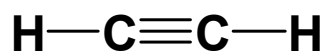


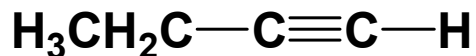
ALKYNES

Alkynes

- Alkynes general formula is C_nH_{2n-2} and alkynes contain **carbon-carbon triple bond**.
- **Terminal alkynes** have a triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond. $R-C\equiv C-H$, and the $H-C\equiv C-H$ are described as "*terminal*" alkynes
- **Internal alkynes** have a carbon atom bonded to each carbon atom of the triple bond. $R-C\equiv C-R'$, are described as "*internal*" alkynes



Ethyne



1-Butyne

Terminal alkyne



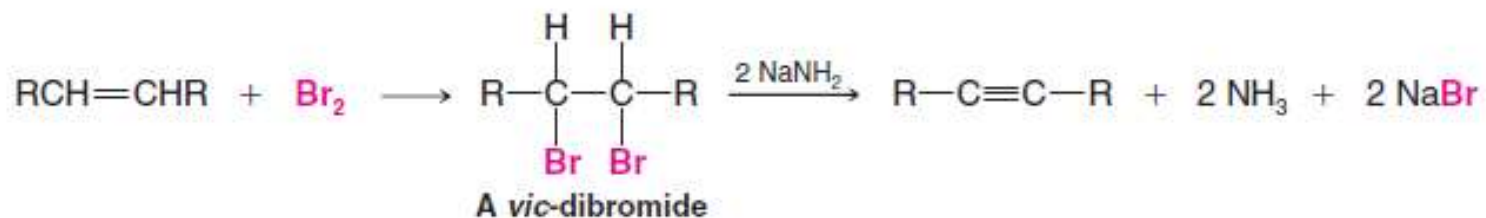
2-Butyne

Internal alkyne

Synthesis of Alkynes by Elimination Reactions

1. From alkenes / vicinal dibromides:

Alkynes can be synthesized from alkenes via compounds called vicinal dihalides. A vicinal dihalide is a compound bearing the halogens on adjacent carbons. A vicinal dibromide, for example, can be synthesized by addition of bromine to an alkene. The vic-dibromide can then be subjected to a double dehydrohalogenation reaction with a strong base to yield an alkyne



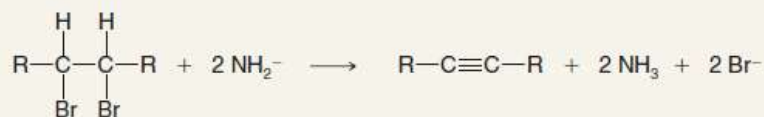
Mechanism of the reaction: NaNH₂ is a very strong base



A MECHANISM FOR THE REACTION

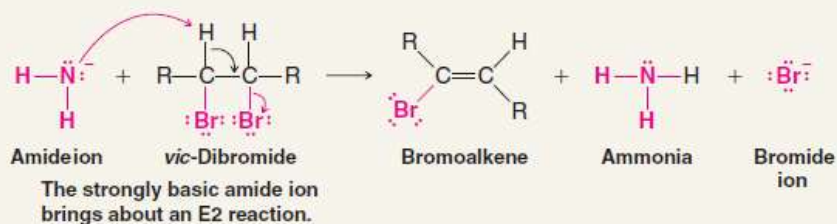
Dehydrohalogenation of vic-Dibromides to Form Alkynes

