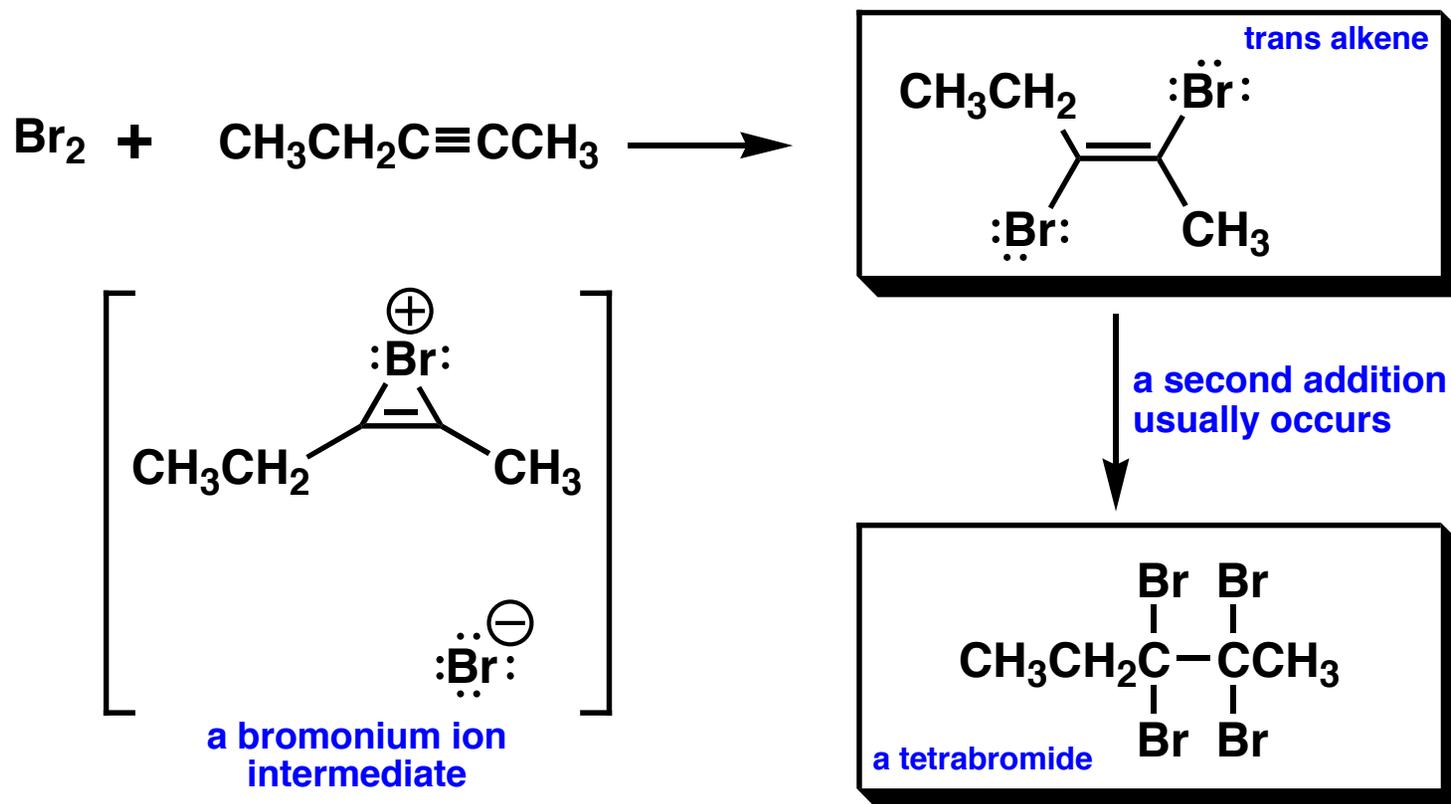


Addition of Br₂ to Alkynes

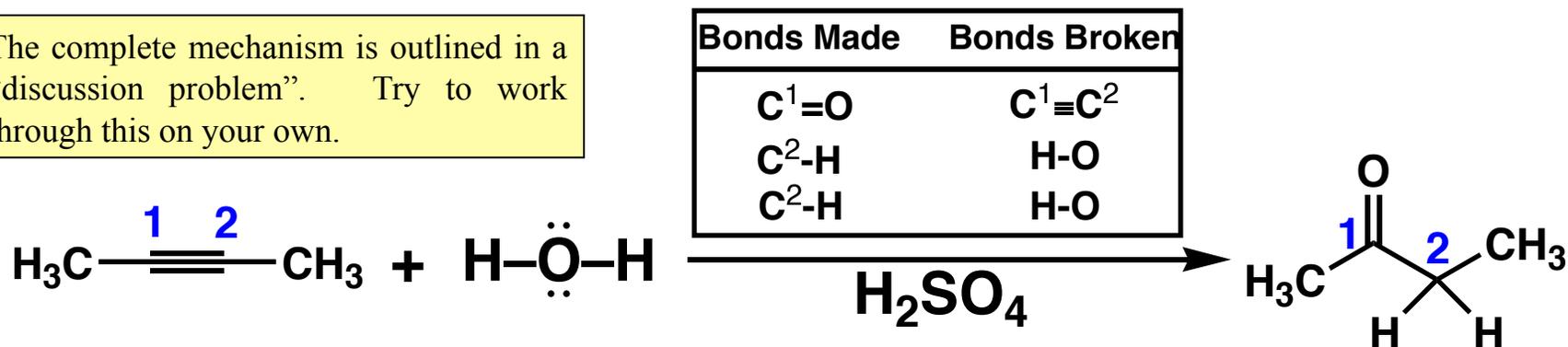


Halogens add to alkynes in a way that is similar to alkenes. An analogous bromonium ion is formed in this case as well, and the subsequent attack of bromide anion results in trans addition. However, this initially formed product usually undergoes a second addition to give a tetrabromoalkane.

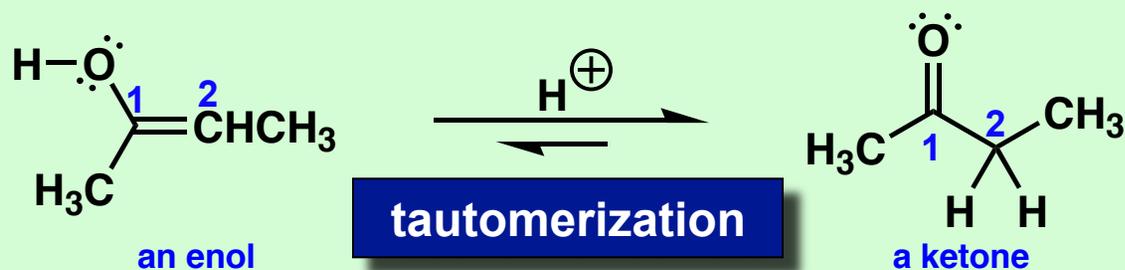


The Addition of Water to Alkynes

The complete mechanism is outlined in a “discussion problem”. Try to work through this on your own.



The addition of water to an alkyne initially results in an **enol**. The enol, whose name is derived from alkene + alcohol, is generally not the form that is most stable. Enols tend to undergo a process known as **tautomerization**, an equilibrium reaction which shifts the position of a double bond together with a C-H, N-H or O-H bond (in this case, an O-H). A bond energy calculation will show why the equilibrium favors the keto form. What we are after right now is not the knowledge that this reaction is a tautomerization, but to understand the mechanism of how tautomerization occurs.



The acid-catalyzed tautomerization mechanism is included with the “discussion problem”. You can fully understand this mechanism using elementary steps that you previously learned.

Acid-Catalyzed Tautomerization Mechanism

To begin, it should not be surprising that the enol is a nucleophilic π -bond capable of undergoing $[A_E]$. This π -bond nucleophile finds an electrophilic partner in H^+ (from H_2SO_4). The new C-H bond must be made at carbon atom C^2 , consistent with the need for a new C^2 -H bond. The resulting carbocation is stabilized by resonance with the lone pair of oxygen (Box 4). This resonance contributor has an octet of electrons on every atom. Moreover, this resonance contributor has the necessary C=O bonding of the final product. All that remains to realize the final product is dissociation of a proton, breaking the final O-H bond in our bonds made / bonds broken list. Notice how H_2SO_4 is regenerated each time it is used, consistent with its use as a **catalyst**.