Objective 13

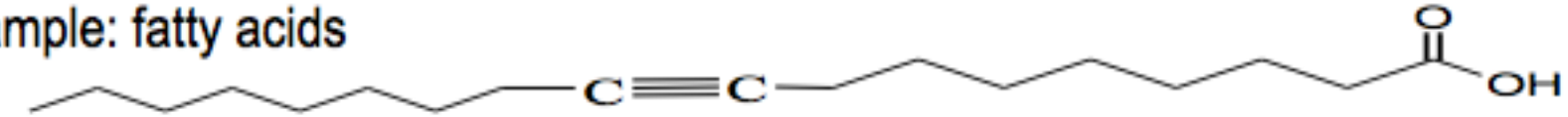
Apply Reactivity Principles to Electrophilic Addition Reactions 2: Alkynes
Identify structural features (pi bond) and electrophiles
Use curved arrows to predict product

Alkynes Are Found in Natural Products

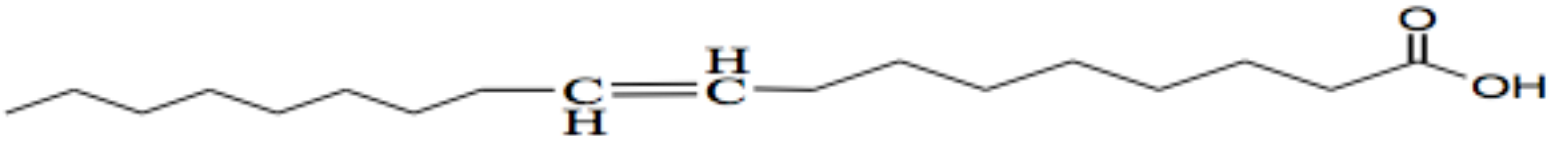
Over 1000 natural products contain carbon-carbon triple bonds.
(see Carey, "Organic Chemistry", 8th ed., p. 361)

Polyacetylenes in Ginseng root: panaxynol, ginsenoyne-A, panaxydol, 10-methoxy heptadeca-1-ene-4, 6-dyne-3, 9-diol, (3R, 9R, 10R)-panaxytriol, panaxyne, and ginsenoyne-C.

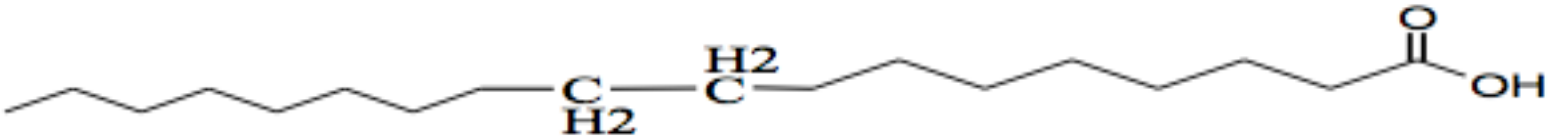
Example: fatty acids



Stearolic Acid



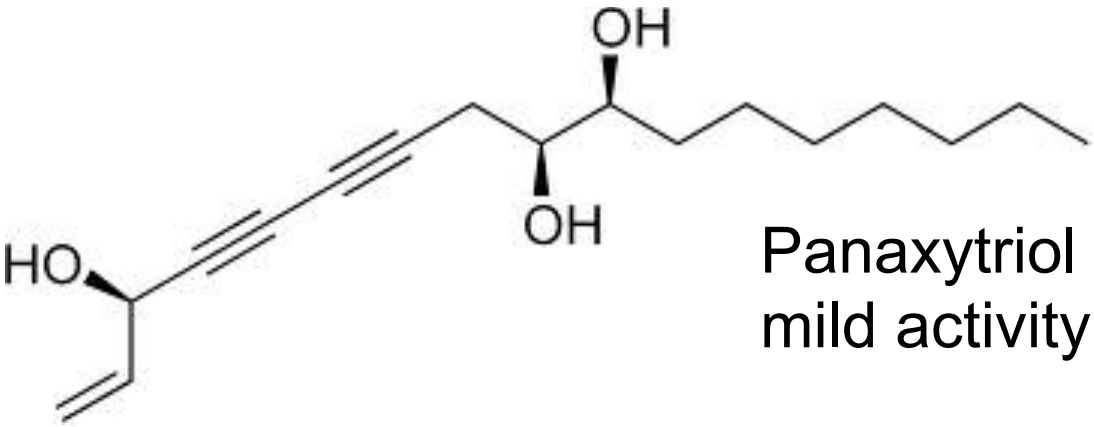
Oleic Acid (cis)/Elaidic Acid (trans)



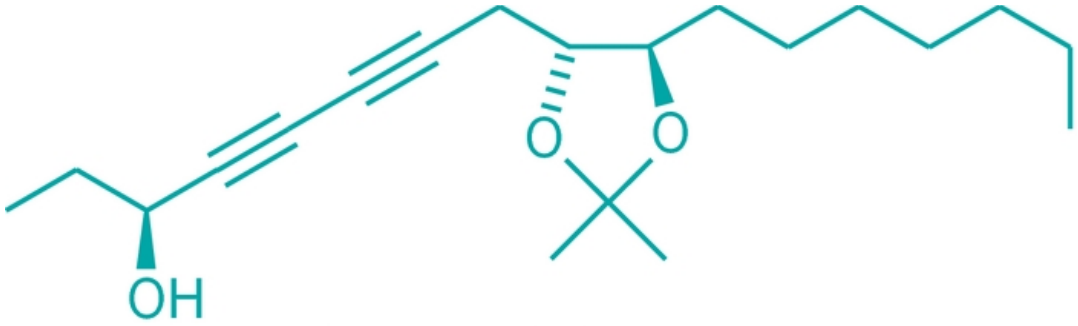
Stearic Acid

http://cen.acs.org/articles/89/i34/Ginseng-Compound-Curbs-Chemo-Effects.html

8/22/11, CEN, p. 39 Ginseng Compound Curbs Chemo Effects



Panaxytriol (Asian Panax ginseng plant)
mild activity against tumors



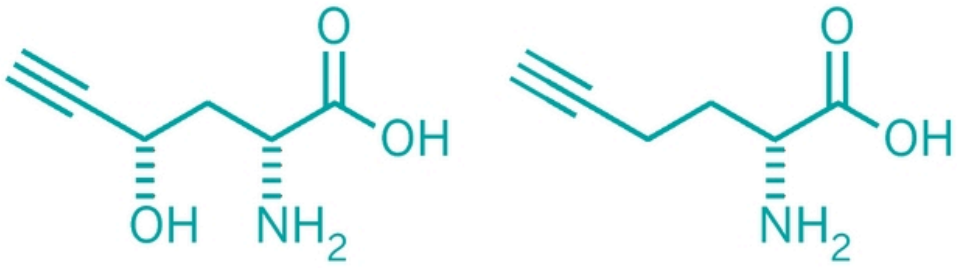
Panaxytriol analog

significantly alleviates the weight loss and nerve damage associated with cancer treatments in mice