REACTION

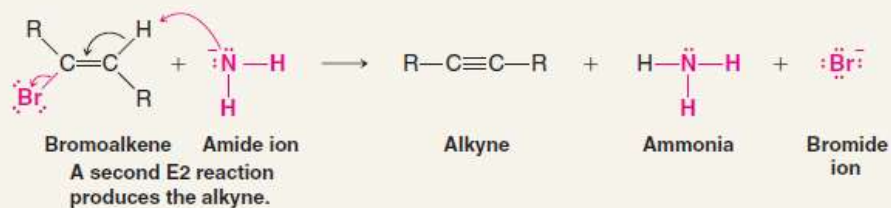


MECHANISM

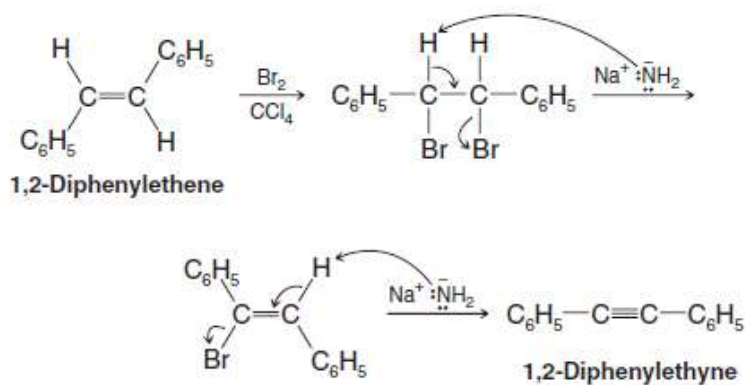
Step 1



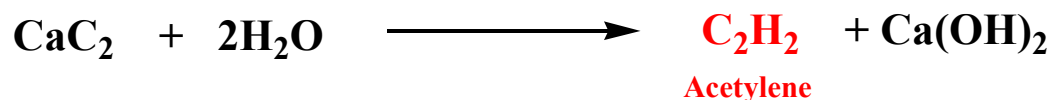
Step 2



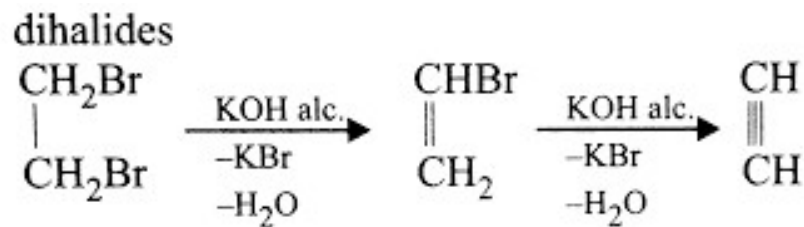
Example



2. By the action of water on calcium carbide

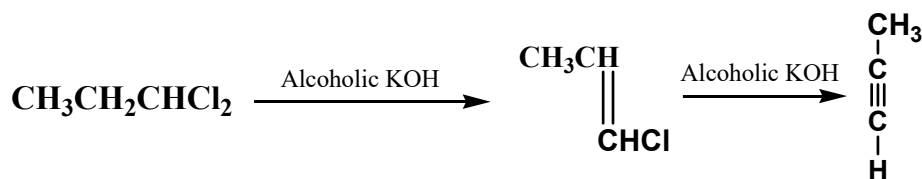
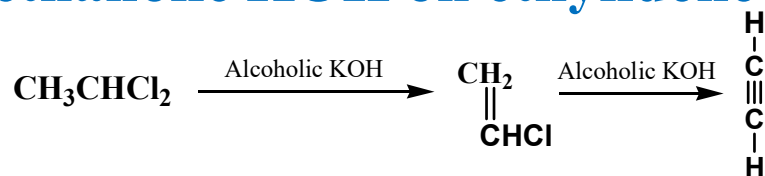


3. By the action of ethanolic KOH on ethylene dibromide



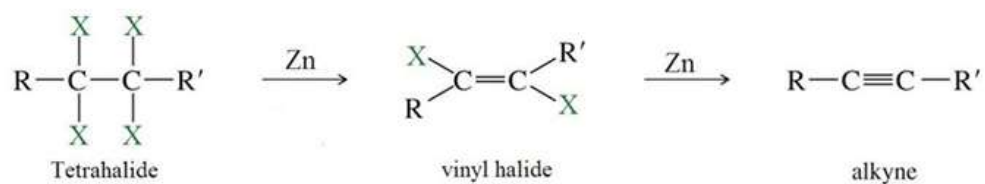
✓ Sodamide can also be used at the place of ethanolic KOH Solution

