Reactions of Alkynes

Nikhila Tippannawar
Chemistry Dept.
Arihant College of Arts,
Commerce and Science

Reactions of Alkynes

Reactions of Alkynes

- ✓ Acidity (Section 9.5)
- Hydrogenation (Section 9.9)
- Metal-Ammonia Reduction (Section 9.10)
- Addition of Hydrogen Halides (Section 9.11)
- Hydration (Section 9.12)
- Addition of Halogens (Section 9.13)
- Ozonolysis (Section 9.14)

Hydrogenation of Alkynes

Hydrogenation of Alkynes

$$RC\equiv CR' \quad + \quad 2H_2 \xrightarrow{\text{cat}} RCH_2CH_2R'$$

catalyst = Pt, Pd, Ni, or Rh

- alkene is an intermediate

Heats of Hydrogenation

$CH_3CH_2C{\equiv}CH$

292 kJ/mol

$CH_3C{\equiv}CCH_3$

275 kJ/mol

Alkyl groups stabilize triple bonds in the same way that they stabilize double bonds. Internal triple bonds are more stable than terminal ones.

Partial Hydrogenation

$$\mathrm{RC{\equiv}CR'} \xrightarrow[\text{cat}]{H_2} \mathrm{RCH{=}CHR'} \xrightarrow[\text{cat}]{H_2} \mathrm{RCH_2CH_2R'}$$

- Alkenes could be used to prepare alkenes if a catalyst were available that is active enough to catalyze the hydrogenation of alkynes, but not active enough for the hydrogenation of alkenes.

Lindlar Palladium

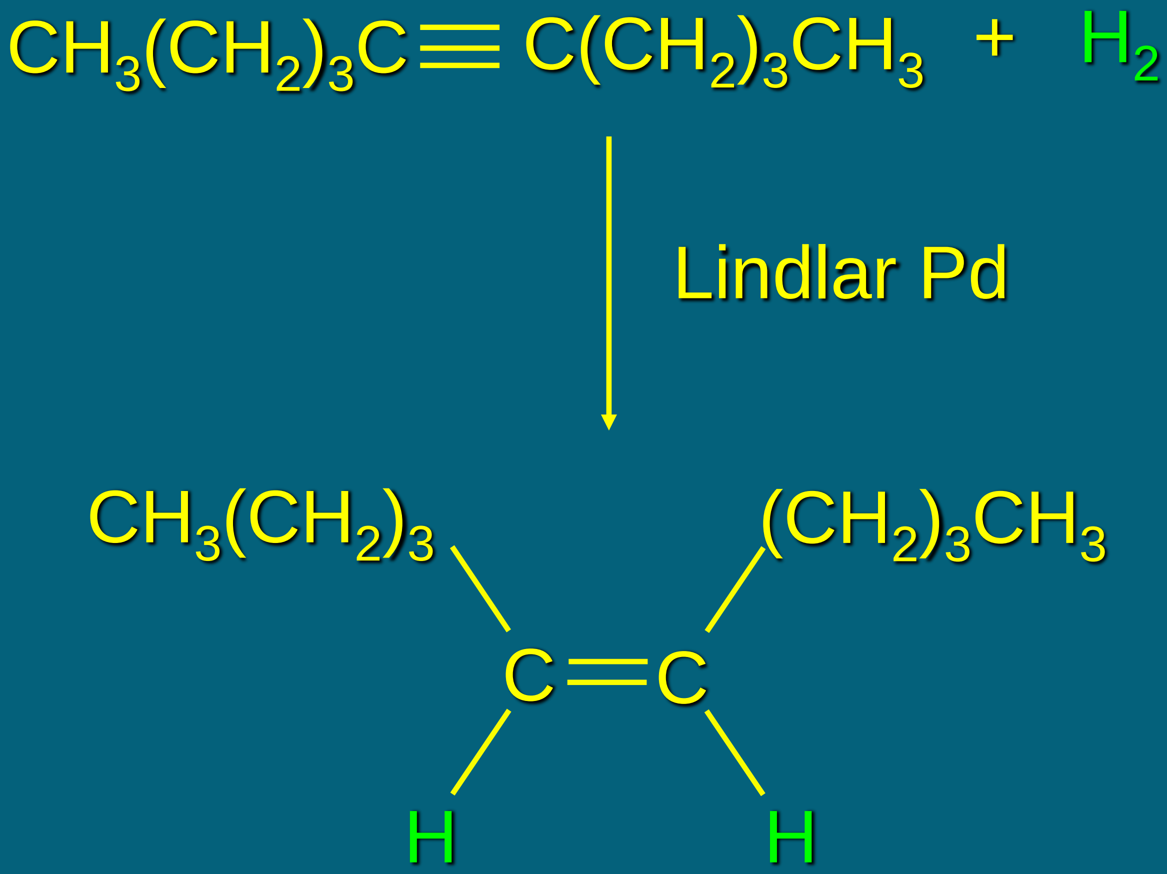
$$RC\equiv CR' \xrightarrow[\text{cat}]{H_2} RCH{=}CHR' \cancel{\xrightarrow[\text{cat}]{H_2}} RCH_2CH_2R'$$

- There is a catalyst that will catalyze the hydrogenation of alkynes to alkenes, but not that of alkenes to alkanes.

- It is called the Lindlar catalyst and consists of palladium supported on $CaCO_3$, which has been poisoned with lead acetate and quinoline.

- *syn*-Hydrogenation occurs; cis alkenes are formed.

Example



$CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3 + H_2$

Lindlar Pd

(87%)

9.10

Metal-Ammonia Reduction of Alkynes

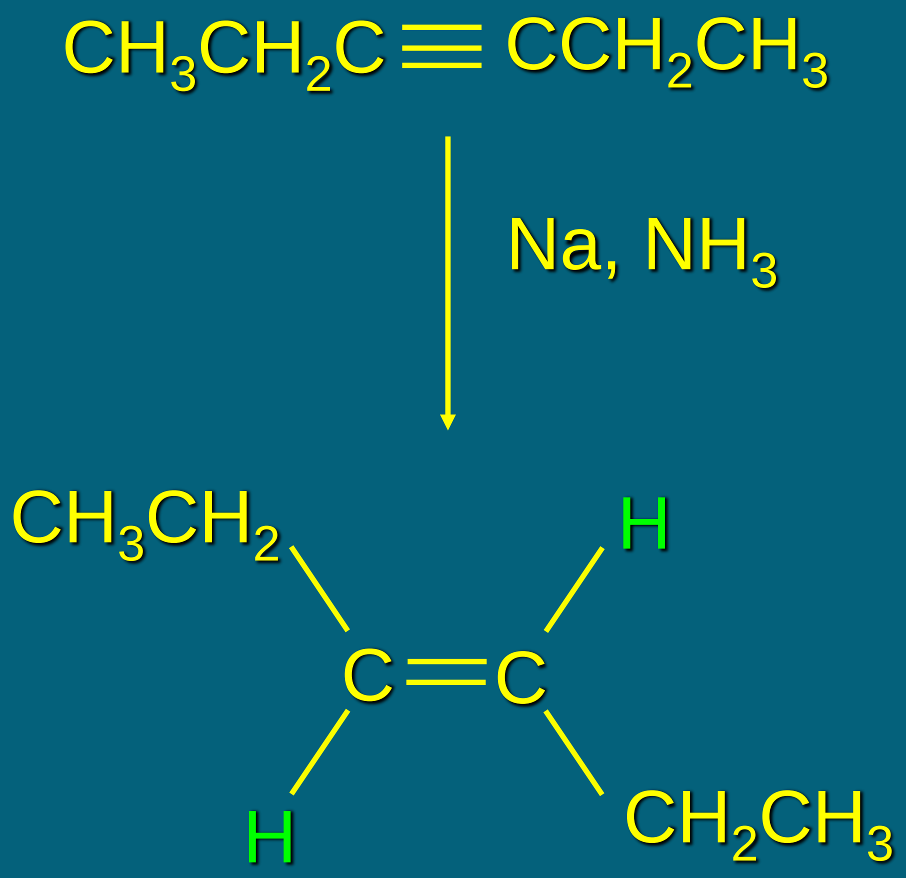
- Alkynes ∅ *trans*-Alkenes

Partial Reduction

$$RC\equiv CR' \longrightarrow RCH{=}CHR' \not\longrightarrow RCH_2CH_2R'$$

- Another way to convert alkynes to alkenes is by reduction with sodium (or lithium or potassium) in ammonia.
- *trans*-Alkenes are formed.