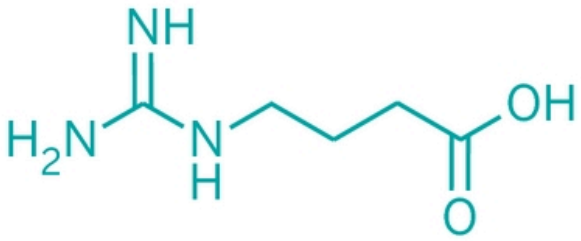
http://cen.acs.org/articles/90/i7/Behind-Mushroom-Scourge.html

2/13/12, CEN, p. 41 “Behind A Mushroom Scourge: Scientists search for the compounds responsible for unexplained deaths”

The deadly mushroom *Trogia venenata* Zhu L. Yang may have claimed hundreds of lives.



New toxic amino acids

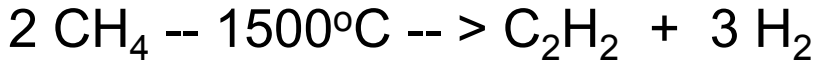


γ-Guanidinobutyric acid

Acetylene is Prepared by 3 Industrial Methods

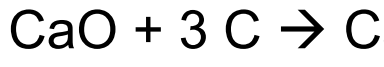
http://www.enotes.com/acetylene-reference/acetylene

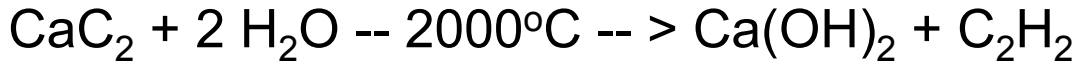
1. Thermal Cracking of Natural Gas (Methane)



2. Dehydrogenation of ethylene:

3. From Lime and Coke:





Acetylene is Used:

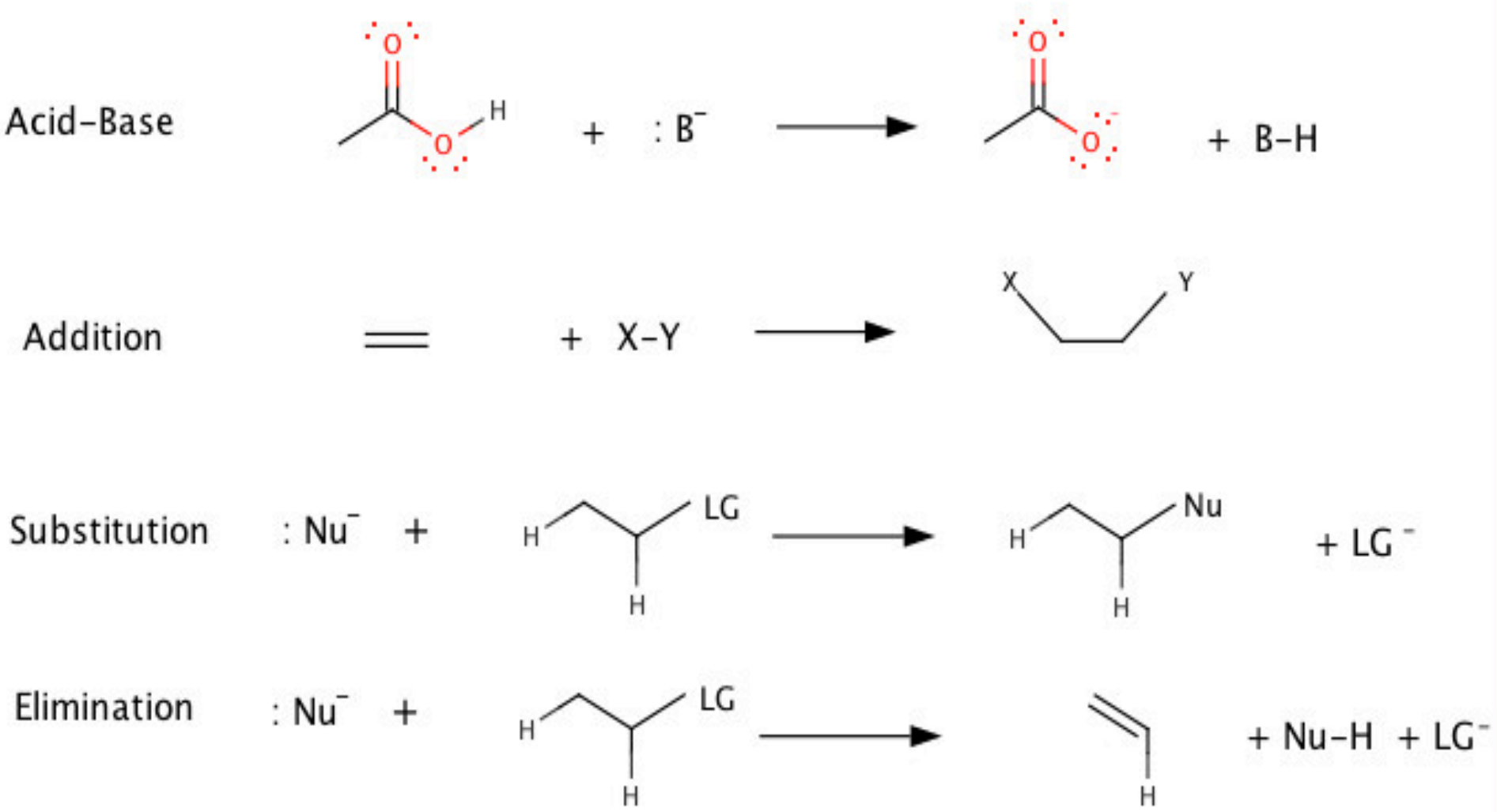
1. Welding (combustion of oxyacetylene flame = 3300°C; hottest burning fuel gas).

2. C_2H_2 ---> C_2H_4 ---> plastics

3. A Starting Material To Make Many Organic Compounds

Reppe Chemistry (http://en.wikipedia.org/wiki/Acetylene)

4 Types of Organic Polar Reactions



Alkynes Have 2 π Bonds and Act Like Alkenes

Functional group/Bonding/Structure/Reactivity:

Reactions:
Acid-Base Reaction: Ethane, Ethylene, Acetylene can lose a H^+
Why is C_2H_2 the strongest acid? (Hint: see conjugate base stability)

Addition Reaction: ***Alkynes are More Reactive than Alkenes***

Alkyne π Bond is more Nucleophilic than Alkene π Bond. Why?

Alkynes Have 2 π Bonds and Act Like Alkenes

Functional group/Bonding/Structure/Reactivity:

Compare **ethane** to **ethylene** to **acetylene**.
Longest carbon-carbon bond?

