SOME FACTS ABOUT TRIPLE BONDS

March 08

3.18

3.19 Orbital Model of a Triple Bond sp Hybridization

- The Structure of Ethyne (Acetylene): *sp* Hybridization
  - Ethyne (acetylene)
    - Propyne is another typical alkyne

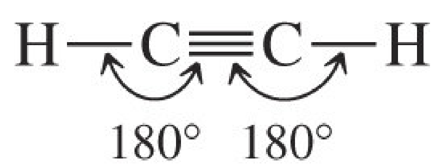
$H-C\equiv C-H$

Ethyne (acetylene) (C_2H_2)

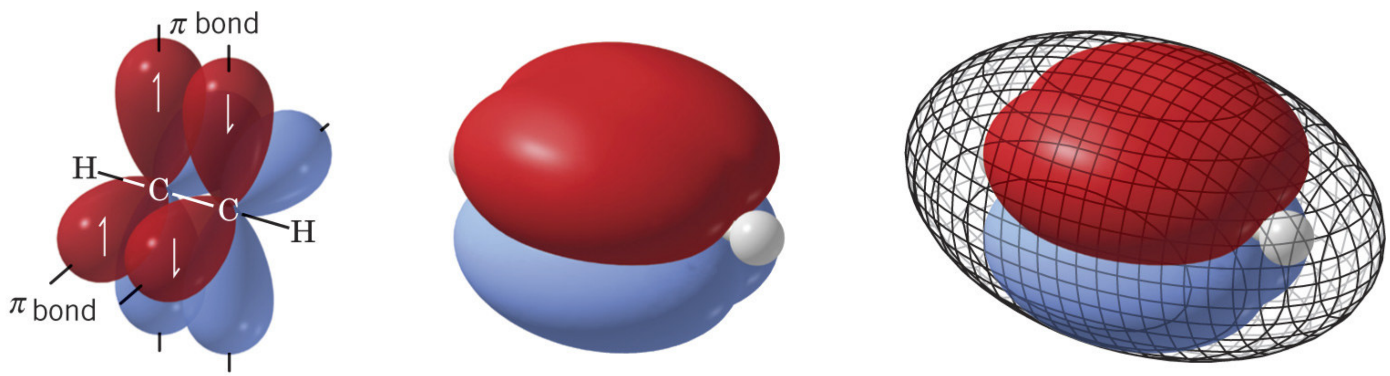
$CH_3-C\equiv C-H$

Propyne (C_3H_4)

