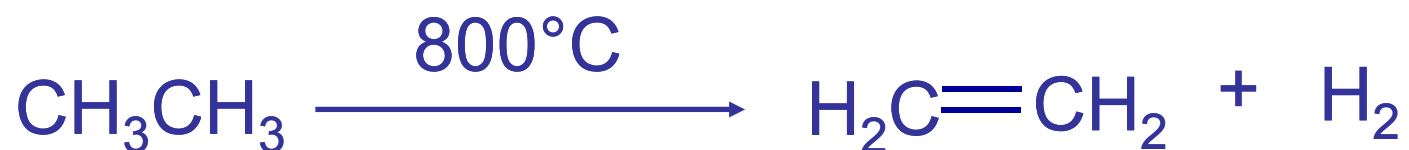


Chapter 9: Alkynes

9.1. Sources of Alkynes. Acetylene

Industrial preparation of acetylene is by dehydrogenation of ethylene



➤ Cost of energy makes acetylene a more expensive industrial chemical than ethylene.

9.2. Nomenclature

➤ Acetylene and ethyne are both acceptable IUPAC names for $\text{HC}\equiv\text{CH}$

➤ Higher alkynes are named in much the same way as alkenes except using an *-yne* suffix instead of *-ene*.



Propyne



1-Butyne



4,4-Dimethyl-2-pentyne

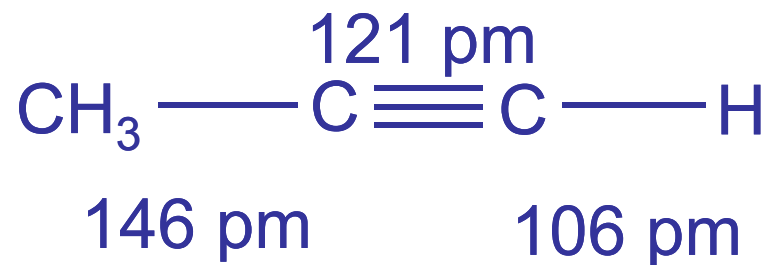
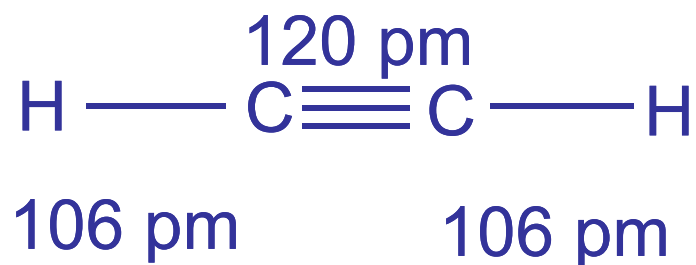
9.3

Physical Properties of Alkynes

The physical properties of alkynes are similar to those of alkanes and alkenes.

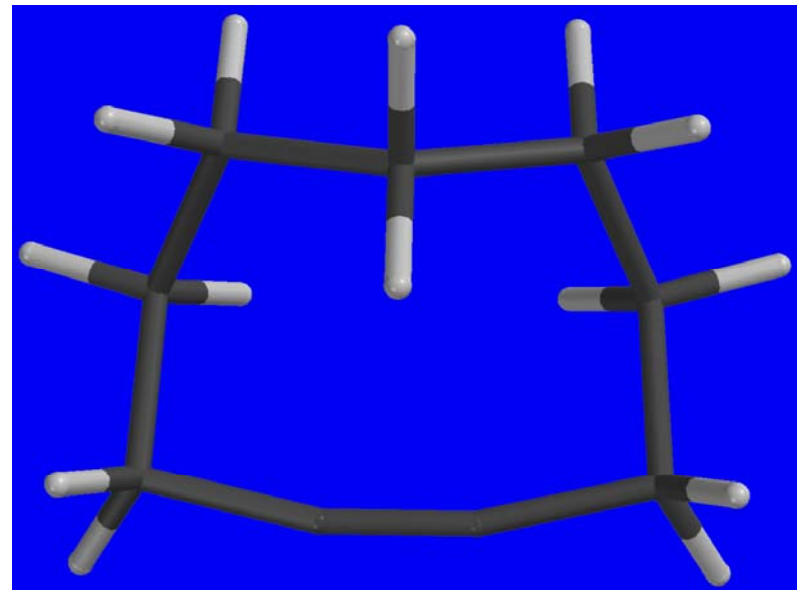
9.4. Structure and Bonding in Alkynes: *sp* Hybridization

Linear geometry for acetylene



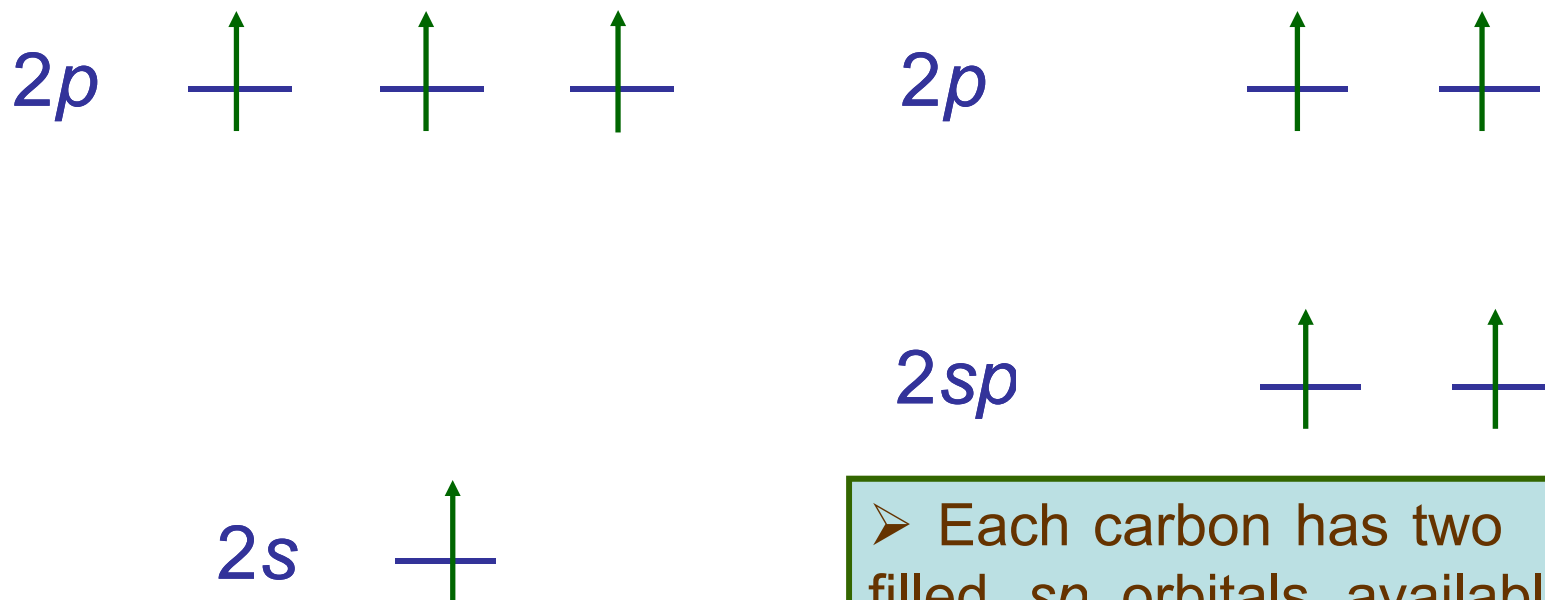
Cyclic Alkynes

- Cyclononyne is the smallest cycloalkyne stable enough to be stored at room temperature for a reasonable length of time.
- Cyclooctyne polymerizes on standing.



Bonding in acetylene is based on sp -hybridization for each carbon

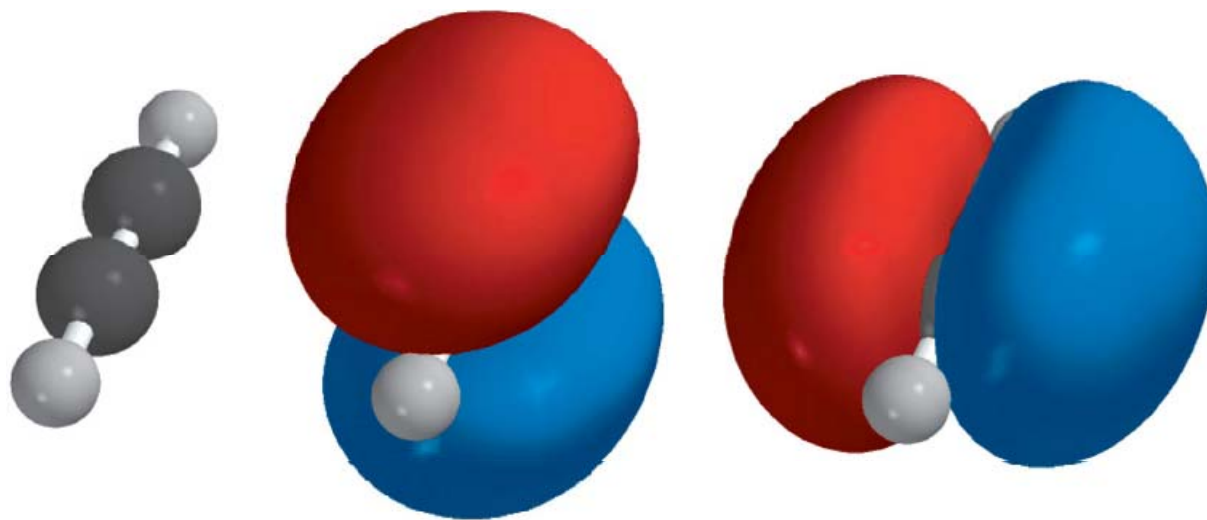
Mix together (hybridize) the 2s orbital and **one** of the three 2p orbitals



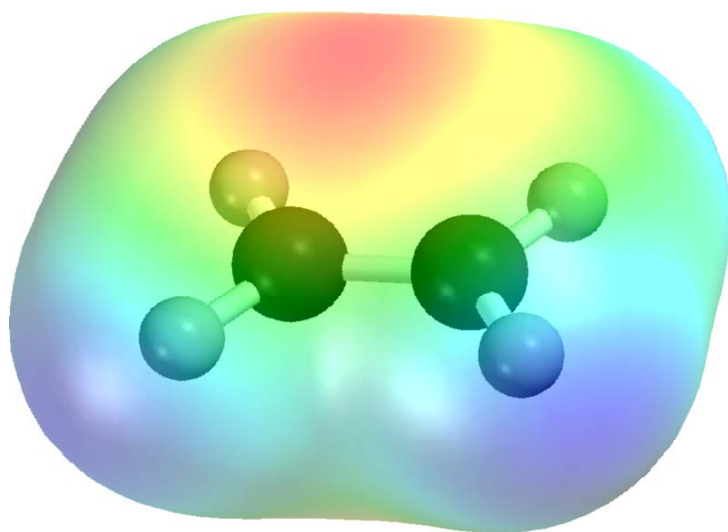
➤ Each carbon has two half-filled sp orbitals available to form σ bonds.

