Alkynes

—C≡C—

Synthesis of Acetylene

Heating coke with lime in an electric furnace to forms calcium carbide.

Then drip water on the calcium carbide.

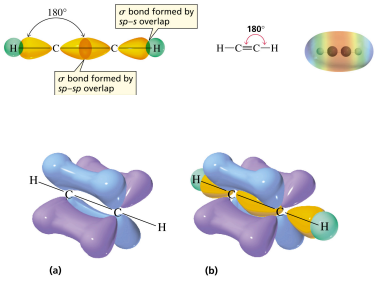
$$3\,C + CaO \longrightarrow CaC_2 + CO$$

(coke; lime)

$$^{*}\,CaC_2 + 2\,H_2O \longrightarrow H{-}C{\equiv}C{-}H + Ca(OH)_2$$

**This reaction was used to produce light for miners' lamps and for the stage.*

The Structure of Alkynes



A triple bond is composed of a σ bond and two π bonds

Question

Arrange ethane, ethene, and ethyne in order of increasing C-C bond length.

A) ethane < ethene < ethyne
B) ethene < ethane < ethyne
C) ethyne < ethene < ethane
D) ethane < ethyne < ethene

Acidity of Acetylene and Terminal Alkynes

H—C≡C—

Acidity of Hydrocarbons

In general, hydrocarbons are very weak acids

Compound	pK_a
HF	3.2
H_2O	16
NH_3	36
$H_2C{=}CH_2$	45
CH_4	60

Acetylene

Acetylene is a weak acid, but not nearly as weak as alkanes or alkenes.

Compound	pK_a	
HF	3.2	
H_2O	16	
HC≡CH		26
NH_3	36	
$H_2C{=}CH_2$	45	
CH_4	60	

Question

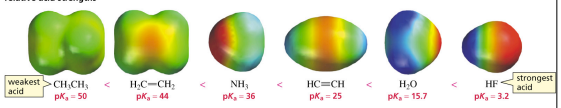
Which one of the following is the strongest acid?

A) water
B) ammonia
C) 1-butene
D) 1-butyne

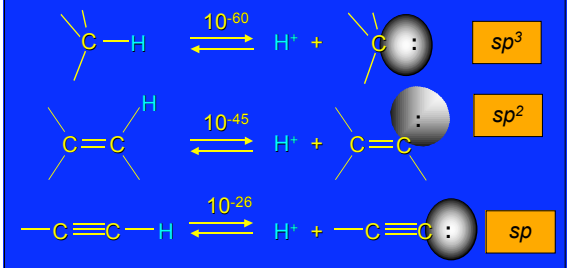
relative electronegativities of carbon atoms

most electronegative: $sp > sp^2 > sp^3$:least electronegative

relative acid strengths



Carbon: Hybridization and Electronegativity



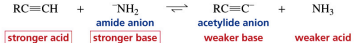
Electrons in an orbital with more *s* character are closer to the nucleus and more strongly held.

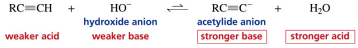
Question

Which one of the following statements best explains the greater acidity of terminal alkynes (RC≡CH) compared with monosubstituted alkenes ($RCH{=}CH_2$)?

A) The *sp*-hybridized carbons of the alkyne are less electronegative than the sp^2 carbons of the alkene.
B) The two π bonds of the alkyne are better able to stabilize the negative charge of the anion by resonance.
C) The *sp*-hybridized carbons of the alkyne are more electronegative than the sp^2 carbons of the alkene.
D) The question is incorrect - alkenes are more acidic than alkynes.

The stronger the acid, the weaker its conjugate base





Sodium Acetylide

Solution: Use a stronger base. Sodium amide is a stronger base than sodium hydroxide.

$NaNH_2 + HC{\equiv}CH \rightleftharpoons NaC{\equiv}CH + NH_3$

$H_2N^- + H{-}C{\equiv}CH \rightleftharpoons H_2N{-}H + {:}C{\equiv}CH^-$

stronger acid $pK_a = 26$ — weaker acid $pK_a = 36$

Ammonia is a weaker acid than acetylene.
The position of equilibrium lies to the right.

Question

Which of the following bases is strong enough to completely deprotonate propyne?