  - The arrangement of atoms around each carbon is linear with bond angles 180°

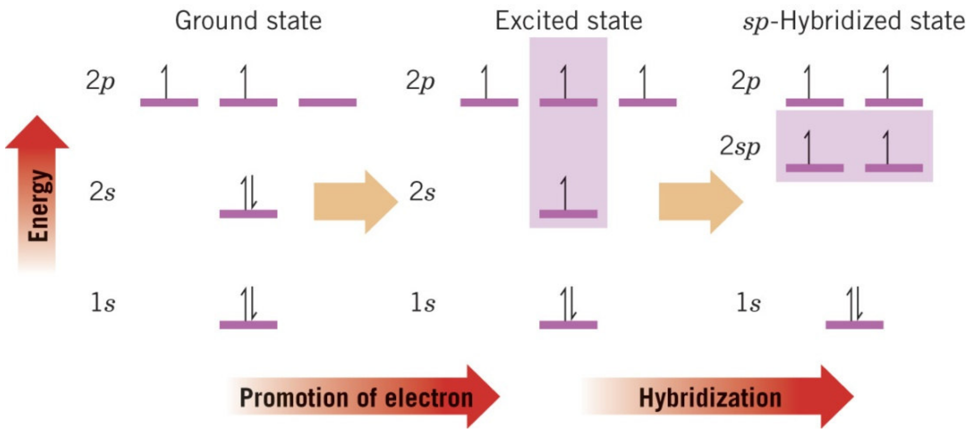


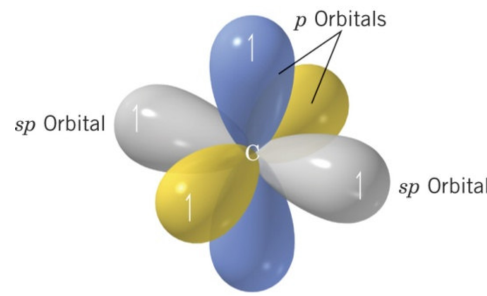
- Depictions of ethyne show that the electron density around the carbon-carbon bond has circular symmetry
  - Even if rotation around the carbon-carbon bond occurred, a different compound would not result



(a) (b) (c)

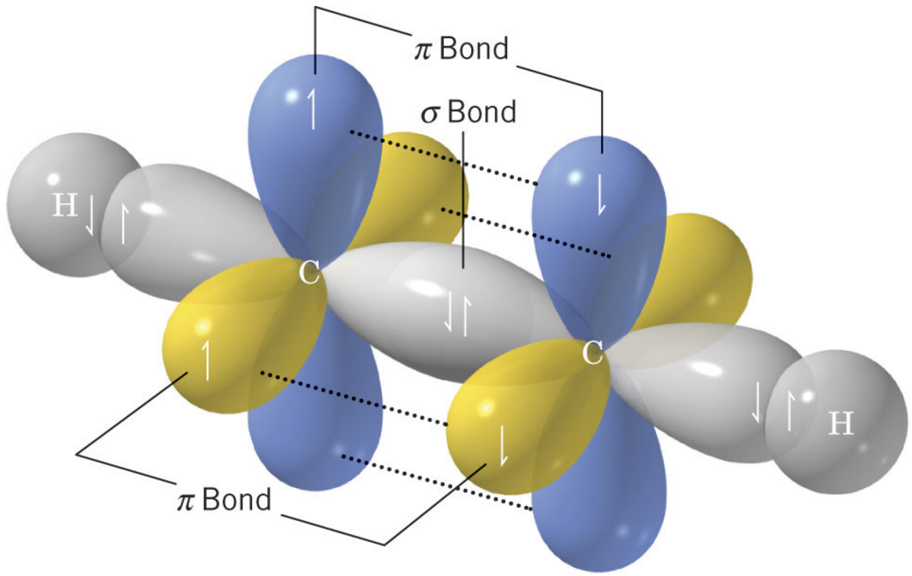
- The carbon in ethyne is *sp* hybridized
  - One *s* and one *p* orbital are mixed to form two *sp* orbitals
  - Two *p* orbitals are left unhybridized





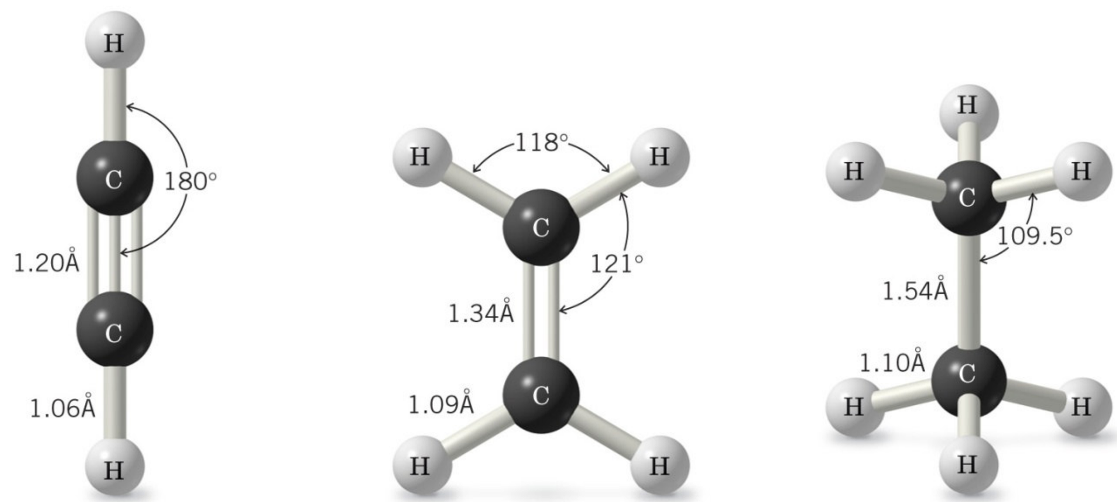
- The two *sp* orbitals are oriented 180° relative to each other around the carbon nucleus
  - The two *p* orbitals are perpendicular to the axis that passes through the center of the *sp* orbitals

