



Chapter 4

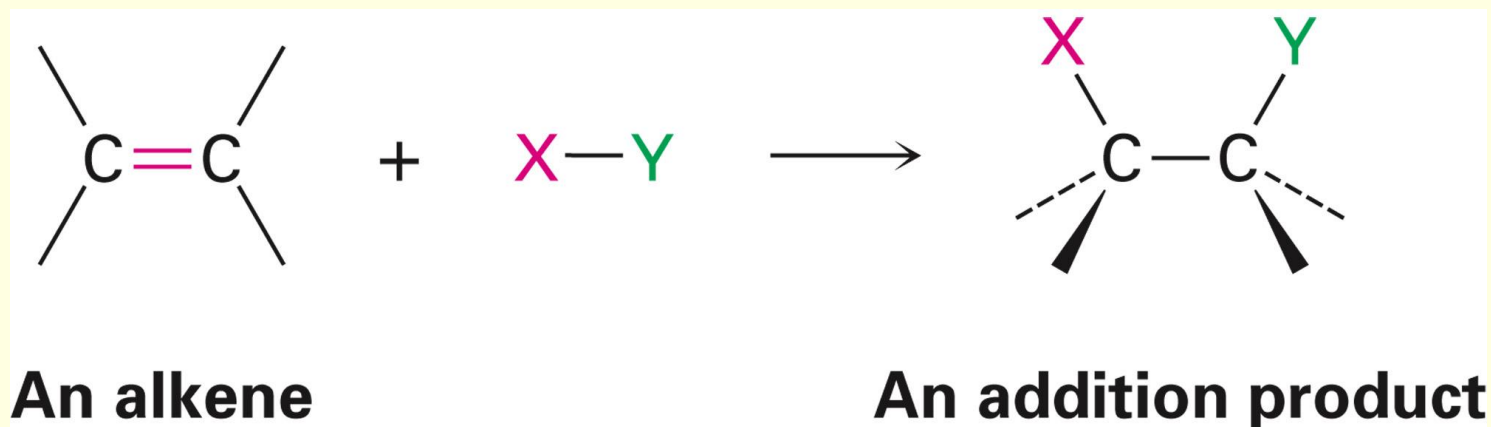
Reactions of Alkenes and Alkynes

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임해균 교수

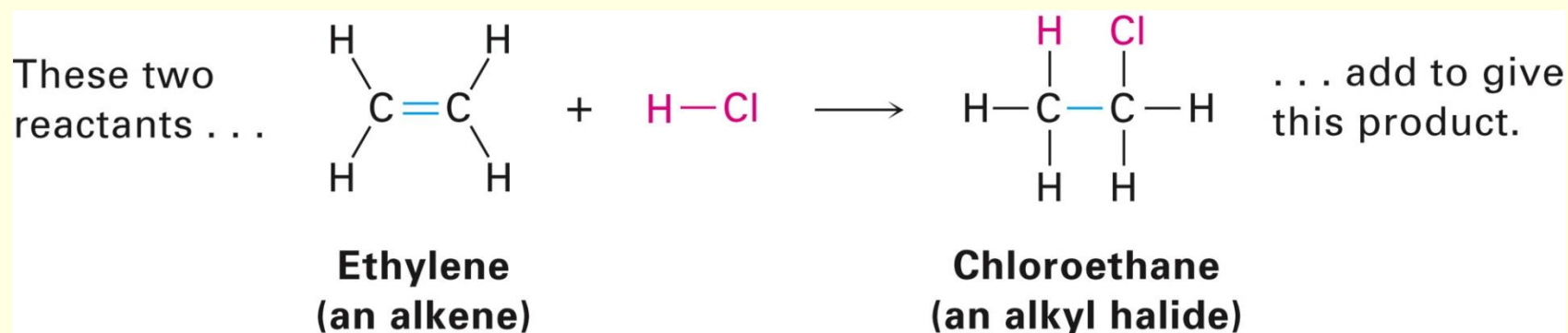
Diverse Reactions of Alkenes

- Alkenes react with many electrophiles to give useful products by addition (often through special reagents)

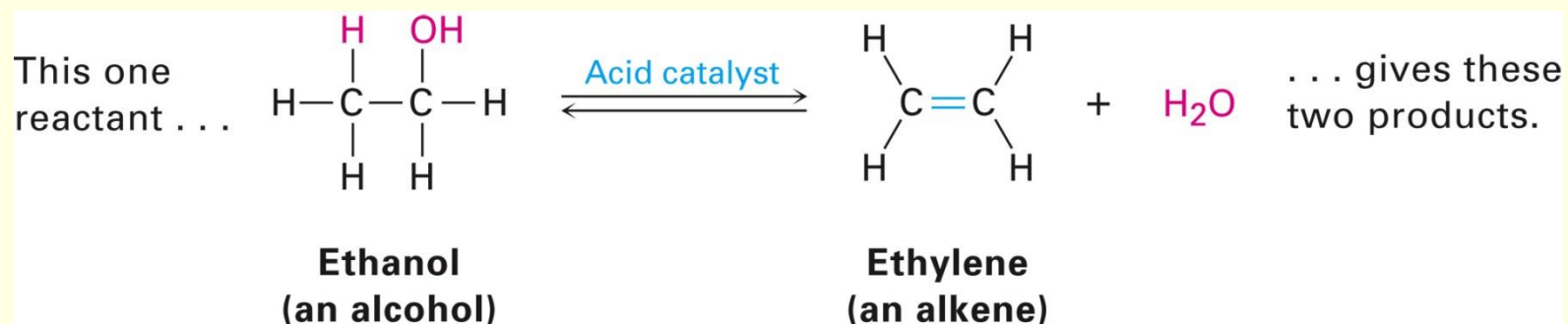


3.5 Kinds of Organic Reactions

- In general, we look at what occurs and try to learn how it happens
- Common patterns describe the changes
 - **Addition** reactions – two molecules combine

