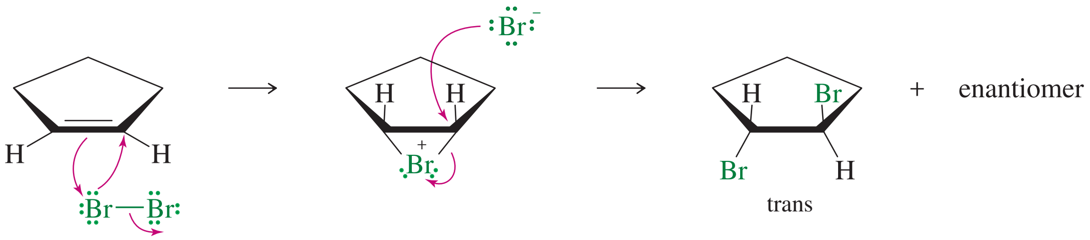
8-8B Stereochemistry of Halogen Addition

The addition of bromine to cyclopentene is a stereospecific **anti addition.**



cyclopentene *trans*-1,2-dibromocyclopentane (92%) (both enantiomers) *cis*-1,2-dibromocyclopentane (not formed)

Anti stereochemistry results from the bromonium ion mechanism. When a nucleophile attacks a halonium ion, it must do so from the back side, in a manner similar to the S_N2 displacement. This back-side attack assures anti stereochemistry of addition.



Halogen addition is another example of a stereospecific reaction, in which different stereoisomers of the starting material give different stereoisomers of the product. Figure 8-5 shows additional examples of the anti addition of halogens to alkenes.

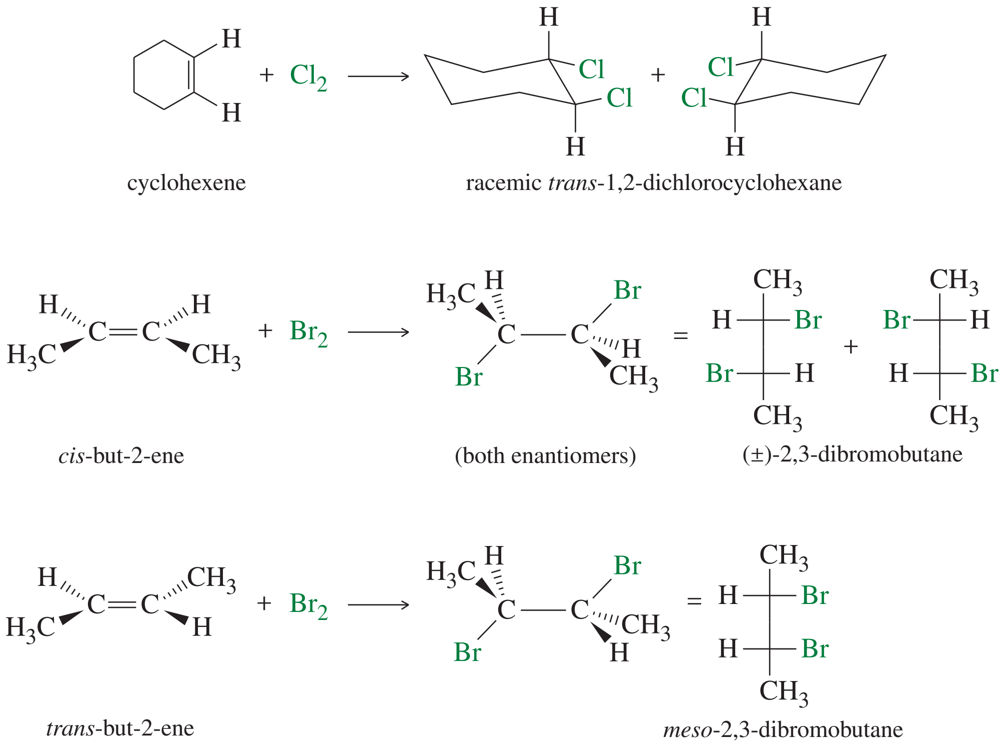


FIGURE 8-5 Examples of the anti addition of halogens to alkenes. The stereospecific anti addition gives predictable stereoisomers of the products.