Alkynes

Alkynes-hydrocarbons with a carbon-carbon triple bond.

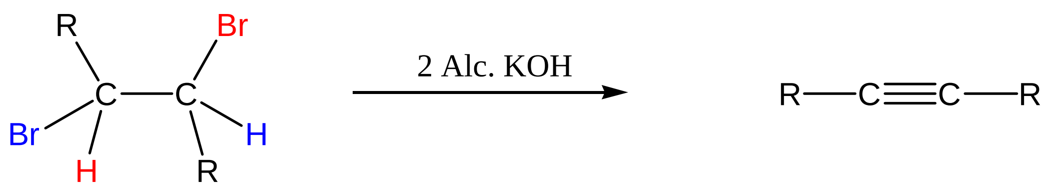
The carbon-carbon triple bond results from the interaction of two sp hybridized carbon atoms. 180 degree angle. Linear.
The carbon-carbon triple bond is the shortest and strongest known carbon-carbon bond. Why? It has the highest percentage of s character.

Type	Hybridization	% s character	% p character
Alkane	sp^3	25	75
Alkene	sp^2	33	67
Alkyne	sp	50	50

<u>Nomenclature</u>
Alkynes are named like alkenes with the following adjustments: 1) Number the carbons on the chain so that the triple bonded carbons receive the lowest possible numbers, 2) Indicate the location of the triple bond by writing the number of the lowest numbered carbon making up the triple bond in front of the name of the parent chain. 3) Change the ending from –ene to –yne.

Reactions to Know
<u>Preparation of Alkynes</u>
Synthesis of Alkynes:

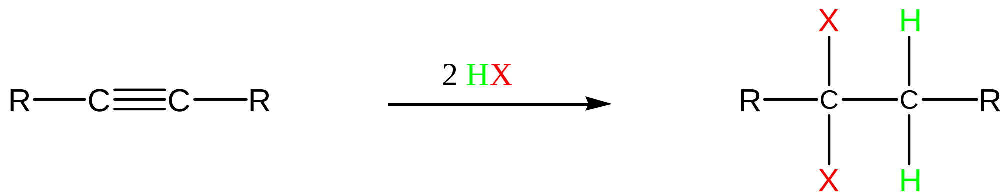
1. Dehydrohalogenation of vicinal dihalides:



Note: vic-dihalides are prepared from alkenes. Thus, in effect, this is a conversion of alkene to alkyne.

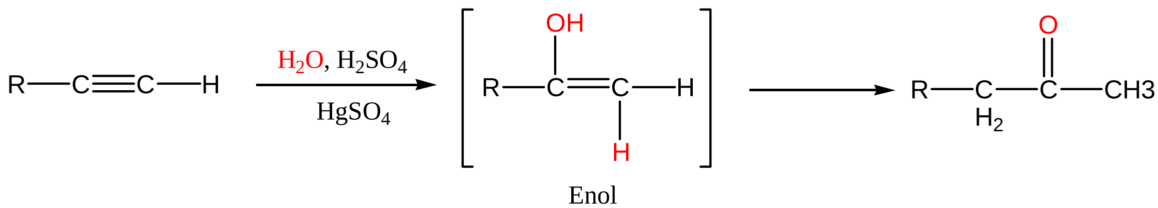
Reactions of Alkynes

1. Hydrohalogenation:



(Geminal Dihalide)

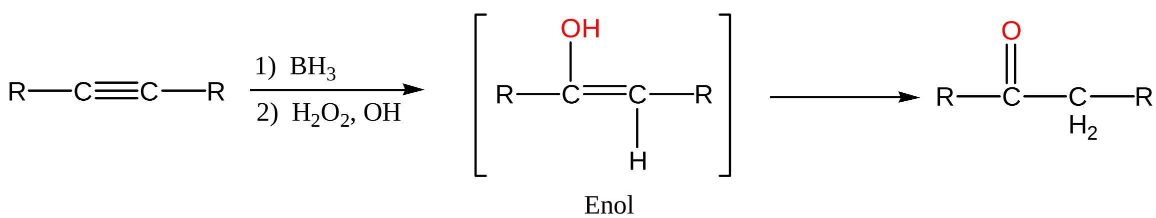
2. Mercury (II)-Catalyzed Hydration:



(Ketone)