σ and π Bonds in Acetylene

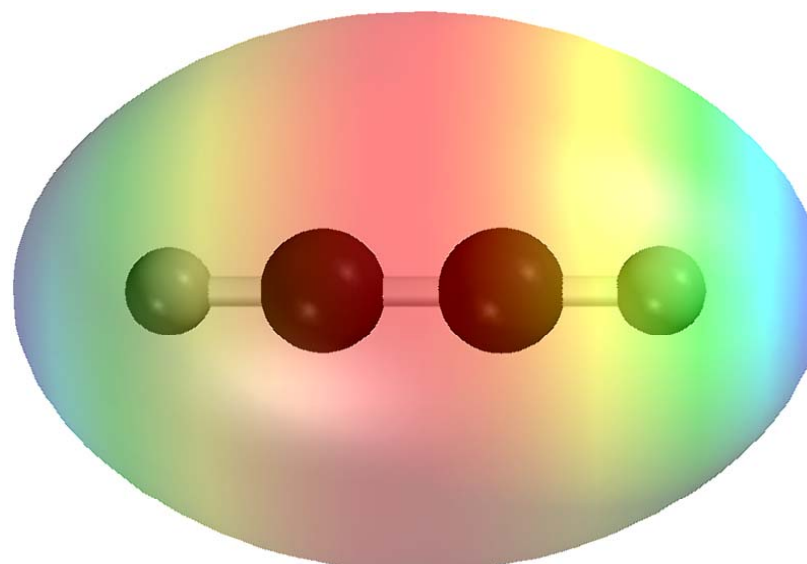
- Each carbon is connected to a hydrogen by a σ bond. The two carbons are connected to each other by a σ bond and two π bonds.



Two π bonds in acetylene at right angles to each other.



➤ The region of highest negative charge lies above and below the molecular plane in ethylene.

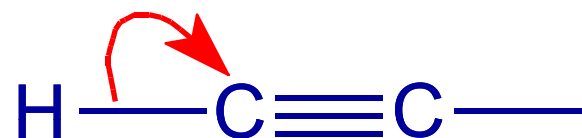


➤ The region of highest negative charge encircles the molecule around its center in acetylene.

Table 9.1. Comparison of ethane, ethylene, and acetylene

	Ethane	Ethylene	Acetylene
C—C distance	153 pm	134 pm	120 pm
C—H distance	111 pm	110 pm	106 pm
H—C—C angles	111.0°	121.4°	180°
C—C BDE	368 kJ/mol	611 kJ/mol	820 kJ/mol
C—H BDE	410 kJ/mol	452 kJ/mol	536 kJ/mol
Hybridization of C	sp^3	sp^2	sp
% s character	25%	33%	50%
pK_a	62	45	26

9.5. Acidity of Acetylene and Terminal Alkynes

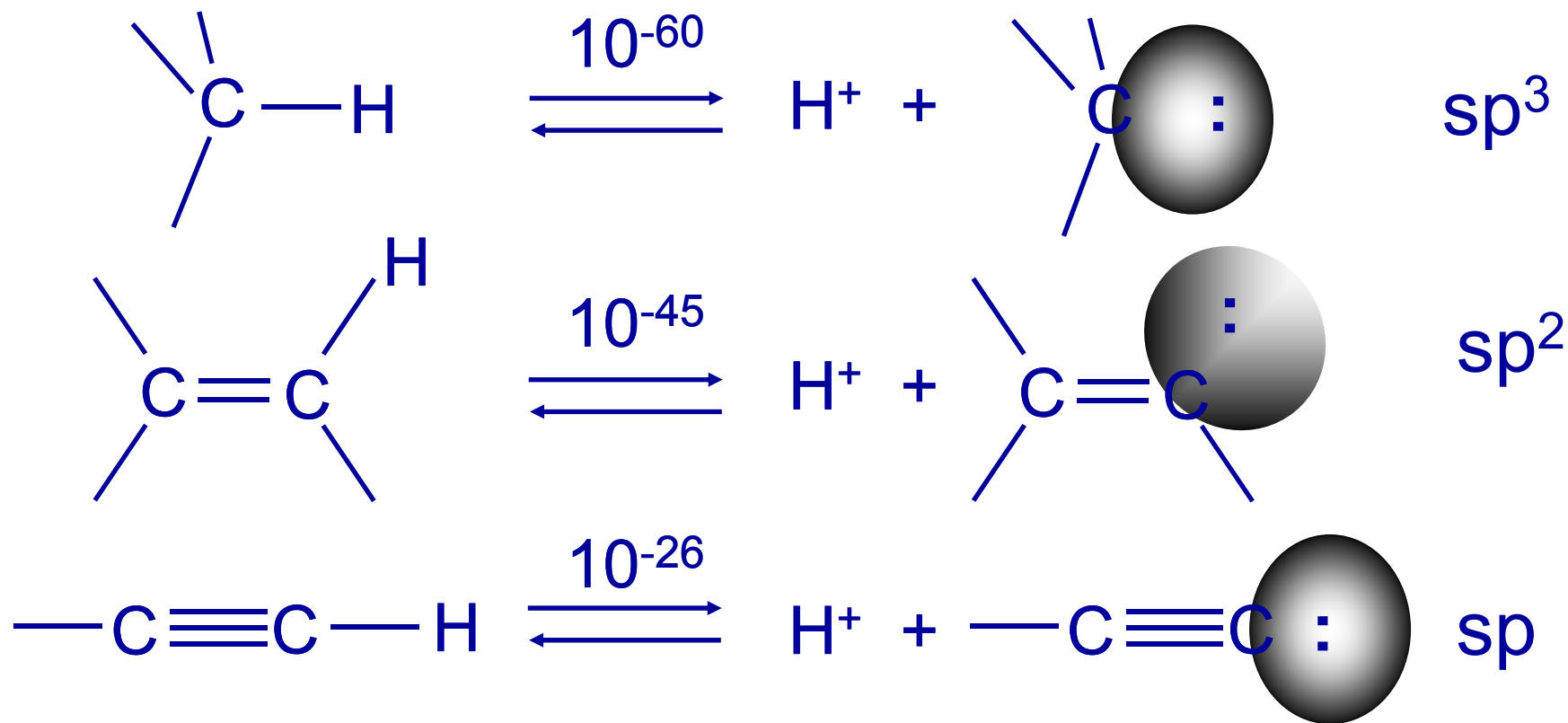


In general, hydrocarbons are exceedingly weak acids

	Compound	pK_a
	HF	3.2
	H ₂ O	16
HC≡CH	-----	----- 26
	NH ₃	36
	H ₂ C=CH ₂	45
	CH ₄	60

Acetylene is a weak acid, but not nearly as weak as alkanes or alkenes.

Electronegativity of carbon increases with its s character



Electrons in an orbital with more s character are closer to the nucleus and more strongly held.

Objective:

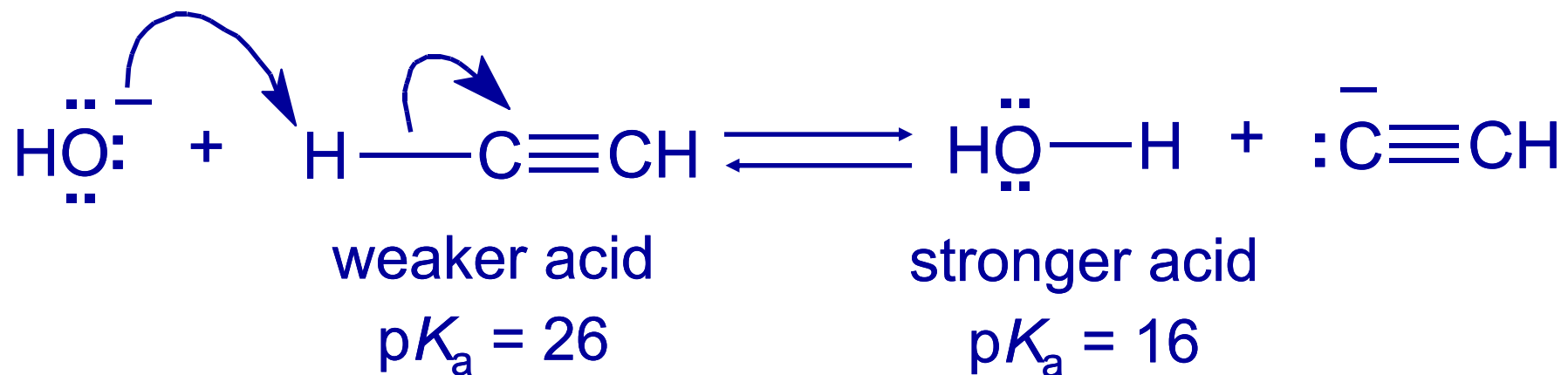
Prepare a solution containing sodium acetylide.



Will treatment of acetylene with NaOH be effective?

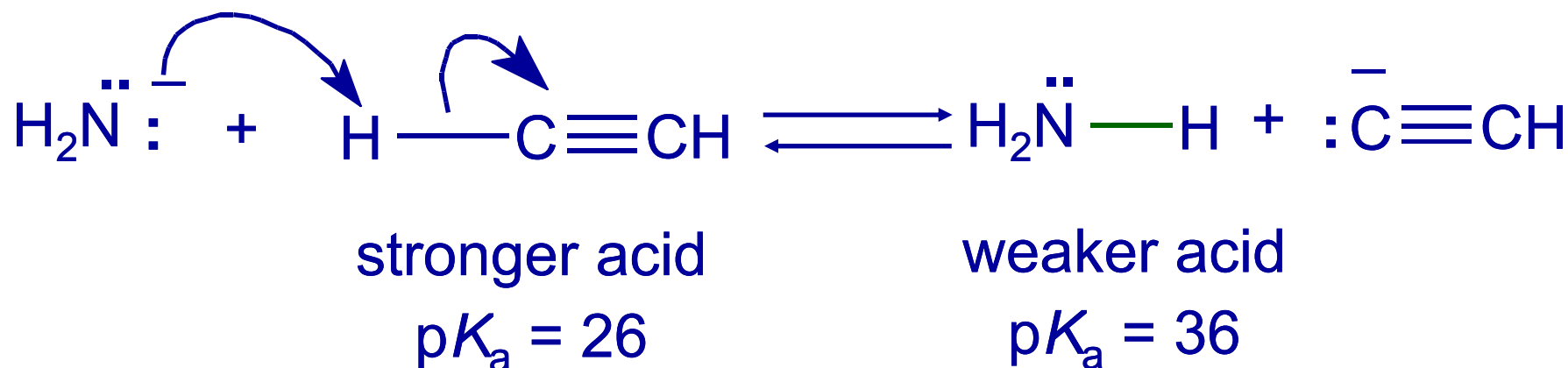


No! Hydroxide is not a strong enough base to deprotonate acetylene.



In acid-base reactions, the equilibrium lies to the side of the weaker acid.

Solution: Use a stronger base. Sodium amide is a stronger base than sodium hydroxide.



Ammonia is a weaker acid than acetylene.
The position of equilibrium lies to the right.