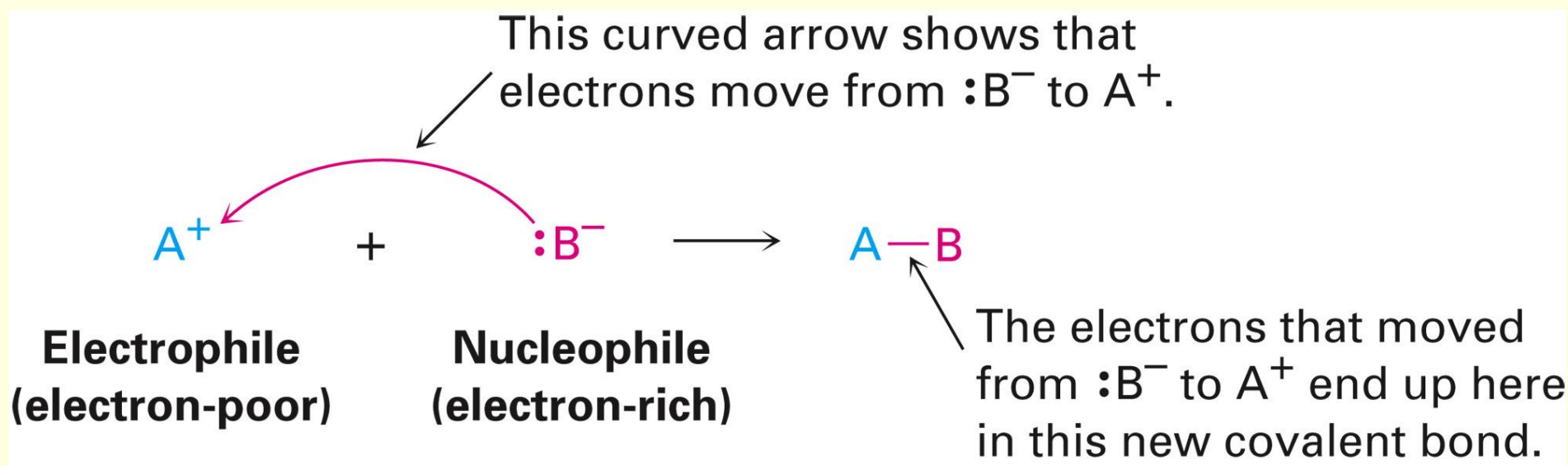


- **Elimination** reactions – one molecule splits into two

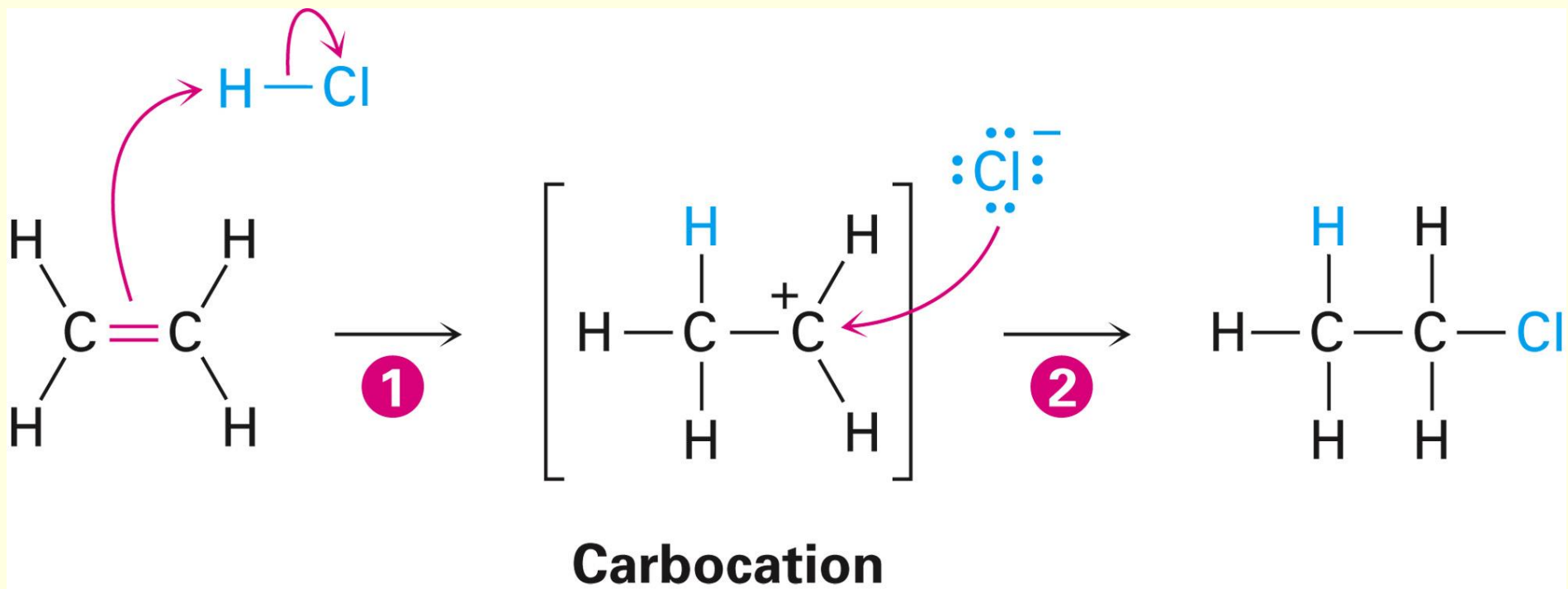


Generalized Polar Reactions

- An **electrophile**, an electron-poor species, combines with a **nucleophile**, an electron-rich species
- The combination is indicated with a curved arrow from nucleophile to electrophile



