

10.3: Reactions of Alkenes- Addition of Water (or Alcohol) to Alkenes

Addition of Water to Alkenes (Hydration of Alkenes)

An alkene does not react with pure water, since water is not acidic enough to allow the hydrogen to act as an electrophile to start a reaction. However, with the presence of small amount of an acid, the reaction does occur with a water molecule added to the double bond of alkene, and the product is an alcohol. This is the acid-catalyzed addition reaction of water to alkene (also called hydration), and this reaction has great utility in large-scale industrial production of certain low-molecular-weight alcohols.

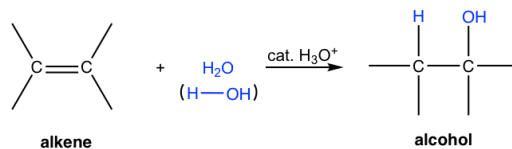


Figure 10.3a Hydration Reaction

The acid most commonly applied to catalyze this reaction is dilute aqueous solution of sulfuric acid (H₂SO₄). Sulfuric acid dissociates completely in aqueous solution and the hydronium ion (H₃O⁺) generated participates in the reaction. Strong organic acid, tosyl acid (TsOH), is used sometimes as well.

The mechanism for acid-catalyzed hydration of alkene is essentially the same as the mechanism for the addition of hydrogen halide, HX, to alkenes, and the reaction therefore follows Markovnikov's rule as well in terms of regioselectivity. The hydration of 1-methylcyclohexene and the reaction mechanism are shown below.

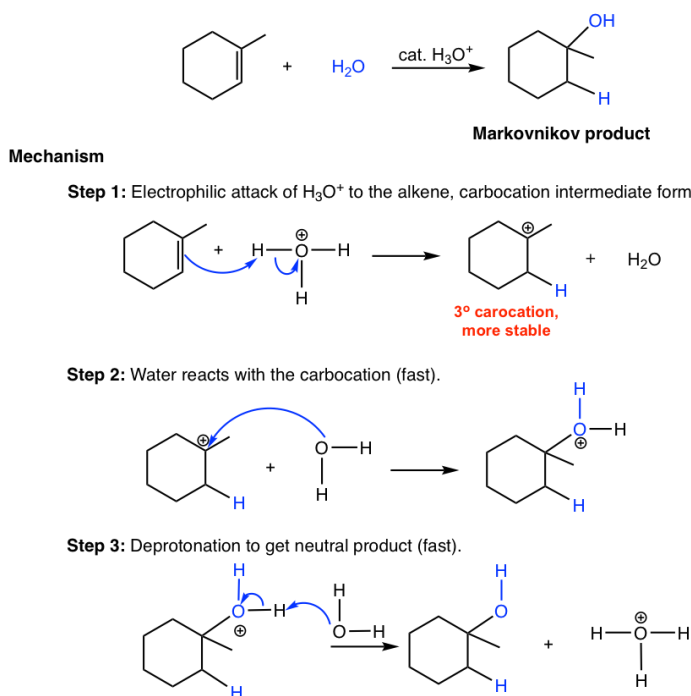


Figure 10.3b Mechanism for acid-catalyzed hydration of alkene

Since water molecule can be regarded as H—OH, so the regioselectivity of alcohol product that follows Markovnikov's rule means the hydrogen atom connects to the double bond carbon that has more hydrogen atoms, and OH group adds to the carbon that has less hydrogen atoms. This can be explained again by the formation of more stable carbocation in the first step of the mechanism. The acidic hydronium ion (H₃O⁺) is regenerated in the last deprotonation step, so only a small amount of acid is required to initiate the reaction, the acid therefore is a catalyst.

Comparing the hydration reaction of alkene to the dehydration reaction of alcohol in section 10.1.2, you would recognize that they are reverse reactions, one is addition and the other is elimination. To produce alcohol from alkene via hydration, water should be in excess to ensure the reaction goes to completion. While to prepare alkene from alcohol through dehydration, high concentration of

acid with elevated temperature favor the elimination process and the product can be removed by distillation as they formed to push the equilibrium to alkene side.

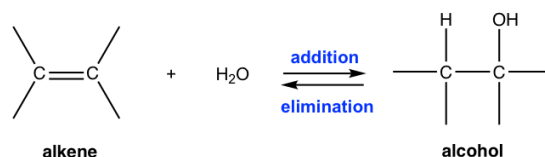


Figure 10.3c Hydration reaction of alkene vs. dehydration reaction of alcohol

Addition of Alcohol to Alkenes

With the presence of acid, an alcohol can be added to the alkene in the same way that water does, and ether formed as product. For example:

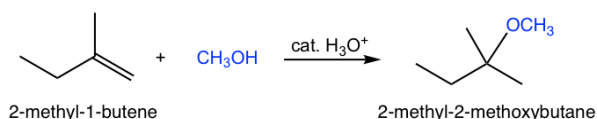


Figure 10.3d Example of addition of Alcohol to Alkenes

Examples: Show the mechanism for above addition reaction of methanol to 2-methyl-1-butene.

Refer to the hydration mechanism.

Solutions:

Mechanism: addition of methanol to 2-methyl-1-butene

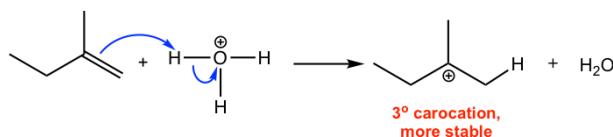
Step 1: Electrophilic attack of H_3O^+ to the alkene, carbocation intermediate formed

Step 2: Methanol reacts with the carbocation

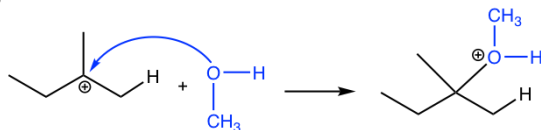
Step 3: Deprotonation to get neutral product

Mechanism: addition of methanol to 2-methyl-1-butene

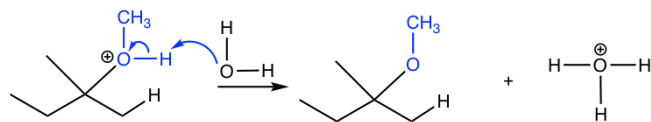
Step 1: Electrophilic attack of H_3O^+ to the alkene, carbocation intermediate formed



Step 2: Methanol reacts with the carbocation



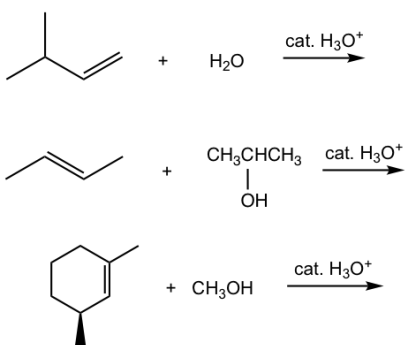
Step 3: Deprotonation to get neutral product



Note: Please keep in mind that for the reaction that involves carbocation intermediate, the rearrangement of carbocation is always an option. Therefore the addition of water/alcohol to alkenes may involve carbocation rearrangement if possible.

Exercises 10.3

Show major product(s) for the following reactions.



Answers to Practice Questions Chapter 10

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