Example



(82%)

Mechanism

Metal (Li, Na, K) is reducing agent; H_2 is not involved

- four steps
  - (1) electron transfer
  - (2) proton transfer
  - (3) electron transfer
  - (4) proton transfer

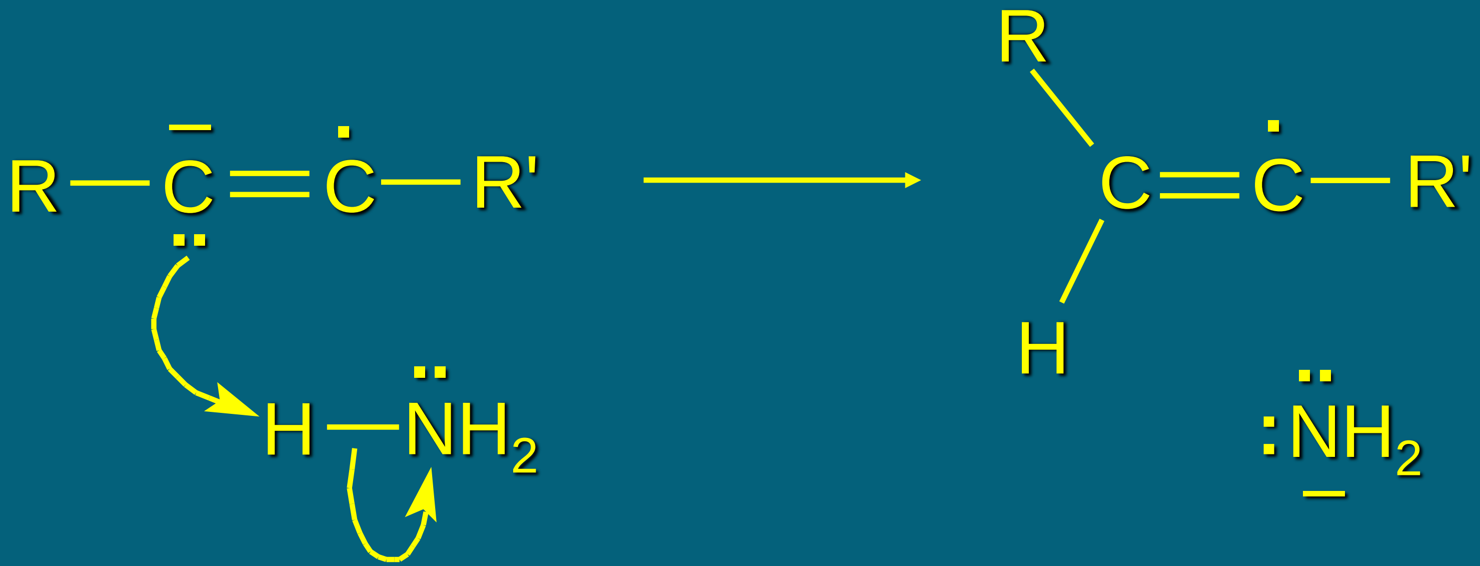
Mechanism

- Step (1): Transfer of an electron from the metal to the alkyne to give an anion radical.

$$R-C\equiv C-R' + M\cdot \longrightarrow R-\overset{M^{+}}{\overset{-}{\ddot{C}}}=\dot{C}-R'$$

Mechanism

- Step (2) Transfer of a proton from the solvent (liquid ammonia) to the anion radical.

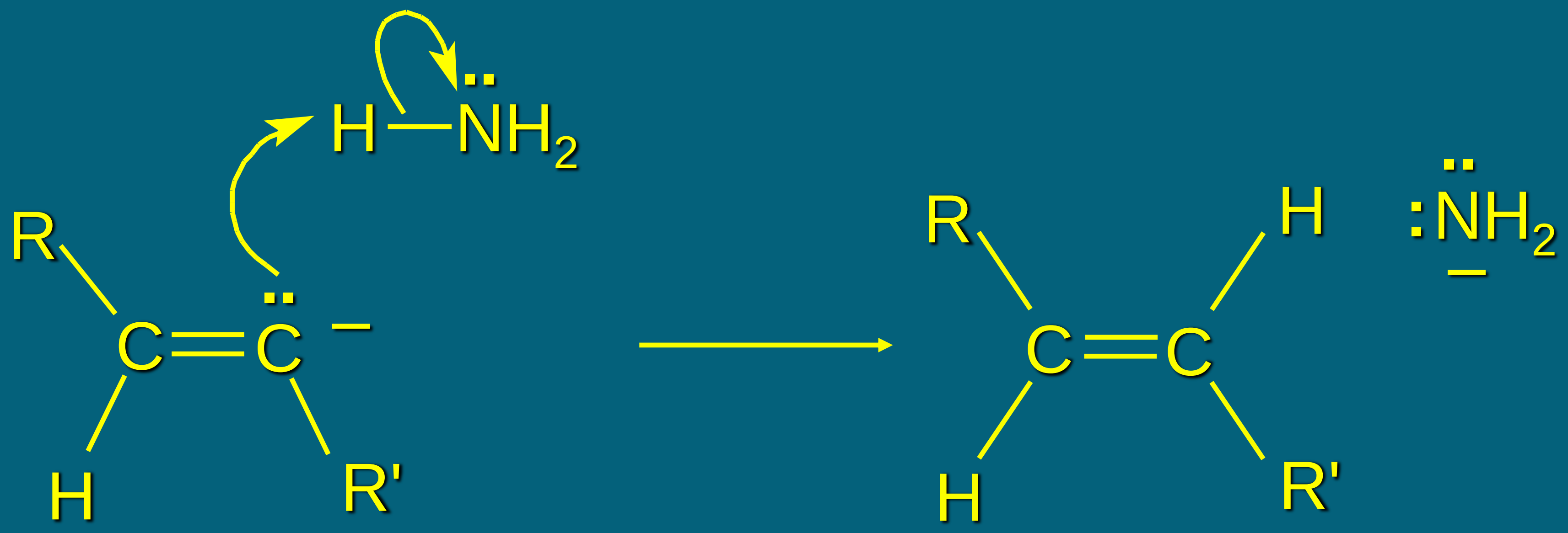


Mechanism

- Step (3): Transfer of an electron from the metal to the alkenyl radical to give a carbanion.

Mechanism

- Step (4) Transfer of a proton from the solvent (liquid ammonia) to the carbanion .

