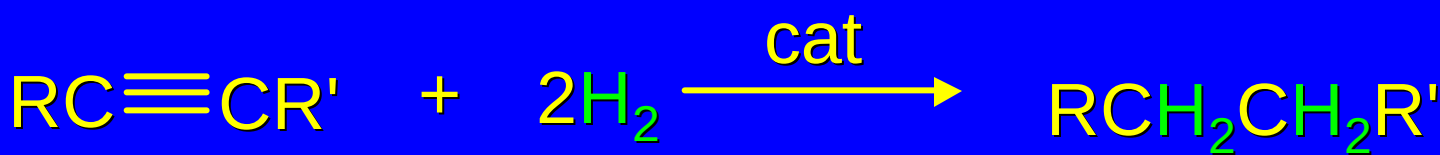
9.8
Reactions of Alkynes

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)

9.9
Hydrogenation of Alkynes

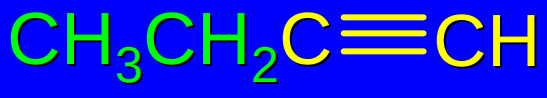
Hydrogenation of Alkynes



catalyst = Pt, Pd, Ni, or Rh

alkene is an intermediate

Heats of Hydrogenation

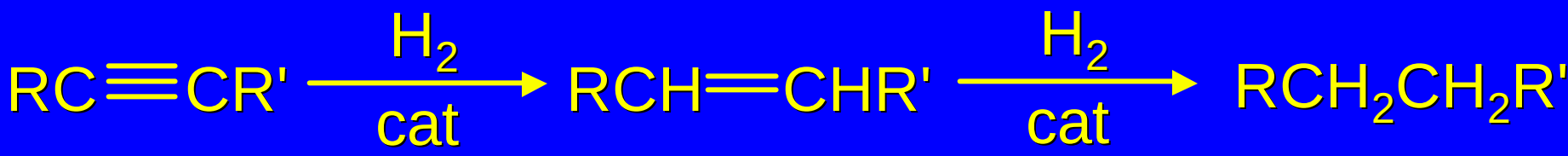


292 kJ/mol

275 kJ/mol

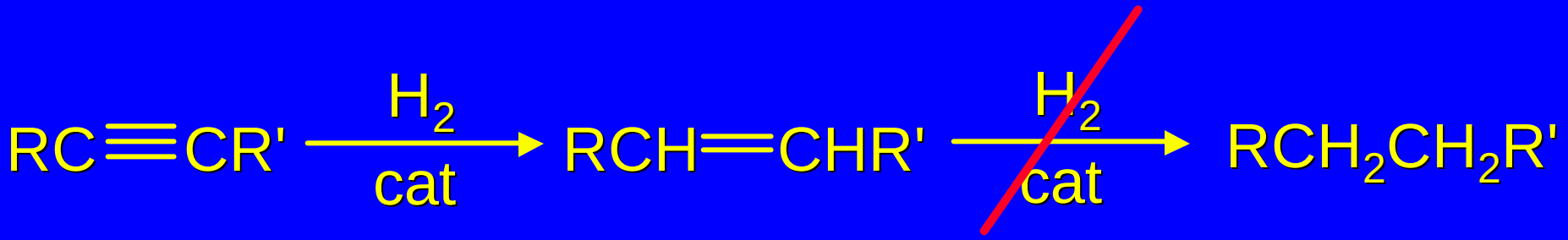
Alkyl groups stabilize triple bonds in the same way that they stabilize double bonds. Internal triple bonds are more stable than terminal ones.

Partial Hydrogenation



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

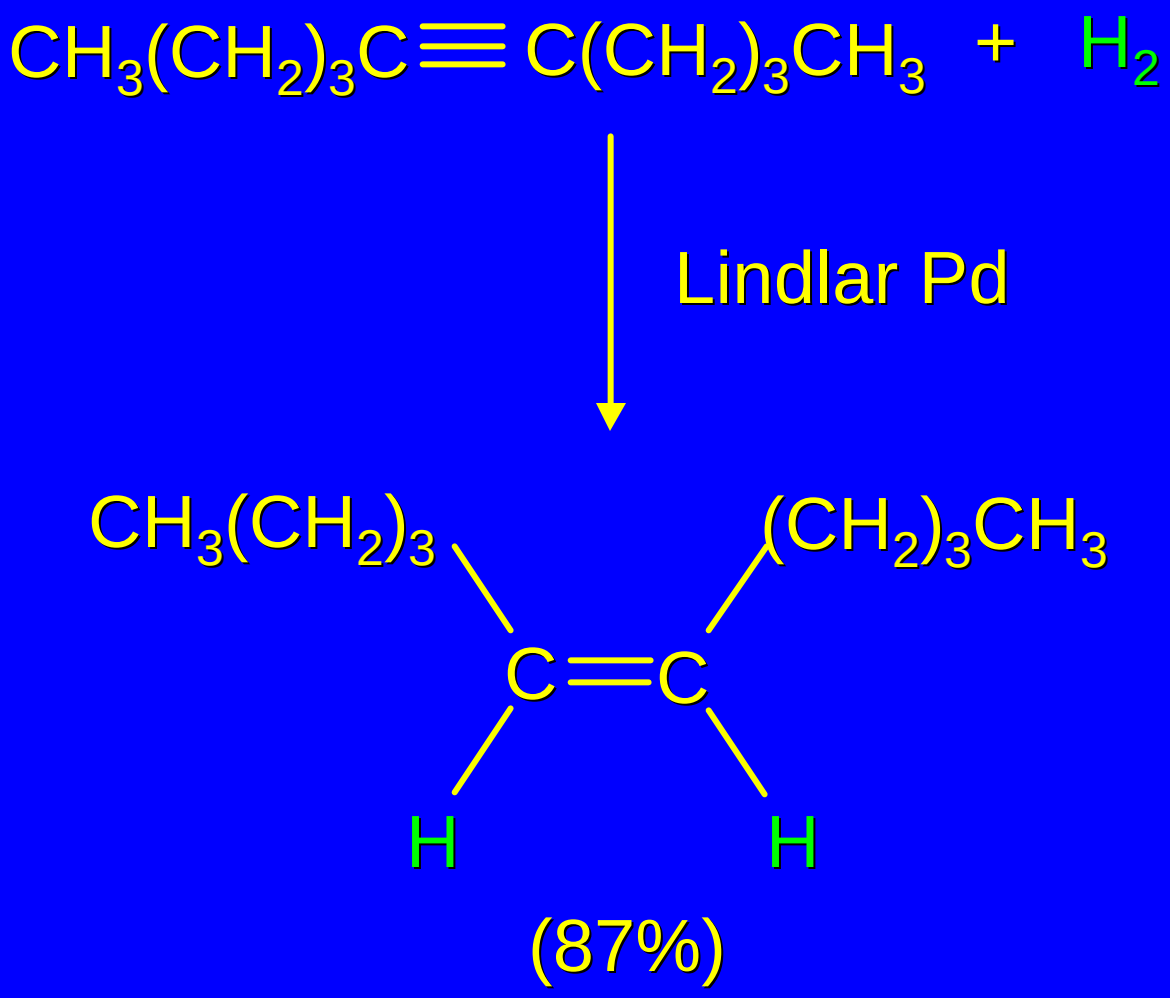


There is a catalyst that will catalyze the hydrogenation of alkynes to alkenes, but not that of alkenes to alkanes.