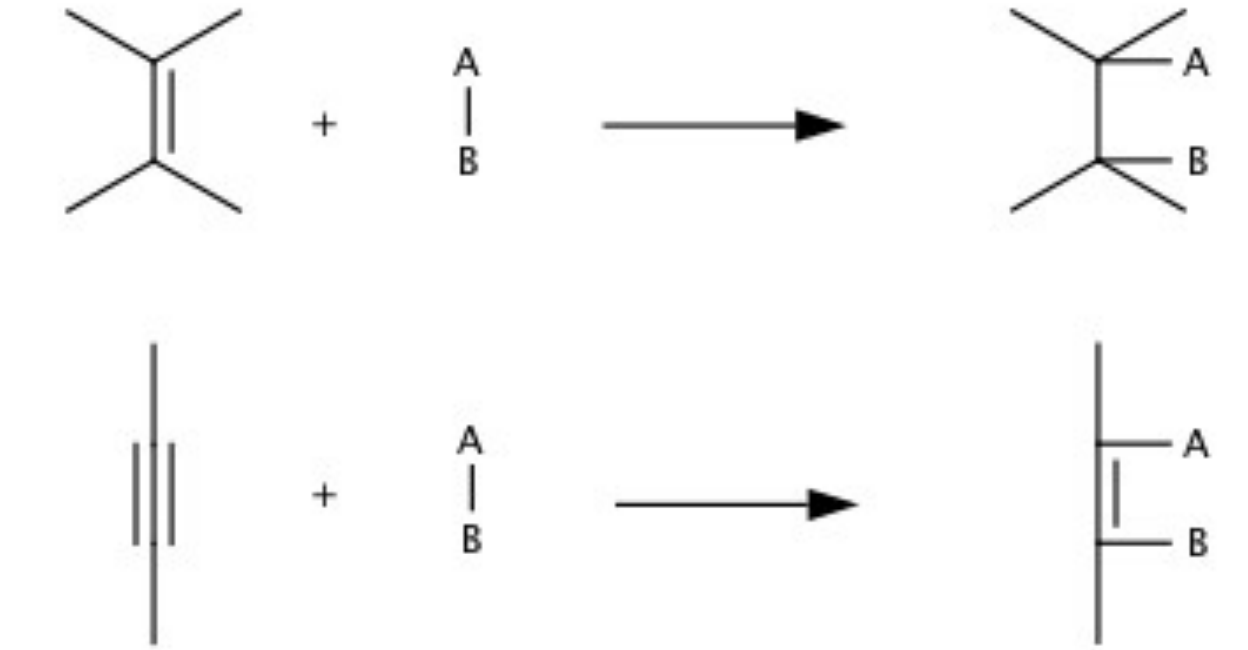
(i) ethane (ii) ethylene (iii) acetylene

Hybridization at each C?

ethane	(a) sp	(b) sp^2	(c) sp^3
ethylene	(d) sp	(e) sp^2	(f) sp^3
acetylene	(g) sp	(h) sp^2	(i) sp^3

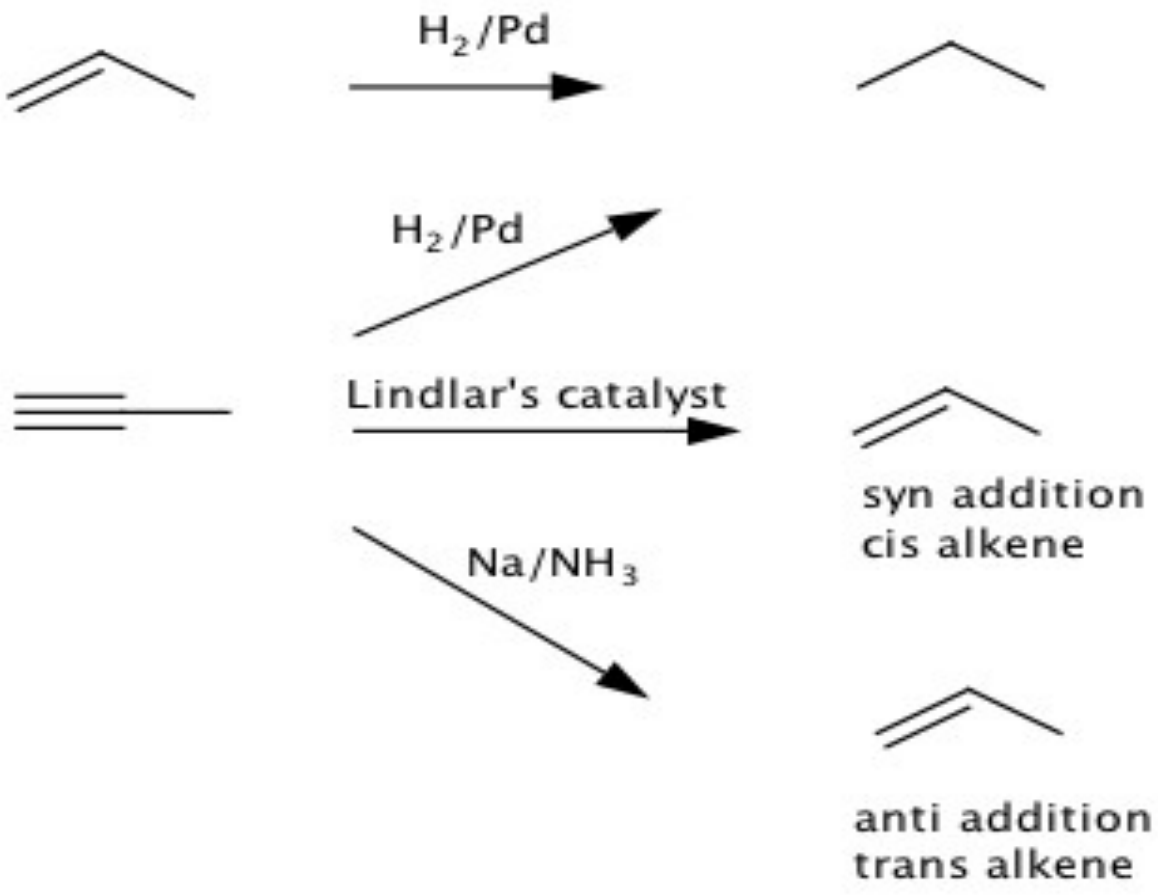
Alkynes are Used as Starting Materials to Make Many Compounds