A) NH_3
B) CH_3OH
C) $NaNH_2$
D) NaOH

Preparation of Various Alkynes
by alkylation reactions with
Acetylide or Terminal Alkynes

Synthesis Using Acetylide Ions: Formation of C–C Bond

$CH_3CH_2C{\equiv}C^- + CH_3CH_2CH_2{-}Br \longrightarrow CH_3CH_2C{\equiv}CCH_2CH_2CH_3 + Br^-$

Alkylation of Acetylene and Terminal Alkynes

$H{-}C{\equiv}C{-}H$

↓

$R{-}C{\equiv}C{-}H$

↓

$R{-}C{\equiv}C{-}R$

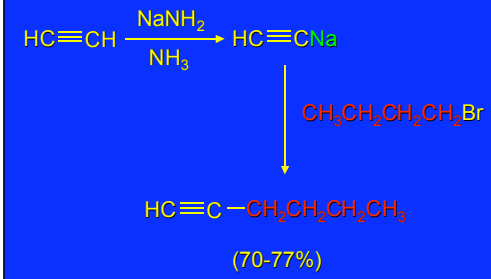
Alkylation of Acetylene and Terminal Alkynes

$H{-}C{\equiv}C{:}^- + R{-}X \xrightarrow{S_N2} H{-}C{\equiv}C{-}R + {:}X^-$

The alkylating agent is an alkyl halide, and the reaction is nucleophilic substitution.

The nucleophile is sodium acetylide or the sodium salt of a terminal (monosubstituted) alkyne.

Example: Alkylation of Acetylene

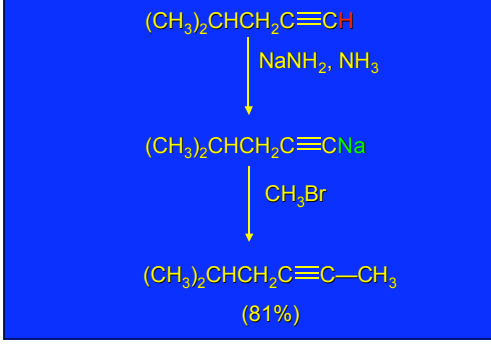


Question

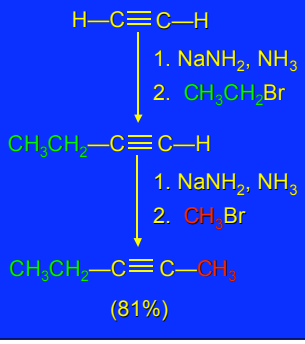
Which alkyl halide will react faster with the acetylide ion (HC≡CNa) in an S_N2 reaction?

A) bromopropane
B) 2-bromopropane
C) *tert*-butyl iodide
D) 1-bromo-2-methylbutane

Example: Alkylation of a Terminal Alkyne



Example: Dialkylation of Acetylene



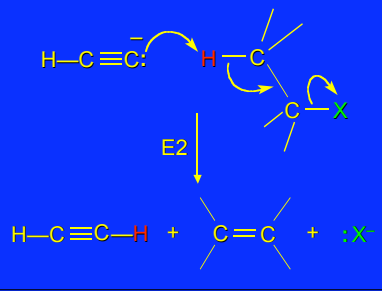
Limitation

Effective only with primary alkyl halides

Secondary and tertiary alkyl halides undergo elimination

Acetylide Ion as a Base

E2 predominates over S_N2 when alkyl halide is secondary or tertiary.



Question

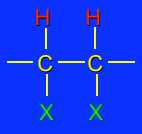
Consider the reaction of each of the following with cyclohexyl bromide. For which one is the ratio of substitution to elimination highest?

A) $NaOCH_2CH_3$, ethanol, 60°C
B) $NaSCH_2CH_3$, ethanol-water, 25°C
C) $NaNH_2$, NH_3, -33°C
D) $NaC{\equiv}CH$, NH_3, -33°C

Preparation of Alkynes by Elimination Reactions

Preparation of Alkynes by "Double Dehydrohalogenation"

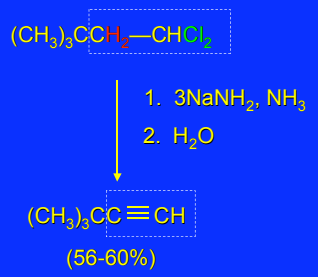
Geminal dihalide



Vicinal dihalide

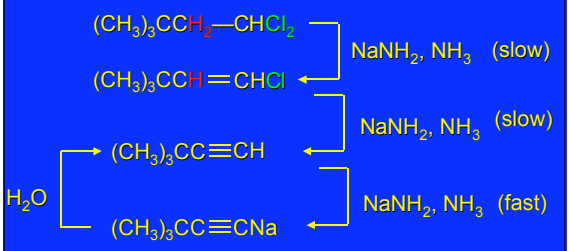
The most frequent applications are in preparation of terminal alkynes.

