

## 9.5: REDUCTION OF ALKYNES

### OBJECTIVES

After completing this section, you should be able to

1. write equations for the catalytic hydrogenation of alkynes to alkanes and *cis* alkenes.
2. identify the reagent and catalyst required to produce a given alkane or *cis* alkene from a given alkyne.
3. identify the product formed from the reaction of a given alkyne with hydrogen and a specified catalyst.
4. identify the alkyne that must be used to produce a given alkane or *cis* alkene by catalytic hydrogenation.
5. write the equation for the reduction of an alkyne with an alkali metal and liquid ammonia.
6. predict the structure of the product formed when a given alkyne is reduced with an alkali metal and liquid ammonia.
7. identify the alkyne that must be used to produce a given alkene by reduction with an alkali metal and ammonia.

### KEY TERMS

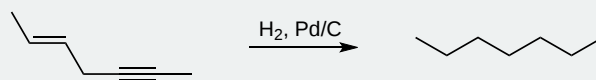
Make certain that you can define, and use in context, the key terms below.

- anion radical
- Lindlar catalyst

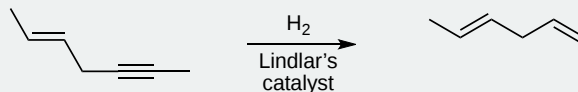
### STUDY NOTES

The Lindlar catalyst allows a chemist to reduce a triple bond in the presence of a double bond.

Thus

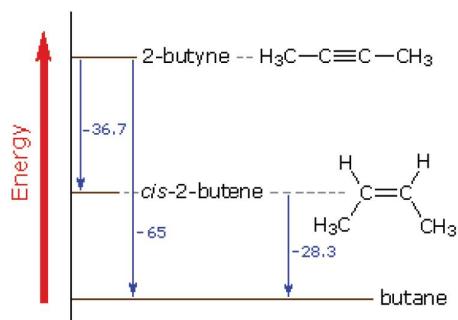


but



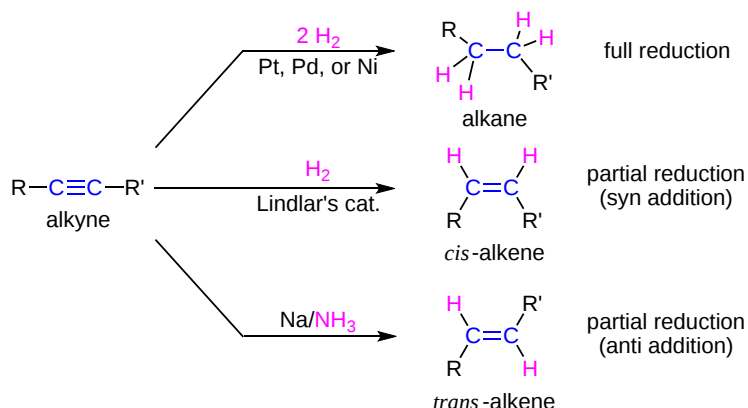
### HYDROGENATION AND THE RELATIVE STABILITY OF HYDROCARBONS

Like alkenes, alkynes readily undergo catalytic hydrogenation partially to *cis*-alkenes or fully to alkanes depending on the reaction employed.



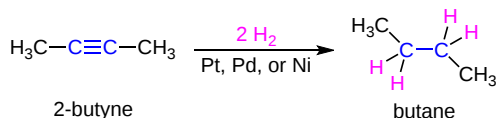
The catalytic addition of hydrogen to 2-butyne provides heat of reaction data that reflect the relative thermodynamic stabilities of these hydrocarbons, as shown above. From the heats of hydrogenation, shown in blue in units of kcal/mole, it would appear that alkynes are thermodynamically less stable than alkenes to a greater degree than alkenes are less stable than alkanes. The standard bond energies for carbon-carbon bonds confirm this conclusion. Thus, a double bond is stronger than a single bond, but not twice as strong. The difference (63 kcal/mole) may be regarded as the strength of the  $\pi$ -bond component. Similarly, a triple bond is stronger than a double bond, but not 50% stronger. Here the difference (54 kcal/mole) may be taken as the strength of the second  $\pi$ -bond. The 9 kcal/mole weakening of this second  $\pi$ -bond is reflected in the heat of hydrogenation numbers ( $36.7 - 28.3 = 8.4$ ).