3.8 Describing a Reaction: Transition States and Intermediates



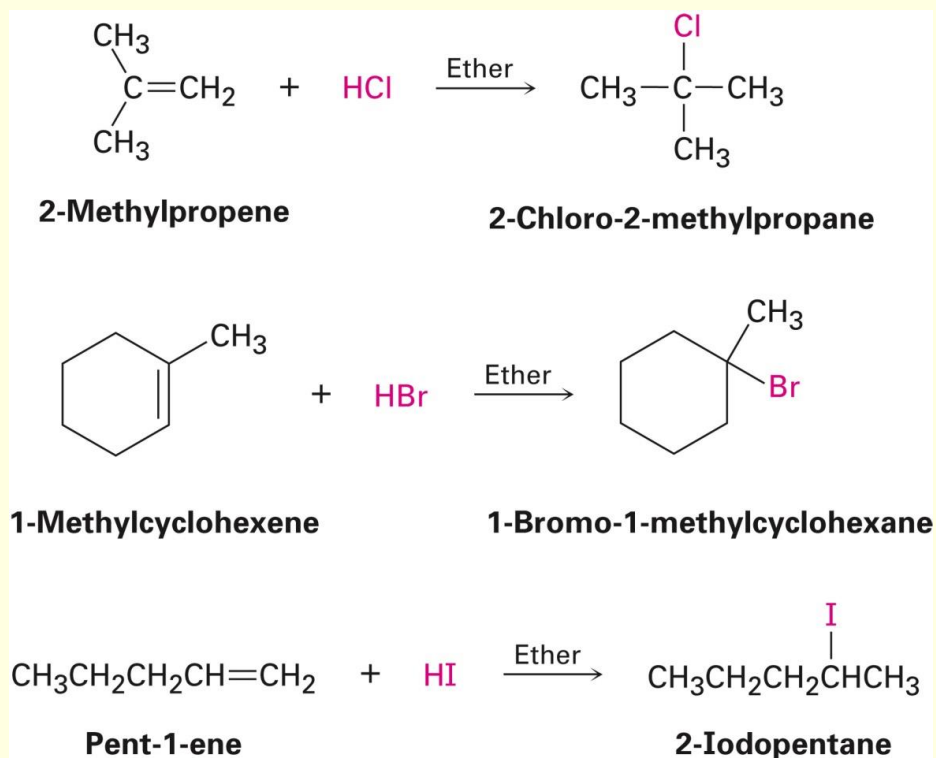
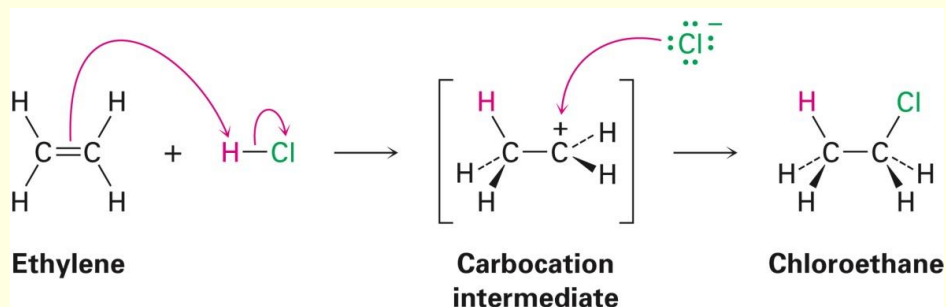
- The highest energy point in a reaction step is called the **transition state**
- The energy needed to go from reactant to transition state is the **activation energy** (ΔG^\ddagger)

Why this chapter?