Alkyne Addition Reactions Are Similar to Alkene Addition Reactions



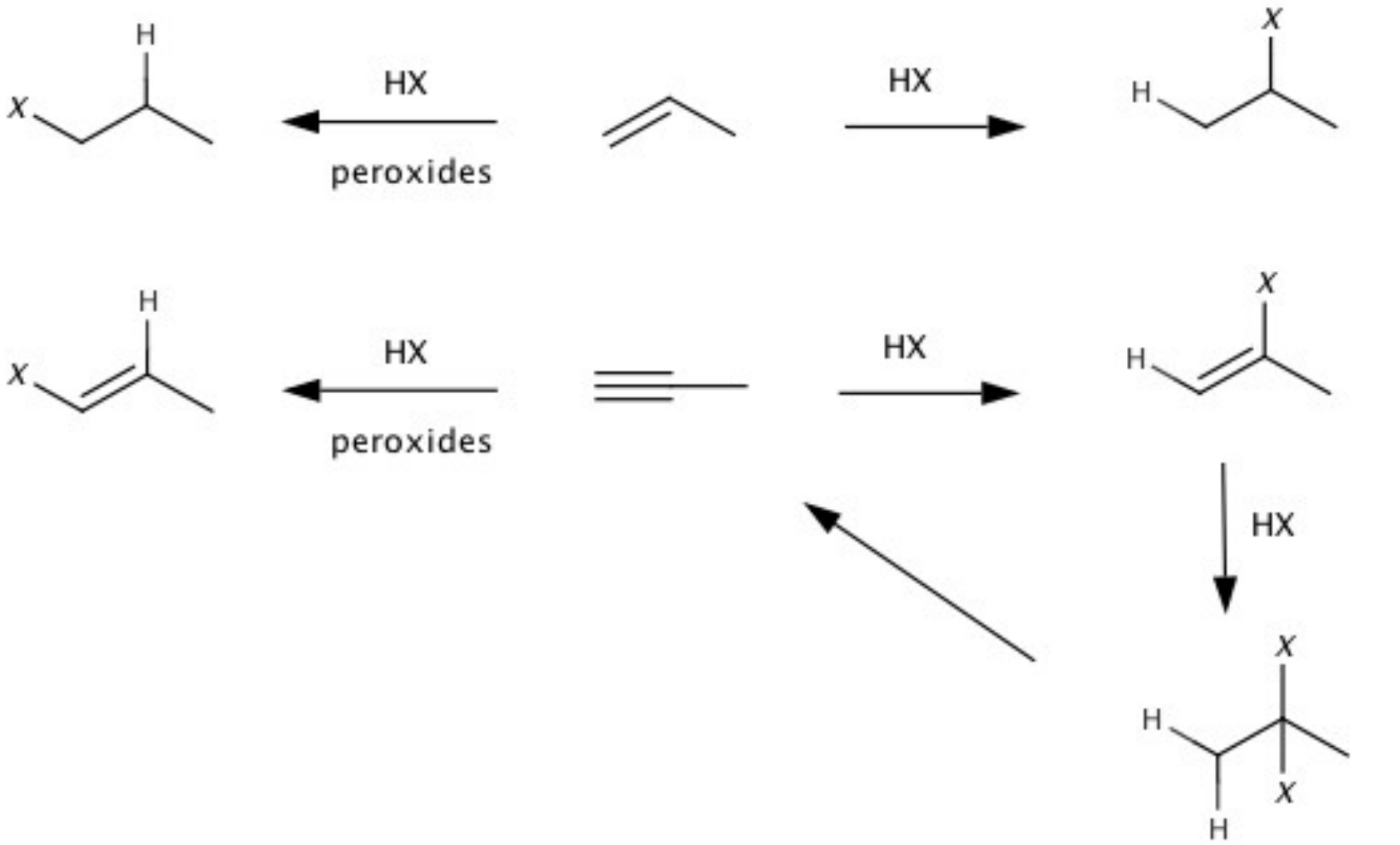
A-B = H_2, HX, X_2, HOH

Addition of H_2: Hydrogenation of Alkyne Produces an Alkene or Alkane



Carey, 8th ed., #9.25a, b

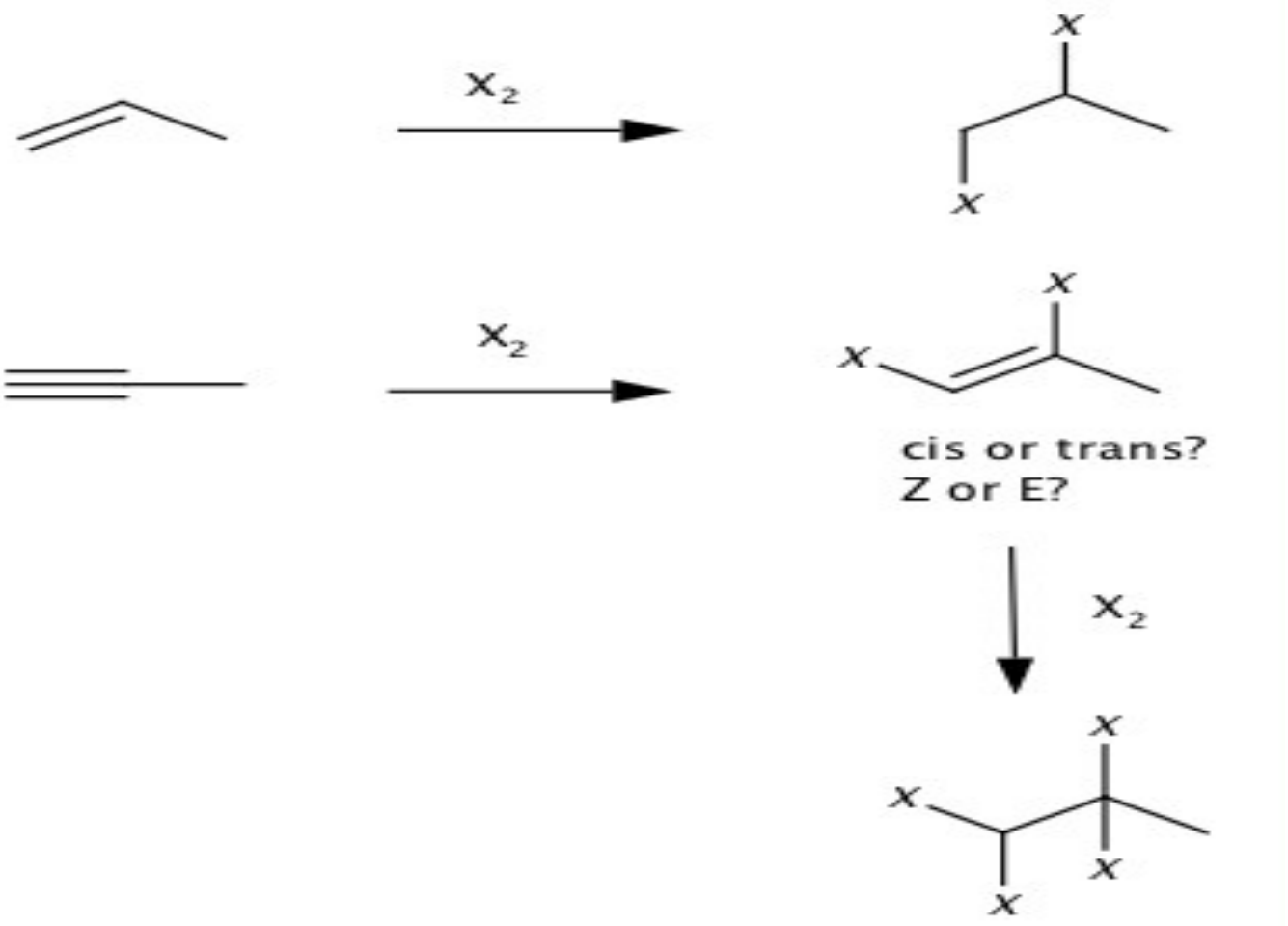
Addition of HX Produces Alkyl Halide or Dihalide with Excess HX



