



Chapter 4

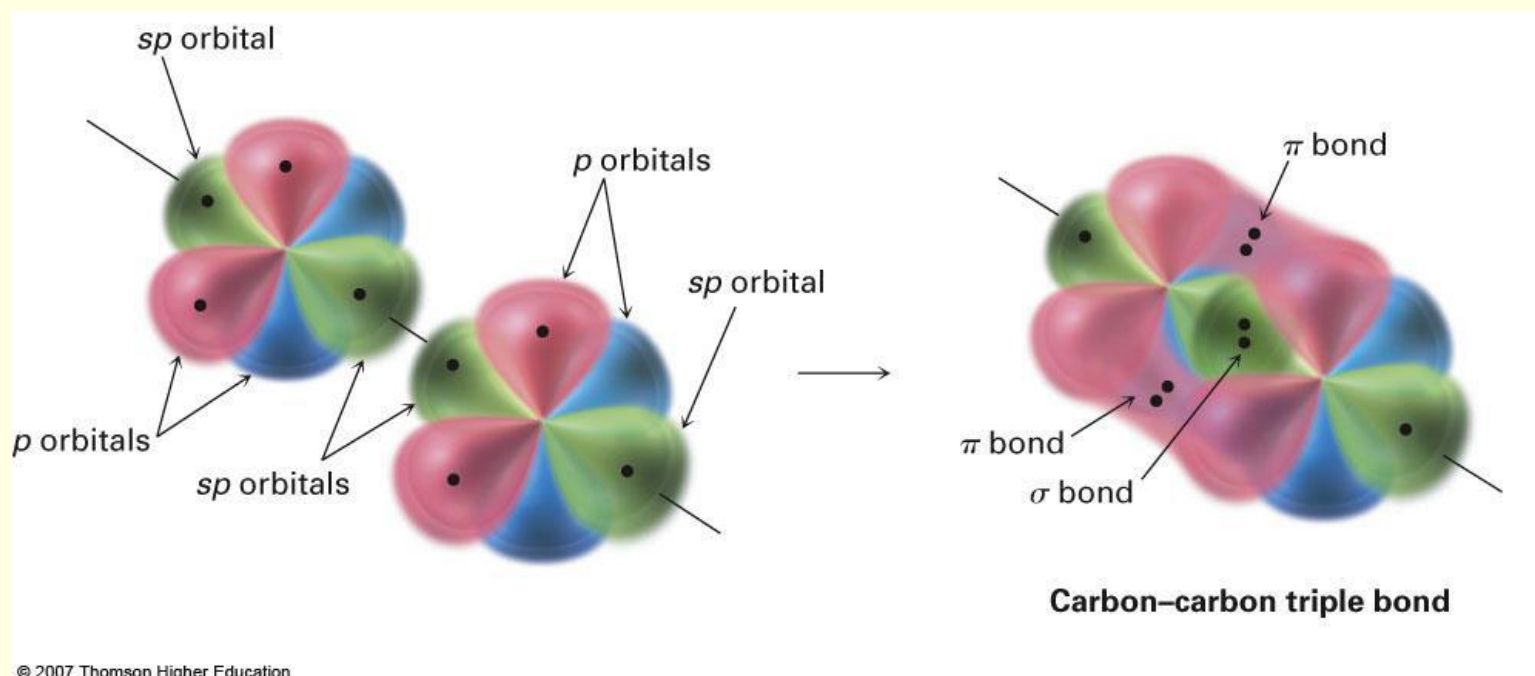
Reactions of Alkenes and Alkynes

스마트헬스케어학부 의공학전공

임해균 교수

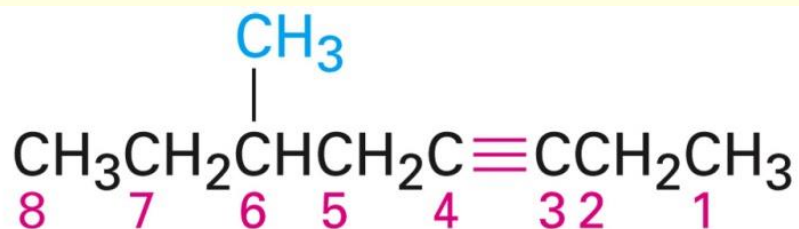
4.11 Alkynes and Their Reactions

- Carbon-carbon triple bond results from **sp orbital** on each C forming a sigma bond and **unhybridized p_x and p_y orbitals** forming π bonds.
- The remaining sp orbitals form bonds to other atoms at 180° to C-C triple bond.



4.11 Alkynes and Their Reactions

- General hydrocarbon rules apply with “-yne” as a suffix indicating an alkyne.
- Numbering of chain with triple bond is set so that the **smallest number possible for the first carbon of the triple bond**.



