# Chapter 6

# Reactions of Alkynes

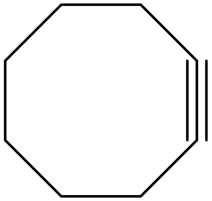
Alkynes

Multistep synthesis

# Alkynes



- HC with ≡
  - $C_nH_{2n-2}$ (acyclic) or $C_nH_{2n-4}$ (cyclic)
  - DU = 2 or 3



smallest cycloalkyne

- nomenclature
  - -yne

| | | | | |
|---|---|---|---|---|
| | $HC{\equiv}CH$ | $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}{\equiv}\overset{1}{C}H$ | $\overset{1}{C}H_3\overset{2}{C}{\equiv}\overset{3}{C}\overset{4}{C}H_2\overset{5}{C}H_3$ | $\overset{4}{C}H_3CH(\overset{5}{C}H_2\overset{6}{C}H_3)\overset{3}{C}{\equiv}\overset{2}{C}\overset{1}{C}H_3$ |
| Systematic: | ethyne | 1-butyne | 2-pentyne | 4-methyl-2-hexyne |
| Common: | acetylene | ethylacetylene | ethylmethylacetylene | *sec*-butylmethyl-acetylene |
| | | a terminal alkyne | an internal alkyne | |



  - alkynes ~ (substituted) acetylenes <cf> paraffins, olefins
  - terminal vs internal alkyne

# nomenclature (cont'd)

- systematic nomenclature ~ the same to alkene

$$CH_2{=}C{=}CH_2$$

systematic: propadiene
common: allene

$$\overset{6}{C}H_3\overset{5}{C}H{=}\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}(CH_3){=}\overset{1}{C}H_2$$

2-methyl-1,4-hexadiene
or
2-methylhexa-1,4-diene

$$CH_3CH(CH_3)C{\equiv}CCH_2C{\equiv}CH$$

6-methyl-1,4-heptadiyne
or
6-methylhepta-1,4-diyne



- for = and ≡
  - same priority
  - list {–ene → -en} first
  - if the same, give = lower number

$$\overset{7}{C}H_3\overset{6}{C}H{=}\overset{5}{C}H\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}{\equiv}\overset{1}{C}H$$

5-hepten-1-yne
*not* 2-hepten-6-yne
because 1 < 2

$$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}{\equiv}\overset{5}{C}\overset{6}{C}H_3$$

2-hexen-4-yne
*not* 4-hexen-2-yne

- for higher priority functional groups
  - give lower # to higher-priority functional group

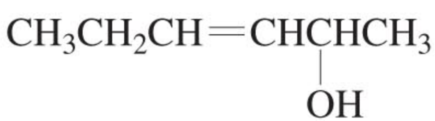
$CH_2{=}CHCH_2OH$

**2-propen-1-ol**

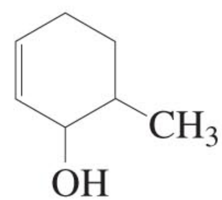
***not* 1-propen-3-ol**

**4-methyl-3-penten-1-ol**

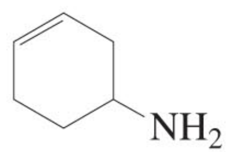
**6-hepten-2-amine**



**3-hexen-2-ol**



**6-methyl-2-cyclohexenol**



**3-cyclohexenamine**



**Table 6.1 Priorities of Functional Group Suffixes**

highest priority $C{=}O > OH > NH_2 > C{=}C = C{\equiv}C$ lowest priority

$= \; > \; \equiv \; > \; -$

**the double bond is given priority over a triple bond only when there is a tie**

# Properties of alkane



- non-polar, hydrophobic, light
  - organic-soluble, water-insoluble, float on water
- higher bp than alkene
  - linear
  - more polarizable ~ loose $\pi$ electrons
    - Alkane is more polarizable than alkene ~ $sp^3$ vs $sp^2$

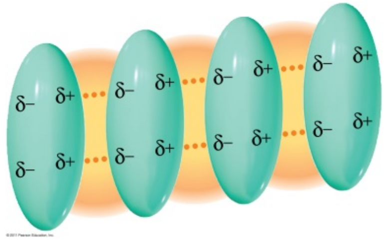
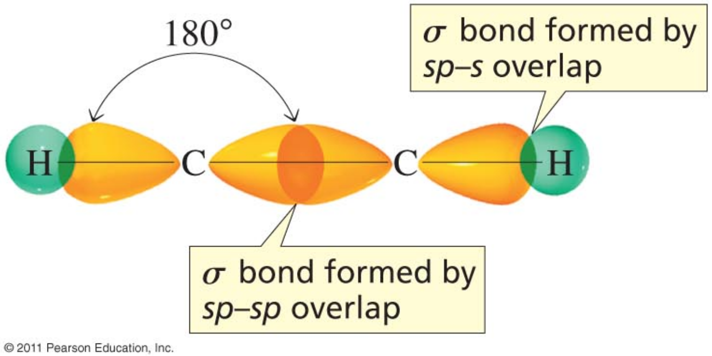


**Table 6.2 Boiling Points of the Smallest Hydrocarbons**

| | bp (°C) | | bp (°C) | | bp (°C) |
|---|---|---|---|---|---|
| $CH_3CH_3$ ethane | −88.6 | $H_2C{=}CH_2$ ethene | −104 | $HC{\equiv}CH$ ethyne | −84 |
| $CH_3CH_2CH_3$ propane | −42.1 | $CH_3CH{=}CH_2$ propene | −47 | $CH_3C{\equiv}CH$ propyne | −23 |
| $CH_3CH_2CH_2CH_3$ butane | −0.5 | $CH_3CH_2CH{=}CH_2$ 1-butene | −6.5 | $CH_3CH_2C{\equiv}CH$ 1-butyne | 8 |
| $CH_3(CH_2)_3CH_3$ pentane | 36.1 | $CH_3CH_2CH_2CH{=}CH_2$ 1-pentene | 30 | $CH_3CH_2CH_2C{\equiv}CH$ 1-pentyne | 39 |
| $CH_3(CH_2)_4CH_3$ hexane | 68.7 | $CH_3CH_2CH_2CH_2CH{=}CH_2$ 1-hexene | 63.5 | $CH_3CH_2CH_2CH_2C{\equiv}CH$ 1-hexyne | 71 |
| | | $CH_3CH{=}CHCH_3$ *cis*-2-butene | 3.7 | $CH_3C{\equiv}CCH_3$ 2-butyne | 27 |
| | | $CH_3CH{=}CHCH_3$ *trans*-2-butene | 0.9 | $CH_3CH_2C{\equiv}CCH_3$ 2-pentyne | 55 |

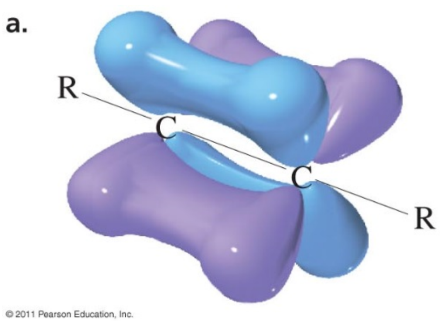
# Structure of alkynes



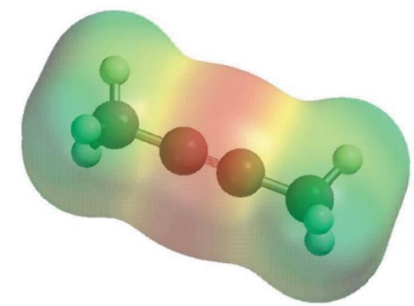




a.




b.