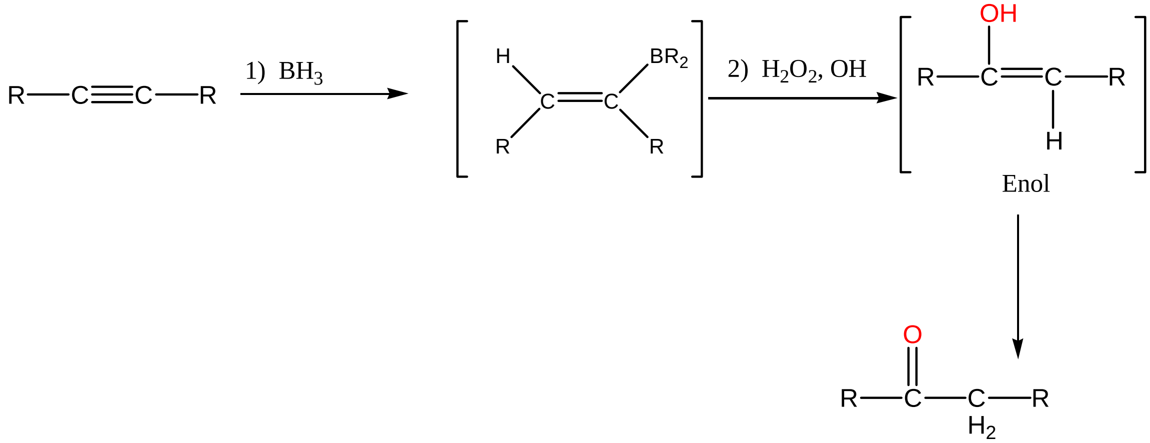
The enol is an intermediate in the reaction. However, it immediately rearranges to form the a ketone through a process called keto-enol tautomerism.

3. **Hydroboration-Oxidation:** (Internal alkynes will give a ketone; terminal alkynes will give an aldehyde).



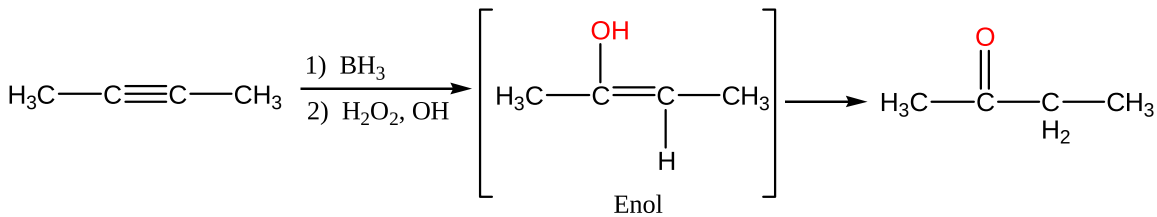
(Ketone)

As in the mercury-catalyzed reaction, the enol is an intermediate which quickly undergoes keto-enol tautomerism to form the ketone.

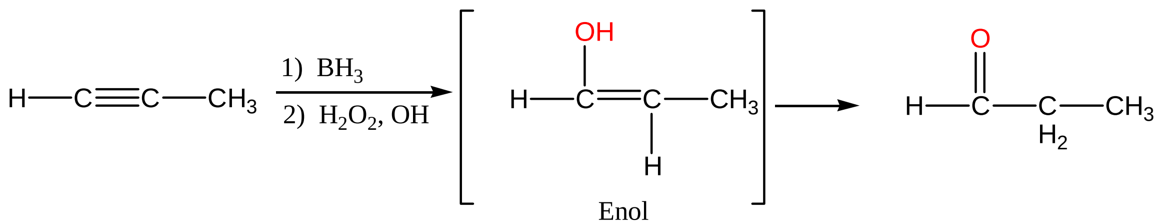


Examples:

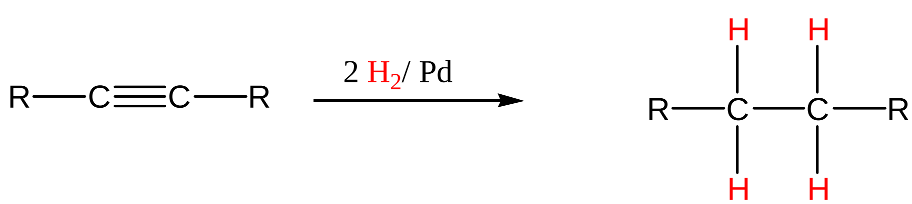
a) Internal alkyne to ketone



b) Terminal alkyne to aldehyde

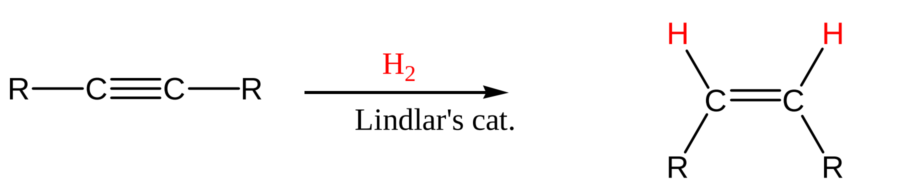


4. Hydrogenation:



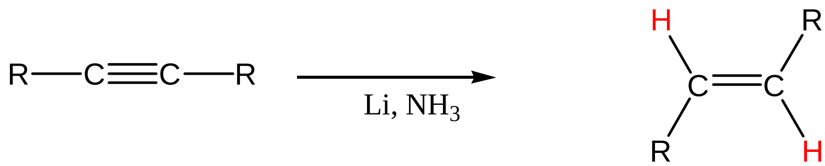
(Alkane)

5. Hydrogenation Using Lindlar Catalyst:



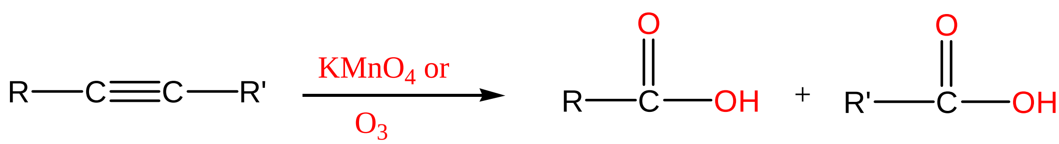
(Cis Alkene)

6. **Hydrogenation Using Lithium and Ammonia** (Na can be used instead of Li):



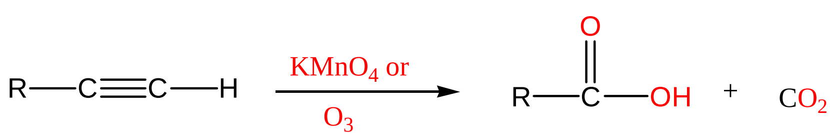
(Trans Alkene)

7. Cleavage of Internal Alkynes:



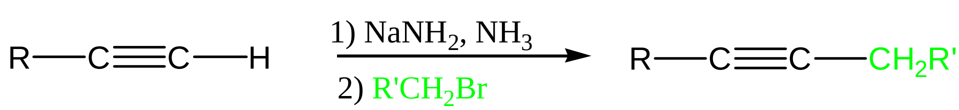
(Carboxylic Acid)

8. Cleavage of Terminal Alkynes:



(Carboxylic Acid and CO_2)

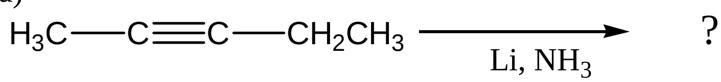
9. Alkylation Using Acetylide Ions:



Practice Problems:

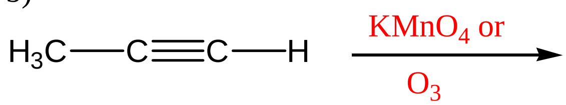
1) What are the products of the following reaction:

a)



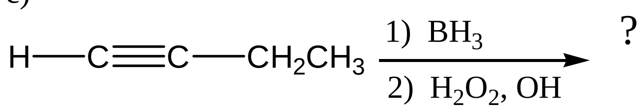
Answer

b)



Answer

c)



Answer

Alkyne Acidity: Forming Acetylide Anions

Terminal alkynes are weakly acidic.

Acidity of simple hydrocarbons:

Alkynes > Alkenes> Alkanes

Why are terminal alkynes more acidic than alkenes or alkanes? Acidity depends upon the stability of the conjugate base. Why are acetylide anions more stable than vinylic or alkyl anions?

1) Hybridization of the negatively charged carbon atom:
   a. Acetylide anion has an sp hybridized carbon. Therefore, the negative charge resides in an orbital that has 50% s characteristic.
   b. Vinylic anion ' sp2 hybridized. 33% s character.
   c. Alkyl anion ' sp3 hybridized. 25% s character.

