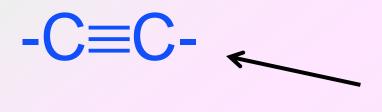
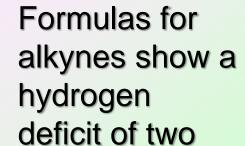


A member of the hydrocarbon family containing a carbon-carbon triple bond as the functional group



Alkynes have triple bonds

 C_nH_{2n-2}



Acetylene

- Simplest member of the alkyne family
 - linear arragement
 - sp hybridization
 - + 2 π bonds & 1 σ bond

One π bond Second π bond

Nomenclature

 Common Names: Derived from acetylene due to replacement of one or both hydrogen atoms

$$H-C \equiv C-C_2H_5$$

 $H-C\equiv C-CH(CH_3)_2$

Ethylacetylene

Isopropylacetylene

Nomenclature

IUPAC Names: Name the carbon group and use the -yne ending

$$H-C \equiv C-C_2H_5$$

 $H-C\equiv C-CH(CH_3)_2$

1-Butyne

3-methyl-1-butyne

Industrial Source of Acetylene

A

coal→coke
$$\longrightarrow$$
 CaC₂ $\xrightarrow{\text{H}_2\text{O}}$ H-C≡C-H

Industrial Source of Acetylene

B.

$$6CH_4 + O_2 \xrightarrow{1500^{\circ}C} 2 \text{ H-C} = C-H + 2 CO + 10 H_2$$

Physical Properties

- Low Polarity
- Similar to alkanes and alkenes
- Insoluble in water
- Soluble in organic solvents
- Less dense than water
- Boiling points -- Table 12.1 page 428

Physical Properties

- Low Polarity
- Similar to alkanes and alkenes
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Table 12.1 ALKYNES

Name	Formula	M.p., °C	В.р., °С	Relative density (at 20 °C)					
					Acetylene	НС≡СН	-82	-75	
					Propyne	$HC \equiv CCH_3$	-101.5	-23	
1-Butyne	HC≡CCH ₂ CH ₃	-122	9						
1-Pentyne	HC≡C(CH ₂) ₂ CH ₃	-98	40	0.695					
1-Hexyne	HC≡C(CH ₂) ₃ CH ₃	-124	72	0.719					
1-Heptyne	$HC \equiv C(CH_2)_4 CH_3$	-80	100	0.733					
1-Octyne	$HC \equiv C(CH_2)_5 CH_3$	-70	126	0.747					
1-Nonyne	$HC \equiv C(CH_2)_6 CH_3$	-65	151	0.763					
1-Decyne	$HC \equiv C(CH_2)_7 CH_3$	36	182	0.770					
2-Butyne	CH ₃ C≡CCH ₃	-24	27	0.694					
2-Pentyne	CH ₃ C≡CCH ₂ CH ₃	-101	55	0.714					
3-Methyl-1-butyne	$HC \equiv CCH(CH_3)_2$		29	0.665					
2-Hexyne	$CH_3C \equiv C(CH_2)_2CH_3$	-92	84	0.730					
3-Hexyne	CH ₃ CH ₂ C≡CCH ₂ CH ₃	-51	81	0.725					
3,3-Dimethyl-1-butyne	$HC \equiv CC(CH_3)_3$	-81	38	0.669					
4-Octyne	$CH_3(CH_2)_2C \equiv C(CH_2)_2CH_3$		131	0.748					
5-Decyne	$CH_3(CH_2)_3C \equiv C(CH_2)_3CH_3$		175	0.769					

PREPARATION OF ALKYNES

PREPARATION OF ALKYNES

1. Dehydrohalogenation of alkyl dihalides. Discussed in Sec. 12.6.

$$\begin{bmatrix} H & H \\ -C = C & \xrightarrow{X_2} \end{bmatrix} \xrightarrow{\begin{array}{c} H & H \\ -C = C \\ \hline \end{array}} \xrightarrow{KOH \, (alc)} \xrightarrow{C} \xrightarrow{C} \xrightarrow{NaNH_2} \xrightarrow{C} = C - \xrightarrow{NaNH_2}$$