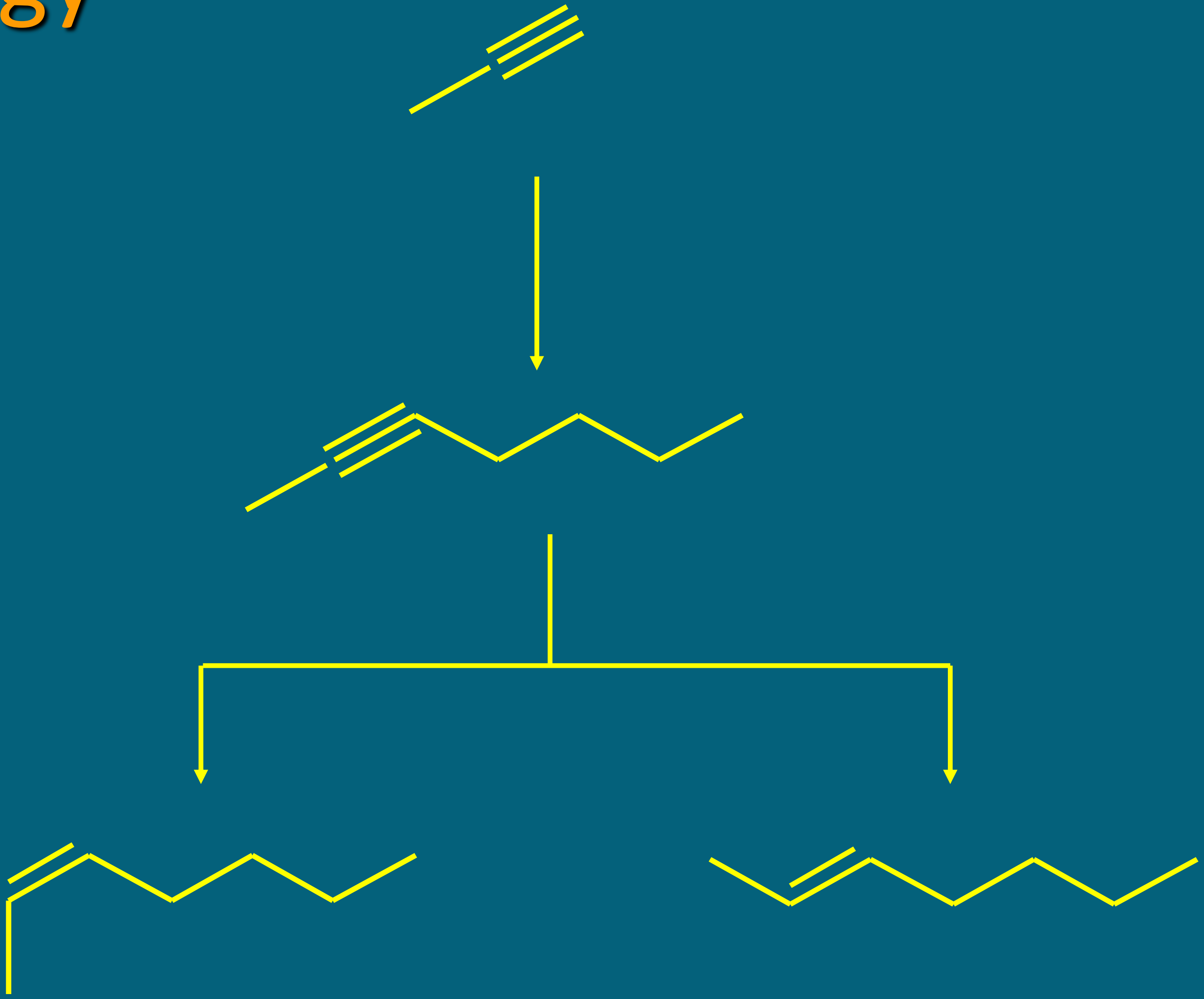


Problem 9.12

- Suggest efficient syntheses of (*E*)- and (*Z*)-2-heptene from propyne and any necessary organic or inorganic reagents.