Carey, 8th ed., #9.25g, h

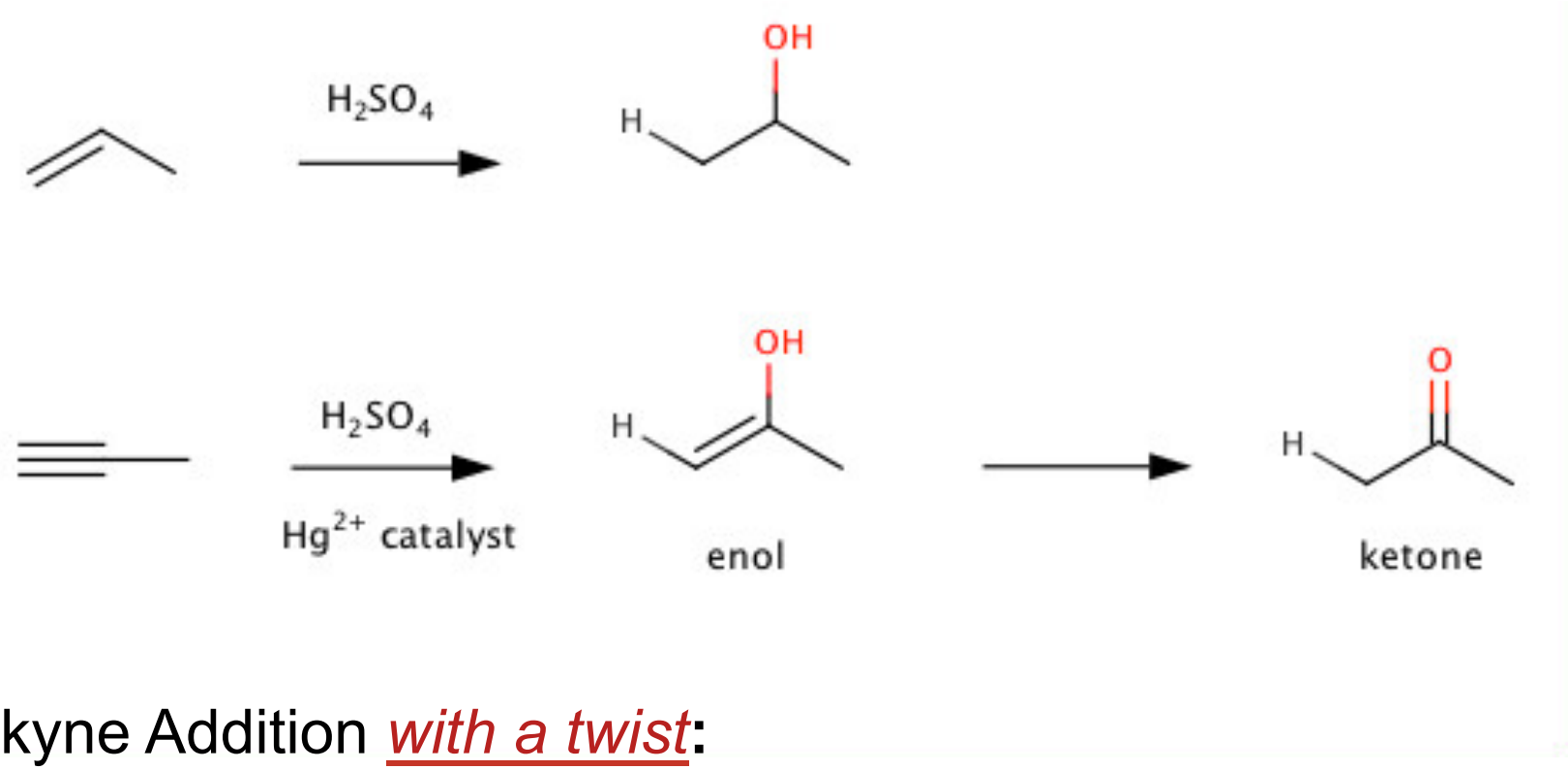
Addition of X_2 Produces 1, 2-dihaloalkene

Is cis or trans alkene formed?



Carey, 8th ed., #9.25i, j

Addition of HOH (H_2SO_4 (aq) and Hg^{2+} catalyst) Produces an Enol



Alkyne Addition *with a twist*:

Enol Tautomerizes into a Ketone

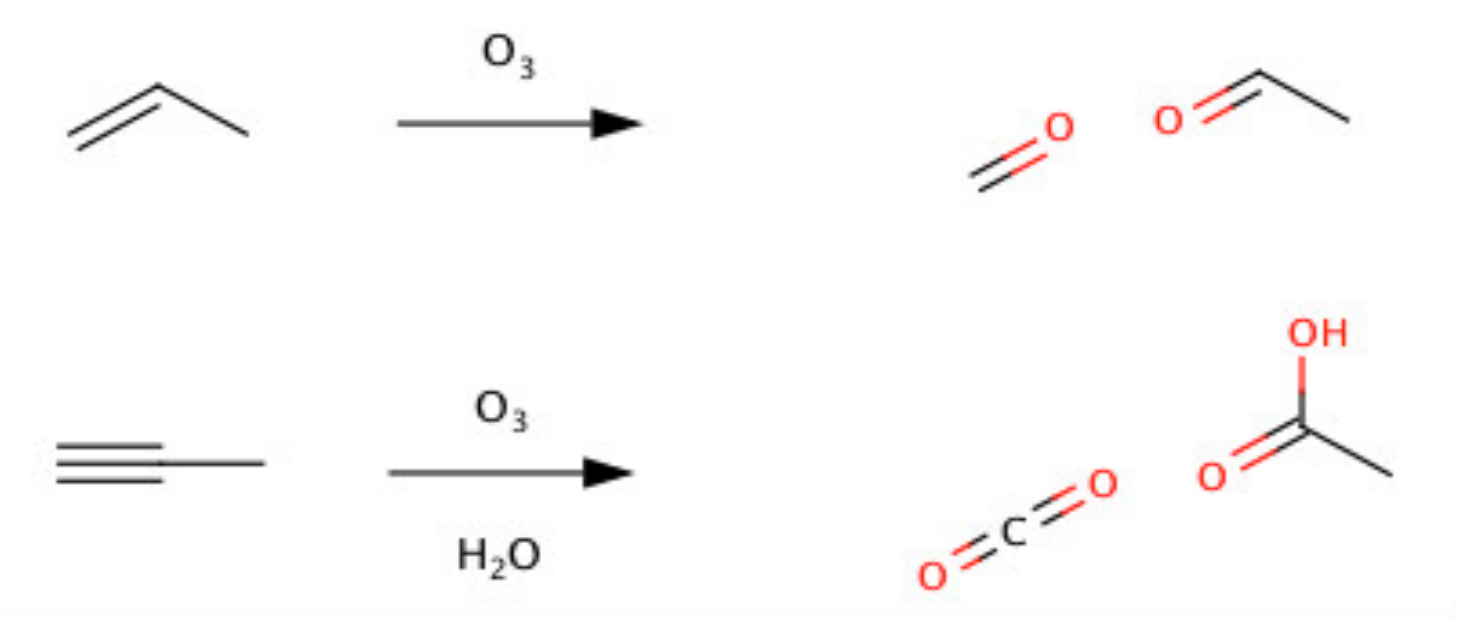
Draw resonance structure of enol.