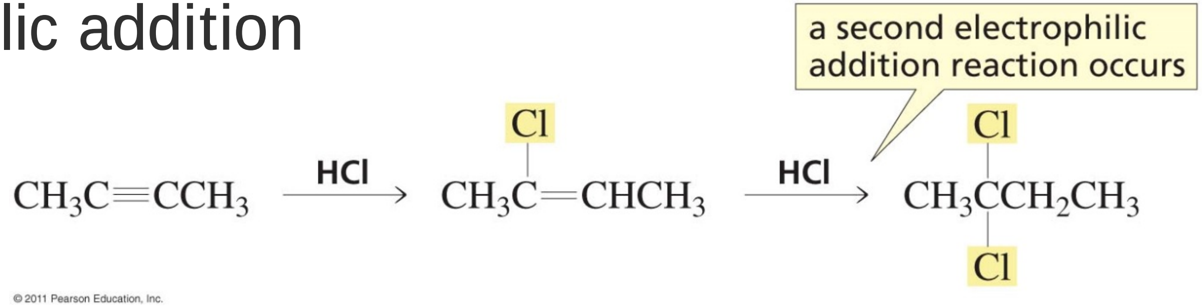


- Internal alkyne is more stable than terminal alkyne.
  - stabilized by hyperconjugation

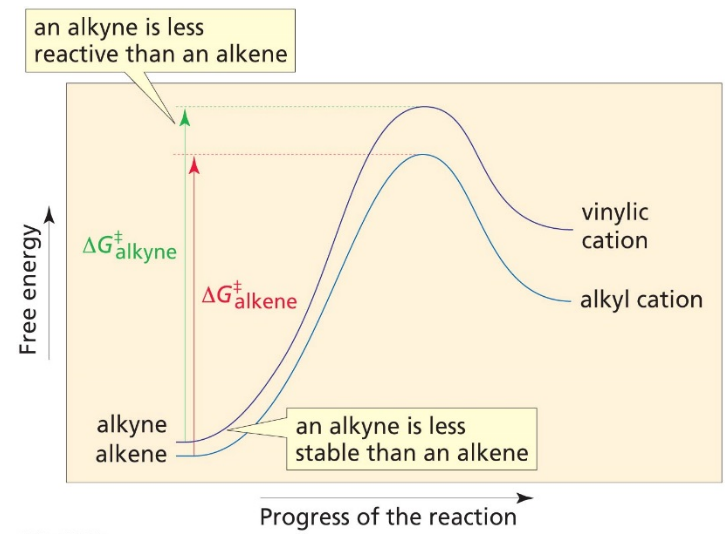
# Reactions of alkynes

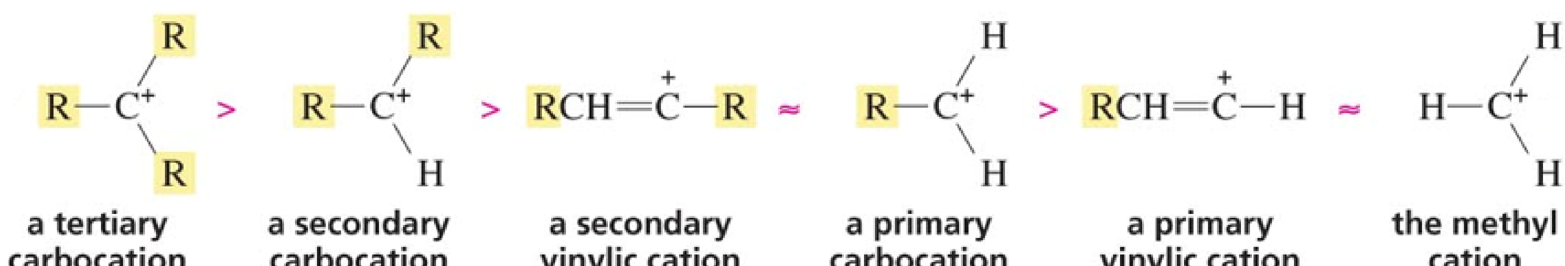


- e-philic addition




  - two times to saturated
  - regioselective
  - Alkyne is less reactive than alkene.
    - less stable vinylic C$^+$
      - sp C more EN than sp$^2$ C, and
      - less effective hyperconjugation

