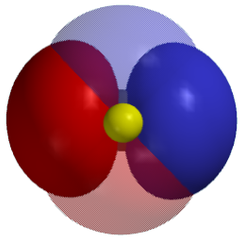
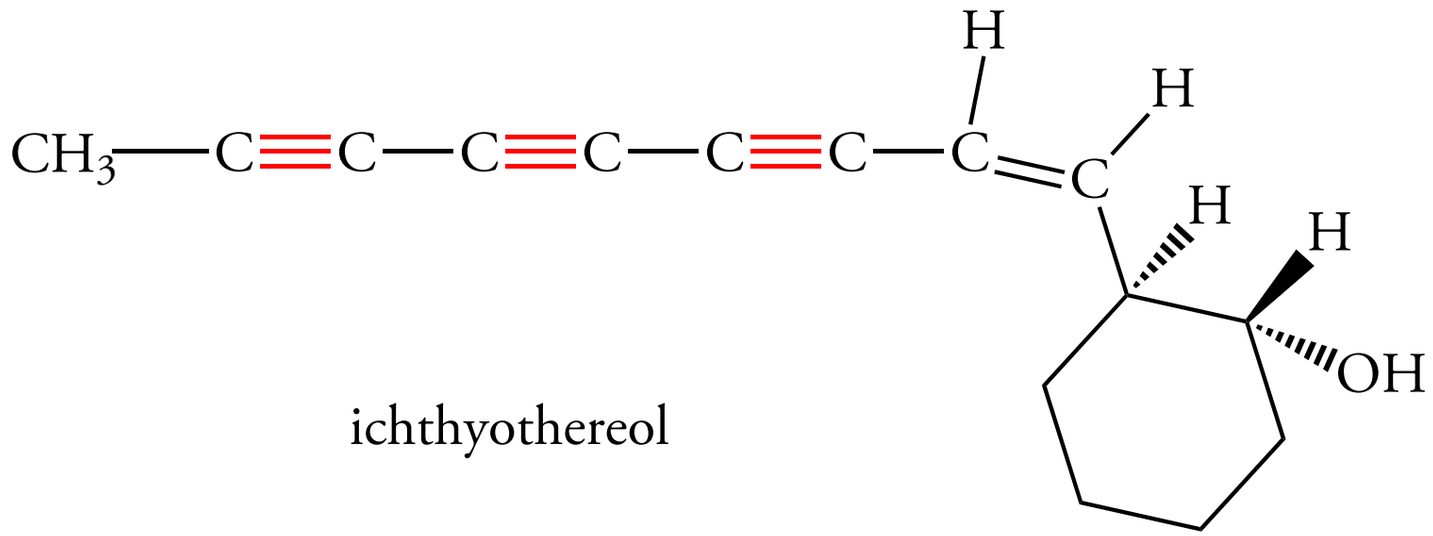
7



ALKYNES



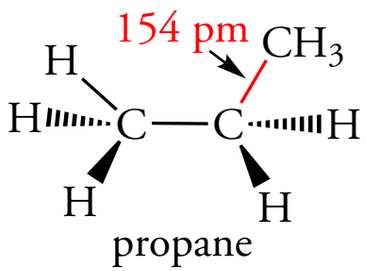
ichthyothereol

7.2 STRUCTURE AND PROPERTIES OF ALKYNES

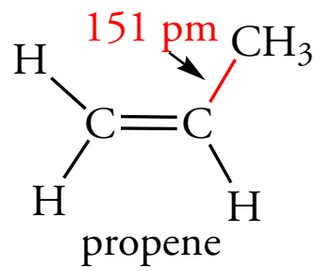
Classification of Alkynes

monosubstituted alkyne (terminal alkyne): R—C≡C—H

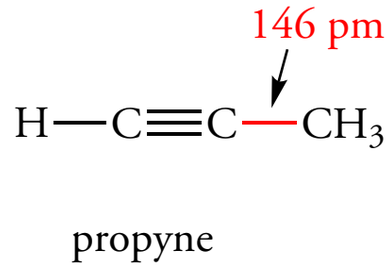
disubstituted alkyne (internal alkyne): R—C≡C—R



propane



propene



propyne

Table 11.1 C—C and C—H Bond Lengths and Bond Strengths in Alkynes, Alkenes, and Alkanes

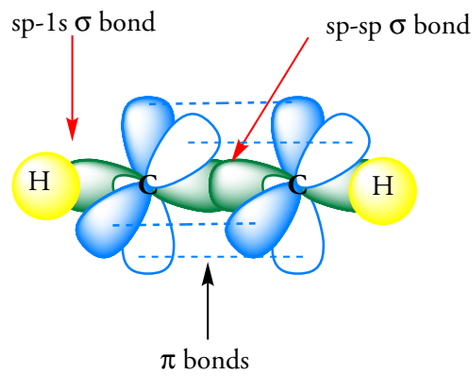
Compound	Bond Length (pm)	Bond Strength (kJ mole^{-1})
C≡C—H (ethyne)	105	536
C=C—H (ethene)	109	470
C—H (ethane)	111	422
C≡C (ethyne)	121	820
C=C (ethene)	133	605
C—C (ethane)	154	368

7.2 STRUCTURE AND PROPERTIES OF ALKYNES

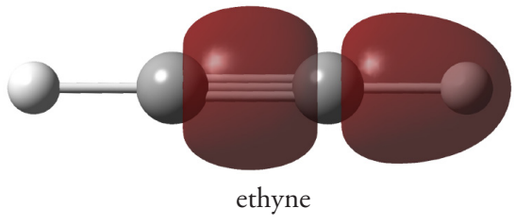
Hybridization, Bond Length, and Bond Energies in Alkynes

Figure 11.1 Structure and Bonding in Ethyne

(a) Schematic diagram. (b) Sigma bonds in ethyne. (c) Electrostatic potential map. We recall that an sp-hybridized carbon is electron deficient relative to an sp^2- or sp^3-hybridized carbon. The regions of partial positive charge surrounding the carbon atoms is shown in red. The negative end of the C—H dipole is shown in blue. (d) Space-filling model.

