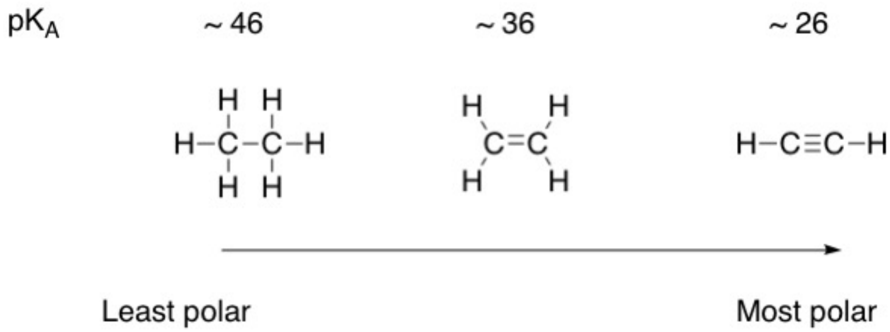
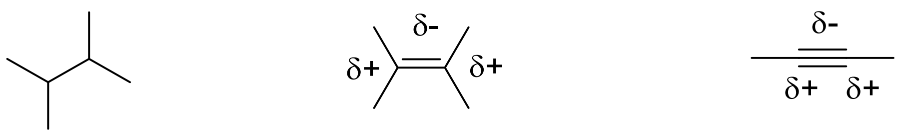
Characteristics of Alkanes, alkenes, and alkynes

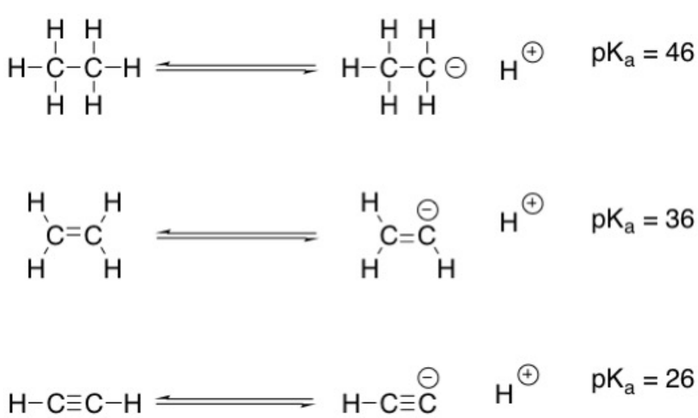


Polarity is due to charge distribution within the molecule:



Alkynes have higher boiling point, melting point, and density. Polarity drops from alkynes to alkanes as well as reactivity and boiling point values (polar substances stick together more strongly than non-polar)

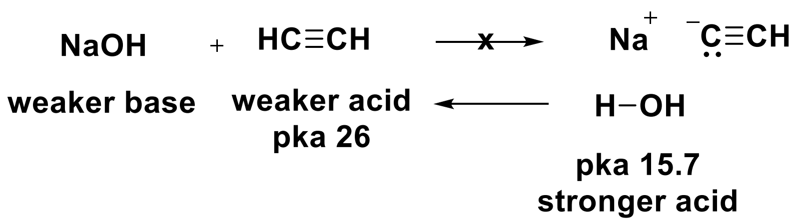
Acidity of Alkanes, Alkenes, and Alkynes



- Equilibrium lies to the left in each of these reactions as alkanes, alkenes, and alkynes are very weakly acidic.

Example

1)



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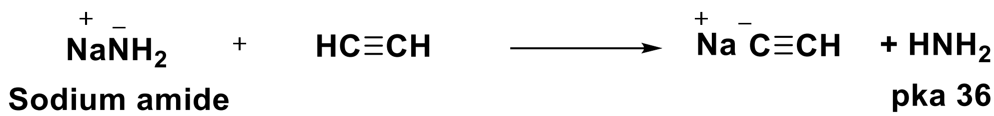