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

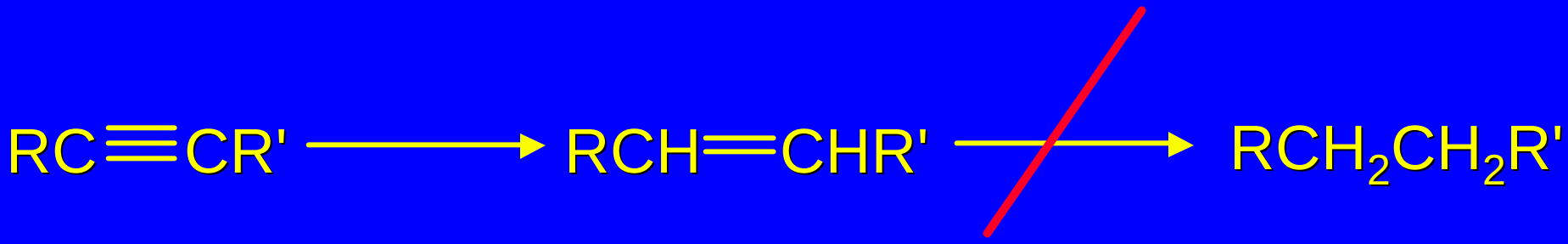


(87%)

