CHAPTER

4

**The Spectra fiber in the bulletproof vests used by police and military is made of ultra high molecular weight polyethylene, a simple alkene polymer.**

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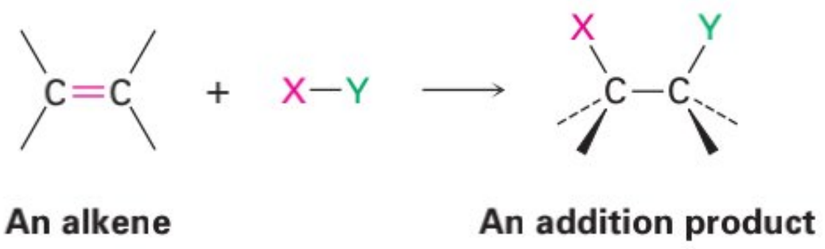
# Reactions of Alkenes and Alkynes



**Much of the background needed to understand organic reactions has been covered, and it's now time to begin a systematic description of the major functional groups.** We'll start in this chapter with a study of the alkene and alkyne families of compounds, and we'll see that the most important reaction of these two functional groups is the addition to the C=C and C≡C multiple bonds of various reagents X–Y to yield saturated products. In fact, all the reactions we'll discuss in this chapter follow the same pattern.




**An alkene** **An addition product**

OWL

Online homework for this chapter can be assigned in OWL, an online homework assessment tool.

## WHY THIS CHAPTER?

Both in this chapter on alkenes and in future chapters on other functional groups, we'll discuss a variety of reactions but will focus on the general principles and patterns of reactivity that tie organic chemistry together. There are no shortcuts; you have to know the reactions to understand organic chemistry.



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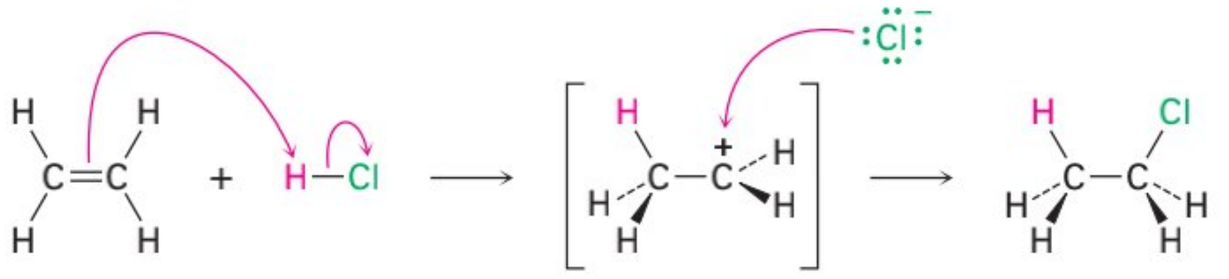
# 4.1 Addition of HX to Alkenes: Markovnikov's Rule

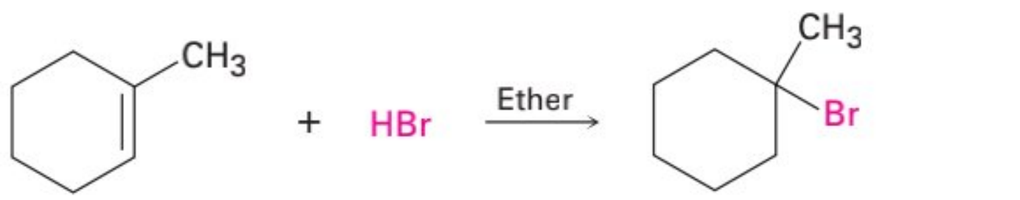
We saw in Section 3.7 that alkenes react with HCl to yield alkyl chloride addition products. For example, ethylene reacts with HCl to give chloroethane. The reaction takes place in two steps and involves a carbocation intermediate.