- In ethyne the *sp* orbitals on the two carbons overlap to form a σ bond
  - The remaining *sp* orbitals overlap with hydrogen 1s orbitals
- The *p* orbitals on each carbon overlap to form two π bonds
- The triple bond consists of one σ and two π bonds



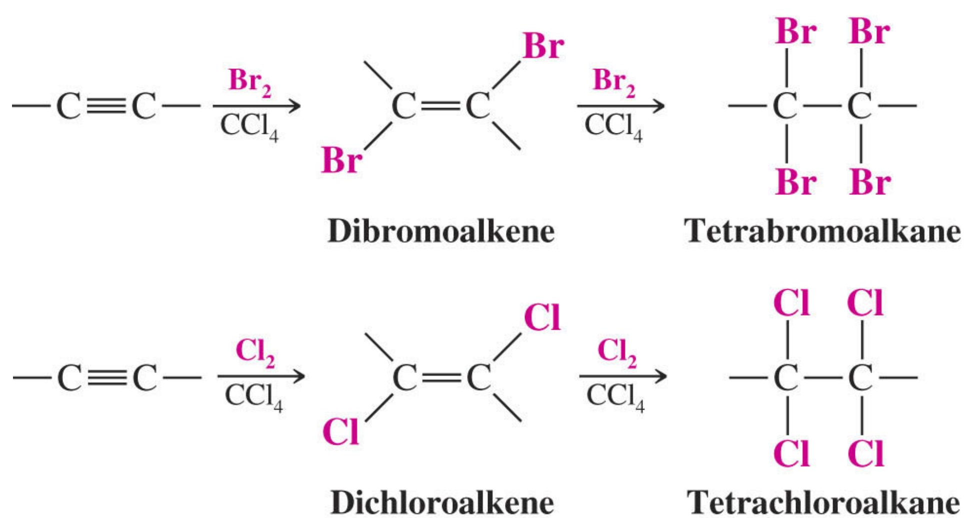
Bond Lengths of Ethyne, Ethene and Ethane

- The carbon-carbon bond length is shorter as more bonds hold the carbons together
  - With more electron density between the carbons, there is more "glue" to hold the nuclei of the carbons together
- The carbon-hydrogen bond lengths also get shorter with more *s* character of the bond
  - 2*s* orbitals are held more closely to the nucleus than 2*p* orbitals
  - A hybridized orbital with more percent *s* character is held more closely to the nucleus than an orbital with less *s* character
  - The *sp* orbital of ethyne has 50% *s* character and its C-H bond is shorter
  - The sp^3 orbital of ethane has only 25% s character and its C-H bond is longer