Example:

2. Reaction of metal acetylides with primary alkyl halides. Discussed in Sec. 12.12.

$$\begin{bmatrix} -C \equiv C - H & \xrightarrow{\text{LiNH}_2} & \end{bmatrix} -C \equiv C : ^-\text{Li}^+ & + & RX & \longrightarrow & -C \equiv C - R + \text{LiX} \\ & R \text{ must be } 1^\circ & \end{bmatrix}$$

HC≡C:
$$^-$$
Li⁺ + CH₃CH₂CH₂CH₂Br → HC≡C−CH₂CH₂CH₂CH₃
Lithium acetylide $^{n-}$ Butyl bromide $^{1-}$ Hexyne $^{(n-}$ Butylacetylene)

REACTIONS OF ALKYNES

Addition Reactions

$$-C \equiv C - + YZ \longrightarrow -C = C - \xrightarrow{YZ} -C - C - C - YZ \xrightarrow{Y} Z$$

1. Addition of hydrogen. Discussed in Sec. 12.8.

$$-C \equiv C - \qquad \begin{array}{c} \text{Na or Li} \\ \text{NH}_3(\text{liq}) \end{array} \longrightarrow \begin{array}{c} \text{H} \\ \text{H} \end{array}$$

$$-C \equiv C - \qquad \begin{array}{c} \text{H}_2 \\ \text{Lindlar catalyst} \end{array} \longrightarrow \begin{array}{c} \text{Syn} \\ \text{H} \end{array}$$

$$CH_3-C \equiv C-CH_3 \xrightarrow{2H_2, N_i} CH_3CH_2CH_2CH_3$$

2-Butyne *n*-Butane

Na, NH₃(liq)

$$C_2H_5C \equiv CC_2H_5$$

3-Hexyne

 $C_2H_5 = CC_2H_5$
 $C_2H_5 = CC_2H_5$

$$-C \equiv C - \xrightarrow{X_2} -C = C - \xrightarrow{X_2} - C - C - C - X_2 = Cl_2, Br_2$$

Example:

3. Addition of hydrogen halides. Discussed in Sec. 12.9.

$$-C = C - \xrightarrow{HX} -C = C - \xrightarrow{HX} -C = C - C - HX = HCl, HBr, HI$$

$$+ X + X + K = HCl, HBr, HI$$

Example:

4. Addition of water. Hydration. Discussed in Sec. 12.10.

$$-C \equiv C - + H_2O \xrightarrow{H_2SO_4, HgSO_4} \begin{bmatrix} -C = C - \end{bmatrix} \xrightarrow{\leftarrow} \begin{bmatrix} H \\ -C = C - \end{bmatrix}$$

$$H O H O$$

$$H-C \equiv C-H + H_2O \xrightarrow{H_2SO_4, HgSO_4} H-C-C-H \\ HO$$
Acetaldehyde

$$CH_{3}-C \equiv C-H+H_{2}O \xrightarrow{H_{2}SO_{4}, HgSO_{4}} H-C-C-C-H$$

$$H O H$$
Acetone

CONTINUED

Reactions as Acids

$$-C \equiv C - H + base \longrightarrow -C \equiv C$$
:

5. Formation of metal acetylides. Discussed in Sec. 12.11.

$$CH_3$$
— $C\equiv C$ — $H + n$ -BuLi $\longrightarrow CH_3C\equiv C^-Li^+ + n$ -BuH
Lithium methylacetylide

$$\begin{array}{c} HC \overline{=} CH + C_2H_5MgBr \longrightarrow HC \overline{=} CMgBr + C_2H_6 \\ Ethynylmagnesium \\ bromide \end{array}$$

