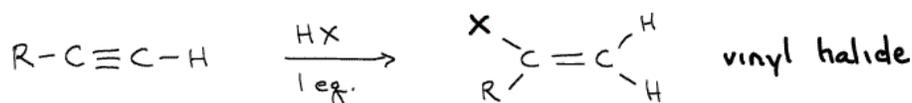


Activity 33. Hydrohalogenation & Hydration of Alkynes

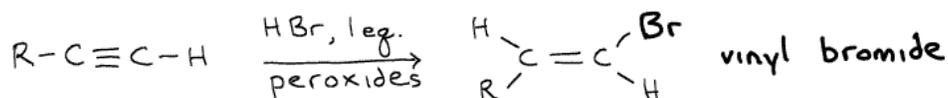
Alkynes undergo many of the same addition reactions that alkenes do, including additions that require carbocation intermediates. Different energy and geometry changes may be required for additions to an alkyne and an alkene so some surprising outcomes may occur with alkynes.

Model 1. Addition of HX

Hydrogen halides (HCl, HBr, HI) add to alkynes to make **vinyl halides**. A carbocation mechanism is followed when the reaction is performed in the dark in a peroxide-free solvent. This addition obeys Markovnikov's rule.

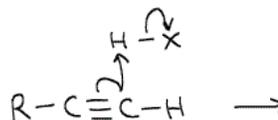
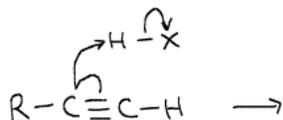


A free-radical-chain mechanism is followed when HBr addition is initiated by organic peroxides. This addition gives an anti-Markovnikov product.

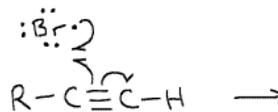
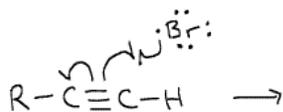


Critical Thinking Questions

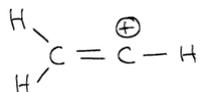
1. Draw the carbocations indicated by the two bouncy curved arrows (below). Based on the observation that the carbocation mechanism yields a Markovnikov product, circle the more stable carbocation.



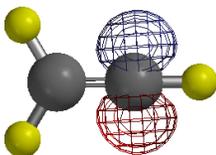
2. (CI) Draw the free radicals indicated by the two competing pathways (below). Based on the observation that the free-radical mechanism yields an anti-Markovnikov product, circle the more stable free radical.



3. The cations and radicals in CTQ #1 and #2 are called **vinyl cations** and **vinyl radicals**, respectively. Based on the regioselectivities reported in Model 1, what effect do alkyl substituents at the charged/radical carbon have on the energies of these species? Is this consistent with, or opposed to, their effect on R_3C^+ and $R_3C\cdot$ species?
4. The geometry of a vinyl cation can be anticipated using VSEPR. Count electron domains in the cation below and predict all of the HCC bond angles.



5. Molecular model calculations yield the following geometry for the cation in CTQ #4. The unoccupied *valence* orbital on C+ is also shown. What kind of AO is this? Use your geometry and orbital data to assign hybrid orbital models to each C.



C unoccupied *valence* AO (mesh surface) _____

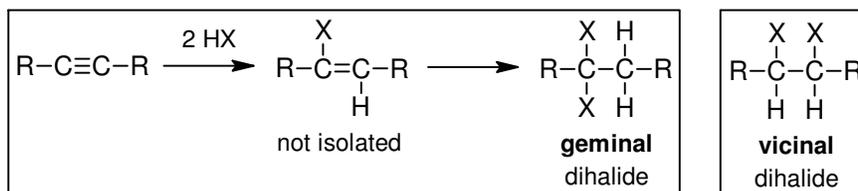
Hybrid orbital model for >C= _____

Hybrid orbital model for C+ _____

6. **(CI)** Describe the atomic/hybrid orbitals that C+ and its neighboring atoms use to create BMO and ABMO (3 bonds \rightarrow 6 MO). Label these BMO/ABMO pairs as σ or π .
7. The model cation shown in CTQ #5 could be produced as a reaction intermediate during the reaction of HBr with acetylene, HC \equiv CH. Circle a hydrogen in the model that could have been delivered by HBr. Draw the product that would be isolated in this experiment.
8. **(CI)** Draw the mechanism and product for the carbocation-mediated addition of 1 eq. HBr to PhC \equiv CH.