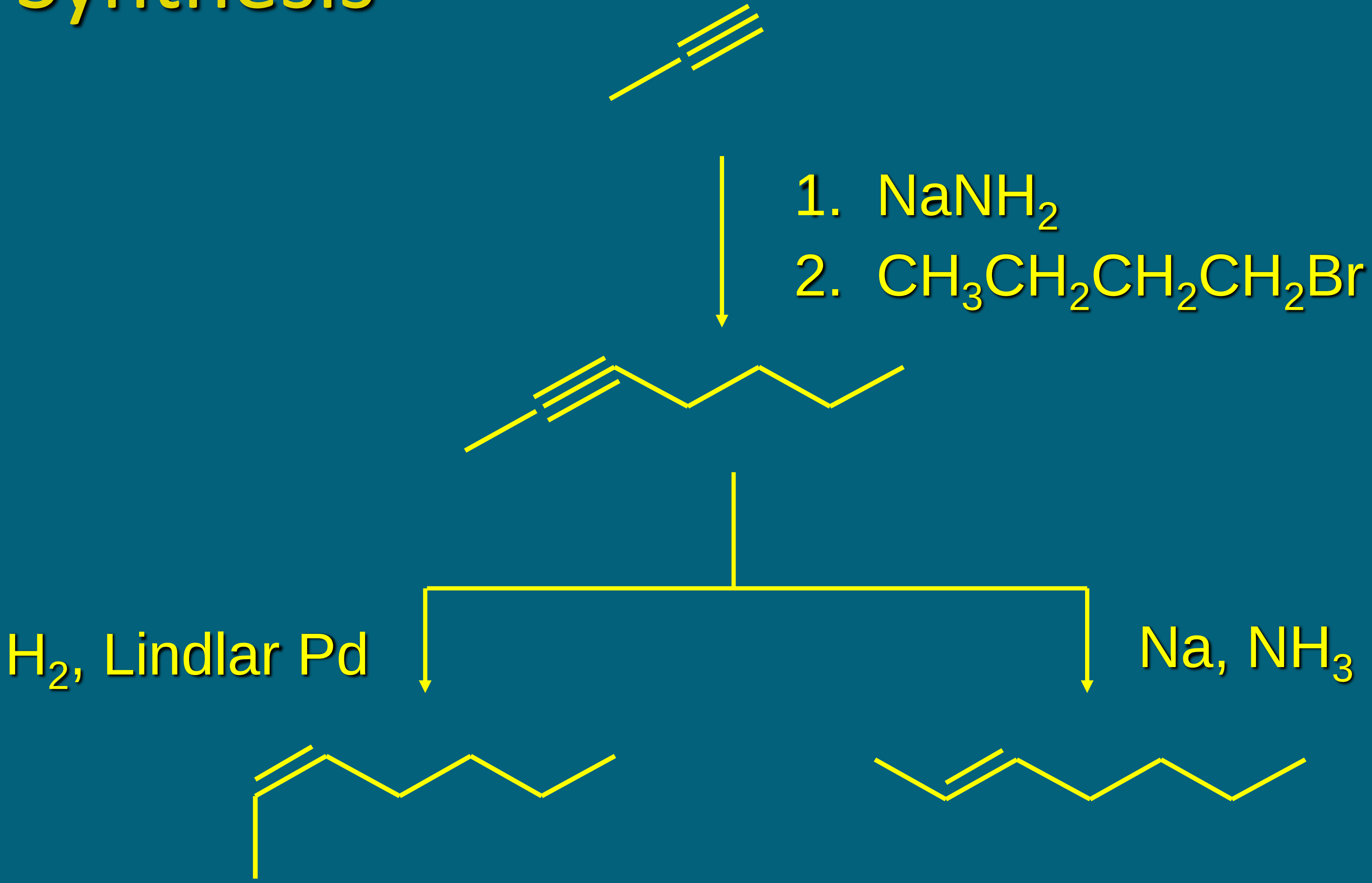
Problem 9.12

Strategy



Problem 9.12

Synthesis



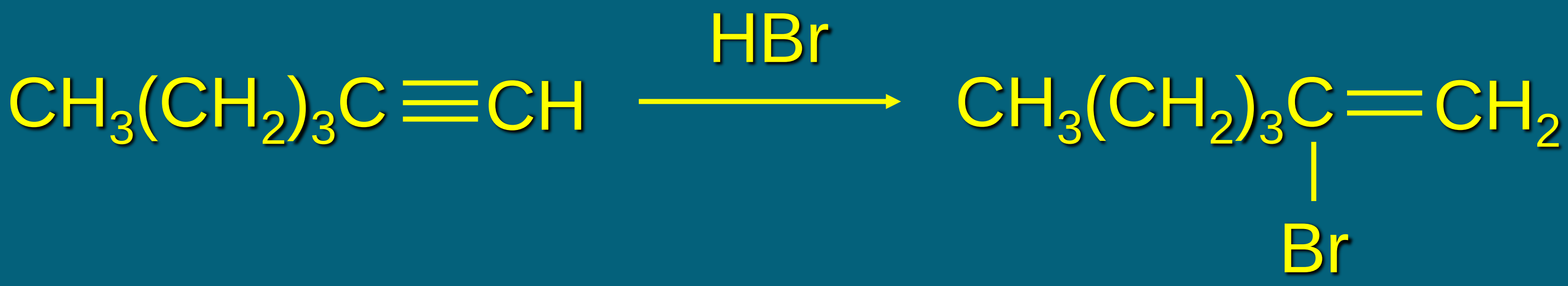
1. $NaNH_2$
2. $CH_3CH_2CH_2CH_2Br$

H_2, Lindlar Pd

Na, NH_3

9.11
Addition of Hydrogen Halides to Alkynes

Follows Markovnikov's Rule

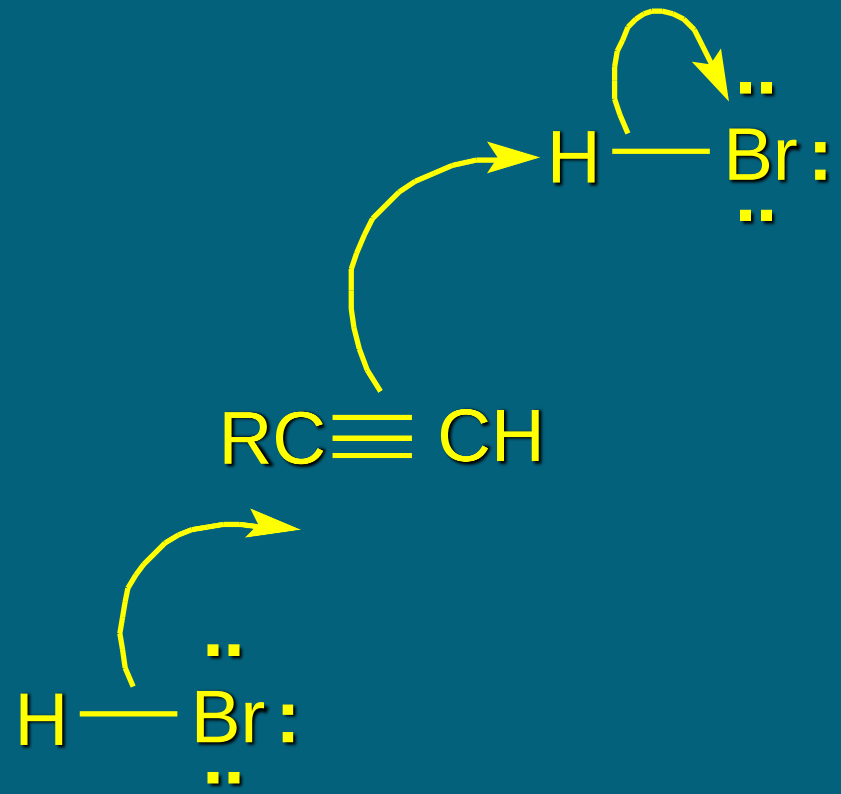


$$CH_3(CH_2)_3C\equiv CH \xrightarrow{HBr} CH_3(CH_2)_3\underset{\underset{Br}{|}}{C}=CH_2$$

(60%)

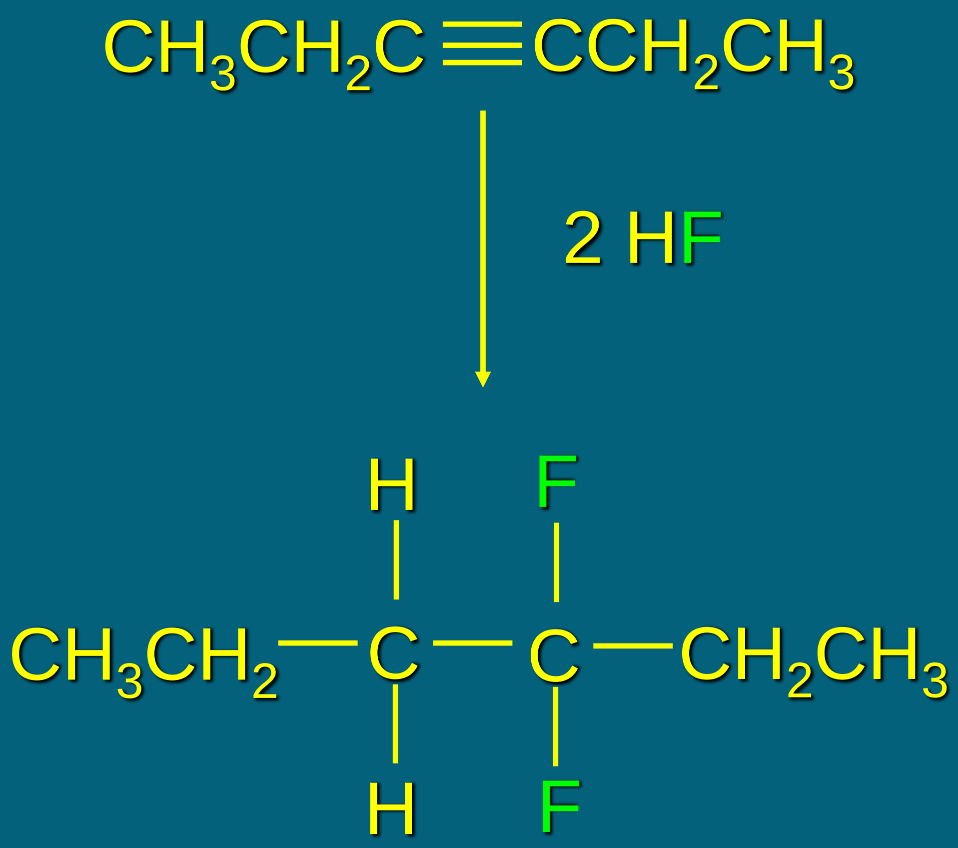
- Alkynes are slightly less reactive than alkenes