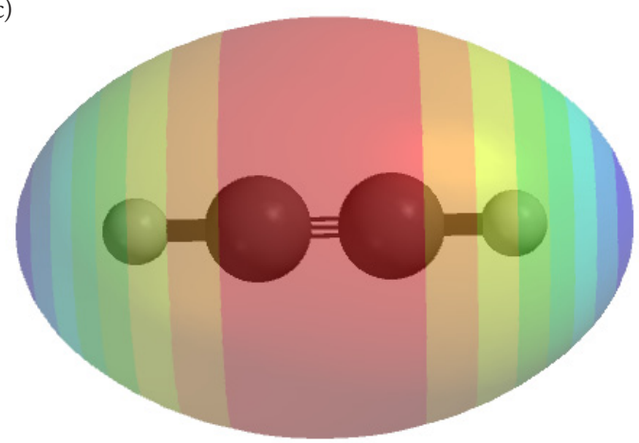


Bonding in ethyne: the carbon-carbon σ bonds are colinear; the π bonds lie above and below, and in front and behind the sigma bonds.

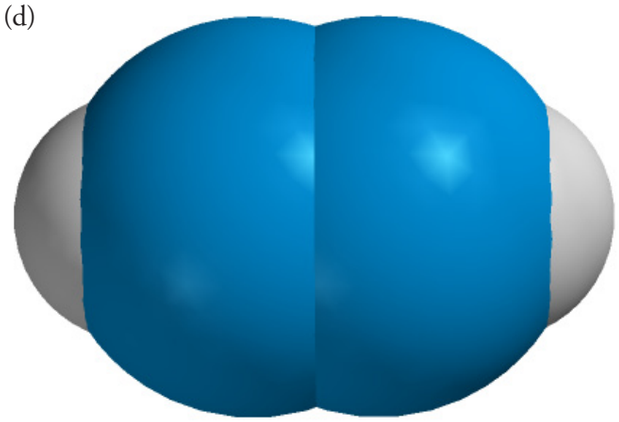


ethyne

(c)



(d)



7.2 STRUCTURE AND PROPERTIES OF ALKYNES

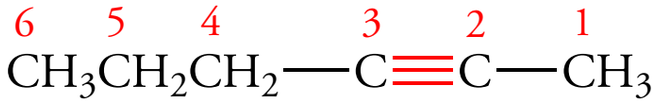
Physical Properties of Alkynes

Table 7.2 Physical Properties of Alkynes

Compound	*Boiling Point (°C)*	*Density (g/cm³)*
1-butyne	8.1	0.678
2-butyne	27	0.091
1-pentyne	40.2	0.690
2-pentyne	56.1	0.711
3-methyl-1-butyne	29	0.666
1-hexyne	71.3	0.716
2-hexyne	84	0.732
3-hexyne	81.5	0.723
4-methyl-1-pentyne	61.1	0.709
4-methyl-2-pentyne	72.0	0.716
3,3-dimethyl-1-butyne	39.5	0.669
1-heptyne	99.7	0.733
2-heptyne	112	0.748
3-heptyne	105.5	0.753
5-methyl-1-hexyne	92	0.727
5-methyl-2-hexyne	102	0.738
2-methyl-3-hexyne	95.2	0.726
4,4-dimethyl-1-pentyne	76.1	0.714
4,4-dimethyl-2-pentyne	82.3	0.718
3-ethyl-1-pentyne	88	0.724

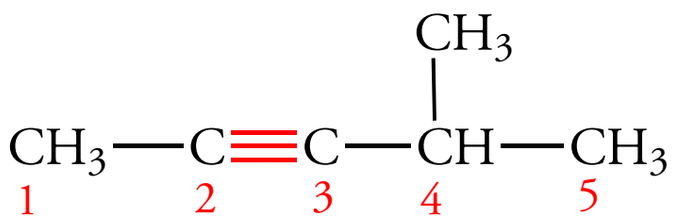
7.3 IUPAC NAMES OF ALKYNES

1. The longest continuous chain that contains the triple bond is the parent.
2. Give the parent the same stem name as an alkane, but replace *-ane* with *-yne*.
3. Number the carbon atoms consecutively from the end of the chain nearer the triple bond. Use the number of the first carbon atom with the triple bond as a prefix separated by a hyphen from the parent name.



Number this compound from right to left.
It is 2-hexyne.

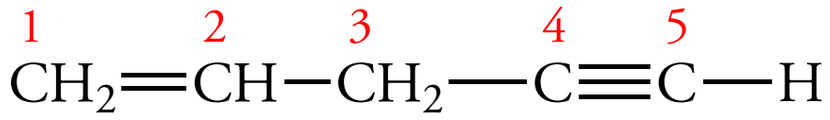
4. Alkyl groups are named, and their positions on the chain determined, by the numbering established by rule 3.



Number this compound from left to right.
It is 4-methyl-2-pentyne.

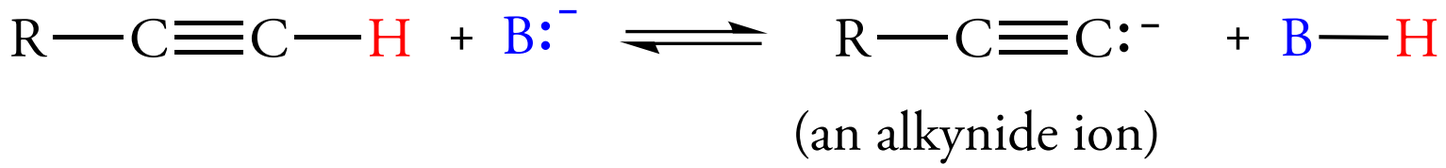
7.3 IUPAC NAMES OF ALKYNES (II)

5. Compounds with multiple triple bonds are diynes, triynes, and so on. Compounds with both double and triple bonds are called *enynes*, <u>not</u> ynenes. Start the numbering of compounds with both double and triple bonds from the end nearer the first multiple bond, regardless of type. When a choice is possible, assign double bonds lower numbers than triple bonds.

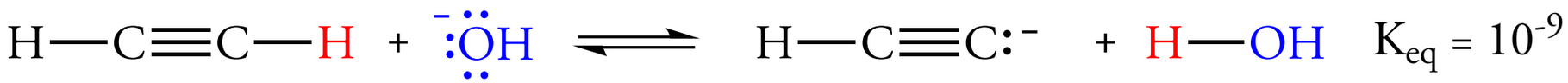


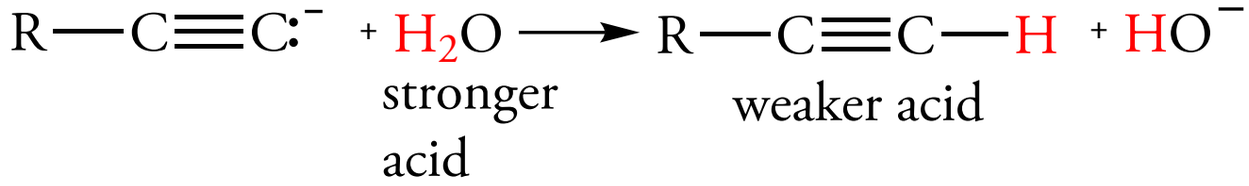
This is 1-penten-4-yne,
not 4=penten-1-yne.

