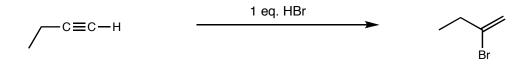
Nomenclature of Alkynes

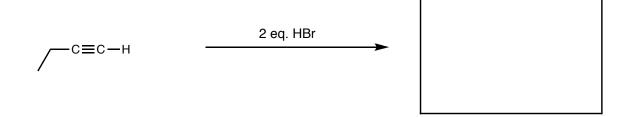
Draw skeletal structures for: acetylene
dimethylacetylene
1-butyne
2-butyne
propargyl chloride

Addition of HX to Alkynes

• Draw a complete curved-arrow mechanism for the following reaction:



• Predict the product and draw a complete curved-arrow mechanism for the following reaction:



Addition of Halogens (X₂) to Alkynes

• Draw a complete curved-arrow mechanism for the following reaction:

• Predict the product and draw a complete curved-arrow mechanism for the following reaction. Be sure to show the **stereochemistry** of the product!

Addition of Water to Alkynes: Enol Formation

• The following reaction produces an **unstable** intermediate known as an **enol** (alkene + alcohol = enol). Draw a complete curved-arrow mechanism for this reaction up to the formation of the enol.

$$G \equiv C - H$$

$$Hg^{2+}, H^+, H_2O$$

$$OH$$

$$enol$$
(unstable)

Addition of Water to Alkynes: Enol Hydrolysis

• The enol is **not** the final product of the reaction of an alkyne with water. The enol reacts rapidly with the aqueous acid to form a carbonyl compound: in this case, a **ketone**. Provide a complete curved-arrow mechanism for the following reaction:

• Show the complete synthetic transformation from an **alkyne** to a **ketone**:

Hydroboration/Oxidation of Alkynes: Enol Formation

• The following reaction produces an **unstable** intermediate known as an **enol** (alk**ene** + alcoh**ol** = **enol**). Draw a complete curved-arrow mechanism for this reaction up to the formation of the enol. You should also explain why the alkene geometry is *trans* (that is, you should explain the **stereochemistry**!)

$$C \equiv C - H$$

1. R_2BH

2. H_2O_2 , OH^-

OH

enol
(unstable)

Hydroboration/Oxidation of Alkynes: Enol Hydrolysis

• The enol is **not** the final product of hydroboration/oxidation of an alkyne. The enol reacts rapidly with the aqueous base (in the oxidation step) to form a carbonyl compound: in this case, an **aldehyde**. Provide a complete curved-arrow mechanism for the following reaction:

• Show the complete synthetic transformation from an **alkyne** to an **aldehyde**:

Hydrogenation of Alkynes: Catalytic Hydrogenation

• Ordinarily, the reaction of an alkyne with H₂ / Pd adds *two* equivalents of hydrogen and yields an alkane. Show the intermediate and final product in the following transformation. Be sure to consider the **stereochemistry**!

an alkene

an alkane

• However, we can use a **poisoned catalyst** (for example, a Lindlar catalyst) to halt the reaction at the alkene stage. This is one of the **best** ways of making a *cis*-alkene:

$$C \equiv C \longrightarrow \frac{H_2}{\text{Lindlar}}$$

a cis-alkene

Hydrogenation of Alkynes: Reduction with Na in NH₃

• We can convert an alkyne into a *trans*-alkene by using a unique reducing agent: sodium metal in liquid ammonia (!). Ammonia is a gas at room temperature; it boils at -33°C. When it is condensed into a liquid it is a tremendously interesting and useful solvent. It dissolves sodium metal to produce a deep blue solution that contains *solvated electrons*:

• Write a balanced equation showing how Na dissolves in NH $_3$ to produce solvated electrons e^-

• These solvated electrons react with the alkyne via an interesting free-radical mechanism that yields a *trans*-alkene as the final product. (You can remember the steps of this mechanism if you note that it involves only 2 kinds of reactions: adding an electron to form an anion, and protonating the anion using NH₃.)

Chemistry S-20ab Week 3

Summary: Reactions of Alkynes

• Show how each of the following products could be synthesized from an alkyne: