

Chapter 9:

Alkynes

Synthesis of Alkynes

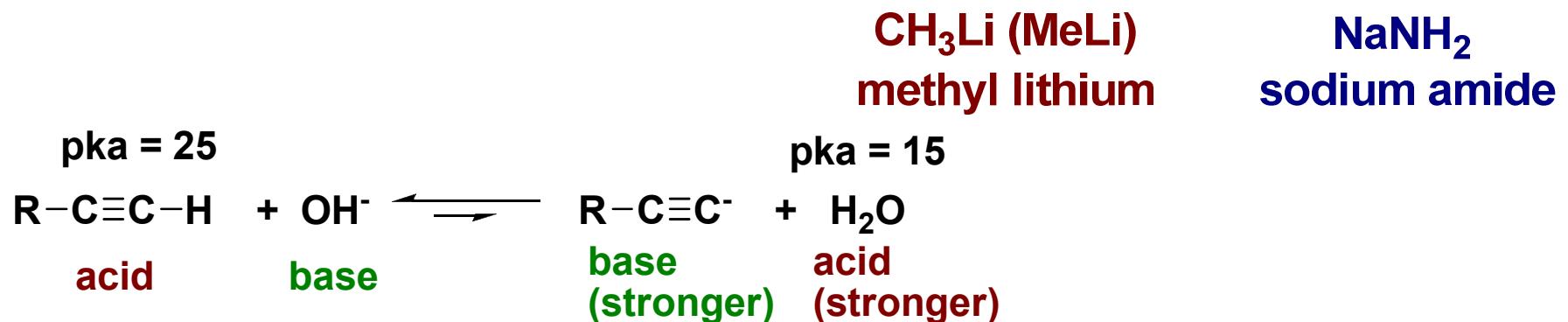
✓ From the Acetylide anion (9-6, 9-7)

The proton of terminal alkynes is **acidic** and can be removed with a **suitable base**. The resulting acetylide anion can be used as nucleophile in S_N2 reactions.

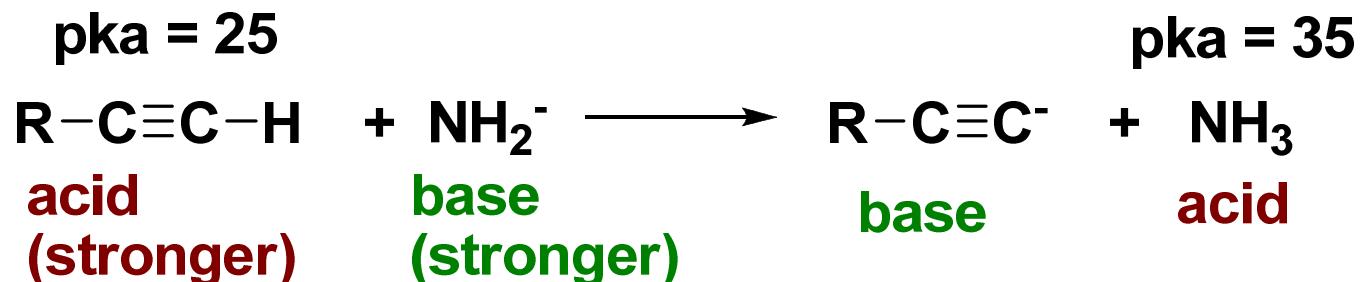
TABLE 9-2

Compound	Conjugate Base	Hybridization	s Character	pK _a	
$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}\left(\begin{array}{c} \text{:} \\ \text{:} \end{array}\right)^- \\ & \\ \text{H} & \text{H} \end{array}$	sp^3	25%	50	weakest acid
$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & =\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}=\text{C}\left(\begin{array}{c} \text{:} \\ \text{:} \end{array}\right)^- \\ \\ \text{H} \end{array}$	sp^2	33%	44	
$:\text{NH}_3$	$:\ddot{\text{N}}\text{H}_2^-$	(ammonia)		35	
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	$\text{H}-\text{C}\equiv\text{C}\left(\begin{array}{c} \text{:} \\ \text{:} \end{array}\right)^-$	sp	50%	25	
$\text{R}-\text{OH}$	$\text{R}-\ddot{\text{O}}\text{:}^-$	(alcohols)		16-18	stronger acid

- ✓ The bases of choice are those capable of removing the proton quantitatively. Bases such as hydroxide ion are not strong enough and create an equilibrium favoring the alkyne. Bases such as the ones below should be used:



since the acetylide anion is the stronger base and water the stronger acid, the reverse reaction is favoured



✓ Deprotonation can be followed by a nucleophilic substitution reaction producing substituted alkynes.



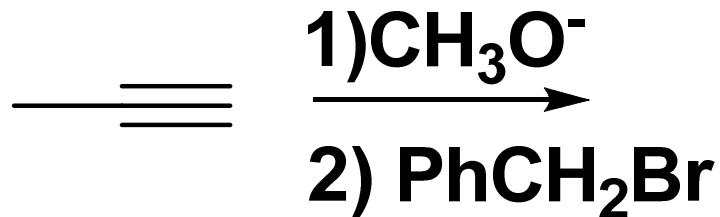
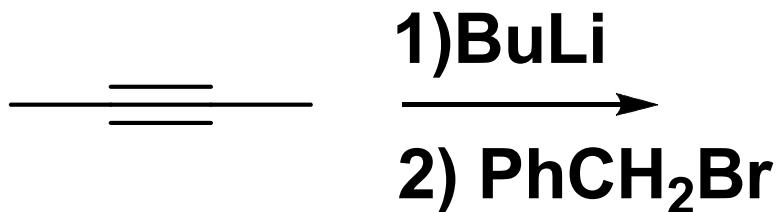
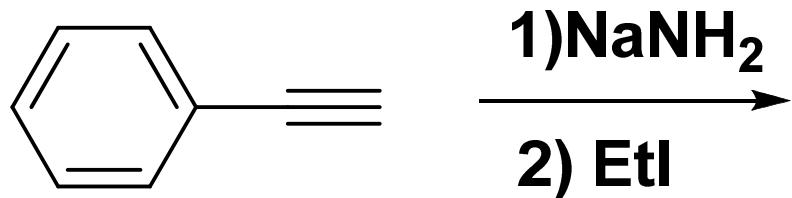
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✓ With **internal alkynes**, there is no reaction since there is **no acidic hydrogen** present



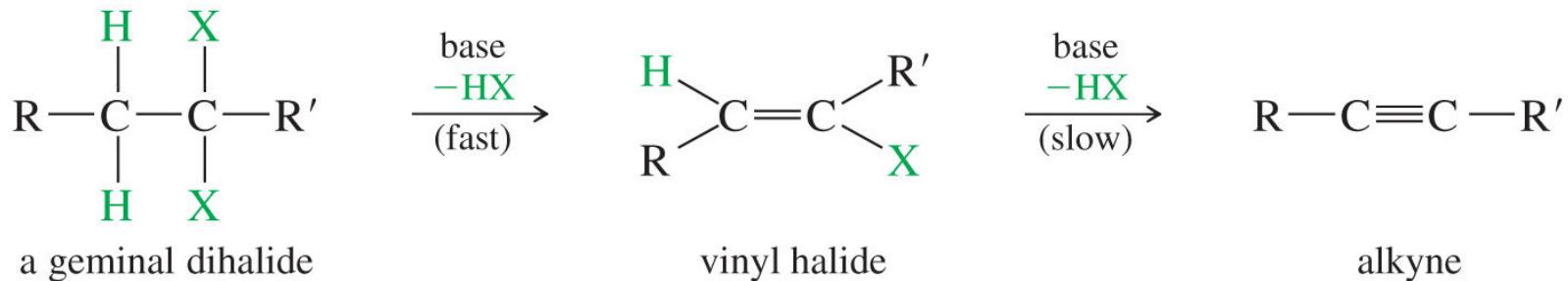
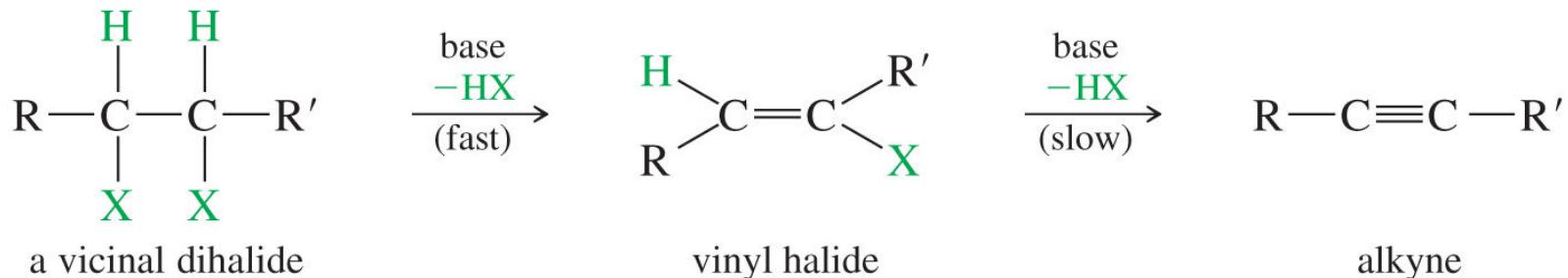
Practice Question

✓ Complete the following reactions.



Synthesis of Alkynes by Elimination Reactions (9-8)

We have seen in Chapter 7 that dehydrohalogenation easily yields alkenes. The same reaction can be performed twice to generate alkynes, however, drastic conditions (KOH, 200°C or NaNH₂, 150°C) are normally required and yields are often low (50%).

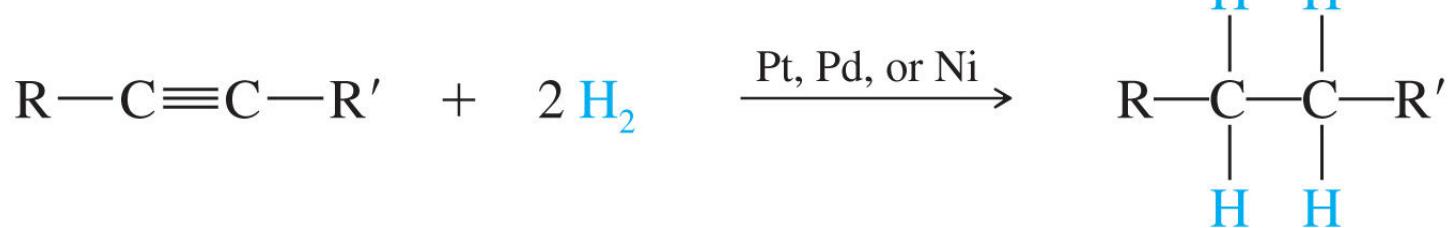


Addition Reactions of Alkynes (9-9)

Many of the reactions of alkynes are similar to those of alkenes since they both type of compound involve π bonds.

Catalytic Hydrogenation to Alkanes

Under normal conditions, the reaction cannot be stopped, producing the alkane.

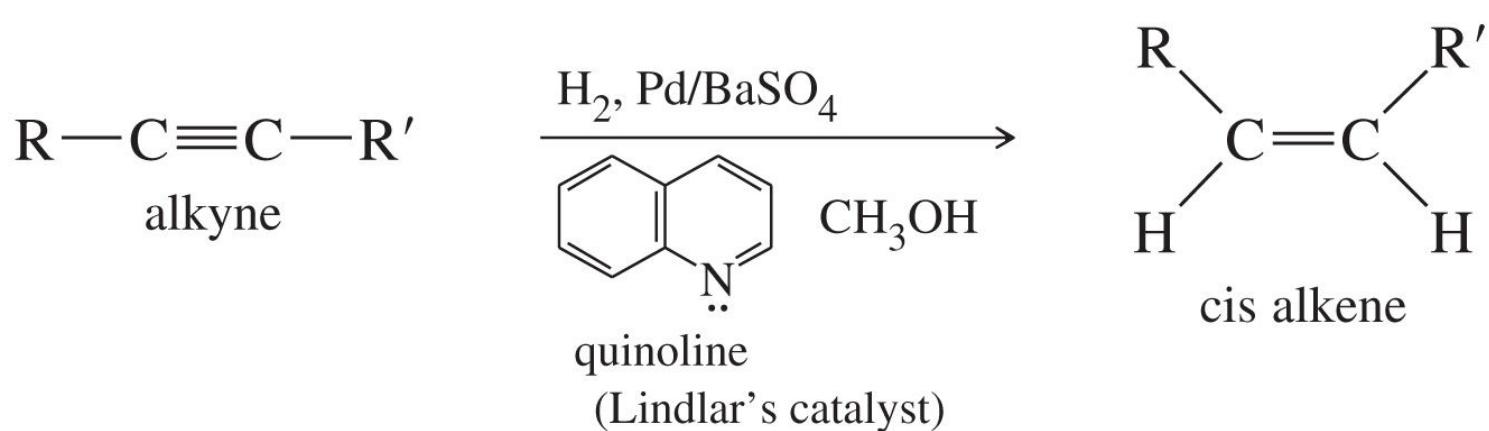


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Hydrogenation to cis-Alkenes

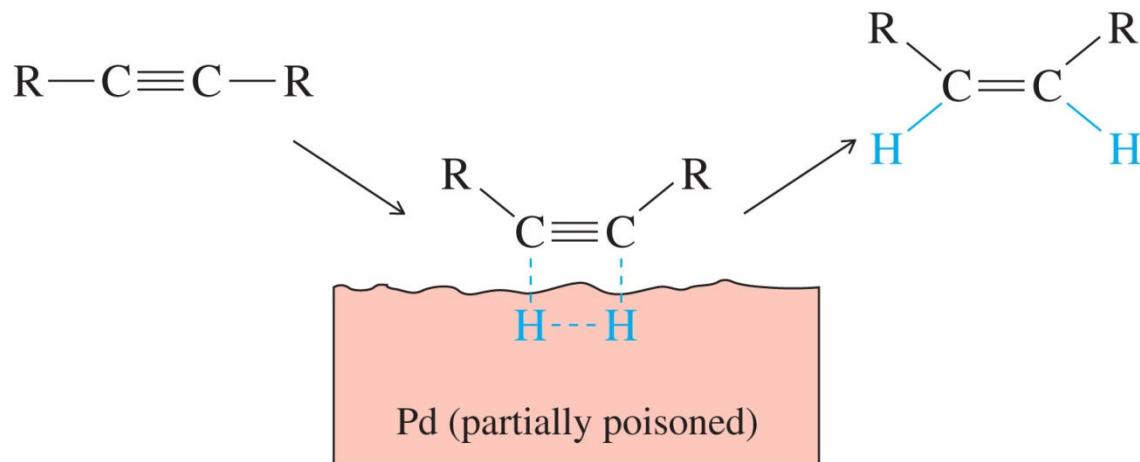
However, It is possible to add **only one equivalent** of hydrogen to the triple bond and produce **cis-alkenes**.

The catalyst used to perform this reaction is known as the **Lindlar's catalyst**.



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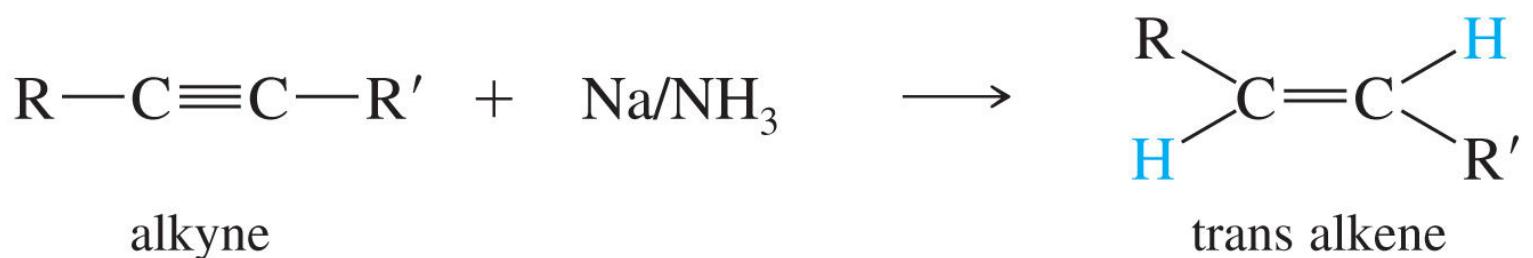
- ✓ The mechanism is the same as for hydrogenation of alkenes, but the catalyst is not active enough (we say that the catalyst is poisoned) to carry out the hydrogenation of the resulting alkene.
- ✓ Gives **cis**-alkenes since hydrogenation is **syn** reaction (same side of triple bond)



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Reduction to trans-Alkenes (6.9)

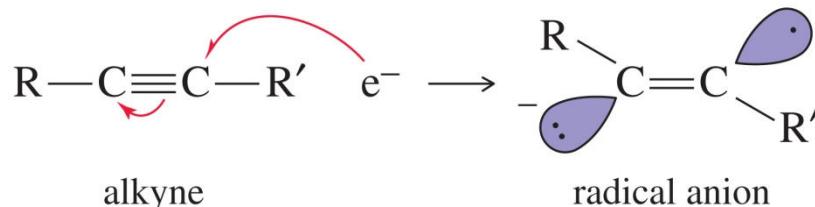
It is also possible to form trans-alkenes from alkynes. In this case hydrogen is not involved, and the reduction is carried out with sodium metal (or lithium) in liquid ammonia by a radical mechanism)



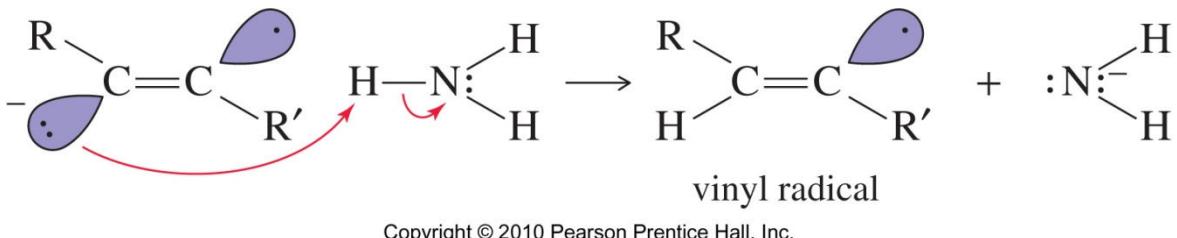
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The **trans** (or anti) stereochemistry results from the greater stability of the vinyl radical (step 3) simply because the alkyl groups are further apart

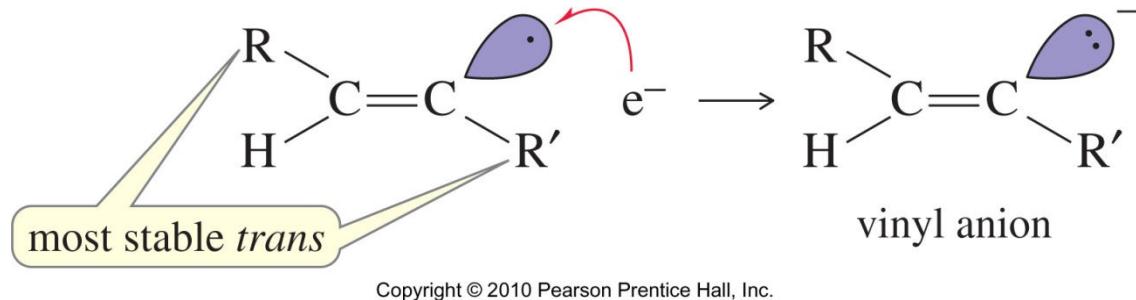
Step 1: An electron adds to the alkyne, forming a radical anion.



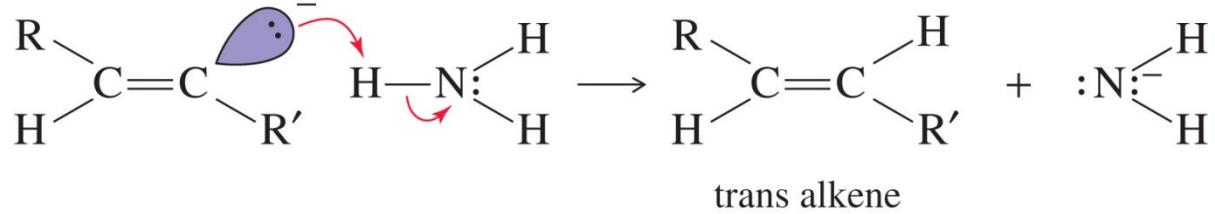
Step 2: The radical anion is protonated to give a radical.



Step 3: An electron adds to the alkyne, forming an anion.



Step 4: Protonation of the anion gives an alkene.



Practice Question

Describe the alkyne and reagent you would use to prepare the following compounds.

pentane

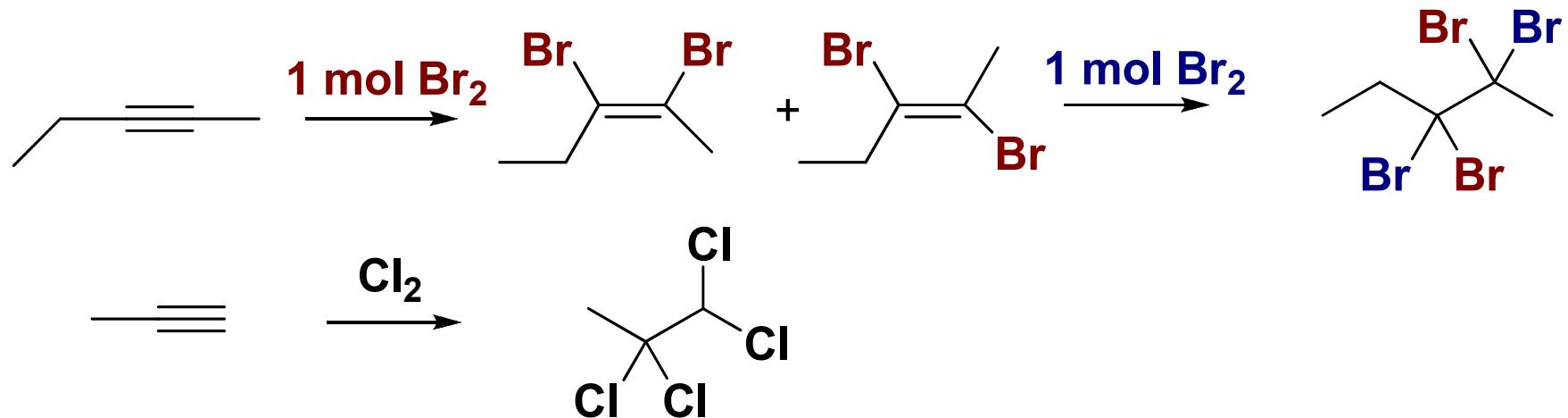
trans-2-butene

cis-2-butene

1-hexene

Addition of Halogens

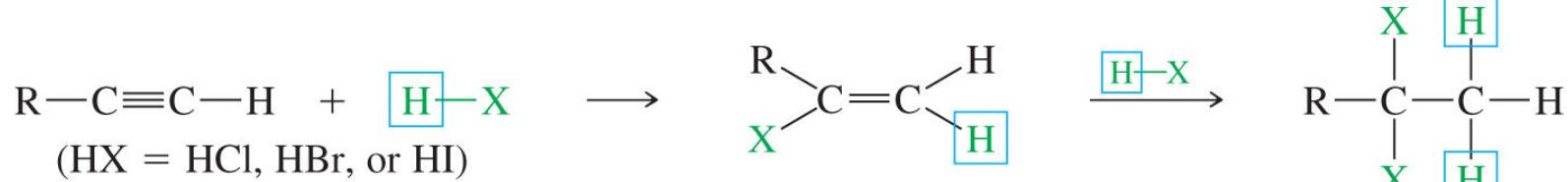
Similar to the reaction we have seen for alkenes. The first equivalent of X_2 normally gives a mixture of vicinal dihalides which quickly react with a second equivalent of X_2 to produce a tetrahalide. Even with only one molar equivalent of X_2 , the reaction normally proceeds to the tetrahalide.



Addition of Hydrogen Halides

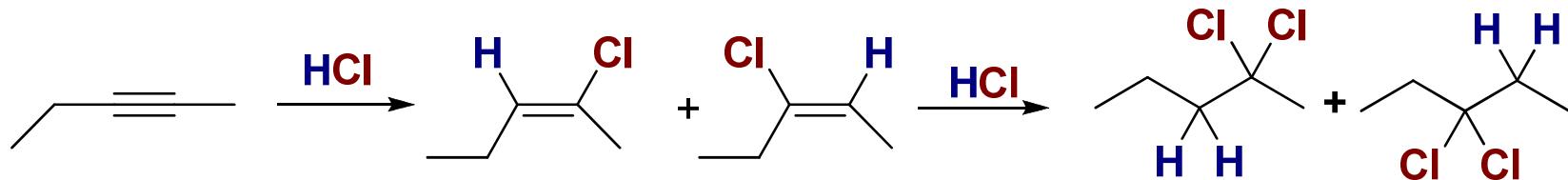
Similar to the reaction we have seen for alkenes, this reaction will produce geminal dihalides.

When the reaction is performed with a terminal alkyne, the orientation follows **Markovnikov** (ie most substituted carbocation is formed).

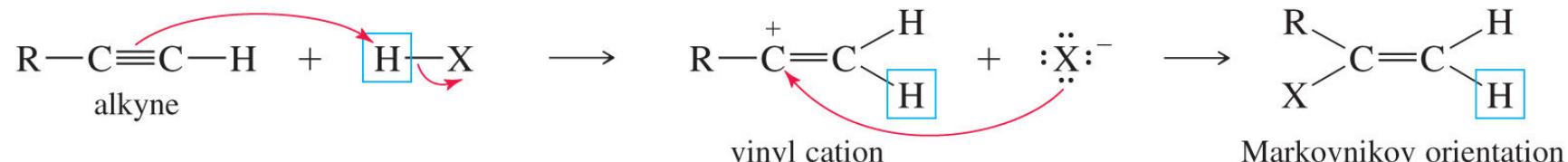


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For unsymmetrical di-substituted alkynes, a mixture of products is obtained.



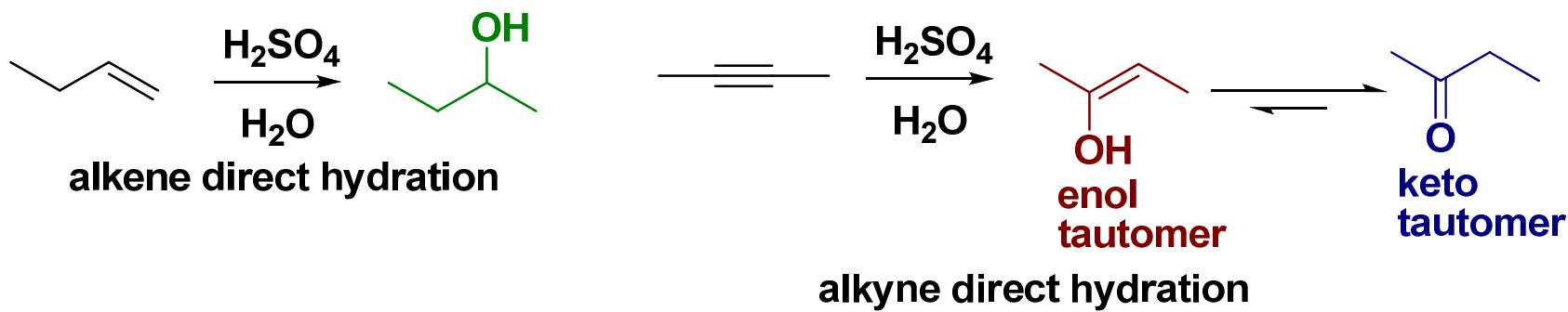
✓ A geminal dihalide is produced because of the stability of the resulting vinyl carbocation. Similar to the normal trend of stability of carbocations ($3^\circ > 2^\circ > 1^\circ$), a more substituted vinyl carbocation is more stable than a less substituted one.



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Hydration of Alkynes to Ketones and Aldehydes

Similar to alkenes, alkynes can be hydrated directly or indirectly. However, the products of these reactions are not alcohols, but rather ketones or aldehydes due to the tautomerism that exist between a ketone/aldehyde and their corresponding enol form.

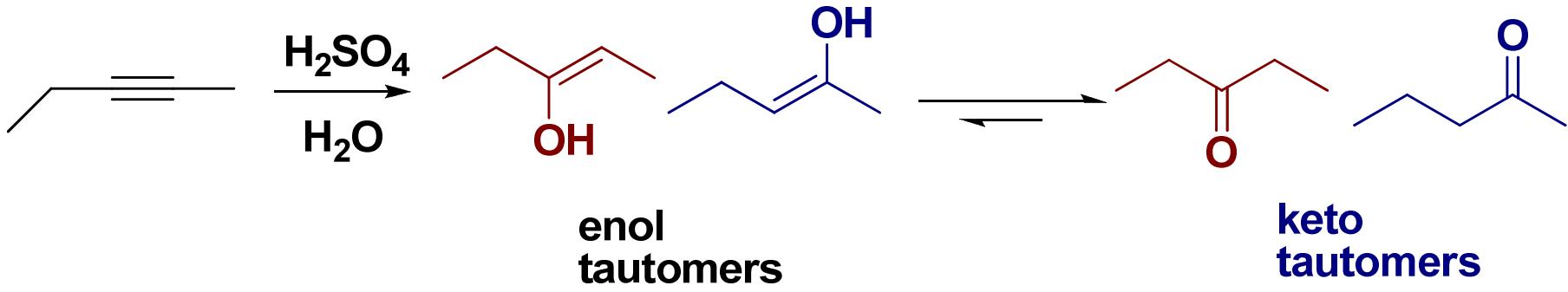
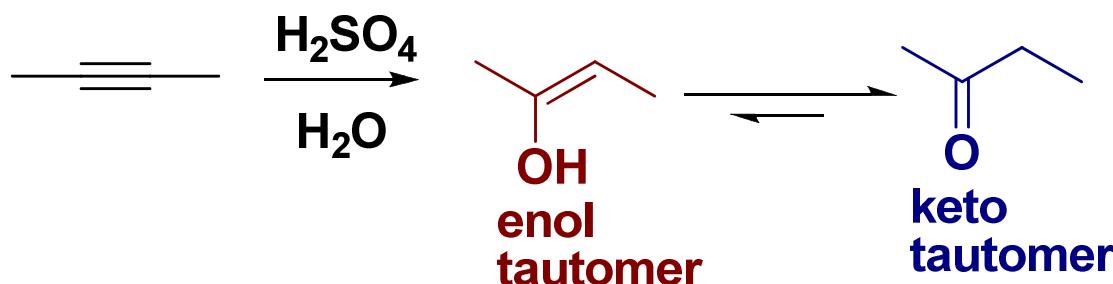


all ketones/aldehydes exist as mixtures of enol and keto tautomers. The keto tautomer is normally the favoured species

[Ketone-enol tautomerism]

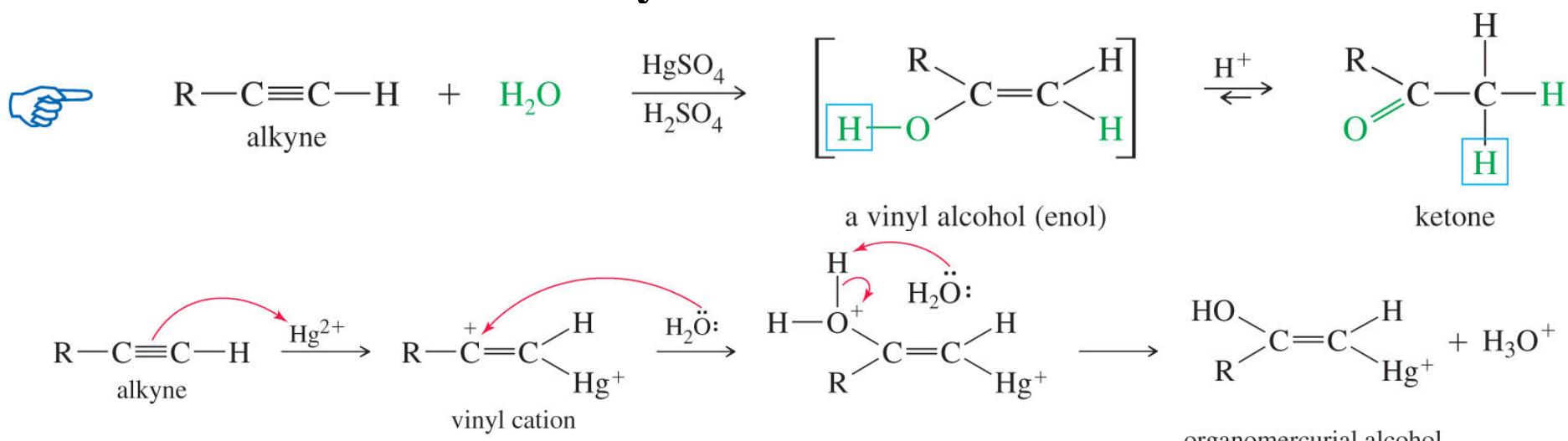
- ✓ Two structures are tautomers of each other when isomeric structures exist as an equilibrium. All ketones and aldehydes exist as an equilibrium between the enol form and the keto form. In most cases, the equilibrium favours the keto structure as shown below.
- ✓ Therefore, in reactions producing the enol form, rearrangement will take place leading to the more stable ketone or aldehyde

With unsymmetrical alkynes, 2 possible enol tautomers will form, therefore a mixture of ketones will be produced.



these two different enol forms
have equivalent stability and are
both formed in equal amounts

✓ The direct hydration of terminal alkynes is difficult under normal acidic conditions but can be catalyzed by HgSO_4 and produces the Markovnikov product (a ketone), i.e. the least substituted enol is formed leading to the **methyl ketone** every time.

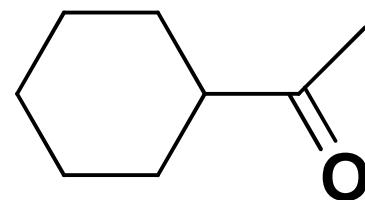
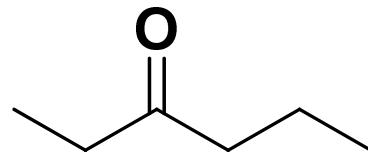
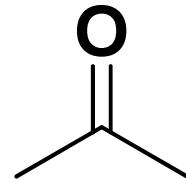


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This mercuric ion will be hydrolyzed leading to the enol, then the methyl ketone

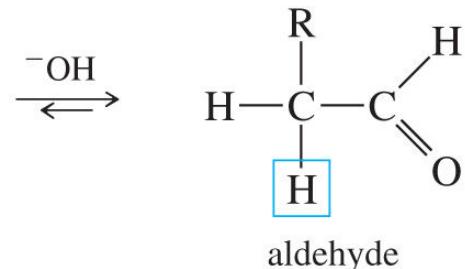
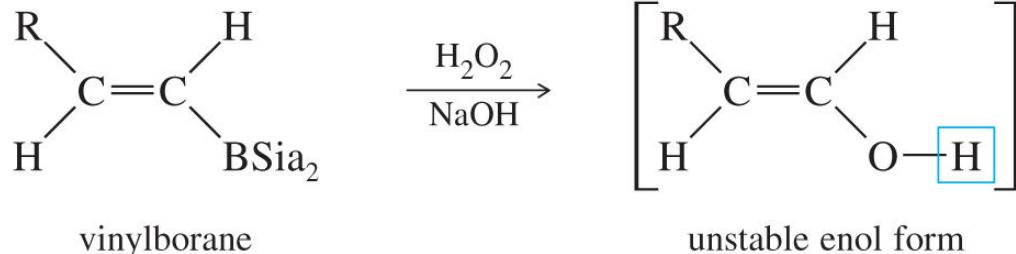
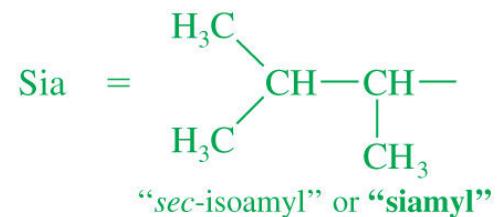
Practice Question

Which alkyne would be the best reagent for the synthesis of each of the following ketones? Show the reaction.



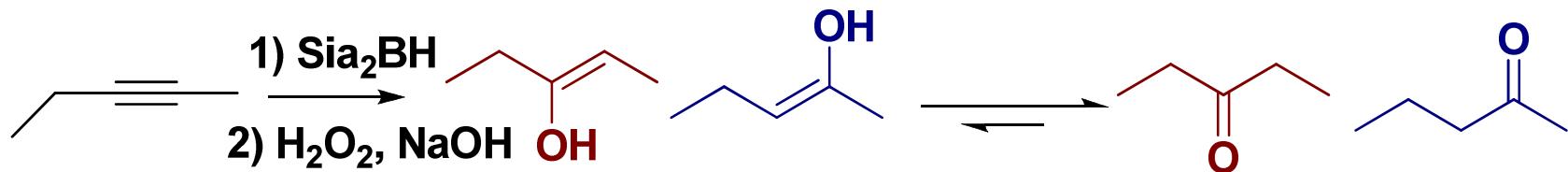
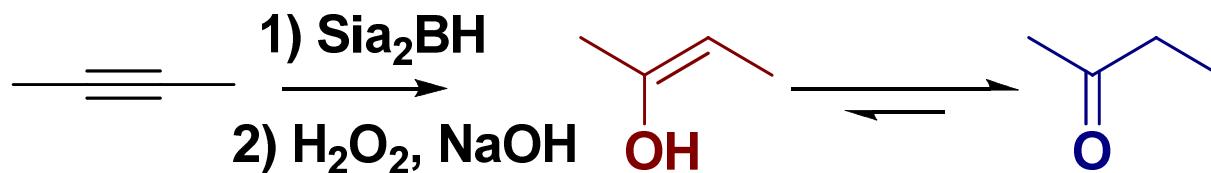
Hydroboration/oxidation

The reaction is similar to the one we have seen for alkenes. However, to prevent the multiple addition of the reagent to the triple bond, a bulky (sterically hindered) borane reagent is needed. The reaction is anti-Markovnikov, meaning that for terminal alkyne, an aldehyde is obtained.

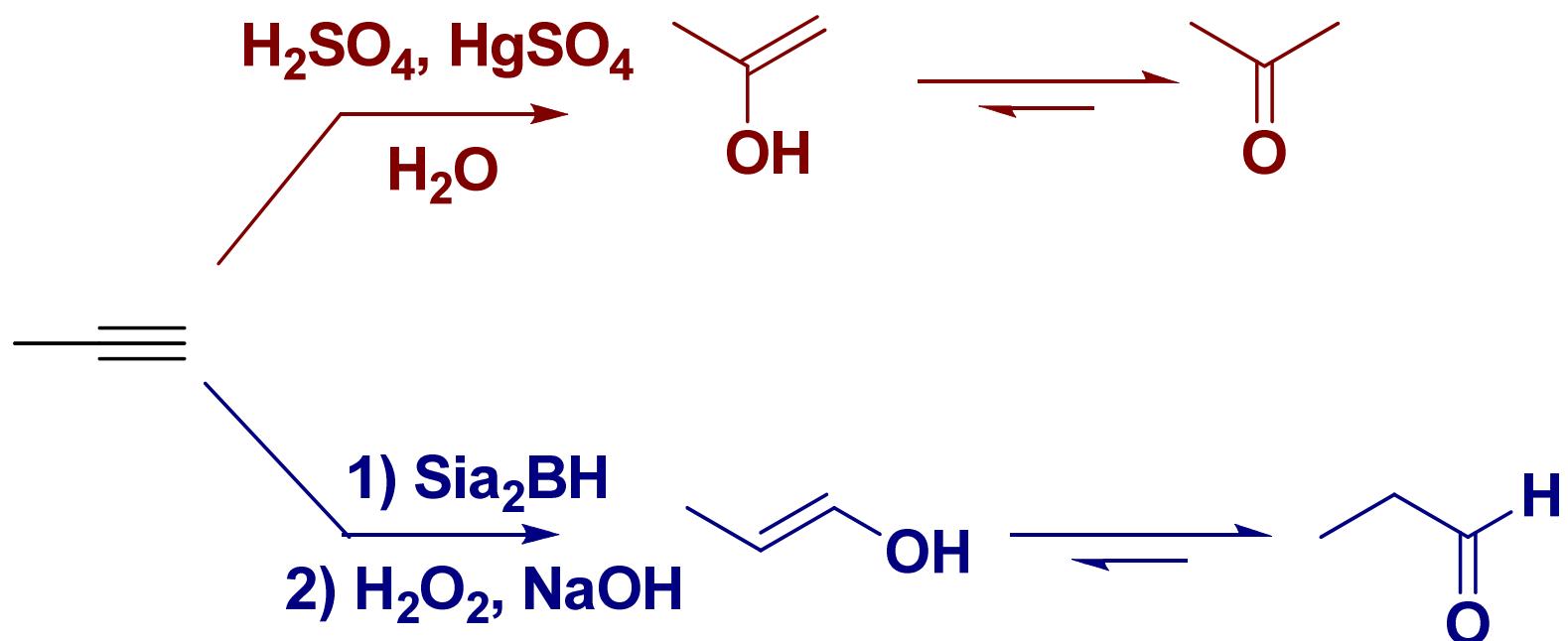


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**For internal alkynes, ketones are obtained.
If the alkynes is symmetrical one product is
formed, but for unsymmetrical alkynes,
mixtures of ketones will be obtained.**

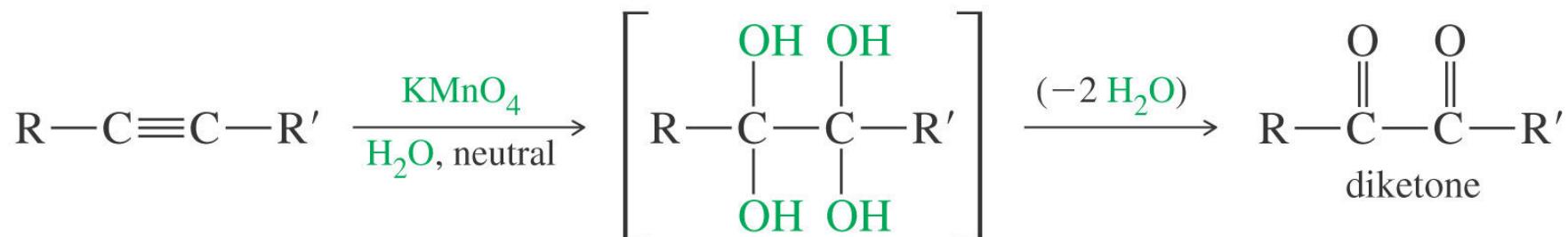


✓ These two indirect hydrations of alkynes are complementary to one another, since you can control the formation of either the ketone or the aldehyde by choosing the correct reaction conditions.



Oxidation (9-10)

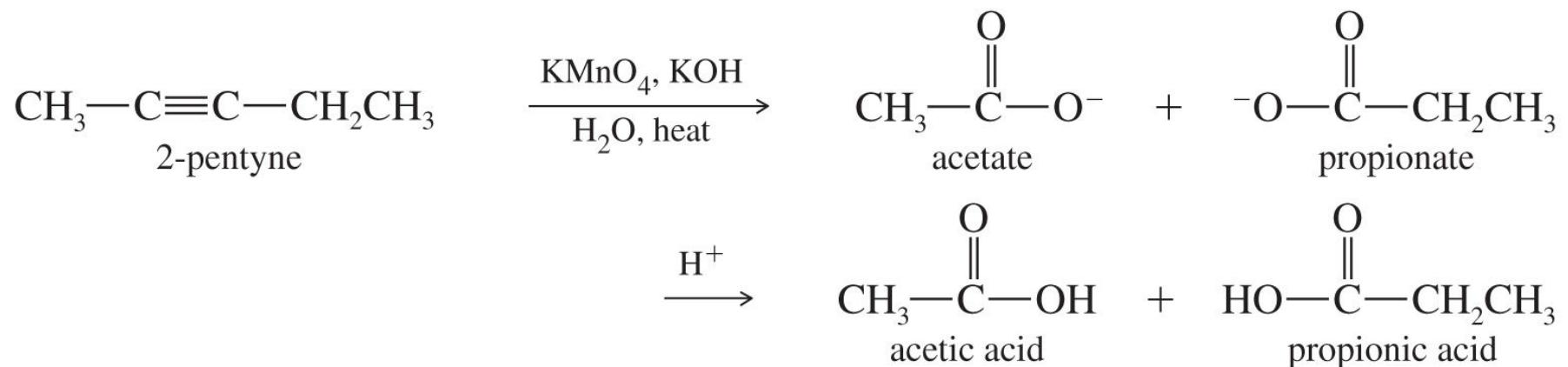
The same reagents that oxidized alkenes can oxidize alkynes in a similar way. Using KMnO₄ under neutral conditions, a vicinal diketones are obtained with internal alkynes



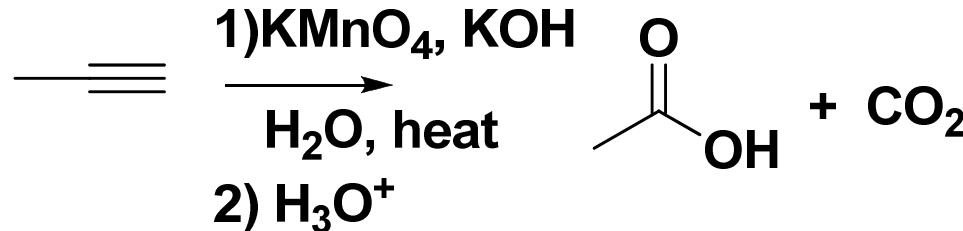
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However, basic conditions cleave the triple bond leading to carboxylate salt. Acidification generate the corresponding carboxylic acids.

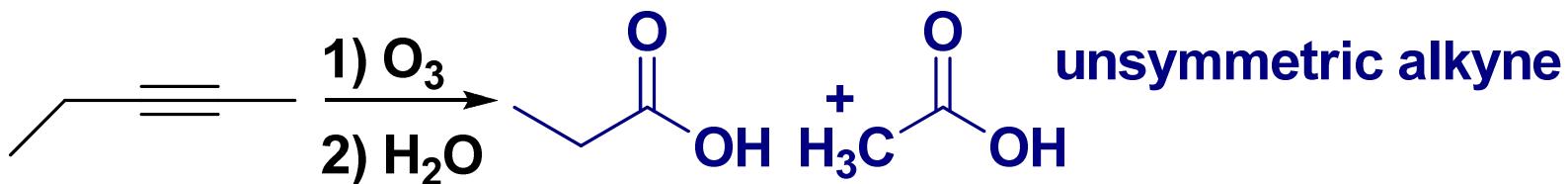
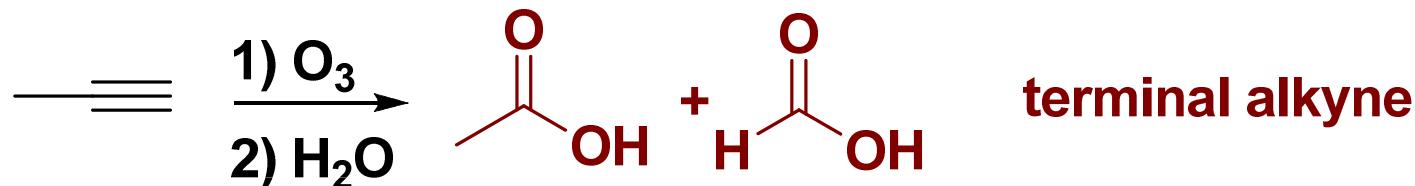
- If the alkyne is unsymmetrical, two products will be formed**



- Terminal alkynes will give a carboxylic acid and CO_2**



Ozonolysis of alkynes is similar to that of alkenes. However, carboxylic acids are formed rather than aldehydes and ketones.



Practice Question

What is the structure of the alkyne that gives each of the following sets of products upon ozonolysis followed by hydrolysis?