Alkynes can undergo reductive hydrogenation reactions similar to alkenes. Due to the presence of two pi bonds within alkynes, reductive hydrogenation reactions can be partial to form an alkene or complete to form an alkane. Since partial reductive hydrogenation of an alkyne produces an alkene, the stereochemistry provided by the reaction's mechanism determines whether a *cis*- or *trans*- alkene is formed. The three most significant alkyne reduction reactions are summarized below:

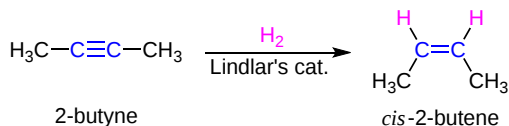


## CATALYTIC HYDROGENATION OF AN ALKYNE

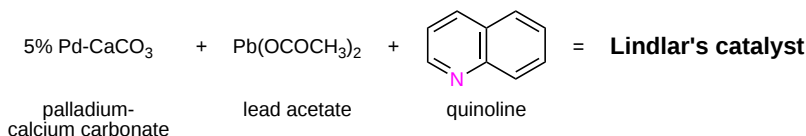
Much like alkenes, alkynes can be fully hydrogenated into alkanes with the help of a platinum, palladium, or nickel catalyst. Because the reaction is catalyzed on the surface of the metal, it is common for these catalysts to be dispersed on carbon (Pd/C) or finely dispersed, such as Raney-Ni. The presence of two pi bonds in the alkyne causes two equivalents of  $H_2$  to be added during the reaction. An alkene intermediate is formed during the reaction but is not isolated.



For catalytic hydrogenation, the Pt, Pd, or Ni catalysts are so effective in promoting the addition of hydrogen to carbon-carbon triple bonds that the alkene intermediate formed cannot be isolated. A less efficient **Lindlar's catalyst**, permits alkynes to be converted to alkenes without further reduction to an alkane. Lindlar's Catalyst transforms an alkyne to a *cis*-alkene because both hydrogen atoms are added to the same side of the alkyne (syn) as shown in the in the previous chapter.

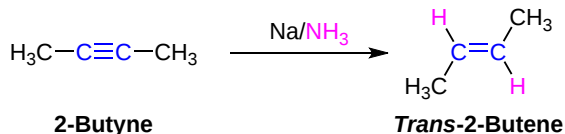


Lindlar's catalyst is prepared by deactivating (or poisoning) a conventional palladium catalyst. Lindlar's catalyst has three components: palladium-calcium carbonate, lead acetate, and quinoline. The quinoline serves to prevent complete hydrogenation of the alkyne to an alkane.



## HYDROGENATION OF AN ALKYNE TO A TRANS-ALKENE

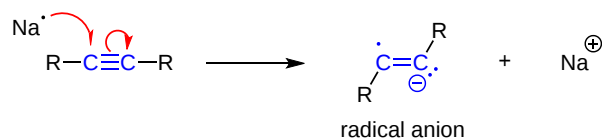
The anti-addition of hydrogen to an alkyne pi bond occurs through reaction with sodium or lithium metal dissolved in ammonia. This reaction, also called a **dissolving metal reduction**, involves a radical mechanism, and produces a *trans*-alkene product.



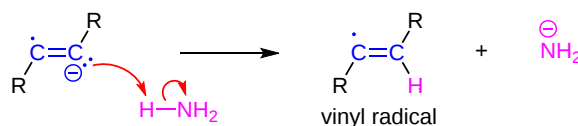
## MECHANISM

Sodium metal is a powerful reducing agent due to the presence of a  $3s^1$  electron in its valence shell. Sodium metal easily gives up this electron to become  $\text{Na}^+$ . The mechanism starts with a sodium atom donating an electron to the alkyne to create an intermediate with a negative charge and an unpaired electron called a radical anion. Next the amine solvent protonates the anion to create a vinyl radical. A second sodium atom then donates an electron to pair the radical to form a vinyl anion. This vinyl anion intermediate rapidly interconverts between *cis* and *trans* conformations and determines the stereochemistry of the reaction. The *trans*-vinyl anion is more stable due to reduced steric crowding and is preferentially formed. Finally, the protonation of the *trans*-vinyl anion creates the *trans*-alkene product.

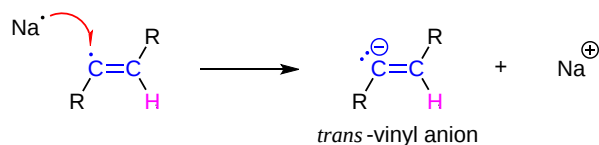
### Step 1: Electron Donation



### Step 2: Protonation



### Step 3: Electron Donation

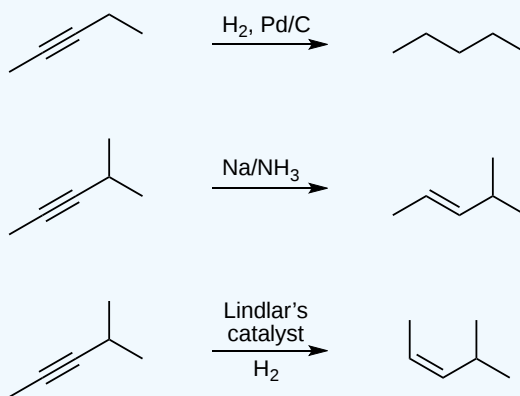


### Step 4: Protonation

## ? EXERCISE 9.5.1

Using any alkyne how would you prepare the following compounds: pentane, *trans*-4-methyl-2-pentene, *cis*-4-methyl-2-pentene.

Answer



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