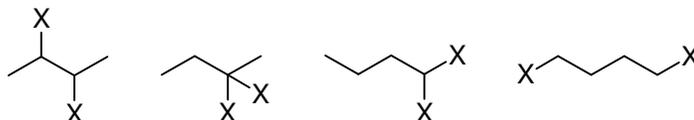
Model 2. Double Addition of HX

If excess halide is used, addition *via* the carbocation mechanism can occur twice. First, a vinyl halide is produced, but this undergoes a second addition yielding a **geminal dihalide**. The second addition is unusual in several respects.



Critical Thinking Questions

9. Circle all geminal dihalides below. Draw a box around all vicinal dihalides.



10. Model 1 reports that 1 eq. HX produces a vinyl halide. This implies something about the relative speeds of reactions #1 and #2 in Model 2. Assuming addition #2 is much faster than #1, what outcome would be expected from 1 eq. HX? (Circle one outcome)



- a. 100% vinyl halide
 b. 50% geminal dihalide + 50% alkyne
 c. 100% alkyne (no reaction)

11. **(CI)** Assuming instead that addition #1 is much faster than #2, which outcome in CTQ #10 would be expected? (Underline one outcome)
12. Recalling the observation given in Model 1, i.e., the reaction in CTQ #10 produces 100% vinyl halide, what can you say about the relative speeds of additions #1 and #2? Which unsaturated compound appears to react more rapidly with HX, alkynes or vinyl halides?

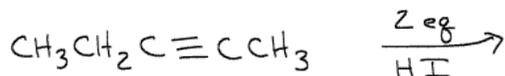
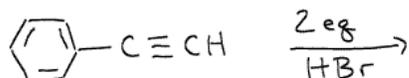
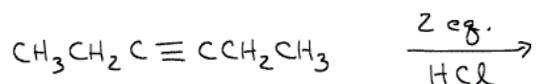
13. Model 2 shows that HX addition to vinyl halides is relatively slow, but regioselective. Draw the carbocation produced by each mode of protonation below. Circle the cation that forms more rapidly.



14. **(CI)** Because Cl carries lone pairs, a second resonance structure can be drawn for the circled carbocation in CTQ #13. Draw this structure.

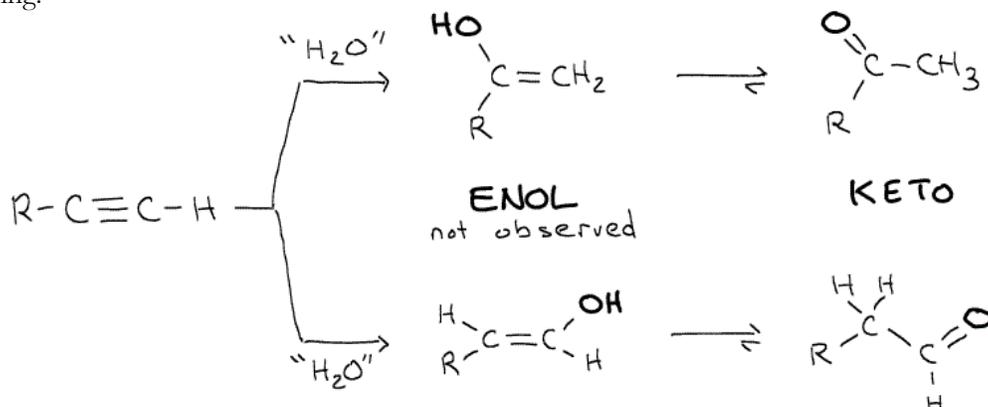
15. What observation(s) provide experimental support for each of the following statements?
- a. A halogen substituent raises the energy for protonating an alkene.
- b. A halogen substituent stabilizes an adjacent carbocation by electron-sharing.

16. (CD) Addition of 2 eq. HX to *symmetric internal* and to *terminal* alkynes gives a single product, while addition to *unsymmetrical internal* alkynes gives two products. Draw the expected products of the following reactions.



Model 3. Hydration of Alkynes and Enol-Keto Equilibrium

Addition of water to an alkyne yields an **enol**, a compound that is structurally analogous to a vinyl halide. Enols are never observed as reaction products, however, because they quickly rearrange to their more stable **keto** isomers. This rearrangement prevents a second hydration reaction from occurring.