9.10
Metal-Ammonia Reduction of Alkynes

Alkynes ∅ *trans*-Alkenes

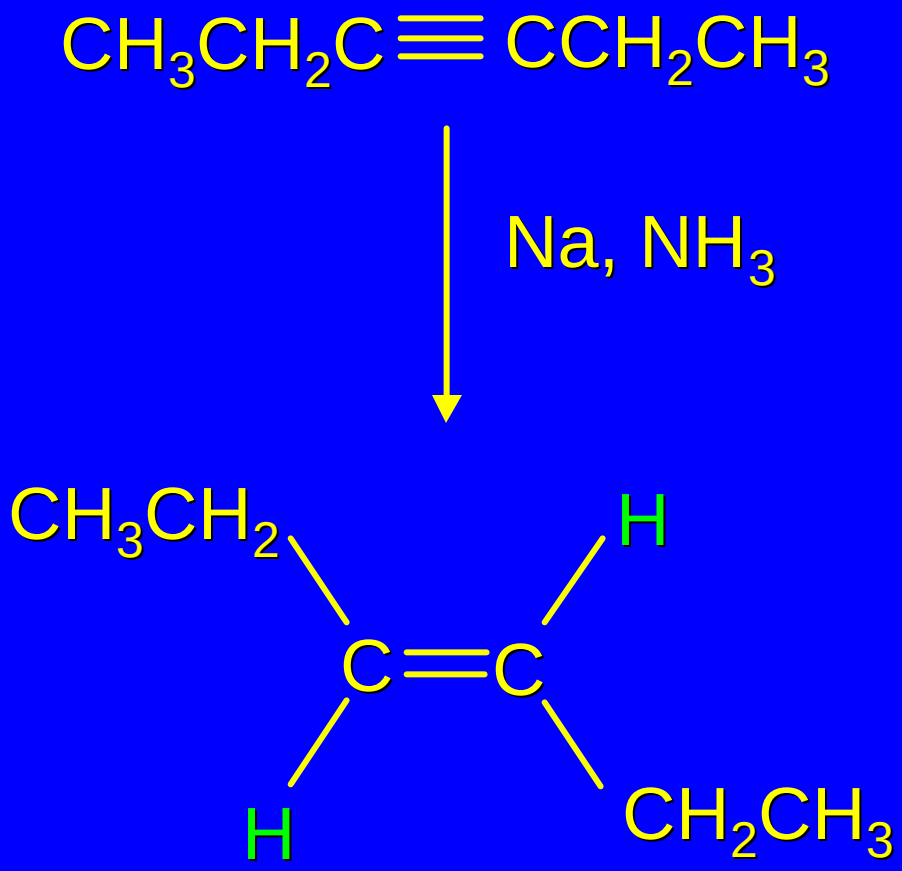
Partial Reduction



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

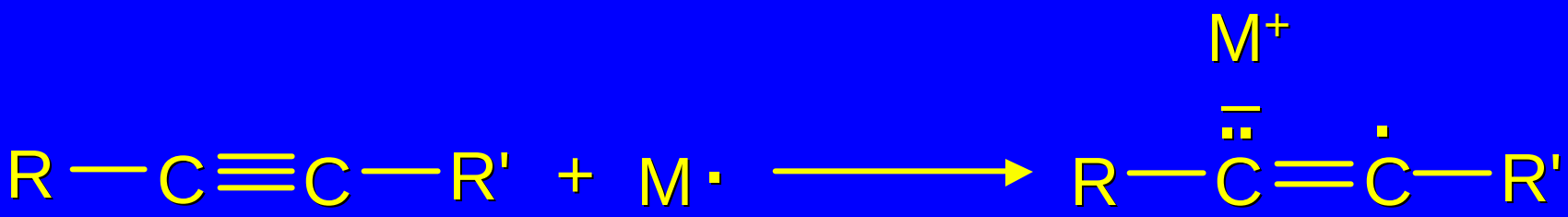
(2) proton transfer

(3) electron transfer

(4) proton transfer

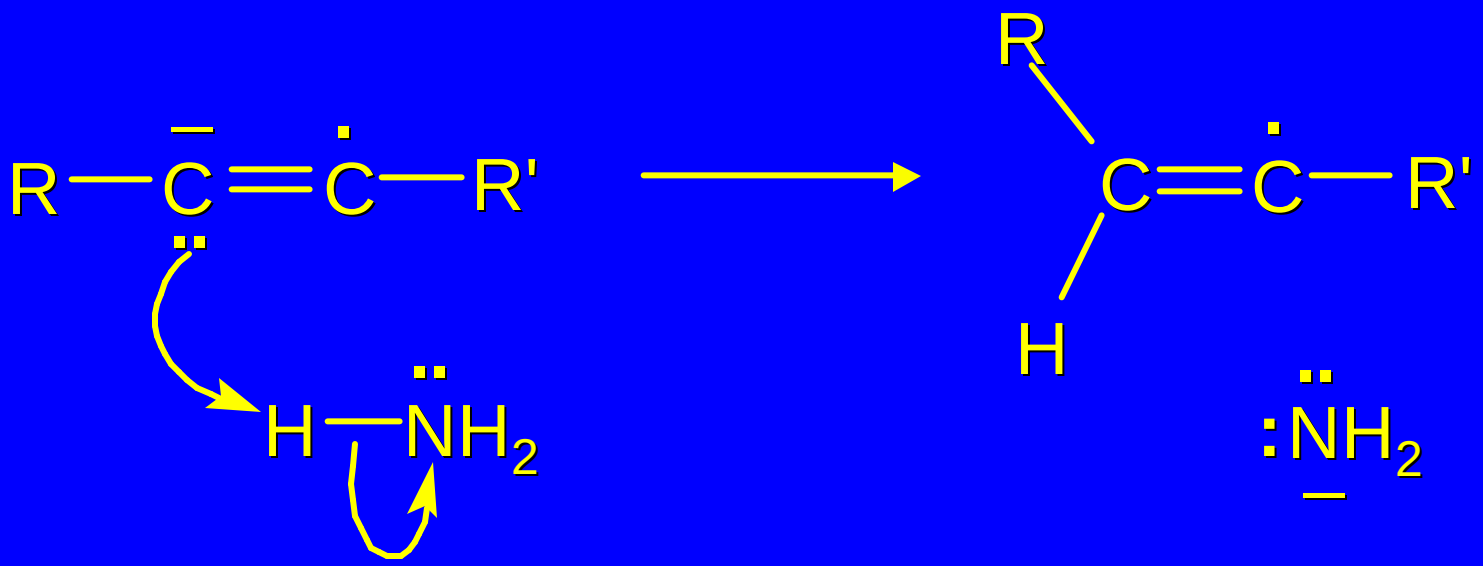
Mechanism

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



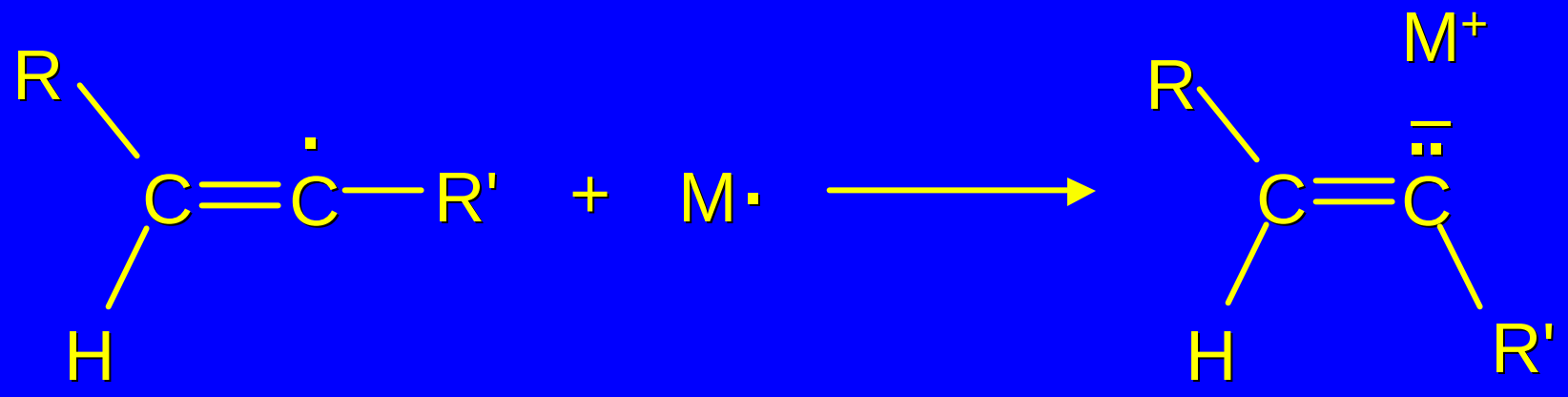
Mechanism

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



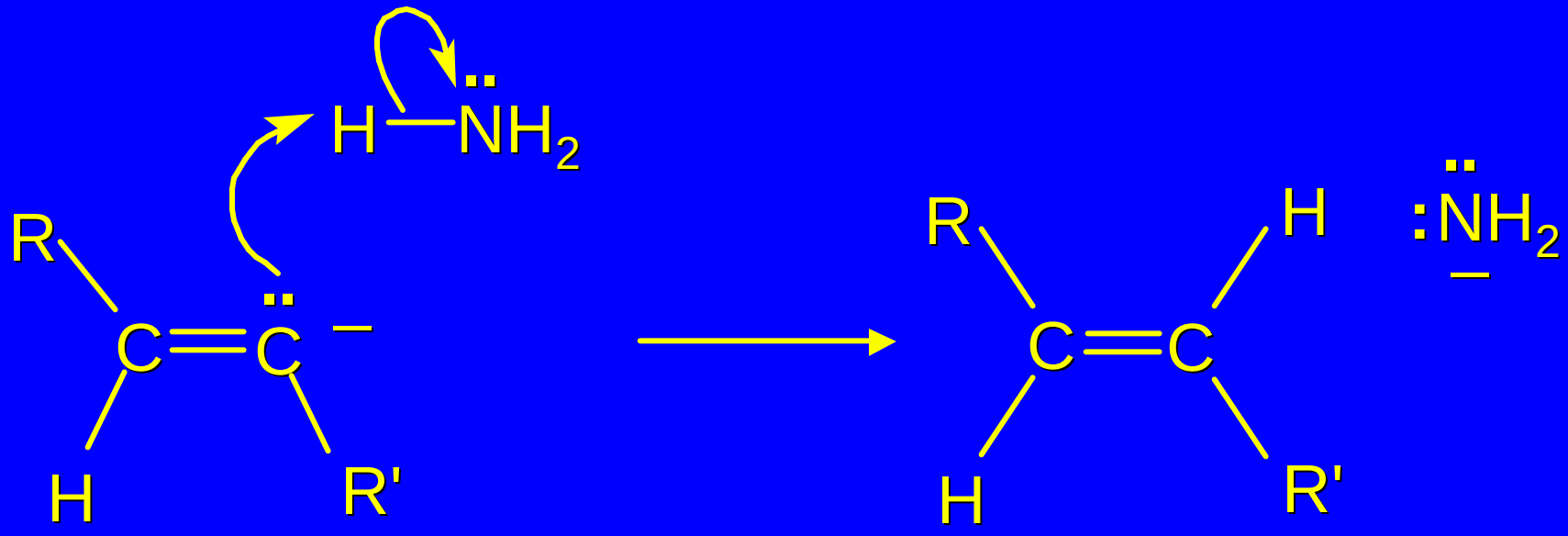
Mechanism

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



Mechanism

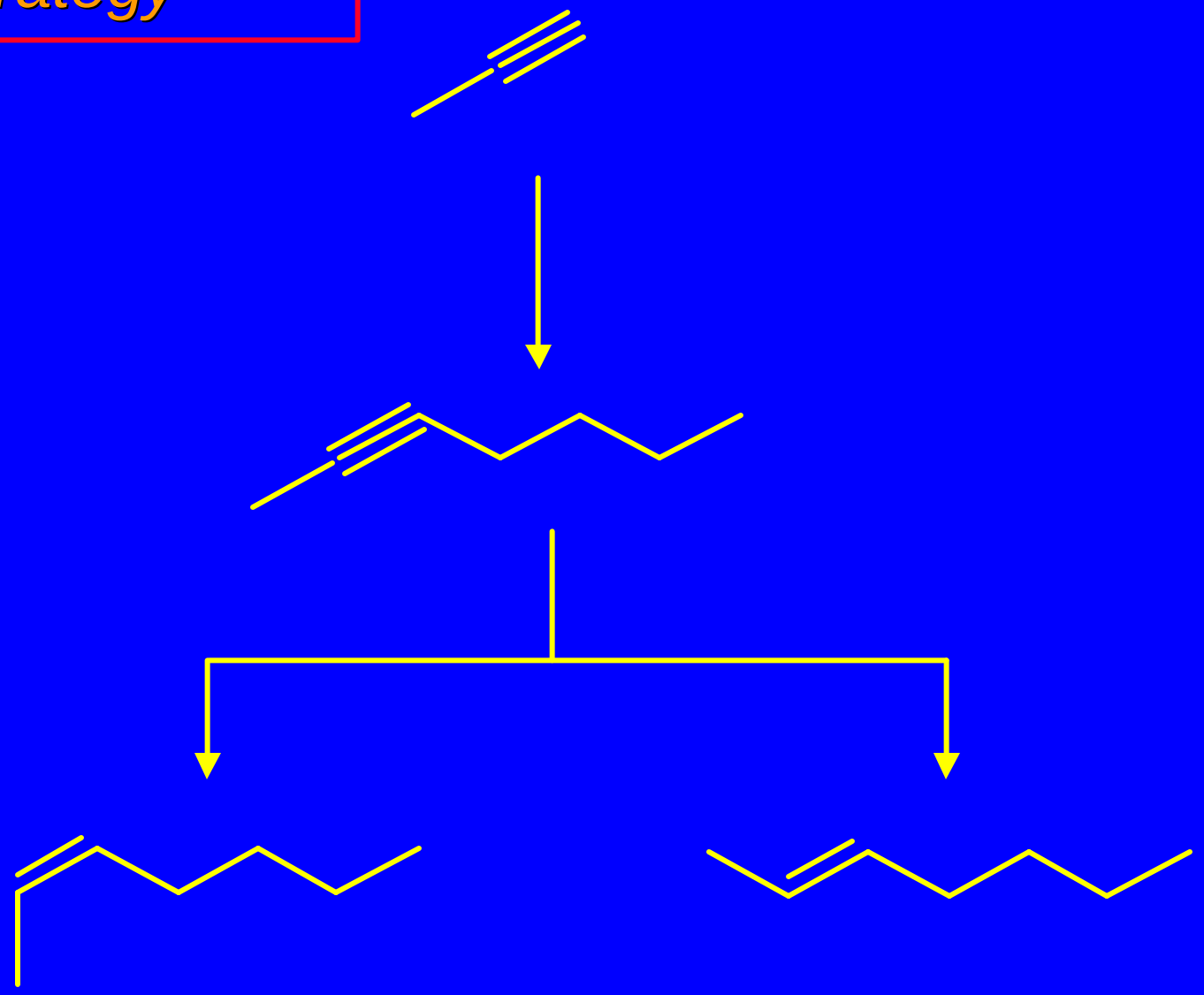
Step (4) Transfer of a proton from the solvent (liquid ammonia) to the carbanion .