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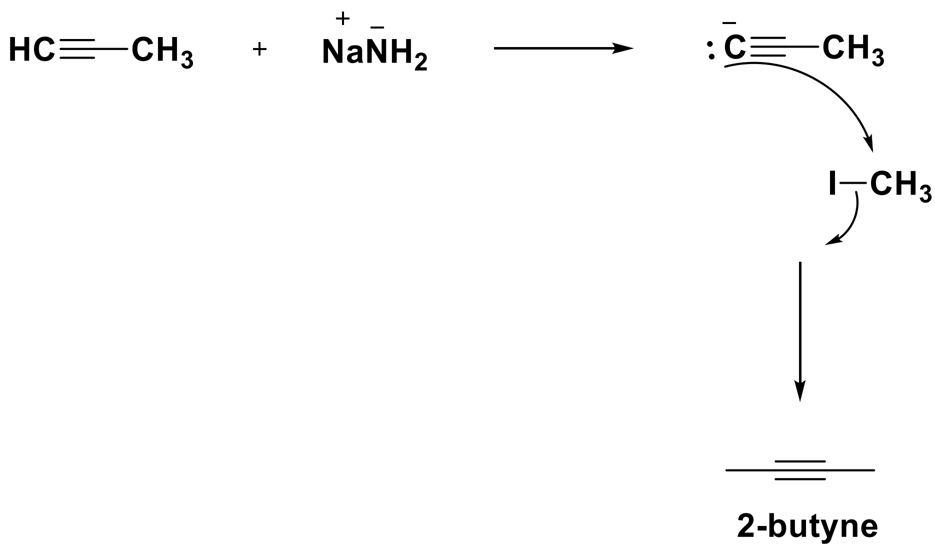

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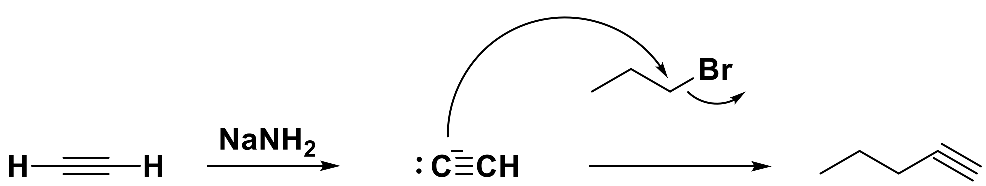

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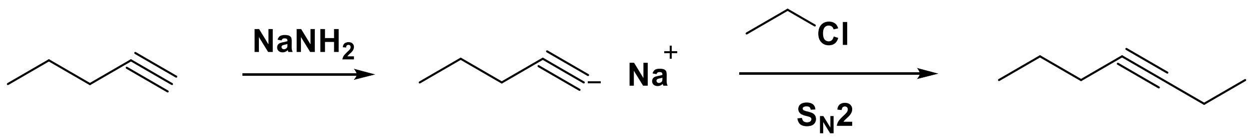
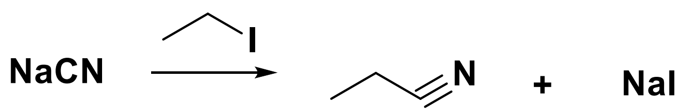


6)

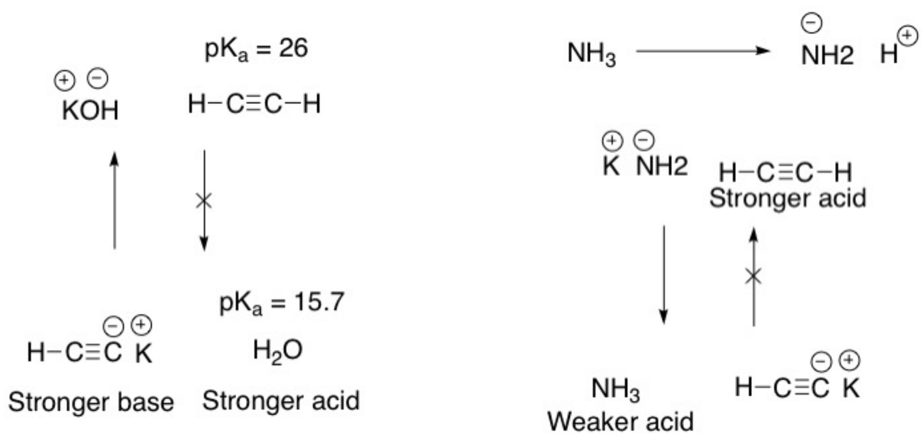
$$HC\equiv N \xrightarrow{NaOH} NaCN + H_2O$$

pka 9 (HC≡N); pka 16 (H_2O)

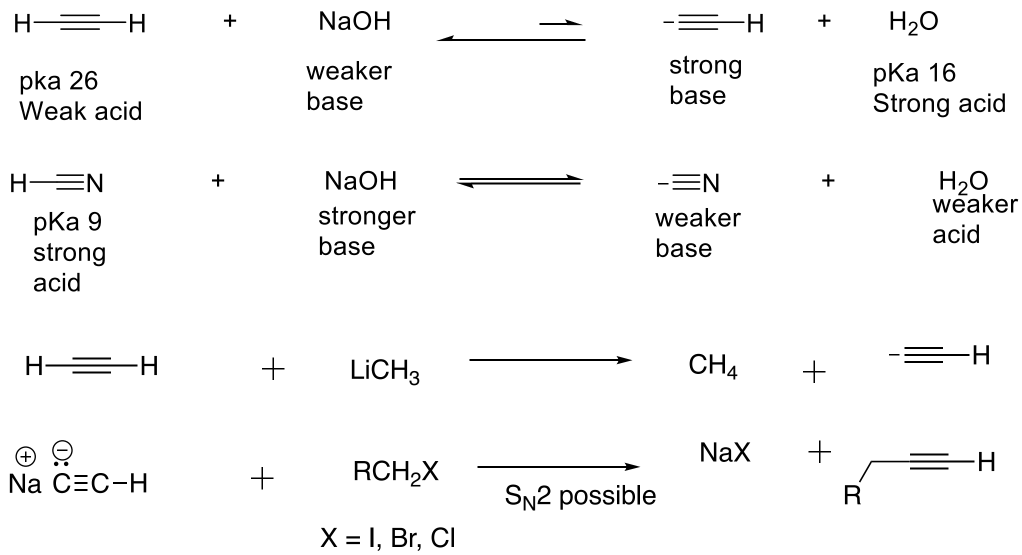
7)



8) Deprotonating acetylenes

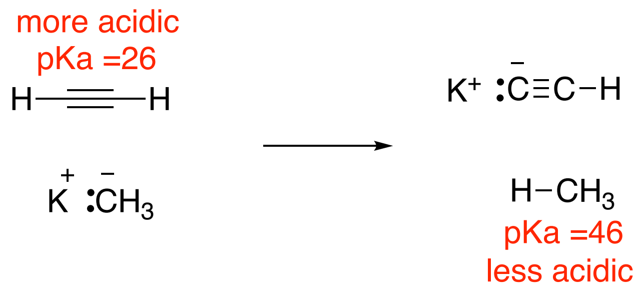


KOH will not deprotonate acetylene because it is a weaker base than acetylenes conjugate base (acetylide).

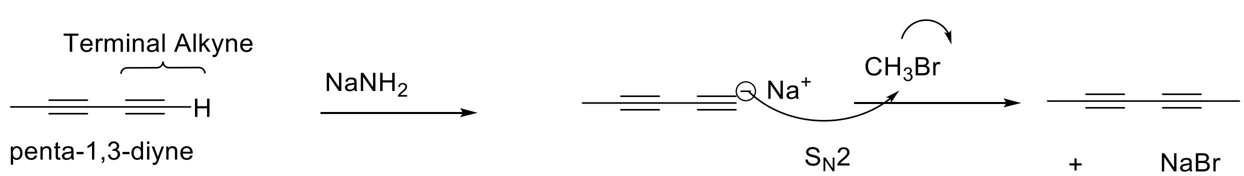


- KNH_2 will deprotonate acetylene, as the resulting acetylide is a weaker base. Ammonia pKa is 36. Other bases such as $NaCH_3$ can also be used to deprotonate acetylene.

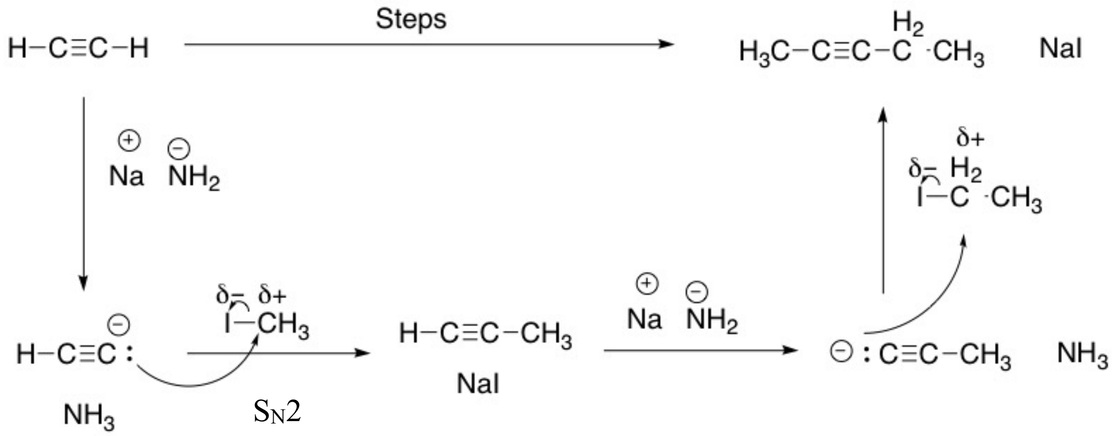
More Example



Example:



Organic synthesis example:

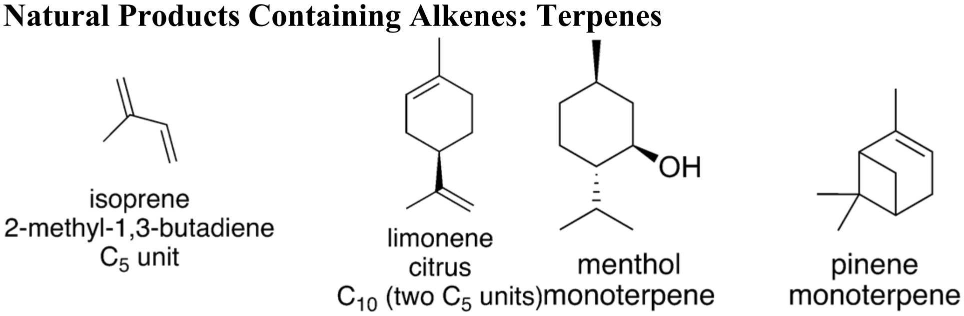


Both substitution reactions involving methyl iodide and ethyl iodide are S_N2, as the primary and secondary carbons will not hold the positive charge that is characteristic of an S_N1 intermediate (tertiary carbocation).

HCN vs C_2H_2

- HCN is more acidic with a pKa of 9.0 due to the N atom being more electronegative than C atom (**Note:** the N atom is pulling the electron density away).
-

Natural Products Containing Alkenes: Terpenes



1 C_5 Hemiterpene

2 C_5 Monoterpene

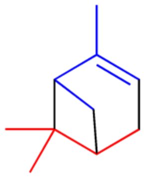
3 C_5 Sesquiterpene

4 C_5 Diterpene

5 C_5 Sesterterpene

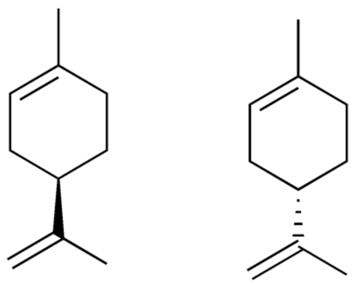
6 C_5 Triterpene

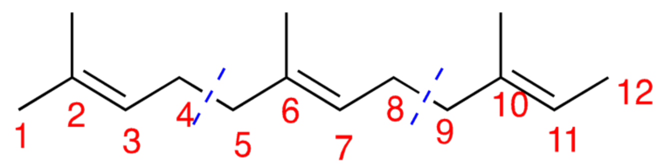
pinene below (in turpentine) is a monoterpene -Pinene is made from two isoprene units