7.4 ACIDITY OF TERMINAL ALKYNES



$CH_3—CH_3$	$CH_2=CH_2$	$HC\equiv CH$
K_a 10^{-50}	$K_a = 10^{-44}$	K_a 10^{-25}





7.5 HYDROGENATION OF ALKYNES

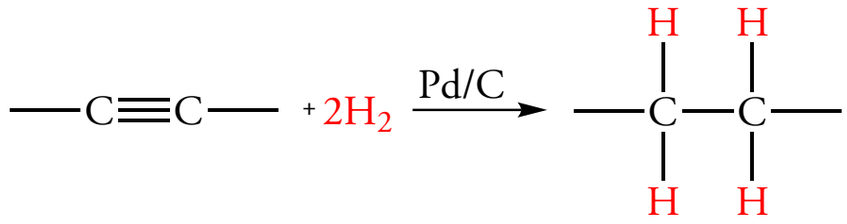
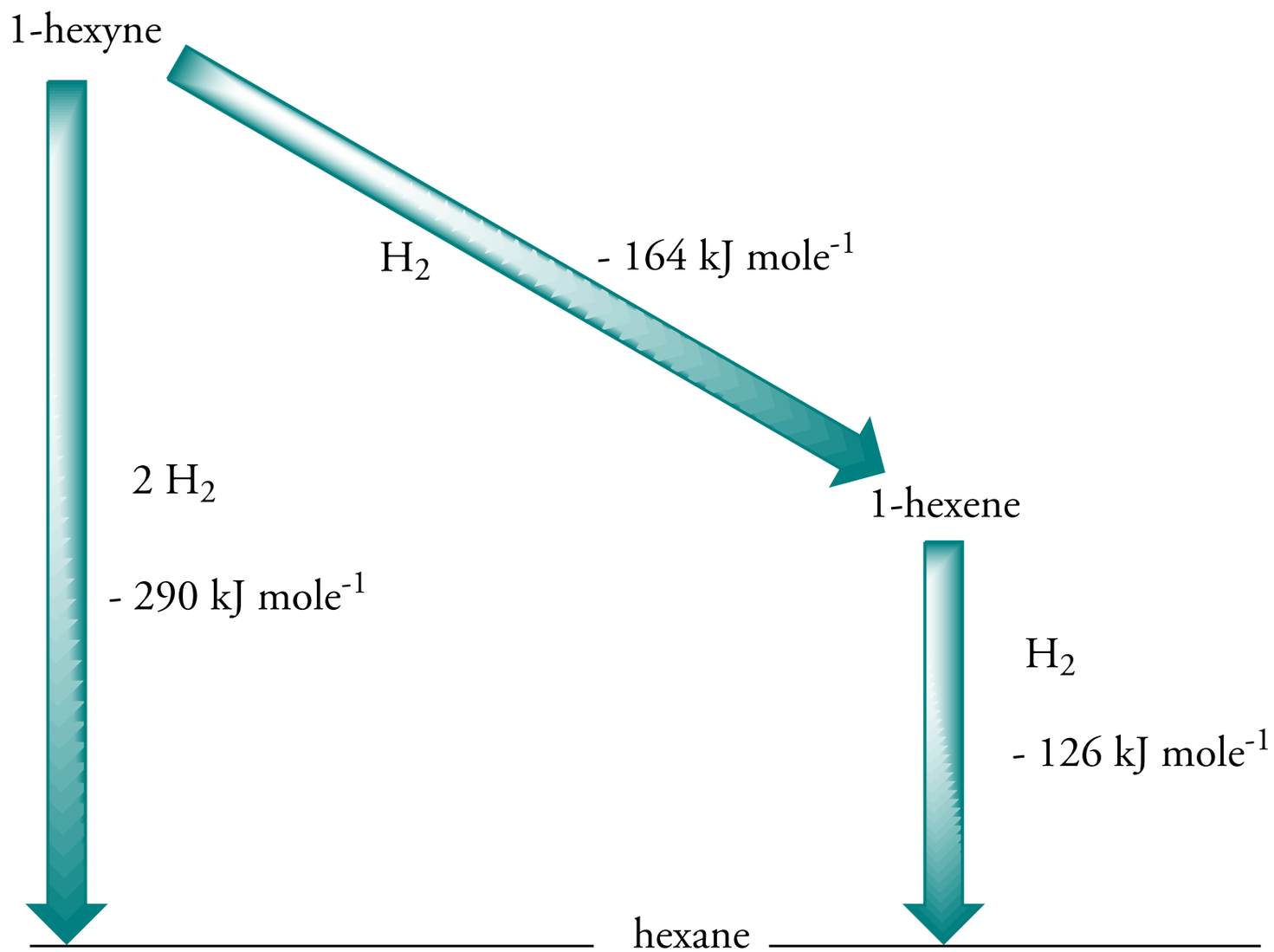
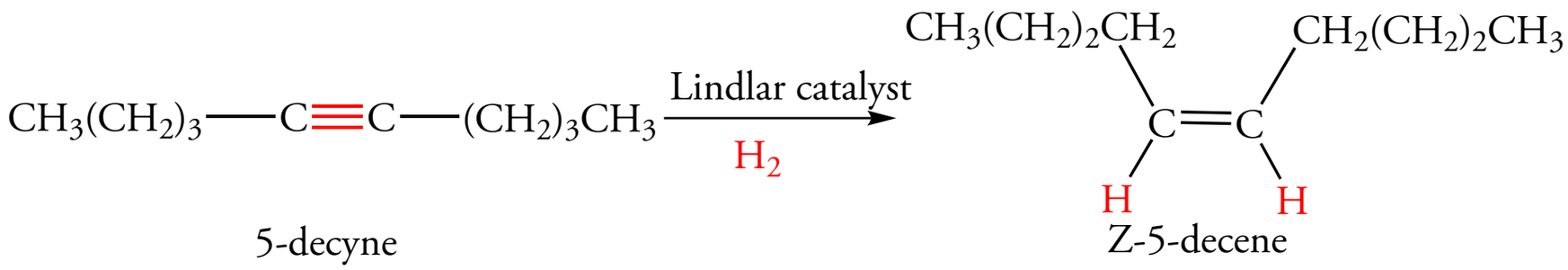