3.20 Addition Reactions of Alkynes

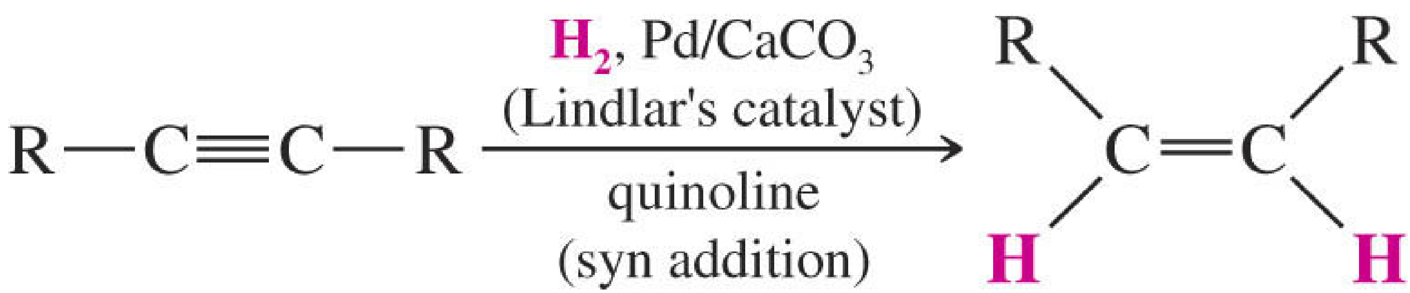
- Addition of Bromine and Chlorine to Alkynes
  - Addition of halogen to alkynes can occur once or twice depending on how many equivalents of the halogen are added
  - Addition of one equivalent usually proceeds to give the trans dihalide



Hydrogenation

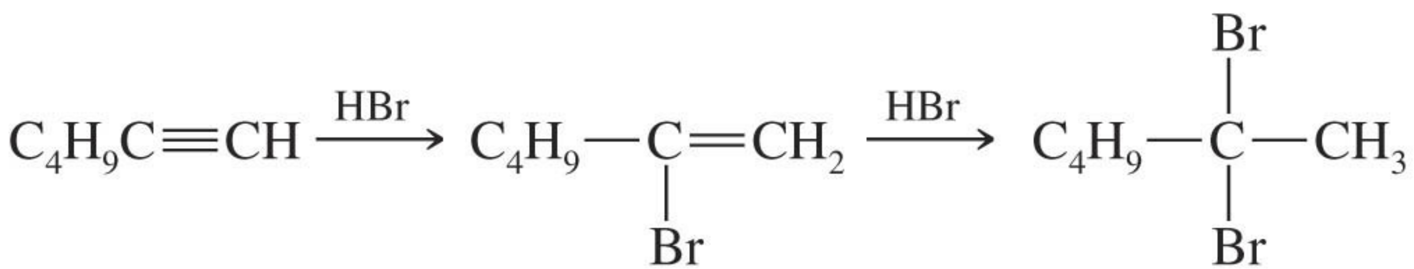
- With ordinary Ni or Pt catalysts, alkynes are hydrogenated all the way to alkanes.

- Lindlar's catalyst produces *cis*-alkenes from alkynes. Only 1 mole H_2 adds.



Addition of Hydrogen Halides to Alkynes

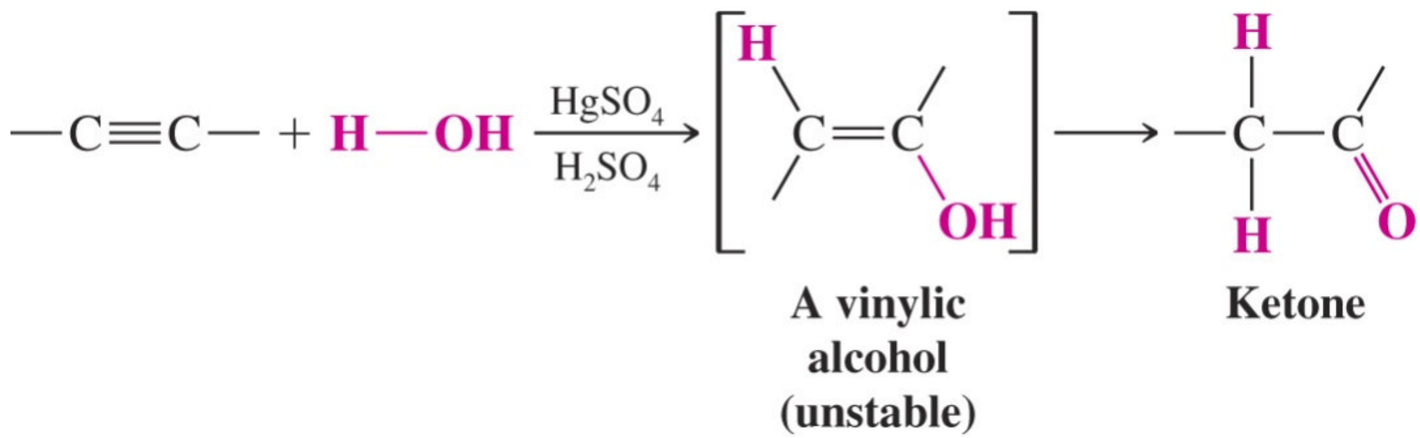
- Addition of hydrogen halides occurs once or twice depending on how many molar equivalent of hydrogen halide are added
- Both additions are Markovnikov and give gem-halides