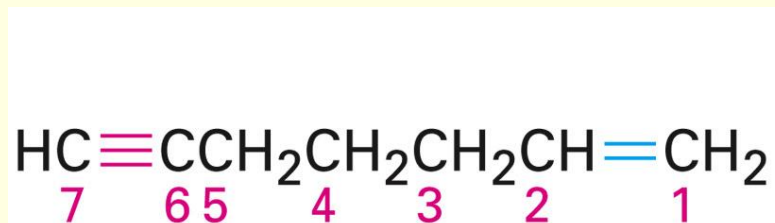
Begin numbering at the end nearer the triple bond.

6-Methyloct-3-yne

(Old name: **6-Methyl-3-octyne**)

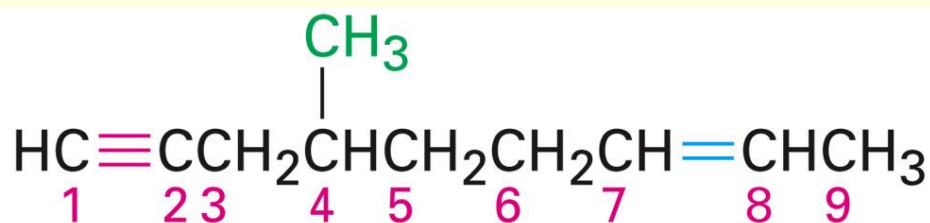
Double & Triple bonds: enyne

- Compounds containing both double and triple bonds are called *enyne*s (not ynenes).
- Numbering of the hydrocarbon chain starts from the end nearer the first multiple bond, whether double or triple.
- If there is a choice in numbering, **double bonds receive lower numbers than triple bonds**.
- For example,



Hept-1-en-6-yne

(Old name: 1-Hepten-6-yne)

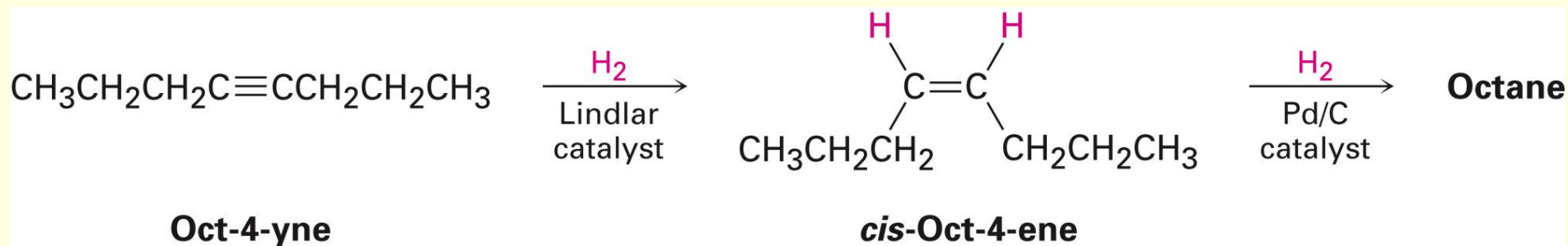


4-Methylnon-7-en-1-yne

(Old name: 4-Methyl-7-nonen-1-yne)