Figure 7.2 Stability of Alkenes and Alkynes



7.5 HYDROGENATION OF ALKYNES

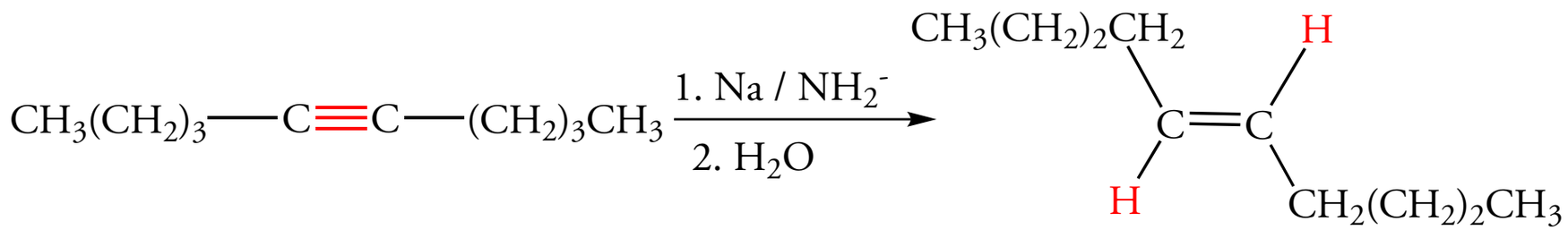
Syn Addition of Hydrogen



5-decyne

Z-5-decene

Anti Addition of Hydrogen

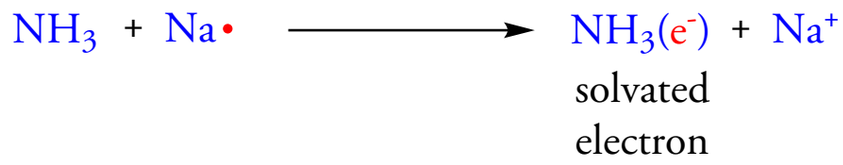


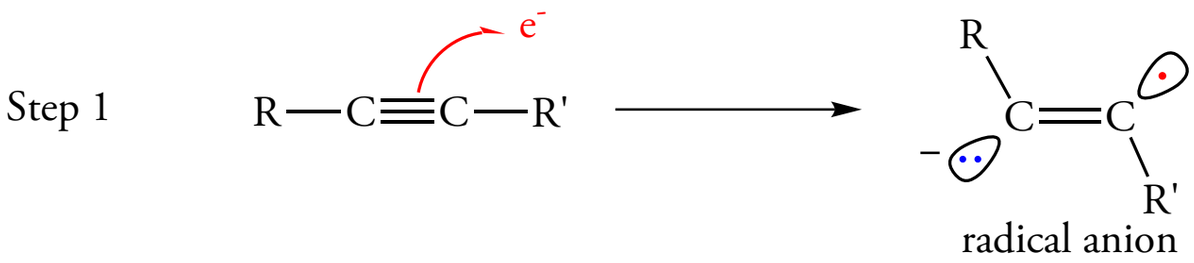
5-decyne

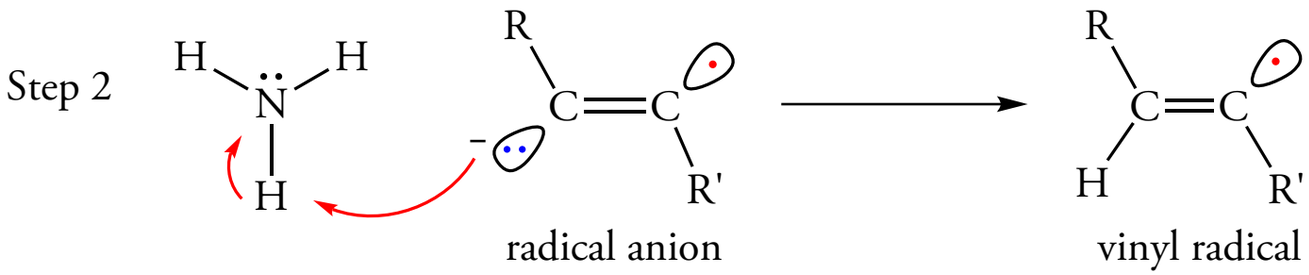
(E)-5-decene

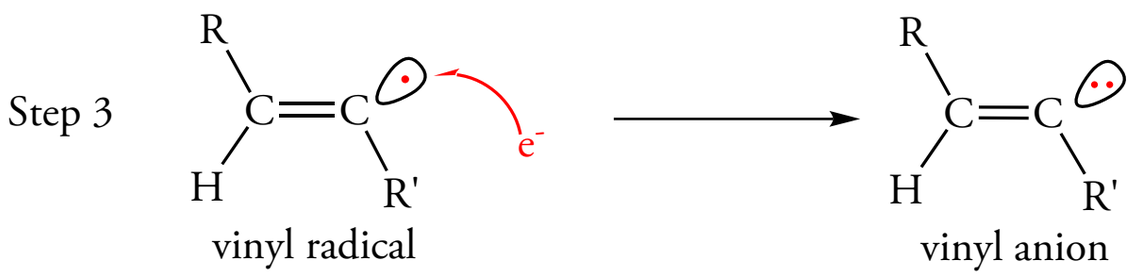
7.5 HYDROGENATION OF ALKYNES

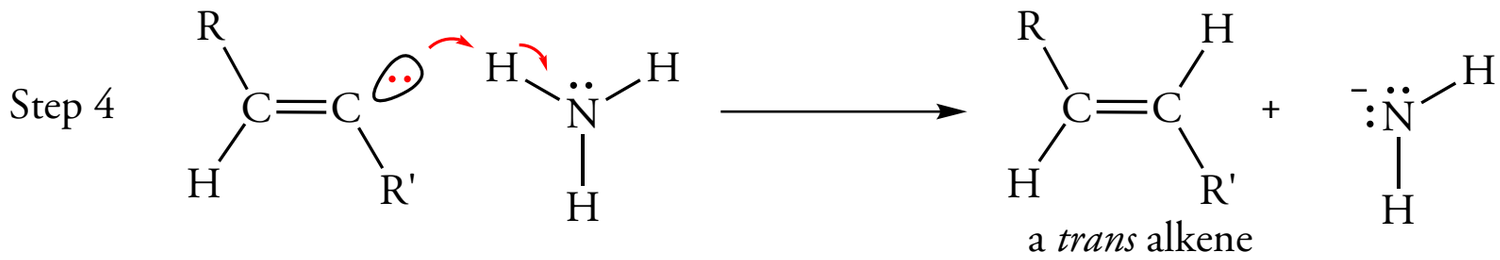
Mechanism of Anti Addition





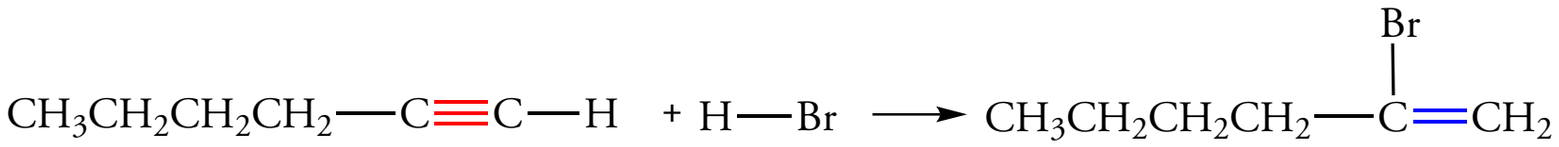