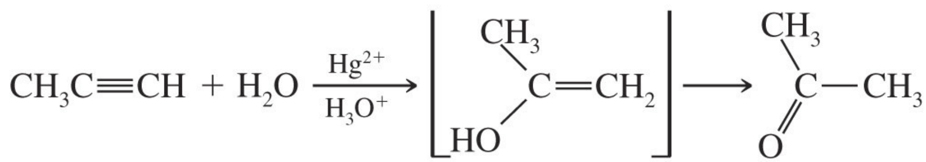
2-Bromo-1-hexene   2,2-Dibromohexane

Addition of Water

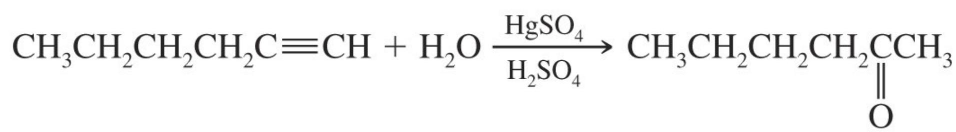
- Addition of water to alkynes requires not only ab acid catalyst but mercuric ion as well.
- Markovnikov hydration of an alkyne initially yields a vinyl alcohol (enol) which then rearranges rapidly to a ketone (keto)



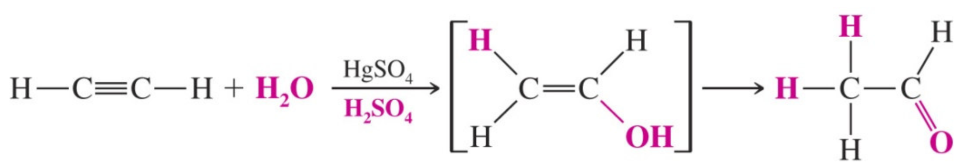
- Terminal alkynes yield ketones because of the Markovnikov regioselectivity of the hydration
  - Ethyne yields acetaldehyde
  - Internal alkynes give mixtures of ketones unless they are symmetrical



Acetone



(80%)

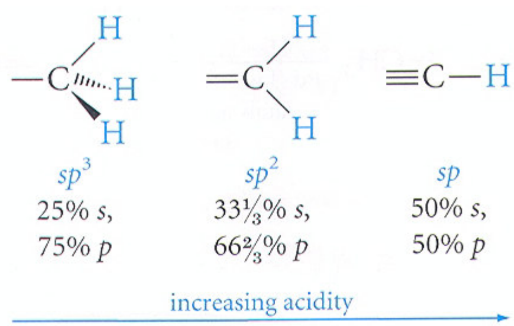


Ethyne

Ethanal (acetaldehyde)

3.21 The Acidity of Terminal Alkynes

- Acetylenic hydrogens have are much more acidic than most other C-H bonds



- Acetylenic hydrogens can be deprotonated with relatively strong bases (sodium amide is typical)
  - The products are called alkynides

$$H{-}C{\equiv}C{-}H + NaNH_2 \xrightarrow{\text{liq. } NH_3} H{-}C{\equiv}C{:}^{-}Na^{+} + NH_3$$

$$CH_3C{\equiv}C{-}H + NaNH_2 \xrightarrow{\text{liq. } NH_3} CH_3C{\equiv}C{:}^{-}Na^{+} + NH_3$$

