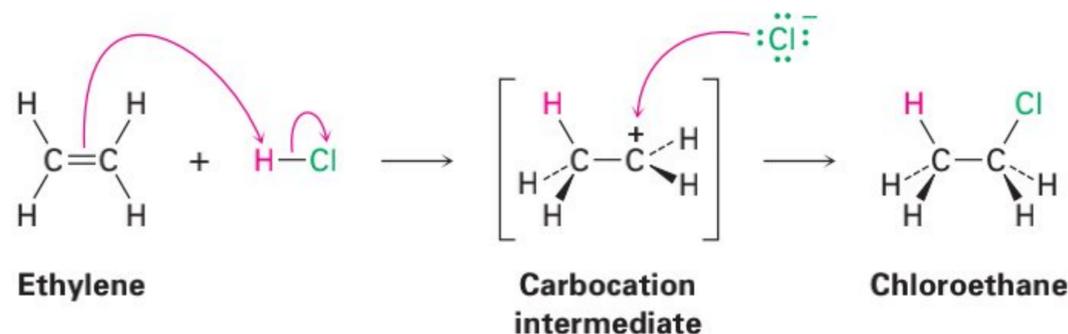


## 4.1 Addition of HX to Alkenes: Markovnikov's Rule

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.

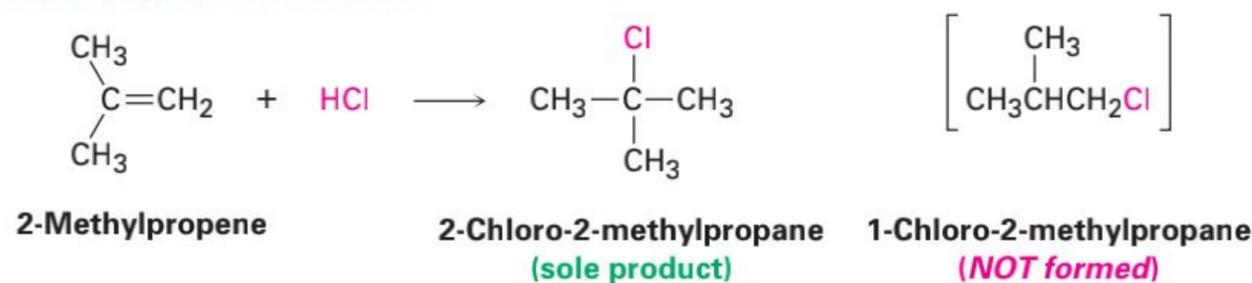


The addition of halogen acids, HX, to alkenes is a general reaction that allows chemists to prepare a variety of halo-substituted alkane products. Thus, HCl, HBr, and HI all add to alkenes.



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 **regio-specific** (ree-jee-oh-specific) when only one of the two possible orientations of addition occurs.

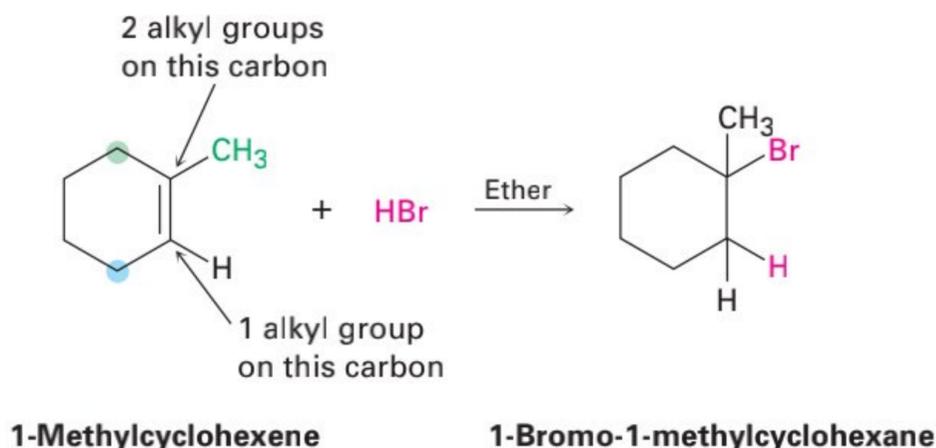
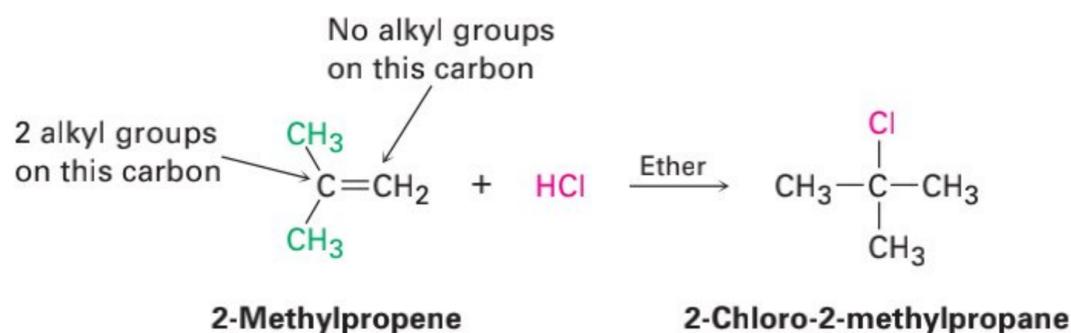
**A regio-specific reaction:**