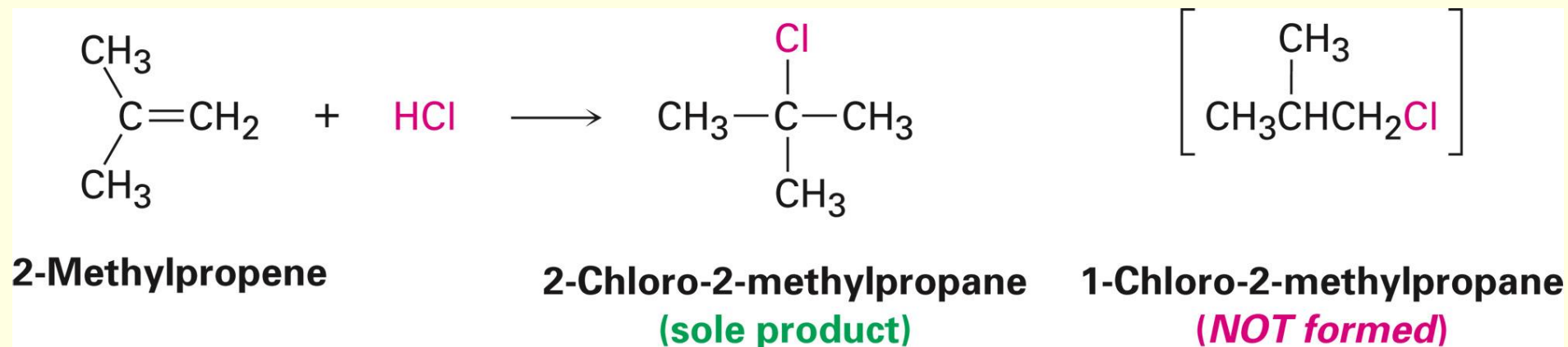
- To begin a **systematic** description of major functional groups
- Begin to focus on general principles and **patterns of reactivity** that tie organic chemistry

4.1 Addition of HX to Alkenes: Markovnikov's Rule

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.

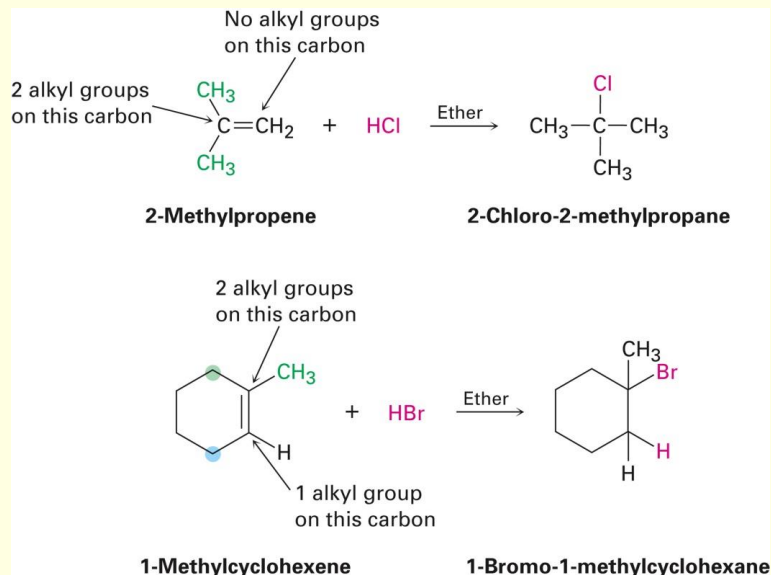


- In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other
- If one orientation predominates, the reaction is **regiospecific**
- **Markovnikov** observed in the 19th century that in the addition of HX to alkene, the H attaches to the carbon with the most H's and X attaches to the other end (to the one with the most alkyl substituents)
 - This is **Markovnikov's rule**

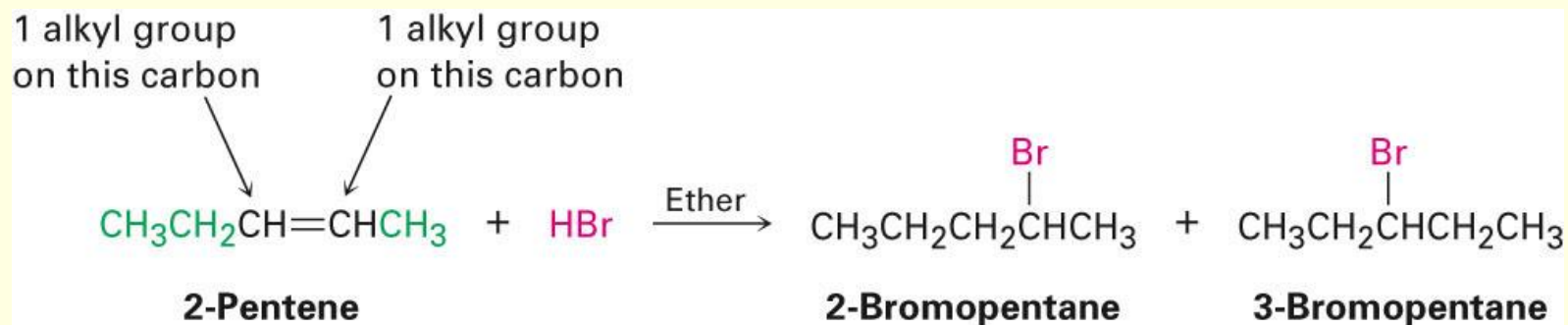


Markovnikov's Rule

- Addition of HCl to 2-methylpropene
- **Regiospecific** – one product forms where two are possible