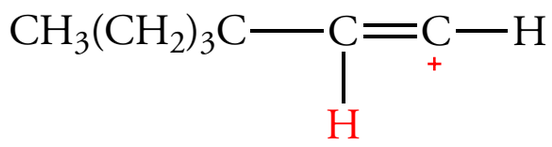
7.6 ELECTROPHILIC ADDITION REACTIONS

Addition of Hydrogen Halides

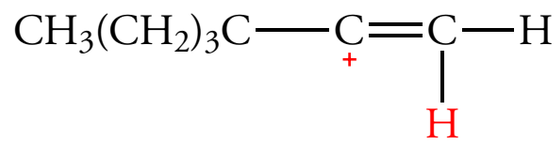


1-hexyne

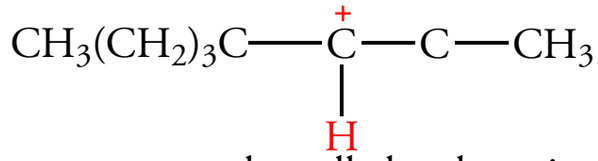
2-bromo-1-hexene



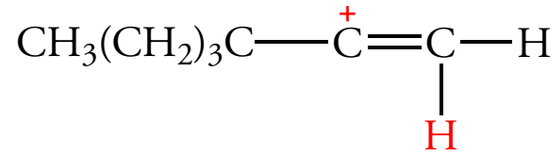
primary alkenyl carbocation
(less stable)



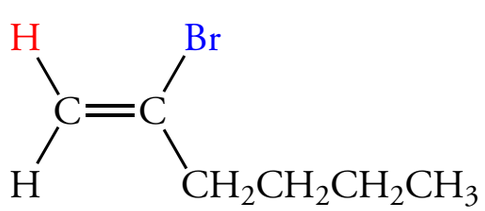
secondary alkenyl carbocation
(more stable)

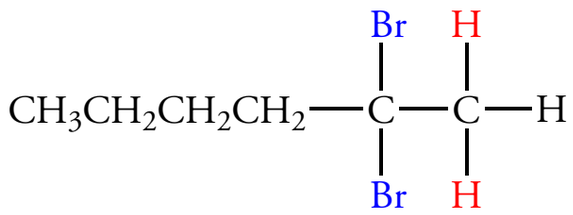


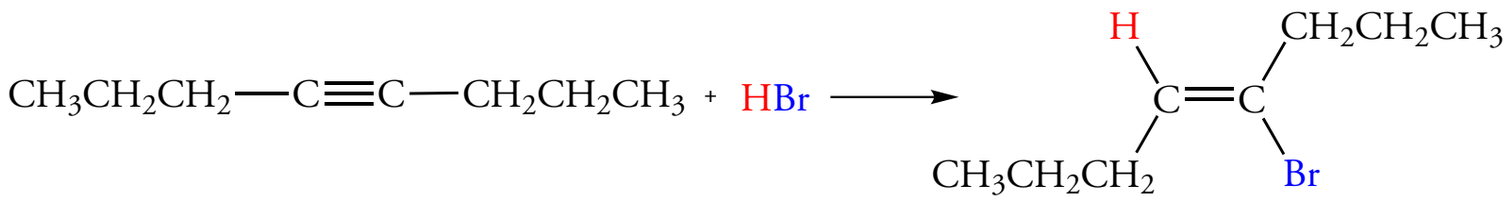
secondary alkyl carbocation
(more stable)



secondary alkenyl carbocation
(less stable)