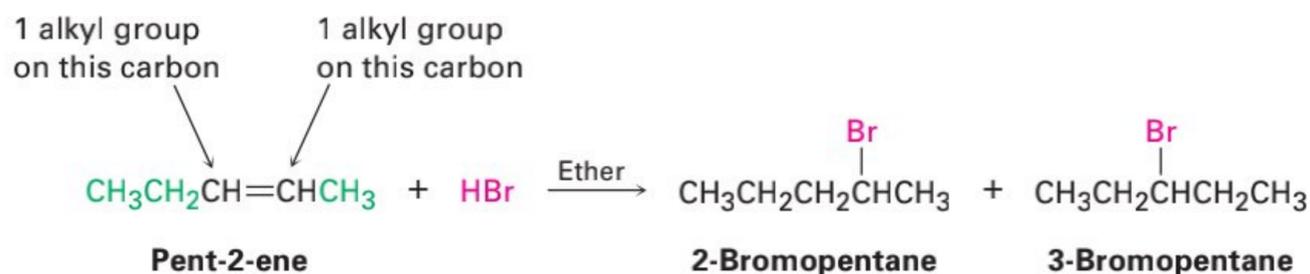
After looking at the results of many such reactions, the Russian chemist Vladimir Markovnikov proposed in 1869 what has become known as **Markovnikov's rule**:

