## Nomenclature of Alkynes (also known as acetylenes)

Rules:

- Find longest chain with max number of multiple bonds
- Number from end to give 1<sup>st</sup> <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

 $H \longrightarrow$ -H ethyne acetylene Structural isomers  $H \longrightarrow CH_3$ H- $H_3C \longrightarrow CH_3$ CH<sub>3</sub> propyne 2-butyne 1-butyne methylacetylene (common name) dimethylacetylene ethylacetylene 1-propyne

## Multiple alkynes end with:

2	с≡с	diyne
3	c≡c	triyne
4	c≡c	tetrayne

Mixed double and triple bond containing compounds are "eneynes."

## **Cyclic Structures with Triple Bonds**



- 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. at -76 C)

- 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 and Morten Meldal)

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.



## 3E,11E-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

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)

## HCN vs C<sub>2</sub>H<sub>2</sub>



- 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).

### **Deprotonating acetylenes**



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

н−≡−н	+	NaOH	<u> </u>	- <u></u> Н	+	H <sub>2</sub> O
pka 26 Weak acid		weaker base		strong base		pKa 16 Strong acid
H──═N pKa 9 strong acid	+	NaOH stronger base	<del>~~`</del>	- <b>≕</b> N weaker base	+	H <sub>2</sub> O weaker acid

#### 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<sub>2</sub> will deprotonate acetylene, as the resulting acetylide is a weaker base. Ammonia pKa is 36. Other bases such as NaCH<sub>3</sub> can also be used to deprotonate acetylene.

## **Example:**



Both substitution reactions involving methyl iodide and ethyl iodide are  $S_N 2$ , as the primary and secondary carbons will not hold the positive charge that is characteristic of an  $S_N 1$  intermediate (tertiary carbocation).