Carey, 8th ed., #9.25k and 29g

Ozonolysis Produces Carbonyl Compound (C=O)

Alkene + O_3 --> Aldehyde/Ketone

Alkyne + O_3 --> Acid or CO_2 from terminal alkyne



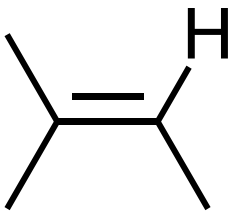
Use in Synthesis: ***reduce*** chain length, make carbonyl

Carey, 8th ed., #9.25l, 29e and f

Alkyne Addition Reactions Are Similar to Alkene Addition Reactions

Predict the product(s) of the following reactions:

Reaction Conditions	Alkene: Propylene	Alkyne: Propyne
H_2/catalyst		
HX		
X_2		
H_2O/H^+ catalyst		
O_3/ H_2O		



Ethylene has a pK_a of 44; acetylene has a pK_a of 25. Acetylene is a _____ acid than ethylene; the conjugate base of acetylene is a _____ base than the conjugate base of ethylene.

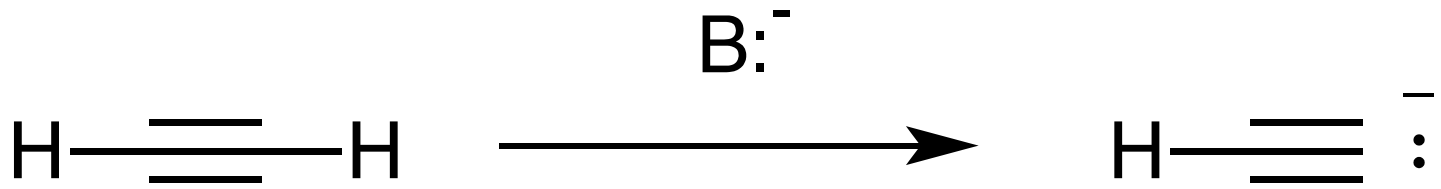
a. stronger/stronger

b. stronger/weaker

c. weaker/stronger

d. weaker/weaker

Acetylene is a Very Weak Acid
Acetylene is a Stronger Acid than Ethylene
Acetylide Ion is a Very Strong Nucleophile



Acid-base: ***Acetylene is Weakly Acidic.***

pK_a of acetylene = 25
pK_a of ethylene = 44
pK_a of ethane = 50

Which base reacts with acetylene?

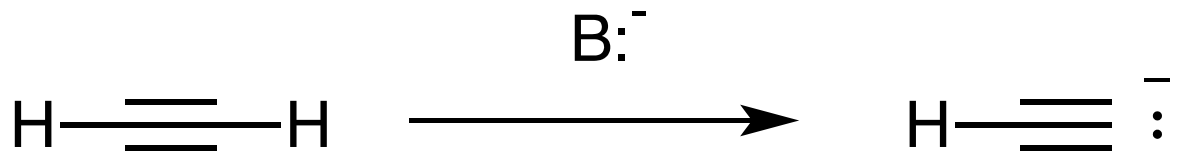
Which base reacts with acetylene?
Draw the structure of the products of the reaction.

a. H_2O

b. OEt^-

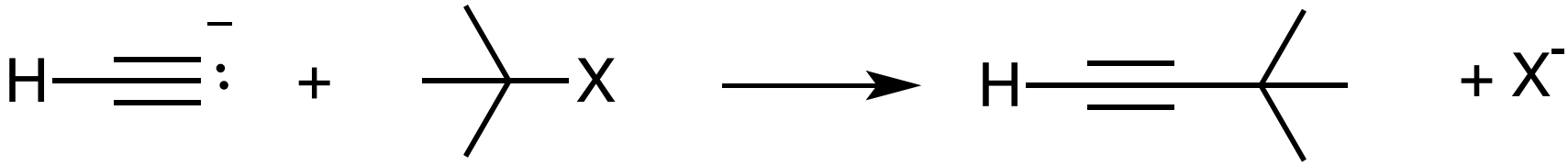
c. NH_2^-

The Acetylide Ion (HC≡C:$^-$) is a <u>Very Strong</u> **Nu:$^-$**



<u>Acetylide ion is used in Synthesis:</u>

Acetylide Ion reacts with R-X in a Substitution Reaction

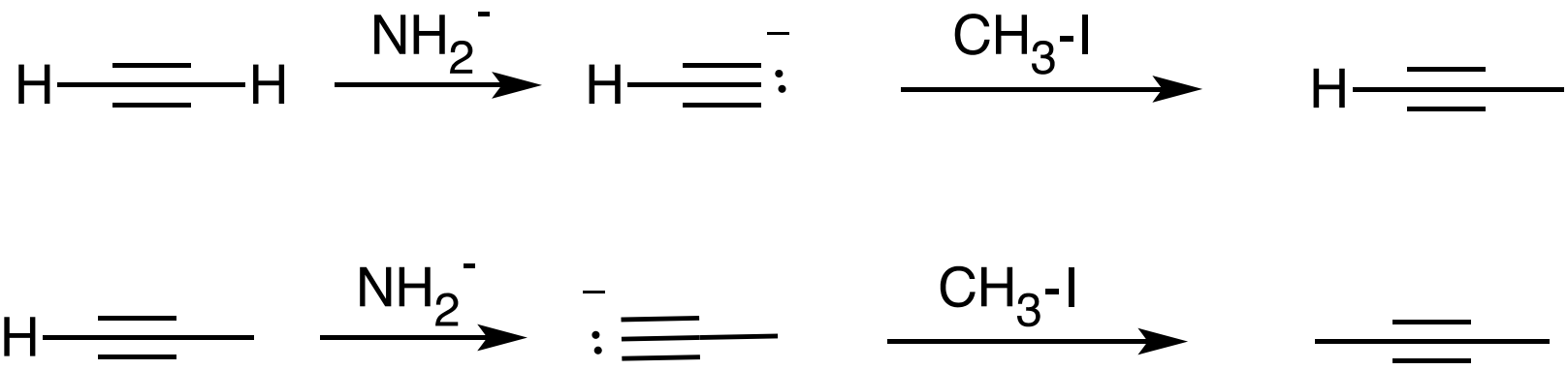


Starting from acetylene, suggest a synthesis of 2-butyne.