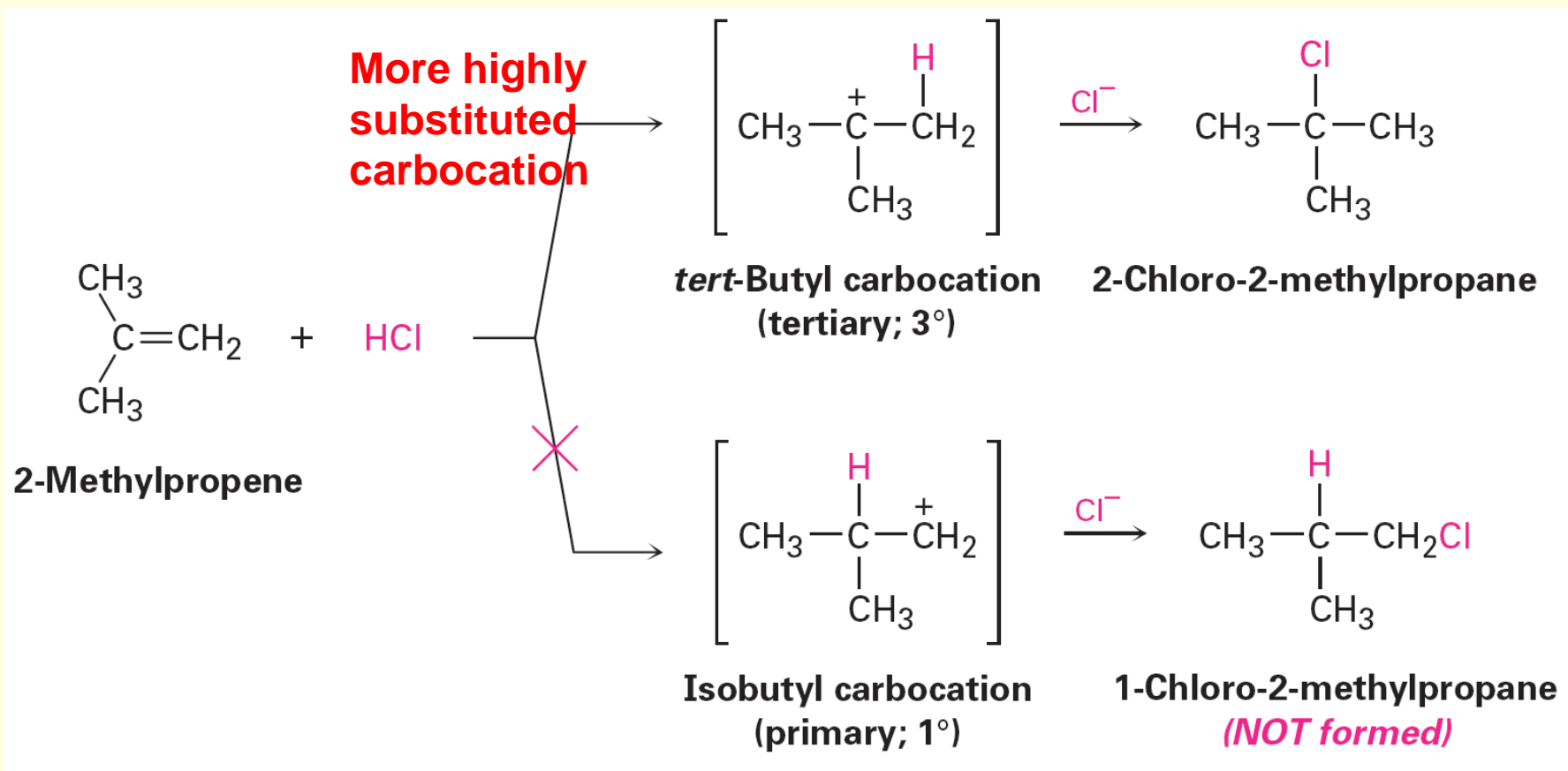


- If both ends have similar substitution, then not regiospecific



Markovnikov's Rule (restated)

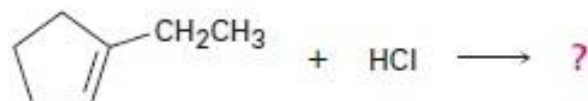
- **More highly substituted carbocation** forms as intermediate rather than less highly substituted one
- Tertiary cations and associated transition states are more stable than primary cations



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?

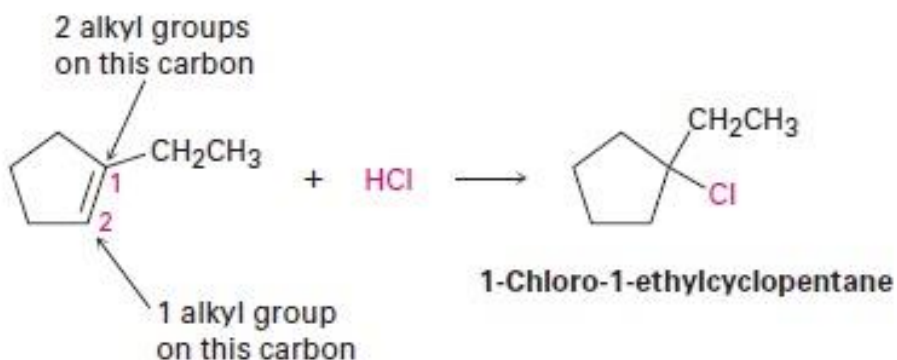


Strategy

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).