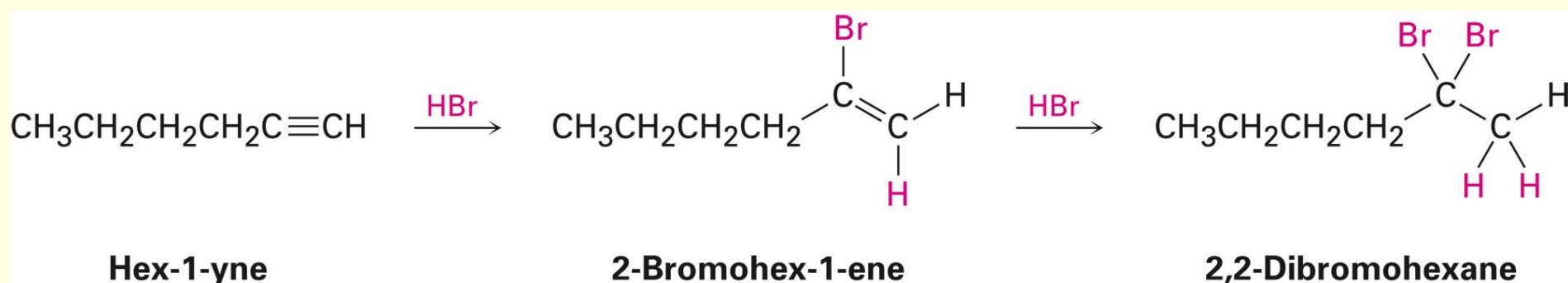
Alkyne Reactions : Addition of H₂

- Addition of H₂ over a metal catalyst (such as palladium on carbon, Pd/C) converts alkynes to alkanes (complete reduction)
- Addition of H₂ using chemically deactivated palladium on calcium carbonate as a catalyst (the *Lindlar catalyst*) produces a *cis* alkene
- The two hydrogens add *syn* (from the same side of the triple bond)



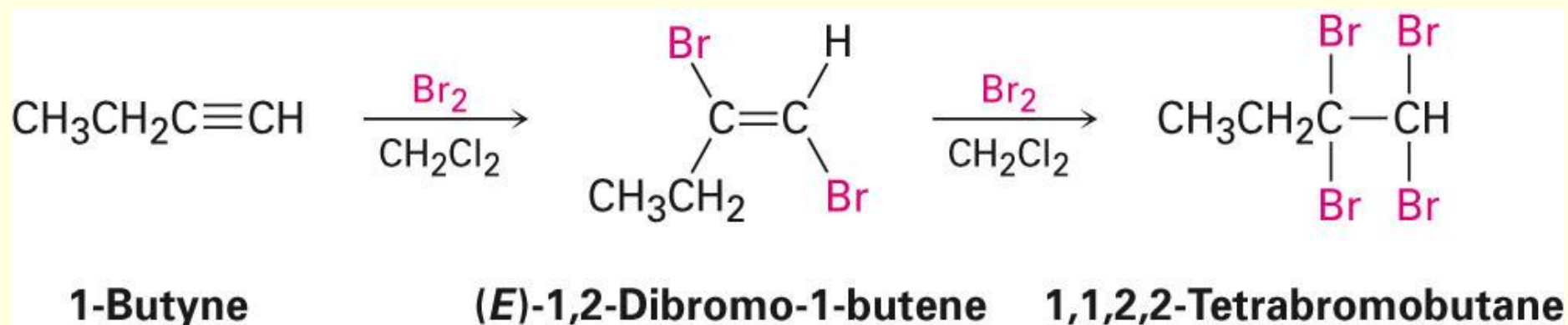
Alkyne Reactions : Addition of HX

- Addition reactions of alkynes are similar to those of alkenes
- Intermediate alkene reacts further with excess reagent
- **Regiospecificity according to Markovnikov**