Termolecular Rate-Determining Step



Observed rate law: rate = k[alkyne][HX]^2

Two Molar Equivalents of Hydrogen Halide



$$CH_3CH_2C\equiv CCH_2CH_3 \xrightarrow{2\ HF} CH_3CH_2-\overset{H}{\underset{H}{C}}-\overset{F}{\underset{F}{C}}-CH_2CH_3$$

(76%)

Free-radical Addition of HBr

$$CH_3(CH_2)_3C\equiv CH \xrightarrow[\text{peroxides}]{HBr} CH_3(CH_2)_3CH=CHBr$$

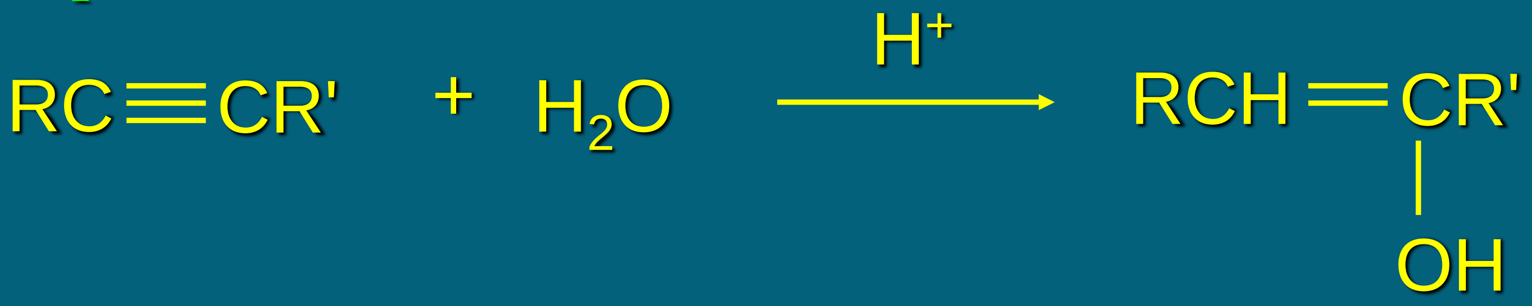
(79%)

- regioselectivity opposite to Markovnikov's rule

9.12
Hydration of Alkynes

Hydration of Alkynes

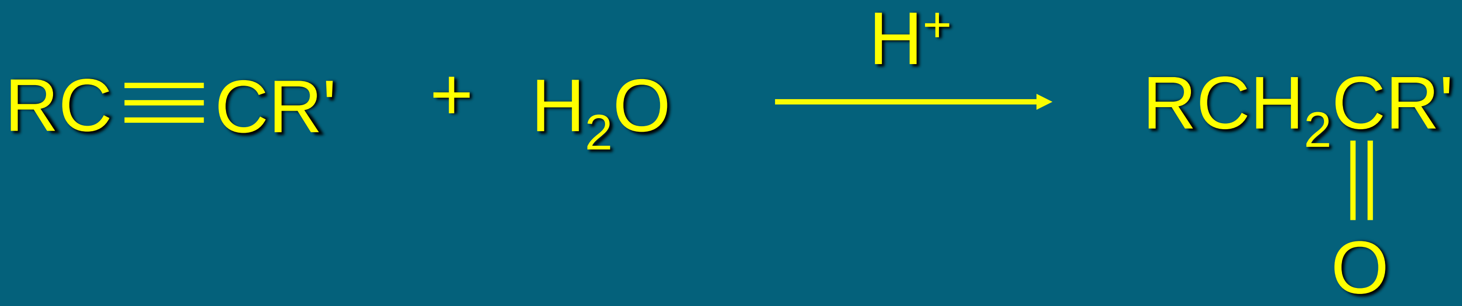
- expected reaction:



$$\mathrm{RC{\equiv}CR' + H_2O \xrightarrow{H^+} RCH{=}\underset{\overset{|}{OH}}{C}R'}$$

enol

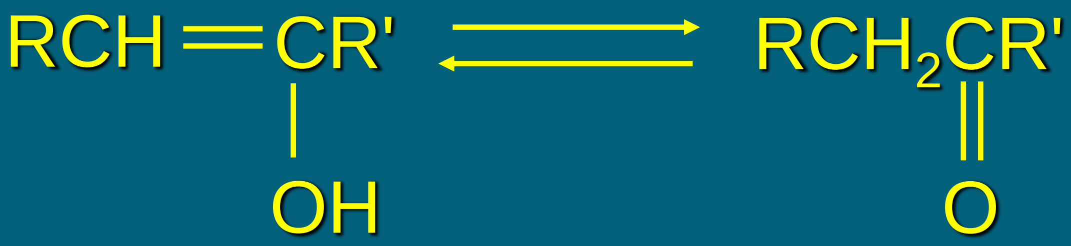
observed reaction:



$$\mathrm{RC{\equiv}CR' + H_2O \xrightarrow{H^+} RCH_2\underset{\overset{\|}{O}}{C}R'}$$

ketone

Enols

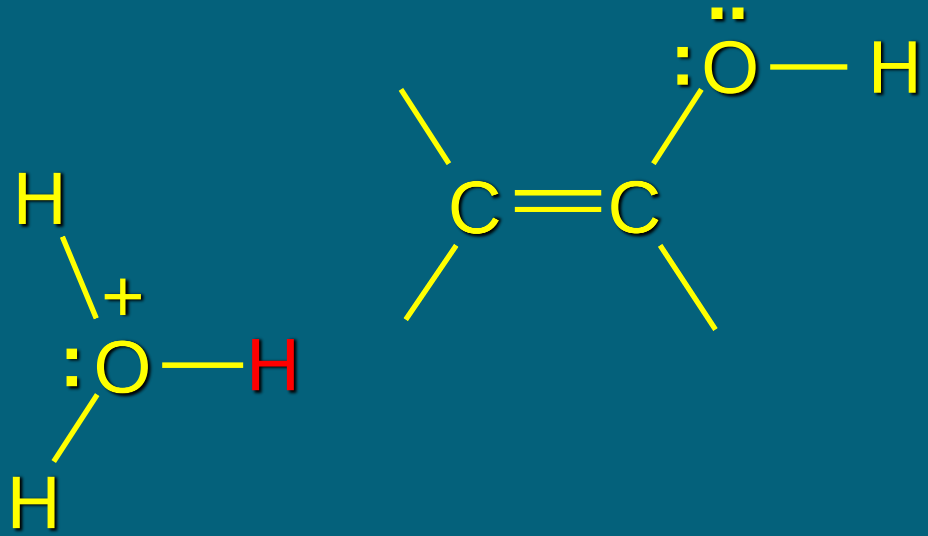


$$RCH{=}C(OH)R' \rightleftharpoons RCH_2C({=}O)R'$$

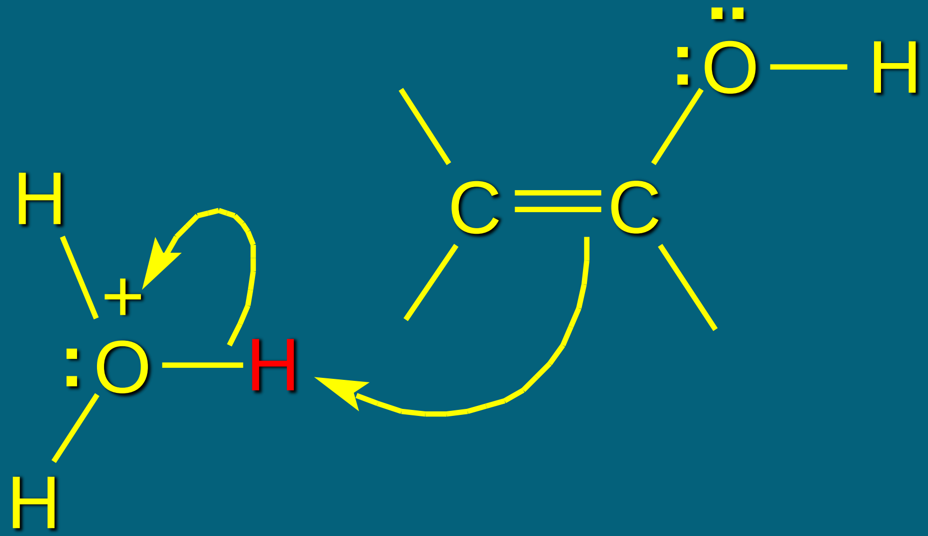
enol *ketone*

- enols are regioisomers of ketones, and exist in equilibrium with them
- keto-enol equilibration is rapid in acidic media
- ketones are more stable than enols and predominate at equilibrium