Geminal dihalide → Alkyne



(56-60%)

Geminal dihalide → Alkyne

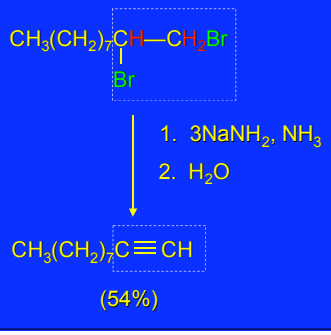


Question

In addition to $NaNH_2$, what other base can be used to convert 1,1-dichlorobutane into 1-butyne?

A) $NaOCH_3$
B) NaOH
C) $NaOCH_2CH_3$
D) $KOC(CH_3)_3$

Vicinal dihalide → Alkyne



Question

Which of the following compounds yield 1-heptyne on being treated with three moles of sodium amide (in liquid ammonia as the solvent) followed by adding water to the reaction mixture?

A) 1,1,2,2-tetrachloroheptane
B) 1-bromo-2-chloroheptane
C) 1,1,2-trichloropentane
D) all of the above

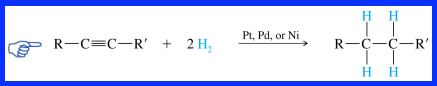
Reactions of Alkynes

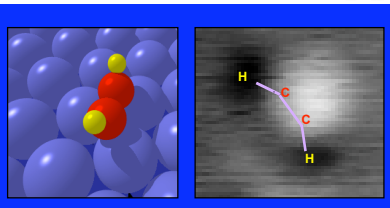
Reactions of Alkynes

- ✓ Acidity
- Hydrogenation
- Metal-Ammonia Reduction
- Addition of Hydrogen Halides
- Hydration
- Addition of Halogens
- Ozonolysis

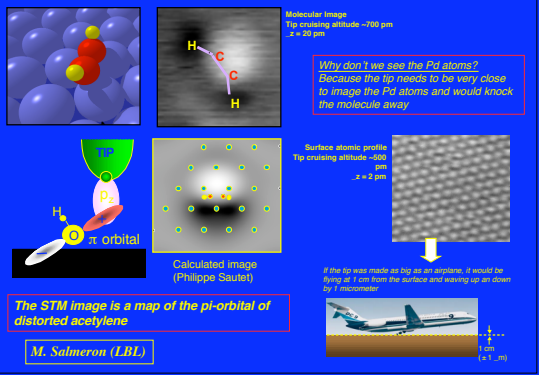
Hydrogenation of Alkynes

Atomic Force Microscopy of Acetylene Lawrence Berkeley Laboratory (LBL)

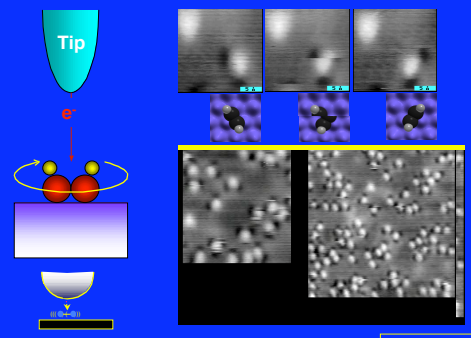




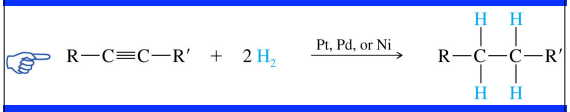
Imaging: acetylene on Pd(111) at 28 K



Excitation of frustrated rotational modes in acetylene molecules on Pd(111) at T = 30 K



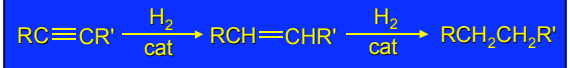
Hydrogenation of Alkynes



catalyst = Pt, Pd, Ni, or Rh

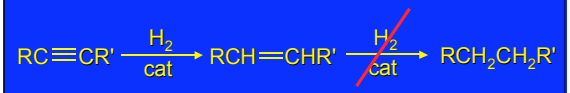
alkene is an intermediate

Partial Hydrogenation



Alkenes could be used to prepare alkenes if a catalyst were available that is active enough to catalyze the hydrogenation of alkynes, but not active enough for the hydrogenation of alkenes.

