11.7: Addition of Hydrogen Halides

Reaction 1: Addition of Hydrogen Halide to an Alkyne

Summary: Reactivity order of hydrogen halides: HI > HB r> HCl > HF.

Follows Markovnikov's rule:

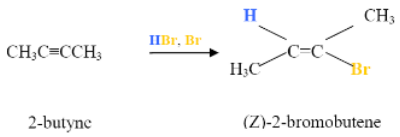
- Hydrogen adds to the carbon with the greatest number of hydrogens, the halogen adds to the carbon with fewest hydrogens.
- Protination occurs on the more stable carbocation. With the addition of HX, haloalkenes form.
- With the addition of excess HX, you get *anti* addition forming a geminal dihaloalkane.

Addition of a HX to an Internal Alkyne

As described in Figure 1, the π electrons will attack the hydrogen of the HBr and because this is a symmetric molecule it does not matter which carbon it adds to, but in an asymmetric molecule the hydrogen will covalently bond to the carbon with the most hydrogens. Once the hydrogen is covalently bonded to one of the carbons, you will get a carbocation intermediate (not shown, but will look the same as depicted in Figure 1) on the other carbon. Again, this is a symmetric molecule and if it were asymmetric, which carbon would have the positive charge?

The final step is the addition of the Bromine, which is a good nucleophile because it has electrons to donate or share. Bromine, therefore attacks the carbocation intermediate placing it on the highly substituted carbon. As a result, you get 2-bromobutene from your 2-butyne reactant, as shown below.

Figure 2



2-butyne (Z)-2-bromobutene

Now, what if you have excess HBr?

Addition due to excess HX present ? yields a geminal dihaloalkane

Figure 3

(Z)-2-bromobutene 2,2-Dibromobutane

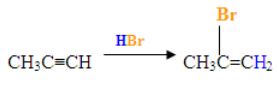
Here, the electrophilic addition proceeds with the same steps used to achieve the product in Addition of a HX to an Internal Alkyne. The π electrons attacked the hydrogen, adding it to the carbon on the left (shown in blue). Why was hydrogen added to the carbon on left and the one on the right bonded to the Bromine?

Now, you will have your carbocation intermediate, which is followed by the attack of the Bromine to the carbon on the right resulting in a haloalkane product.

Addition of HX to Terminal Alkyne

- Here is an addition of HBr to an asymmetric molecule.
- First, try to make sense of how the reactant went to product and then take a look at the mechanism.

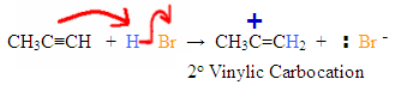
Figure 4



Propyne 2-Bromopropene

Mechanism:

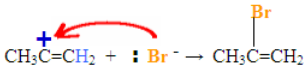
1)



2° Vinylic Carbocation

The π electrons are attacking the hydrogen, depicted by the electron pushing arrows and the Bromine gains a negative charge. The carbocation intermediate forms a positive charge on the left carbon after the hydrogen was added to the carbon with the most hydrogen substituents.

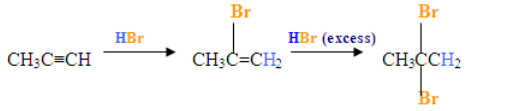
2)



The Bromine, which has a negative charge, attacks the positively charged carbocation forming the final product with the nucleophile on the more substituted carbon.

Addition due to excess HBr present

Figure 5

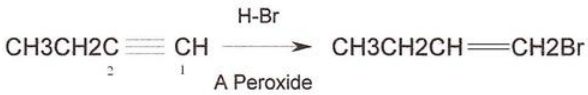


Propyne 2-Bromopropene 2,2-Dibromopropane

Most Hydrogen halide reactions with alkynes occur in a Markovnikov-manner in which the halide attaches to the most substituted carbon since it is the most positively polarized. A more substituted carbon has more bonds attached to 1) carbons or 2) electron-donating groups such as Fluorine and other halides. However, there are two specific reactions among alkynes where anti-Markovnikov reactions take place: the radical addition of HBr and Hydroboration Oxidation reactions. For alkynes, an anti-Markovnikov addition takes place on a terminal alkyne, an alkyne on the end of a chain.

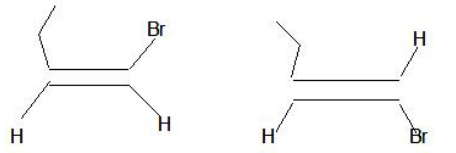
HBr Addition With Radical Yields 1-bromoalkene

The Br of the Hydrogen Bromide (H-Br) attaches to the less substituted 1-carbon of the terminal alkyne shown below in an anti-Markovnikov manner while the Hydrogen proton attaches to the second carbon. As mentioned above, the first carbon is the less substituted carbon since it has fewer bonds attached to carbons and other substituents. The H-Br reagent must also be reacted with heat or some other radicial initiator such as a peroxide in order for this reaction to proceed in this manner. This presence of the radical or heat leads to the anti-Markovnikov addition since it produces the most stable reaction. For more on Anti-Markovnikov additions:Radical Additions--Anti-Markovnikov Product Formation



The product of a terminal alkyne that is reacted with a peroxide (or light) and H-Br is a 1-bromoalkene.

Regioselectivity: The Bromine can attach in a ***syn*** or ***anti*** manner which means the resulting alkene can be both ***cis*** and ***trans***. ***Syn*** addition is when both Hydrogens attach to the same face or side of the double bond (i.e. ***cis***) while the ***anti*** addition is when they attach on opposite sides of the bond (***trans***).



Cis-1-bromo-1-butene *Trans*-1-bromo-1-butene

Contributors

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