

STUDY GUIDE FOR CHAPTER 9

1. Nomenclature of Alkynes – alkynes are molecules with triple carbon – carbon bonds. The triple bond introduces two elements of unsaturation in the alkyne molecule.
 - A. As in the case of alkenes, one seeks the longest chain, containing the triple bond, for the base of the name. Numbering from the terminus closer to the triple bond. If equidistant, from the terminus closer to a substituent.
 - B. Alkynes with the triple bond at position 1 are called *terminal alkynes*. All other are called *internal alkynes*.
 - C. If more than one functional group is present, one can form names with combined endings – enynes (double and triple bond), endiynes (double + two triple bonds), etc.
 - D. Substituent Groups – they are called alkynyl groups (ethynyl, propynyl, etc.)
 - E. Trivial names – they are based on the word acetylene. Terminal alkynes are then considered alkylacetylenes, while internal alkynes are dialkylacetylenes. It is useful when naming materials with ring sub-structures – phenylacetylene, cyclohexylacetylene, etc.
2. Physical Properties of Alkynes – very similar to alkanes and alkenes. Alkynes are also hydrocarbons, with weak London forces between molecules. Bp gradually increases with increasing size of the molecule.
3. Commercial Use and Preparation of Acetylene.
 - A. It is used as a fuel in the welding torch, since it gives the highest amount of heat per mole of products, thus achieving the highest temperature of the products.
 - B. Acetylene is prepared from calcium carbide in reaction with water. It can also be made by a very short duration, high temperature pyrolysis of methane (natural gas). The latter reaction is driven by the large positive entropy change, even though it is endothermic.
4. Electronic Structure. The Triple Bond.
 - A. Triple bond consists of $1\sigma + 2\pi$ bonds. The two π -bonds are in mutually perpendicular planes.
 - B. The triple bond is much shorter, which is partially due to the high *s*-character of the *sp*-hybrid orbitals. Electrons are held closer to the nucleus and more tightly if the corresponding orbital has a higher *s*-character (i.e. higher percentage of *s*-participation). The *s*-character increases from 25% for sp^3 to 33% for sp^2 to 50% for *sp*. The bond between the *sp*-C and hydrogen also becomes shorter.
5. Acidity of Alkynes.
 - A. As explained earlier (see handout for acids and bases strength) the increased *s*-character of the *sp*-orbital makes it capable of stabilizing negative charge to an extent that makes alkynes much more acidic, compared to the rest of the hydrocarbons. Acetylene is at least 10^{25} times as acidic as ethane and 10^{19} times more acidic than ethylene. In fact it is about 10^{10} (difference of pK's is about 10!) more acidic than ammonia, which makes it possible to react terminal alkynes with the conjugate base of ammonia, the amide anion, to produce the conjugate base of the alkyne, the acetylide anion, and a molecule of ammonia. The acetylide anion is in the form of an alkaline metal salt (usually sodium or potassium). **REMEMBER:** Only terminal alkynes are acidic, since they have hydrogen directly bound to an *sp*-carbon.
6. Synthesis of Alkynes.
 - A. From Acetylides.
 - 1) Alkylation of Acetylide Anions – these anions are powerful nucleophiles and enter readily into S_N2 reactions with methyl, primary or secondary halides. Secondary halides give a mixture of substitution and elimination products. Tertiary halides give only elimination products.
 - B. Via Elimination Reactions.

- 1) Strong bases can eliminate two molecules of HX from *geminal or vicinal dihalides*, to give alkynes. If the base is very strong, such as NaNH_2 , then the terminal alkyne is deprotonated and thus taken out of the equilibrium process.
7. Reactions of Alkynes – much like the double bond, the triple bond is also an electron donor and enters into a variety of reactions of electrophilic addition.
- A. Hydrogenation (Reduction) of Alkynes.
 - 1) Exhaustive hydrogenation – this is the process of conversion of alkynes to alkanes, i.e. full (exhaustive) saturation. Achieved by transition metal catalysts – Pt, Pd, Ni.
 - 2) Hydrogenation to *cis*-alkenes – the above process of exhaustive hydrogenation occurs via an alkene as an intermediate, but the latter is not isolated and reacts further in these conditions. To stop the reaction at the alkene stage, one needs to “poison” the catalyst, i.e. reduce its activity. One way to achieve this is by coating some powdered BaSO_4 with Pd (the catalyst) and poisoning it with quinoline. The resultant combination of some 10% Pd over CaCO_3 + quinoline + lead acetate is known as the Lindlar’s catalyst. The hydrogenation does not go beyond the alkene stage. And since the mechanism is again a surface promoted bond dissociation followed by addition to the triple bond, the result is an alkene derived via syn-addition of hydrogen.
 - 3) Hydrogenation to *trans*-alkenes – it is done by the action of alkaline metal (usually sodium) in liquid ammonia. The actual reagent is the solvated electron. The intermediate is a vinyl radical anion. Since the latter is a disubstituted alkene-type species, its more stable form is the trans, leading to a *trans*-alkene.
 - B. Polar addition reactions.
 - 1) Addition of Hydrogen Halides.
 - a. The polar addition obeys the Markovnikov rule. The intermediate product is a haloalkene. The second molecule adds also according to the Markovnikov rule, to give a *geminal (gem)* dihaloalkane.
 - b. The radical addition of HBr is also possible, with an anti-Markovnikov product.
 - 2) Addition of Water to Alkynes (Hydration of Alkynes).
 - a. It is a process catalyzed by acids and mercuric salts. The initial electrophilic attack is by the mercuric cation.
 - b. The product of addition of ONE molecule of water is an *enol*. The enols are usually unstable and quickly rearrange (catalyzed by the acid) to the more stable *keto* form. This is a typical tautomeric equilibrium (tautomerism).
 - c. Since water adds according to the Markovnikov rule, the end product (the keto form) is always a ketone (You cannot make an aldehyde this way!!). The only exception is acetylene.
 - 3) Addition of halogen – first product is a dihaloalkene (usually E, so some stereospecificity!!). Often the reaction goes on further to a tetrahaloalkane.
 - C. Radical addition of HBr – possible when peroxides are present. Leads to anti-Markovnikov product.
 - D. Ozonolysis.
 - 1) Ozonolysis, followed by hydrolysis, also leads to the complete cleavage of the triple bond, producing two carboxylic acid molecules.