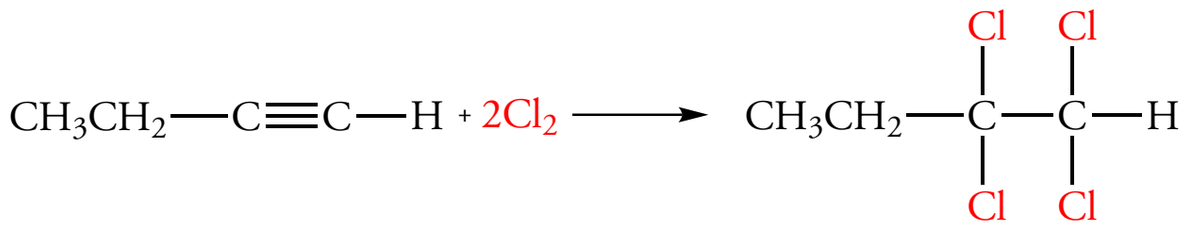


4-octyne

(Z)-4-bromo-4-octene

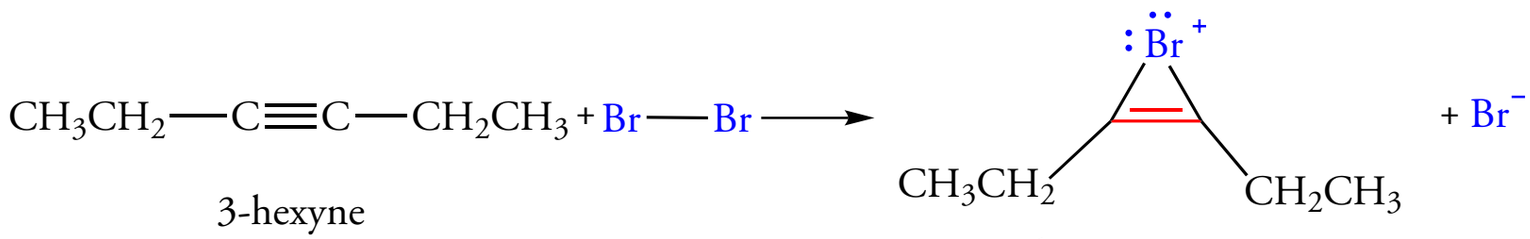
7.6 ELECTROPHILIC ADDITION REACTIONS

Addition of Halogens



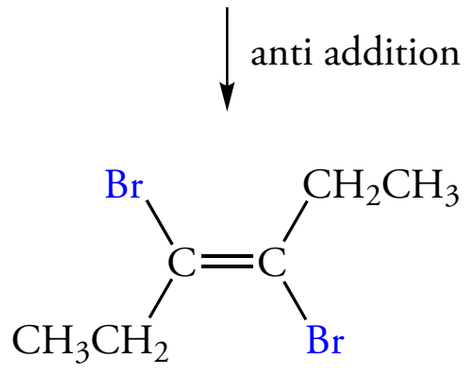
1-butyne

1,1,2,2-tetrachlorobutane



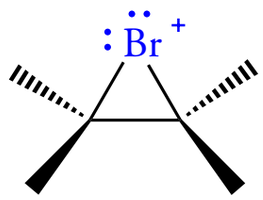
3-hexyne

bromonium ion



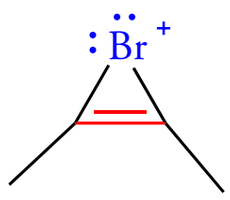
(E)-3,4-dibromo-3-hexene

cyclic bromonium ion
from alkene addition



more stable

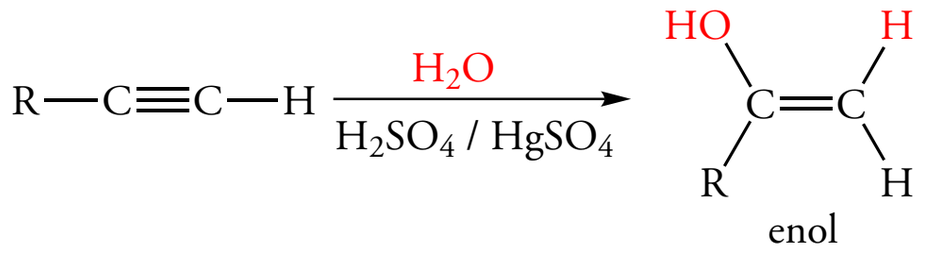
cyclic bromonium ion
from alkyne addition



