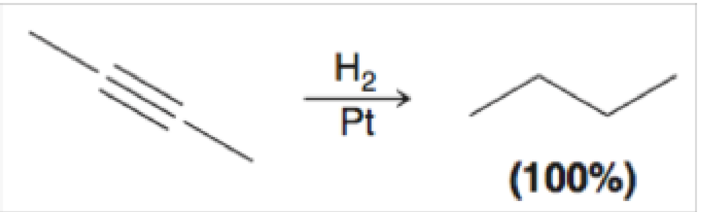
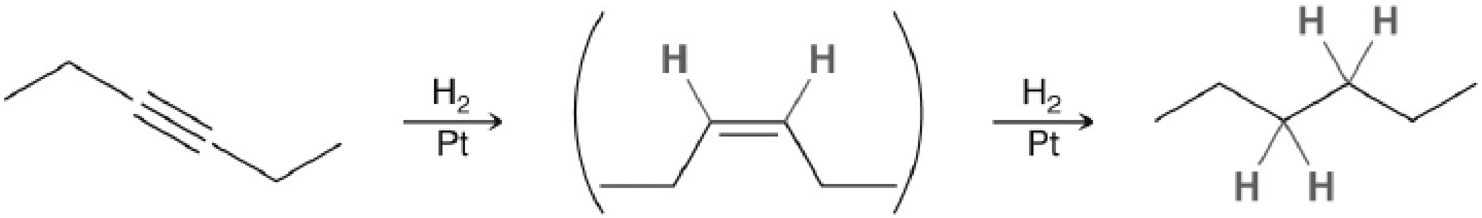
Reactions of alkynes

Reduction of Alkynes

- **Catalytic hydrogenation** – alkyne is concerted to an alkane by addition of two equivalents of H2

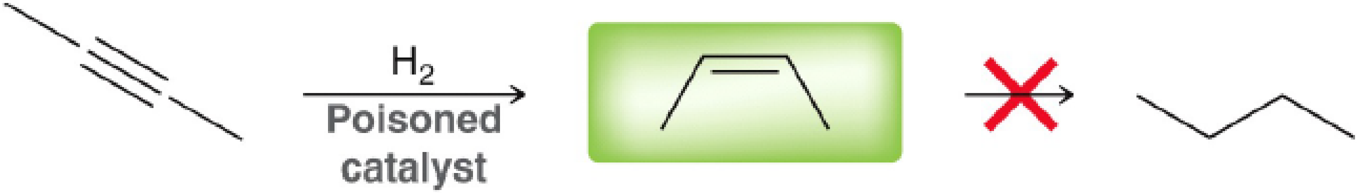


- The first addition produces a *cis* alkene (via ***syn* addition**) which then undergoes addition to yield the alkane



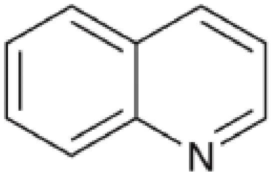
Reduction of Alkynes

- A deactivated or poisoned catalyst can be used to stop the reaction at the *cis* alkene, without further reduction:



- **Lindlar's catalyst** and **P-2 (Ni_2B complex)** are common examples of a poisoned catalysts

Lindlar's catalyst =

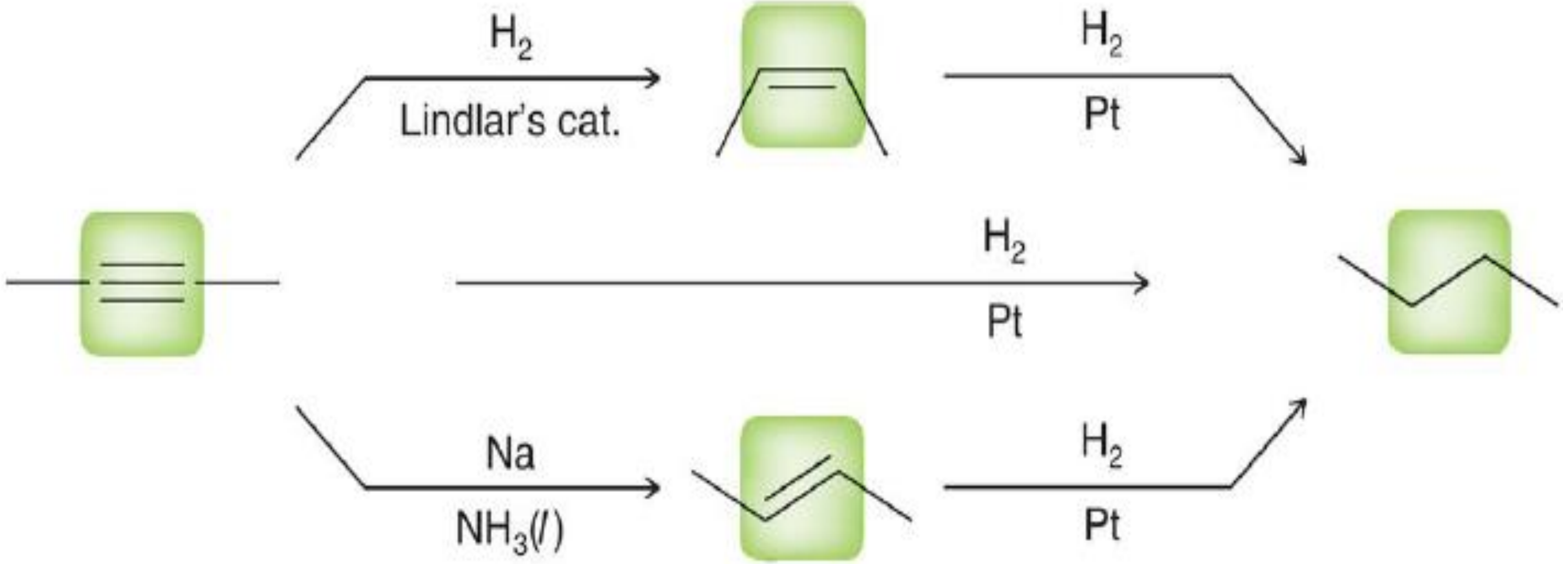


, Pd / $BaSO_4$, CH_3OH

Quinoline

Reduction of Alkynes - Summary

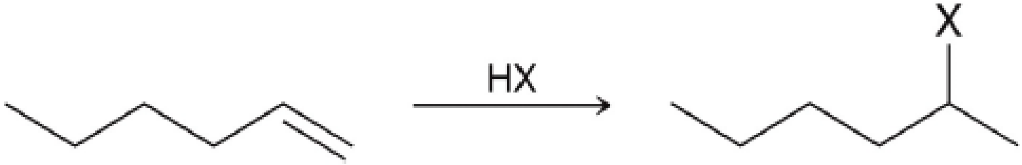
- Know the reagents needed to reduce an alkyne to an alkane, a *cis* alkene, or a *trans* alkene.



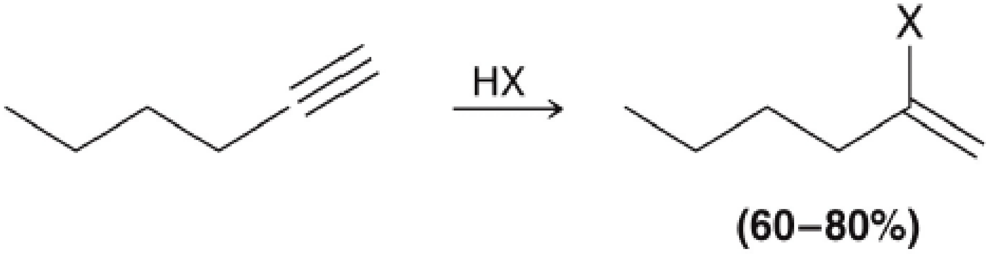
Hydrohalogenation of Alkynes

- **Hydrohalogenation** affords Markovnikov addition of **H and X** to an alkyne, same as with an alkene.