Solved Problems

PROBLEM 3.29 Write equations for the following reactions:

a. $CH_3C{\equiv}CH + Br_2$ (1 mole)
b. $CH_3C{\equiv}CH + Cl_2$ (2 moles)
c. 1-butyne + HBr (1 and 2 moles)
d. 1-pentyne + H_2O (Hg^{2+}, H^+)

a. $CH_3C{\equiv}CH + Br_2 \longrightarrow CH_3CBr{=}CHBr$

b. $CH_3C{\equiv}CH + 2\,Cl_2 \longrightarrow CH_3CCl_2{-}CHCl_2$

c. $HC{\equiv}CCH_2CH_3 + HBr \longrightarrow CH_2{=}CBrCH_2CH_3$

$HC{\equiv}CCH_2CH_3 + 2\,HBr \longrightarrow CH_3CBr_2CH_2CH_3$

d. $HC{\equiv}CCH_2CH_2CH_3 + H{-}OH \xrightarrow[H^+]{Hg^{++}} CH_3\overset{\overset{\large O}{\|}}{C}CH_2CH_2CH_3$

PROBLEM 3.30 Write an equation for the reaction of 1-hexyne with sodium amide in liquid ammonia.

$$CH_3(CH_2)_3C{\equiv}C{-}H \quad + \quad NaNH_2 \longrightarrow CH_3(CH_2)_3C{\equiv}C^- \; Na^+ \quad + \quad NH_3$$

PROBLEM 3.31 Write an equation for the reaction of a sodium acetylide with water.

$$HC{\equiv}C^- \; Na^+ \quad + \quad H_2O \longrightarrow HC{\equiv}CH \quad + \quad NaOH$$

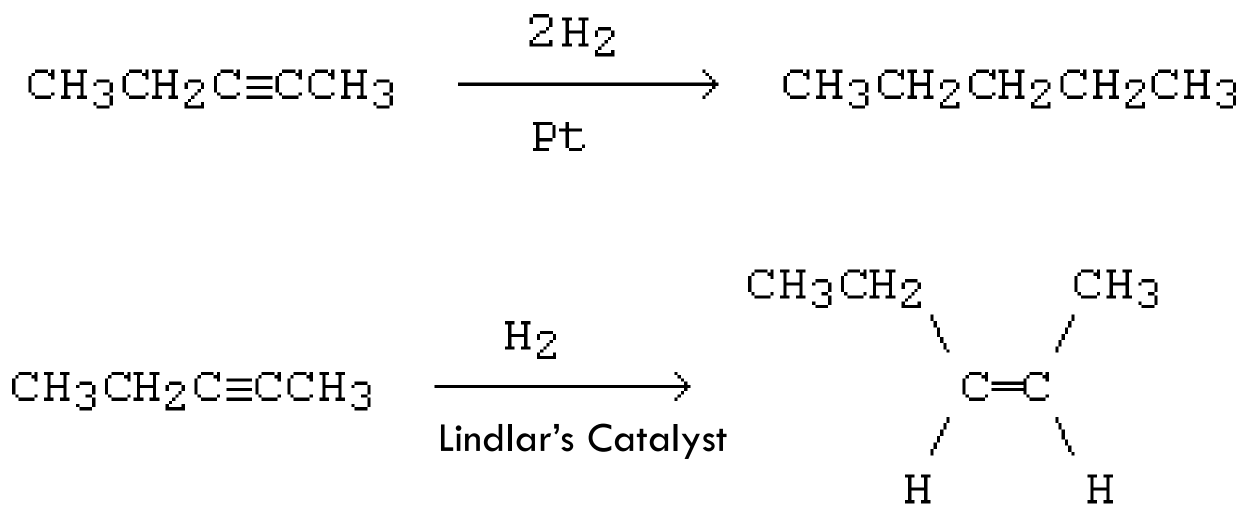
PROBLEM 3.32 Will 2-butyne react with sodium amide? Explain.