The Acetylide Ion is Used to Make C-C Bonds

Synthesis: Acetylide as an Alkylating Agent to Lengthen Chain

Starting from acetylene, suggest a synthesis of 2-butyne.



Acetylide ion undergoes substitution with:

(i) 1° RX (ii) 2° RX (iii) 3° RX

What is the mechanism type? (iv) S_N1 (v) S_N2

The Acetylide Ion is Used to Make C-C Bonds

Synthesis: Acetylide as an Alkylating Agent to Lengthen Chain

Acetylide reacts with 1° RX via S_N2 mechanism.

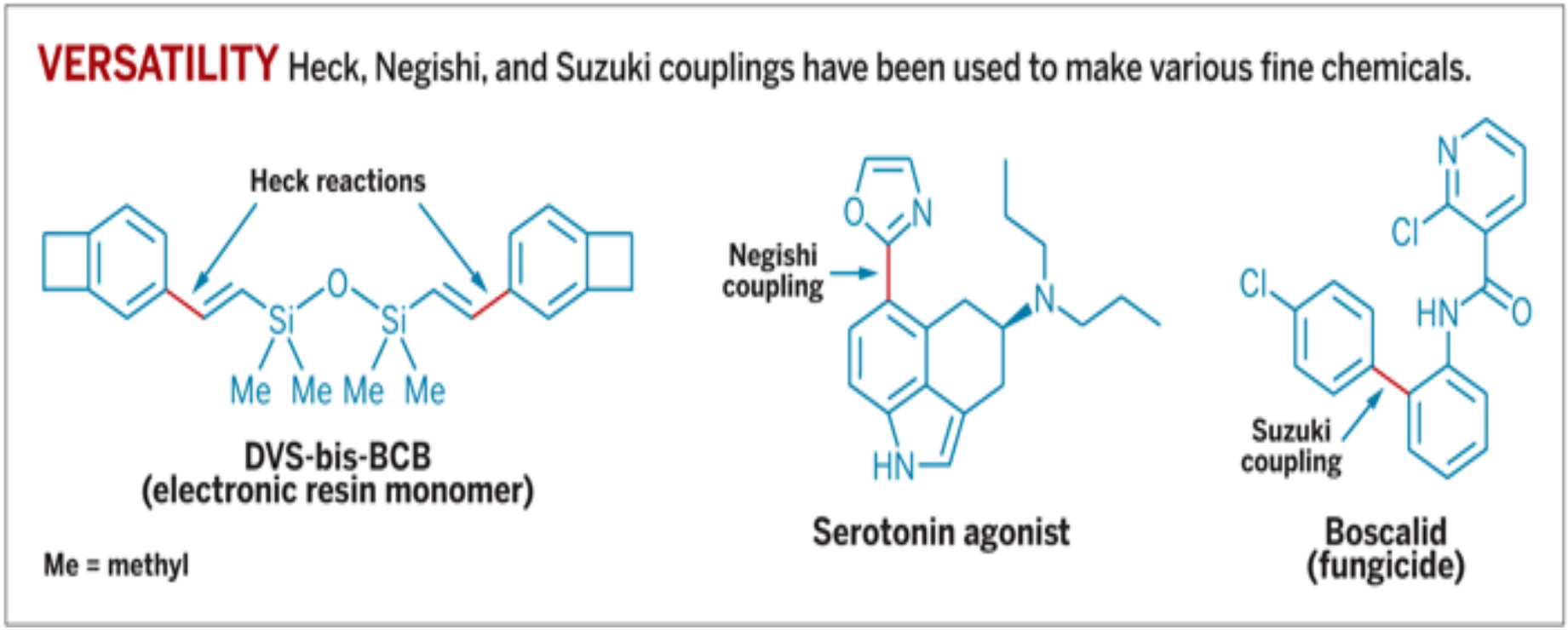
Use CH_3OH instead of CH_3I. Will same product form? Give reasons.

??

Carey, "Organic Chemistry", 8th ed., #9.25d and e, 29a and d.