addition to an alkene



addition to an alkyne

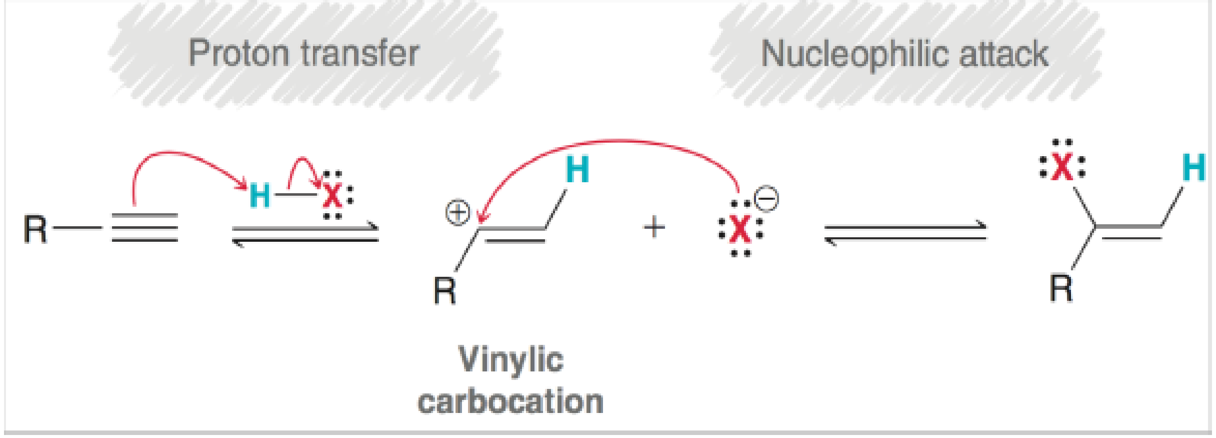


- Excess HX affords a geminal dihalide

geminal dihalide

Hydrohalogenation of Alkynes

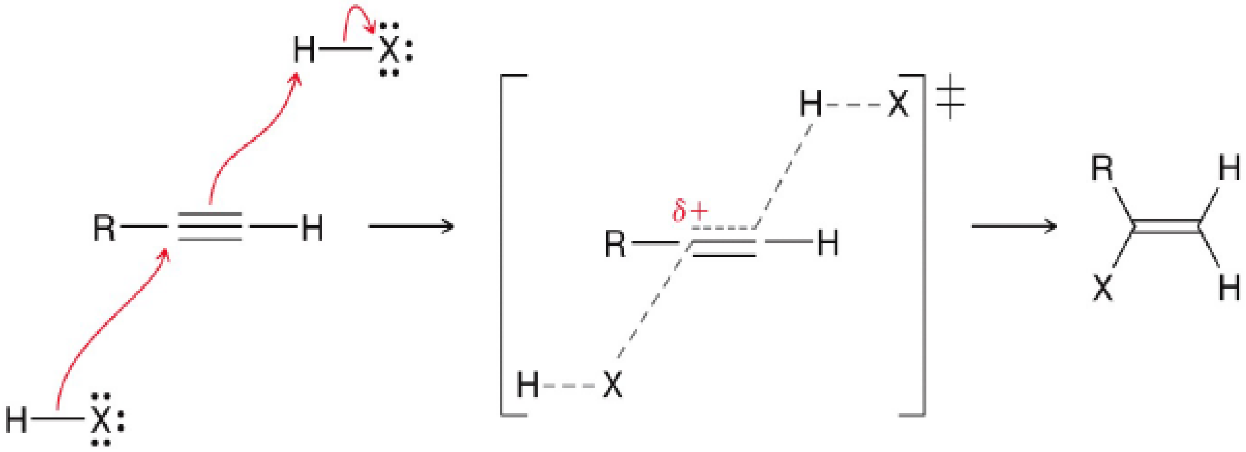
- If the mechanism was analogous to HX addition to an alkene, it would require the formation of a vinyl carbocation:



- Vinyl carbocations are extremely unstable, so this mechanism is unlikely
- Kinetic data also suggests a different mechanism is in play

Hydrohalogenation of Alkynes

- Proposed mechanism

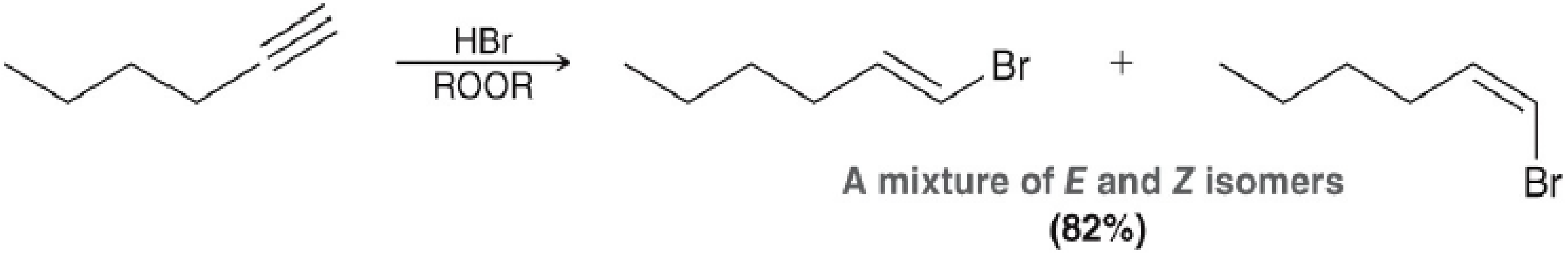


Transition state

- Its possible several competing mechanisms are occurring.

Hydrohalogenation of Alkynes

- HBr with peroxides promotes *anti*-Markovnikov addition, just like with alkenes

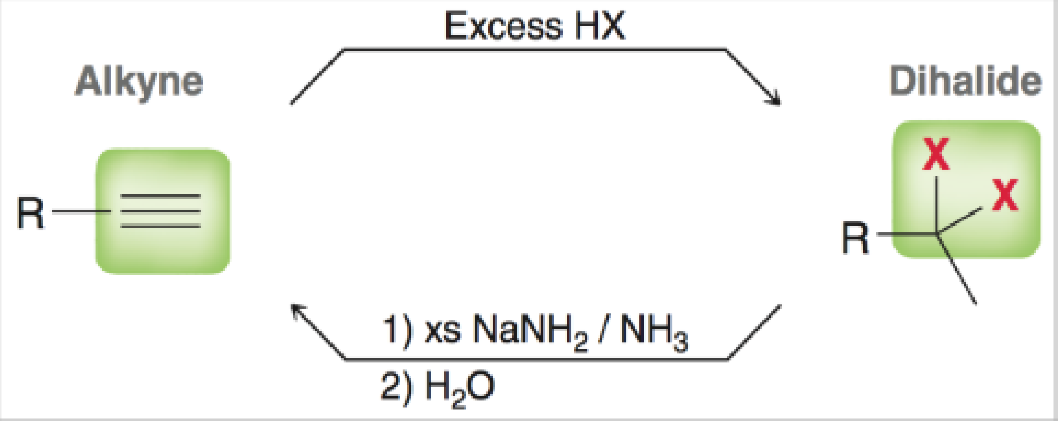


A mixture of *E* and *Z* isomers
(82%)

- This only works with HBr (not with HCl or HI)