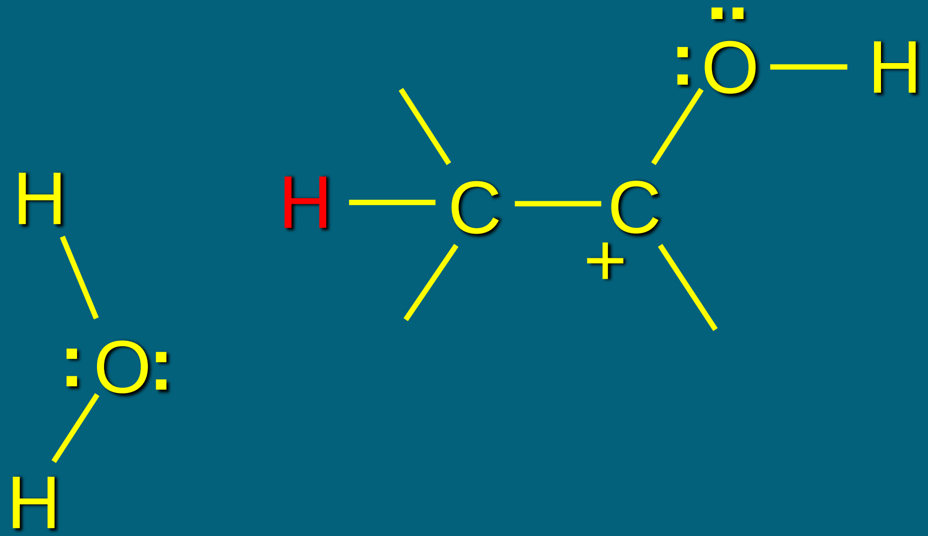
Mechanism of conversion of enol to ketone



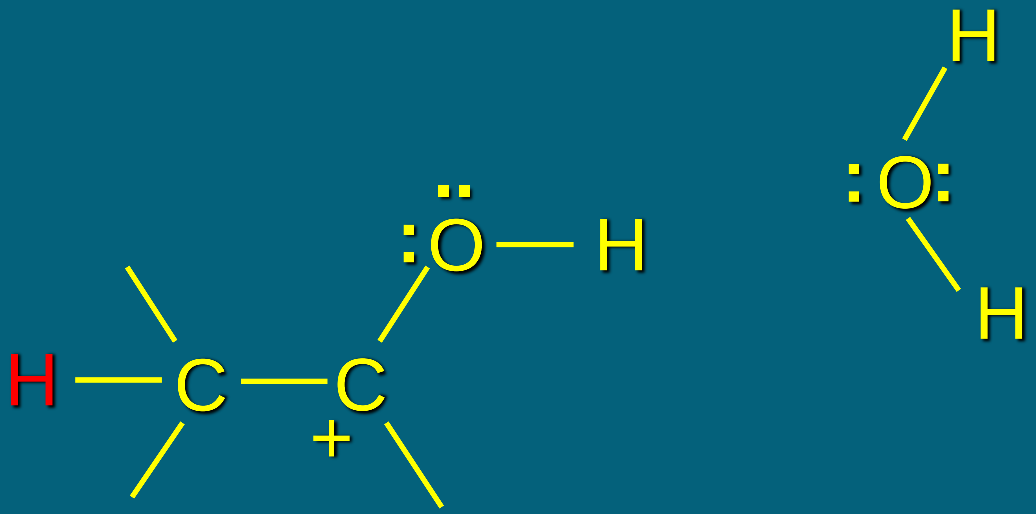
Mechanism of conversion of enol to ketone



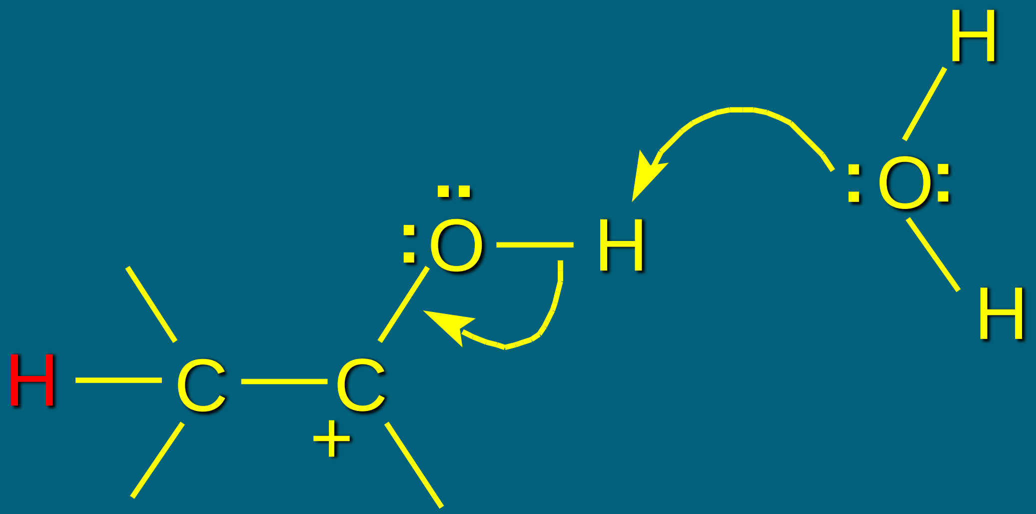
Mechanism of conversion of enol to ketone



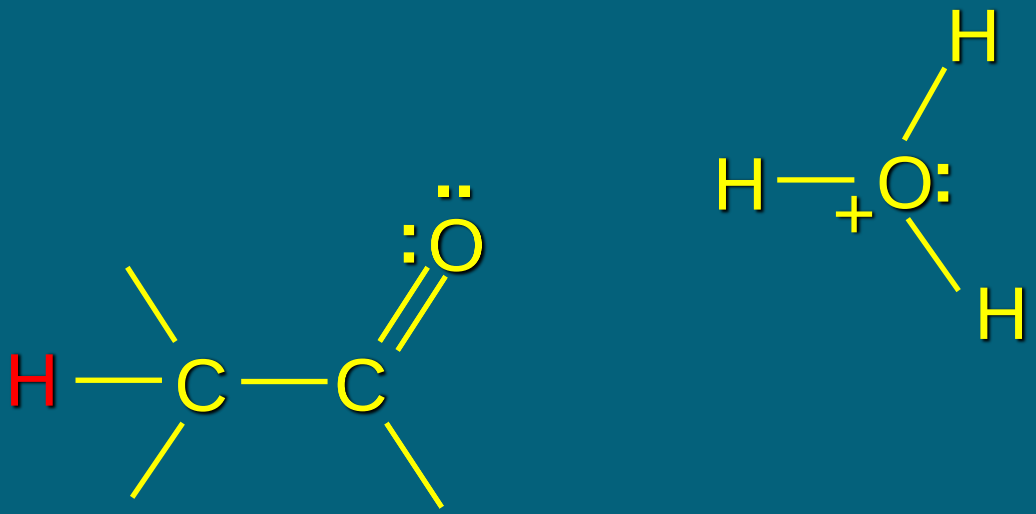
Mechanism of conversion of enol to ketone