Lindlar Palladium

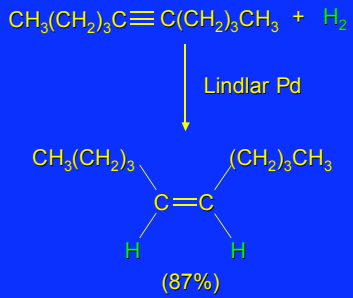


There is a catalyst that will catalyze the hydrogenation of alkynes to alkenes, but not that of alkenes to alkanes.

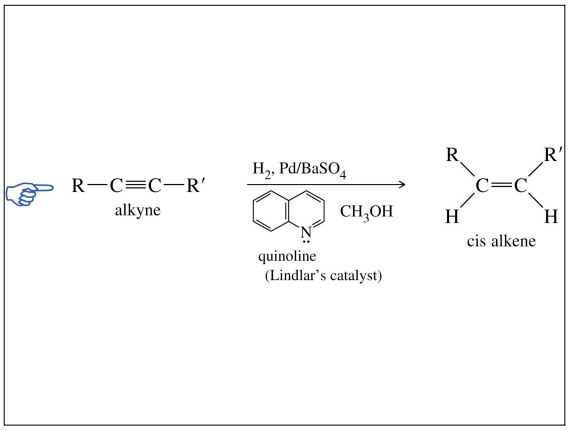
It is called the Lindlar catalyst and consists of palladium supported on $CaCO_3$, which has been poisoned with lead acetate and quinoline.

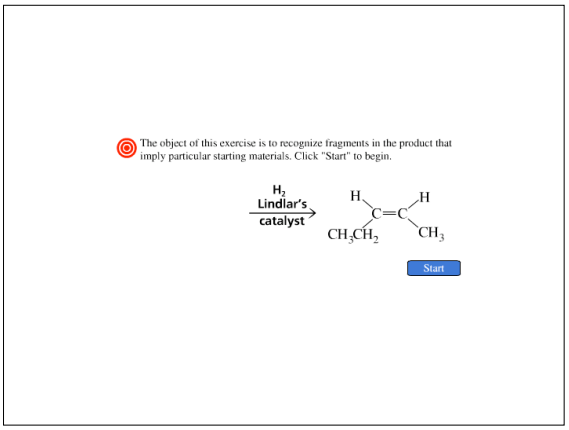
syn-Hydrogenation occurs; cis alkenes are formed.

Example



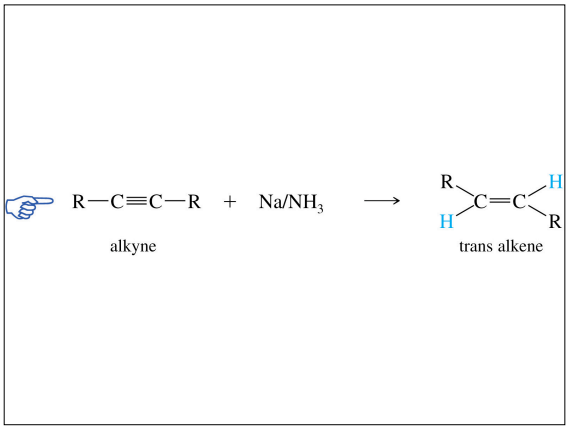
(87%)





Metal-Ammonia Reduction of Alkynes

Alkynes → *trans*-Alkenes



Partial Reduction

$RC{\equiv}CR' \longrightarrow RCH{=}CHR' \not\longrightarrow RCH_2CH_2R'$

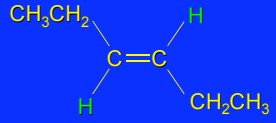
Another way to convert alkynes to alkenes is by reduction with sodium (or lithium or potassium) in ammonia.

trans-Alkenes are formed.