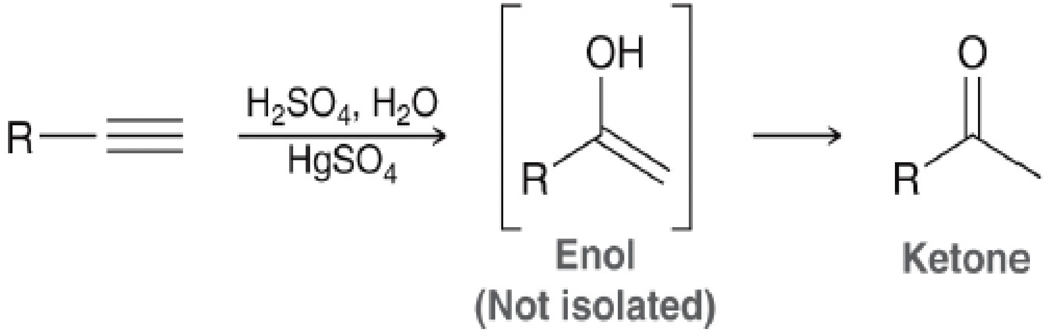
9.6 Dihalide/alkyne interconversion

- **Hydrohalogenation of alkynes**, and **elimination of dihalides** represent complimentary reactions:



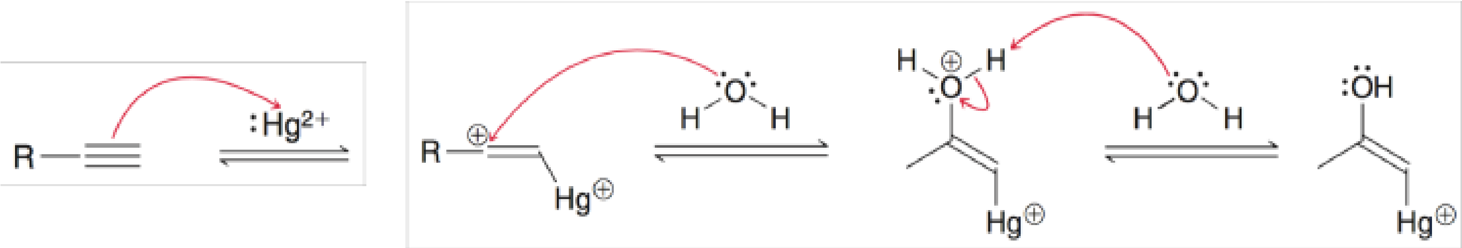
Hydration of Alkynes

- Alkynes can also undergo acid catalyzed Markovnikov hydration
- The process is generally catalyzed with $HgSO_4$ to compensate for the slow reaction rate that results from the formation of vinylic carbocation

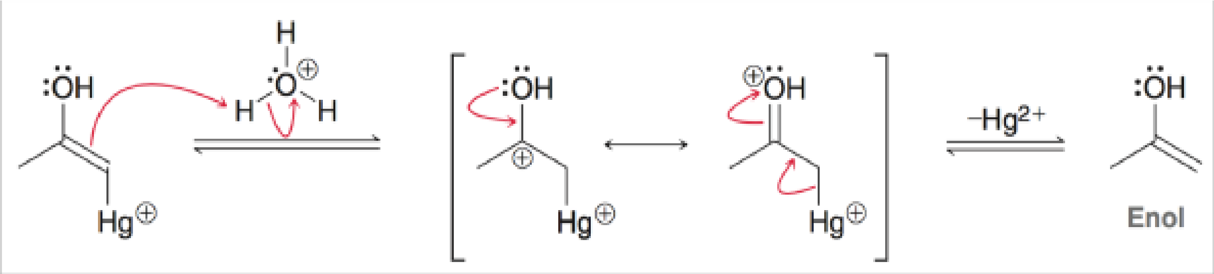


Hydration of Alkynes - mechanism

- The alkyne attacks the mercury cation to form the **mercurinium ion intermediate**, which is attacked by water, followed by deprotonation

