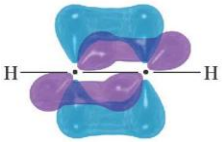
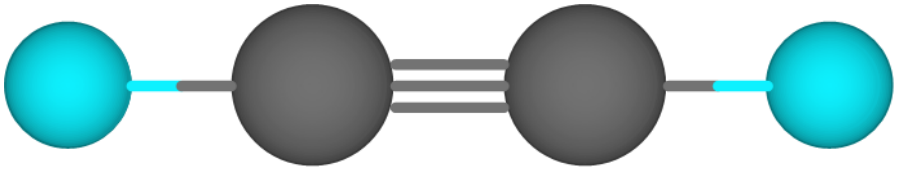
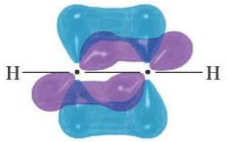


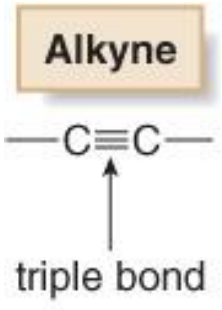
Alkynes

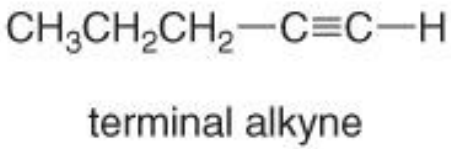


Alkynes

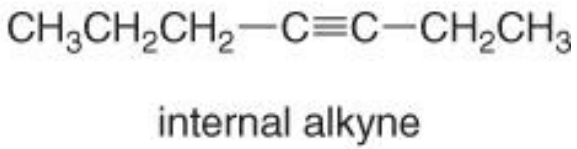


- General formula is C*n*H2*n*-2.
- Two elements of unsaturation for each triple bond.
- Some reactions resemble the reactions of alkenes, like addition and oxidation.
- Some reactions are specific to alkynes.
- Alkynes contain a triple bond, the triple bond can be terminal or internal.



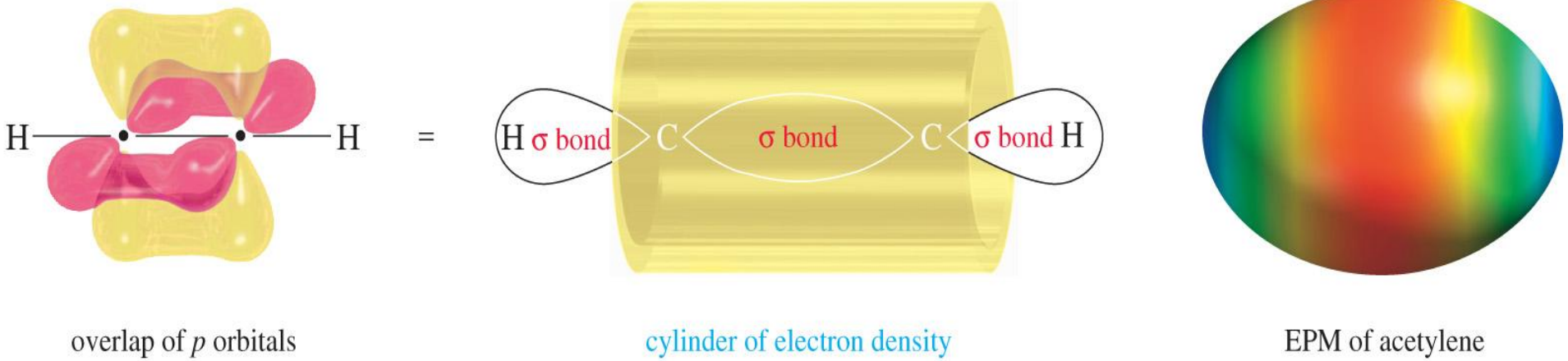


terminal alkyne



internal alkyne

Molecular Structure of Acetylene



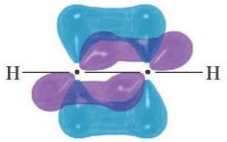
overlap of *p* orbitals

cylinder of electron density

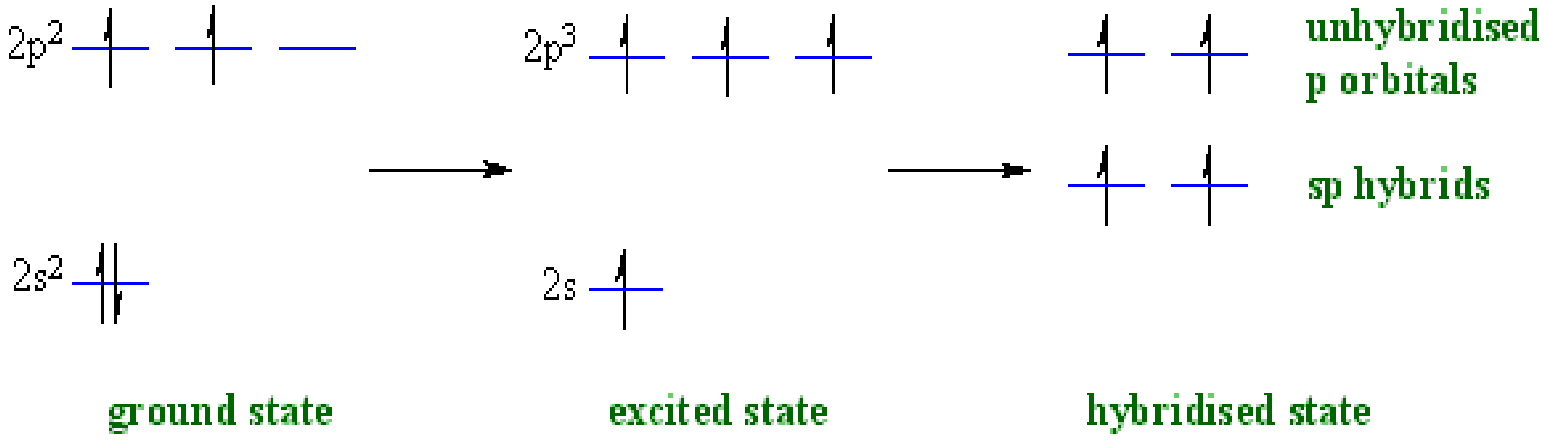
EPM of acetylene

- **Triple-bonded carbons have *sp* hybrid orbitals.**
- **A sigma bond is formed between the carbons by overlap of the *sp* orbitals.**
- **Sigma bonds to the hydrogens are formed by using the second *sp* orbital.**
- **Since the *sp* orbitals are linear, acetylene will be a linear molecule.**

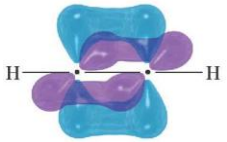
sp hybridization

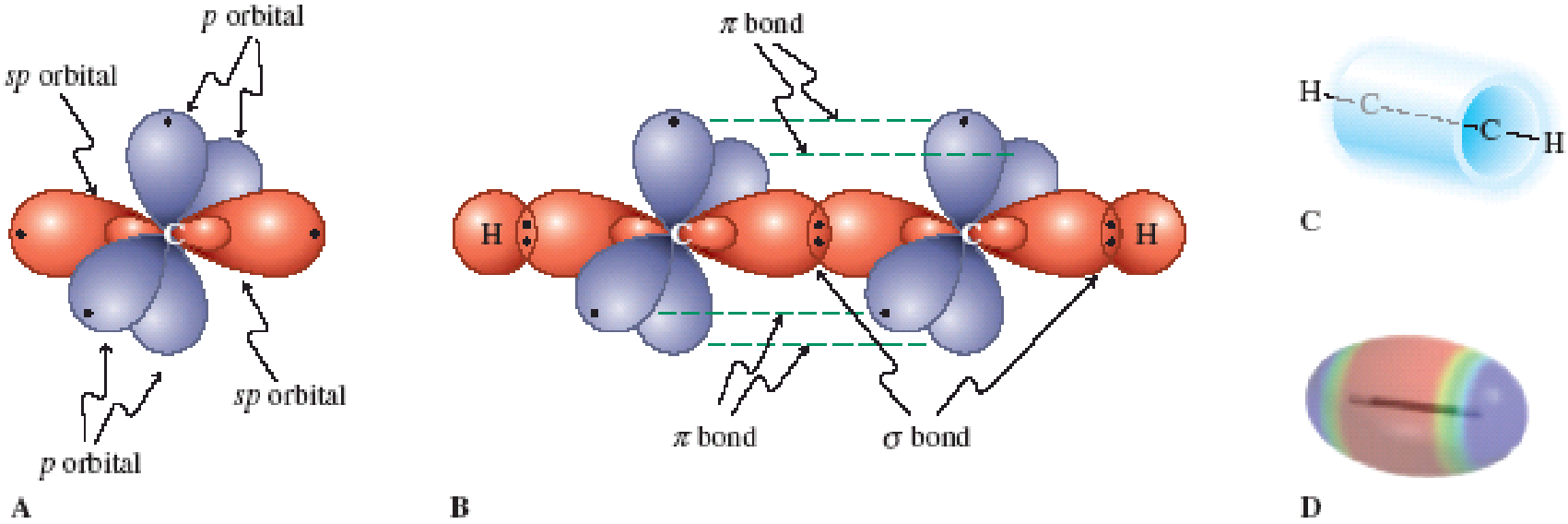


This involves the mixing of one s- and one p-orbital forming two sp-hybrid orbitals. The two sp-hybrid orbitals are oriented in a linear arrangement and bond angle is 180°.



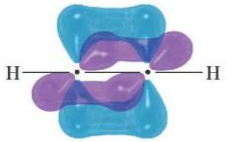
Overlap of the *p* Orbitals of Acetylene





- Carbon-carbon triple bond results from sp orbital on each C forming a sigma bond and unhybridized p_X and p_y orbitals forming π bonds.
- The remaining sp orbitals form bonds to other atoms at 180º to C-C triple bond.
- The bond is shorter and stronger than single or double

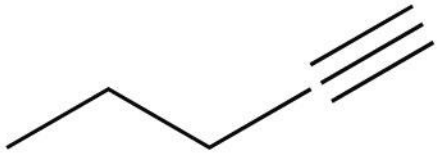
Nomenclature



- General hydrocarbon rules apply with Change *-ane* ending to *-yne*.

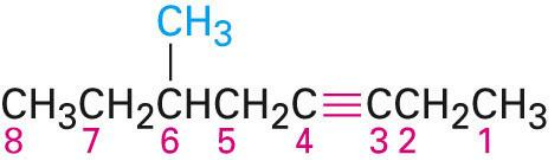
Pentane

Pentene



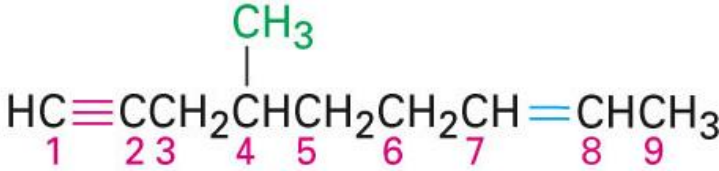
Pentyne

- Numbering of chain with triple bond is set so that the smallest number possible for the first carbon of the triple bond
- Multiple triple bonds are: diynes, triynes, etc…
- Double and triple bonds are: enynes
  - Number nearest a multiple bond (either double or triple)
  - If you have a choice, double bond lower number than triple



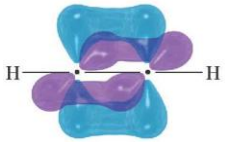
6-Methyl-3-octyne

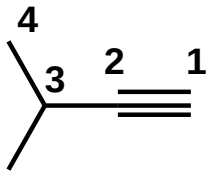
1-Hepten-6-yne



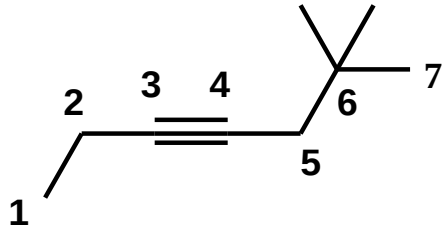
4-Methyl-7-nonen-1-yne

Examples of Nomenclature

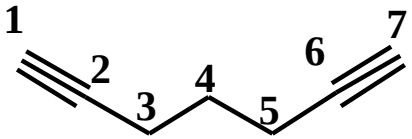




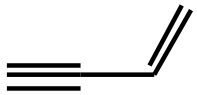
3-Methyl-1-butyne



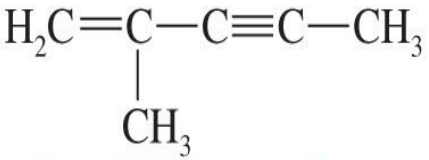
6,6-Dimethyl-3-heptyne

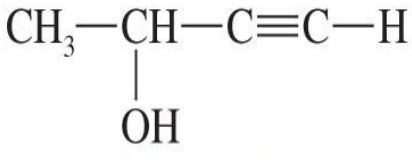


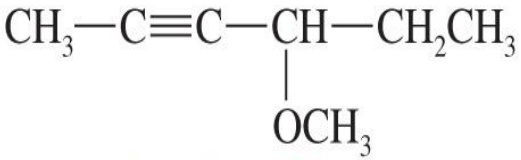
1,6-Heptadiyne



IUPAC name:	**2-Butyne**	**1-Buten-3-yne**
Common name:	**Dimethylacetylene**	**Vinylacetylene**

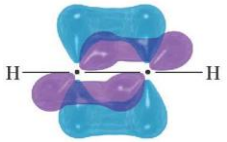






IUPAC name:	2-methyl-1-penten-3-yne	3-butyn-2-ol	4-methoxy-2-hexyne
new IUPAC name:	2-methylpent-1-en-3-yne	but-3-yn-2-ol	4-methoxyhex-2-yne

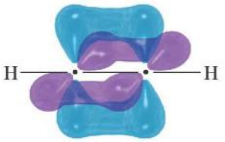
Physical Properties



- Nonpolar, insoluble in water.
- Soluble in most organic solvents.
- Boiling points are similar to alkane of same size.
- Less dense than water.
- Up to four carbons, gas at room temperature.

Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density at 20°C (g/mL)
Ethyne	$HC{\equiv}CH$	-81	-84	(a gas)
Propyne	$CH_3C{\equiv}CH$	-102	-23	(a gas)
1-Butyne	$CH_3CH_2C{\equiv}CH$	-126	8	(a gas)
2-Butyne	$CH_3C{\equiv}CCH_3$	-32	27	0.691
1-Pentyne	$CH_3(CH_2)_2C{\equiv}CH$	-90	40	0.690
1-Hexyne	$CH_3(CH_2)_3C{\equiv}CH$	-132	71	0.716
1-Octyne	$CH_3(CH_2)_5C{\equiv}CH$	-79	125	0.746
1-Decyne	$CH_3(CH_2)_7C{\equiv}CH$	-36	174	0.766

Relative Stability of Alkynes



The heats of hydrogenation of alkyne isomers can be used to determine their relative stabilities:

$$CH_3CH_2C{\equiv}CH + 2\,H_2 \xrightarrow{\text{Catalyst}} CH_3CH_2CH_2CH_3 \qquad \Delta H^\circ = -69.9 \text{ kcal mol}^{-1} \; (-292.5 \text{ kJ mol}^{-1})$$

$$CH_3C{\equiv}CCH_3 + 2\,H_2 \xrightarrow{\text{Catalyst}} CH_3CH_2CH_2CH_3 \qquad \Delta H^\circ = -65.1 \text{ kcal mol}^{-1} \; (-272.4 \text{ kJ mol}^{-1})$$

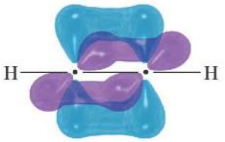
Unnumbered figure pg 564c
Organic Chemistry, Fifth Edition

The greater relative stabililty of internal alkynes is due to hyperconjugation.

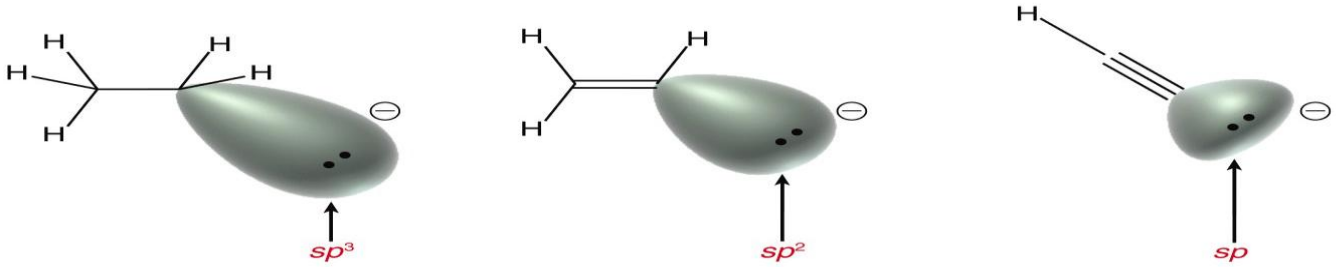
Relative Stabilities of the Alkynes

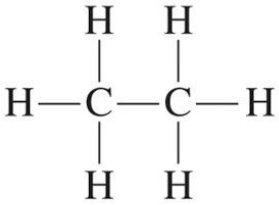
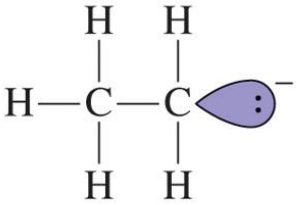
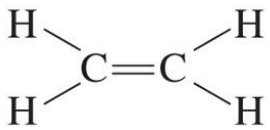
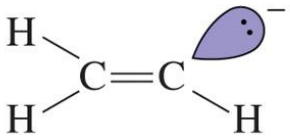
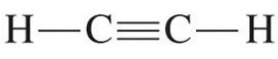
$$RC{\equiv}CH < RC{\equiv}CR'$$

Acidity

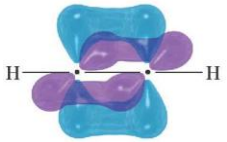


- A major difference between the chemistry of alkynes and that of alkenes and alkanes is the acidity of the hydrogen bonded to a triply bonded carbon



Compound	Conjugate Base	Hybridization	*s* Character	pK_a	
		sp^3	25%	50	weakest acid
		sp^2	33%	44	
$:NH_3$	$:\ddot{N}H_2^-$	(ammonia)		35	
		sp	50%	25	
R—OH	R—$\ddot{O}:^-$	(alcohols)		16–18	stronger acid

Acidity of Alkynes



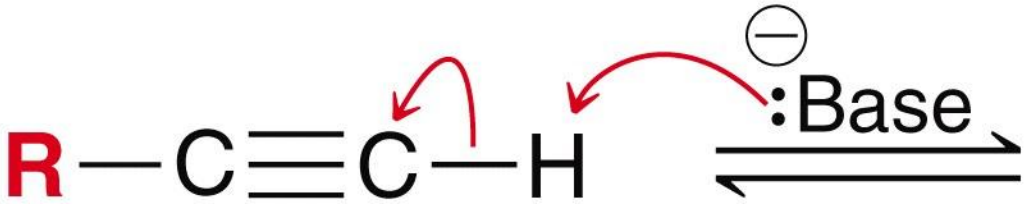
- Terminal alkynes, are more acidic than other hydrocarbons due to the higher *s* character of the *sp* hybridized carbon.
- Terminal alkynes can be deprotonated quantitatively with strong bases such as sodium amide (-NH2), sodium hydride or lithium diisopropylamide (LDA)

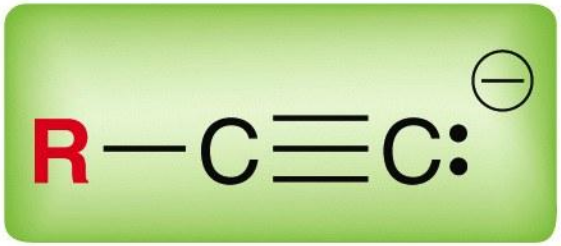
$Na^+ H^-$

Sodium hydride

$[(CH_3)_2CH]_2N^- Li^+$

Lithium diisopropylamide (LDA)

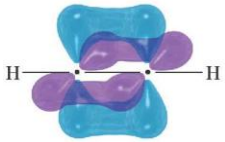




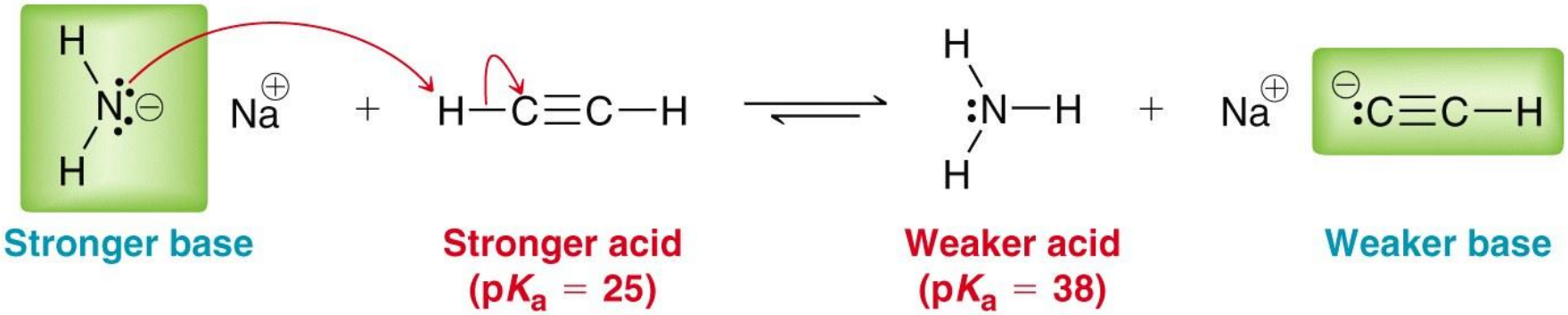
An alkyne

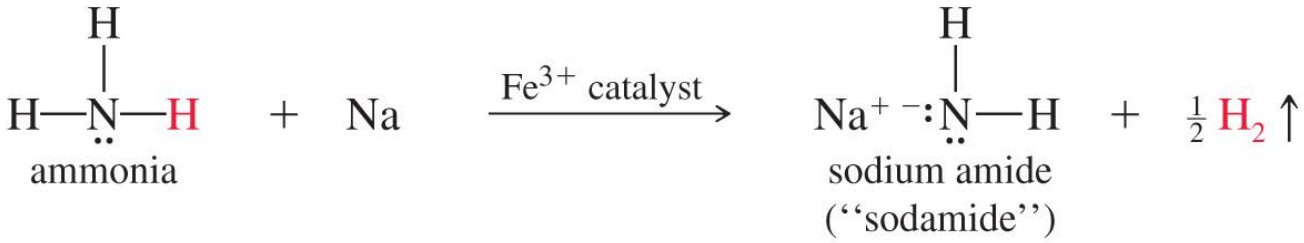
An alkynide ion

Formation of Acetylide Ions

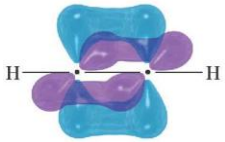


- Acetylene reacts with sodium amide to form sodium acetylide

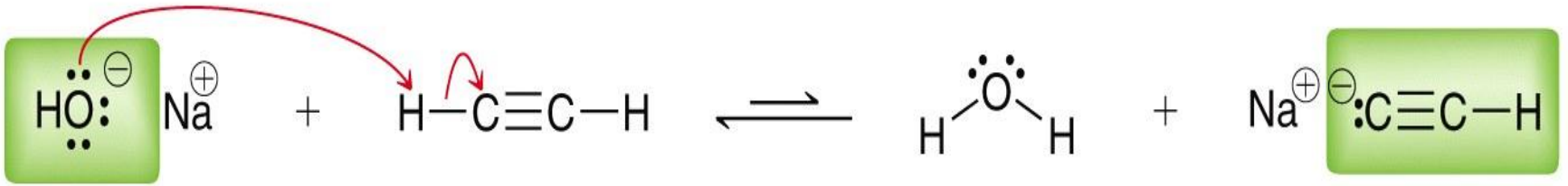




Acidity



- **Water is a stronger acid than acetylene; Hydroxide and alkoxide bases are not strong enough to deprotonate the alkyne quantitatively to its anion**



Weaker base

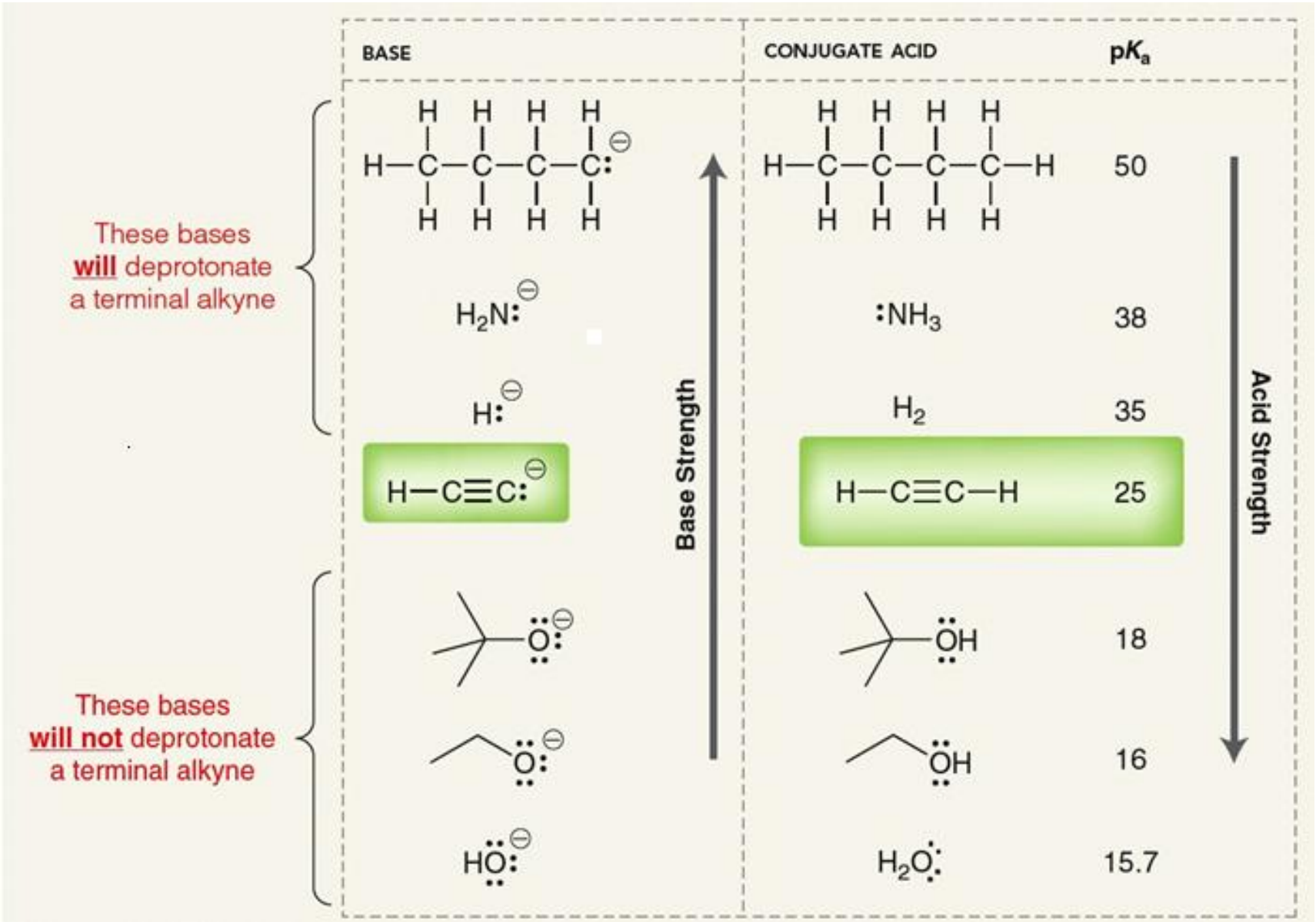
Weaker acid (pK_a = 25)