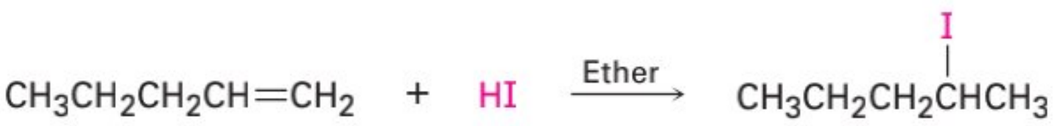
**Ethylene** **Carbocation intermediate** **Chloroethane**

The addition of halogen acids, HX, to alkenes is a general reaction that allows chemists to prepare a variety of halo-substituted alkane products. Thus, HCl, HBr, and HI all add to alkenes.

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



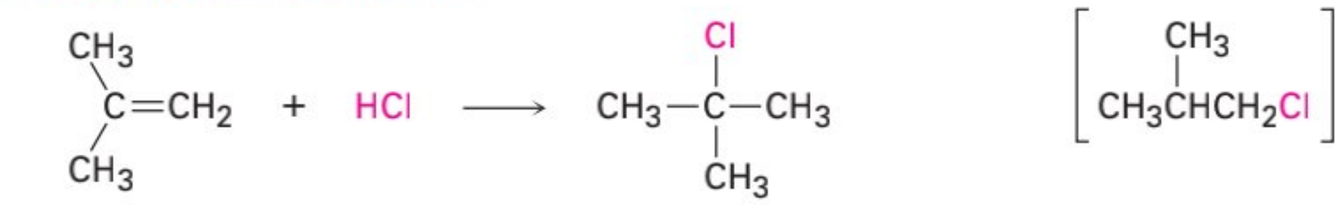
**1-Methylcyclohexene** **1-Bromo-1-methylcyclohexane**



**Pent-1-ene** **2-Iodopentane**

Look carefully at the three reactions just shown. In each case, an unsymmetrically substituted alkene has given a single addition product rather than the mixture that might have been expected. For example, 2-methylpropene *might* have reacted with HCl to give 1-chloro-2-methylpropane in addition to 2-chloro-2-methylpropane, but it didn't. We say that such reactions are **regiospecific** (**ree**-jee-oh-specific) when only one of the two possible orientations of addition occurs.

A regiospecific reaction:



**2-Methylpropene** **2-Chloro-2-methylpropane** (sole product) **1-Chloro-2-methylpropane** (*NOT formed*)

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**:

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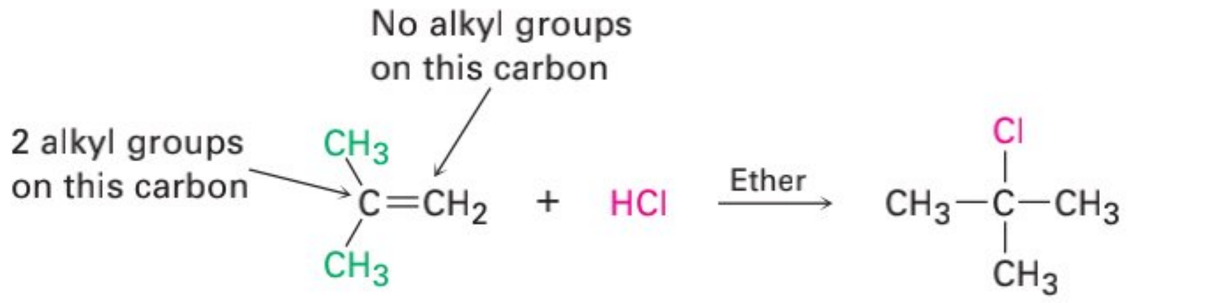
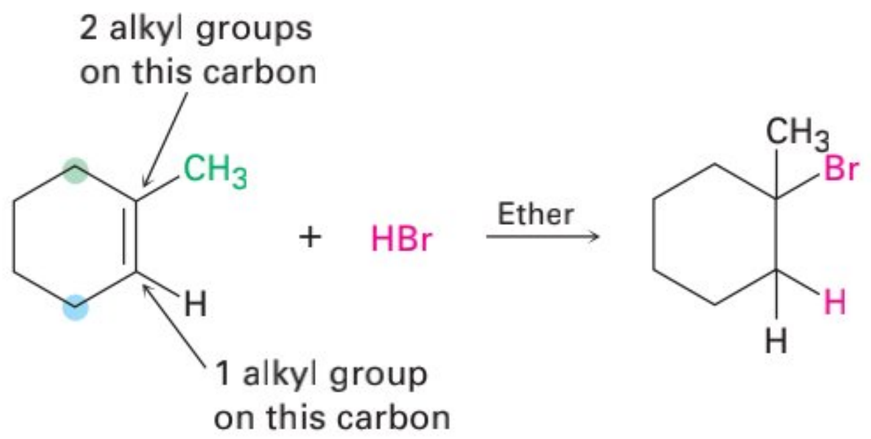
**MARKOVNIKOV'S RULE** In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents.