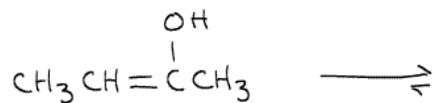


Historical note: The enol-keto pairs shown above are called **tautomers**. This label is applied to any pair of isomers that differ in the location of an "acidic" proton *and* one or more double bonds. Tautomers also appear throughout biochemistry. For example, different tautomers can be drawn for the four nucleotide bases (A, T, G, C) found in DNA. One reason why Watson and Crick were able to figure out DNA's structure ahead of Linus Pauling were the different assumptions they made regarding the most stable set of nucleotide tautomers. Unlike the tautomers chosen by Pauling, the structures chosen by Watson and Crick led naturally to A-T and G-C hydrogen bonding.

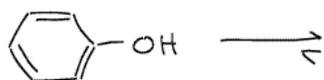
Critical Thinking Questions

17. Which hydrogen in an enol changes its position to make the corresponding keto isomer?

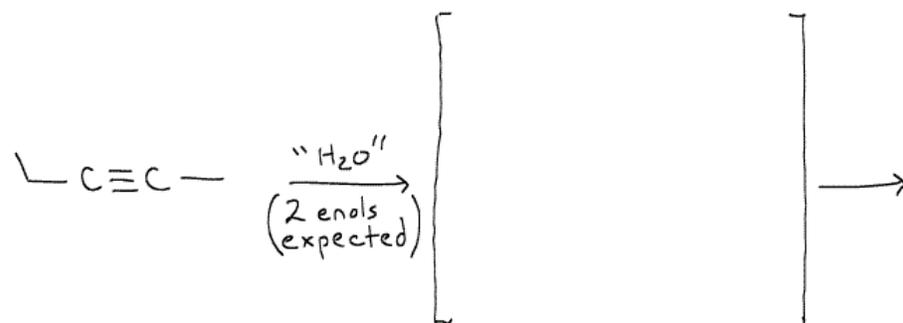
18. Draw the keto isomers of these enols. Note: the third compound is not a true enol, but the same logic applies.



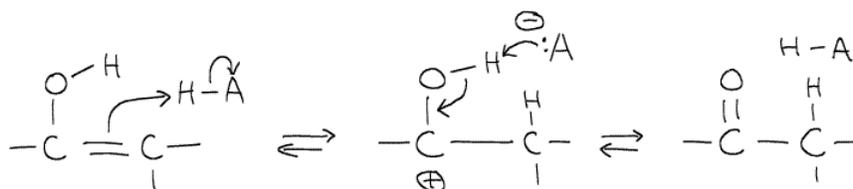
19. In special molecules, an enol may be favored over its keto tautomer. Two examples are shown below. Draw the missing keto tautomers and explain why each enol is favored.



20. Draw the unobserved enols and the ketos expected from the following hydration reactions.



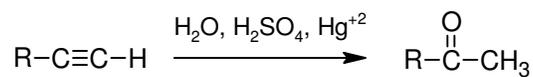
21. Enol-keto exchange is catalyzed by trace quantities of acid or base. It cannot be stopped for enols in solution. The acid-catalyzed mechanism consists of two proton transfers (below). Explain the regioselectivity of the initial protonation step. (Hint: see CTQ # 14.)



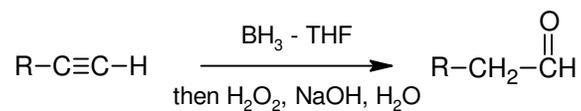
Model 4. Hydrating Agents

Water and a strong acid, e.g., H_2SO_4 , will hydrate some alkynes, but a more reliable procedure is to combine these reagents with a powerful Lewis acid, a salt containing Hg^{+2} . The mechanism resembles that of the alkene oxymercuration-reduction, but a reducing agent is not required.

The following reaction illustrates how chemists draw this reaction. Notice that the enol intermediate, the initial product of Markovnikov addition of water across the triple bond, is not drawn.



Hydroboration-oxidation hydrates alkynes in anti-Markovnikov fashion. Loudon points out that this reaction doesn't always work cleanly with terminal alkynes and introduces another hydroboration reagent, **disiamylborane**, that is more reliable. This advice is well-intentioned advice, but you can ignore it and draw $\text{BH}_3\text{-THF}$ as your reagent for hydroborating all alkynes.



Critical Thinking Questions

22. Draw the enol precursor of each keto product shown in Model 4 and confirm the regioselectivity of each addition.

23. **(CI)** Draw the alkyne and reagent(s) needed to make each compound.