Stronger acid (pK_a = 15.7)

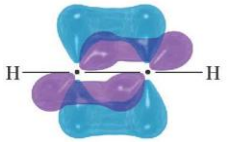
Stronger base

Equilibrium favors the weaker acid and weaker base

Bases and Their Congugate acids



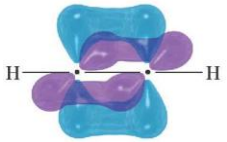
Alkylation of Acetylides



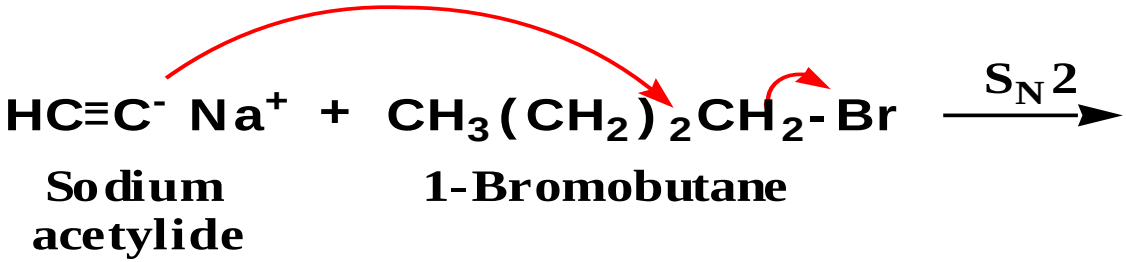
- **Acetylide anions are both strong bases and good nucleophiles**
- **They undergo S_N2 reactions with alkyl halides, tosylates, and mesylates to form new C-C bonds to alkyl groups; that is, they undergo alkylation**

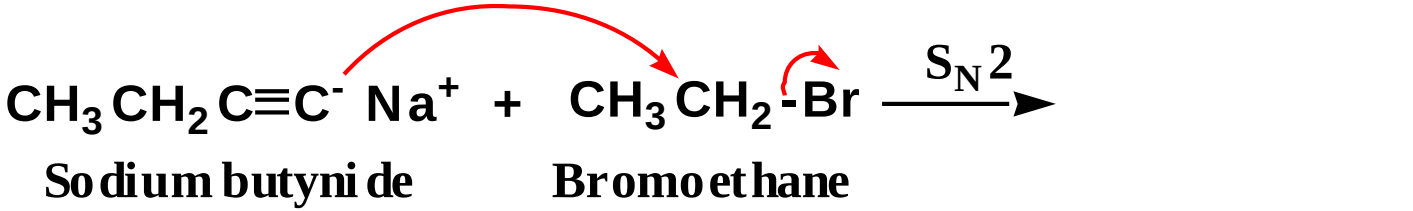
  - **because acetylide anions are also strong bases, alkylation is practical only with methyl and 1° halides**
  - **with 2° and 3° halides, E2 is the major reaction.**

Alkylation of Acetylides

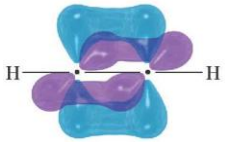


- Alkylation of acetylide anions is the most convenient method for the synthesis of terminal alkynes
- Alkylation can be repeated and a terminal alkyne can be converted to an internal alkyne

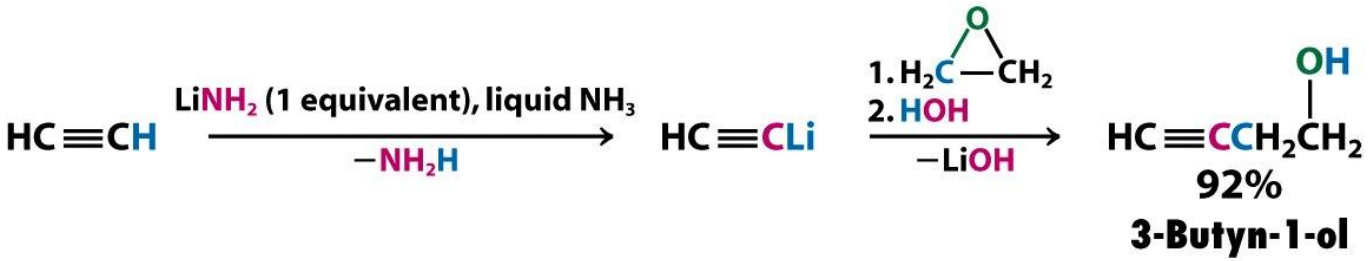


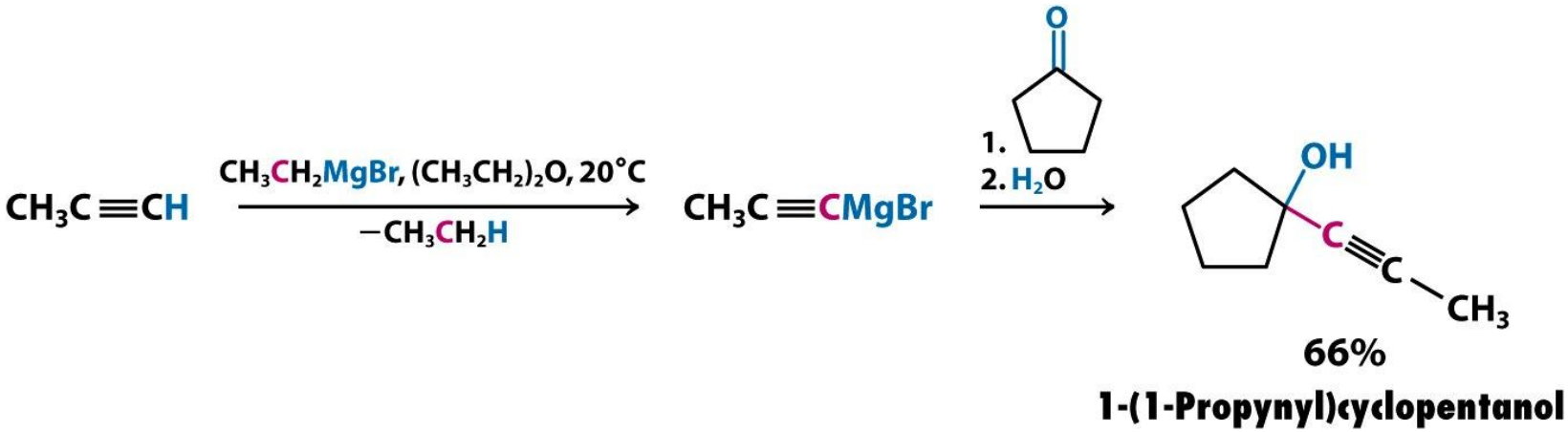


Other reactions of alkynyl anions



Reactions of Alkynyl Anions

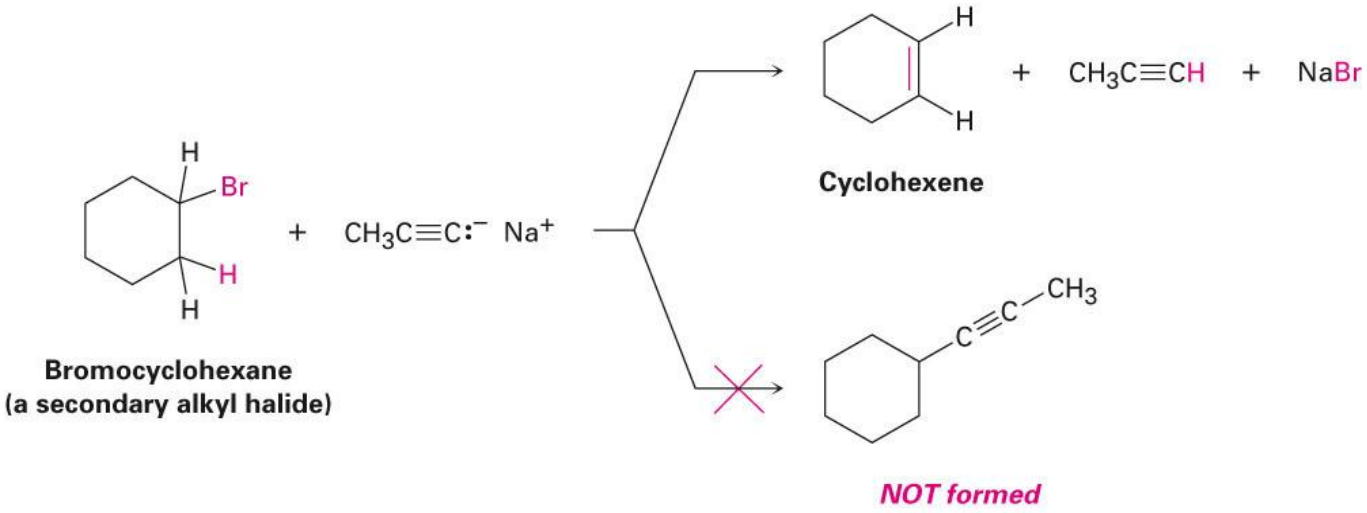




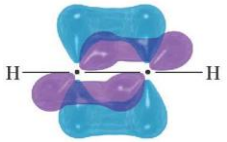
Unnumbered figure pg 572a
Organic Chemistry, Fifth Edition

Limitations of Alkyation of Acetylide Ions

- **Reactions only are efficient with 1º alkyl bromides and alkyl iodides**
- **Reactions with 2º and 3º alkyl halides gives dehydrohalogenation, converting alkyl halide to alkene**



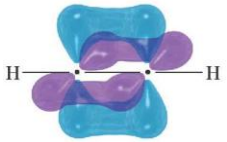
Reduction



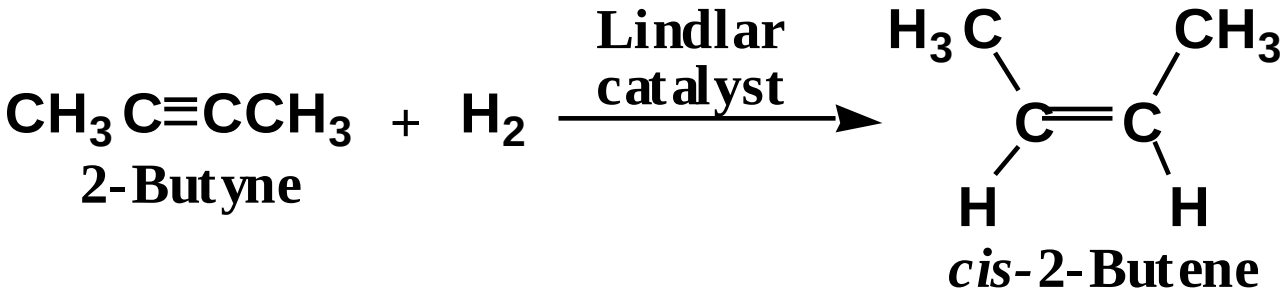
- **Treatment of an alkyne with hydrogen in the presence of a transition metal catalyst, most commonly Pd, Pt, or Ni, converts the alkyne to an alkane**

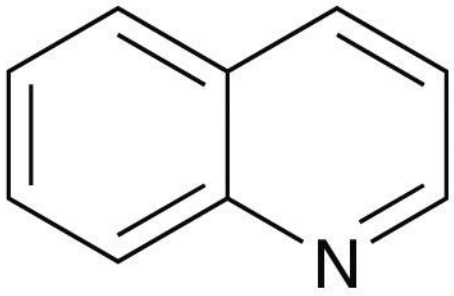
$$\underset{\text{2-Butyne}}{CH_3C{\equiv}CCH_3} + 2H_2 \xrightarrow[3\ \text{atm}]{\text{Pd, Pt, or Ni}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

Reduction



- **With the Lindlar catalyst, reduction stops at addition of one mole of H_2**
  - **this reduction shows syn stereoselectivity**