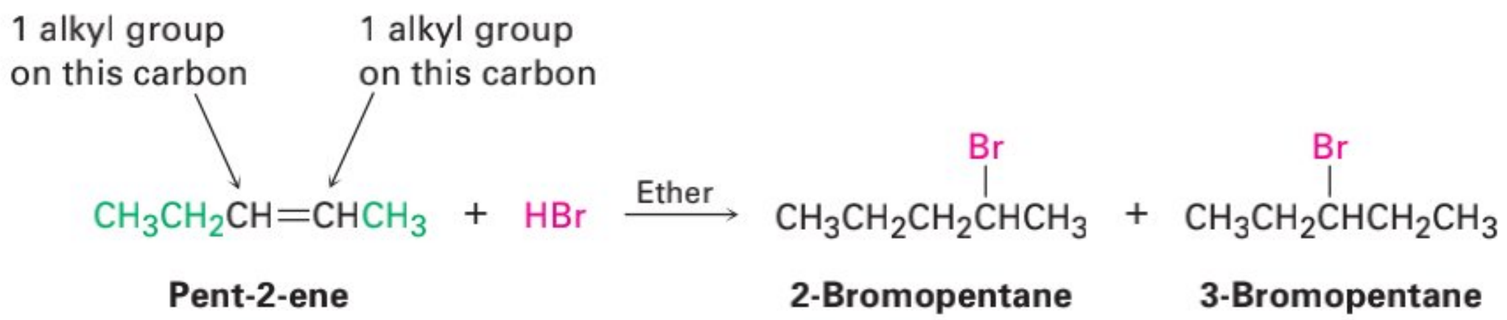



**2-Methylpropene** **2-Chloro-2-methylpropane**




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

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

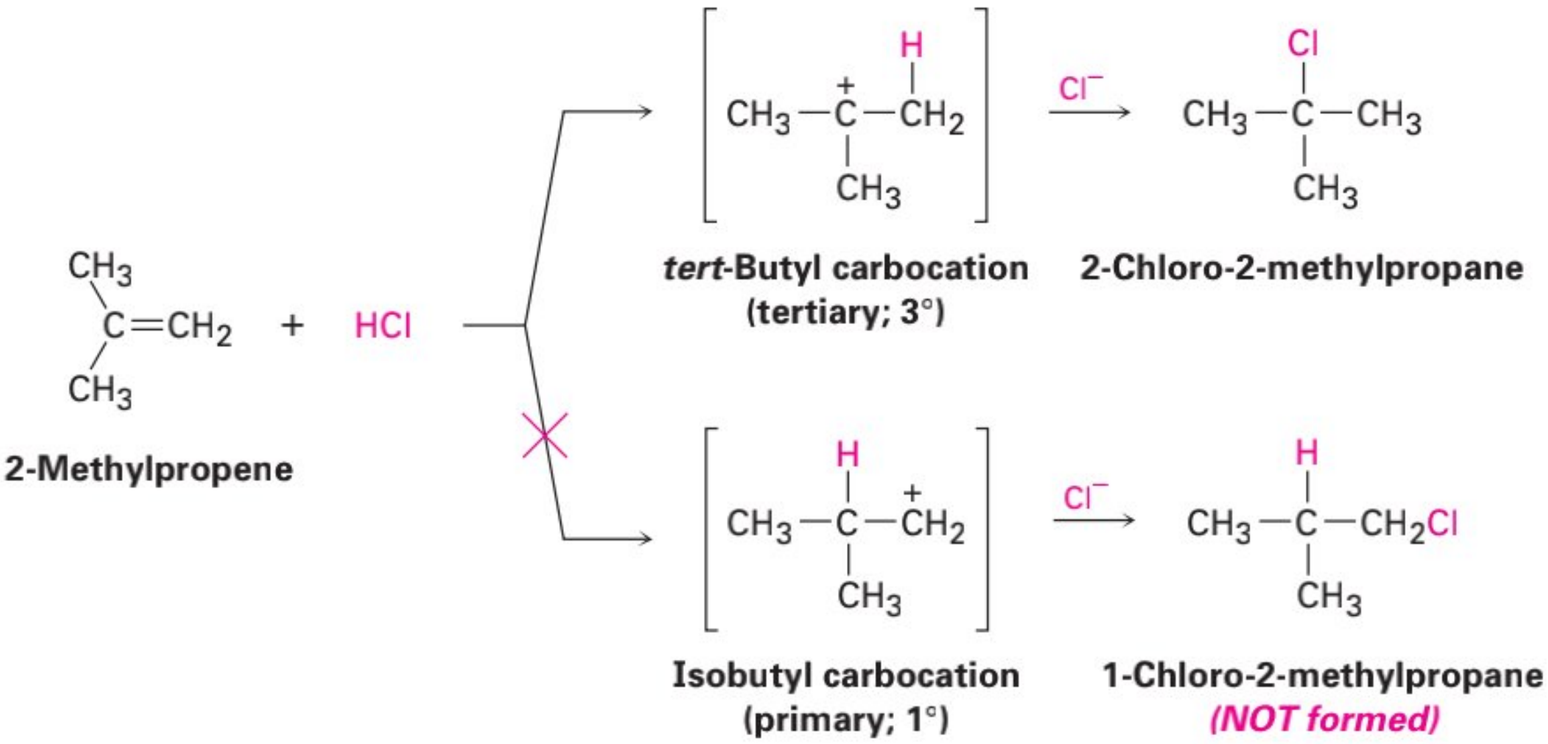



**Pent-2-ene** **2-Bromopentane** **3-Bromopentane**

Because carbocations are involved as intermediates in these reactions (Section 3.8), Markovnikov's rule can be restated.

**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 $H^+$ to 2-methylpropene yields the intermediate *tertiary* carbocation rather than the alternative primary carbocation. Why should this be?




**2-Methylpropene**

***tert*-Butyl carbocation (tertiary; 3°)** **2-Chloro-2-methylpropane**

**Isobutyl carbocation (primary; 1°)** **1-Chloro-2-methylpropane *(NOT formed)***

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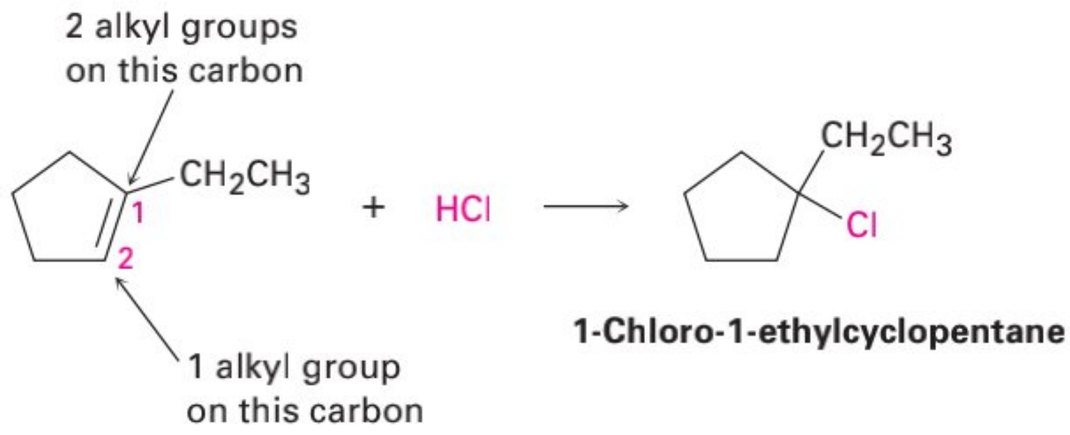
## Worked Example 4.1 Predicting the Product of an Alkene Addition Reaction

What product would you expect from the reaction of HCl with 1-ethylcyclopentene?