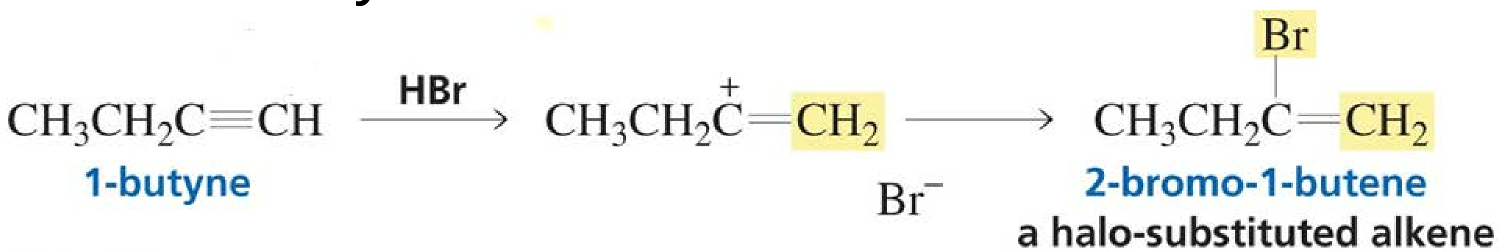


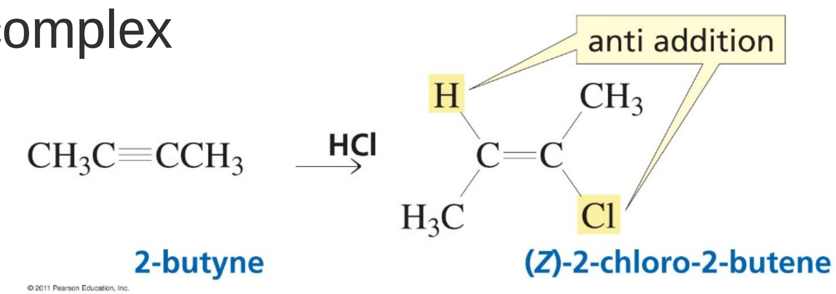
# Addition of HX

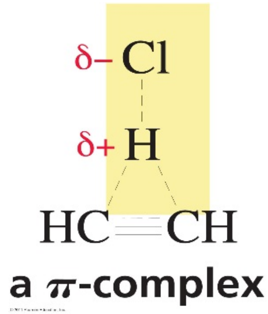


- to terminal alkyne with 1 mol of HX



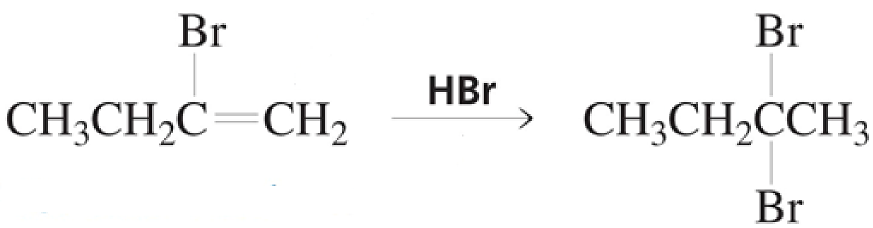

  - stops here
    - alkyne more reactive than haloalkene ← induction effect of X
  - regioselective ← 2° vinylic $C^+$ more stable than 1°
  - through vinylic $C^+$? maybe not.
    - stability similar to 1° alkyl $C^+$
    - maybe thru $\pi$-complex