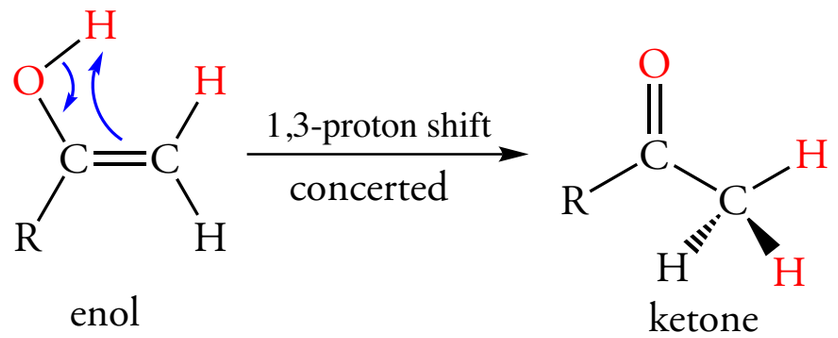
less stable

7.6 ELECTROPHILIC ADDITION REACTIONS

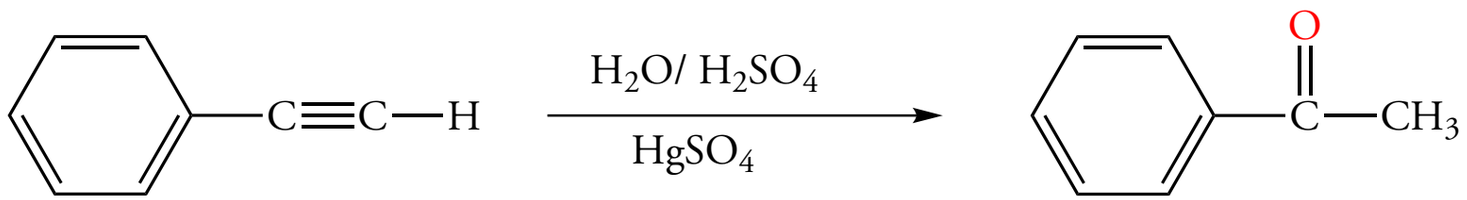
Hydration of Alkynes



enol

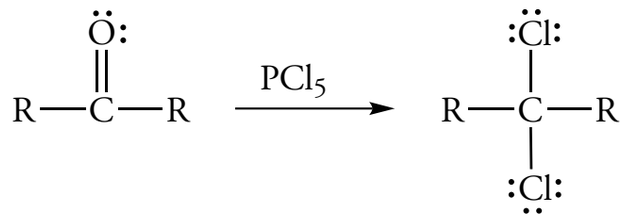


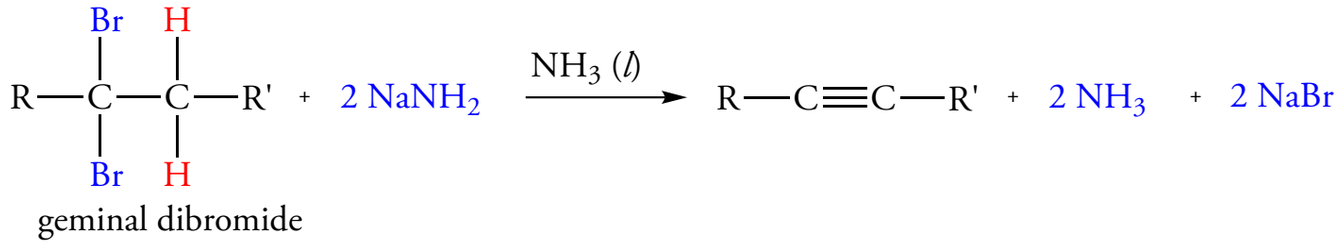
enol ketone



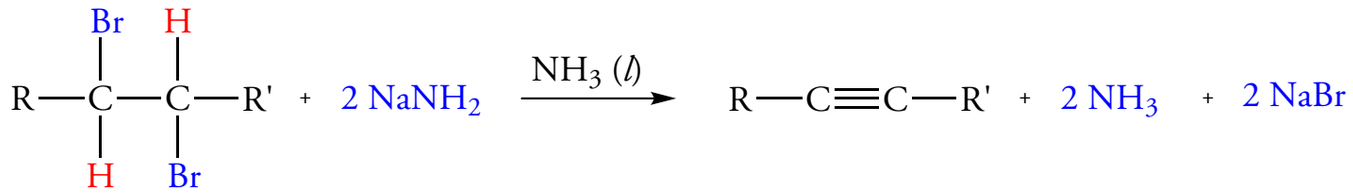
7.7 SYNTHESIS OF ALKYNES

Elimination Reactions of Dihalides

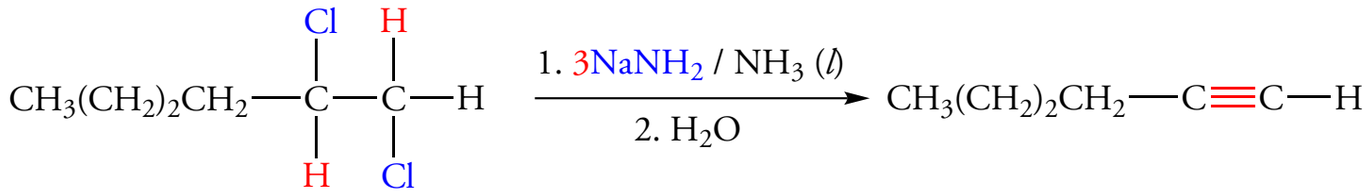




geminal dibromide

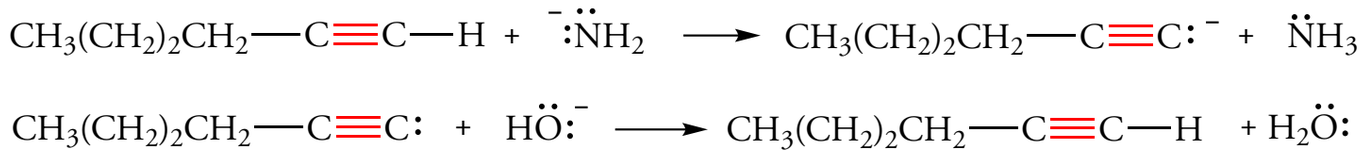


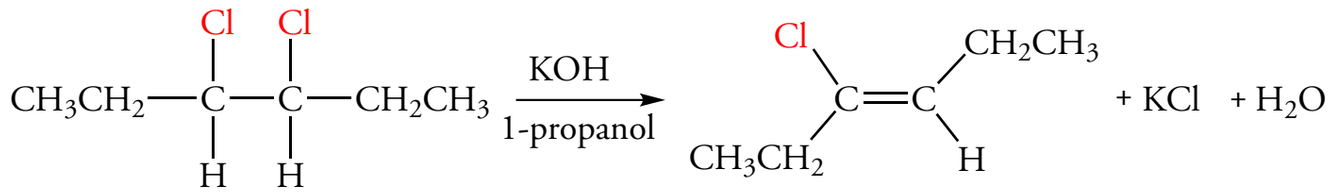
vicinal dibromide



1,2-dichlorohexane

1-hexyne





3,4-dichloroexane

7.6 ELECTROPHILIC ADDITION REACTIONS

Alkylation of Alkynes