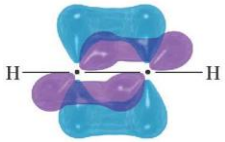


Lindlar's catalyst = 

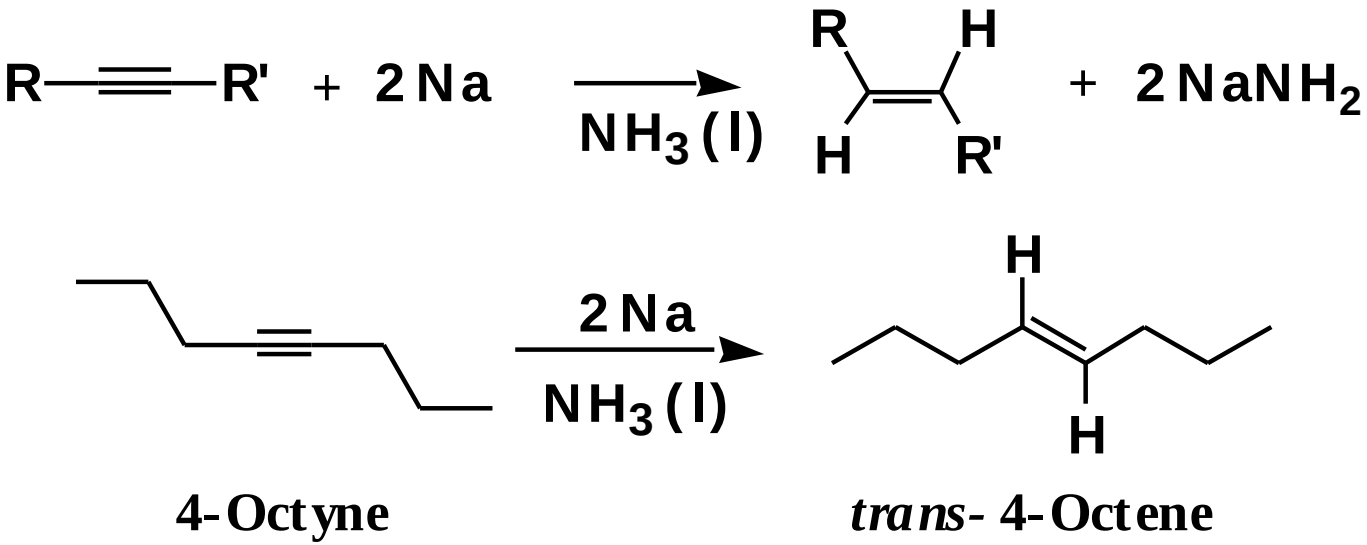
, Pd / $BaSO_4$, CH_3OH

Quinoline

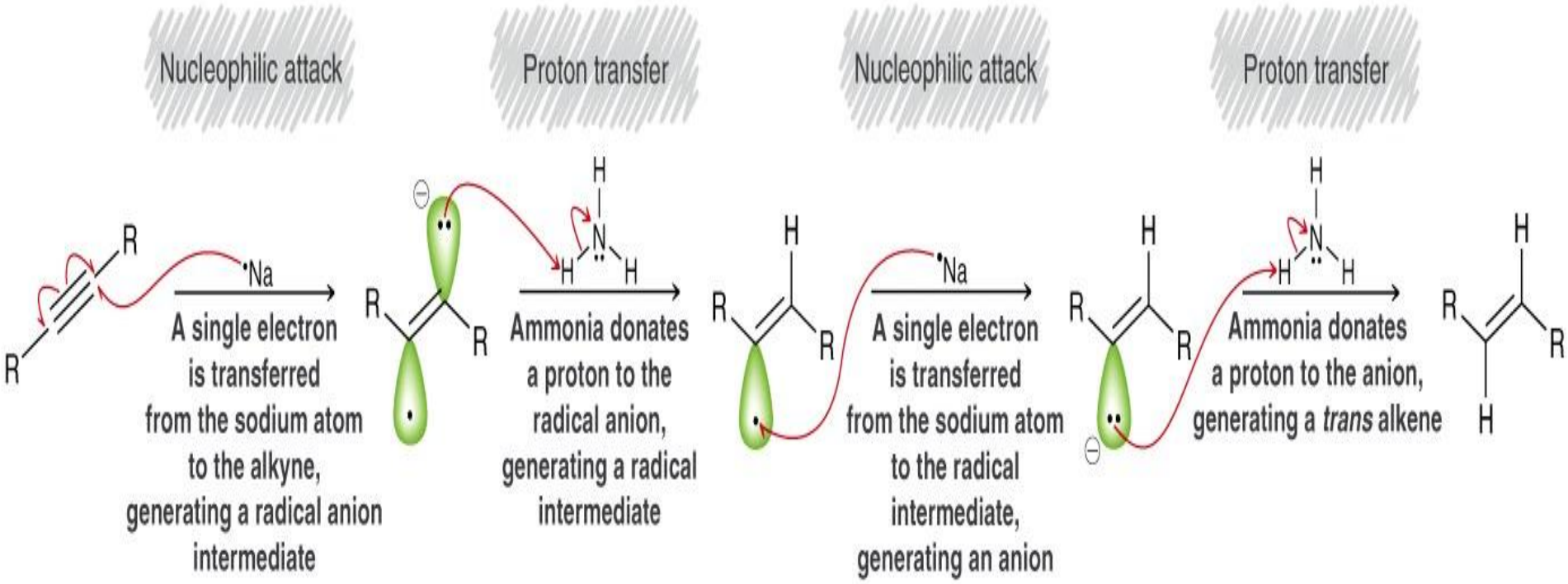
Reduction

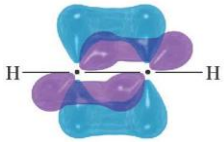


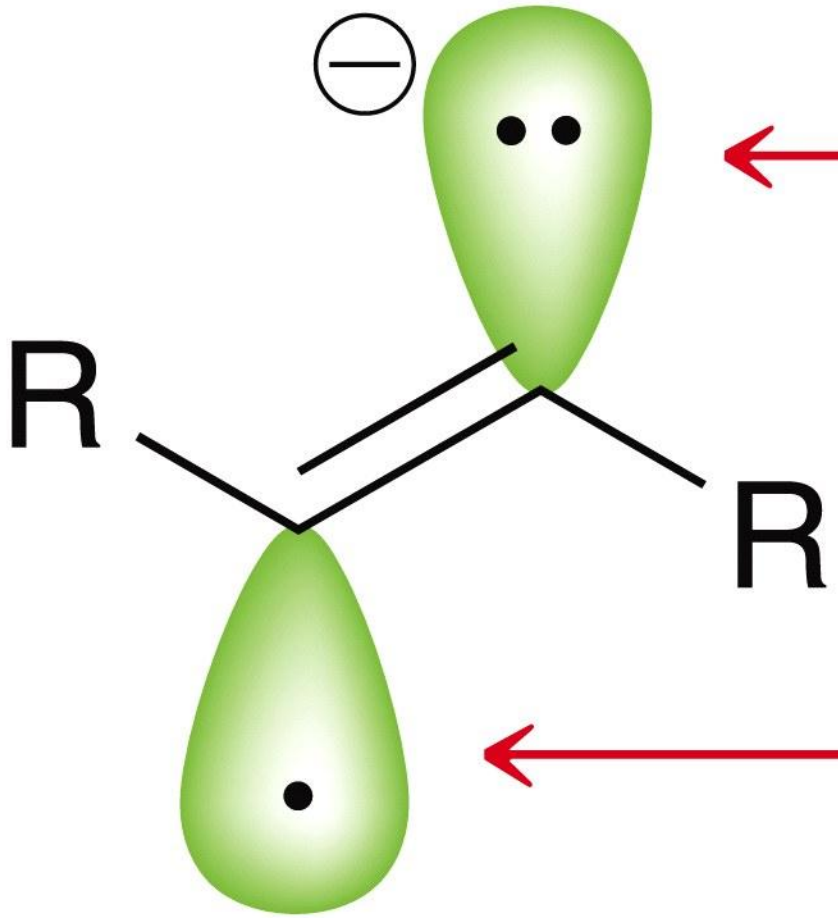
- **Reduction of an alkyne with Na or Li in liquid ammonia converts an alkyne to an alkene with anti stereoselectivity**



Na/NH_3 Reduction

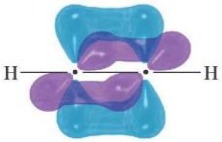


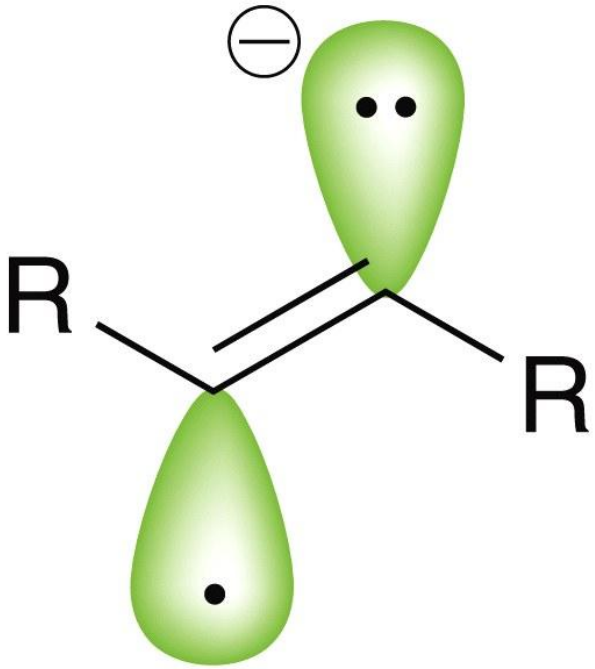




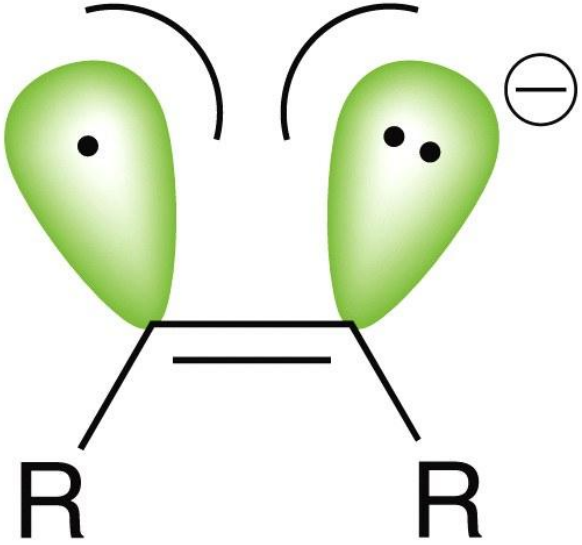
Anion

Radical





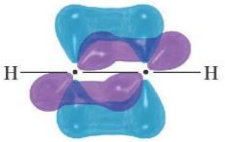
Repulsion



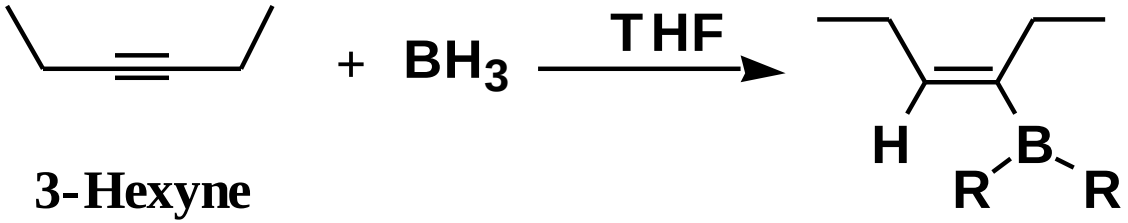
Lower energy

Higher energy

Hydroboration



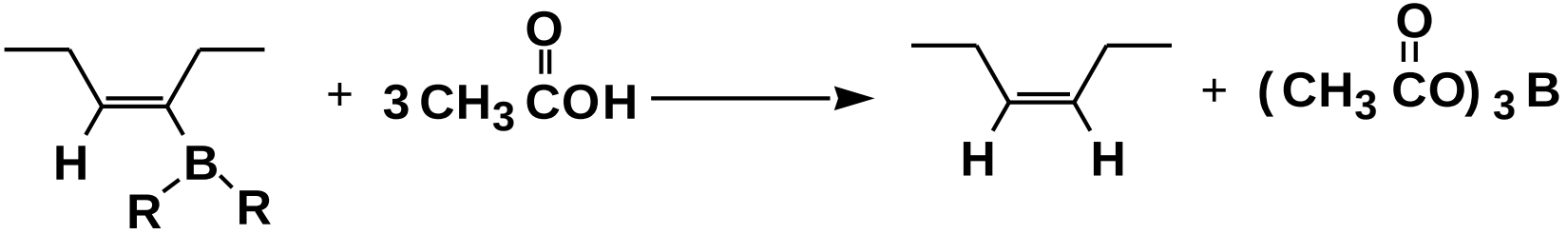
- **Addition of borane to an internal alkynes gives a trialkenylborane**



3-Hexyne

A trialkenylborane
(R = *cis*-3-hexenyl group)

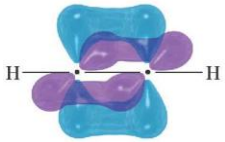
- **Treatment of a trialkenylborane with acetic acid results in stereoselective replacement of B by H**



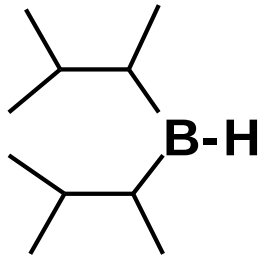
A trialkenylborane

cis-3-Hexene

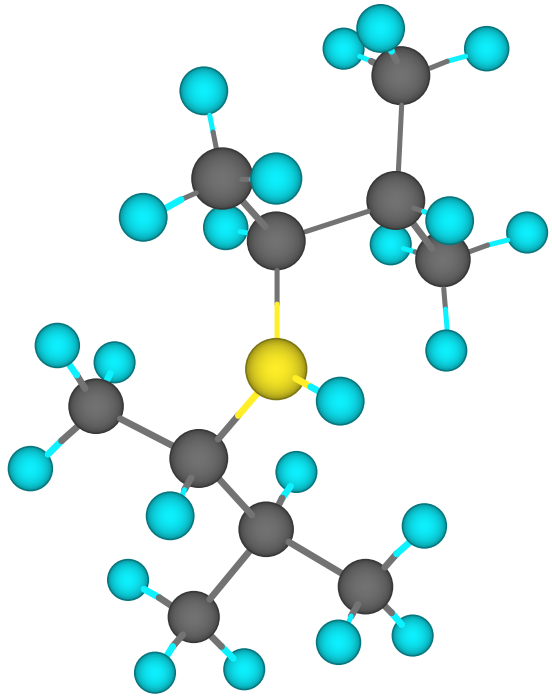
Hydroboration



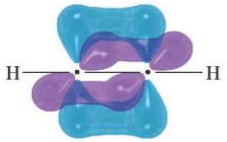
- To prevent dihydroboration with terminal alkynes, it is necessary to use a sterically hindered dialkylborane, such as $(sia)_2BH$



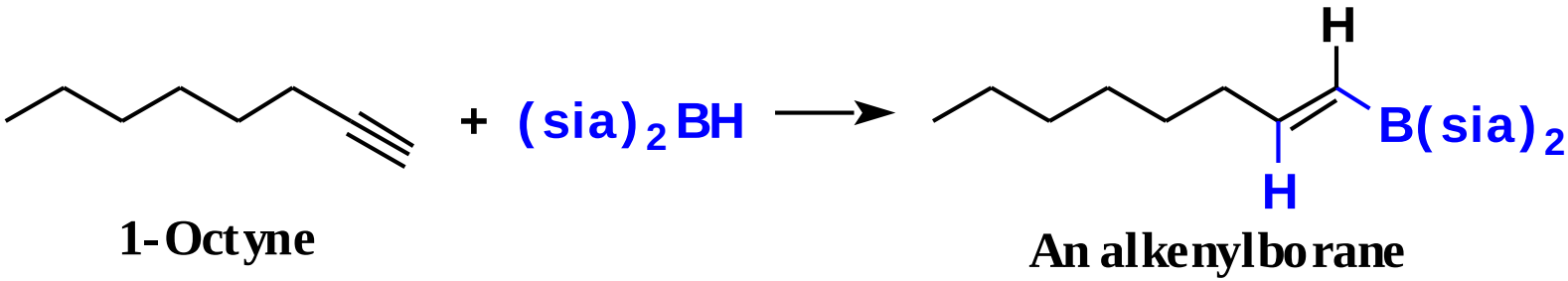
Di-sec-isoamylborane
$[(sia)_2BH]$



Hydroboration



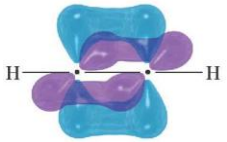
- **Treatment of a terminal alkyne with $(sia)_2BH$ results stereospecific and regioselective hydroboration**



1-Octyne

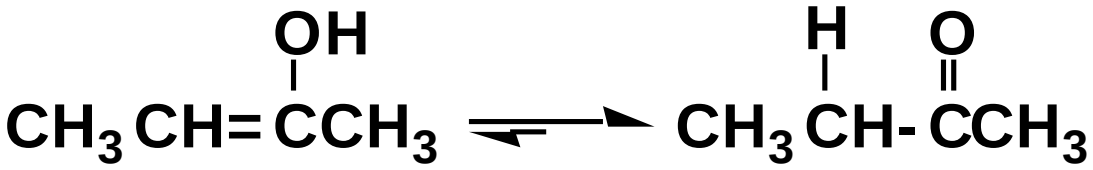
An alkenylborane

Hydroboration



- Treatment of an alkenylborane with H_2O_2 in aqueous NaOH gives an enol

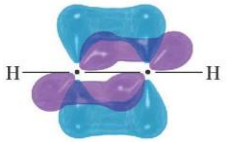
$$CH_3C{\equiv}CCH_3 \xrightarrow[2.\ H_2O_2,\ NaOH]{1.\ BH_3}$$



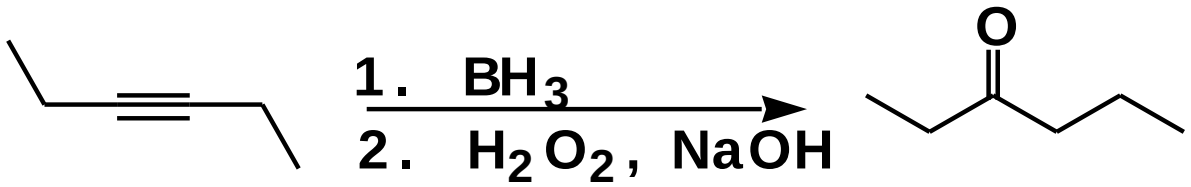
2-Buten-2-ol (an enol) ⇌ 2-Butanone (a ketone)

$K_{eq} = 6.7 \times 10^6$ (for keto-enol tautomerism)

Hydroboration/oxidation



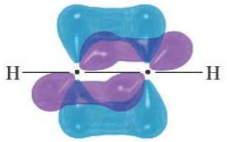
- **Hydroboration/oxidation of an internal alkyne gives a ketone**



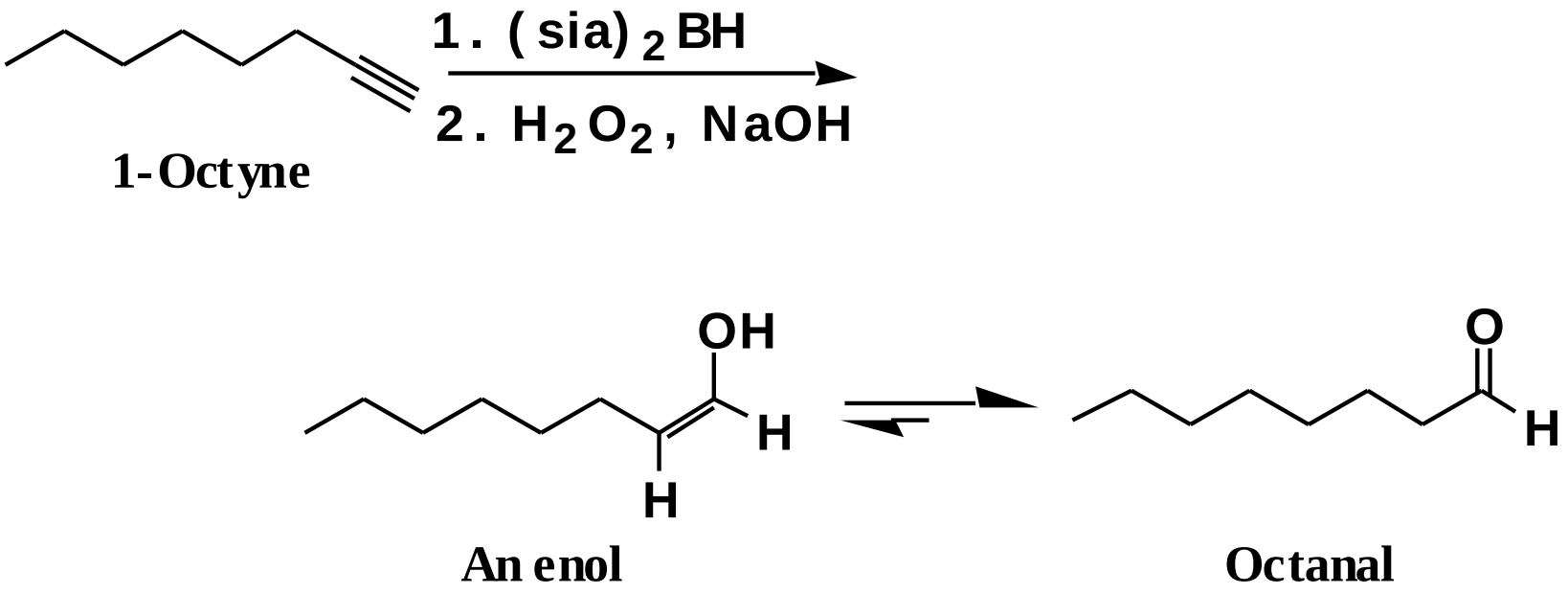
3-Hexyne

3-Hexanone

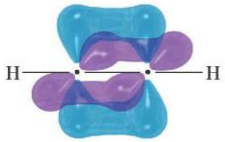
Hydroboration/oxidation



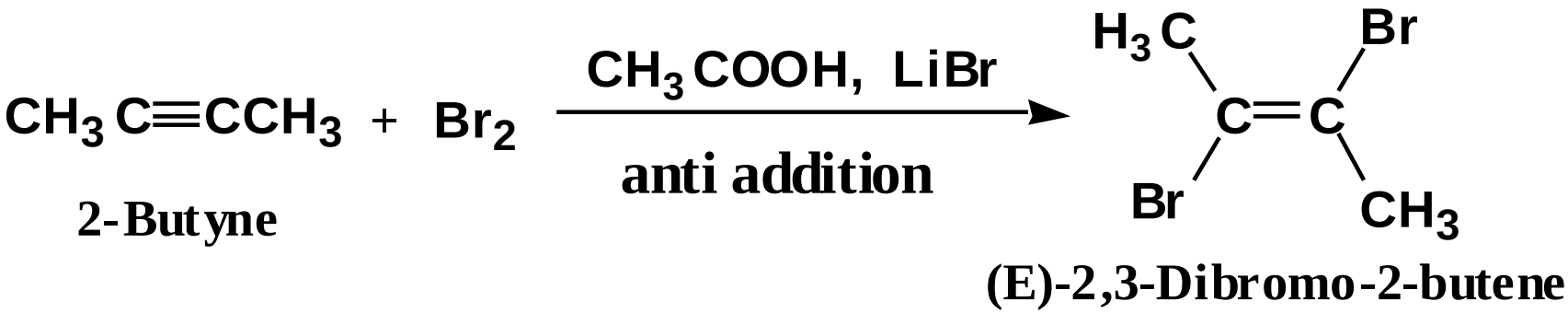
- **Hydroboration/oxidation of a terminal alkyne gives an aldehyde**



Addition of X_2



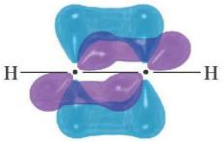
- **Alkynes add one mole of bromine to give a dibromoalkene**
  - **addition shows anti stereoselectivity**



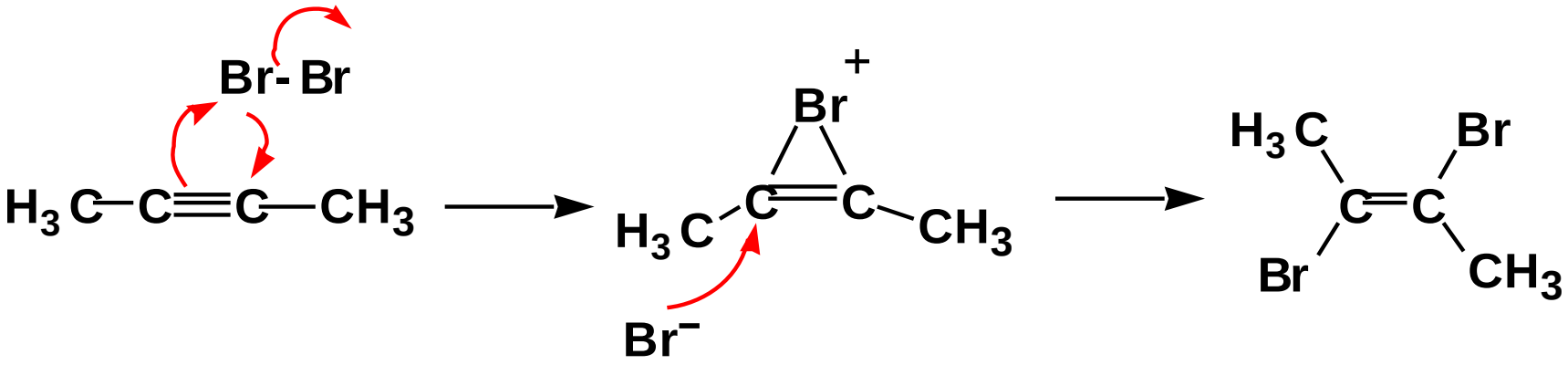
2-Butyne

(E)-2,3-Dibromo-2-butene

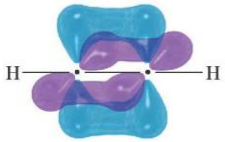
Addition of X_2



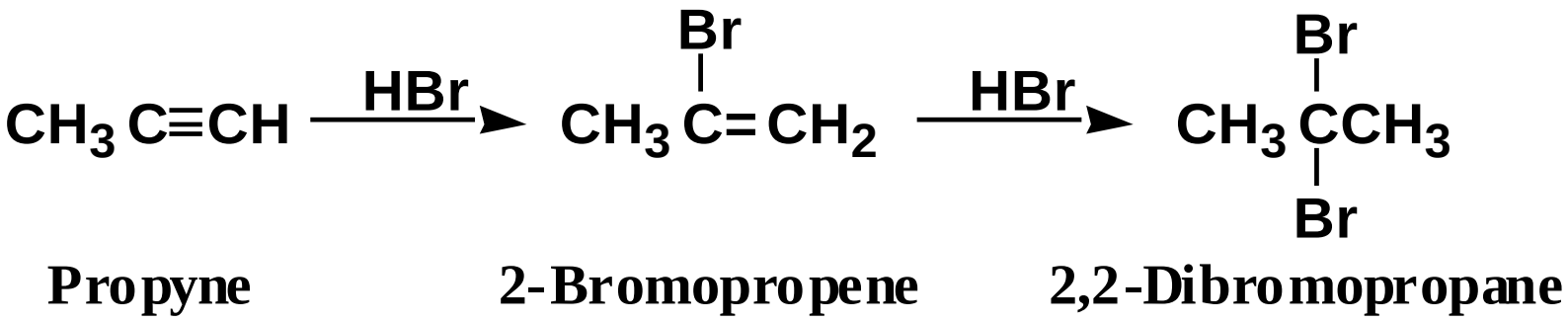
- **The intermediate in bromination of an alkyne is a bridged bromonium ion**