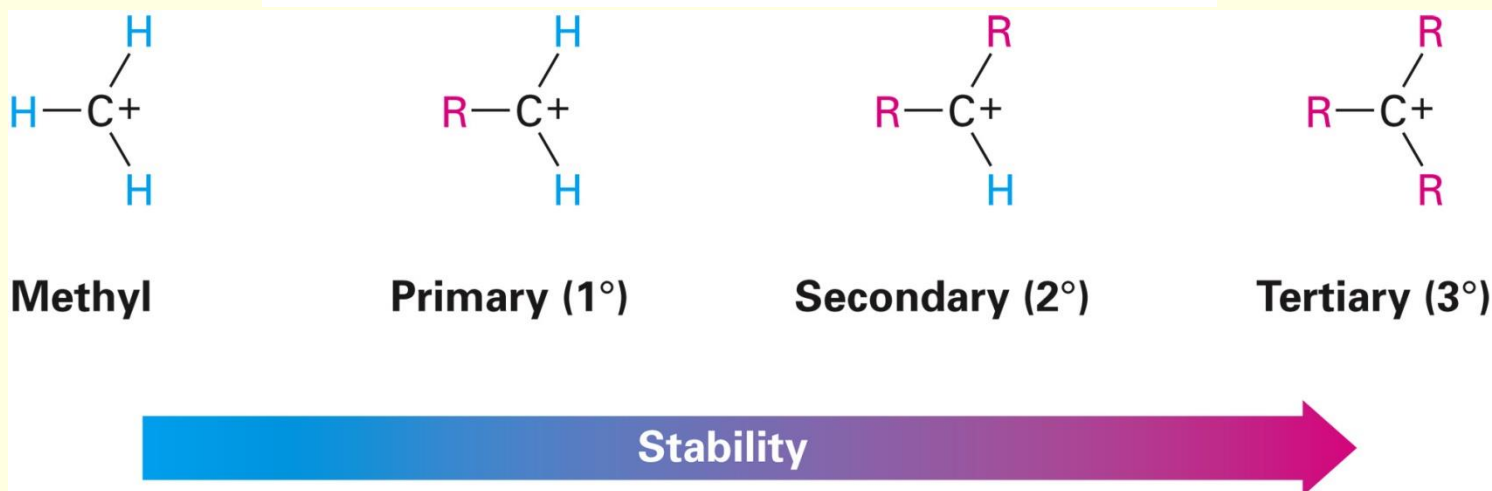
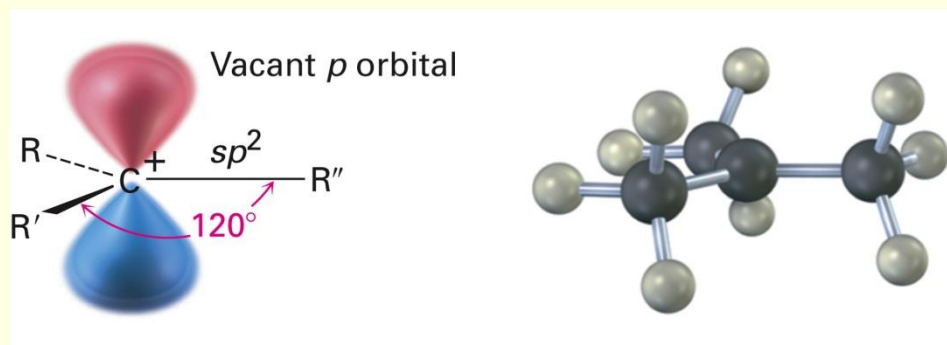
Solution