Example

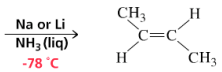
$CH_3CH_2C{\equiv}CCH_2CH_3$

↓ Na, NH_3



(82%)

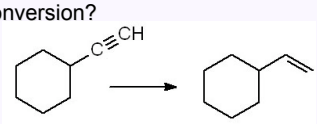
The object of this exercise is to recognize fragments in the product that imply particular starting materials. Click "Start" to begin.



Start

Question

How would you accomplish the following conversion?

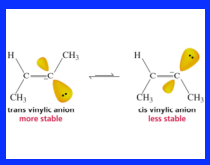


A) $NaNH_2$
B) H_2, Lindlar Pd
C) Na, NH_3
D) either B or C

Mechanism

Metal (Li, Na, K) is reducing agent;
H_2 is not involved; proton comes from NH_3

four steps
(1) electron transfer
(2) proton transfer
(3) electron transfer
(4) proton transfer



Question

Select the most effective way to synthesize *cis*-2-pentene from 1-propyne.

A) 1) $NaNH_2$ 2) CH_3CH_2Br 3) H_2, Pd
B) 1) $NaNH_2$ 2) CH_3Br 3) H_2, Lindlar Pd
C) 1) $NaNH_2$ 2) CH_3CH_2I 3) H_2, Lindlar Pd
D) 1) $NaNH_2$ 2) CH_3CH_2Br 3) Na,NH_3

Answer

Select the most effective way to synthesize *cis*-2-pentene from 1-propyne.

A) 1) $NaNH_2$ 2) CH_3CH_2Br 3) H_2, Pd
B) 1) $NaNH_2$ 2) CH_3Br 3) H_2, Lindlar Pd
C) 1) $NaNH_2$ 2) CH_3CH_2I 3) H_2, Lindlar Pd
D) 1) $NaNH_2$ 2) CH_3CH_2Br 3) Na,NH_3

Question

Which reagent would accomplish the transformation of 3-hexyne into *trans*-3-hexene?

A) H_2/Ni
B) H_2, Lindlar Pd
C) Na, NH_3
D) $NaNH_2$, NH_3

Answer

Which reagent would accomplish the transformation of 3-hexyne into *trans*-3-hexene?

A) H_2/Ni

B) H_2, Lindlar Pd

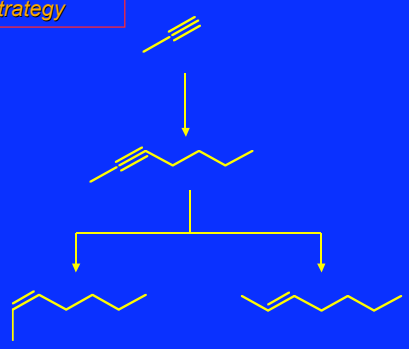
C) Na, NH_3

D) $NaNH_2$, NH_3

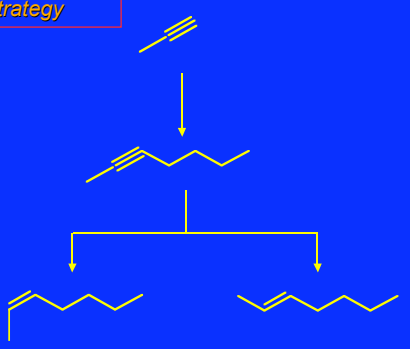
Problem

Suggest an efficient syntheses of (*E*)- and (*Z*)-2-heptene from propyne and any necessary organic or inorganic reagents.

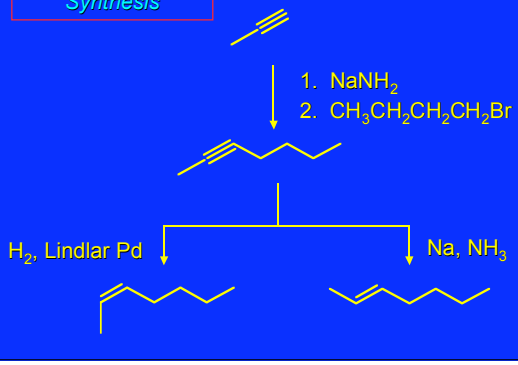
Problem
Strategy



Problem
Strategy



Problem
Synthesis



Question

Which would be the best sequence of reactions to use in order to prepare *cis*-3-nonene from 1-butyne?