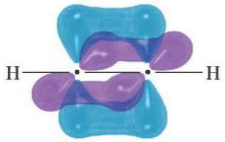
Addition of HX



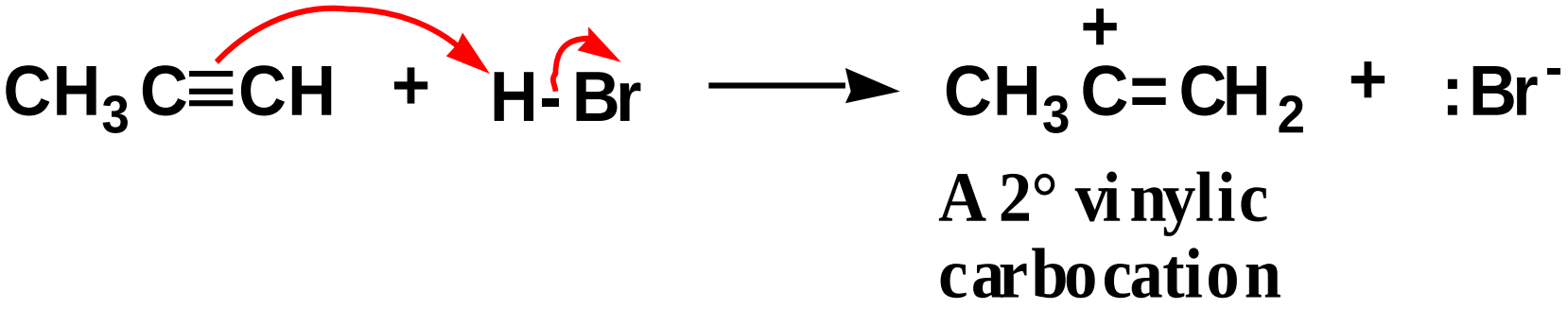
- **Alkynes undergo regioselective addition of first one mole of HX and then a second mole to give a dibromoalkane**



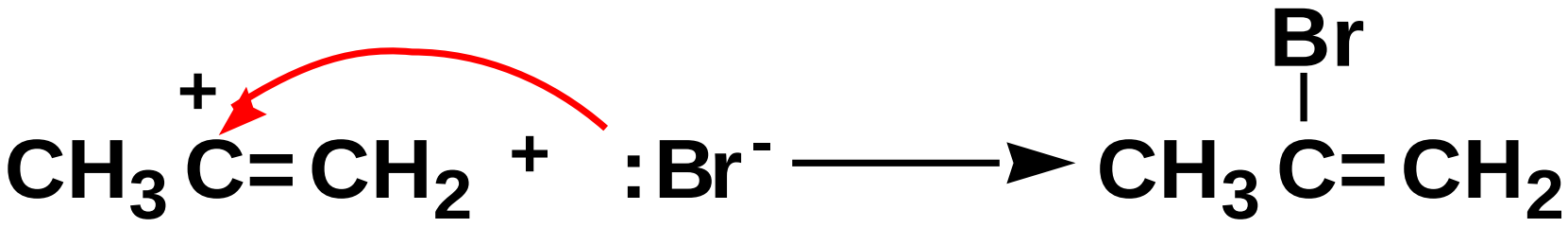
Addition of HX



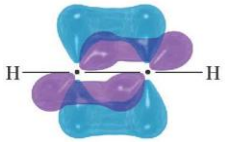
- the intermediate in addition of HX is a 2° vinylic carbocation



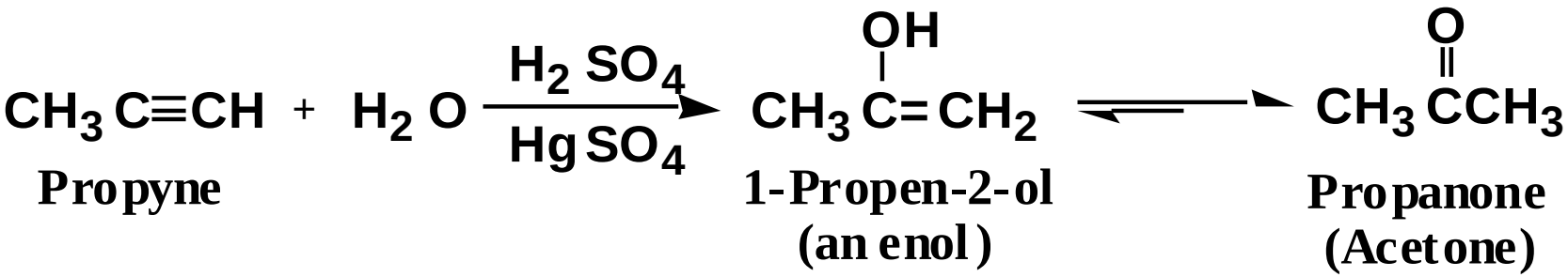
- reaction of the vinylic cation with halide ion gives the product



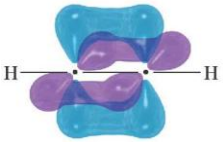
Addition of H_2O:hydration



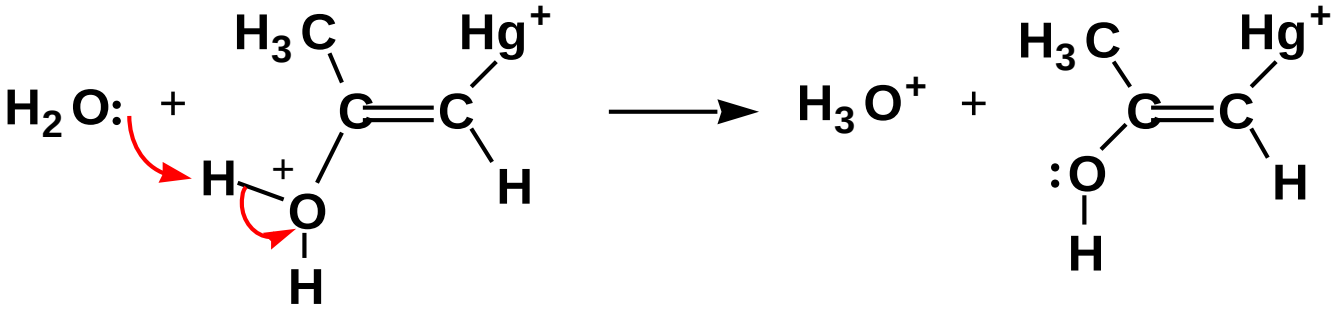
- In the presence of sulfuric acid and Hg(II) salts, alkynes undergo addition of water



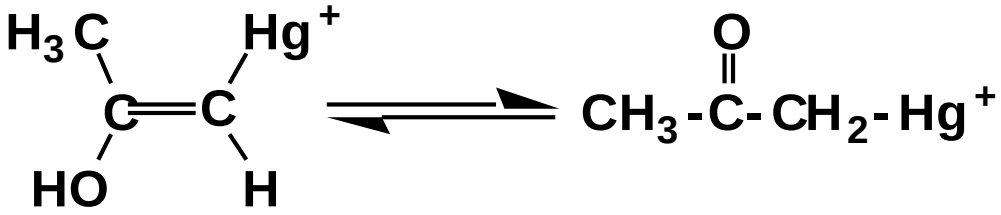
Addition of H_2O:hydration



- proton transfer to solvent



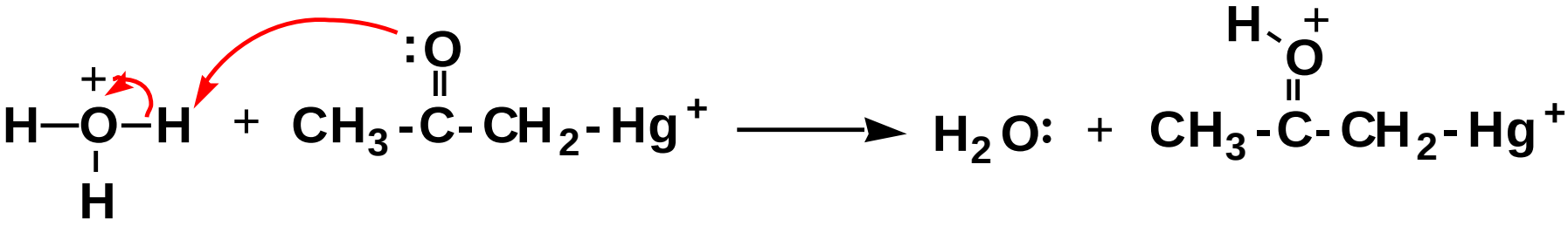
- tautomerism of the enol gives the keto form



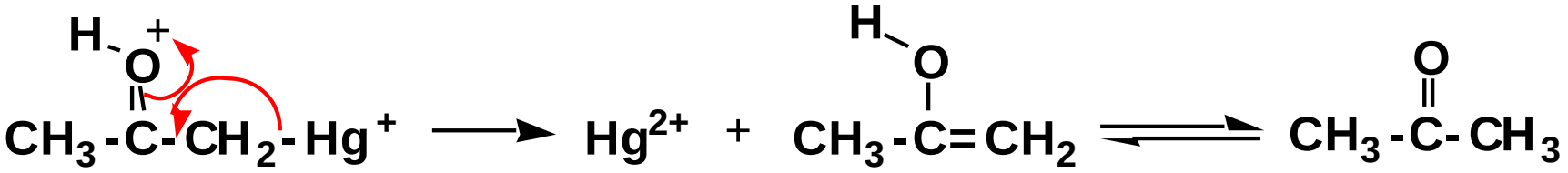
Enol form Keto form

Addition of H_2O:hydration

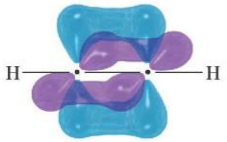
- **proton transfer to the carbonyl oxygen gives an oxonium ion**



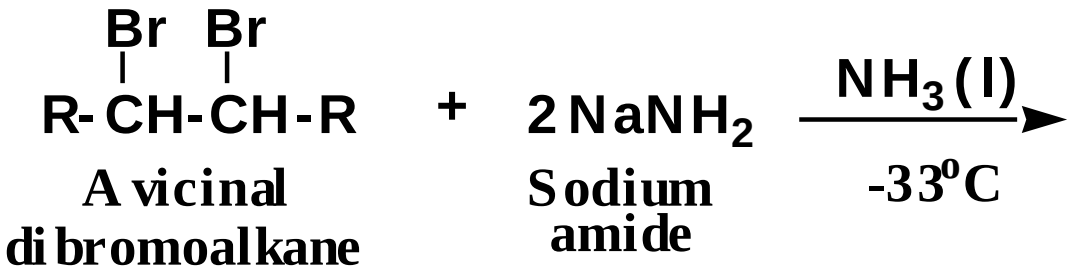
- **loss of Hg^{2+} gives an enol; tautomerism of the enol gives the ketone**

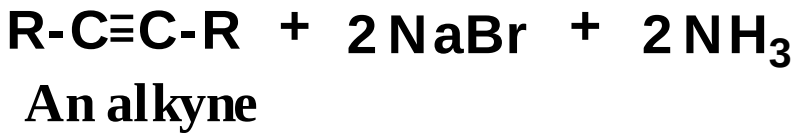


Preparation

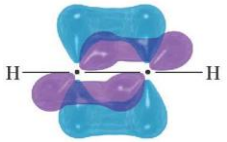


- **Treatment of a vicinal dibromoalkane with two moles of base, most commonly sodium amide, results in two successive E2 reactions and formation of an alkyne**

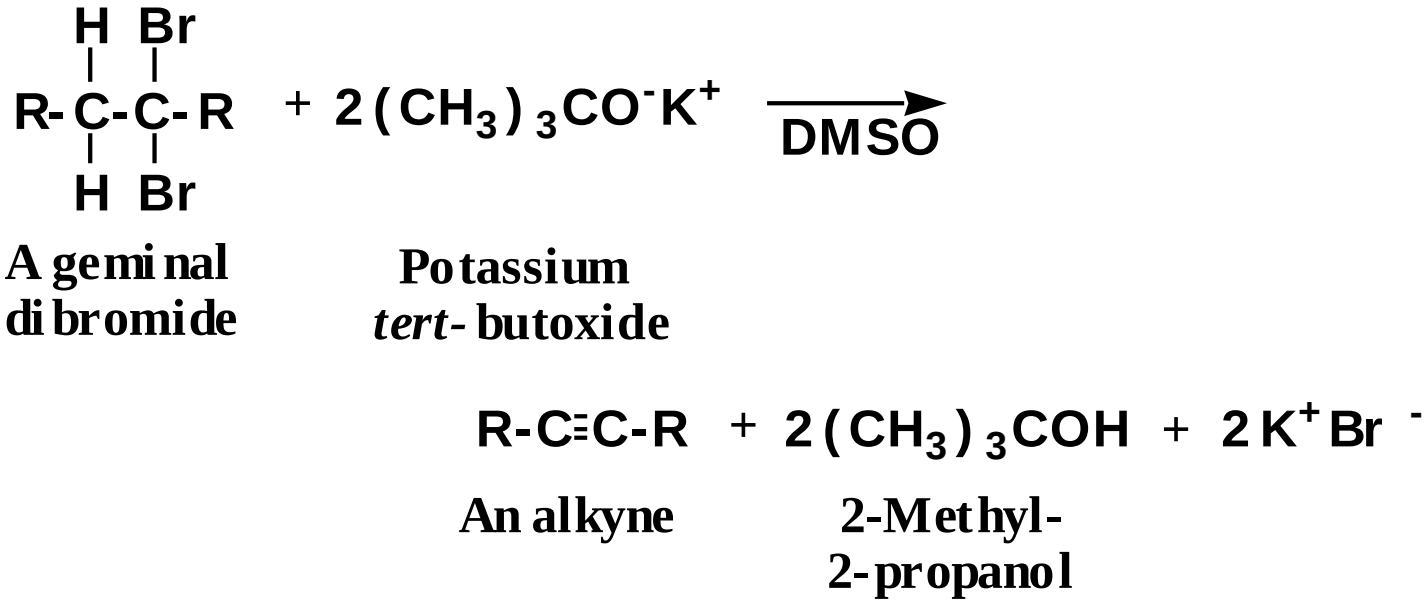




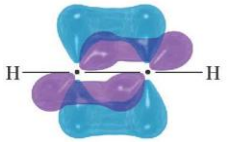
Preparation



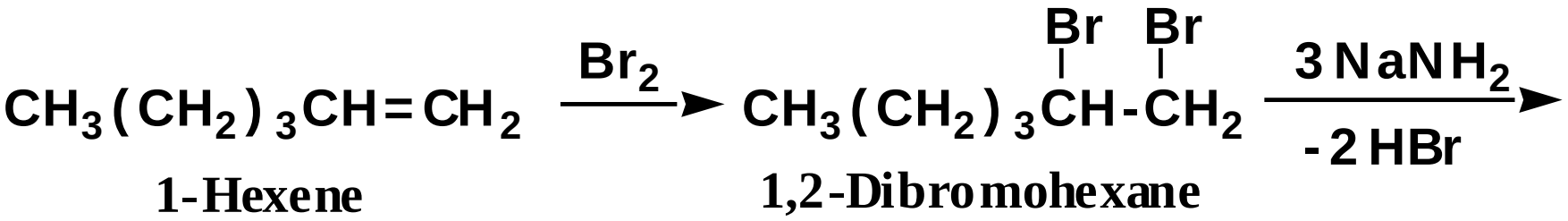
- **Alkynes are also prepared by double dehydrohalogenation of geminal dihalides**