4. By the action of ethanolic KOH on ethylidene dichloride (*geminal dihalides*)

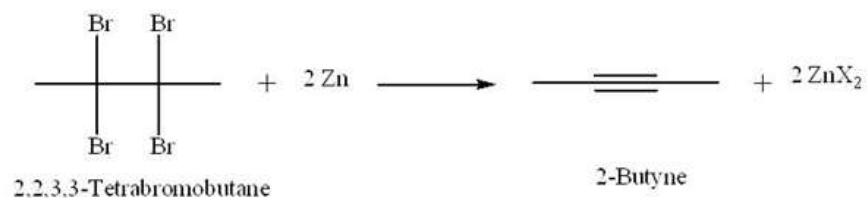


5. From tetrahalides

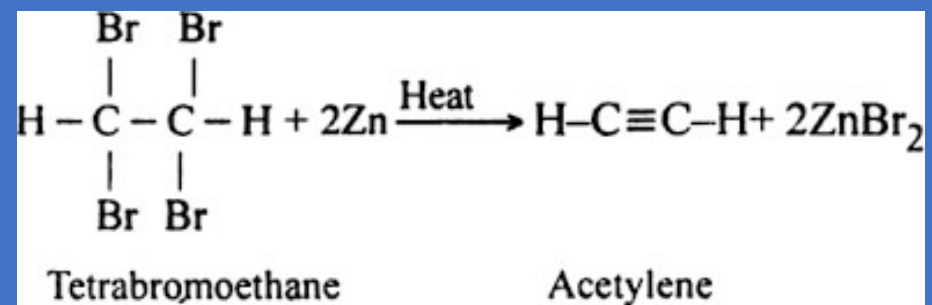
General Examples



Example:

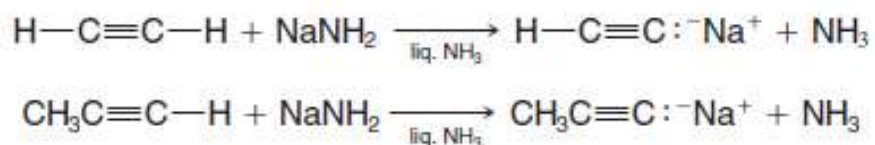


Synthesis of acetylene



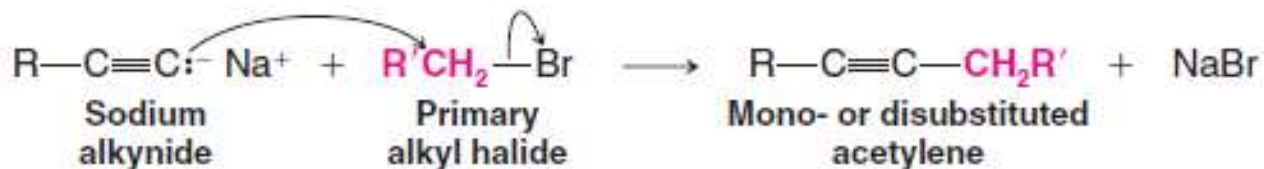
6. Substitution of the Acetylenic Hydrogen Atom of Terminal Alkynes: *Conversion of terminal alkynes into internal alkynes*

Sodium ethynide and other **sodium alkynides** can be prepared by treating terminal alkynes with sodium amide in liquid ammonia:



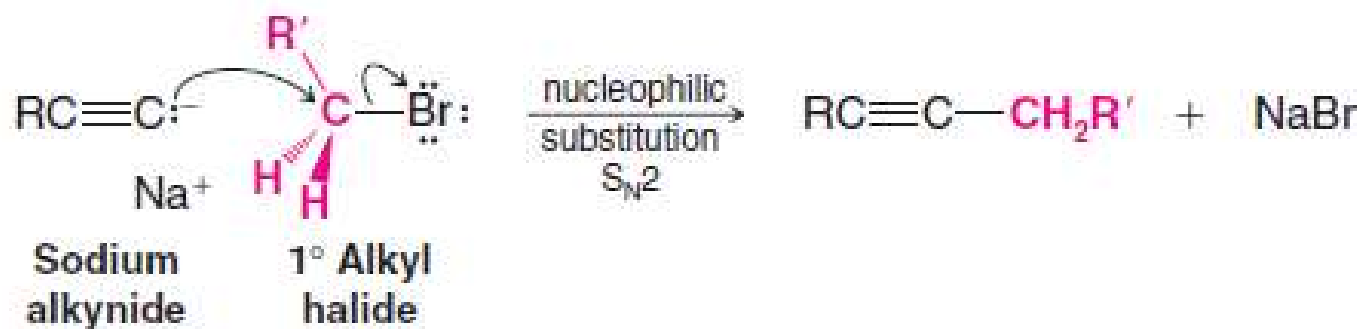
Remember: Na / liq. NH₃ can also be used.