- Steroids are made from triterpenes

Examples:





Enantiomers of Limonene

a monoterpene

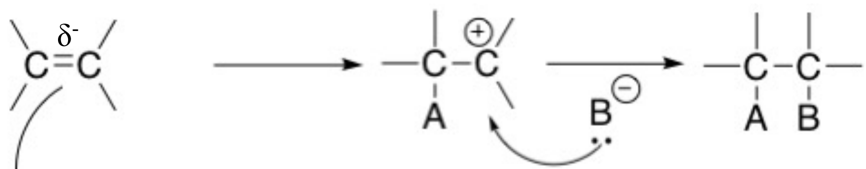
2,6,10-trimethyldodeca-2,6,10-triene

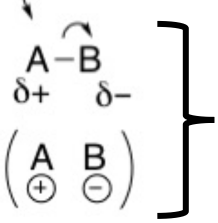
2,6,10-trimethyl-2,6,10-dodecatriene

<u>Addition to Alkene and Alkynes Reaction:</u>

- Large amount of negative charge concentrated on the π-bond (δ^-). An **electrophile**, a species that seeks negative charge (electron-loving), would then get attacked by the electrons in the π-bond, hence forming a new bond.

General Mechanism

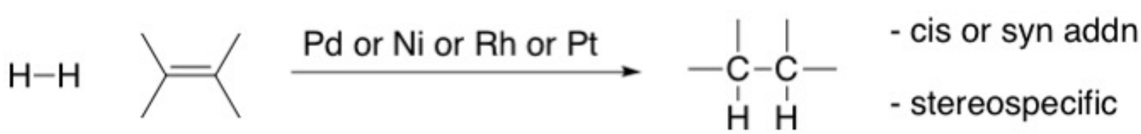




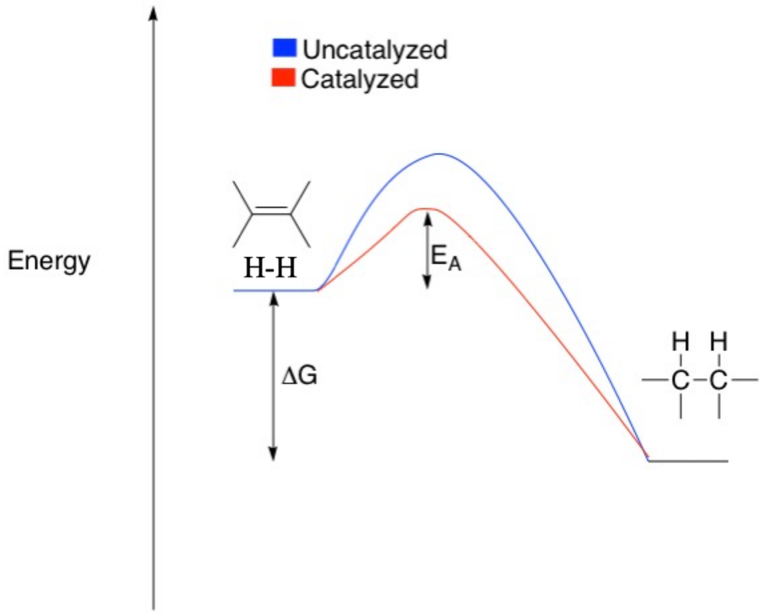
- H_2 – with Pd / Pt / Ni / Rh
- X_2 – halogen possibly with H-O-H and R-OH (X = Cl, Br, I)
- H^+ with X^- possible with H-O-H and R-OH (X = Cl, Br, I)
- BH_3

A is an electrophile – seeks electrons
B is a nucleophile – seeks nucleus
Alkene = olefin