Alkyne Reactions : Addition of X_2

- Initial addition gives **trans** intermediate
- Product with excess reagent is **tetrahalide**



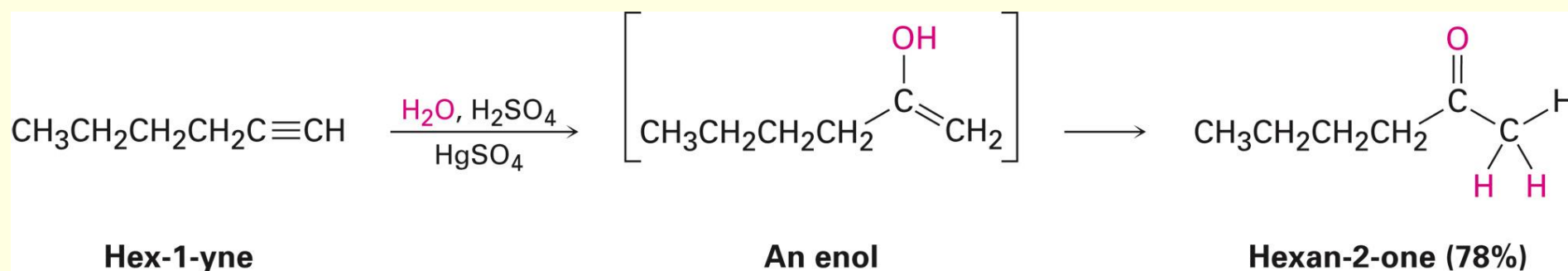
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Alkyne Reactions : Addition of H₂O

- Addition of H-OH as in alkenes

- Mercury (II) catalyzes Markovnikov oriented addition

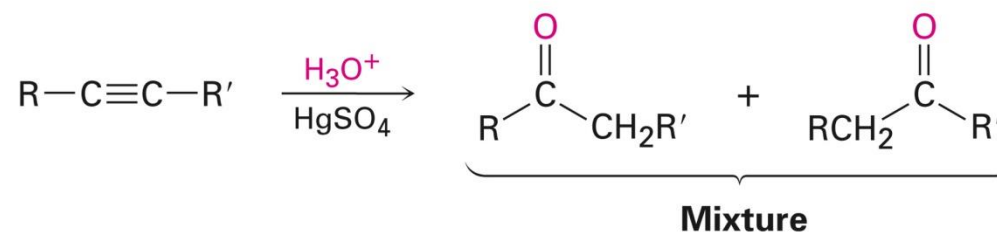
- Addition of water takes place when an alkyne is treated with aqueous sulfuric acid in the presence of mercuric sulfate catalyst.
- Markovnikov regioselectivity is found for the hydration reaction, with the H attaching to the less substituted carbon and the OH attaching to the more substituted carbon.
- Interestingly, though, the product is **not** the expected vinylic alcohol, or *enol* (*ene* alkene; *ol* alcohol). Instead, the enol rearranges to a more stable **ketone isomer** ($R_2C=O$).



Alkyne Reactions : Addition of H₂O

- Addition of H-OH as in alkenes
 - Mercury (II) catalyzes Markovnikov oriented addition
- A mixture of both possible ketones results when an **internal alkyne** is hydrated, but only a single product is formed from reaction of a **terminal alkyne**.