These are acid–base reactions. The amide ion, by virtue of its being the anion of a very weak acid, ammonia ($pK_a = 38$), is able to remove the acetylenic protons of terminal alkynes ($pK_a = 25$). These reactions, for all practical purposes, go to completion. Sodium alkynides are useful intermediates for the synthesis of other alkynes. These syntheses can be accomplished by treating the sodium alkynide with a primary alkyl halide:



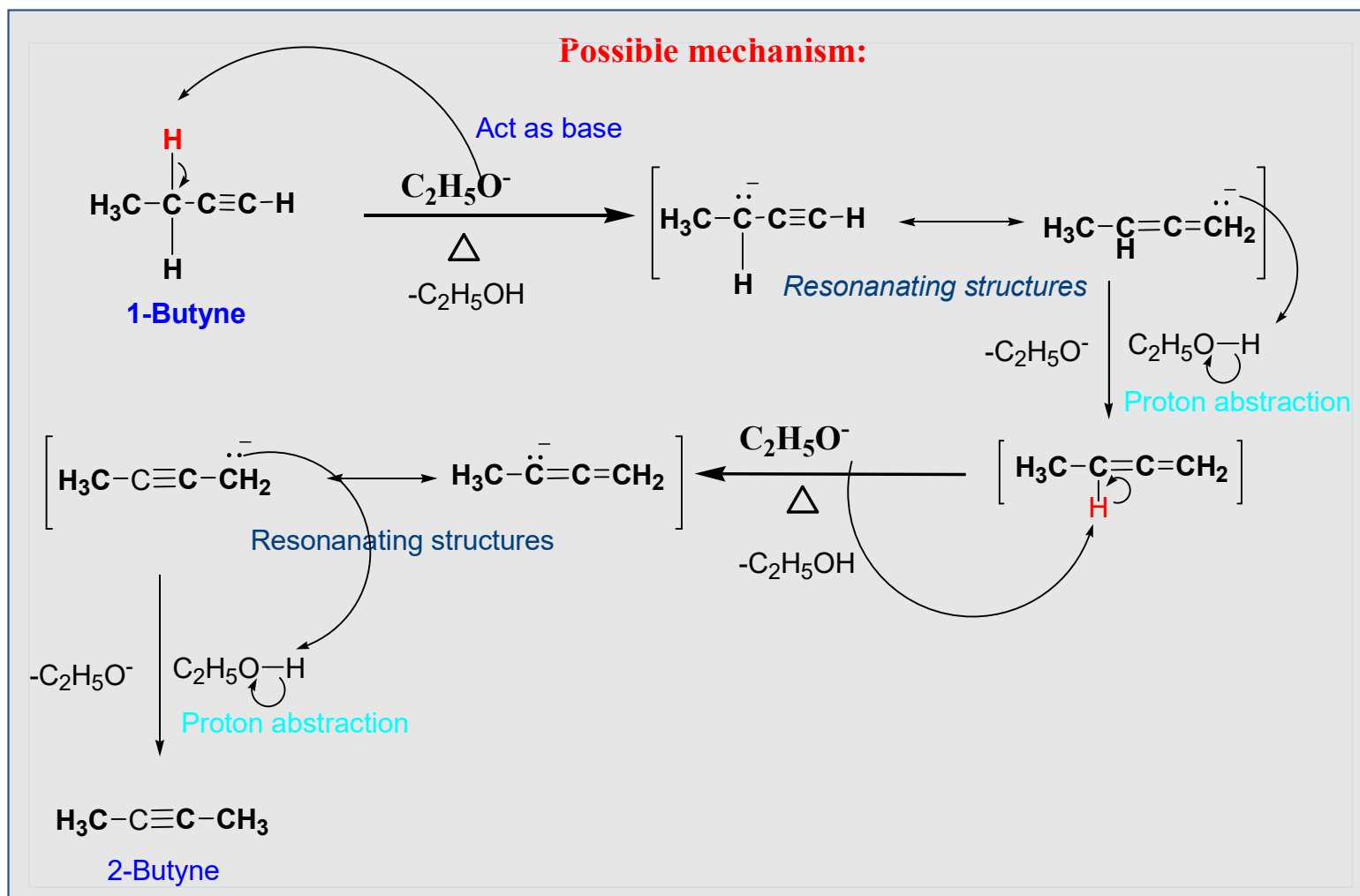
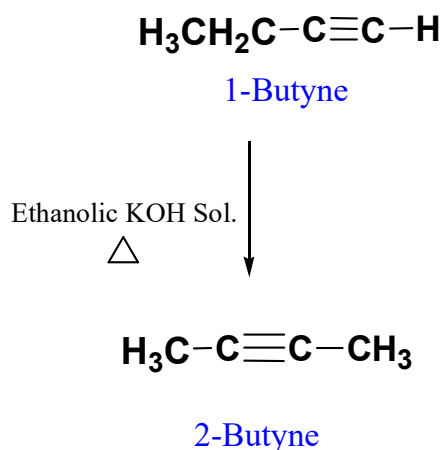
(R or R' or both may be hydrogen.)