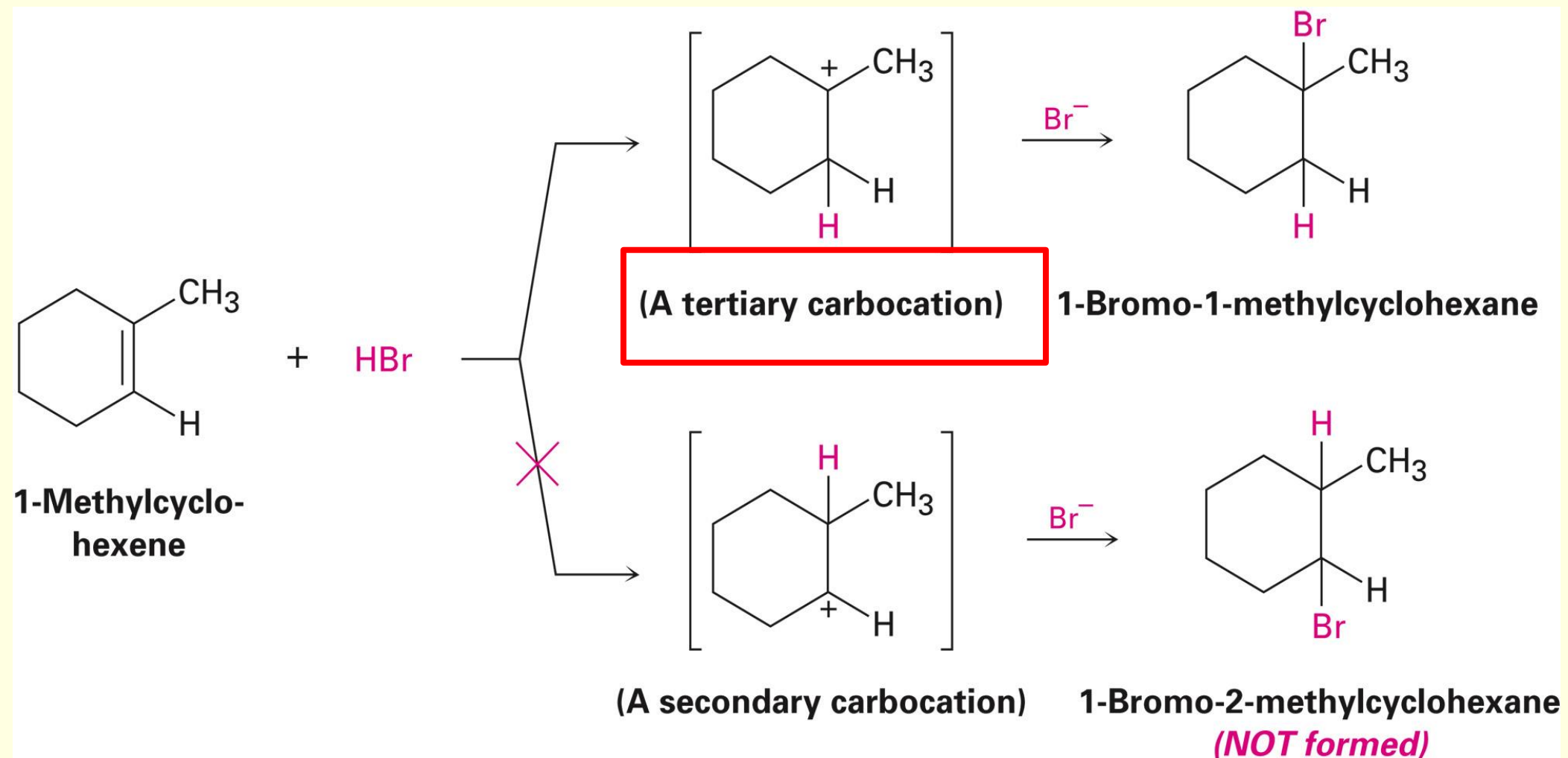
The expected product is 1-chloro-1-ethylcyclopentane.



4.2 Carbocation Structure and Stability

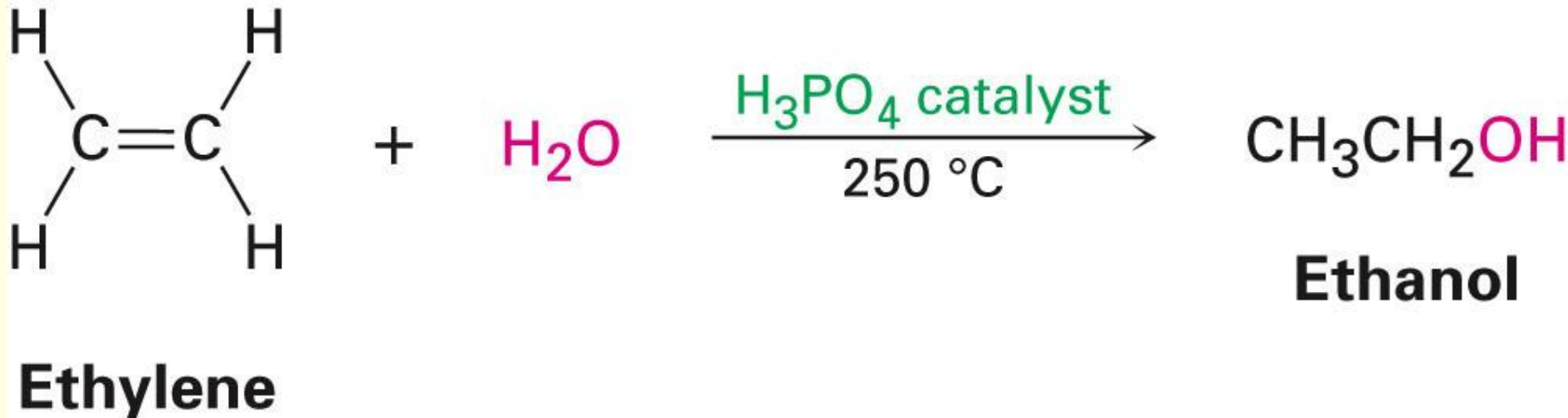
- Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in sp^2 orbitals
- The fourth orbital on carbon is a vacant p -orbital
- The stability of the carbocation (measured by energy **needed** to form it from R-X) is increased by the presence of alkyl substituents