An internal alkyne

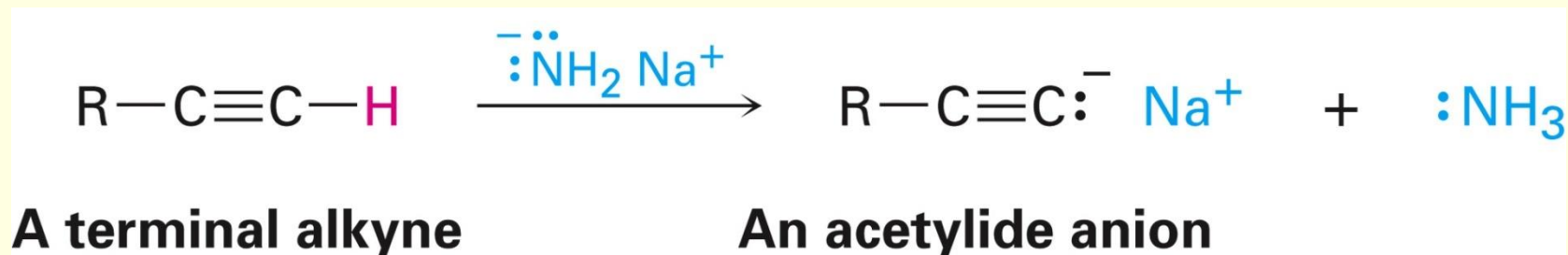


A terminal alkyne



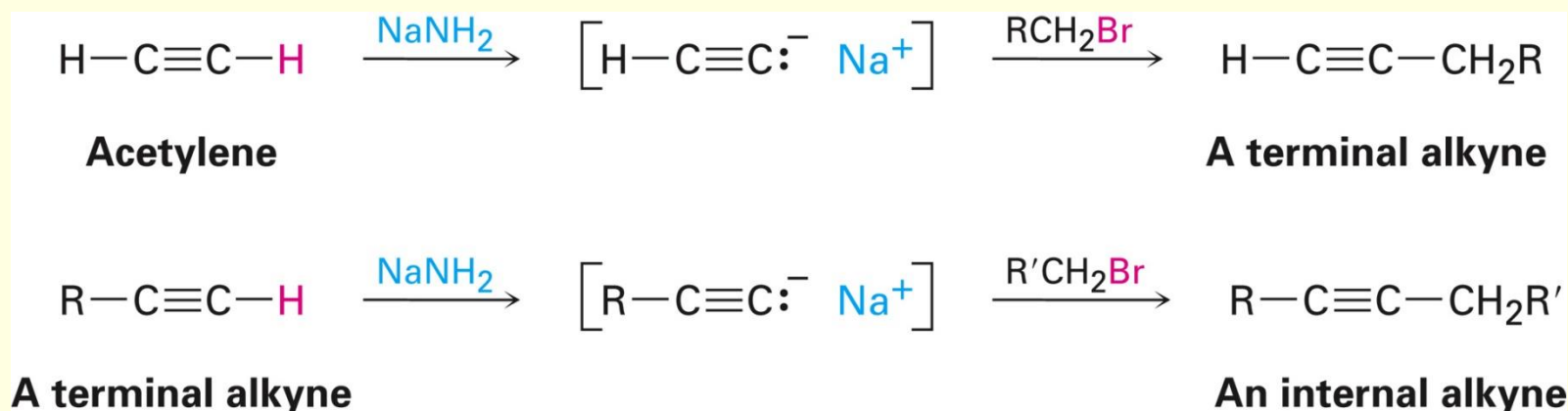
Alkyne Reactions: Formation of Acetylide Anions

- Terminal alkynes are weak Brønsted acids ($pK_a \sim 25$)
- Alkenes ($pK_a \sim 44$) and alkanes are much less acidic
- When a terminal alkyne is treated with a strong base such as sodium amide, NaNH_2 , the terminal hydrogen is removed and an **acetylide anion** is formed.



Alkyne Reactions: Formation of Acetylide Anions

- The presence of an unshared electron pair on the negatively charged alkyne carbon makes **acetylide anions both basic and nucleophilic**.
 - As a result, acetylide anions react with **alkyl halides** such as bromomethane to substitute for the **halogen** and yield a new alkyne product.
 - **Terminal alkynes** can be prepared by reaction of acetylene itself
 - **Internal alkynes** can be prepared by further reaction of a terminal alkyne.
- Reaction with a primary **alkyl halide** produces a **hydrocarbon** that contains carbons from both partners.