9.6. Preparation of Alkynes by Alkylation of Acetylene and Terminal Alkynes

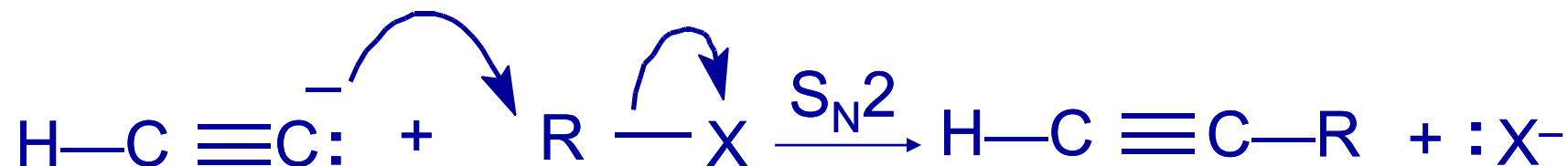
There are two main methods for the preparation of alkynes:

- Carbon-carbon bond formation:
alkylation of acetylene and terminal alkynes
- Functional-group transformations:
elimination

Alkylation of acetylene and terminal alkynes

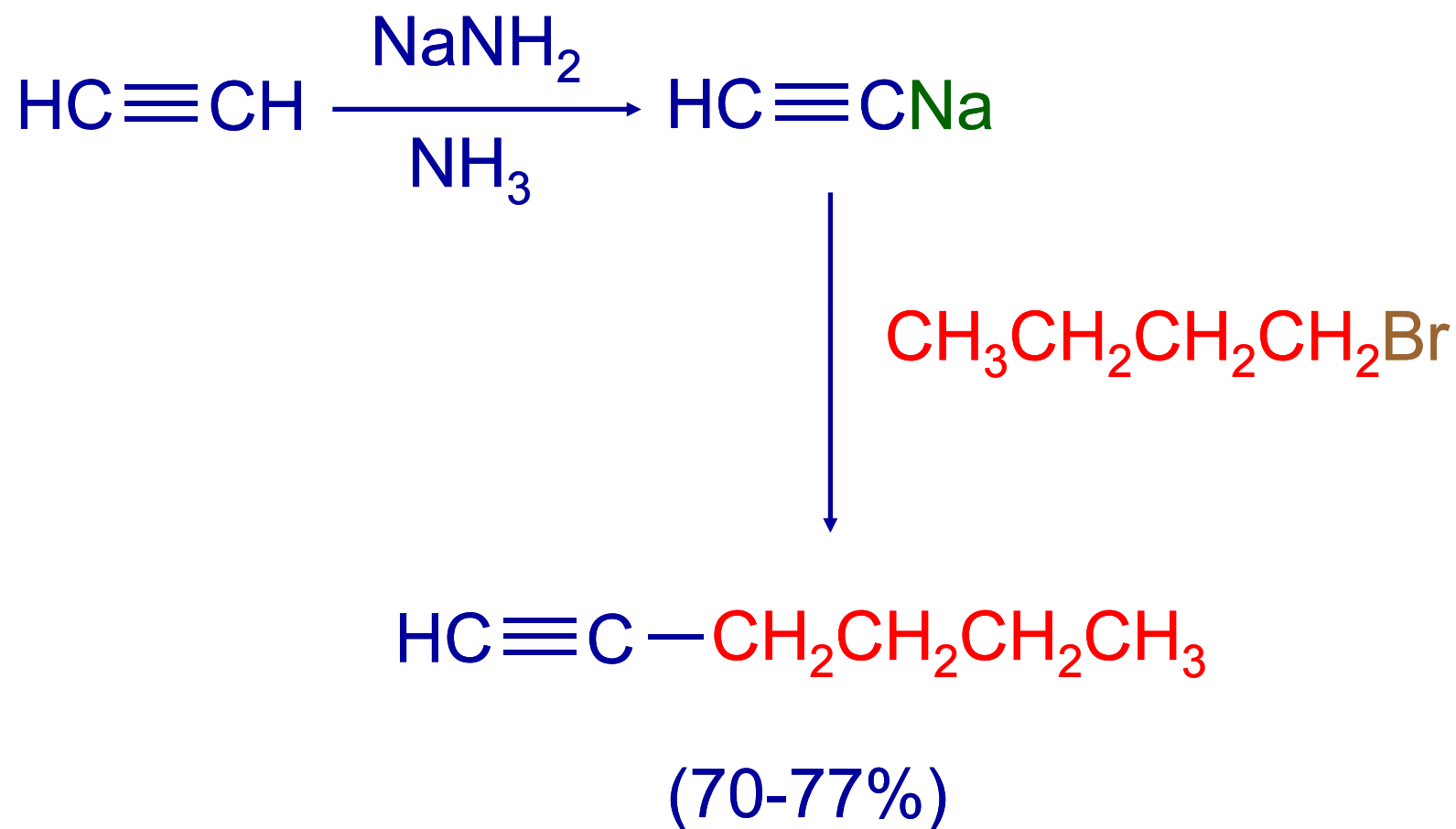


Alkylation of acetylene and terminal alkynes

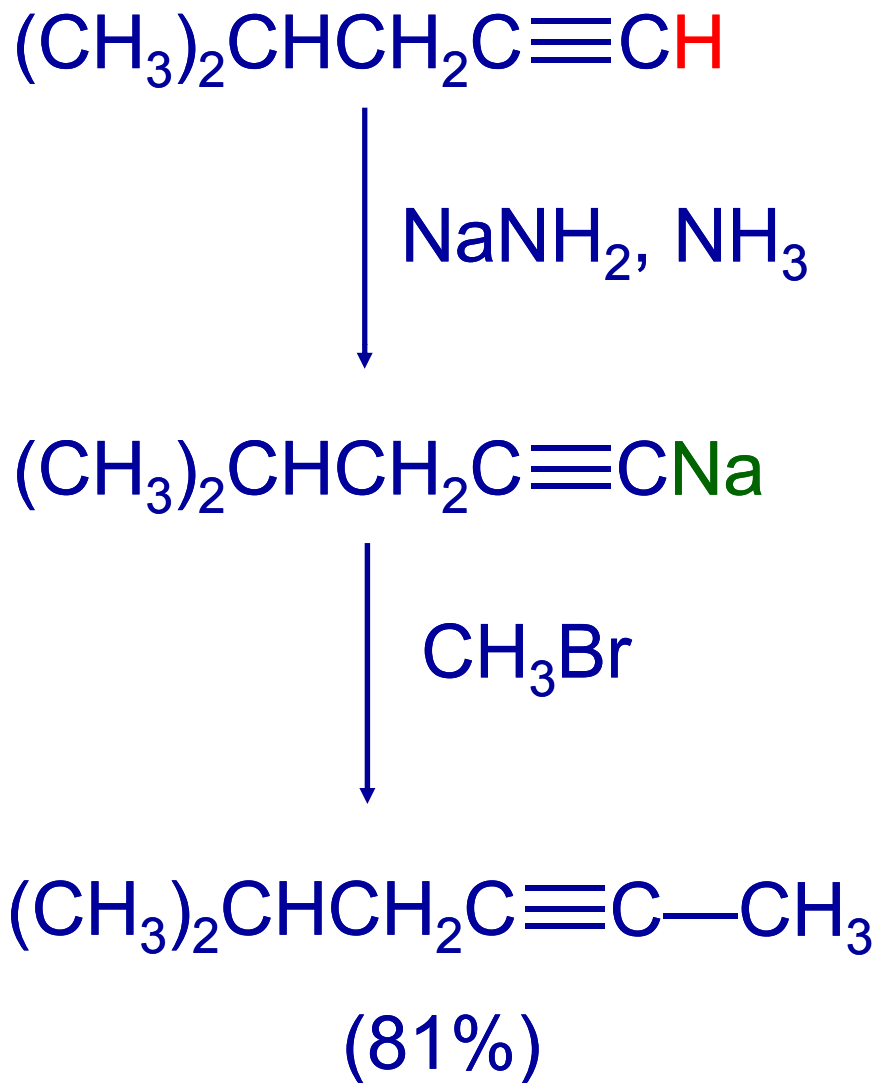


- The alkylating agent is an alkyl halide, and the reaction is nucleophilic substitution.
- The nucleophile is sodium acetylide or the sodium salt of a terminal (monosubstituted) alkyne.