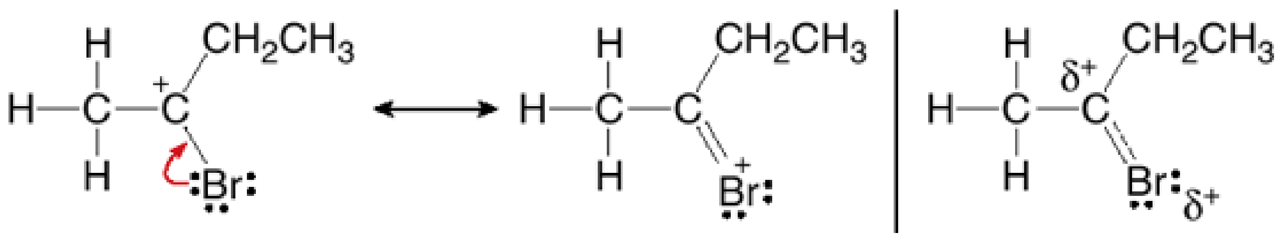



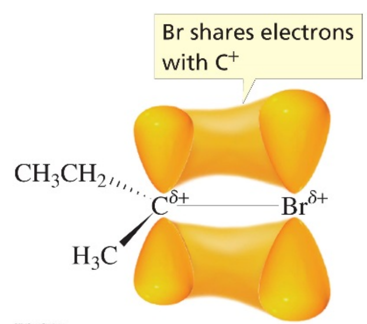

    - intermediate not clear

- with > 1 mol

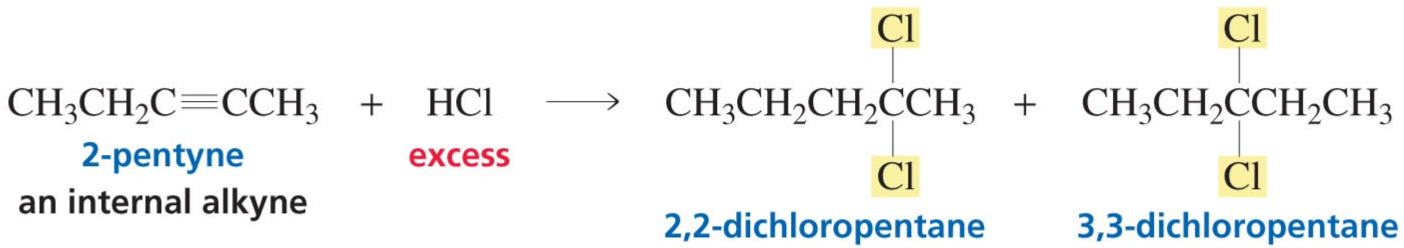



  - to geminal dihalide
  - regioselective ~ Markovnikov-type

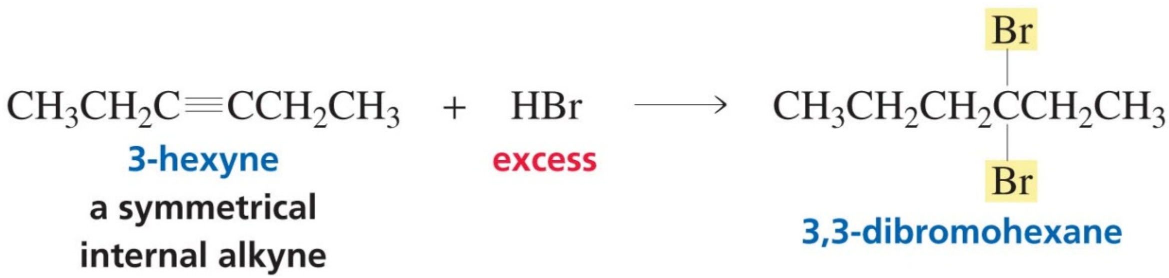




- to internal alkyne



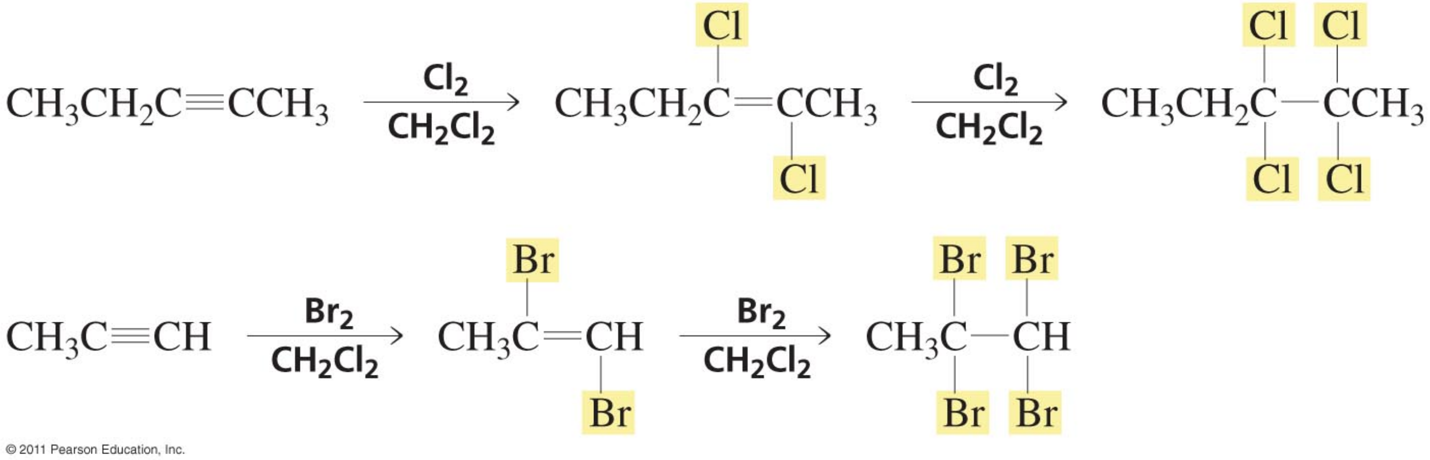


# Addition of $X_2$



- through vicinal dihaloalkene to tetrahaloalkane

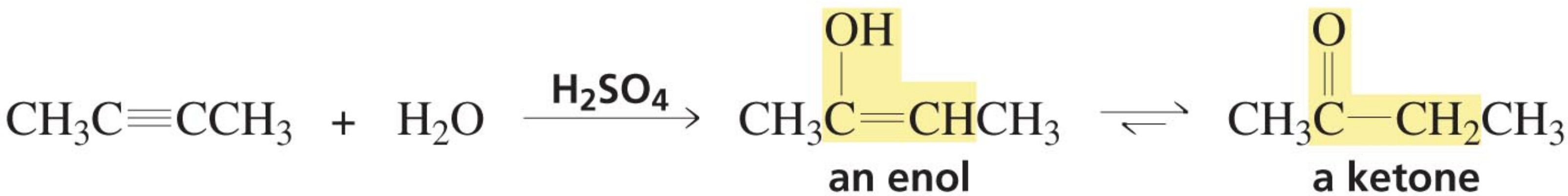



  - anti addition ← cyclic halonium ion intermediate

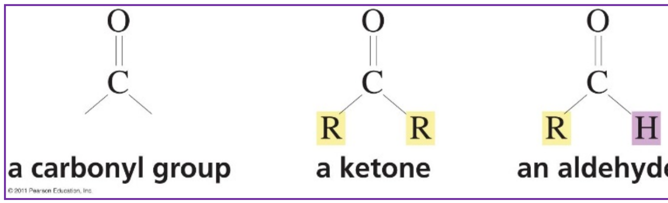
# Addition of $H_2O$



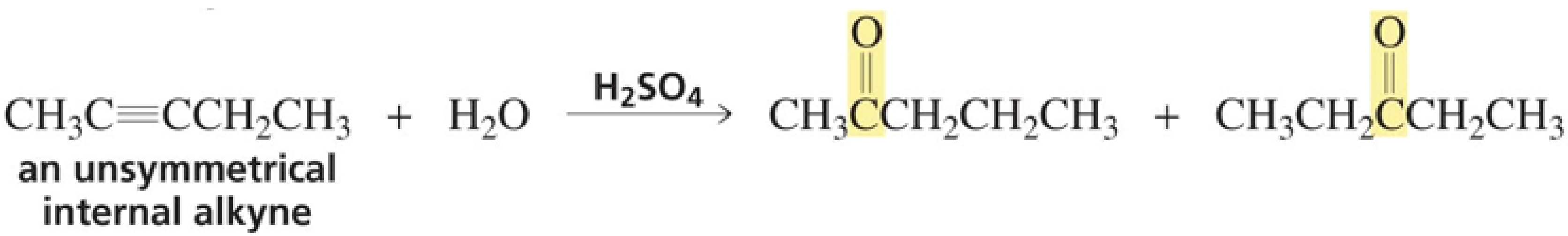
- to form ketone





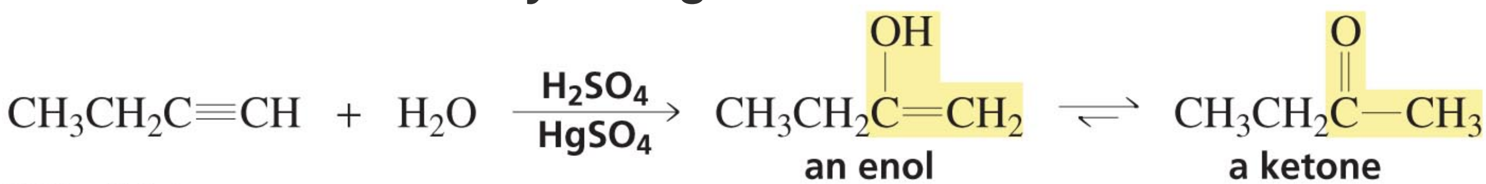




- keto-enol tautomerism p836
  - tautomerization ~ an isomerization
  - equilibrium (heavily) favored to keto form [tautomer]



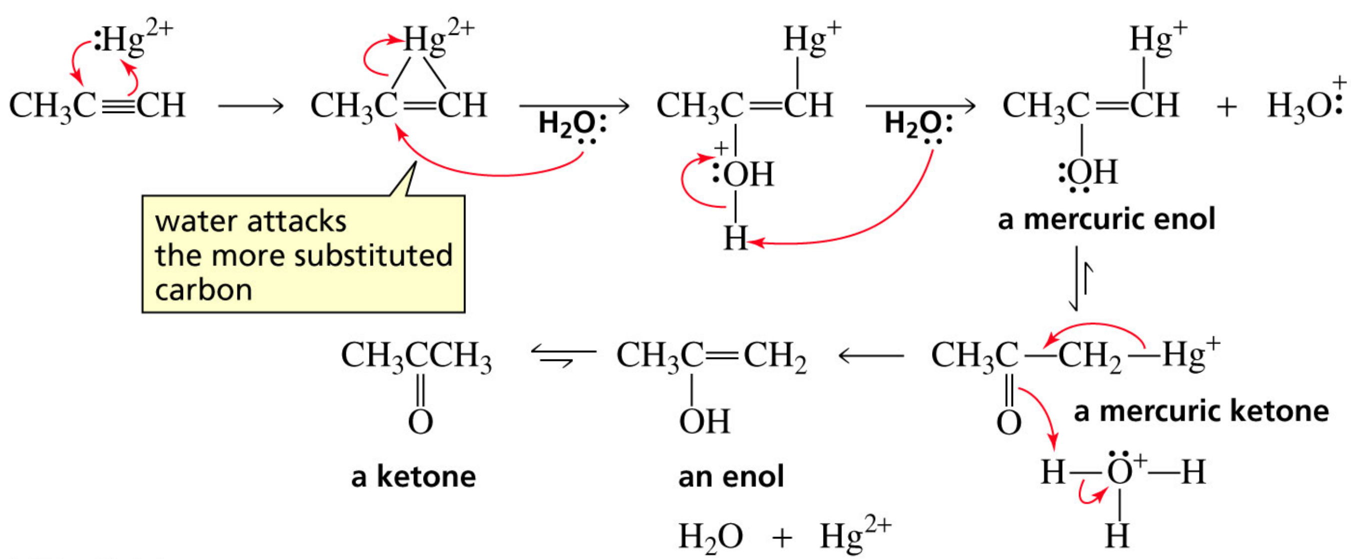

- mechanism ~ $C^+$ ~ Markovnikov

- terminal alkyne
  - need additional catalyst, $Hg^{2+}$





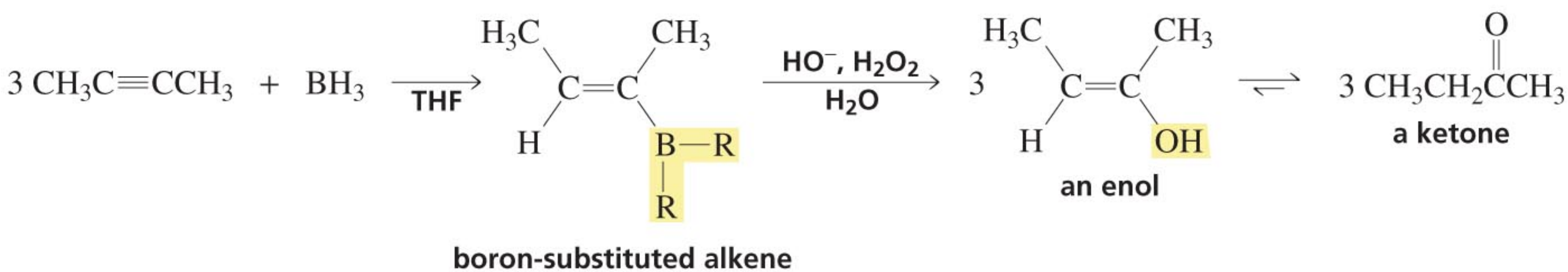

  - mechanism ~ cyclic mercurinium interm
    - regiospecific ~ Markovnikov



# Hydroboration-oxidation

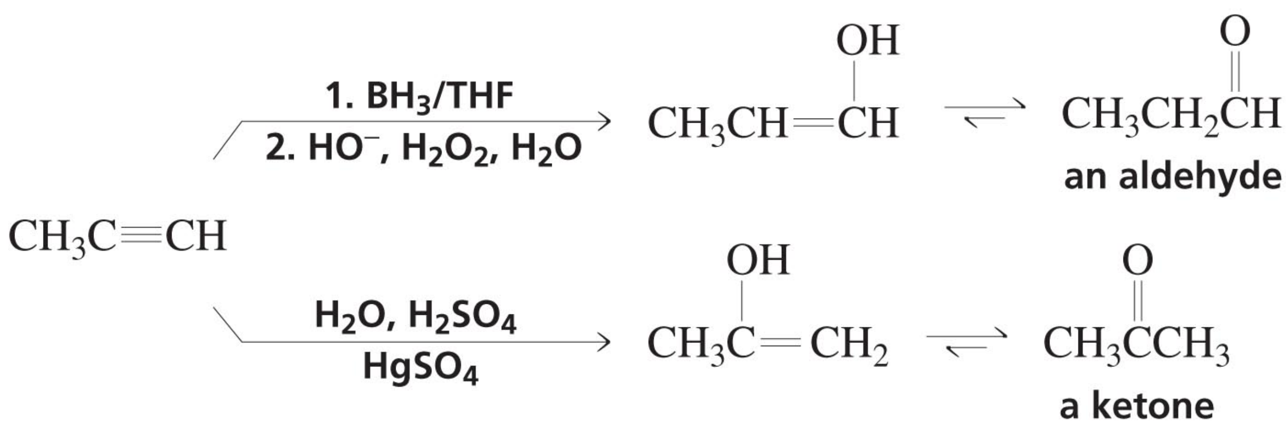


- internal alkyne to form ketone