2-Butyne has no hydrogens on the triple bond:

$$CH_3C{\equiv}CCH_3$$

Therefore, it does not react with sodium amide.

Which of the following reductions of an alkyne is NOT correct?



All Correct

What characteristic(s) of alkynes would make it difficult to prepare cyclohexyne?

1. The requirement for linearity at the triple bond center
2. The large electron density between carbons of a triple bond
3. The short carbon-carbon triple bond length
4. The need that the carbon-carbon triple bond be internal in the chain
5. All of these

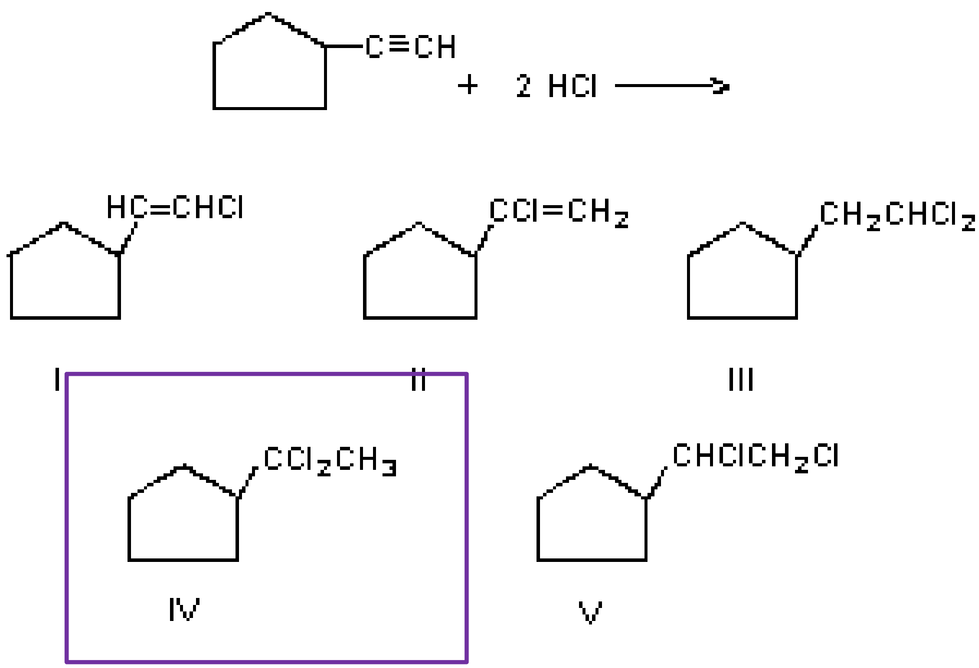
Which of these compounds will react with each of these reagents?