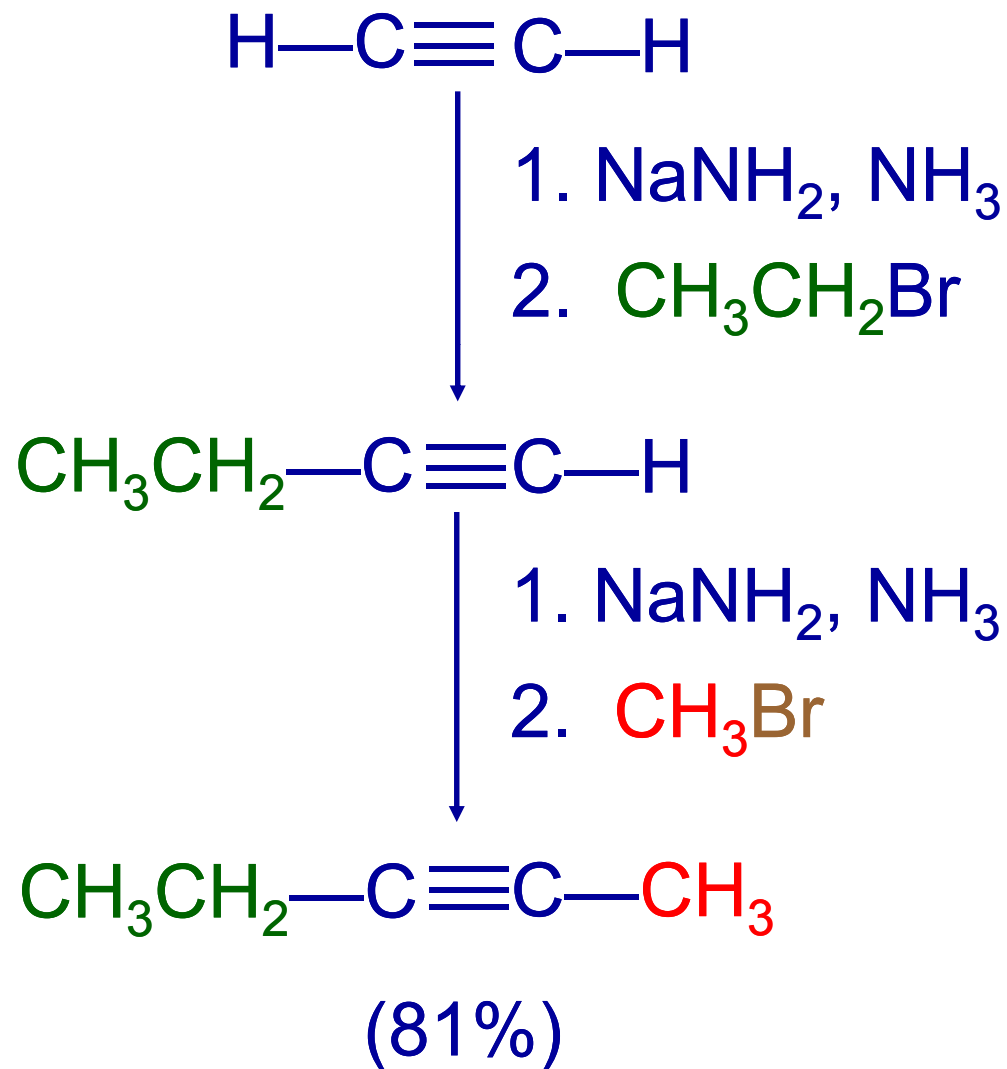
Example: Alkylation of acetylene



Example: Alkylation of a terminal alkyne



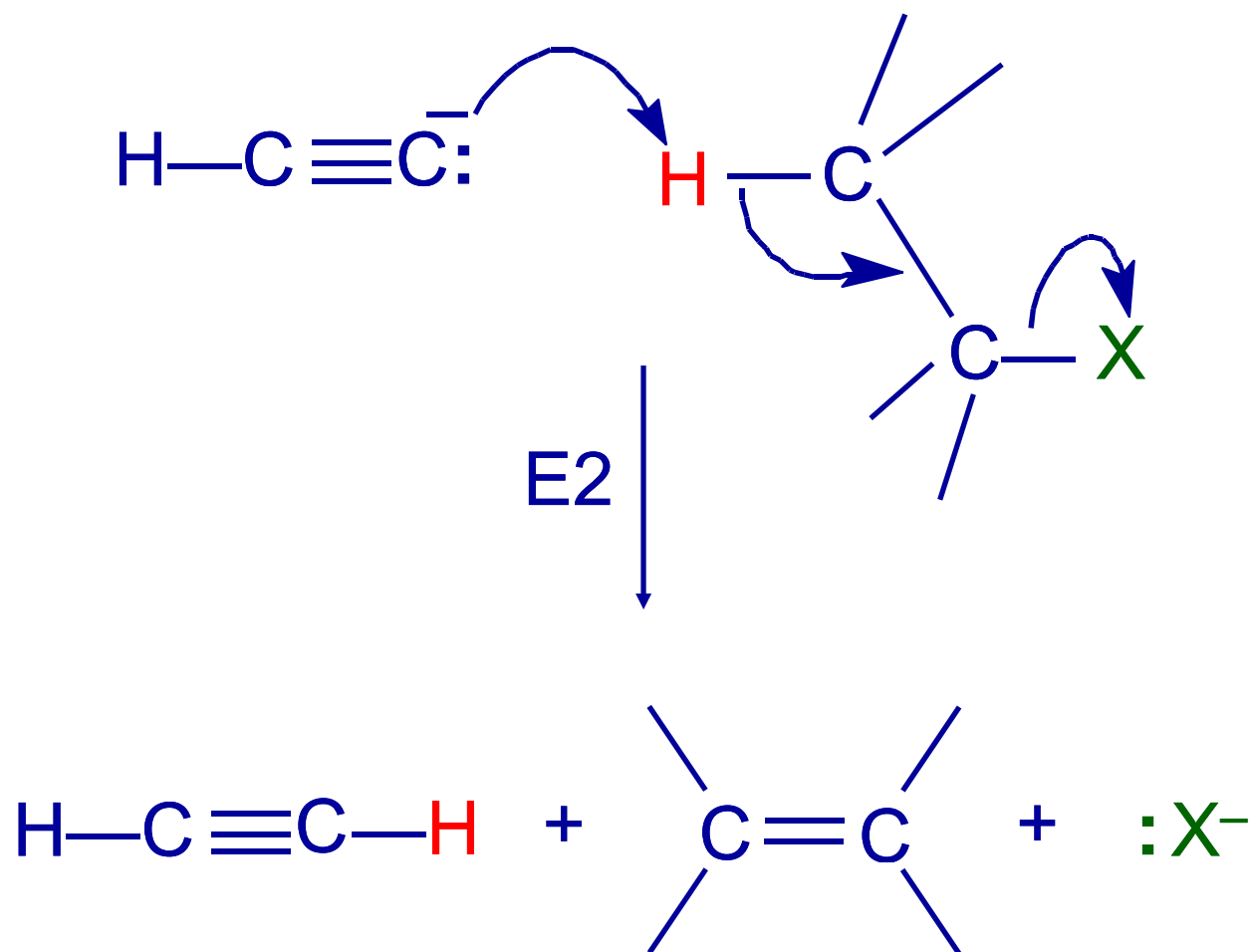
Example: Dialkylation of acetylene



➤ **LIMITATION!**

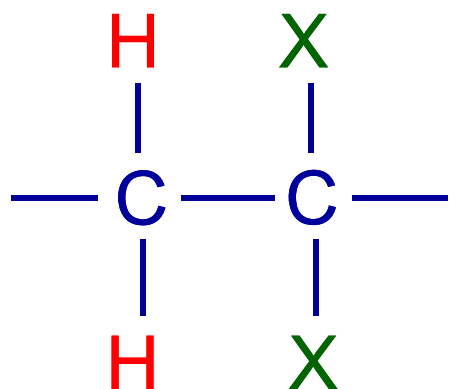
Effective only with primary alkyl halides. *Secondary and tertiary alkyl halides undergo elimination.*

E2 predominates over S_N2 when alkyl halide is secondary or tertiary

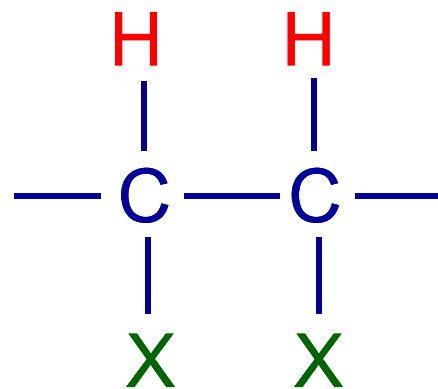


9.7. Preparation of Alkynes by Elimination Reactions

Double Dehydrohalogenation



Geminal dihalide



Vicinal dihalide

The most frequent applications are in preparation of terminal alkynes.

Geminal dihalide \rightarrow Alkyne



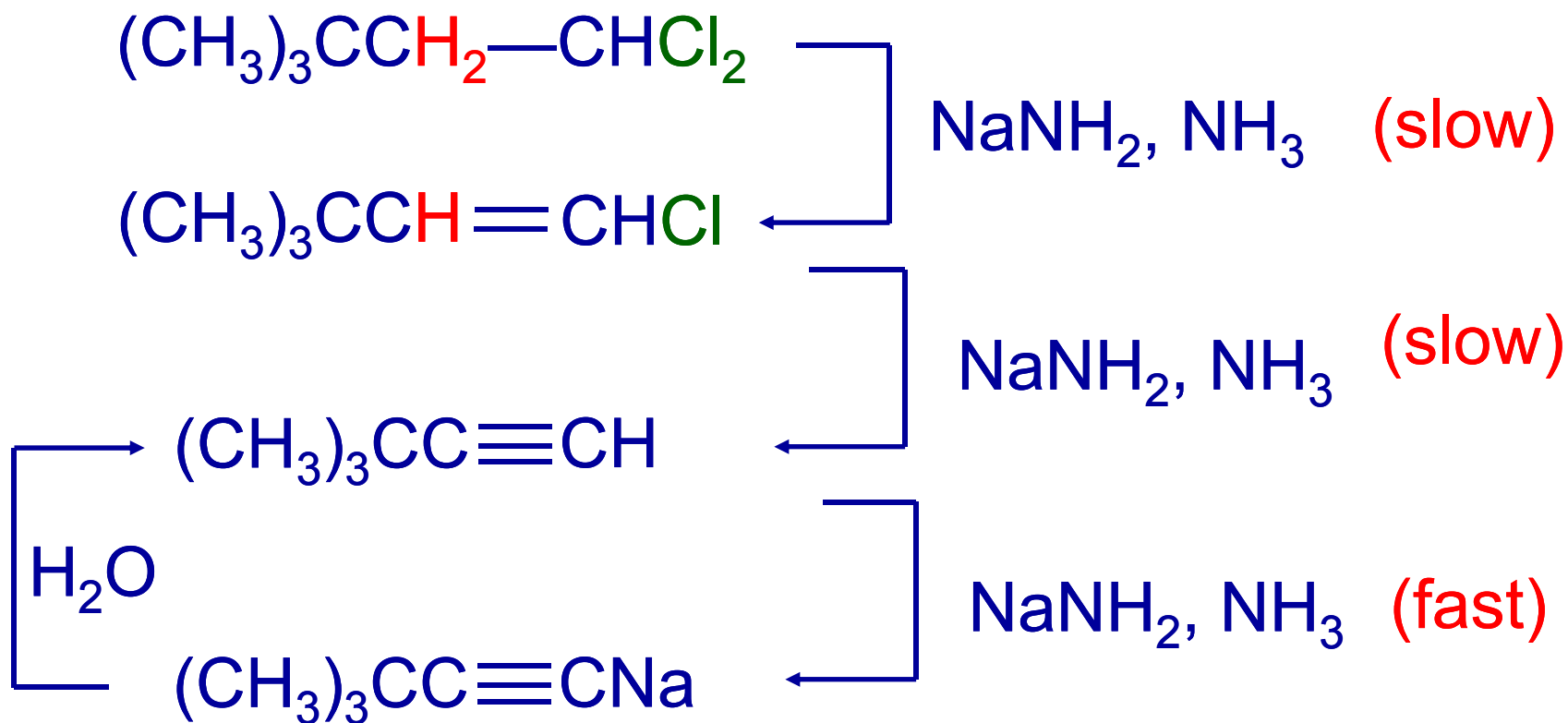
1. $3\text{NaNH}_2, \text{NH}_3$

2. H_2O

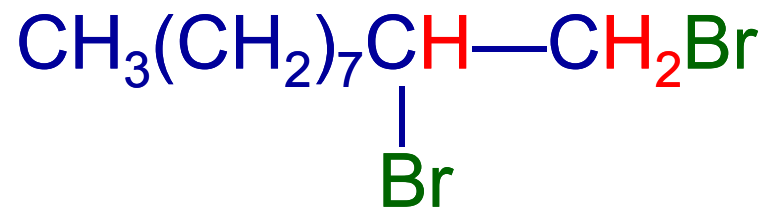


(56-60%)

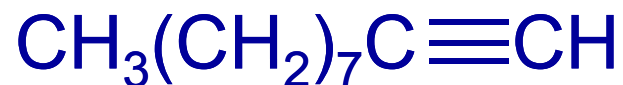
Geminal dihalide \rightarrow Alkyne



Vicinal dihalide \rightarrow Alkyne

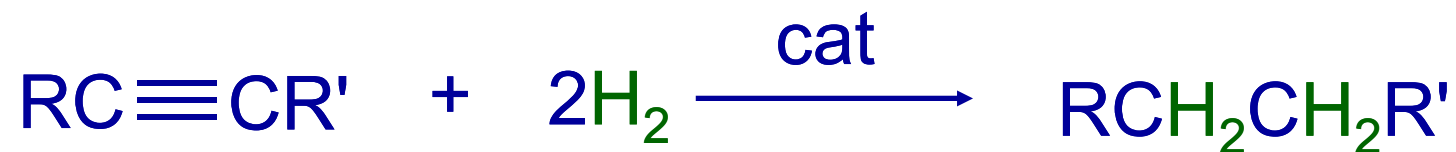


1. $3\text{NaNH}_2, \text{NH}_3$
2. H_2O



(54%)

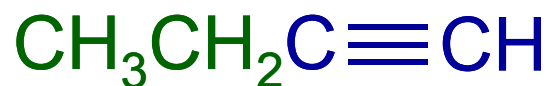
9.9. Hydrogenation of Alkynes



catalyst = Pt, Pd, Ni, or Rh

alkene is an intermediate

Heats of Hydrogenation



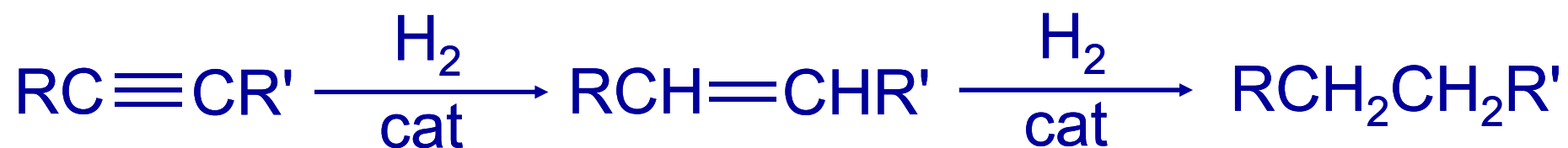
292 kJ/mol



275 kJ/mol

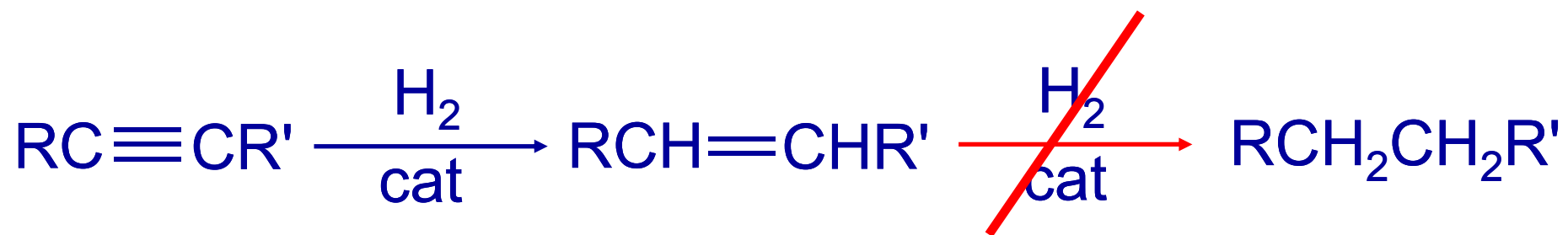
- Alkyl groups stabilize triple bonds in the same way that they stabilize double bonds. Internal triple bonds are more stable than terminal ones.