Mechanism of conversion of enol to ketone



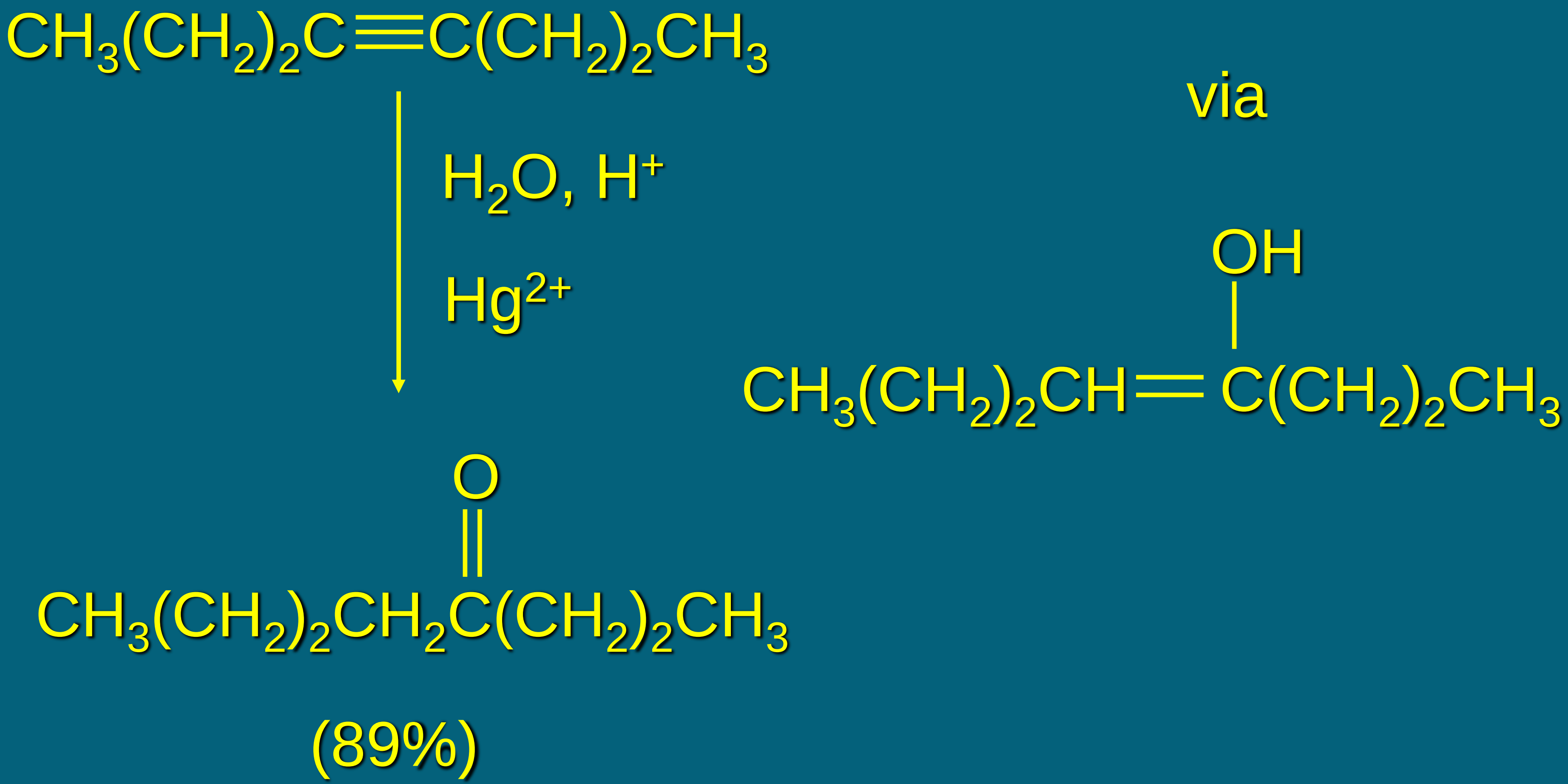
Mechanism of conversion of enol to ketone



Key Carbocation Intermediate

Carbocation is stabilized by
electron delocalization (resonance)

Example of Alkyne Hydration



$$CH_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3 \xrightarrow[Hg^{2+}]{H_2O,\ H^+} CH_3(CH_2)_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_2CH_3$$

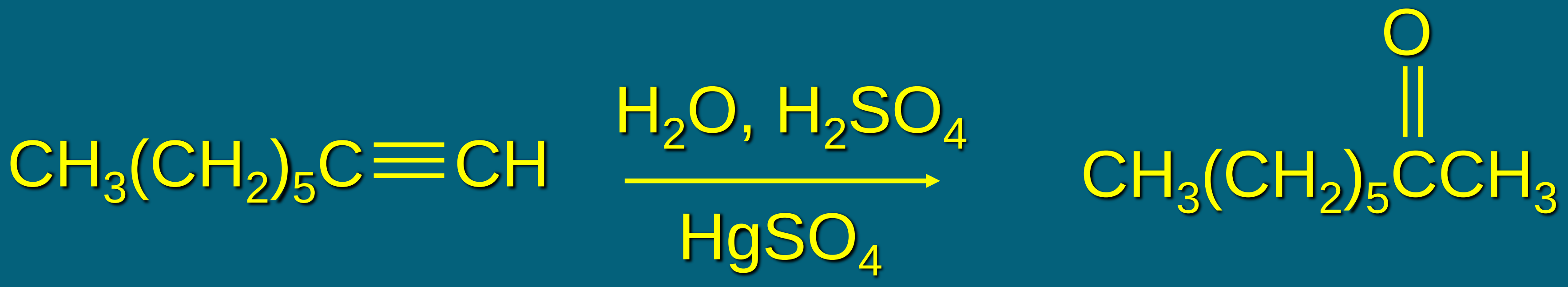
(89%)

via

$$CH_3(CH_2)_2CH{=}\overset{\overset{\displaystyle OH}{|}}{C}(CH_2)_2CH_3$$

Regioselectivity

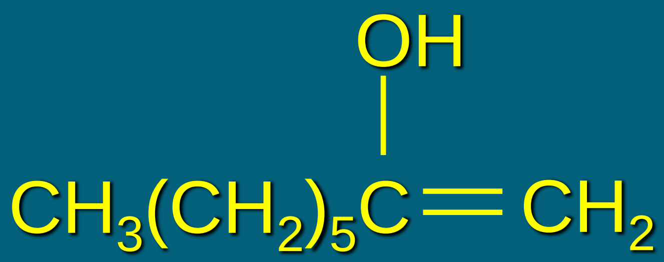
Markovnikov's rule followed in formation of enol



$$CH_3(CH_2)_5C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3(CH_2)_5\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