The alkynide ion acts as a nucleophile and displaces a halide ion from the primary alkyl halide. We now recognize this as an S_N2 reaction. The unshared electron pair of the alkynide ion attacks the back side of the carbon atom that bears the halogen atom and forms a bond to it. The halogen atom departs as a halide ion.

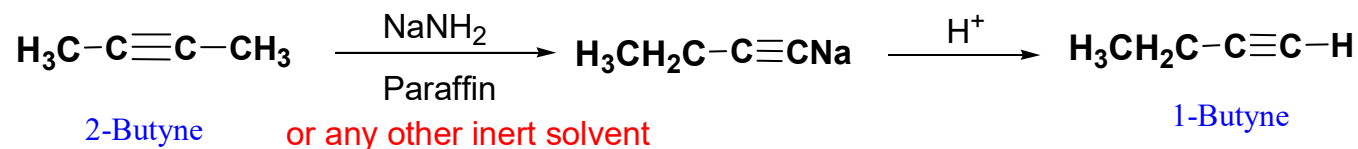


7. Isomerization of **terminal alkynes** of type (R-C≡CH) into **internal alkynes** in the presence of ethanolic KOH solution under heating condition

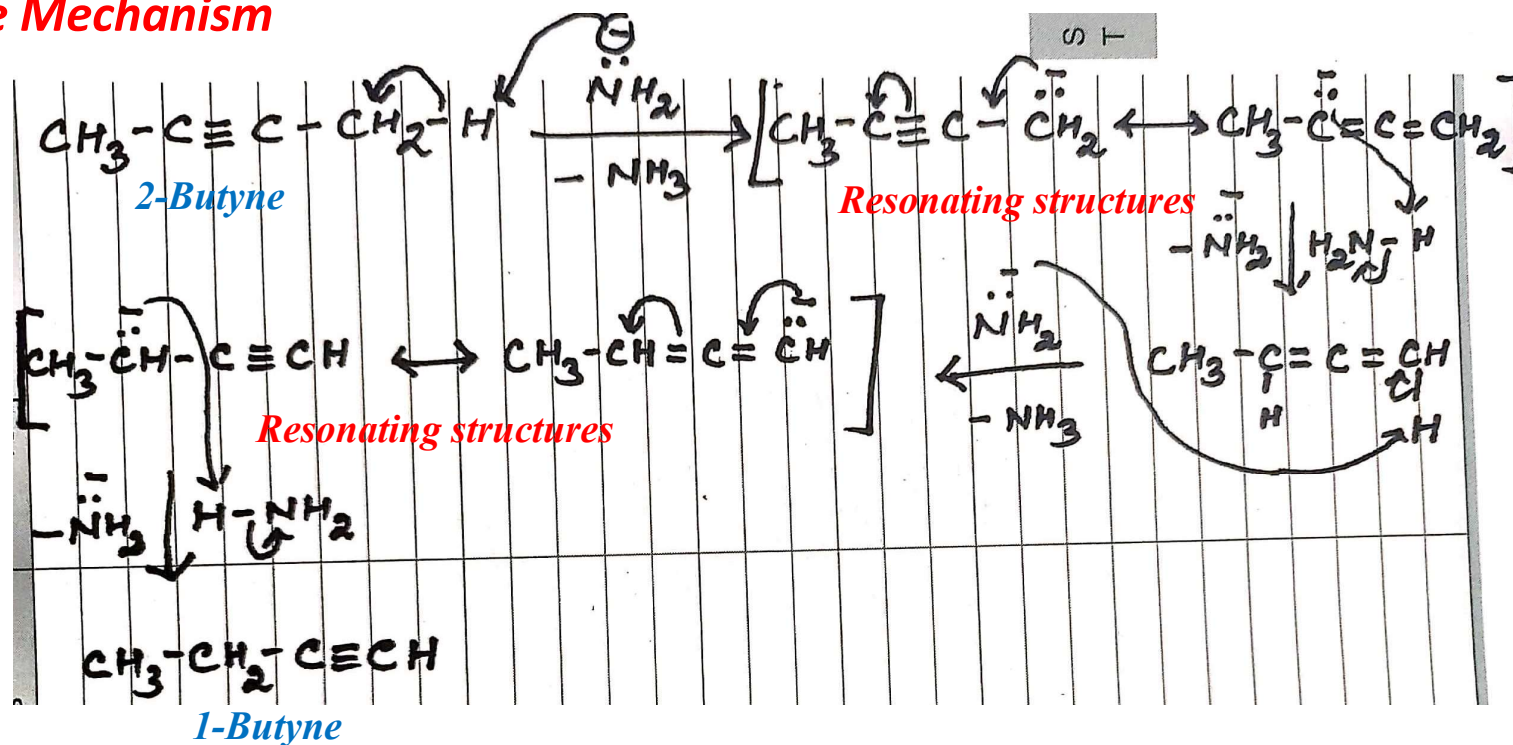
Chemical reaction



8. When internal alkynes are heated with NaNH_2 in an inert solvent e.g. paraffin the triple bond moves towards the end of the chain

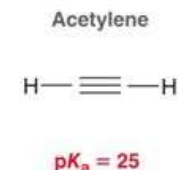
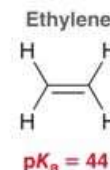