Partial Hydrogenation



- Alkynes 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



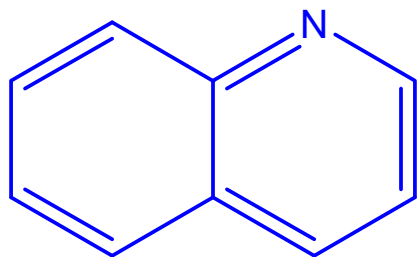
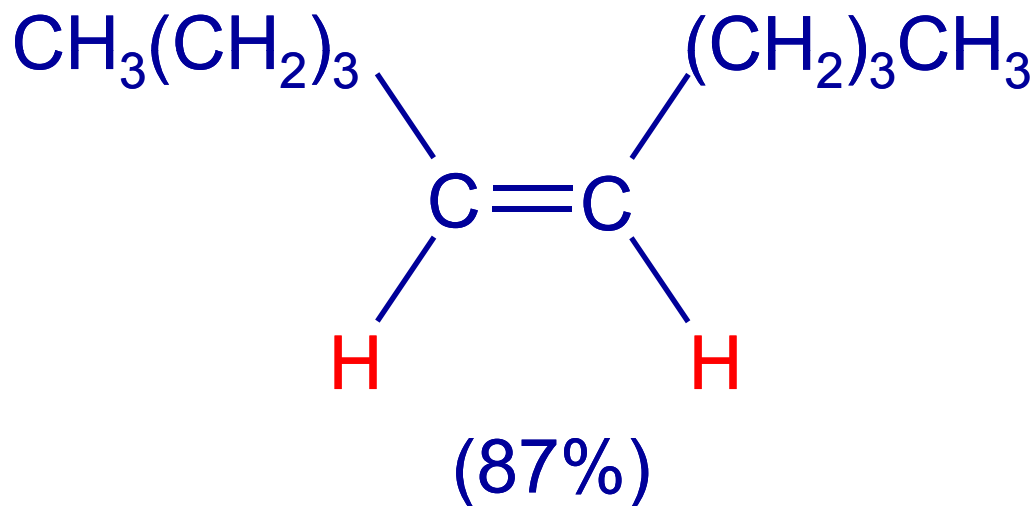
➤ There is a catalyst that will catalyze the hydrogenation of alkynes to alkenes, but not that of alkenes to alkanes. It is called the **Lindlar catalyst** and consists of palladium supported on CaCO_3 , which has been poisoned with lead acetate and quinoline.

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



Lindlar Pd

➤ Lindlar Pd: Pd on CaCO_3 ; $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ and quinoline added to it.

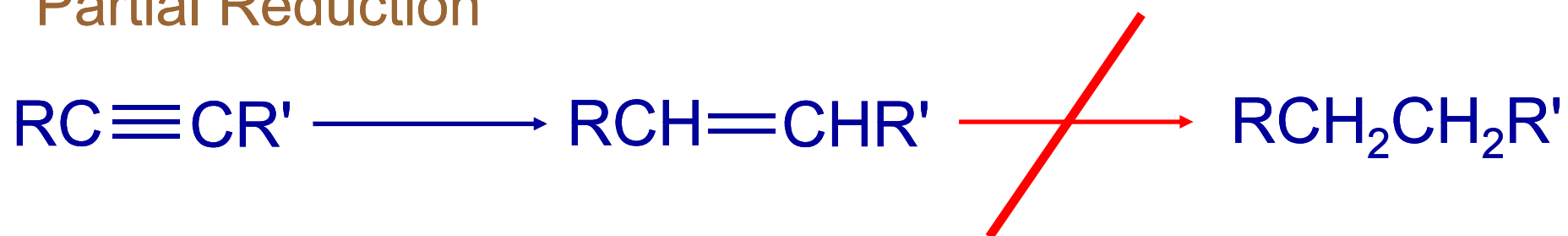


Quinoline

9.10. Metal-Ammonia Reduction of Alkynes

Alkynes \rightarrow *trans*-Alkenes

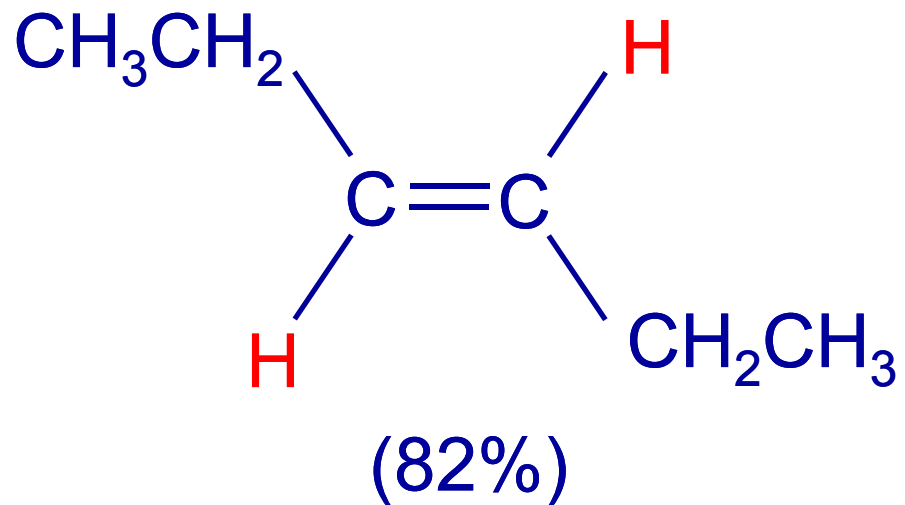
Partial Reduction



➤ Another way to convert alkynes to alkenes is by reduction with sodium (or lithium or potassium) in ammonia.

trans-Alkenes are formed.

Example



Mechanism

➤ Metal (Li, Na, K) is reducing agent; H₂ is not involved.

Four steps:

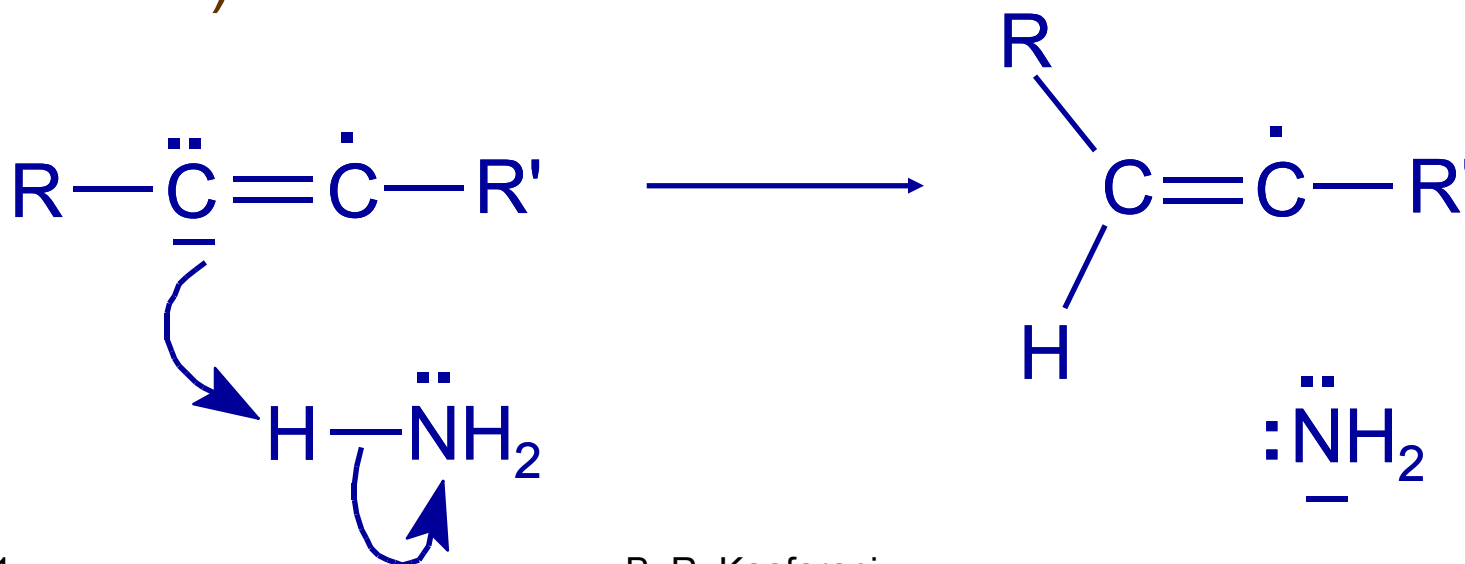
- (1) Electron transfer
- (2) Proton transfer
- (3) Electron transfer
- (4) Proton transfer

Mechanism

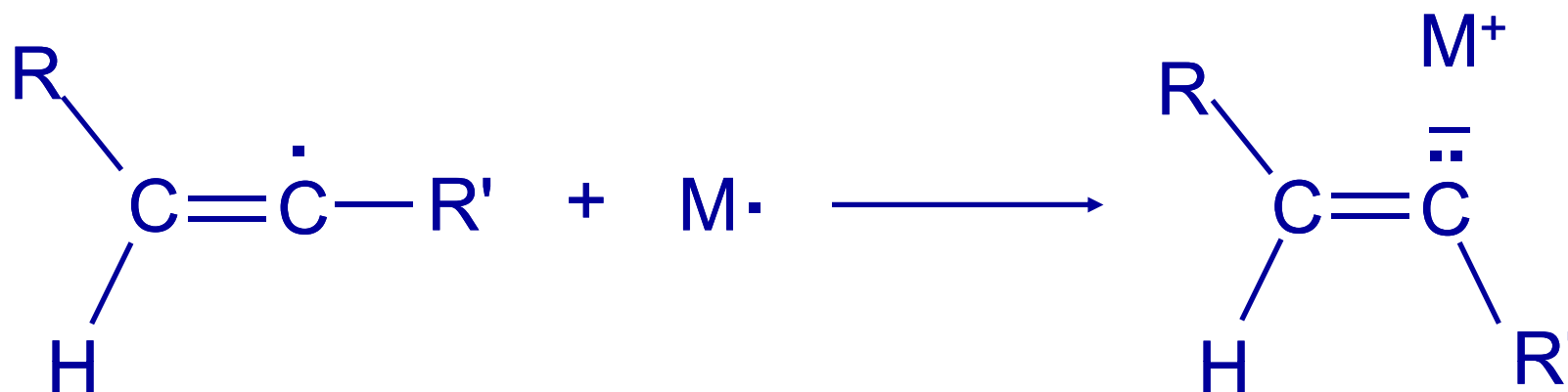
Step (1): Transfer of an electron from the metal to the alkyne to give an anion radical.