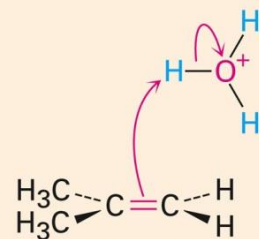
4.3 Addition of Water to Alkenes

- **Hydration of an alkene** is the addition of H-OH to to give an alcohol
- Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol



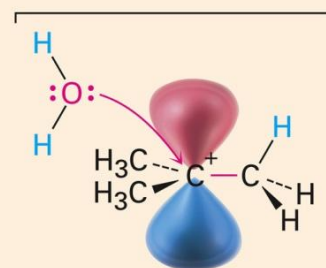
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- 1 A hydrogen atom on the electrophile H_3O^+ is attacked by π electrons from the nucleophilic double bond, forming a new C-H bond. This leaves the other carbon atom with a + charge and a vacant p orbital. Simultaneously, two electrons from the H-O bond move onto oxygen, giving neutral water.



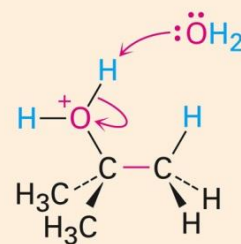
2-Methylpropene

1



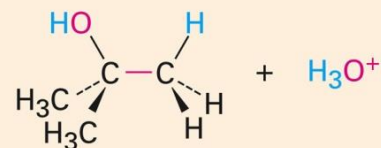
Carbocation

2



Protonated alcohol

3

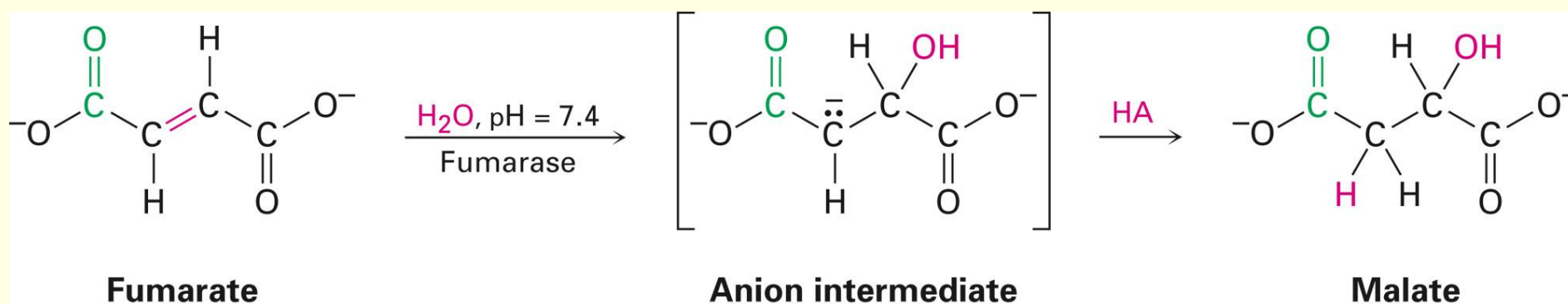


2-Methylpropan-2-ol

- 2 The nucleophile H_2O donates an electron pair to the positively charged carbon atom, forming a C-O bond and leaving a positive charge on oxygen in the protonated alcohol addition product.

- 3 Water acts as a base to remove H^+ , regenerating H_3O^+ and yielding the neutral alcohol addition product.

Biological hydration



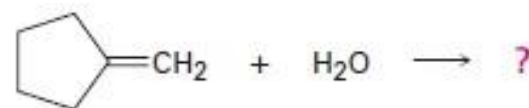
Hydration of carbon–carbon double bonds **also occurs in various biological pathways**, although **not by the carbocation** mechanism. Instead, biological hydrations usually require that the double bond be adjacent to a carbonyl group ($\text{C}=\text{O}$) for reaction to proceed.

We'll see the function of the nearby carbonyl group in Section 9.10 but might note for now that the reaction occurs through a mechanism that involves formation of an **anion intermediate** followed by protonation by an acid HA .

Worked Example 4.2

Predicting the Product of an Alkene Hydration Reaction

What product would you expect from acid-catalyzed addition of water to methylenecyclopentane?

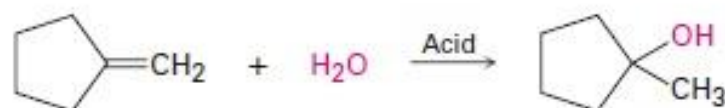


Methylenecyclopentane

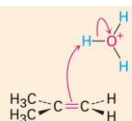
Strategy

According to Markovnikov's rule, H^+ adds to the carbon that already has more hydrogens (the $=\text{CH}_2$ carbon) and OH adds to the carbon that has fewer hydrogens (the ring carbon). Thus, the product will be a tertiary alcohol.

Solution

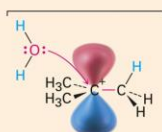


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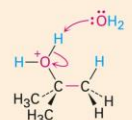
2-Methylpropene

1



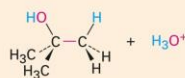
Carbocation

2



Protonated alcohol

3



2-Methylpropan-2-ol

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