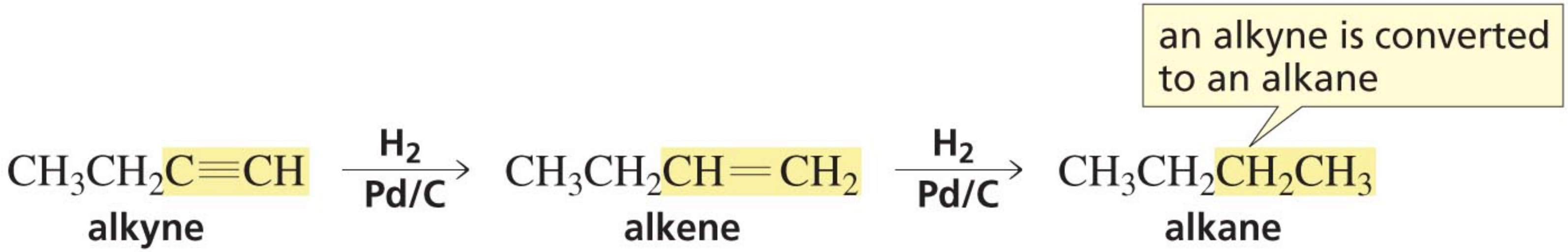

- terminal alkyne to form alhehyde



# Addition of $H_2$

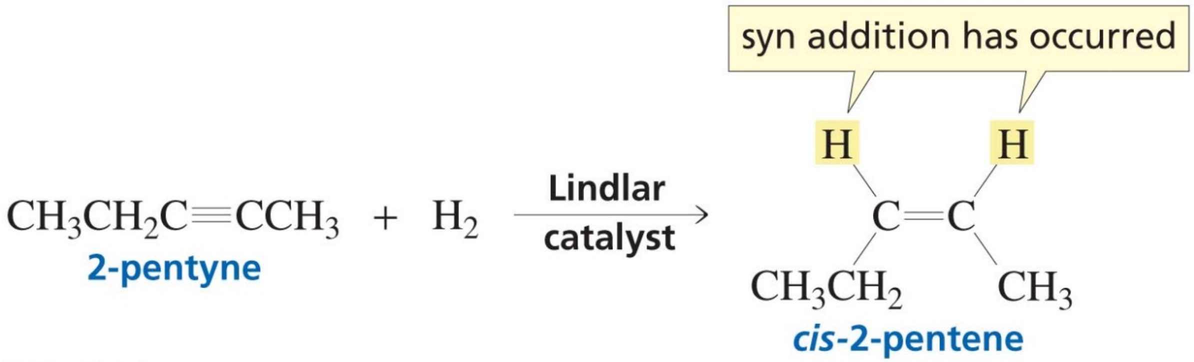


- all the way to alkane

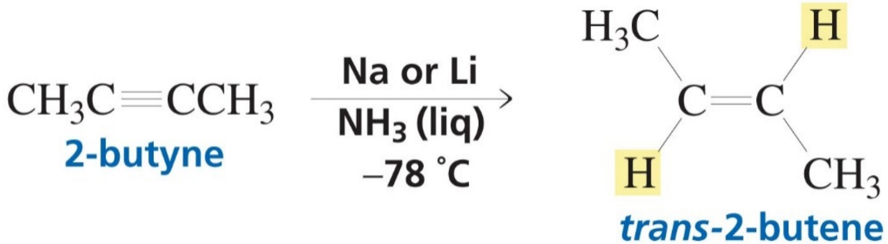




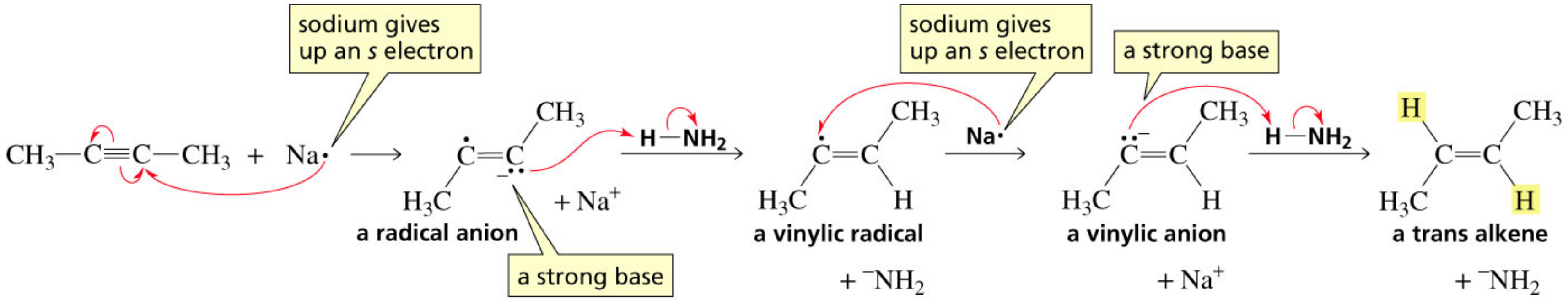

- to stop at alkene
  - use partially deactivated [‘poisoned’] catalyst
  - eg, Lindlar catalyst



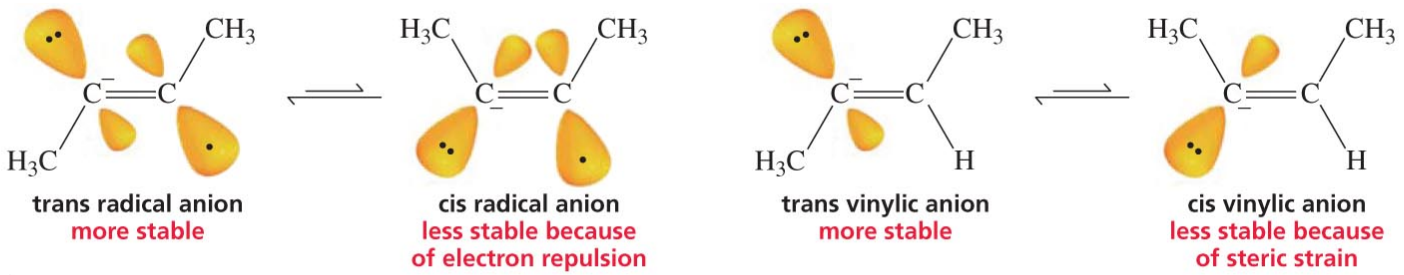
- to prepare *trans* alkene





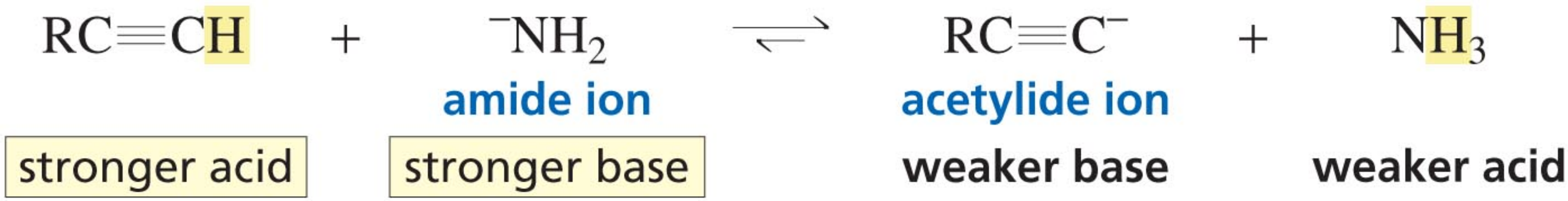


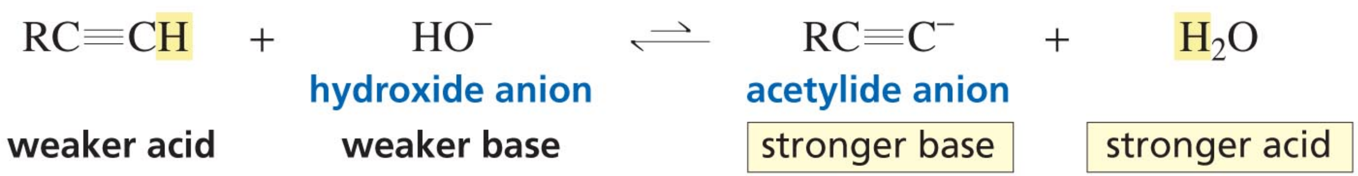
# Reaction with ≡C⁻



- acetylide ion
  - need very strong base to prepare

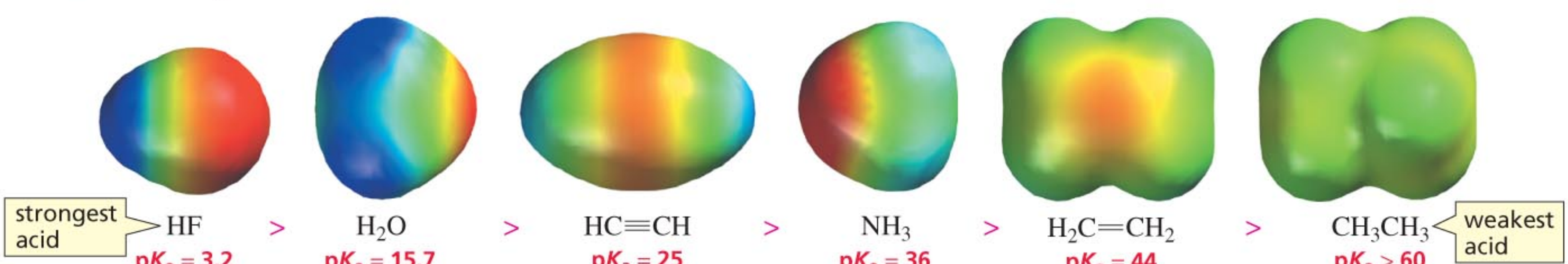







relative acid strengths

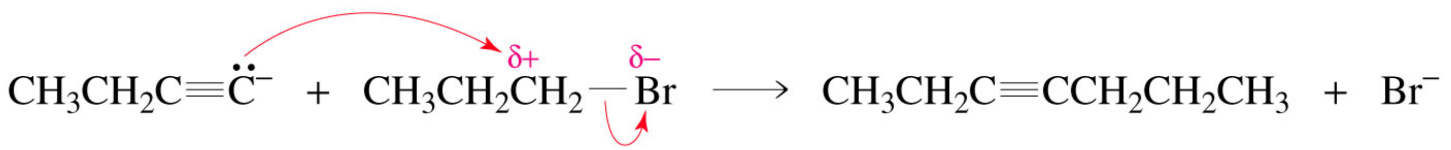


# Alkylation using acetylide ion

$$CH_3CH_2C{\equiv}C^- + CH_3CH_2CH_2Br \longrightarrow \underset{\text{3-heptyne}}{CH_3CH_2C{\equiv}CCH_2CH_2CH_3} + Br^-$$



- a nucleophilic substitution reaction Chapter 8






  - works (much) better with 1° alkyl or methyl halide
- converting a terminal alkyne to an internal alkyne

$$\underset{\text{1-pentyne}}{CH_3CH_2CH_2C{\equiv}CH} \xrightarrow{NaNH_2} CH_3CH_2CH_2C{\equiv}C^- \xrightarrow{CH_3CH_2Br} \underset{\text{3-heptyne}}{CH_3CH_2CH_2C{\equiv}CCH_2CH_3}$$



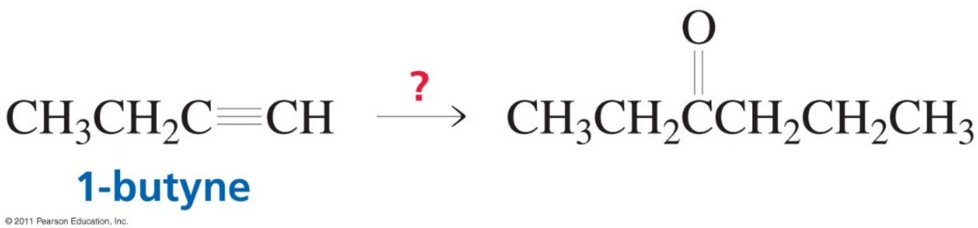
- increasing the # of C

# Designing synthesis

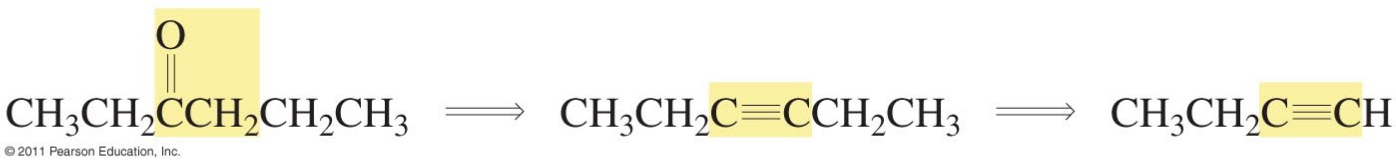


- retrosynthetic analysis
  - target compound ⇒ precursor ⇒  ⇒ starting material(s)
    - ⇒ ~ retrosynthetic arrow
  - considering
    - time ~ fewer # of steps
    - cost ~ cheaper reactant(s)
    - yield ~ higher
- ‘total synthesis’
  - complex comp’d from simple pieces
    - biological from petrochemical (bulk)
    - without the aid of biological process
  - developing new route

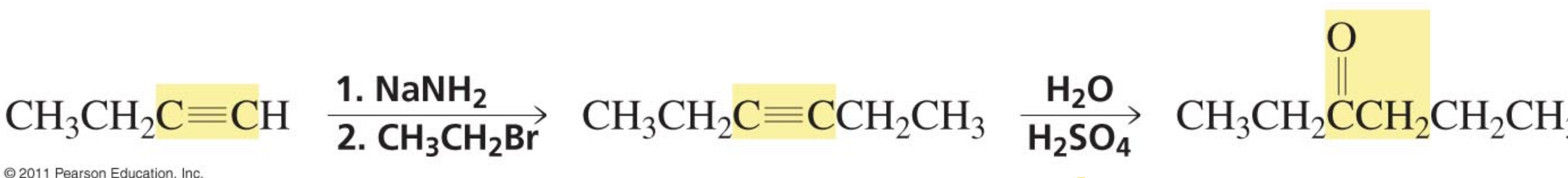
## <Ex 1>




retrosynthetic analysis

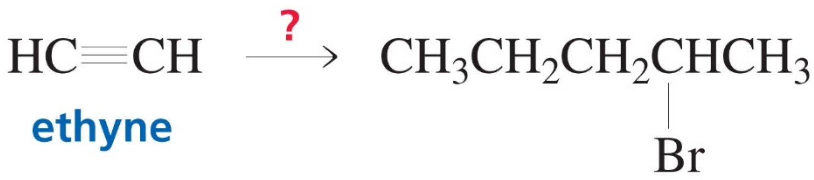



synthesis




hydroboration-oxidation?