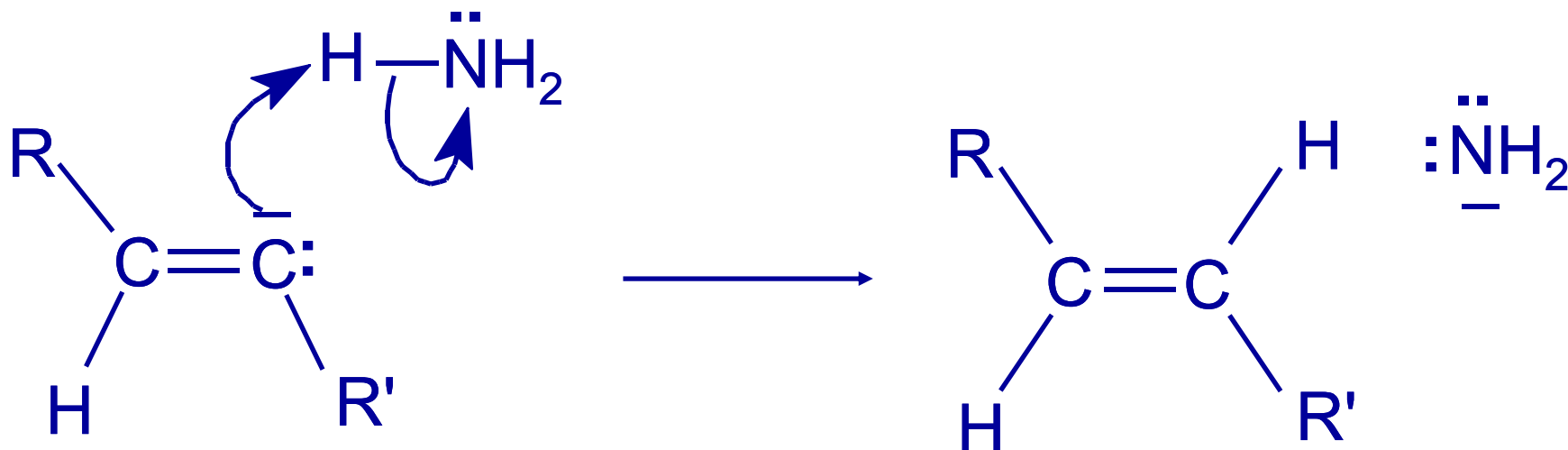
Step (2) Transfer of a proton from the solvent (liquid ammonia) to the anion radical.



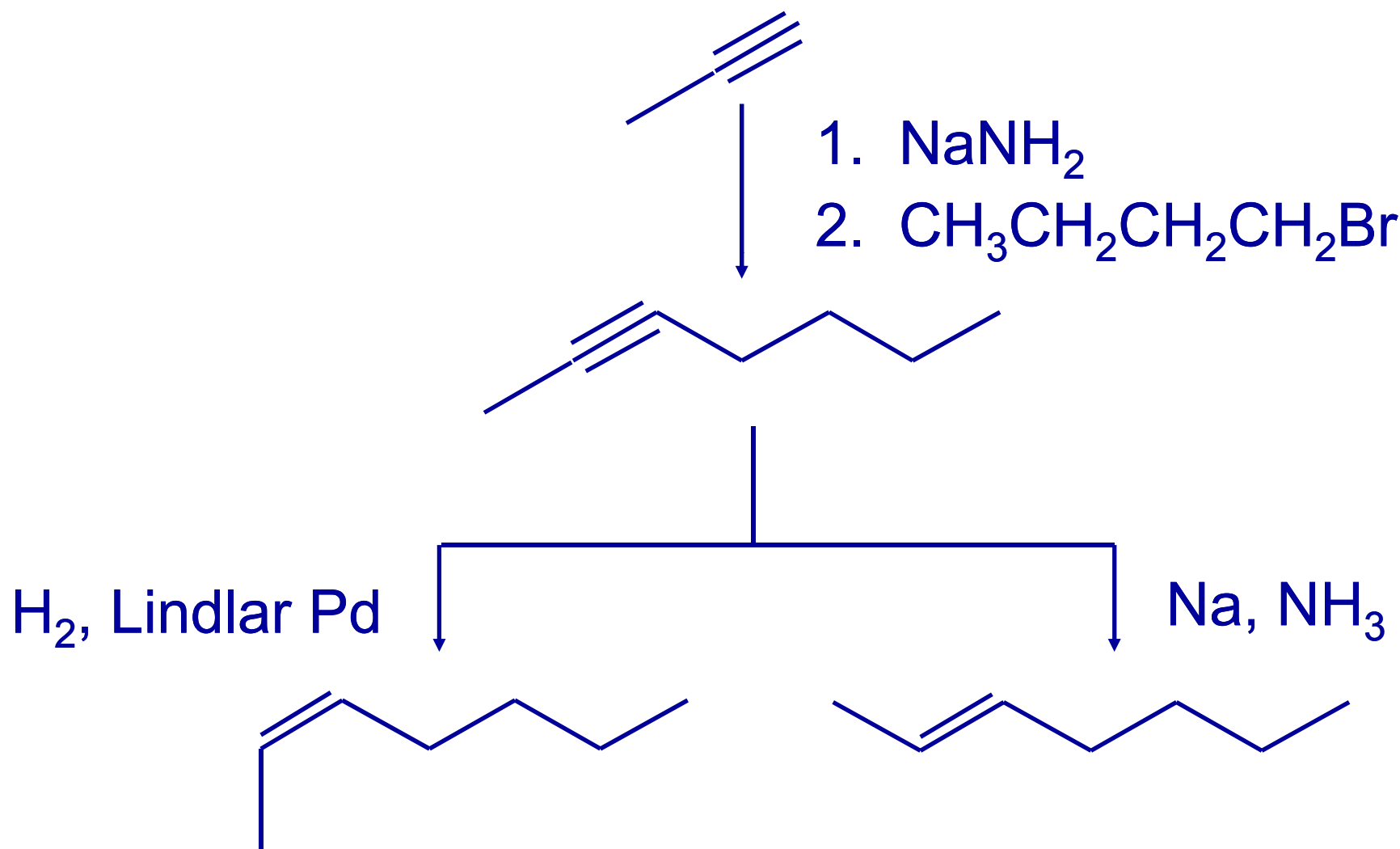
Step (3): Transfer of an electron from the metal to the alkenyl radical to give a carbanion.



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

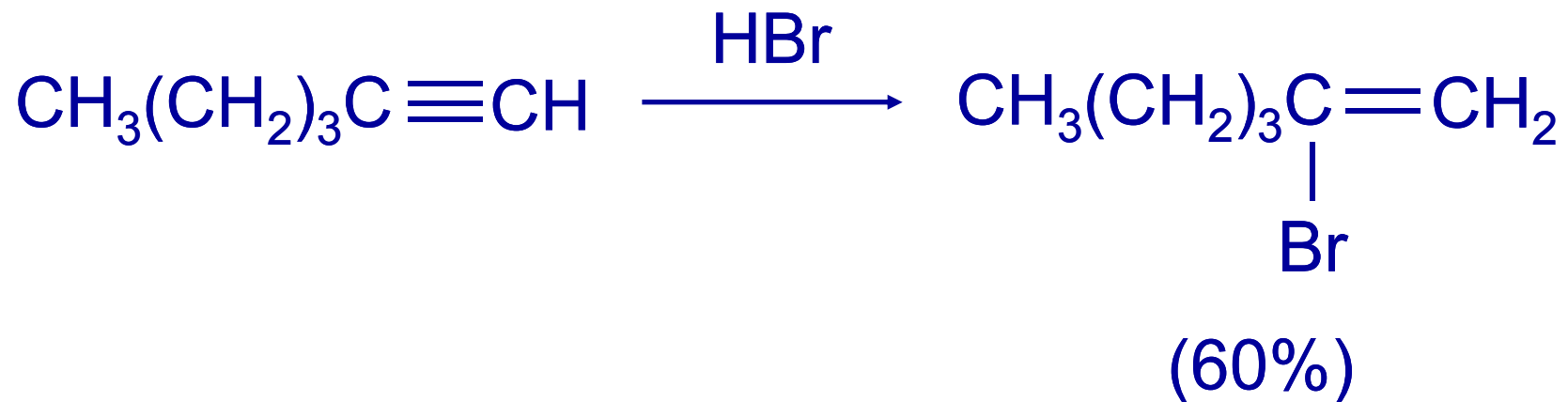


➤ Suggest efficient syntheses of (*E*)- and (*Z*)-2- heptene from propyne and any necessary organic or inorganic reagents.



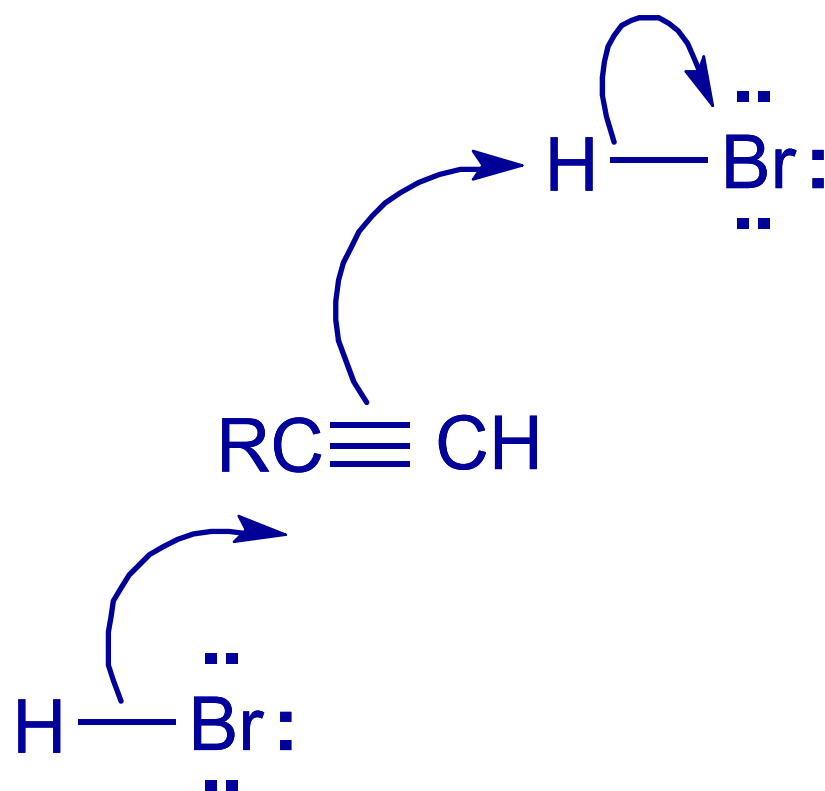
9.11. Addition of Hydrogen Halides to Alkynes

Follows Markovnikov's Rule



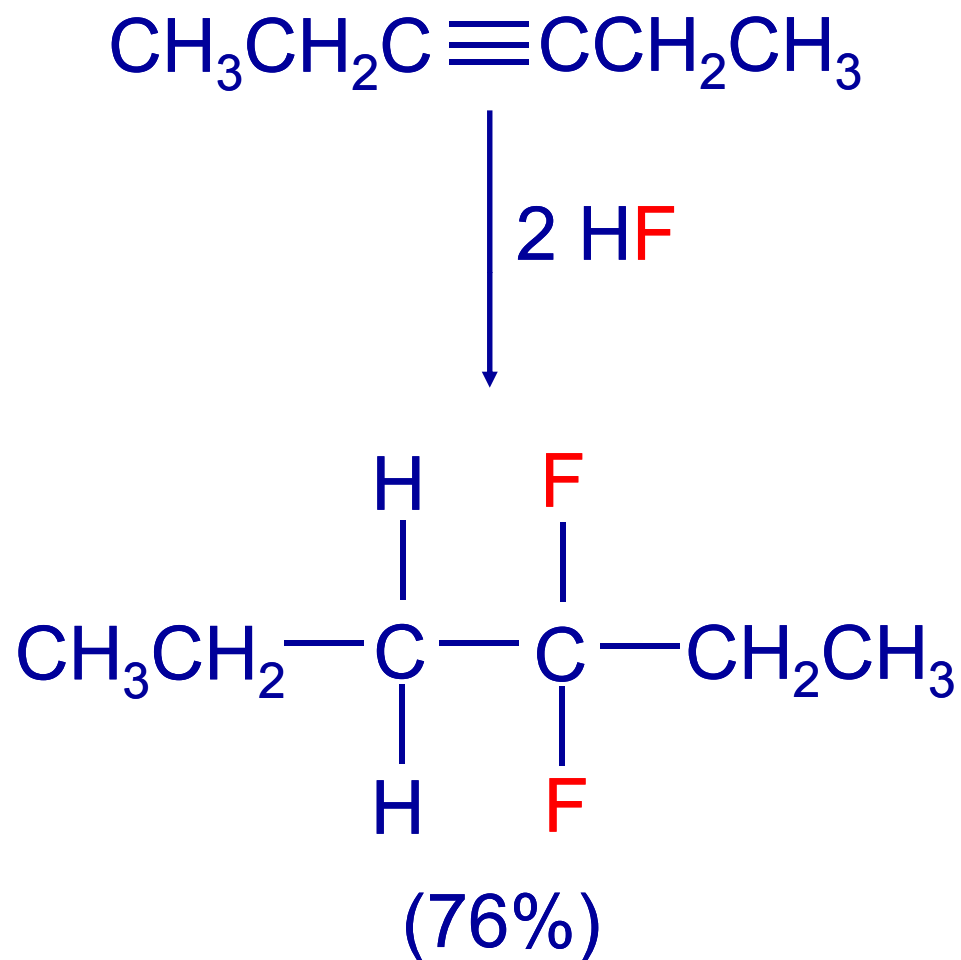
Alkynes are slightly *less* reactive than alkenes.