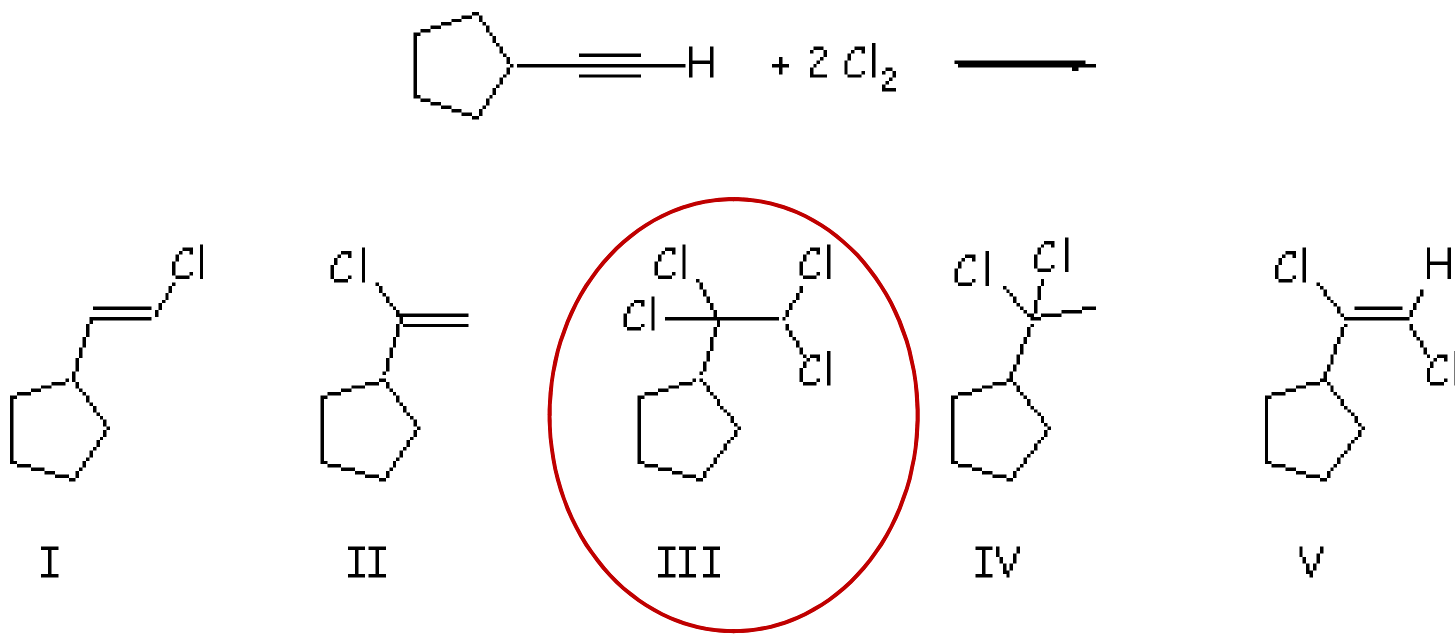
cold concd. H_2SO_4

Br_2 in CCl_4

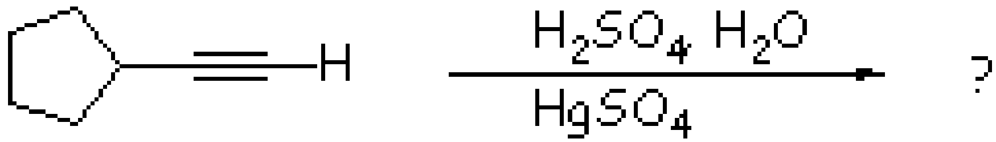
1. $CH_3CH_2CH{=}CHCH_3$
2. $CH_3CH_2CH_2CH{=}CH_2$
3. $CH_3CH_2C{\equiv}CCH_3$
4. $(CH_3)_2CHC{\equiv}CH$
5. All of these

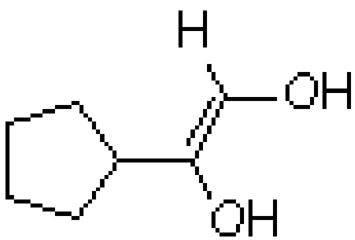
Select the structure of the major product formed in the following reaction.



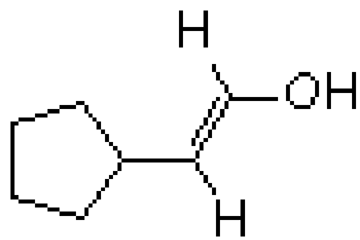


I II III IV V

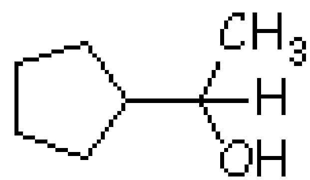




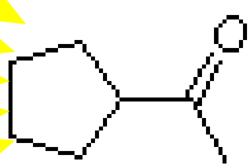
I



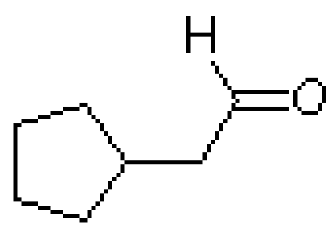
II



III



IV



V

End of Chapter 3

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