**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.



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

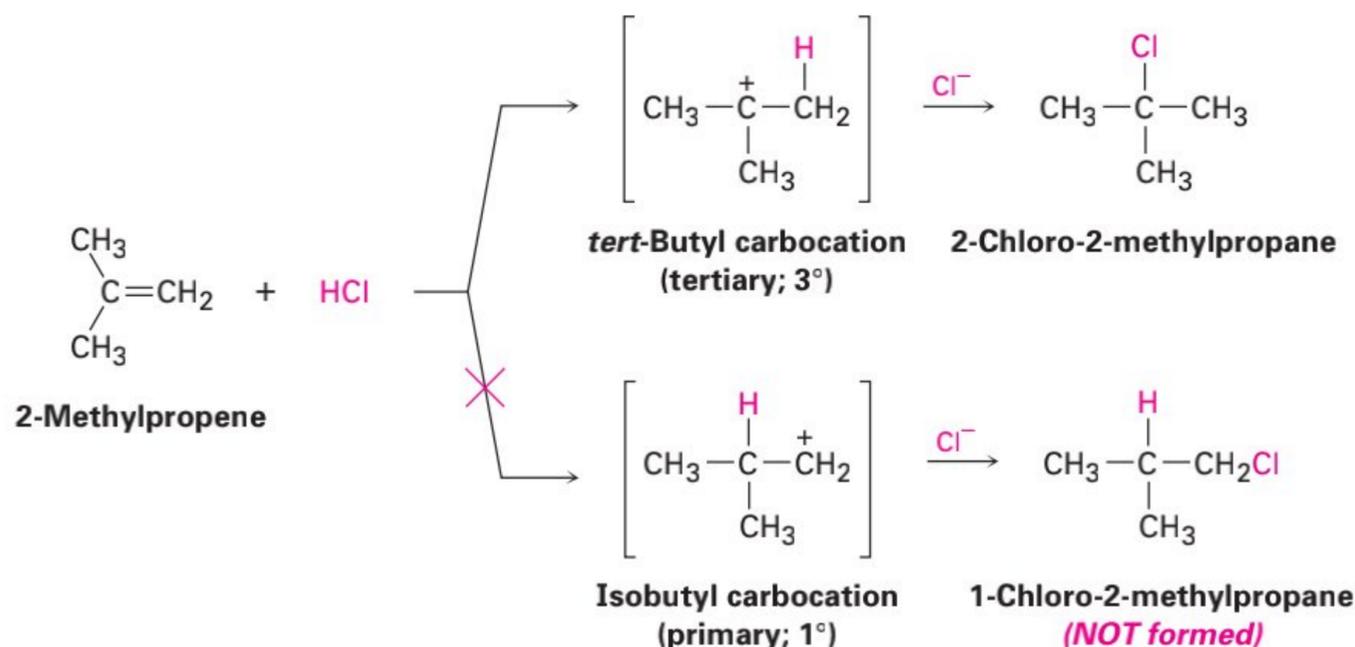


Because carbocations are involved as intermediates in these reactions (Section 3.8), Markovnikov's rule can be restated.

**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.

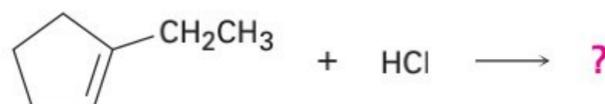
For example, addition of H<sup>+</sup> to 2-methylpropene yields the intermediate *tertiary* carbocation rather than the alternative *primary* carbocation. Why should this be?



## 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?

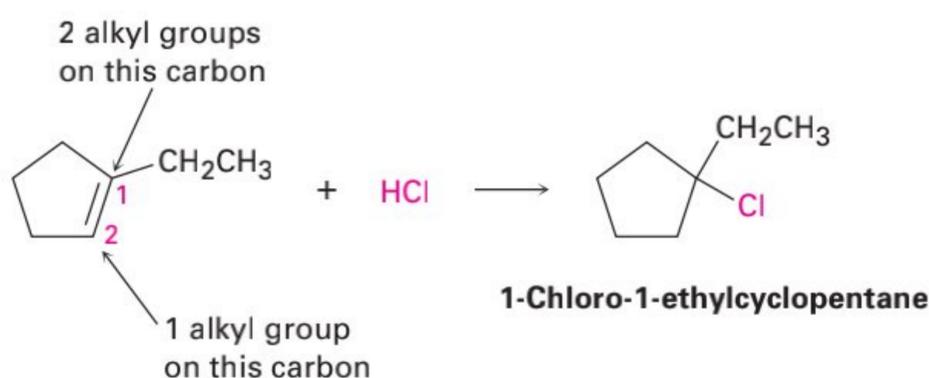


## Strategy

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  $\text{H}^+$  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).

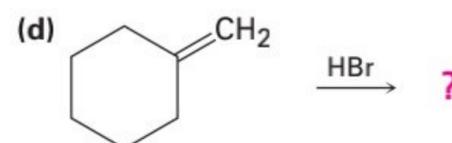
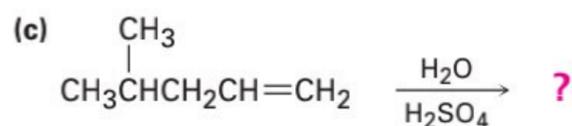
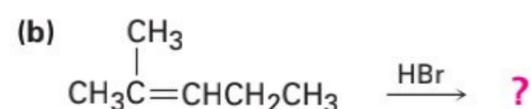
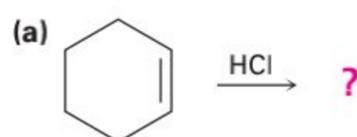
## Solution

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



## Problem 4.1

Predict the products of the following reactions:



(Addition of  $\text{H}_2\text{O}$  occurs.)

## Problem 4.2

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