Problem 9.12

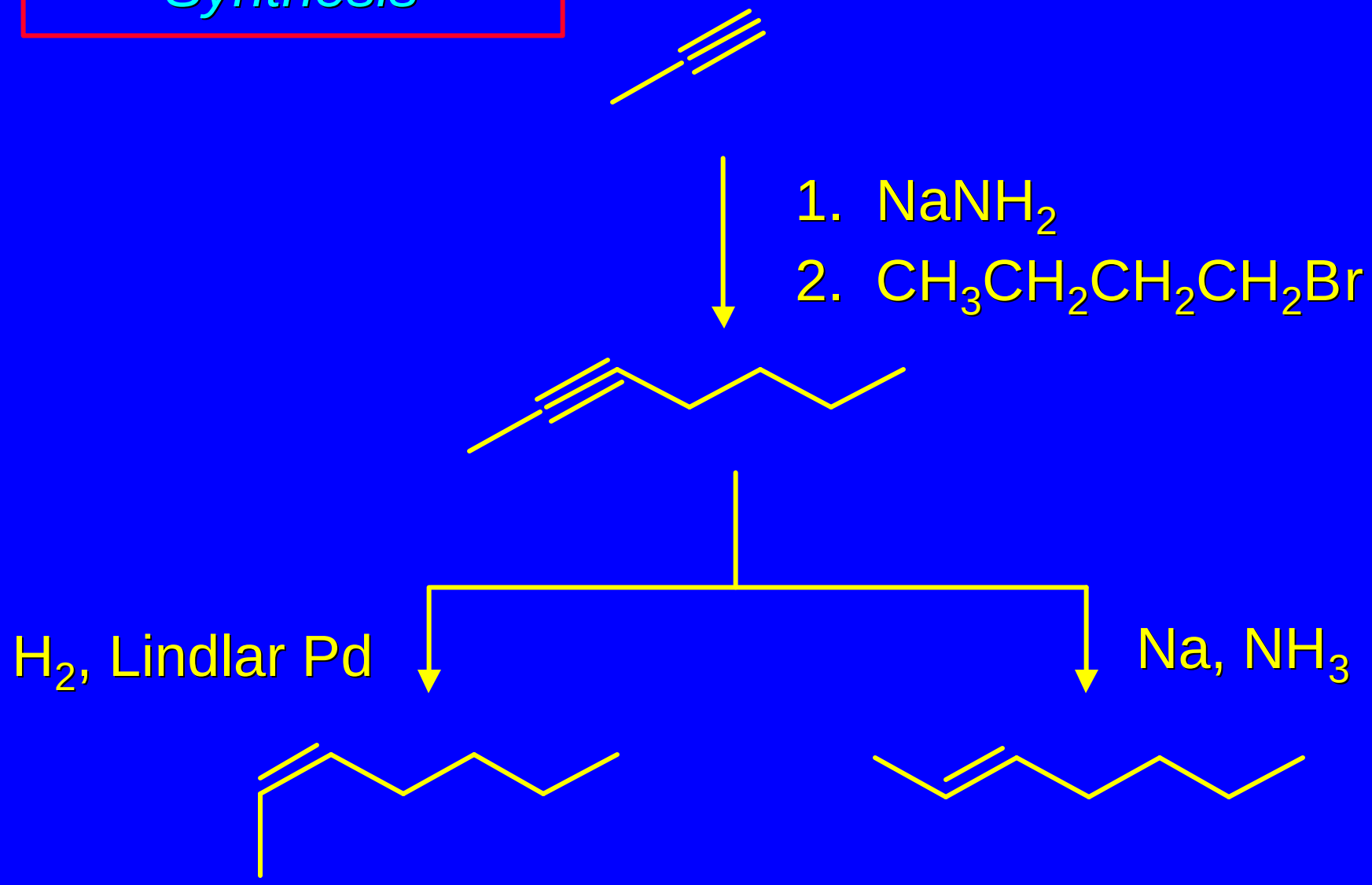
Suggest efficient syntheses of (*E*)- and (*Z*)-2-heptene from propyne and any necessary organic or inorganic reagents.

Problem 9.12
Strategy



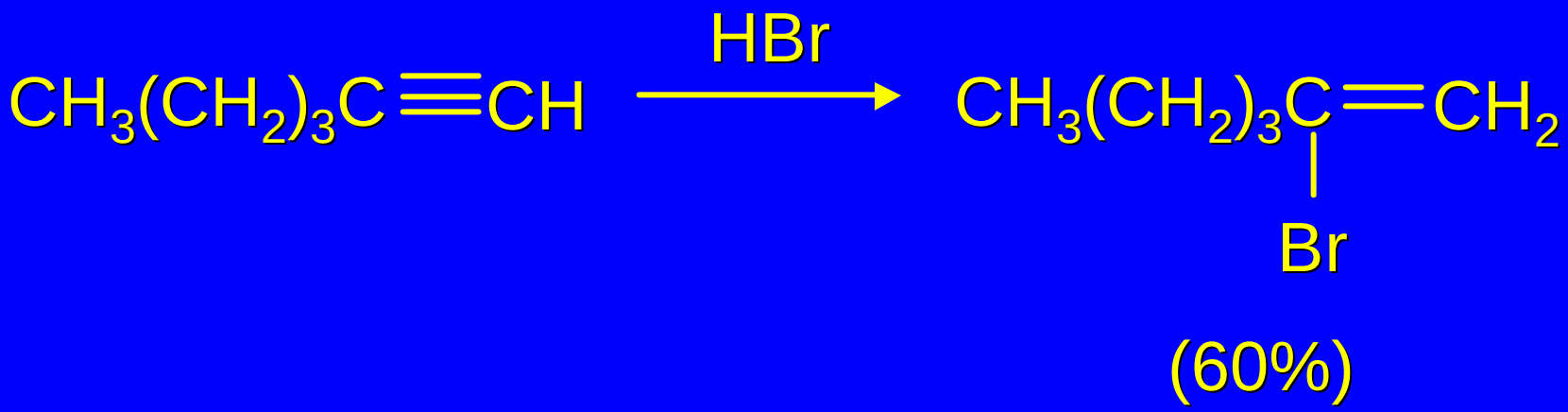
Problem 9.12

Synthesis



9.11
Addition of Hydrogen Halides to Alkynes

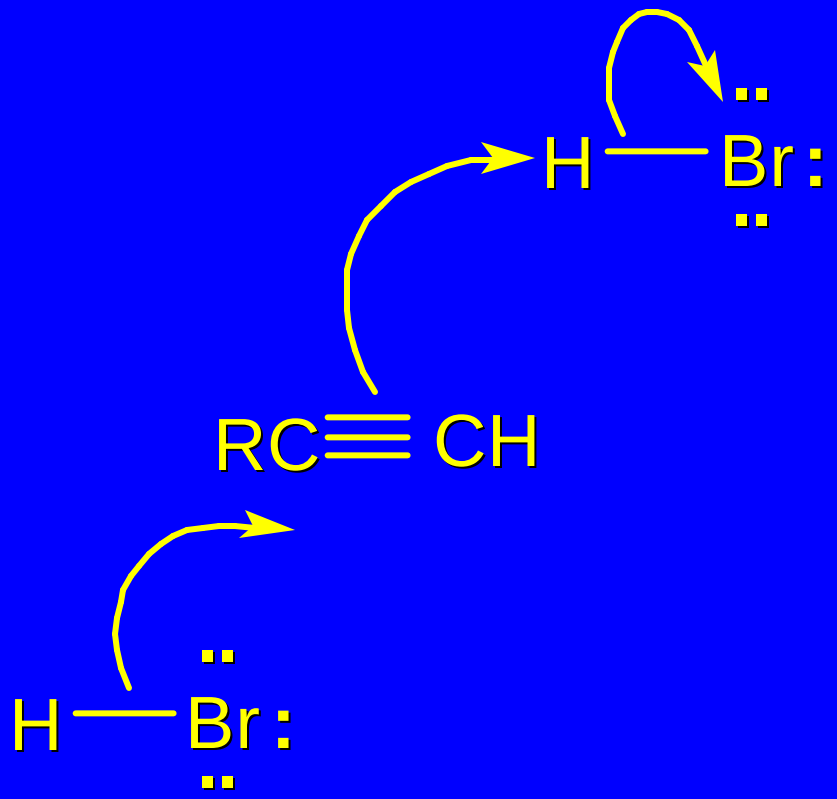
Follows Markovnikov's Rule



(60%)

