

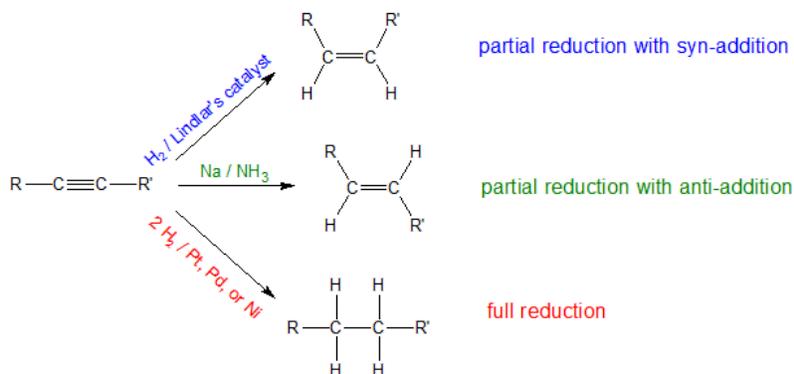
10.6: 10.6 REDUCTION OF ALKYNES

Learning Objective

- predict the products and specify the reagents for the full or partial reduction of alkynes

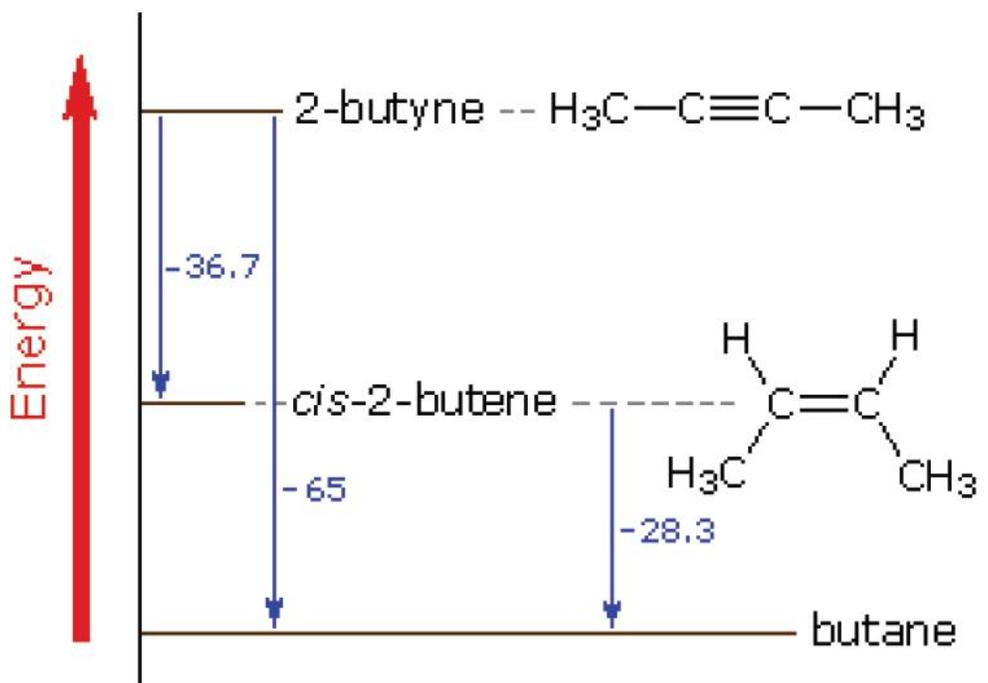
INTRODUCTION AND OVERVIEW

Alkynes can undergo reduction reactions similar to alkenes. These reactions are also called hydrogenation reactions. With the presence of two pi bonds within the carbon-carbon triple bonds, the reduction reactions can be partial or complete depending on the reagents. Since partial reduction of an alkyne produces an alkene, the stereochemistry of the addition mechanism determines whether the cis- or trans-alkene is formed. The three most significant alkyne reduction reactions are summarized below.



HYDROGENATION AND THE RELATIVE STABILITY OF HYDROCARBONS

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

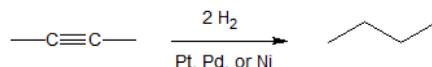


The catalytic addition of hydrogen to 2-butyne provides heat of reaction data that reflect the relative thermodynamic stabilities of these hydrocarbons, as shown above. From the heats of hydrogenation, shown in blue in units of kcal/mole, it would appear that alkynes are thermodynamically less stable 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 π -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 π -bond. The 9 kcal/mole weakening of this second π -bond is reflected in the heat of hydrogenation numbers (36.7 - 28.3 = 8.4).