(91%)

via

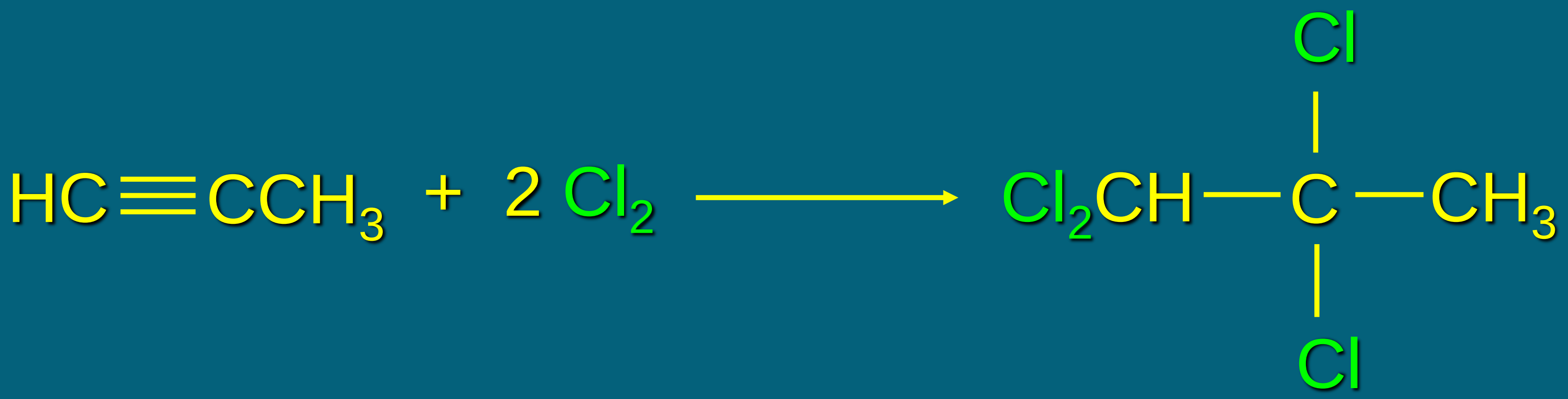


$$CH_3(CH_2)_5\overset{\overset{\displaystyle OH}{|}}{C}{=}CH_2$$

9.13

Addition of Halogens to Alkyn

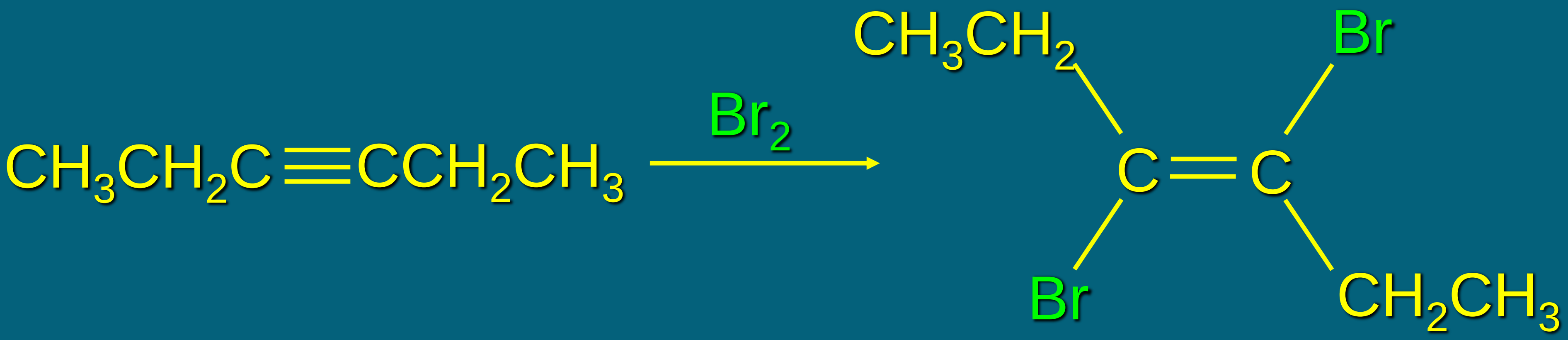
Example



$$HC\equiv CCH_3 + 2\,Cl_2 \longrightarrow Cl_2CH-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CH_3$$

(63%)

Addition is anti

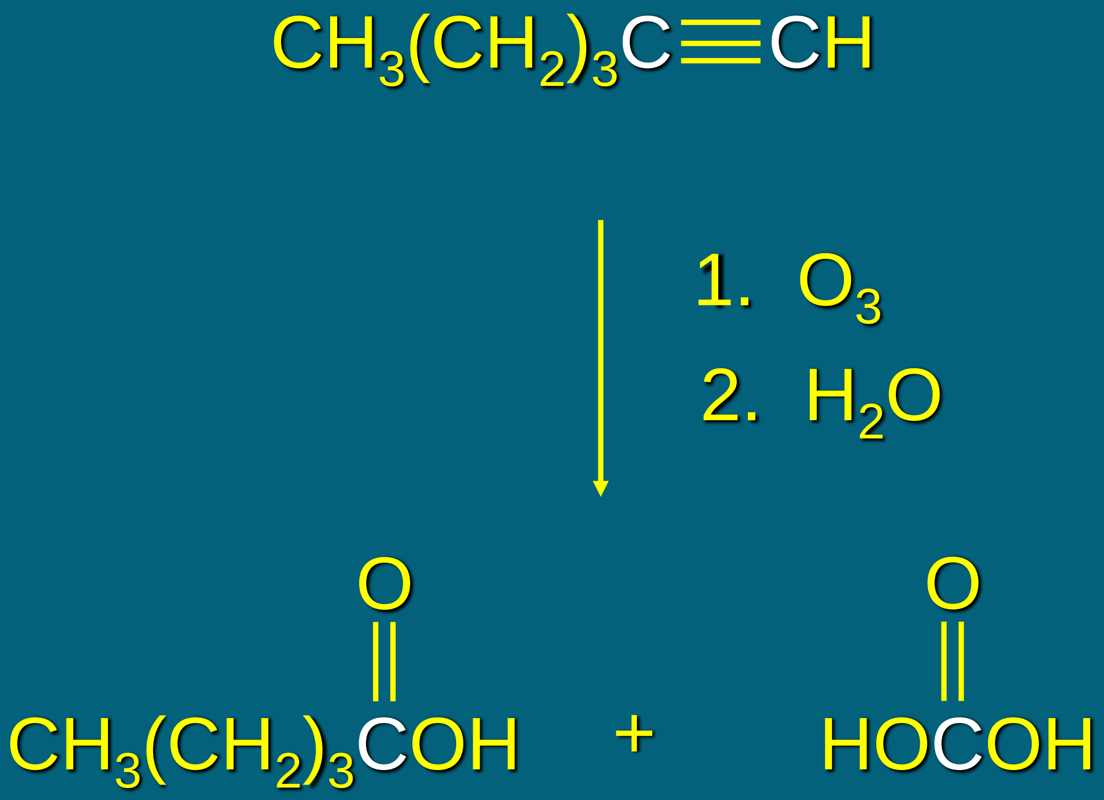


(90%)

9.14
Ozonolysis of Alkynes

- gives two carboxylic acids by cleavage of triple bond

Example



$$\mathrm{CH_3(CH_2)_3C{\equiv}CH} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{O_3}} \mathrm{CH_3(CH_2)_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH} \quad + \quad \mathrm{HO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH}$$

(51%)