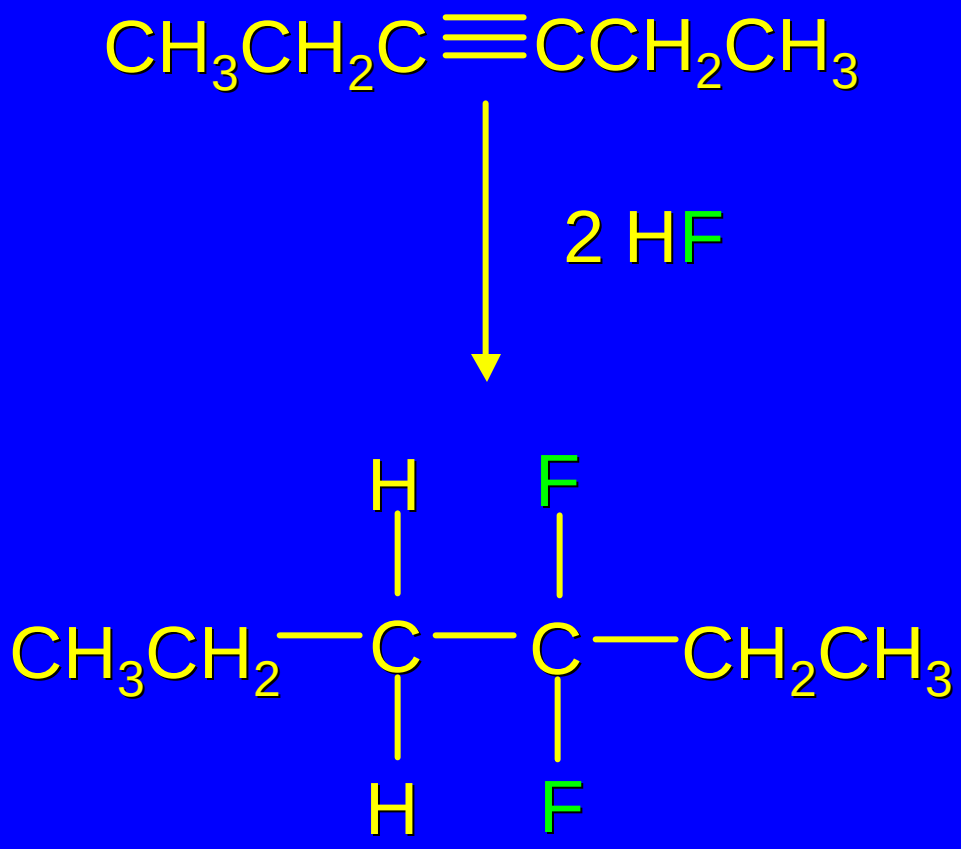
Alkynes are slightly less reactive than alkenes

Termolecular Rate-Determining Step



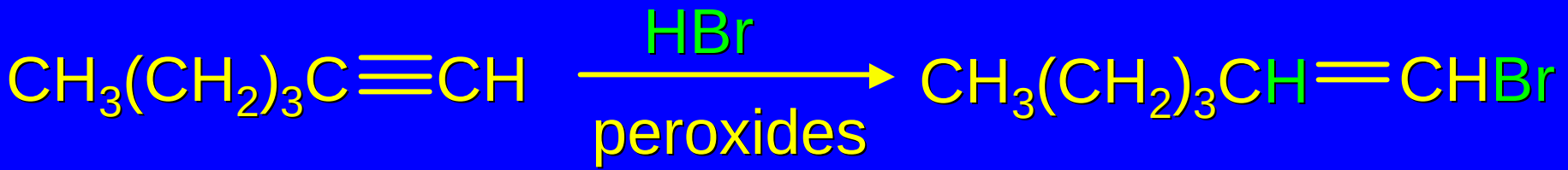
Observed rate law: rate = k[alkyne][HX]^2

Two Molar Equivalents of Hydrogen Halide



(76%)

Free-radical Addition of HBr



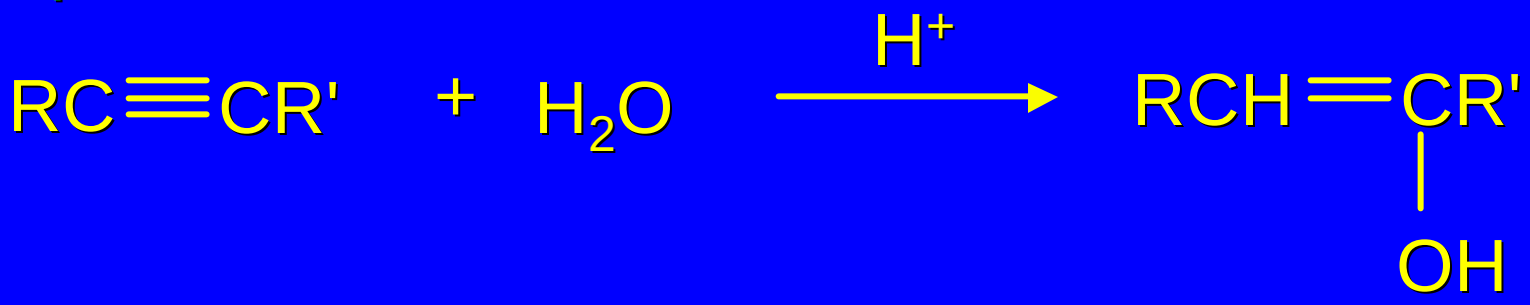
(79%)

regioselectivity opposite to Markovnikov's rule

9.12
Hydration of Alkynes

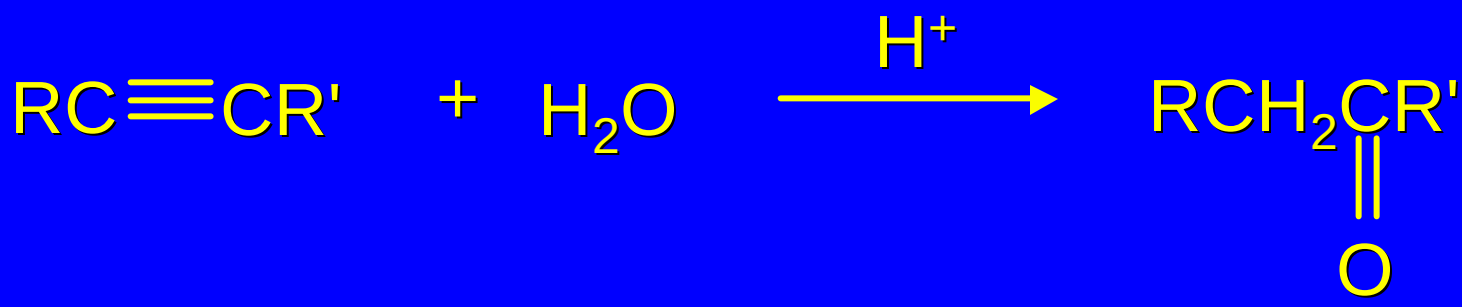
Hydration of Alkynes

expected reaction:



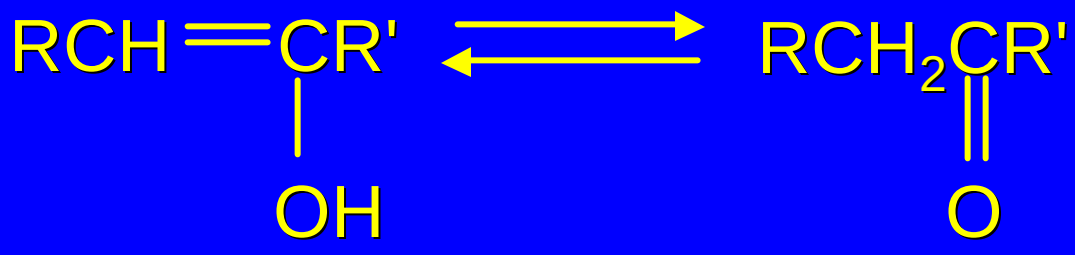
enol

observed reaction:



ketone

Enols



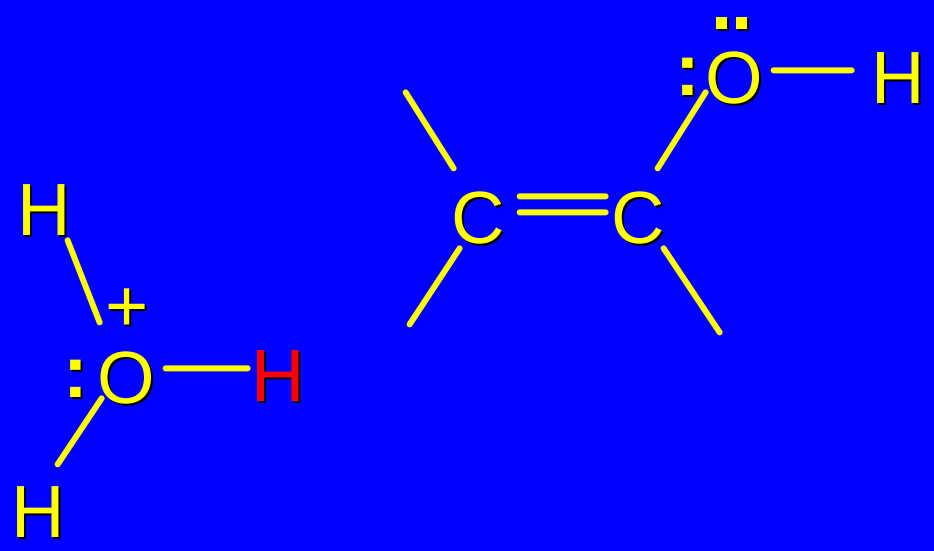
enol *ketone*

enols are regioisomers of ketones, and exist in equilibrium with them

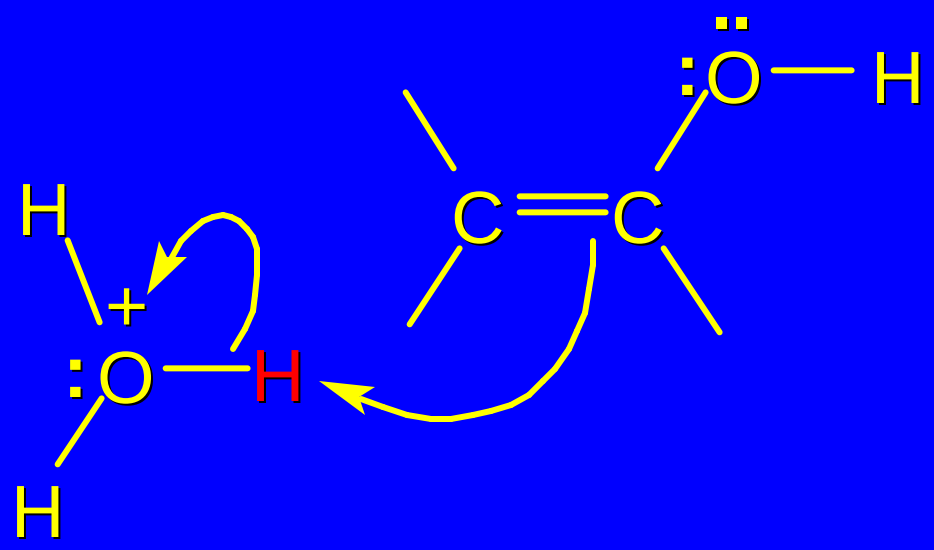
keto-enol equilibration is rapid in acidic media

ketones are more stable than enols and predominate at equilibrium

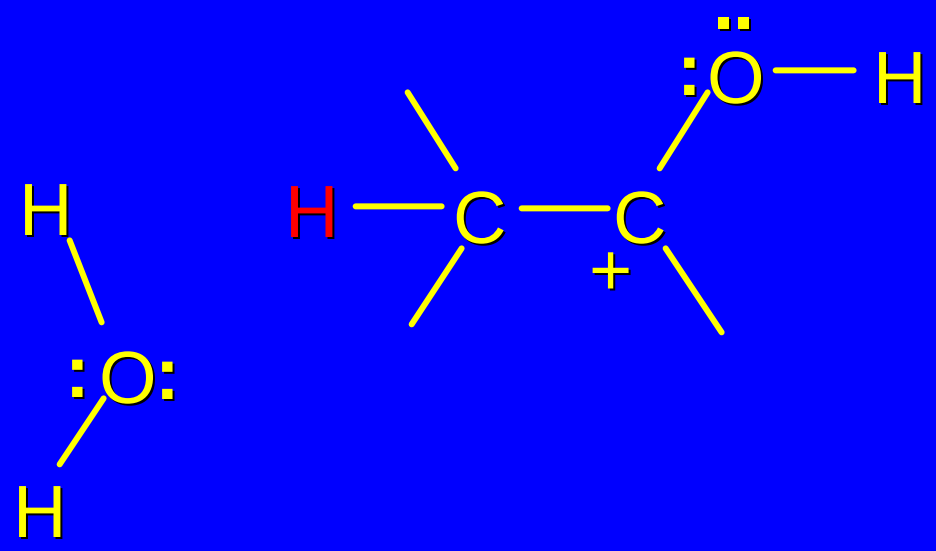
Mechanism of conversion of enol to ketone



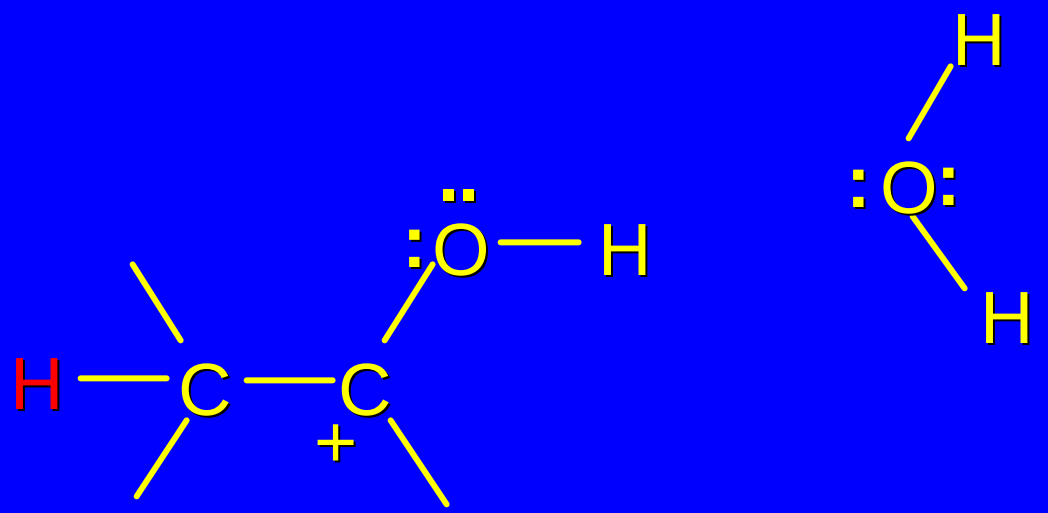
Mechanism of conversion of enol to ketone