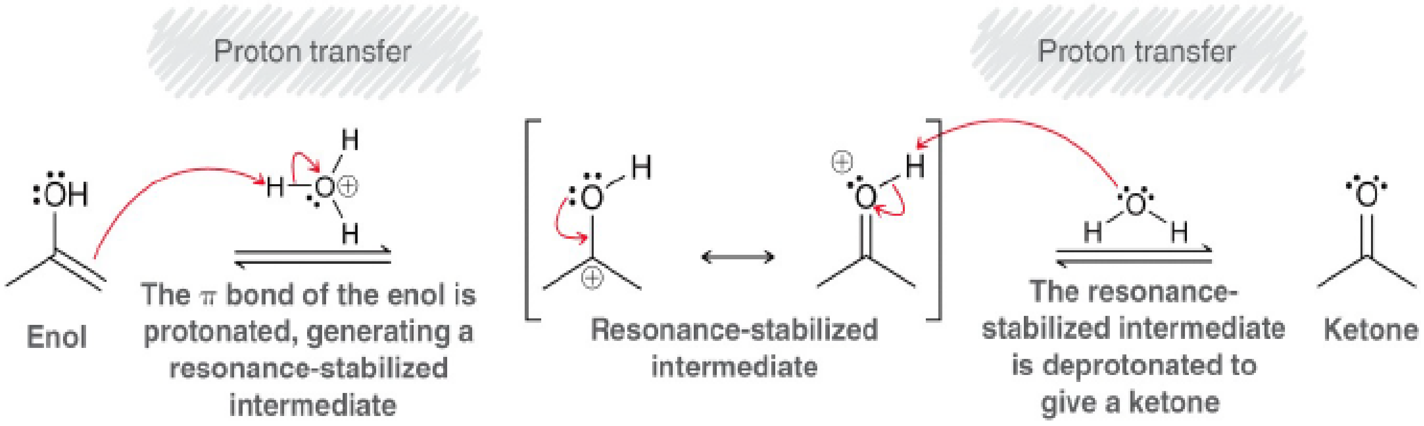


- A proton then replaces the Hg^{2+} to form an **enol intermediate**



Hydration of Alkynes

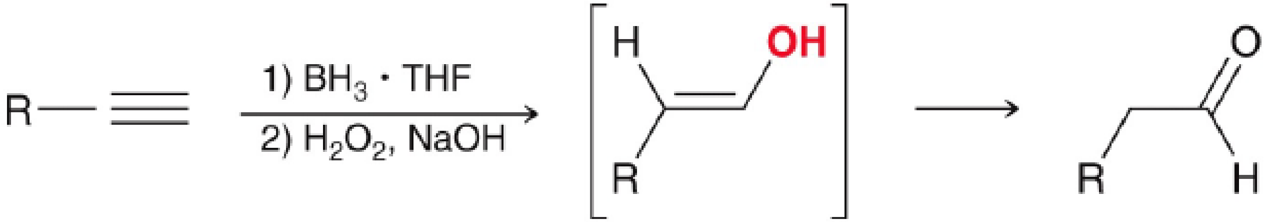
- The enol then **tautomerizes** to the ketone.
- Process is called **keto-enol tautomerization**



- The enol and the ketone are **tautomers** of one another
- Equilibrium generally favors the ketone