## <Ex 2>

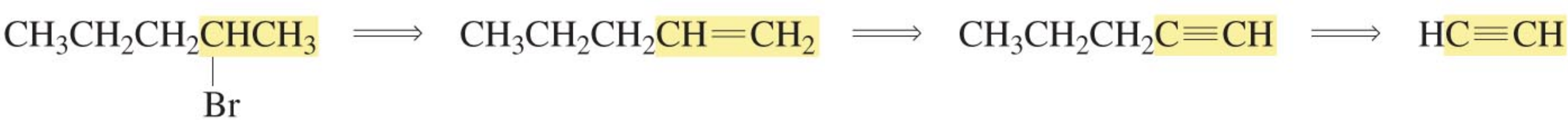



ethyne

2-bromopentane

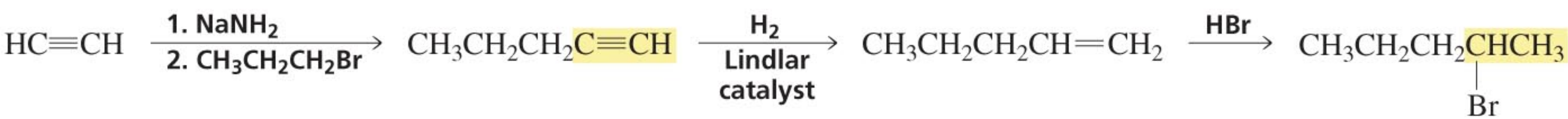


retrosynthetic analysis

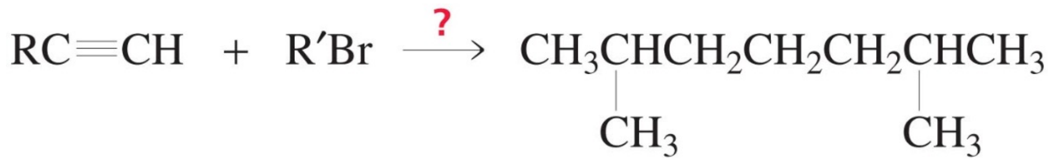





synthesis



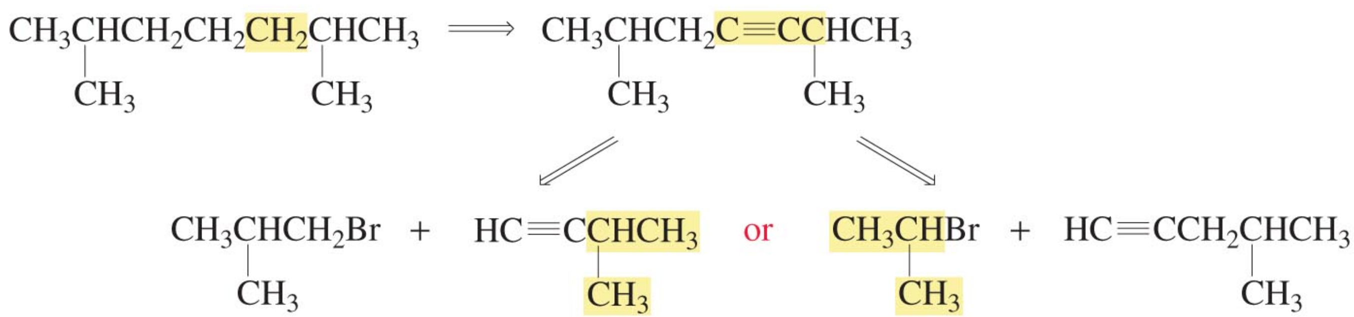
## <Ex 3>



2,6-dimethylheptane

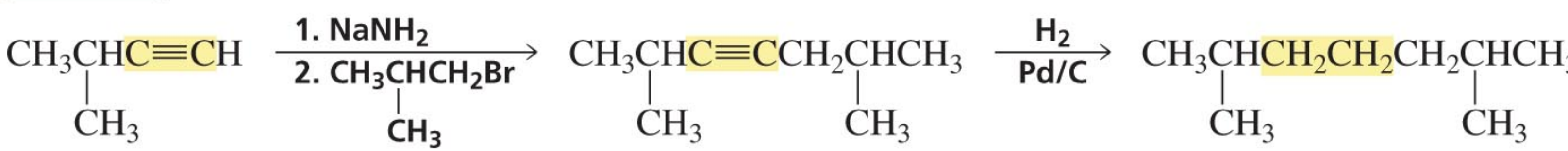


retrosynthetic analysis





synthesis



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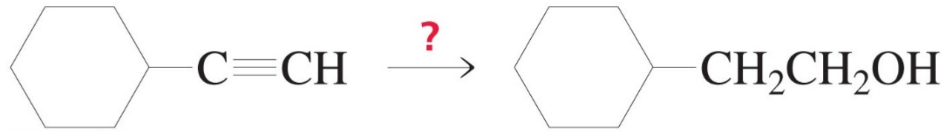
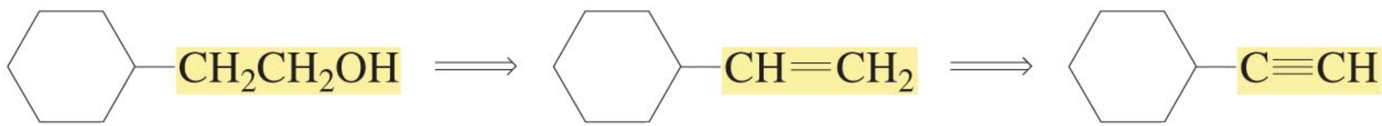





retrosynthetic analysis



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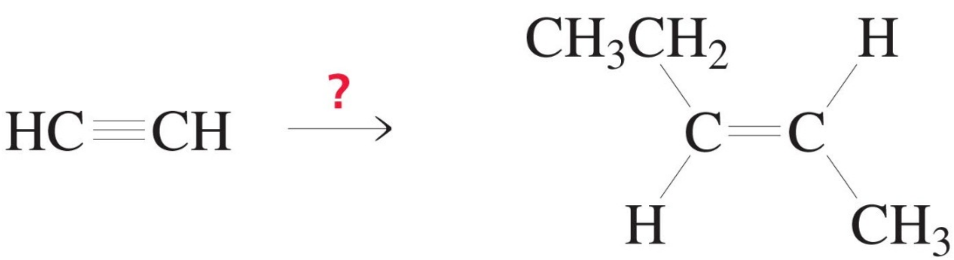
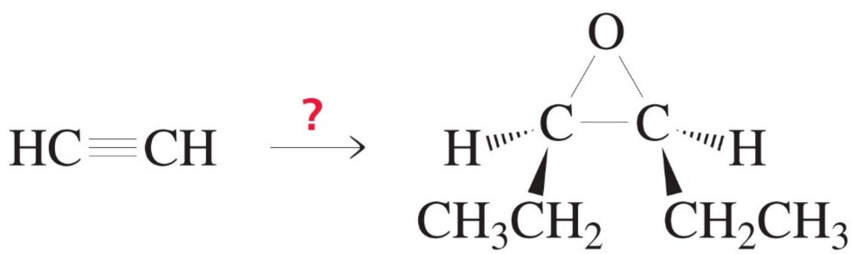



(*E*)-2-pentene

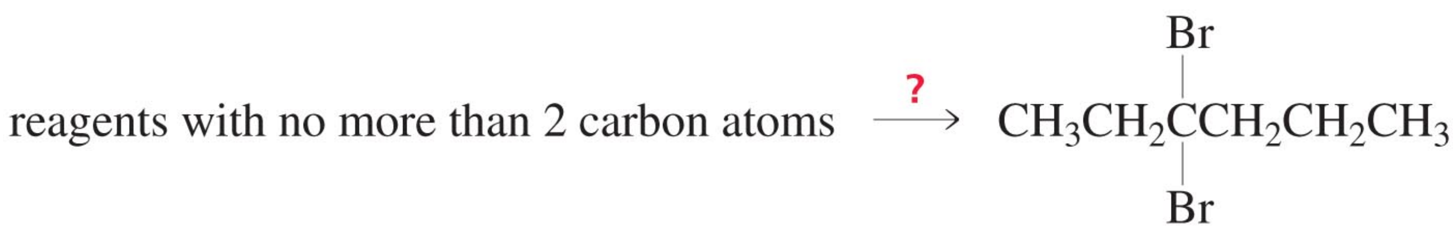
## <Ex 6>




***cis*-2,3-diethyloxirane**



## <Ex 7>




**3,3-dibromohexane**