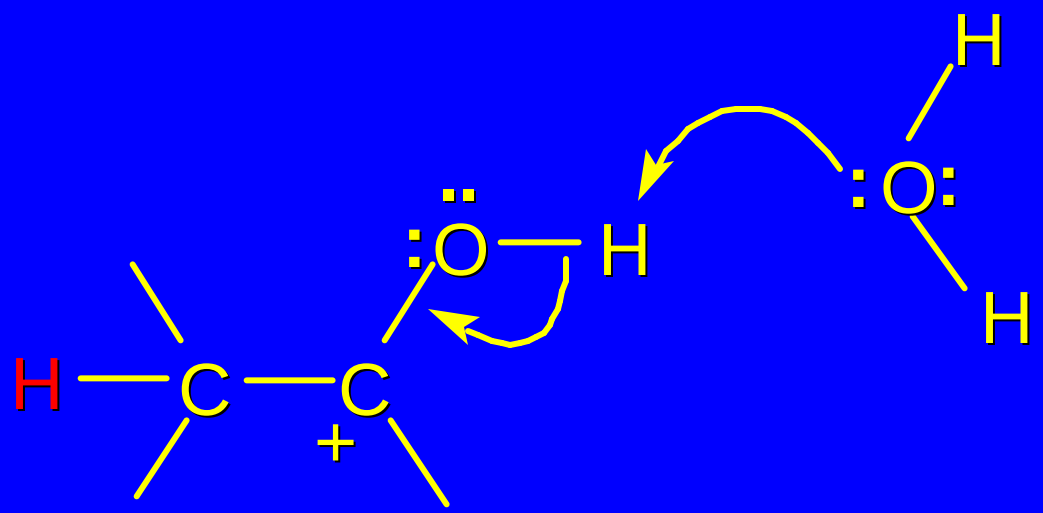
Mechanism of conversion of enol to ketone



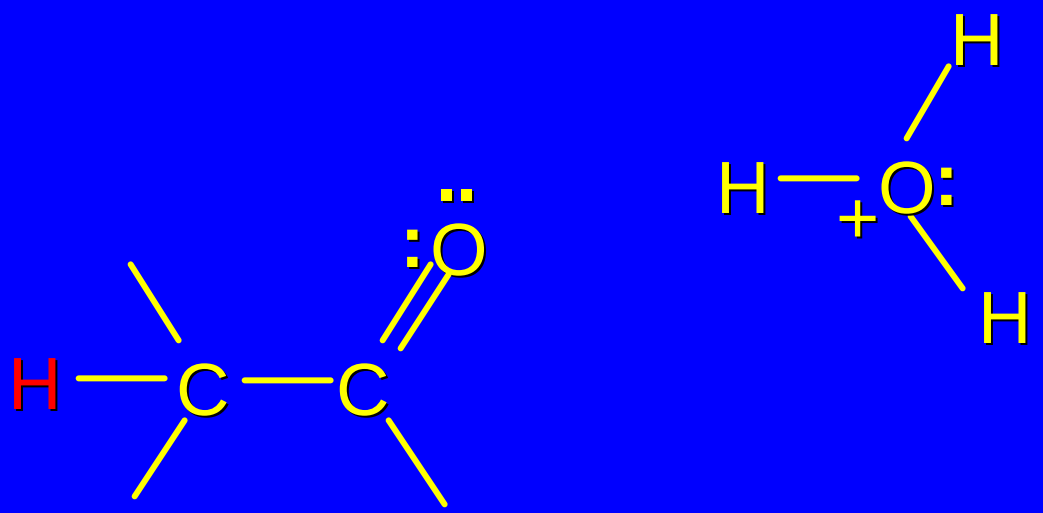
Mechanism of conversion of enol to ketone



Mechanism of conversion of enol to ketone

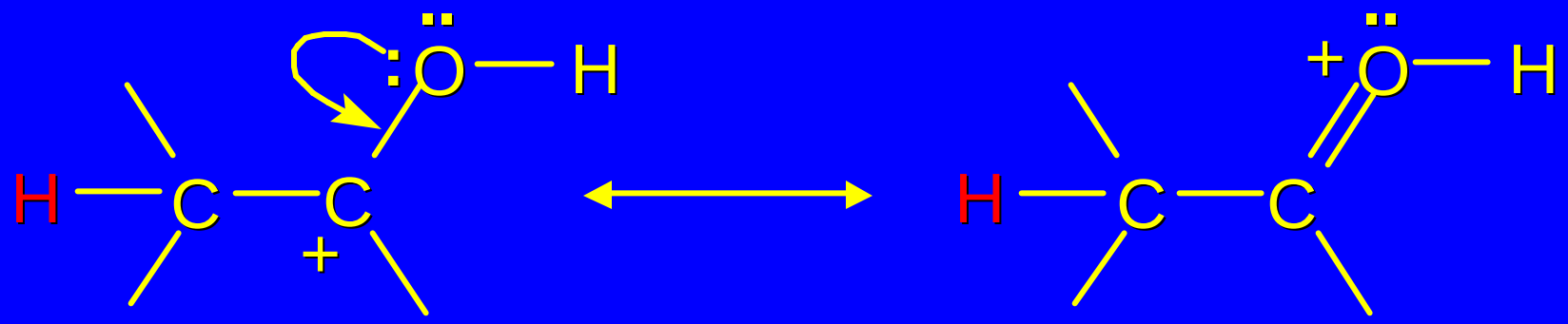


Mechanism of conversion of enol to ketone

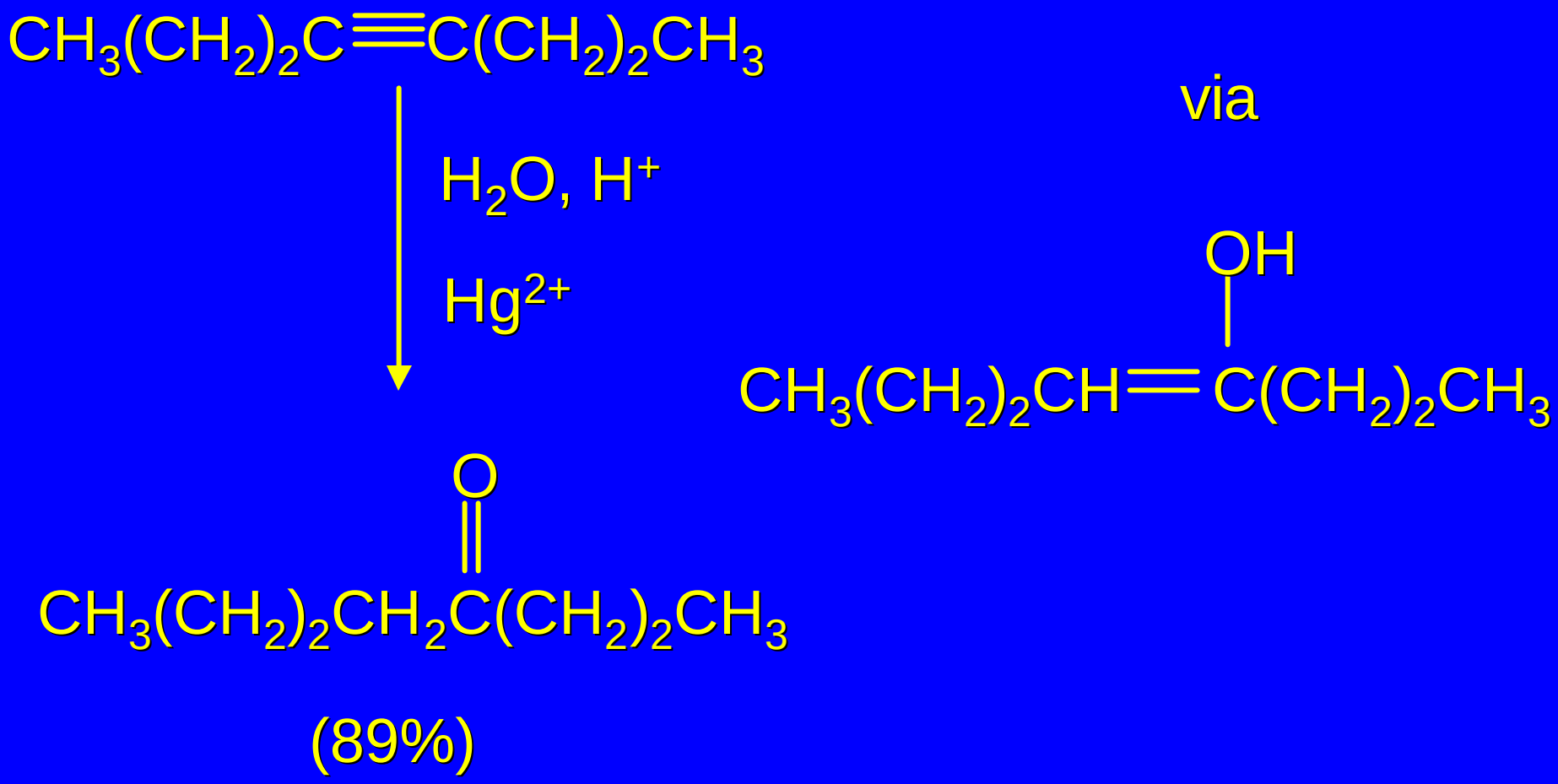


Key Carbocation Intermediate

Carbocation is stabilized by electron delocalization (resonance)