9.7 Hydroboration-Oxidation of Alkynes

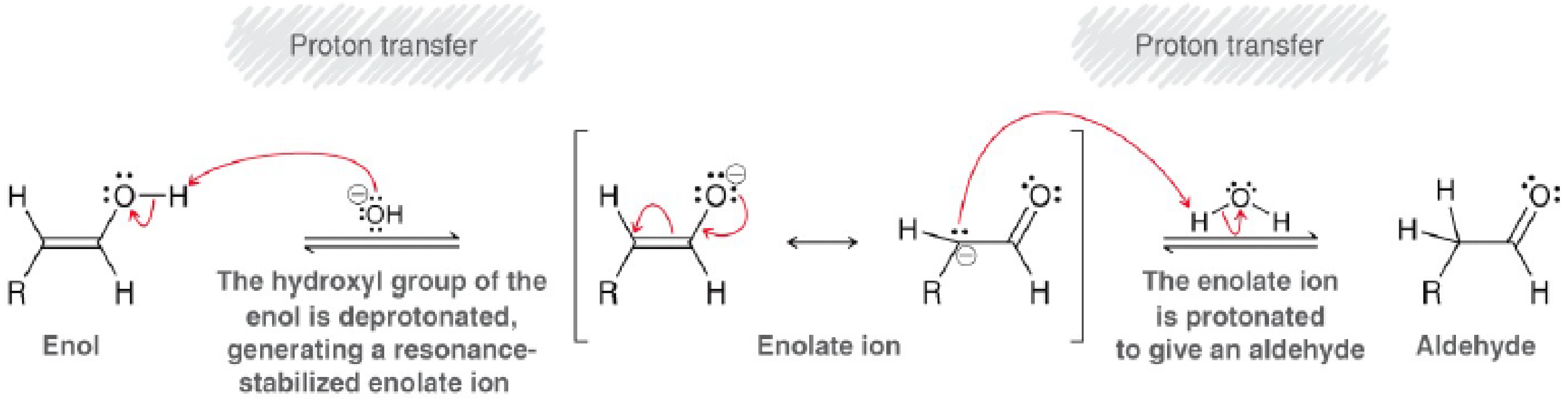
- **Hydroboration-oxidation** of alkynes is the same as for alkenes
- **Regioselective** for *anti*-Markovnikov addition
- It also produces an enol that tautomerizes to aldehyde



- In this case, tautomerization is base-catalyzed (OH^-)

Hydroboration-Oxidation of Alkynes

- **Base-catalyzed tautomerization mechanism:**



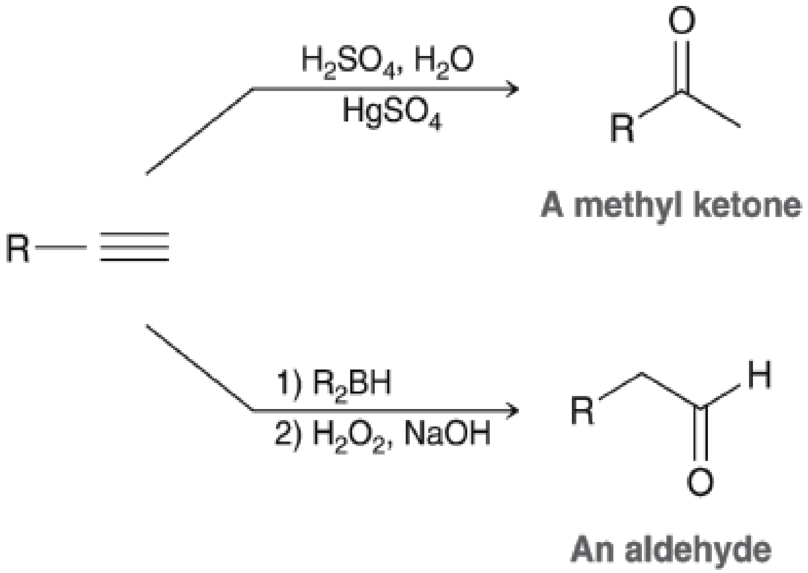
The hydroxyl group of the enol is deprotonated, generating a resonance-stabilized enolate ion

The enolate ion is protonated to give an aldehyde

- Enol is deprotonated to form an **enolate**, which is protonated at the carbon to produce the aldehyde.

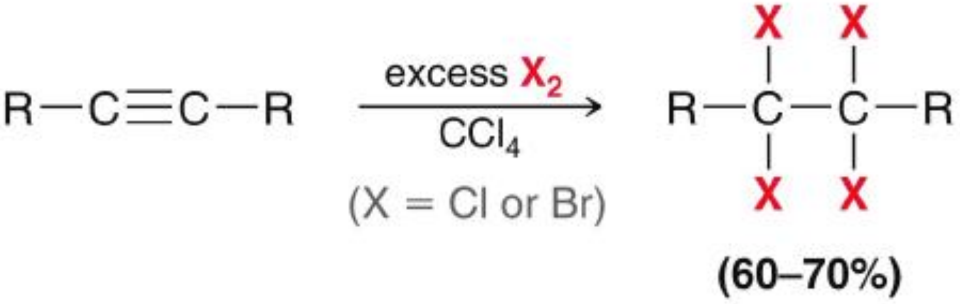
Controlling Hydration Regiochemistry

- For a **terminal alkyne**:
  - **Markovnikov** hydration yields **a ketone**
  - ***Anti* Markovnikov** hydration yields **an aldehyde**