Worked Example 4.6

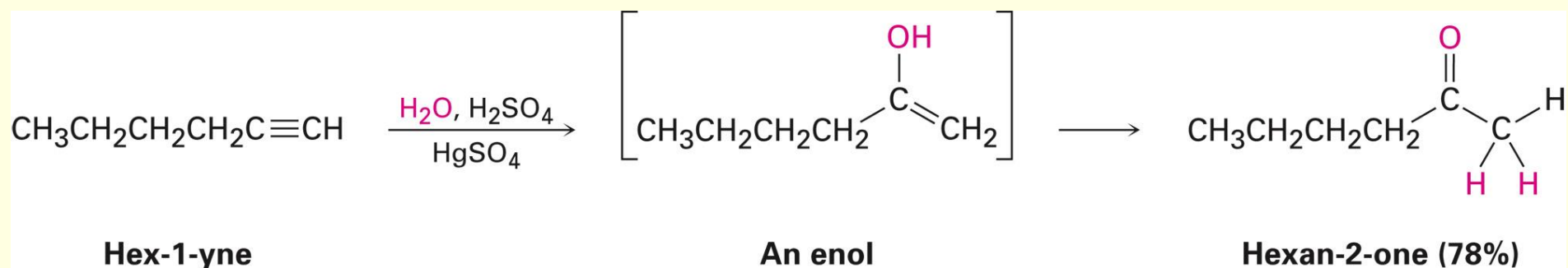
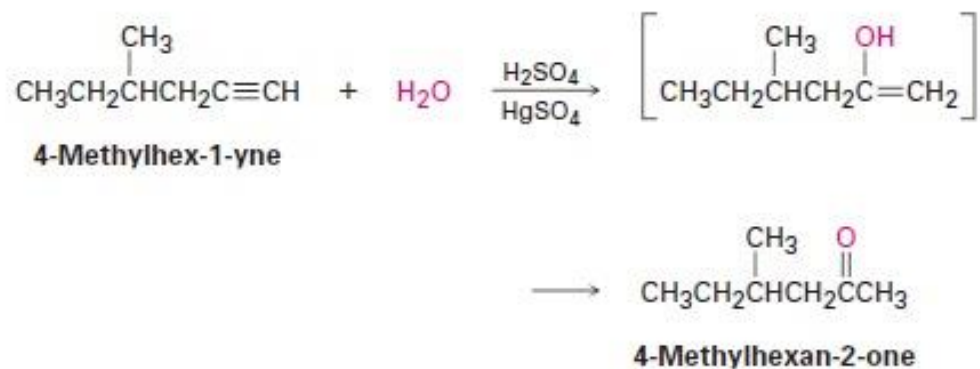
Predicting the Product of an Alkyne Hydration Reaction

What product would you obtain by hydration of 4-methylhex-1-yne?

Strategy

Ask yourself what you know about alkyne addition reactions. Addition of water to 4-methylhex-1-yne according to Markovnikov's rule will yield a product with the OH group attached to C2 rather than C1. This initially formed enol will then isomerize to yield a ketone.

Solution



Worked Example 4.7

Synthesizing an Alkyne

What alkyne and what alkyl halide would you use to prepare pent-1-yne?

Strategy

As always when synthesizing a compound, work the problem backward. Draw the structure of the target molecule, and identify the alkyl group(s) attached to the triple-bonded carbons. In the present case, one of the alkyne carbons has a propyl group attached to it and the other has a hydrogen attached. Thus, pent-1-yne could be prepared by treatment of acetylene with NaNH_2 to yield sodium acetylide, followed by reaction with 1-bromopropane.

Solution