A) 1. $NaNH_2$ in NH_3; 2. 1-bromopentane; 3. H_2, Lindlar Pd

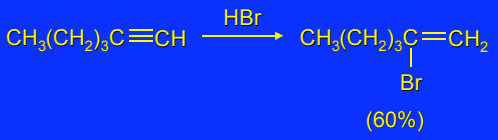
B) 1. $NaNH_2$ in NH_3; 2. 1-bromopentane; 3. Na, NH_3

C) 1. H_2, Lindlar Pd; 2. $NaNH_2$ in NH_3; 3. 1-bromopentane

D) 1. Na, NH_3; 2. $NaNH_2$ in NH_3; 3. 1-bromopentane

Addition of Hydrogen Halides to Alkynes

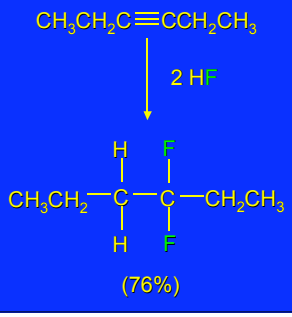
Follows Markovnikov's Rule



(60%)

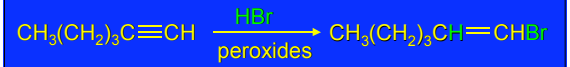
Alkynes are slightly less reactive than alkenes

Two Molar Equivalents of Hydrogen Halide



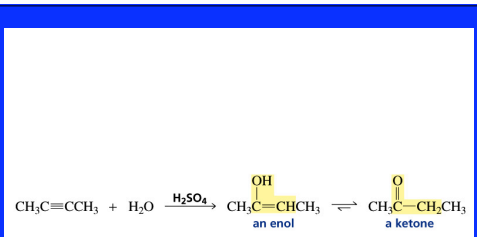
(76%)

Free-radical Addition of HBr



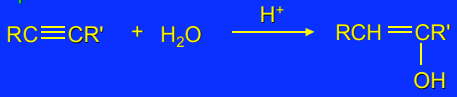
(79%)

regioselectivity opposite to Markovnikov's rule



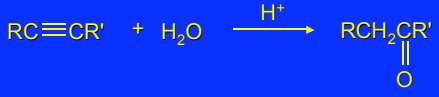
Hydration of Alkynes

expected reaction:



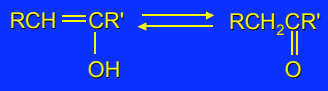
enol

observed reaction:



ketone

Enols



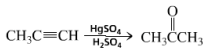
enol *ketone*

enols are regioisomers of ketones, and exist in equilibrium with them

keto-enol equilibration is rapid in acidic media

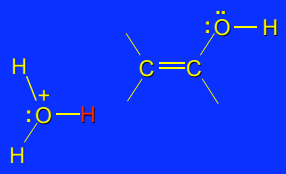
ketones are more stable than enols and predominate at equilibrium

Click "Start" to learn about each step in the mechanism.

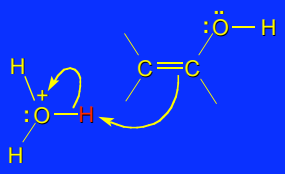


Start

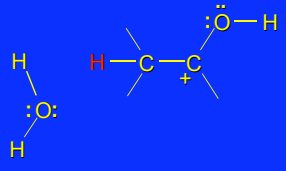
Mechanism of conversion of enol to ketone



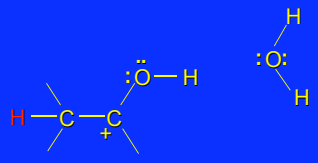
Mechanism of conversion of enol to ketone



Mechanism of conversion of enol to ketone

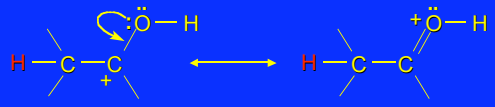


Mechanism of conversion of enol to ketone

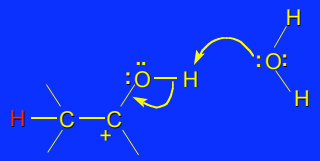


Key Carbocation Intermediate

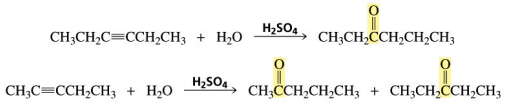
Carbocation is stabilized by electron delocalization (resonance).