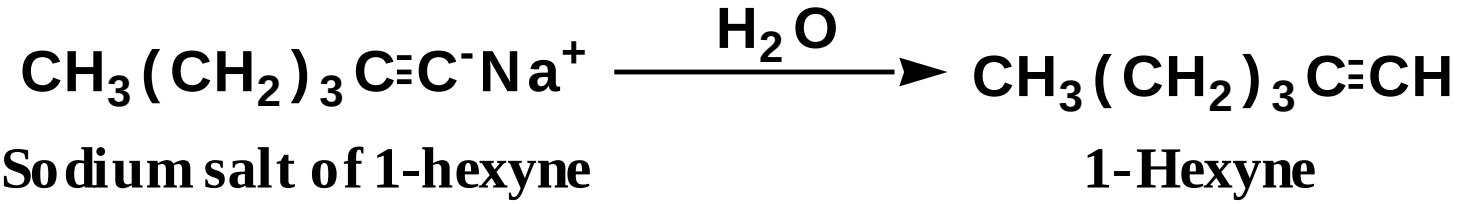


Preparation

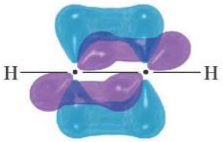


- **An alkene can be converted to an alkyne**
  - **for a terminal alkene to a terminal alkyne, 3 moles of $NaNH_2$ are required**
  - **for an internal alkene to an internal alkyne, only 2 moles of $NaNH_2$ are required**

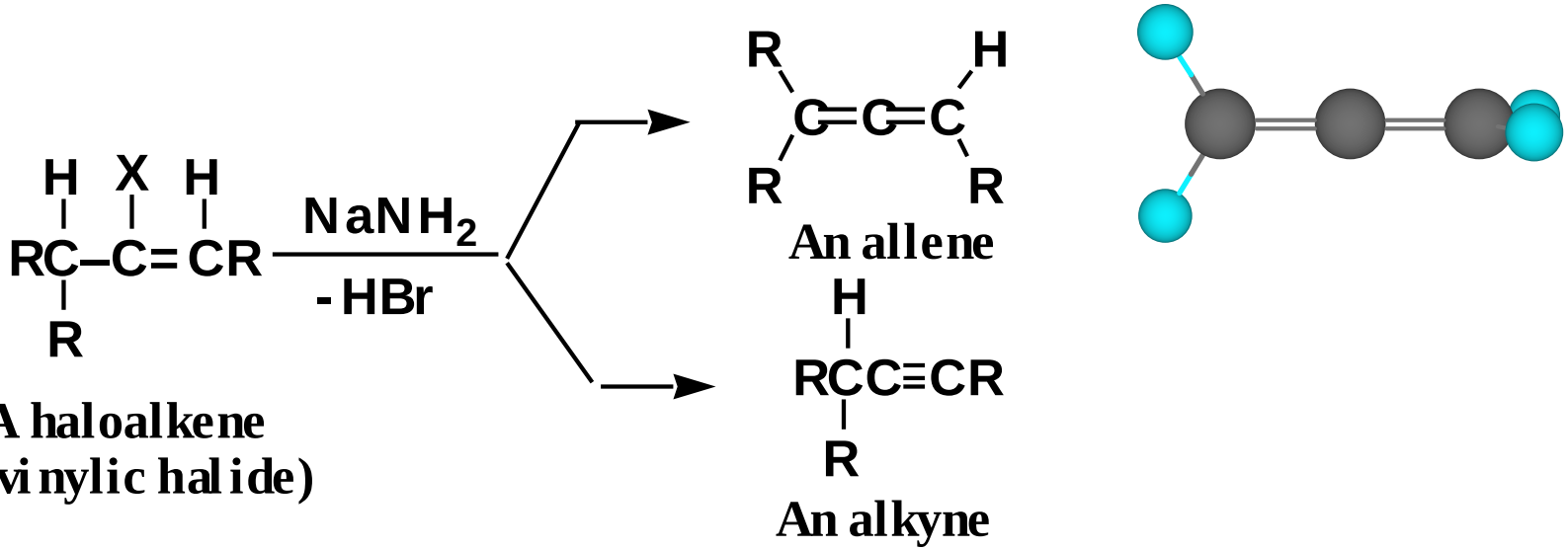




Preparation

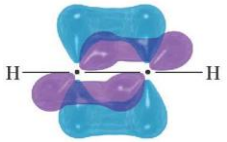


- A side product may be an allene, a compound containing adjacent carbon-carbon double bonds, C=C=C



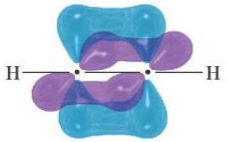
- Most allenes are less stable than their isomeric alkynes, and are generally only minor products in alkyne-forming dehydrohalogenation reactions

Organic Synthesis



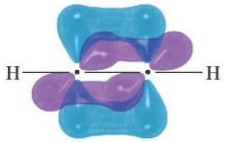
- **A successful synthesis must**
  - **provide the desired product in maximum yield**
  - **have the maximum control of stereochemistry and regiochemistry**
  - **do minimum damage to the environment (it must be a "green" synthesis)**
- **Our strategy will be to work backwards from the target molecule**

Organic Synthesis



- **We analyze a target molecule in the following ways**
  - **the carbon skeleton: how can we put it together. Our only method to date for forming new a C-C bond is the alkylation of acetylide anions**
  - **the functional groups: what are they, how can they be used in forming the carbon-skeleton of the target molecule, and how can they be changed to give the functional groups of the target molecule**

Organic Synthesis



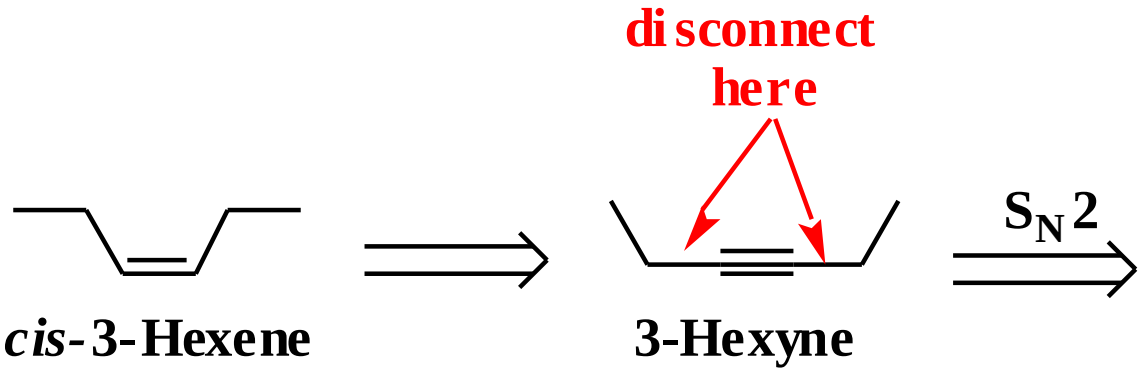
- We use a method called a retrosynthesis and use an open arrow to symbolize a step in a retrosynthesis

target molecule ⟹ starting materials

- **Retrosynthesis:** a process of reasoning backwards from a target molecule to a set of suitable starting materials

Organic Synthesis

- **Target molecule: *cis*-3-hexene**



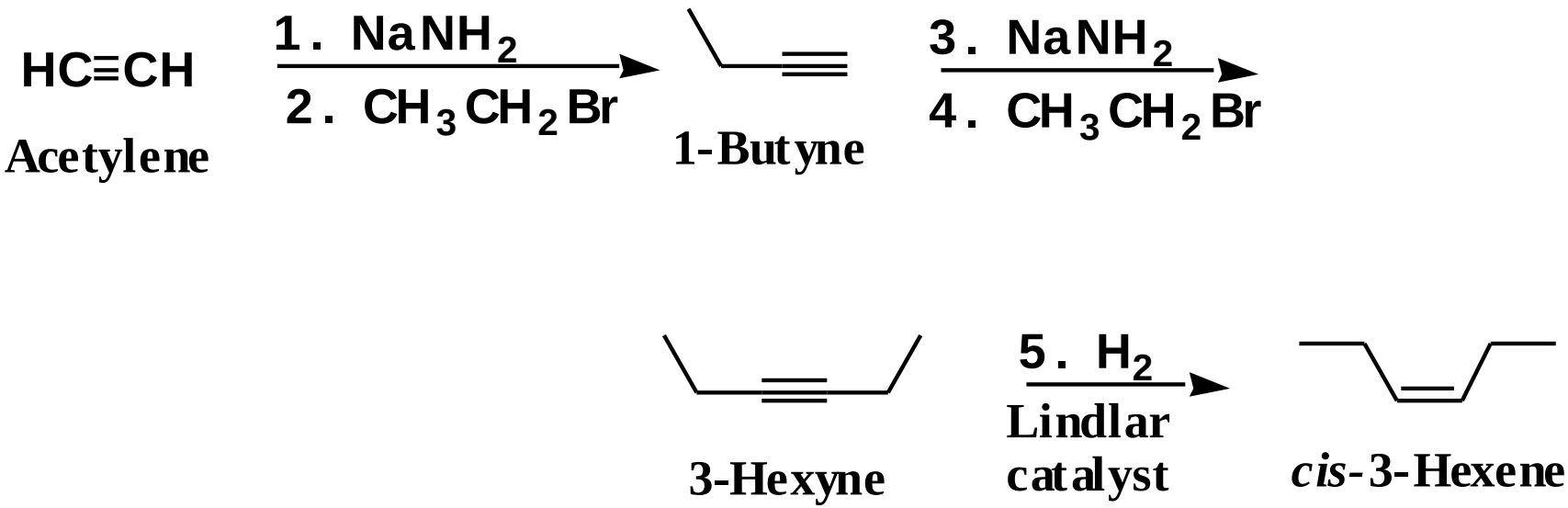
$^{-}:C{\equiv}C:^{-}$ + $2\,CH_3CH_2Br$

Acetylide dianion

Bromoethane

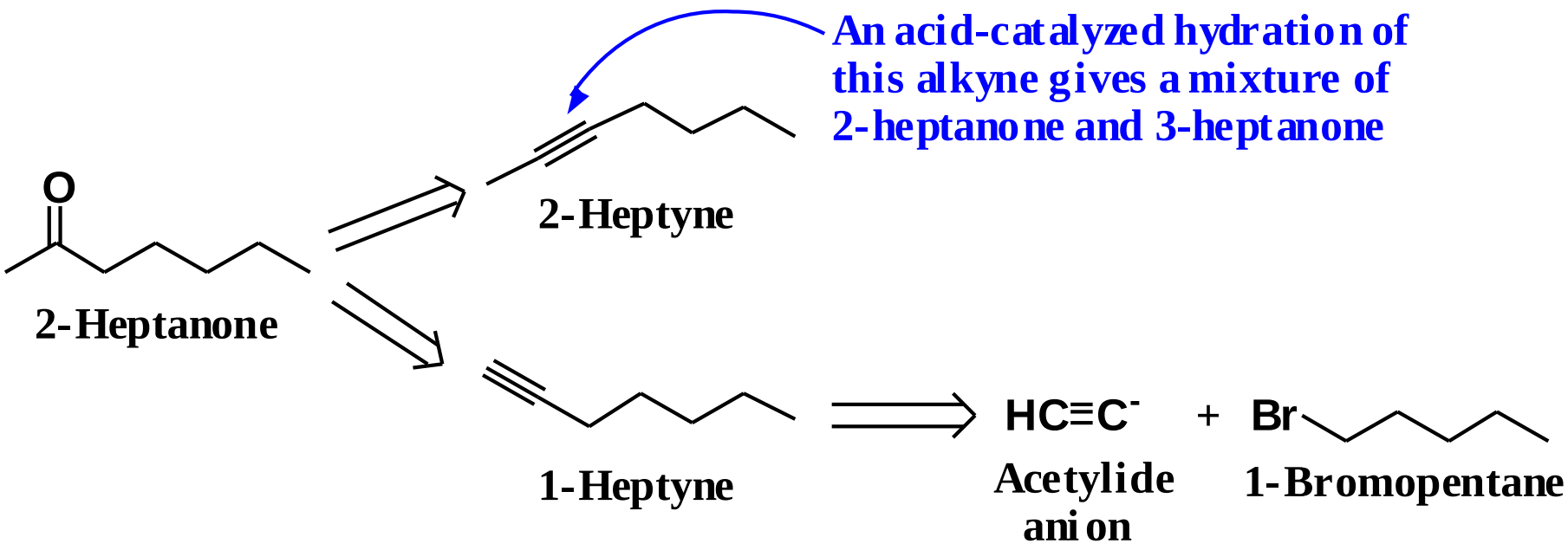
Organic Synthesis

- **starting materials are acetylene and bromoethane**



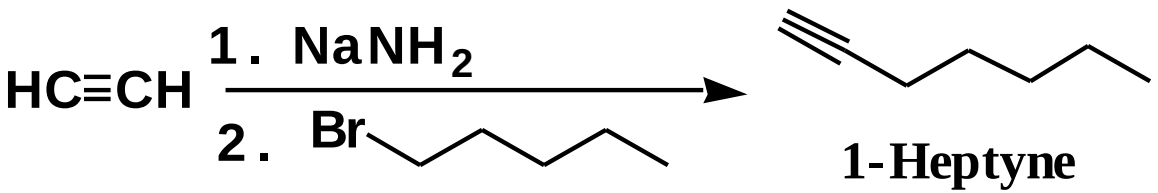
Organic Synthesis

- **Target molecule: 2-heptanone**

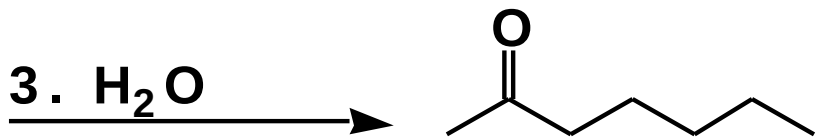


Organic Synthesis

- **starting materials are acetylene and 1-bromopentane**

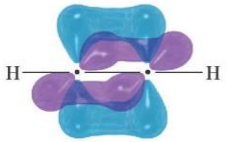


1-Heptyne



2-Heptanone

Problem



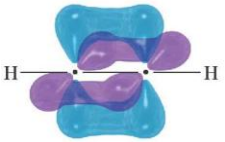
Show how to prepare each alkyne from the given starting material.