Termolecular Transition State

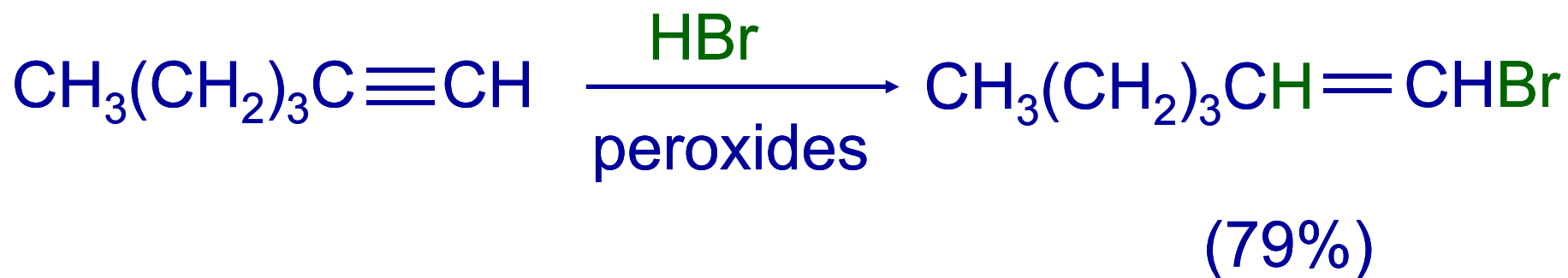


Observed rate law: $\text{rate} = k[\text{alkyne}][\text{HX}]^2$

Reaction with two moles of a hydrogen halide yields a geminal dihalide



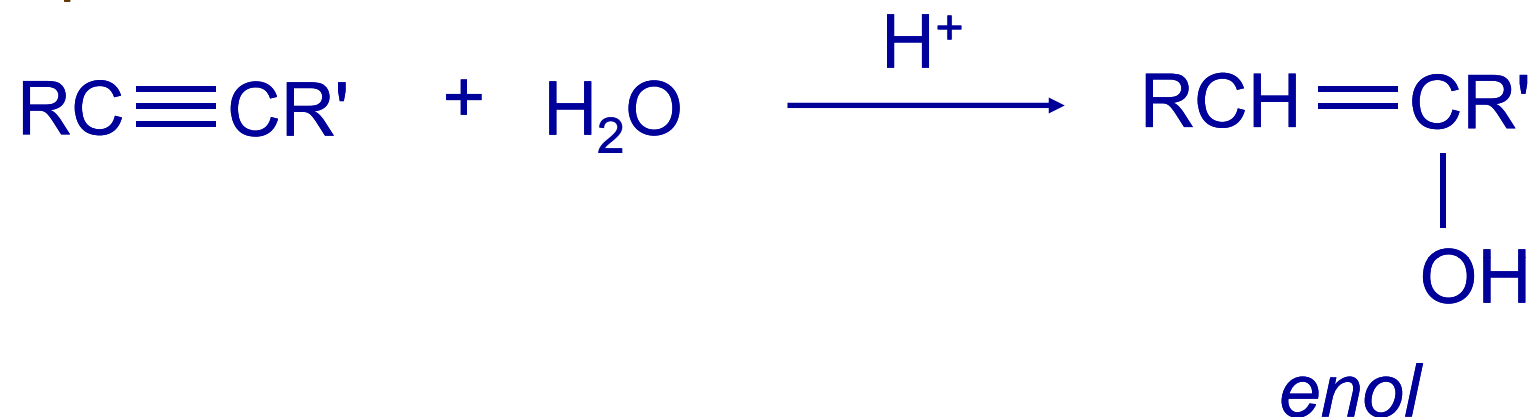
Free-radical addition of HBr occurs when peroxides are present



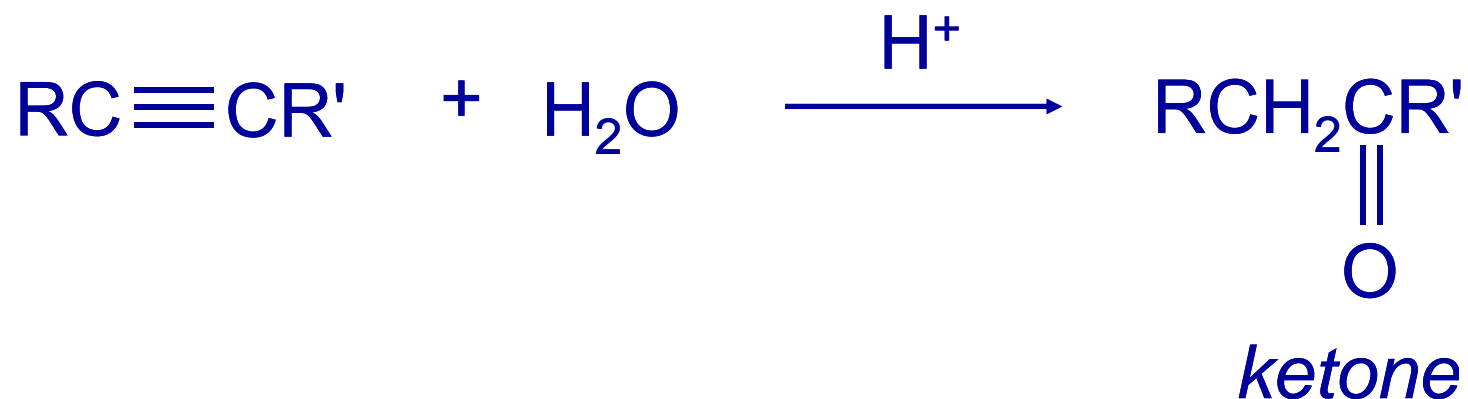
- Regioselectivity opposite to Markovnikov's rule.

9.12. Hydration of Alkynes

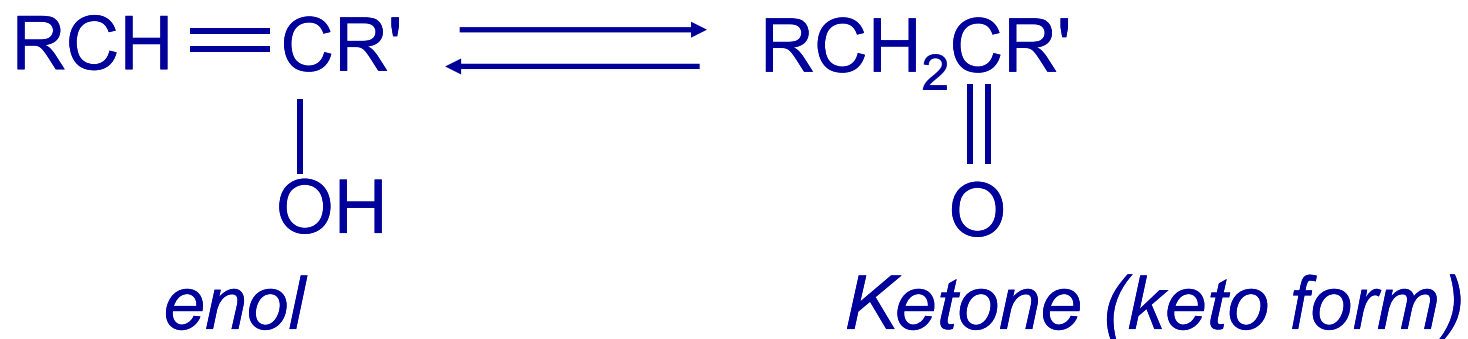
Expected reaction:



Observed reaction:

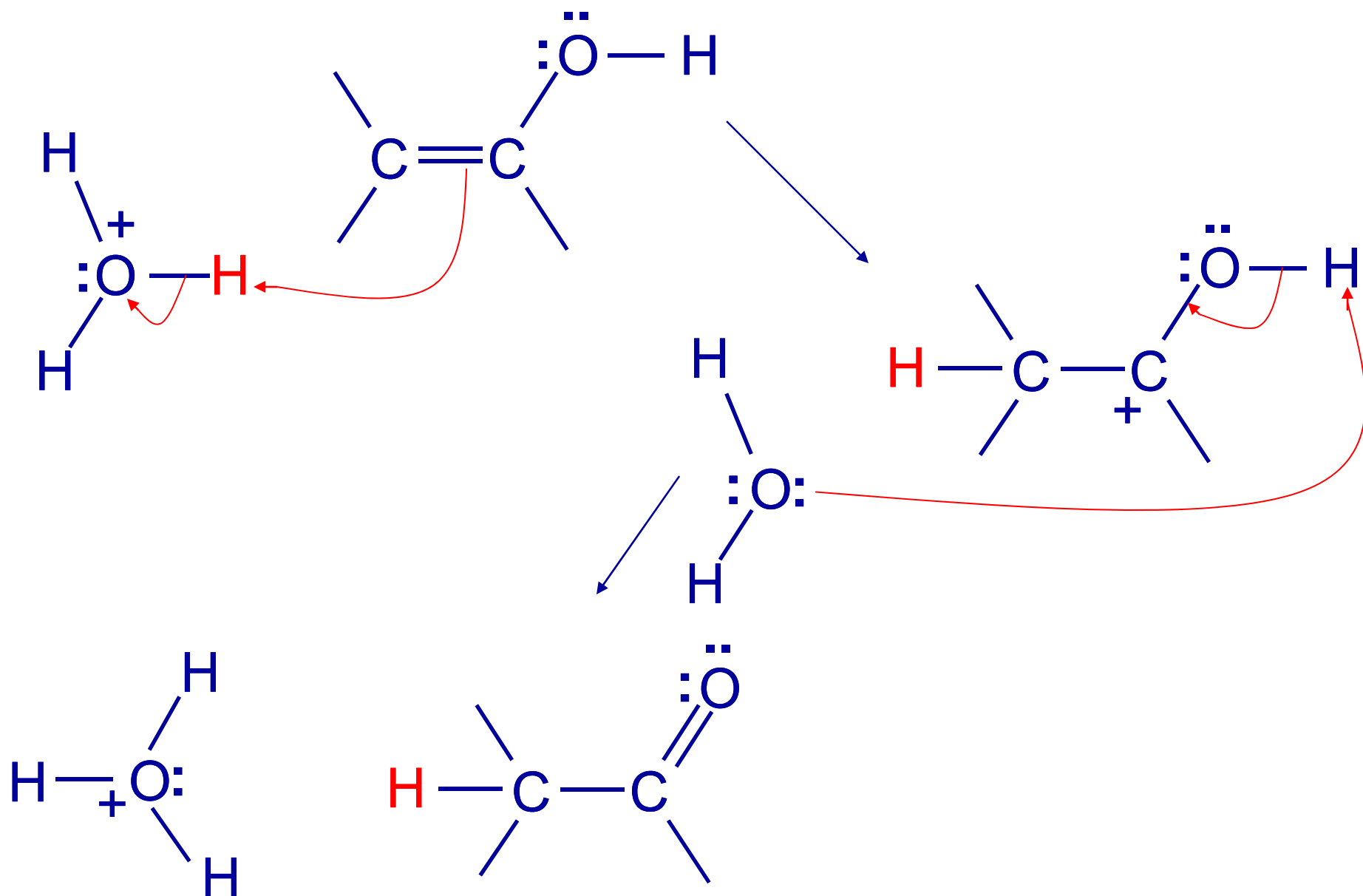


Tautomerism

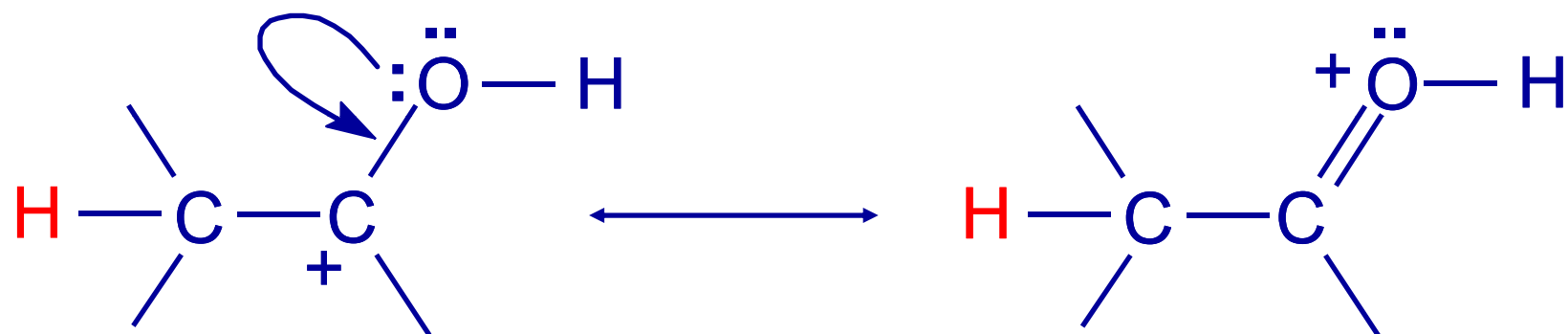


- Enols are regioisomers of ketones, and exist in equilibrium with them.
- Keto-enol equilibration is rapid in acidic media.
- Ketones are more stable than enols and predominate at equilibrium.
- Tautomers are constitutional isomers that equilibrate by migration of an atom or group. The equilibrium is called tautomerism.

Mechanism of conversion of enol to ketone



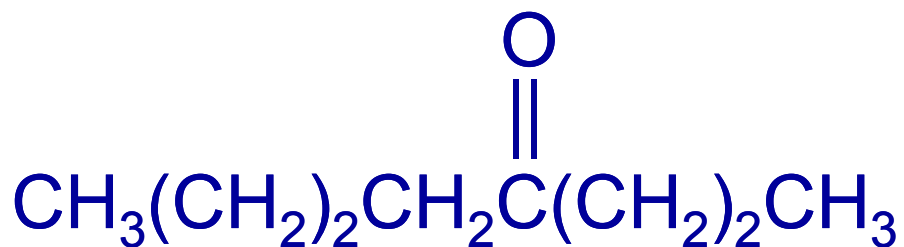
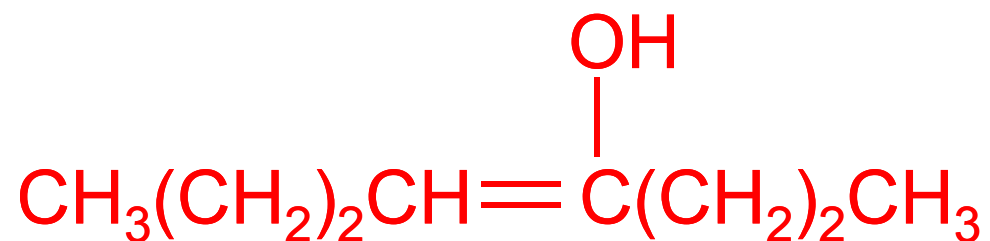
Key carbocation intermediate is stabilized by electron delocalization (resonance)



Example

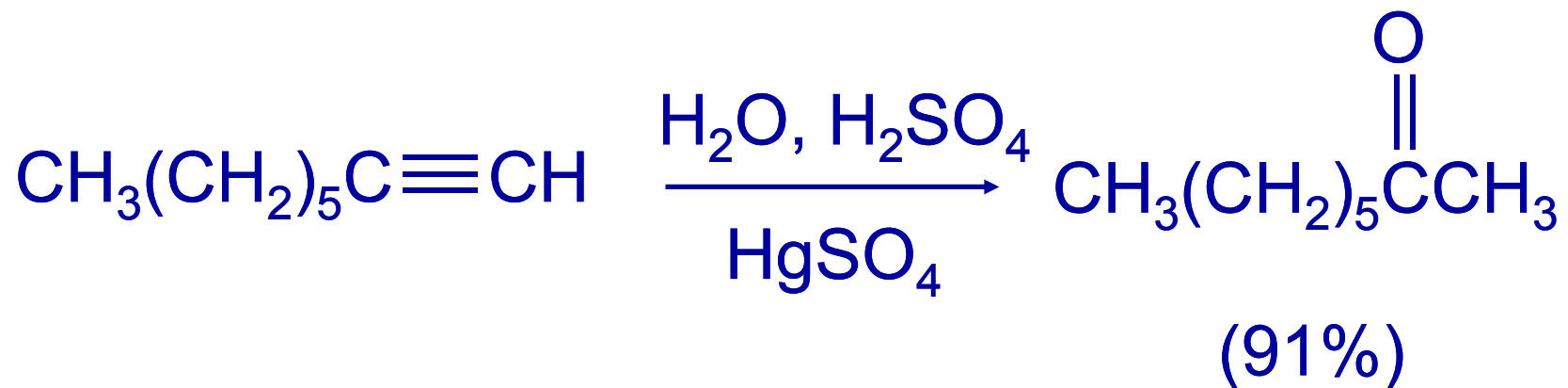


via

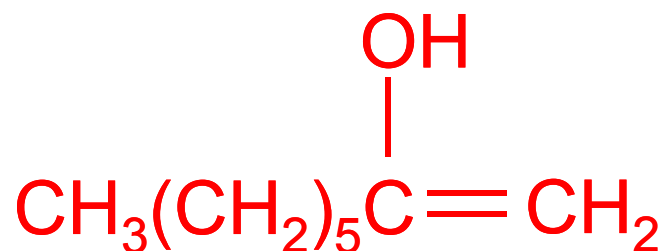


(89%)

Markovnikov's rule followed in formation of enol

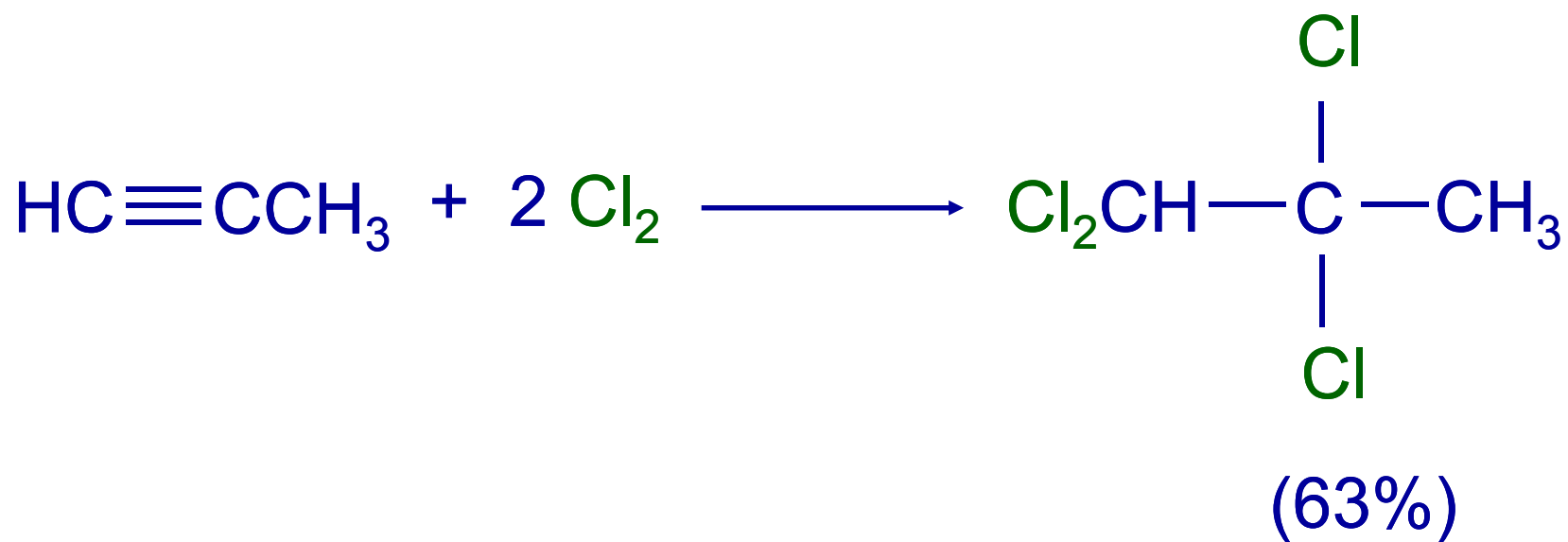


via

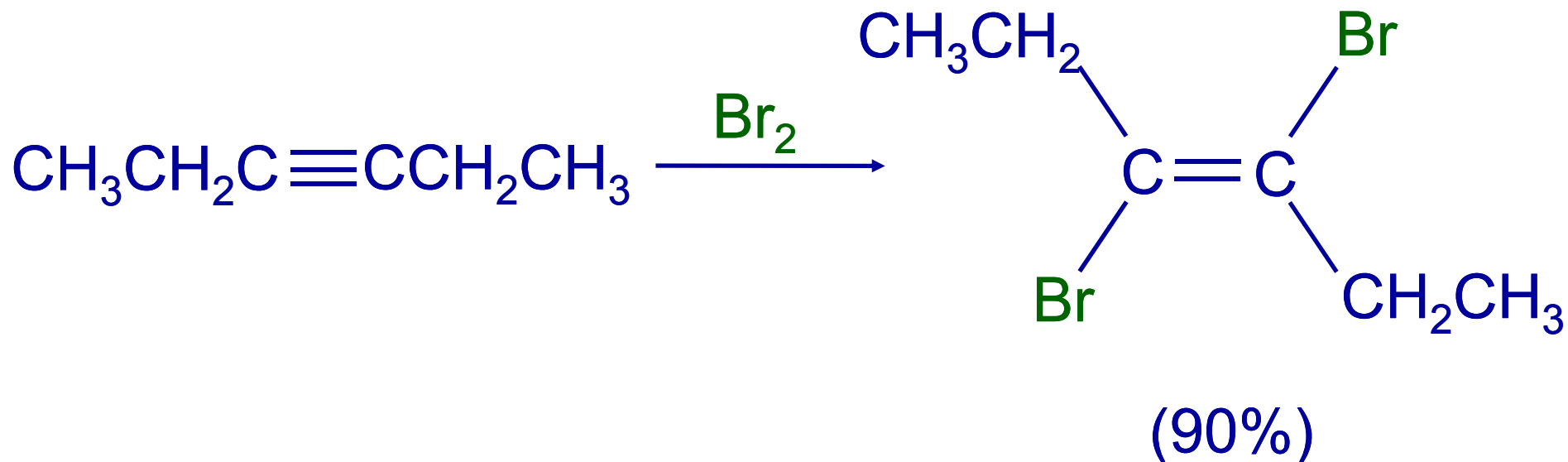


9.13. Addition of Halogens to Alkynes

Example



Addition is *anti*



➤ Intermediate can be isolated when 1:1 molar ratio is used.

9.14. Ozonolysis of Alkynes

Gives two carboxylic acids by cleavage of triple bond

Example

