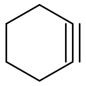
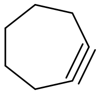
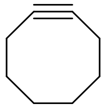
Cyclic Structures with Triple Bonds



extremely unstable
Cyclohexyne



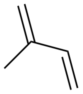
$T_{1/2}$ approx 1 h
very reactive
Cycloheptyne



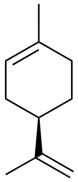
Cyclooctyne

- Cycloalkynes are very reactive as the triple bonds wants to assume a 180° bond angle.
- Cycloheptyne is more stable as the angle is larger ($T_{1/2}$=1 h)
- Cyclooctyne is known to be relatively stable compound used in azide-alkyne [3+2] cycloadditions (used in biorthogonal coupling – Nobel Prize 2022 Carolyne Betozzi & Barry Sharpless)

Terpenes or Isoprenoids or Terpenoids

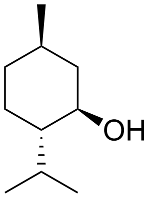


isoprene
2-methyl-1,3-butadiene
C_5 unit

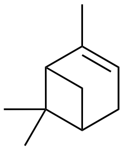


limonene
citrus
C_{10} (two C_5 units)

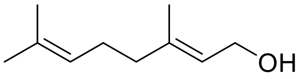
1 C_5 Hemiterpene
2 C_5 Monoterpene
3 C_5 Sesquiterpene
4 C_5 Diterpene
5 C_5 Sesterterpene
6 C_5 Triterpene



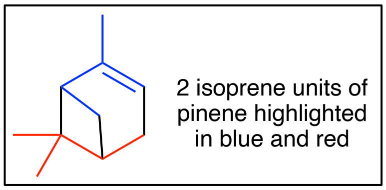
menthol
monoterpene



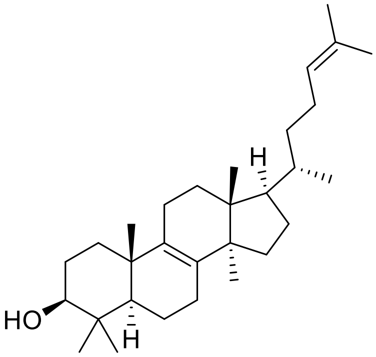
pinene
monoterpene



Geraniol



2 isoprene units of pinene highlighted in blue and red



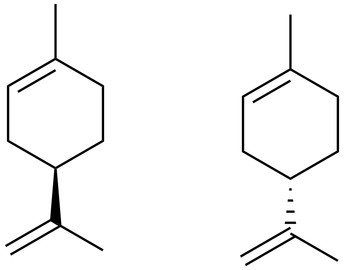
lanosterol

- Steroids are made from triterpenes

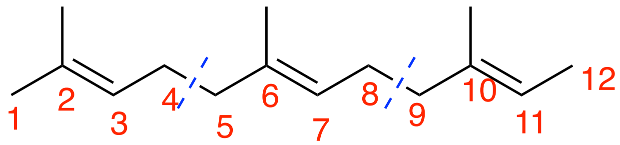
-Pinene is made from two isoprene units

- Leopold Ruzicka: did significant work with terpenes

Examples:



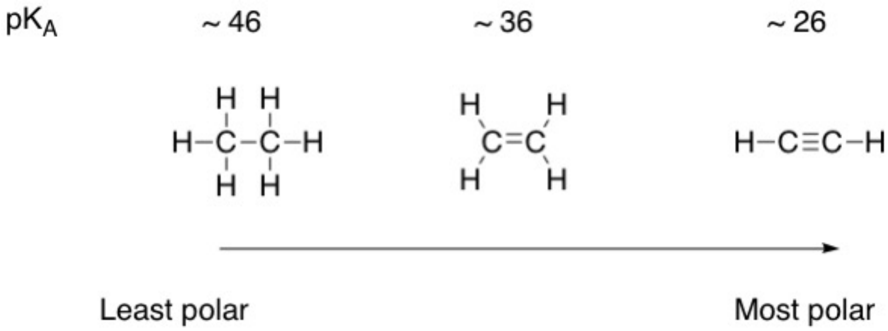
Enatiomers of Limonene



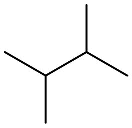
2,6,10-trimethyldodeca-2,6,10-triene

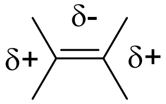
2,6,10-trimethyl-2,6,10-dodecatriene

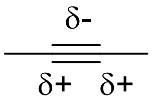
Characteristics of Alkanes, alkenes, and alkynes



Polarity is due to charge distribution within the molecule:

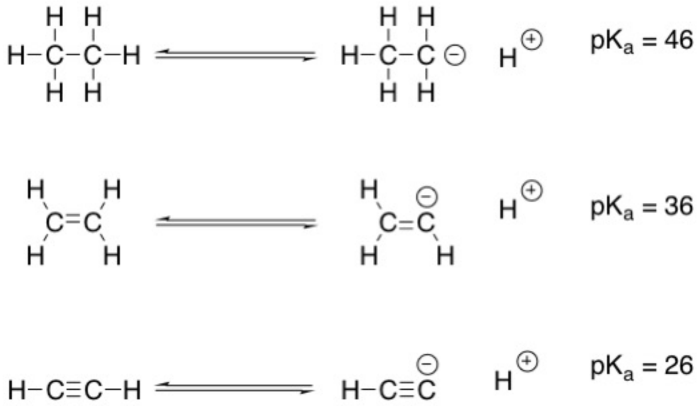






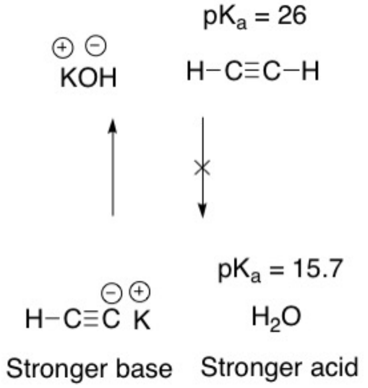
Alkynes have higher boiling point, melting point, and density. Polarity drops from alkynes to alkanes as well as reactivity and boiling point values (polar substances stick together more strongly than non-polar)

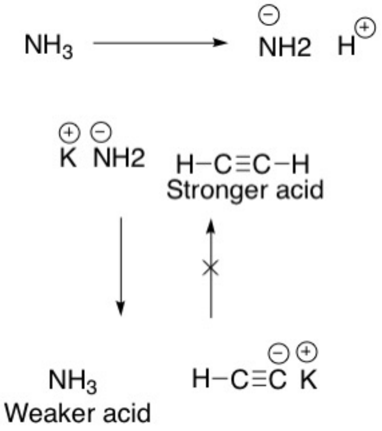
Acidity of Alkanes, Alkenes, and Alkynes



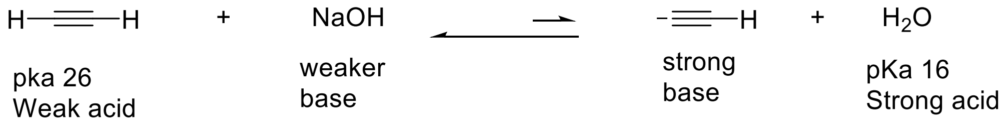
- Equilibrium lies to the left in each of these reactions as alkanes, alkenes, and alkynes are very weakly acidic.

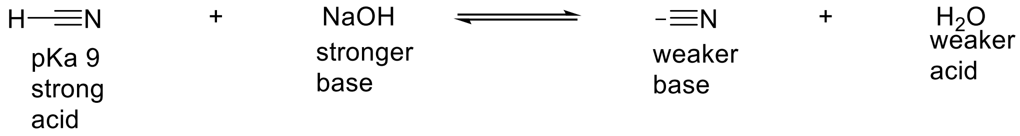
Deprotonating acetylenes

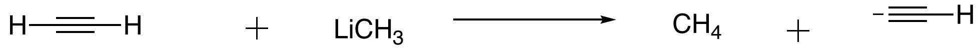


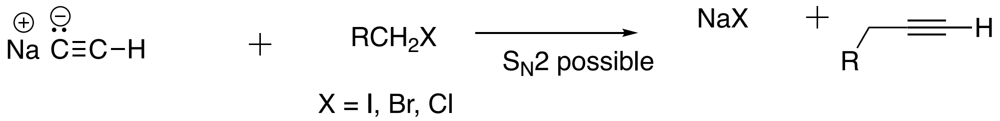


KOH will not deprotonate acetylene because it is a weaker base than acetylenes conjugate base (acetylide).



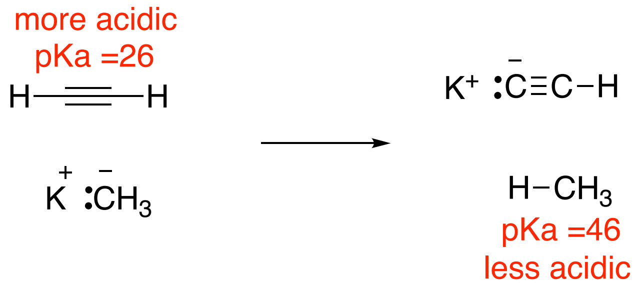




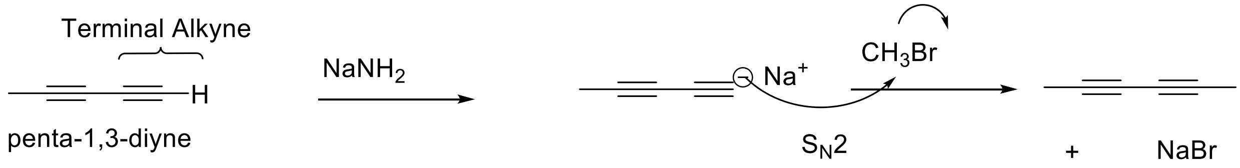


- KNH_2 will deprotonate acetylene, as the resulting acetylide is a weaker base. Ammonia pKa is 36. Other bases such as $NaCH_3$ can also be used to deprotonate acetylene.

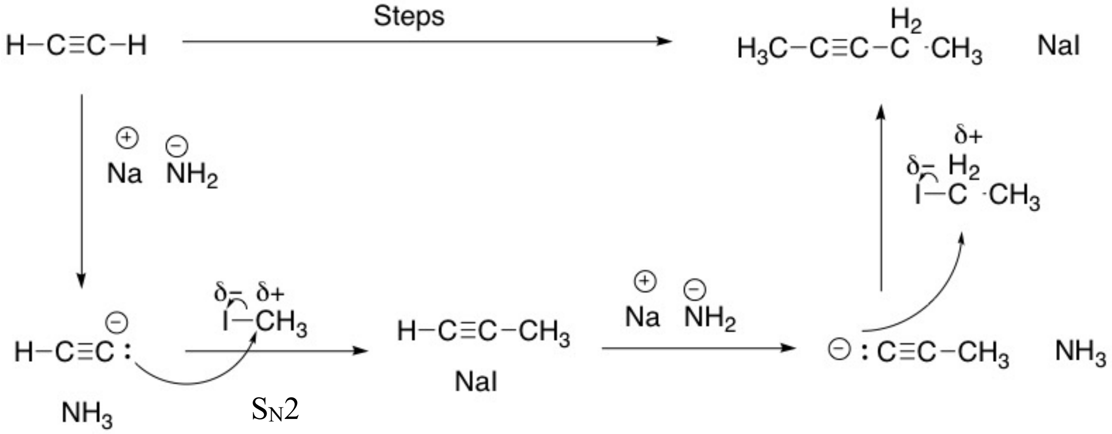
More Example



Example:



Organic synthesis example:

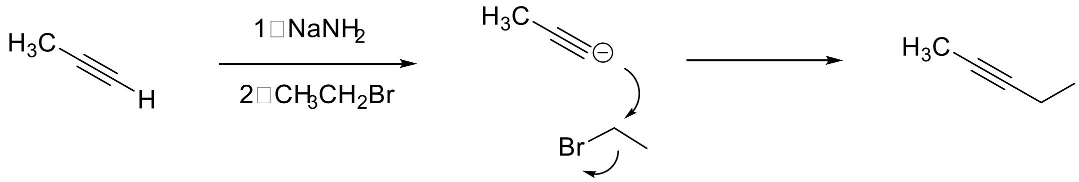


Both substitution reactions involving methyl iodide and ethyl iodide are S_N2, as the primary and secondary carbons will not hold the positive charge that is characteristic of an S_N1 intermediate (tertiary carbocation).

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).

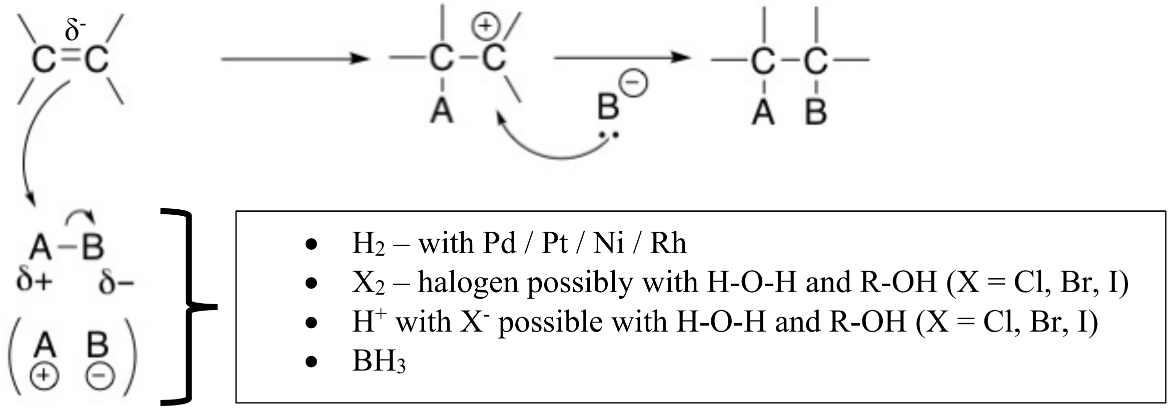
Example.



Addition to Alkene and Alkynes Reaction:

- 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.

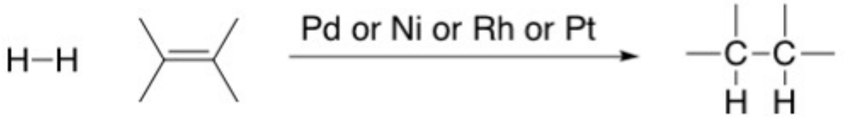
General Mechanism



- 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

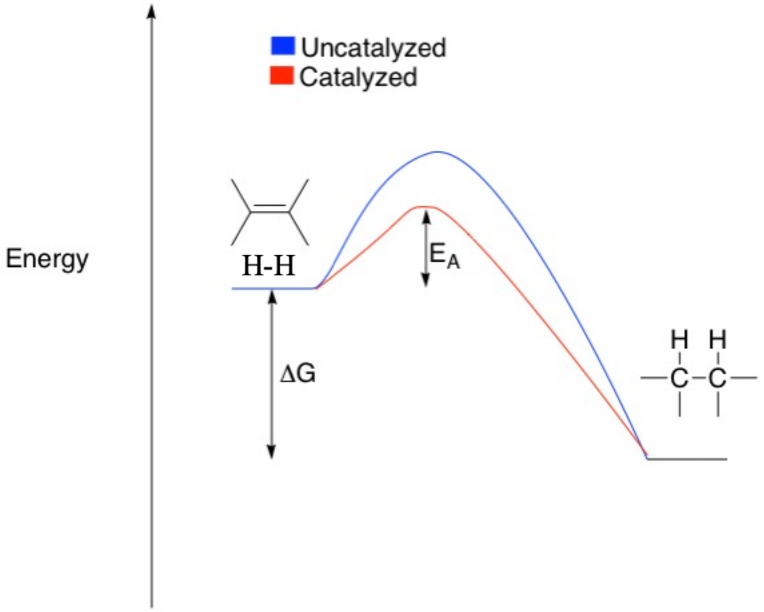
Hydrogenation Addition of H_2



- cis or syn addn

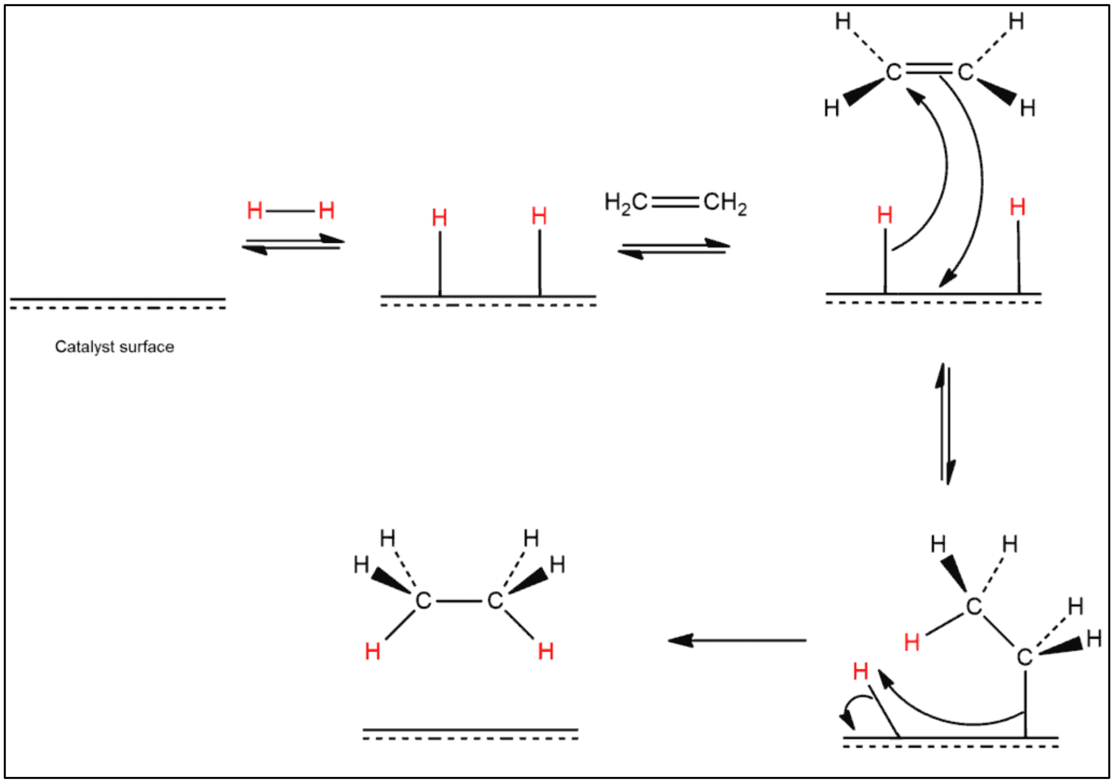
- stereospecific

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.



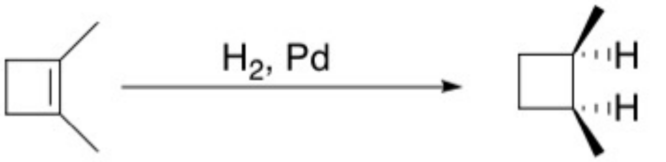
Catalysts accelerate the reaction rate by providing a lower energy pathway (red curve above). In general, they are not permanently converted to other products