(a) $CH_3CH_2CH_2CH{=}CH_2 \longrightarrow CH_3CH_2CH_2C{\equiv}CH$

(b) $CH_3(CH_2)_5\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \longrightarrow CH_3(CH_2)_4C{\equiv}CCH_3$

(c) $CH_3CH_2CH_2C{\equiv}CH \longrightarrow CH_3CH_2CH_2C{\equiv}CD$

Problem



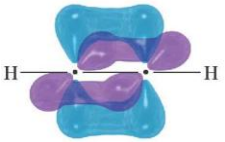
Complete each acid-base reaction and predict whether the equilibrium lies toward the left or toward the right.

(a) $CH_3C{\equiv}CH + (CH_3)_3CO^-K^+ \xrightleftharpoons{(CH_3)_3COH}$

(b) $CH_2{=}CH_2 + Na^+NH_2^- \xrightleftharpoons{NH_3(l)}$

(c) $CH_3C{\equiv}CCH_2OH + Na^+NH_2^- \xrightleftharpoons{NH_3(l)}$

Problem

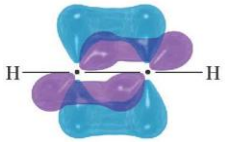


Draw a structural formula for the enol intermediate and the carbonyl compound formed in each reaction.

(a) $CH_3(CH_2)_5C{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$ (an enol) $\longrightarrow$

(b) $CH_3(CH_2)_5C{\equiv}CH \xrightarrow[2.\ NaOH/H_2O_2]{1.\ (sia)_2BH}$ (an enol) $\longrightarrow$

Problem



Show how to convert propene to each compound.

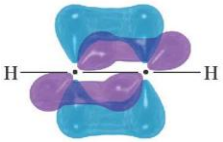
(a) $CH_3C(Br)(Br)CH(Br)(Br)$

(b) $CH_3C(Br)(Br)CH_3$

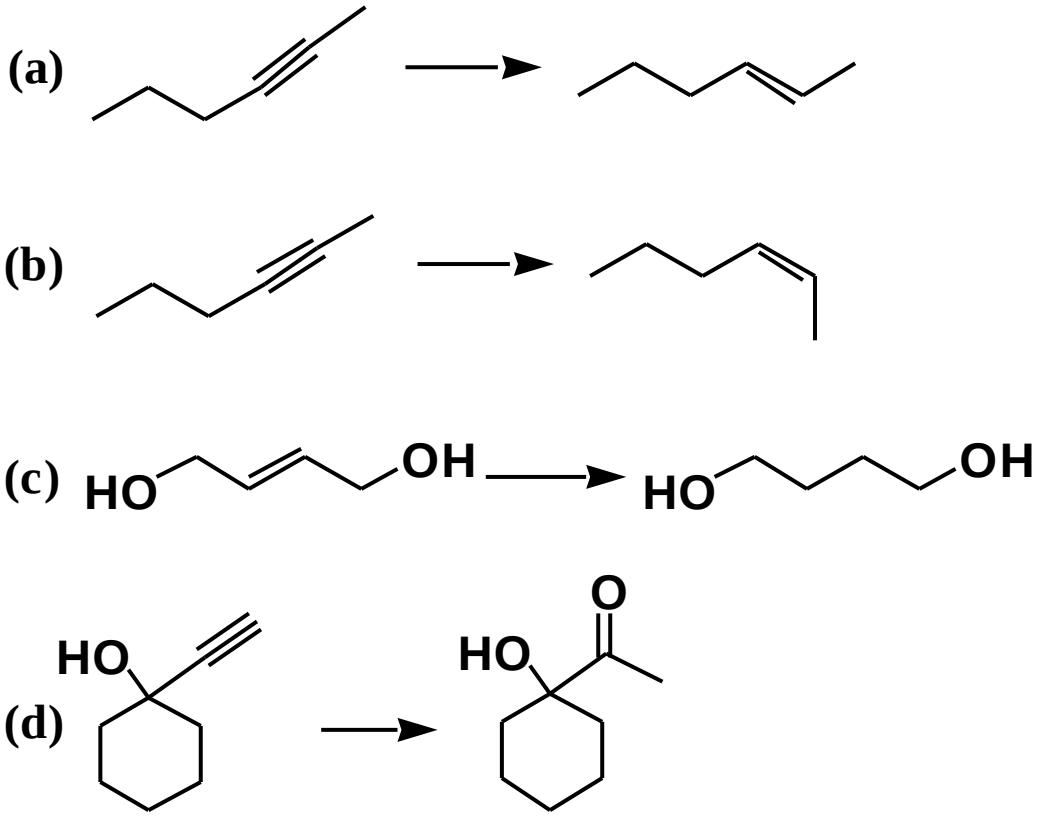
(c) $CH_3C(=O)CH_3$

(d) $CH_3CH_2CH(=O)$

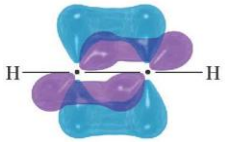
Problem

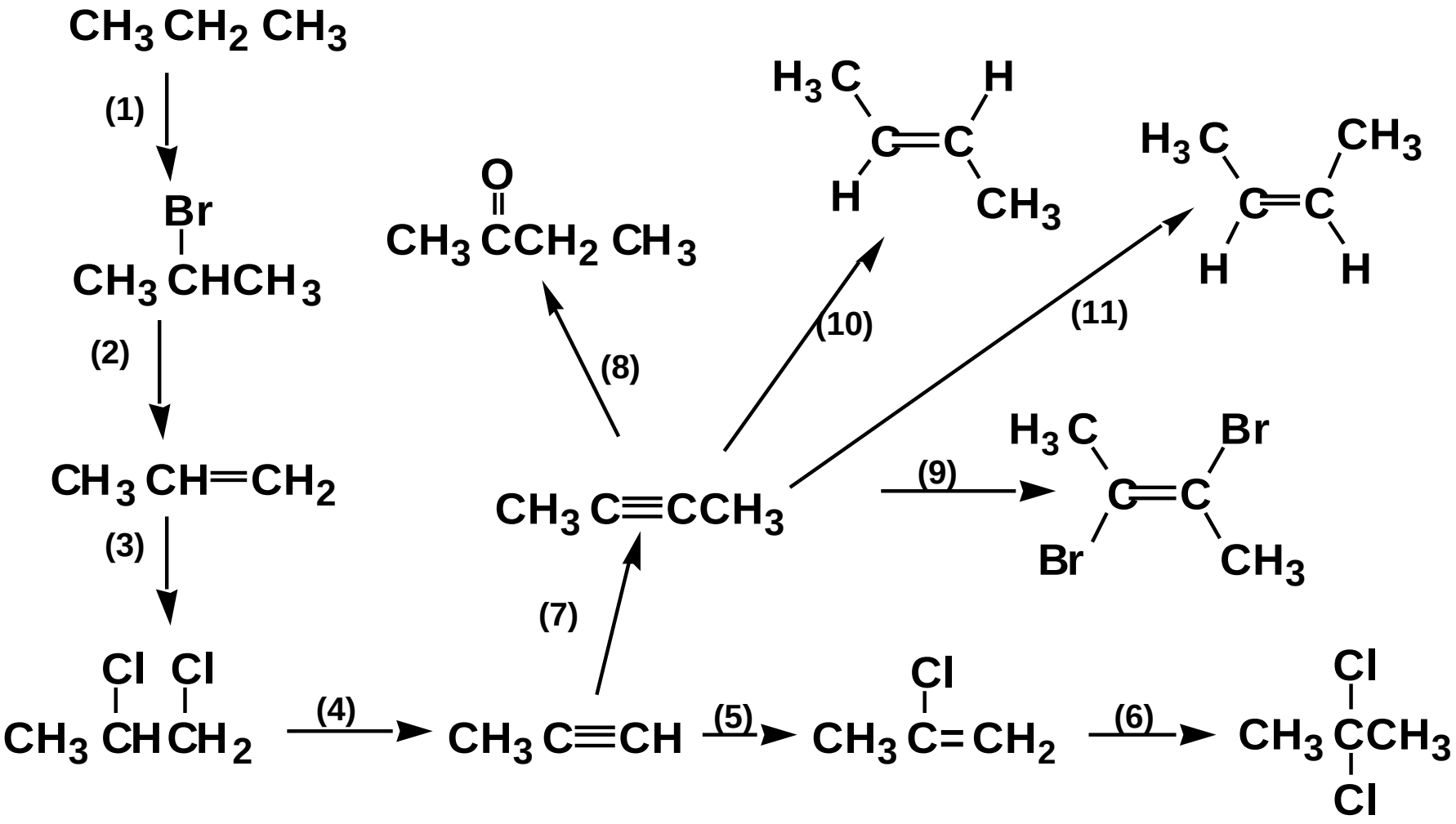


Show how to bring about each conversion.

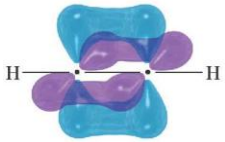


Problem

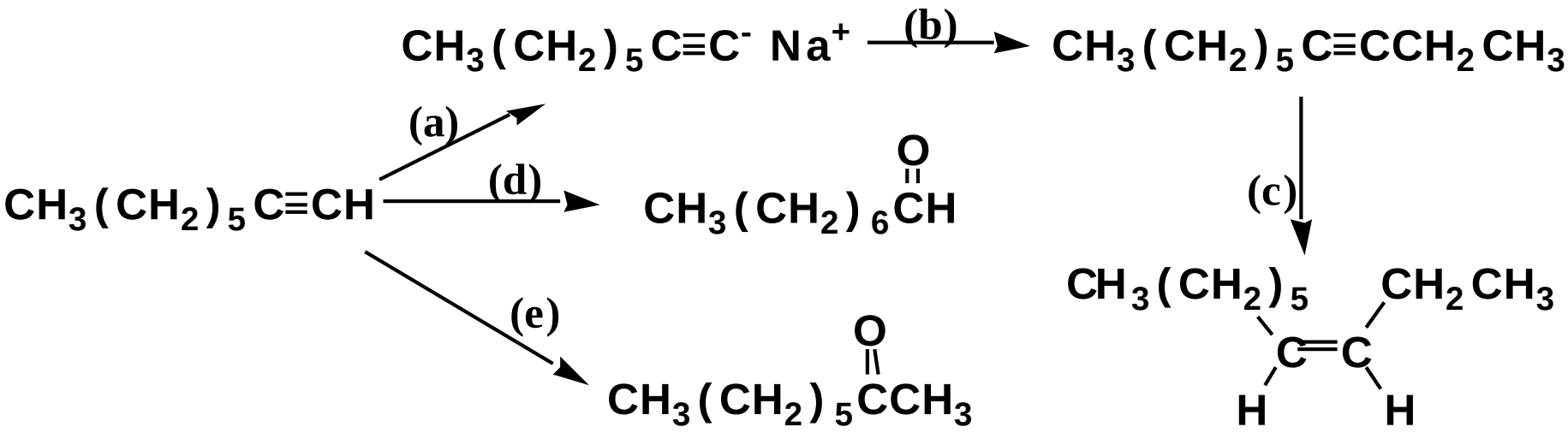



CH3 CH2 CH3
(1)
Br
CH3 CHCH3
(2)
CH3 CH=CH2
(3)
Cl Cl
CH3 CHCH2
(4)
CH3 C≡CH
(5)
Cl
CH3 C= CH2
(6)
CH3 CCH3
Cl
(7)
O
CH3 CCH2 CH3
(8)
CH3 C≡CCH3
(9)
H3 C Br
C=C
Br CH3
(10)
H3 C H
C=C
H CH3
(11)
H3 C CH3
C=C
H H

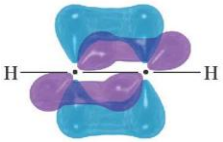
Problem



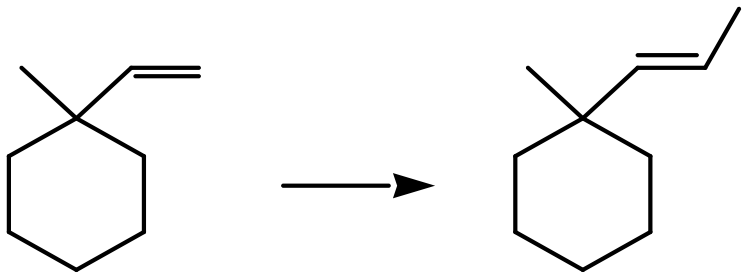
Show how to bring about each conversion.



Problem



Show how to bring about this conversion.



Visual test for alkynes