Nomenclature of Alkynes (also known as acetylenes)

Rules:

- Find longest chain with max number of multiple bonds
- Number from end to give 1st <u>multiply</u> bonded position the lowest number
- Drop “ane” and add “yne”
- For multiple triple bonds, drop “ne” and add “diyne”,” triyne”, etc.
- Halides and alkyl substituents take lower priority than double or triple bonds

$H-\equiv-H$

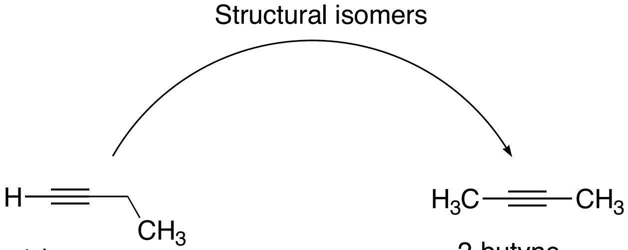
ethyne
acetylene

$H-\equiv-CH_3$

propyne

methylacetylene (common name)

1-propyne



1-butyne

ethylacetylene

2-butyne

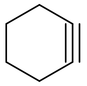
dimethylacetylene

Multiple alkynes end with:

2	$C\equiv C$	diyne
3	$C\equiv C$	triyne
4	$C\equiv C$	tetrayne

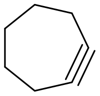
Mixed double and triple bond containing compounds are “eneynes.”

Cyclic Structures with Triple Bonds



extremely unstable

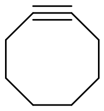
Cyclohexyne



$T_{1/2}$ 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)

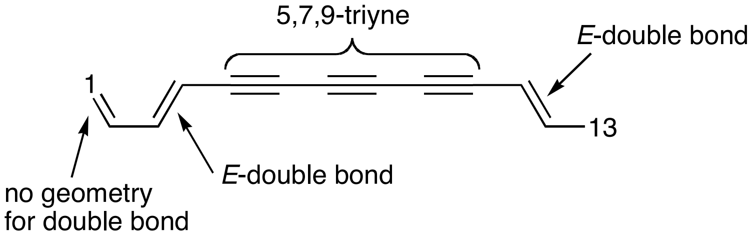
Example 1:

2,4 - Octadiyne
(octa-2,4-diyne)

Example 2:

The below example is from canola – defense substance (anti-nematode)

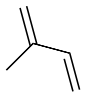
- Parent alkane of 13 carbons is tridecane – hence trideca
- Start numbering the chain such that the **first multiply bonded position** gets the lowest number possible.



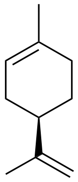
3*E*,11*E*-trideca-1,3,11-triene-5,7,9-triyne

Note: alkene stereochemistry can go right to the numbers indicating positions of double bonds: **trideca-1,3*E*,11*E*-triene-5,7,9-triyne**

Terpenes

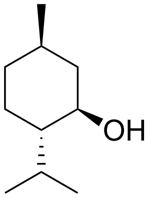


isoprene
2-methyl-1,3-butadiene
C_5 unit

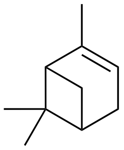


limonene
citrus
C_{10} (two C_5 units)

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



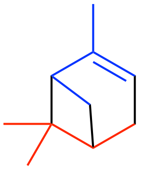
menthol
monoterpene



pinene
monoterpene

- Steroids are made from triterpenes

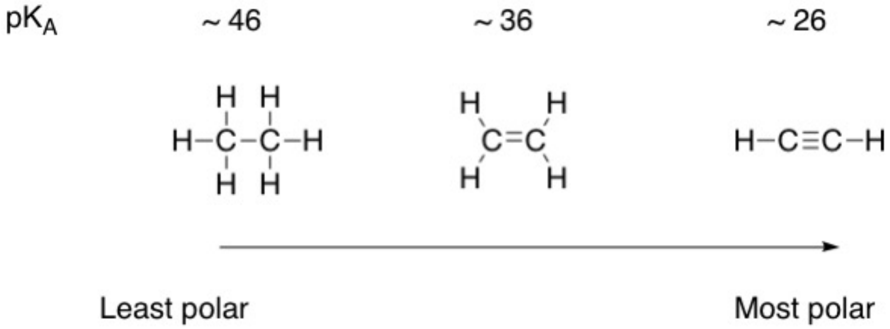
-Pinene is made from two isoprene units



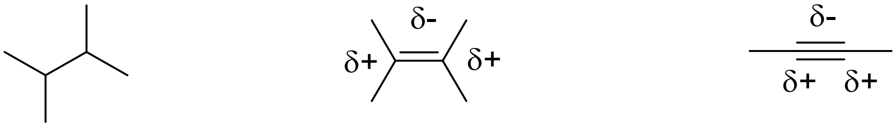
2 isoprene units of pinene highlighted in blue and red

- Leopold Ruzicka: did significant work with terpenes

Characteristics of Alkanes, alkenes, and alkynes

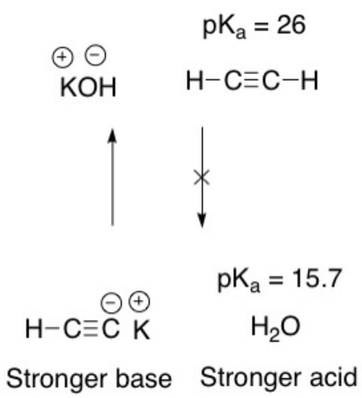


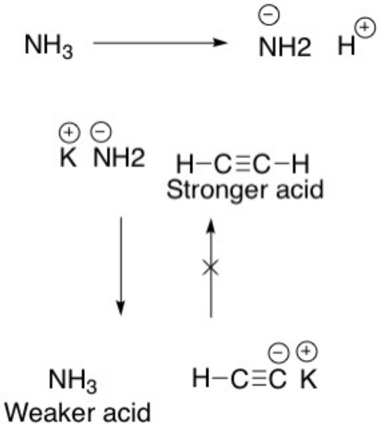
Polarity is due to charge distribution within the molecule:



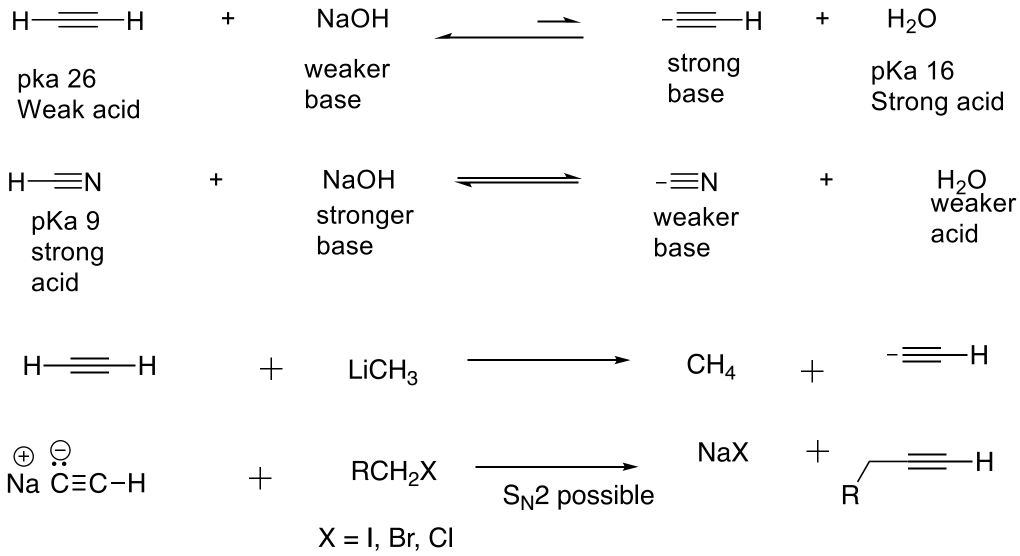
Alkynes have higher boiling point, melting point, and density. Polarity drops from alkynes to alkanes as well as reactivity and boiling point values (polar substances stick together more strongly than non-polar)