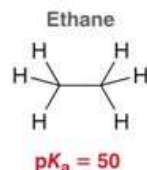


Possible Mechanism

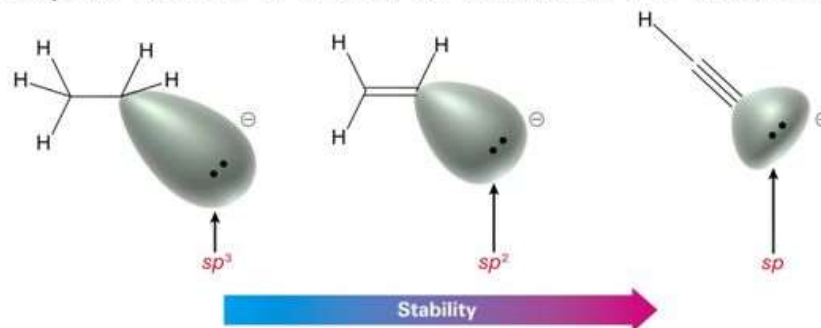


Acidity of Alkynes

- Terminal alkynes are weak acids
 - More acidic than alkenes or alkanes
- Conjugate base = acetylide ion or alkynide ion



- Conjugate base is somewhat stable
 - Electron pair closer to nucleus with more s character



More stable the conjugate base smaller is the pK_a value or higher the acidity strength is.

Questions: Carry out the following conversions.

1. Convert ethanol into ethyne.
2. Convert ethene into ethyne.
3. Convert 1-propyne into 2-butyne.
4. Convert propyl chloride into propyne.
5. Acetylene into propyne and 2-butyne.
6. Butanol into 1-butyne.
7. 1-Butyne into 2-butyne.
8. 2-Butyne into 1-butyne.
9. Propane into propyne.