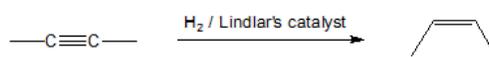
CATALYTIC HYDROGENATION OF AN ALKYNE

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 as nickel (Raney-Ni). The full reduction of 2-butyne is shown below as an example.

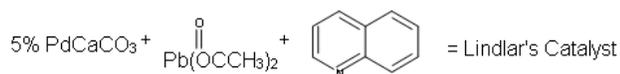


HYDROGENATION OF AN ALKYNE TO A CIS-ALKENE

Since alkynes are thermodynamically less stable than alkenes, we expect addition reactions of alkynes to be more exothermic and relatively faster than equivalent reactions of alkenes. For catalytic hydrogenation, the Pt, Pd, or Ni catalysts are so effective in promoting addition of hydrogen to both double and triple carbon-carbon bonds that the alkene intermediate formed by hydrogen addition to an alkyne cannot be isolated. A less efficient catalyst, 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 the hydrogenation reaction is occurring on the surface of the metal. Both hydrogen atoms are added to the same side of the alkyne as shown in the syn-addition mechanism for hydrogenation of alkenes in the previous chapter.

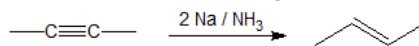


Lindlar's catalyst is prepared by deactivating (or poisoning) a conventional palladium catalyst. Lindlar's catalyst has three components: palladium-calcium carbonate, lead acetate and quinoline. The quinoline serves to prevent complete hydrogenation of the alkyne to an alkane. This approach is similar to the one used for hydration of alkynes using a dialkyl borane for hydroboration. A strong reagent is modified into a less reactive form.

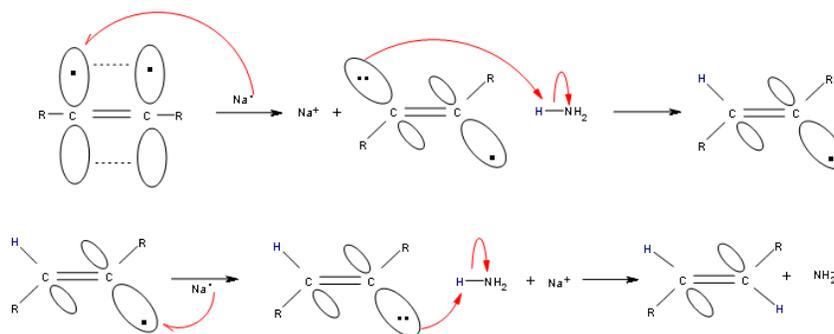


HYDROGENATION OF AN ALKYNE TO A TRANS-ALKENE

Alkynes can be reduced to trans-alkenes with the use of sodium dissolved in an ammonia solvent. A sodium radical donates an electron to one of the p-orbitals in the carbon-carbon triple bond. This reaction forms an anion that can be protonated by a hydrogen atom in the ammonia solvent which prompts another sodium radical to donate an electron to the second p-orbital. The resulting anion is also protonated by a hydrogen from the ammonia solvent to produce a trans-alkene according to the mechanism shown below.



Mechanism for Hydrogenation of Alkynes to trans-Alkenes

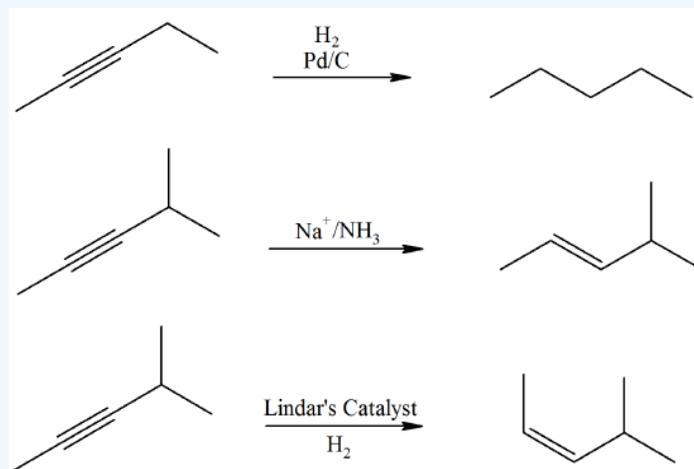


Exercise

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

Answer

1.


CONTRIBUTORS

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