Deprotonating acetylenes

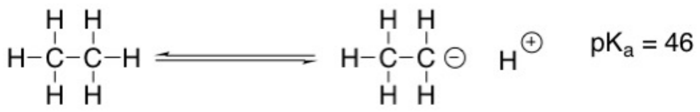


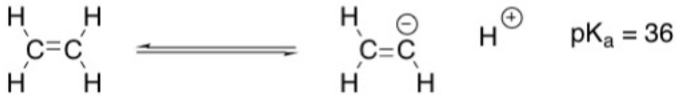


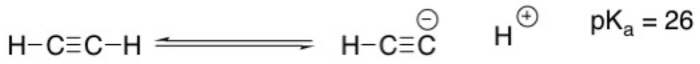
KOH will not deprotonate acetylene because it is a weaker base than acetylenes conjugate base (acetylide).



More examples:



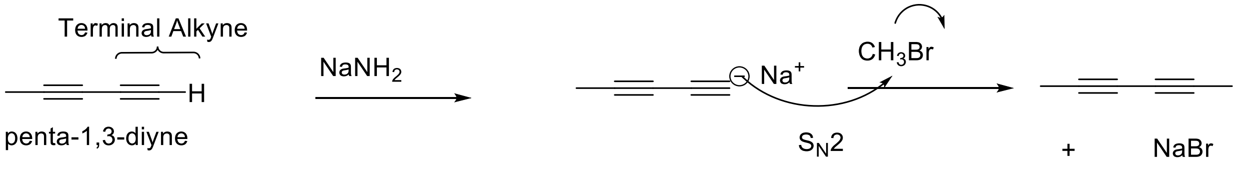




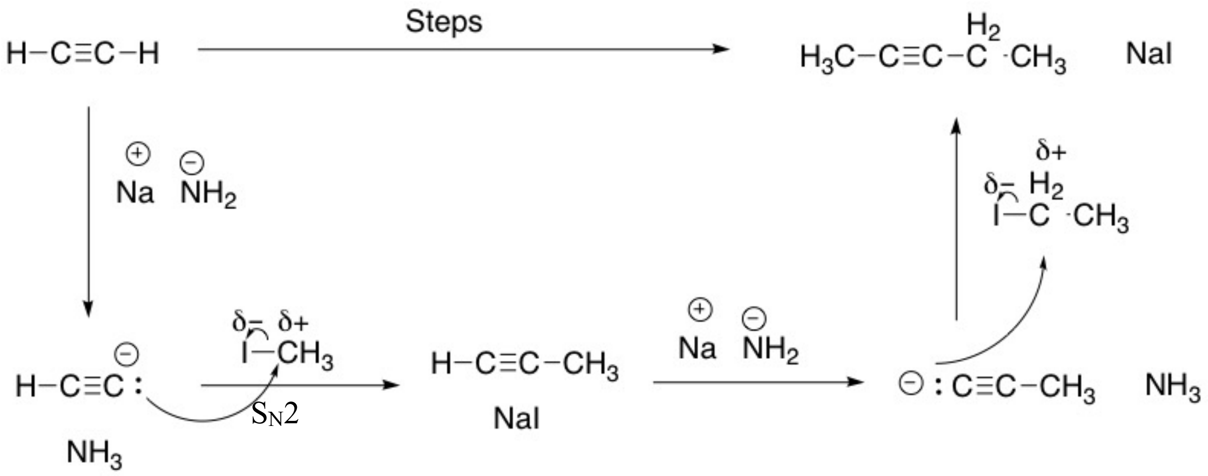
- Equilibrium lies to the left in each of these reactions as alkanes, alkenes, and alkynes are very weakly acidic.

- On the other hand, 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.

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).