

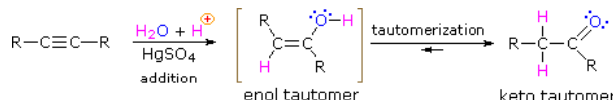
10.4: HYDRATION OF ALKYNES FOR MARKOVNIKOV PRODUCTS

Learning Objective

- predict the products and specify the reagents for the Markovnikov-products of alkyne hydration

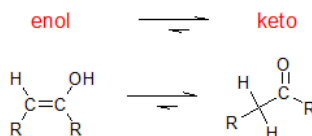
REACTION: HYDRATION OF ALKYNES (MARKOVNIKOV'S RULE)

Hydration of alkynes begins similar to the hydration of alkenes through the addition of the first water molecule. However, this first hydration reaction forms an enol, an alcohol bonded to a vinyl carbon. Enols immediately undergo a special type of isomerization reaction called tautomerization to form carbonyl groups - aldehydes or ketones. To keep things simple, this reaction is called "enol-keto" tautomerization with the understanding that aldehydes form on terminal alkyne carbons. As with alkenes, hydration (addition of water) to alkynes requires a strong acid, usually sulfuric acid with a mercuric sulfate catalyst as shown below.



ENOL-KETO TAUTOMERS

Tautomers are defined as rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom (colored red here) and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples. The three examples shown below illustrate these reactions for different substitutions of the triple-bond. The tautomerization step is indicated by a red arrow. For terminal alkynes the addition of water follows the Markovnikov rule, as in the second example below, and the final product is a methyl ketone (except for acetylene, shown in the first example). For internal alkynes (the triple-bond is within a longer chain) the addition of water is not regioselective. If the triple-bond is not symmetrically located (i.e. if R & R' in the third equation are not the same) two isomeric ketones will be formed.



With the addition of water, alkynes can be hydrated to form enols that spontaneously tautomerize to ketones. The reaction is catalyzed by mercury ions and follows Markovnikov's Rule. A useful functional group conversion for multiple -step syntheses is to hydrate terminal alkynes to produce methyl ketones.

HYDRATION OF ALKYNE MECHANISM

The first step is an acid/base reaction where the π electrons of the triple bond acts as a Lewis base and reacts with the proton therefore protonating the carbon with the most hydrogen substituents as expected by Markovnikov's Rule. In the second step, the nucleophilic water molecule reacts with the electrophilic carbocation to produce an oxonium ion. The oxonium ion is deprotonated by a base to produce an enol which immediately tautomerizes into a ketone. The hydration reaction for propyne is shown below with its mechanism to illustrate the electron flow of the mechanism.

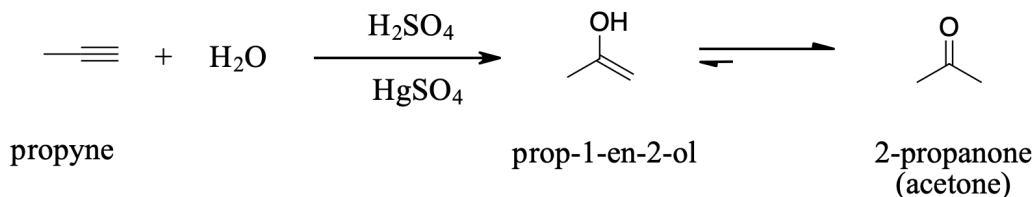
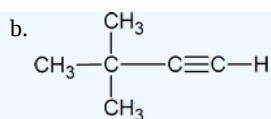


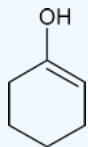
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Exercise

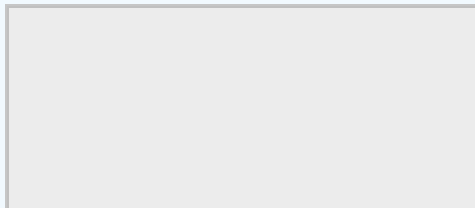
- Draw the structure of the product formed when each of the substances below is treated with $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ in the presence of HgSO_4 .
 - CH_3CHCCH



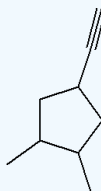
2. Draw the structure of the keto form of the compound shown below. Which form would you expect to be the most stable?



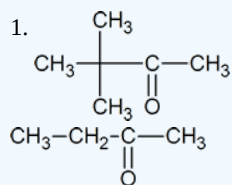
3. What alkyne would you start with to gain the following products, in an oxidation reaction? Keep in mind resonance.



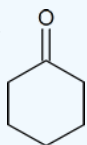
4. Propose a reaction scheme for the following compound starting from the alkyne and showing required reagents and intermediates.



Answer

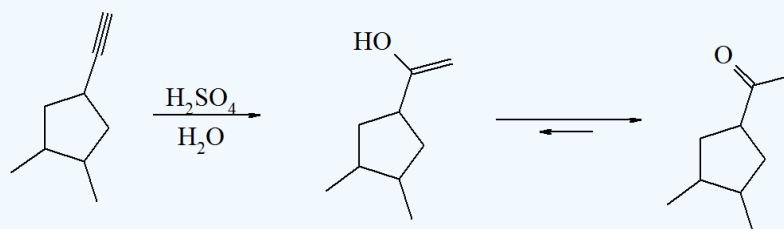


2. ; The keto form should be the most stable.



3.

4.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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