**Strategy** When solving a problem that asks you to predict a reaction product, begin by looking at the functional group(s) in the reactants and deciding what kind of reaction is likely to occur. In the present instance, the reactant is an alkene that will probably undergo an electrophilic addition reaction with HCl. Next, recall what you know about electrophilic addition reactions, and use your knowledge to predict the product. You know that electrophilic addition reactions follow Markovnikov's rule, so $H^+$ will add to the double-bond carbon that has one alkyl group (C2 on the ring) and Cl will add to the double-bond carbon that has two alkyl groups (C1 on the ring).

**Solution** The expected product is 1-chloro-1-ethylcyclopentane.




**1-Chloro-1-ethylcyclopentane**

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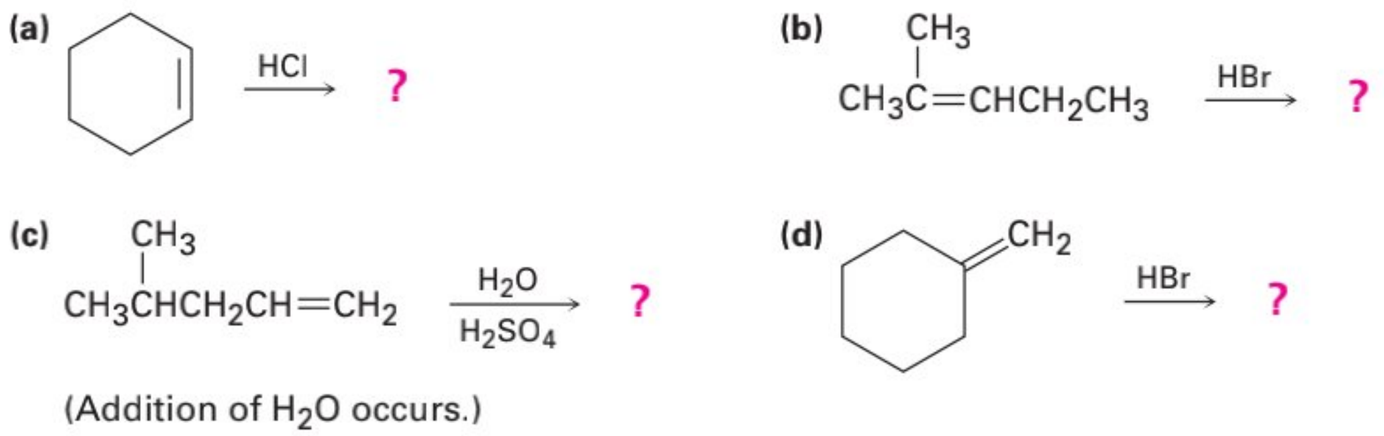
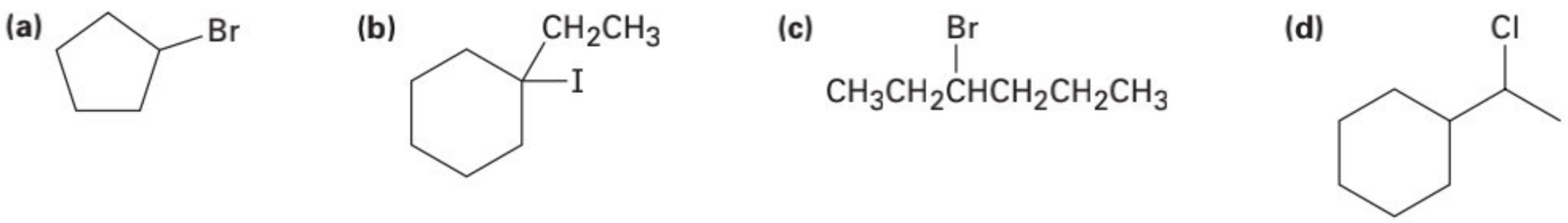
**Problem 4.1** Predict the products of the following reactions:




**Problem 4.2** What alkenes would you start with to prepare the following alkyl halides?

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