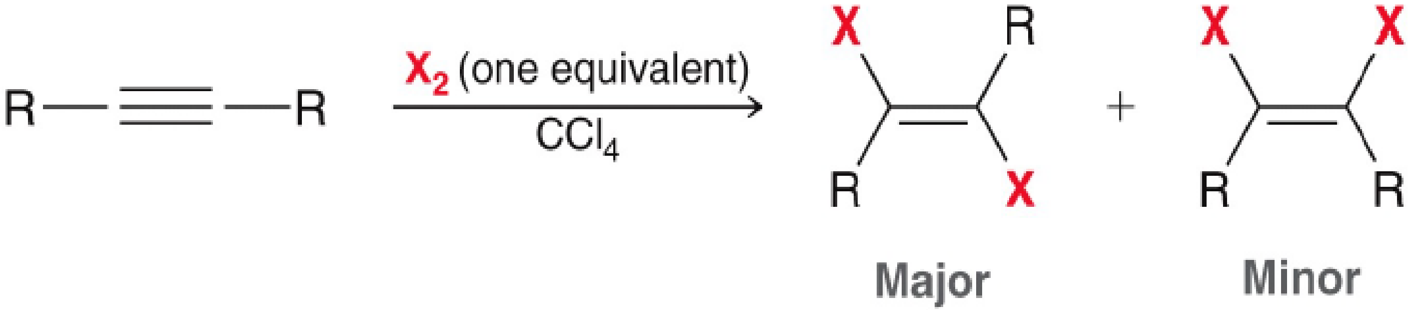
Halogenation of Alkynes

- **Halogenation** of alkynes yields a **tetrahalide**
- Two equivalents of halogen are added with excess X_2



Halogenation of Alkynes

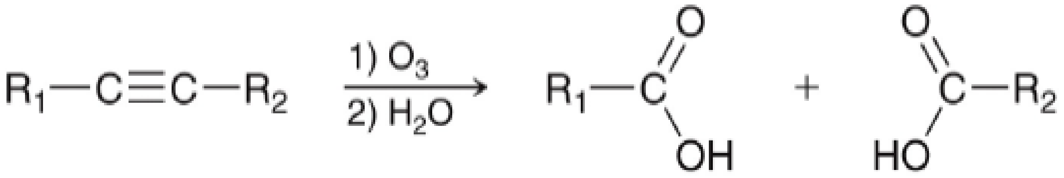
- When one equivalent of halogen is added to an alkyne, both *anti* and *syn* addition is observed



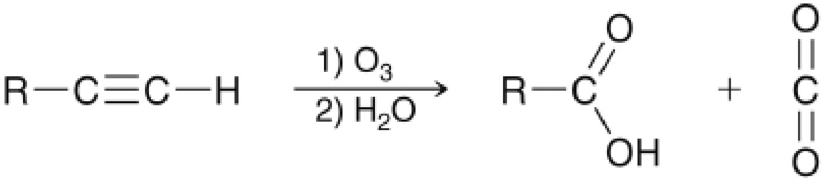
- The mechanism for alkyne halogenation is not fully understood. If it was like halogenation of an alkene, only the *anti* product would be obtained.

Ozonolysis of Alkynes

- **Ozonolysis** of an **internal alkyne** produces **two carboxylic acids**



- **Ozonolysis** of a **terminal alkyne** yields a **carboxylic acid and carbon dioxide**.



9.11 Reactions of Alkynes - Summary