Mechanism of conversion of enol to ketone



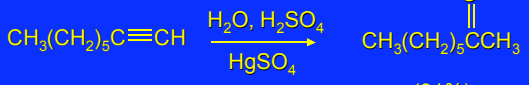
Useful for symmetrical starting alkynes to produce a single product.



Unsymmetrical starting alkynes that are not terminal produce a mixture of ketones…non-regioselectively.

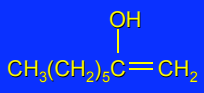
Regioselectivity

Markovnikov's rule followed in formation of enol, Useful with terminal alkynes.

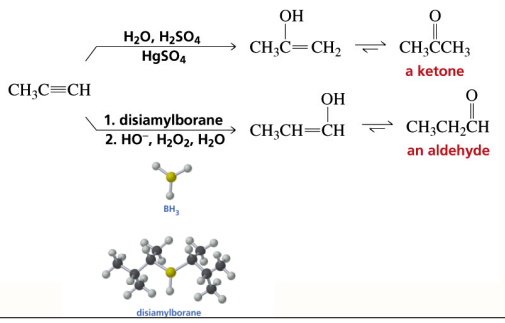


(91%)

via

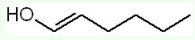


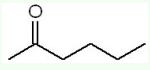
Aldehyde vs. Ketone

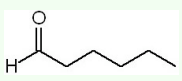


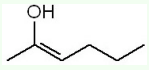
Question

What is the product of the acid catalyzed hydration of 1-hexyne?

A) 

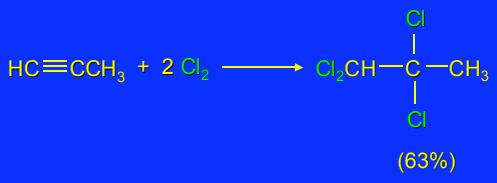
B) 

C) 

D) 

Addition of Halogens to Alkynes

Example



(63%)

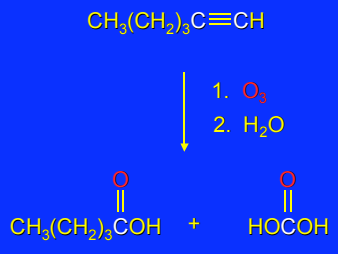
Addition is anti

(90%)

Ozonolysis of Alkynes

gives two carboxylic acids by cleavage of triple bond

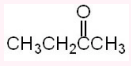
Example

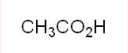


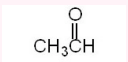
(51%)

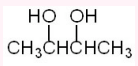
Question

What product is formed when 2-butyne is subjected to ozonolysis?

A) 

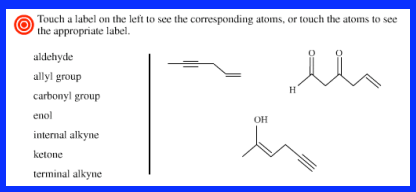
B) 

C) 

D) 

Alkynes
Synthesis & Functions

Can you identify and name the function?



retrosynthetic analysis

$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \Longrightarrow$$

retrosynthetic analysis

$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \Longrightarrow CH_3CH_2C{\equiv}CCH_2CH_3 \Longrightarrow$$

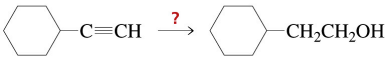
retrosynthetic analysis

$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \Longrightarrow CH_3CH_2C{\equiv}CCH_2CH_3 \Longrightarrow CH_3CH_2C{\equiv}CH$$

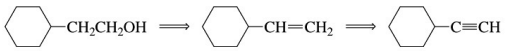
synthesis

$$CH_3CH_2C{\equiv}CH \xrightarrow[2.\ CH_3CH_2Br]{1.\ NaNH_2} CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[H_2SO_4]{H_2O} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$$

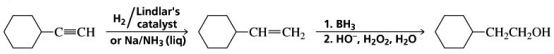
Example



retrosynthetic analysis



synthesis



Question

What is the structure of **Compound Y** in the following synthetic sequence?

A) pentane
B) *cis*-2-pentene
C) *trans*-2-pentene
D) 2-pentyne