Mechanism of hydrogenation



Hydrogenation examples

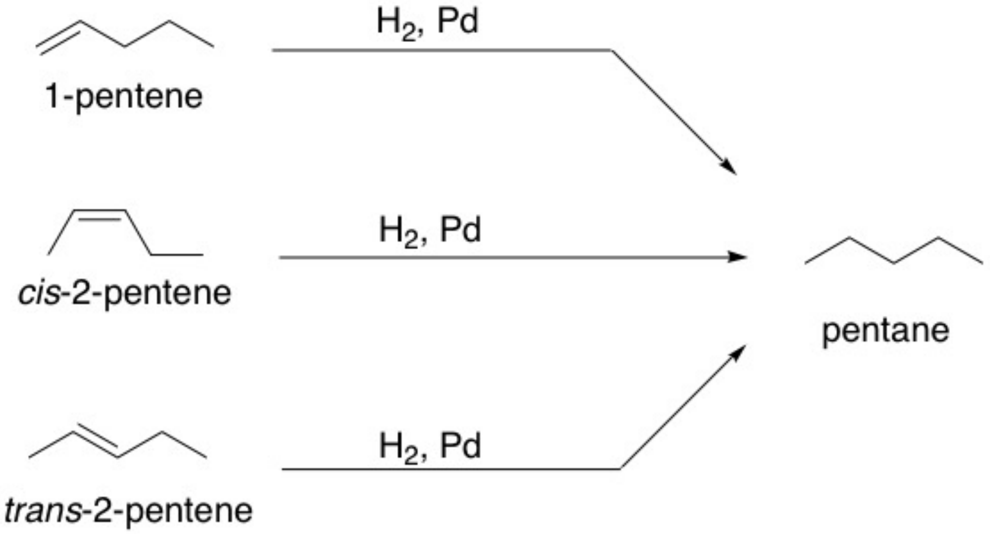
Example 1: 1,2-dimethylcyclobutene



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

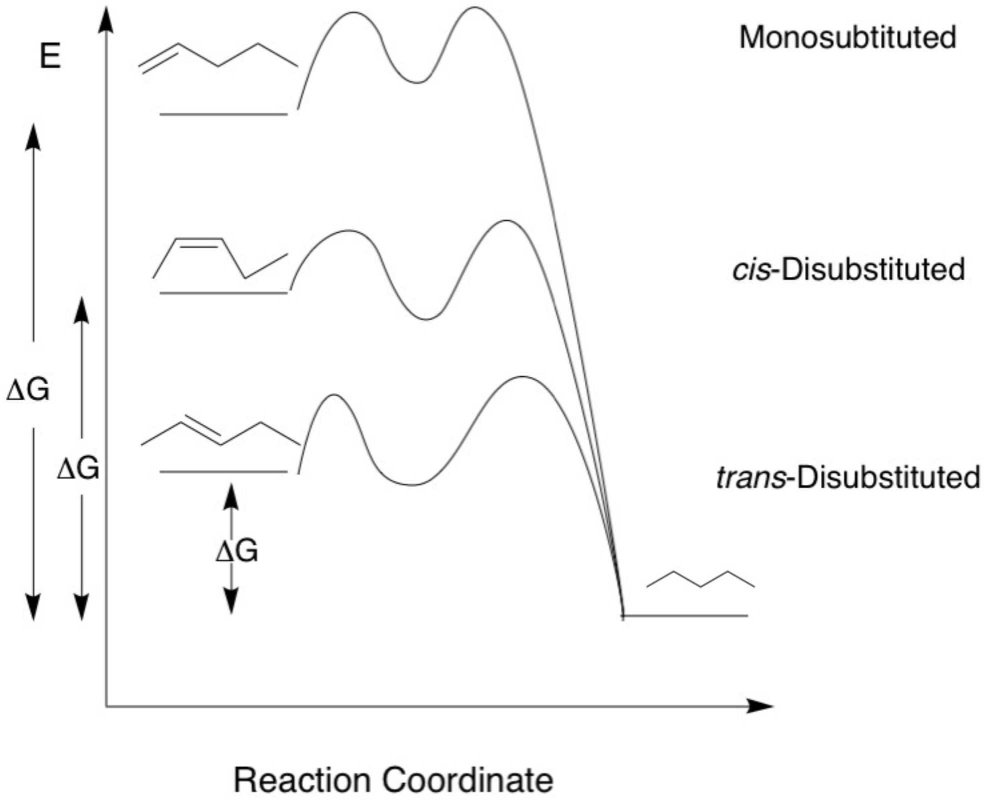
The hydrogenation can occur from the top or the bottom, which in this case produces the same product (cis isomer of 1,2-dimethylcyclobutane). The starting material is achiral, and the product is a **meso compound** (two stereogenic centers, but a plane of symmetry)

Example 2: Pentene



Energy is released in each of these reactions, the energy released implies stabilization caused from transforming the starting material into the product

Energy diagram



ΔG *trans*-isomer < ΔG *cis*-isomer < ΔG 1-pentene isomer

Alkenes with more substituents are more stable. Carbons in a double bond have a δ+ (electron-deficient), this is stabilized by the **electron donating effects** of alkyl groups. Hydrogens are less electron donating and so less substituted alkenes are less stable.

Cis alkenes are less stable than trans alkenes as they have methyl groups facing the same direction which causes unfavorable steric interactions.