Hydrogenation Addition of H_2

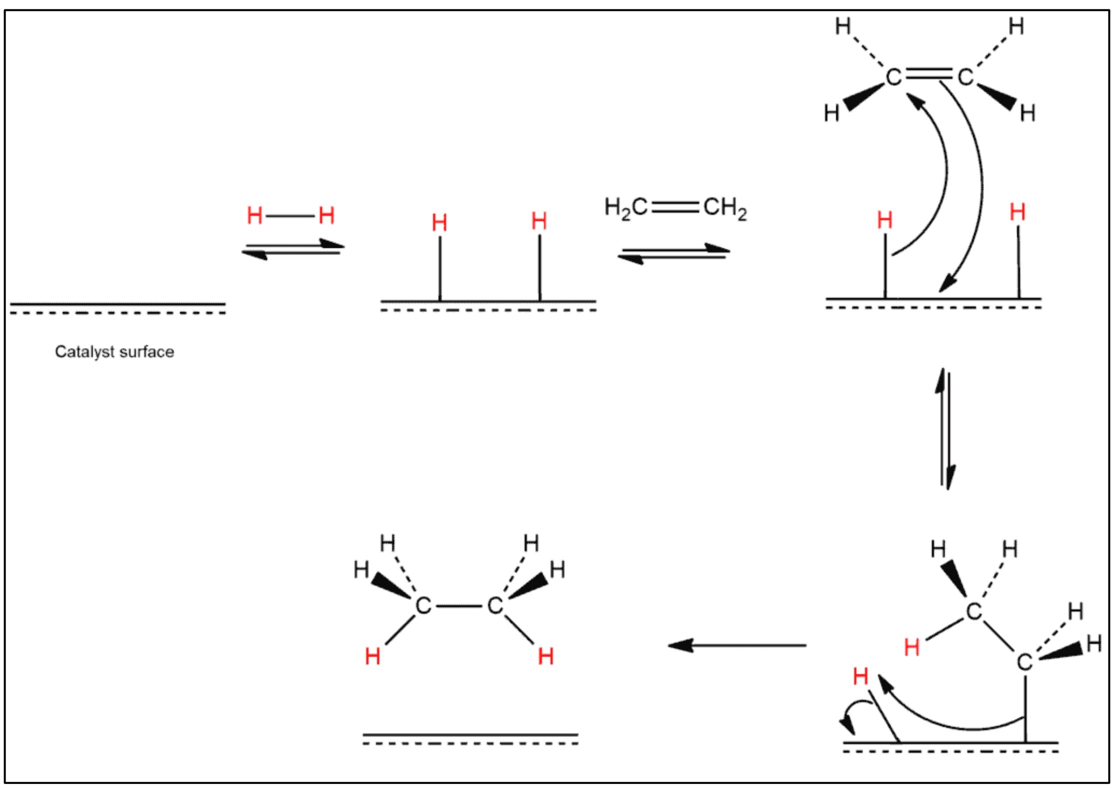


This reaction is **stereospecific**, meaning that the stereochemistry of the starting material determines the stereochemistry of the product (in this reaction, **cis**). Needs a catalyst for the reaction to proceed. The metals palladium (Pd), nickel (Ni), rhodium (Rh), and platinum (Pt) act as catalysts to facilitate this reaction.



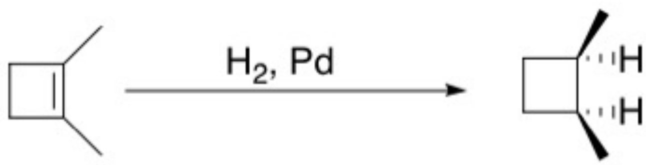
Catalysts accelerate the reaction rate by providing a lower energy pathway (red curve above). In general, they are not permanently converted to other products

Mechanism of hydrogenation



Hydrogenation examples

Example 1: 1,2-dimethylcyclobutene



1,2-dimethylcyclobutene *cis*-1,2-dimethylcyclobutane

The hydrogenation can occur from the top or the bottom, which in this case produces the same product (cis isomer of 1,2-dimethylcyclobutane). The starting material is achiral, and the product is a **meso compound** (two stereogenic centers, but a plane of symmetry)