Since s orbitals are nearer the positive nucleus and are lower in energy than p orbitals, the negative charge is stabilized to a greater extent.

1. Formation of Acetylide Anions

Acetylide anion

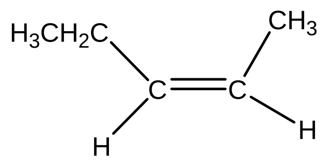
Acetylide Anions are important to organic synthesis because they can be used to make a carbon chain longer.

2. Alkylation of Acetylide Anions

$RC\equiv C:^{-}$ + 1° RX $\rightarrow$ $RC\equiv CR$

You'll learn the mechanism for this reaction in a later chapter.

Practice Synthesis Problem:

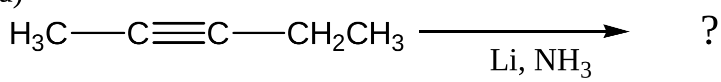
2) How could you prepare  from $H_3CH_2CC\equiv CH$ and any needed reagents?

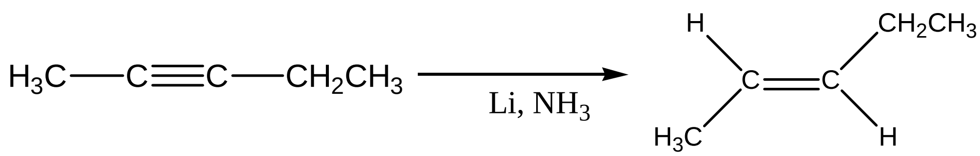
Answer

Answer

1) What are the products of the following reaction:

   a)



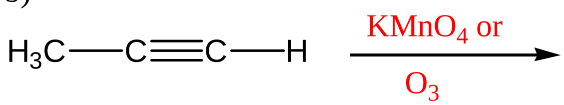


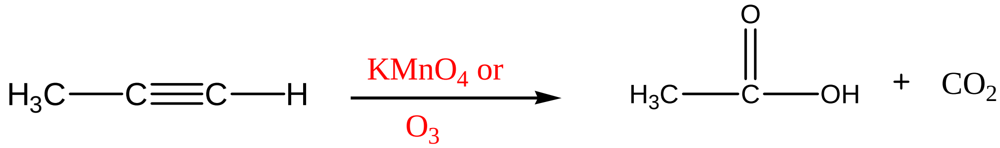
Return to Problem

Answer

1) What are the products of the following reaction:

b)



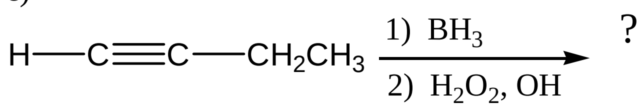


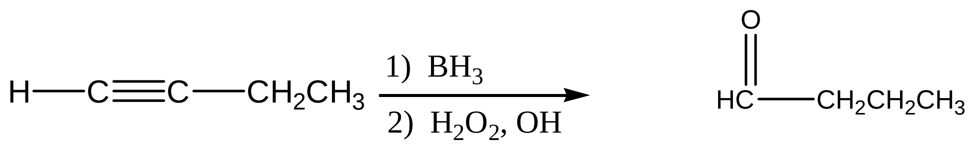
Return to Problem

Answer

1) What are the products of the following reaction:

c)

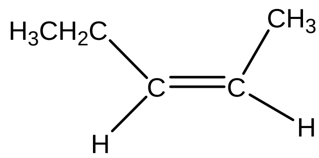




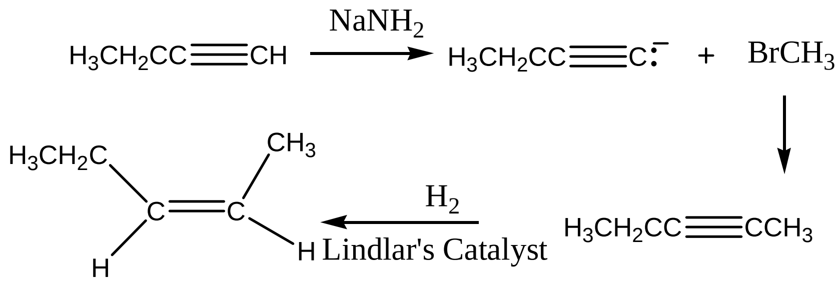
Return to Problem

Answer:

2) How could you prepare



from $H_3CH_2CC\equiv CH$ and any needed reagents?



Return to Problem