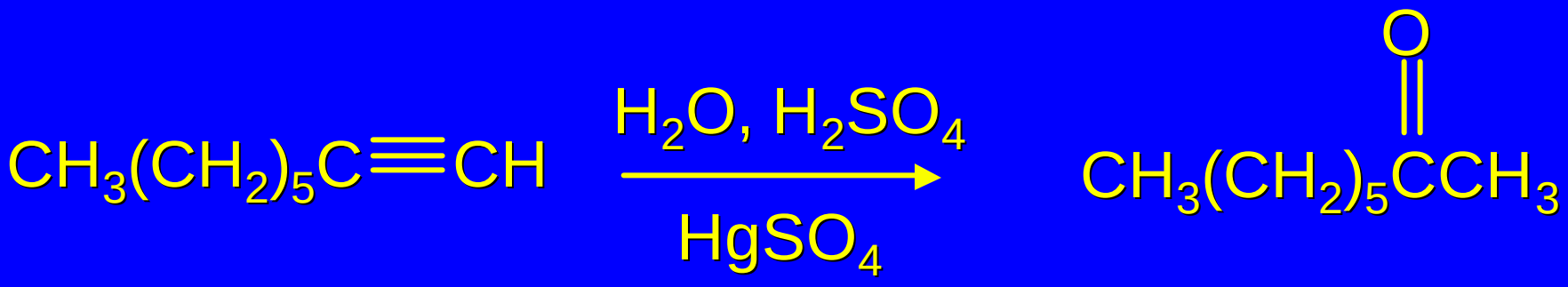


Example of Alkyne Hydration



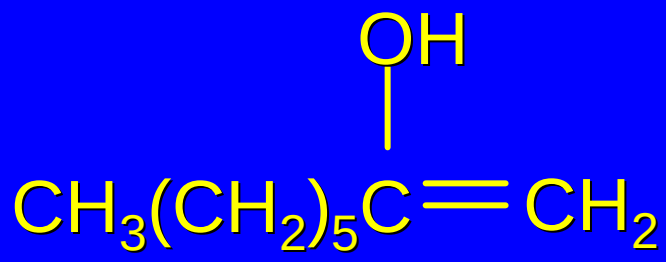
Regioselectivity

Markovnikov's rule followed in formation of enol



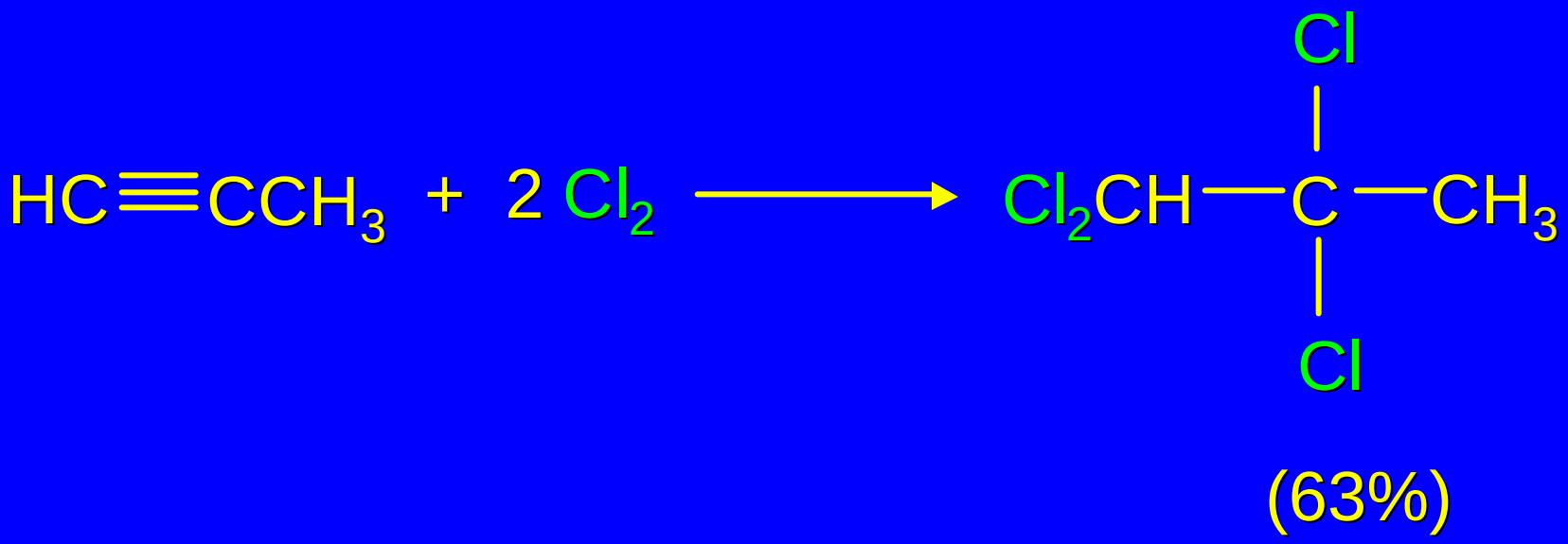
(91%)

via



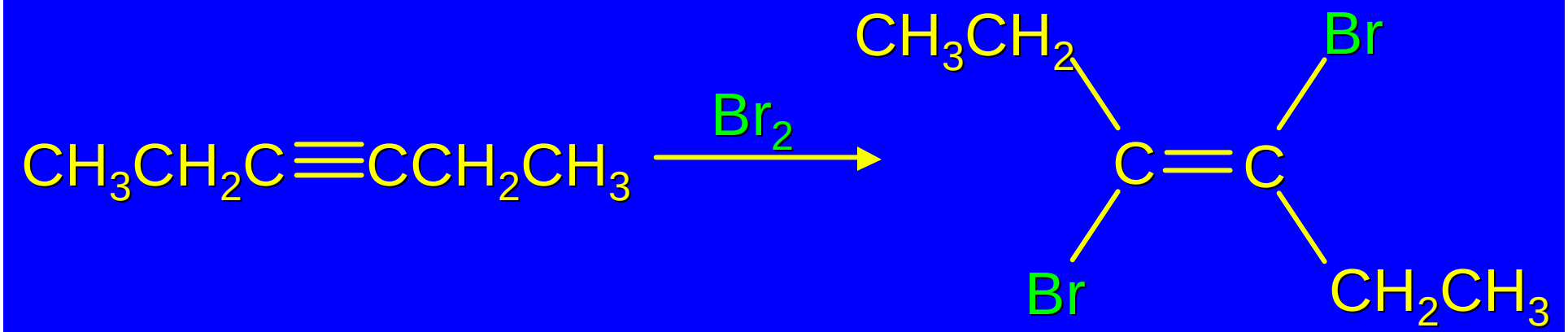
9.13
Addition of Halogens to Alkynes

Example



(63%)

Addition is anti



(90%)

9.14

Ozonolysis of Alkynes

gives two carboxylic acids by cleavage of triple bond

Example