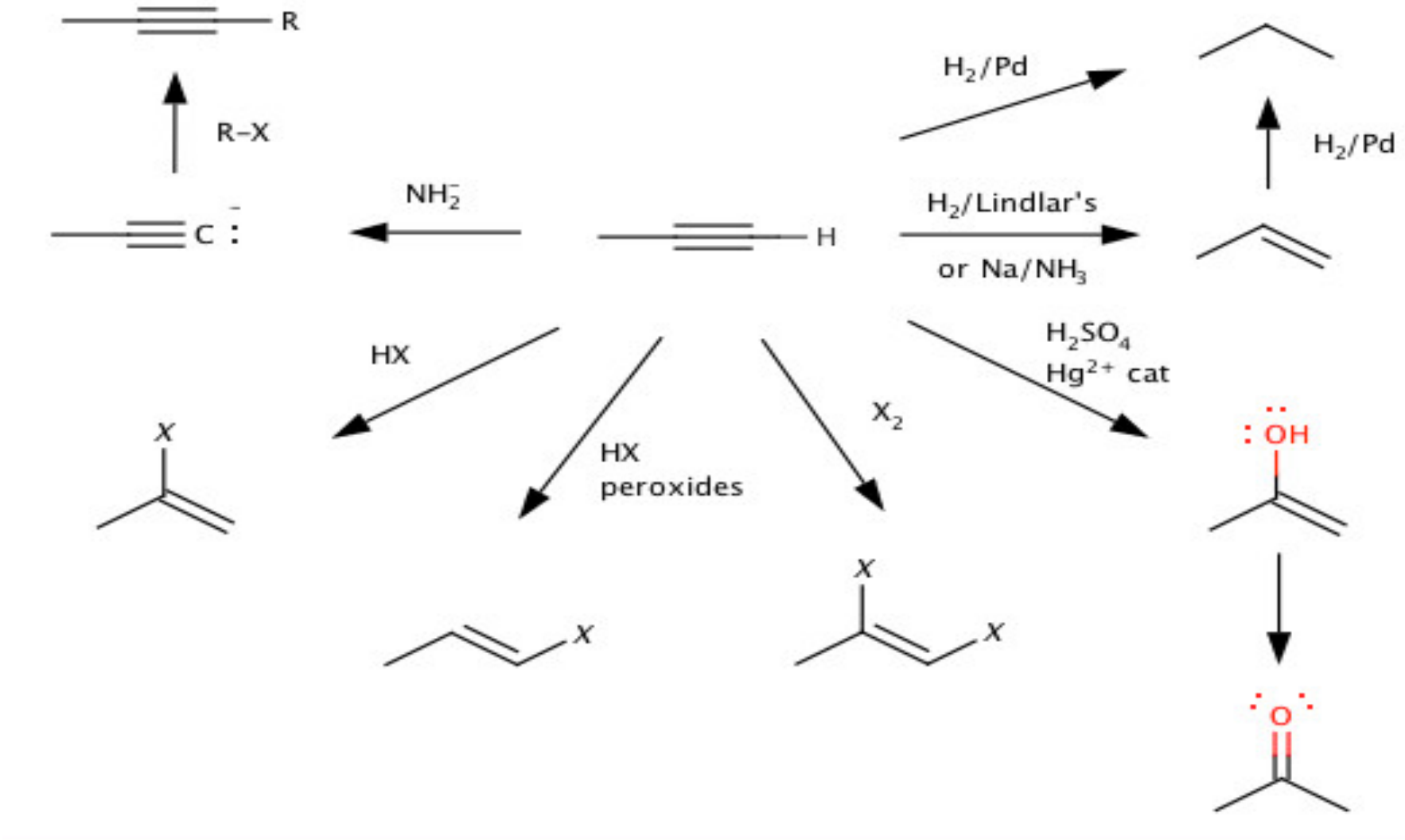
Making C-C Bonds Is Important in Synthesis

1. Acetylide ion: $HCC^{:-}$ + R-X →
2. 1912 Nobel Prize in Chemistry: Grignard reagent (Chem 12B)
   RMgX + aldehyde/ketone →
3. 2010 Nobel Prize in Chemistry: Pd catalyzed cross coupling



Chemical and Engineering News, 10/11/10, p. 7.

Acetylide Ion is Used to Form C-C Bonds (Lengthen Chain)
Alkynes Undergo Addition Reactions



Acetylene or Ethylene is Often used as a Starting Material in Synthesis

Alkynes can be Converted to Alkenes which can be converted to Alkanes

Many Syntheses Start from an Alkene or ***Go Through an Alkene*** *to make the Target compound* **(alkene as "hub")**

Acetylene is used to Lengthen a Carbon Chain (via Substitution Rxn)

Klein, Ch. 10#53

Alkynes Are Like Alkenes

Alkynes, like Alkenes, are Prepared via ***Elimination*** Reaction

Alkynes, like Alkenes, undergo ***Addition*** Reactions

Alkynes are ***Stronger Acids*** than Alkenes

===> Acetylene (HC≡CH) + $B:^-$ ---> Acetylide ion ($HC\equiv C:^-$)

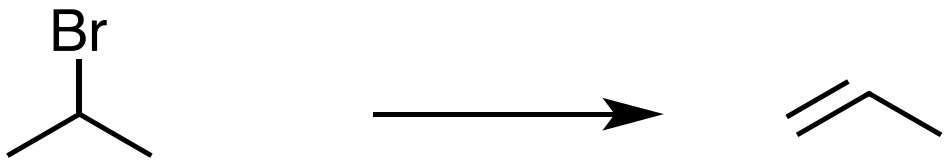
The Acetylide ion ($HC\equiv C:^-$) is a very good $Nu:^-$

===> used in Substitution reactions

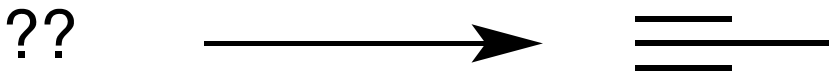
===> used to make C-C bonds

Alkynes are Like Alkenes

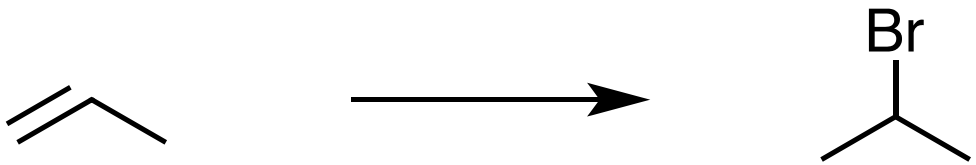
How do you make an alkene?



How do you make an alkyne?



What is the alkene addition product?



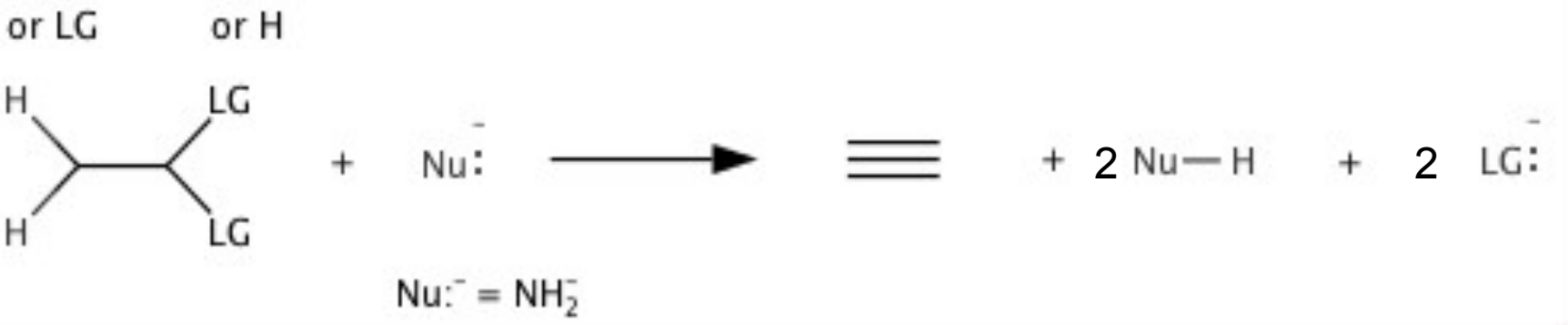
What is the alkyne addition product?

Lab: Alkynes are Prepared by an Elimination Reaction from a Dihalide

Elimination Reaction: R-LG + Nu:$^-$ --> alkene + Nu-H + LG$^-$

What LG is used?

$R\text{-}LG_2 + NaNH_2 \rightarrow$ alkyne + Nu-H + LG$^-$ where LG = X

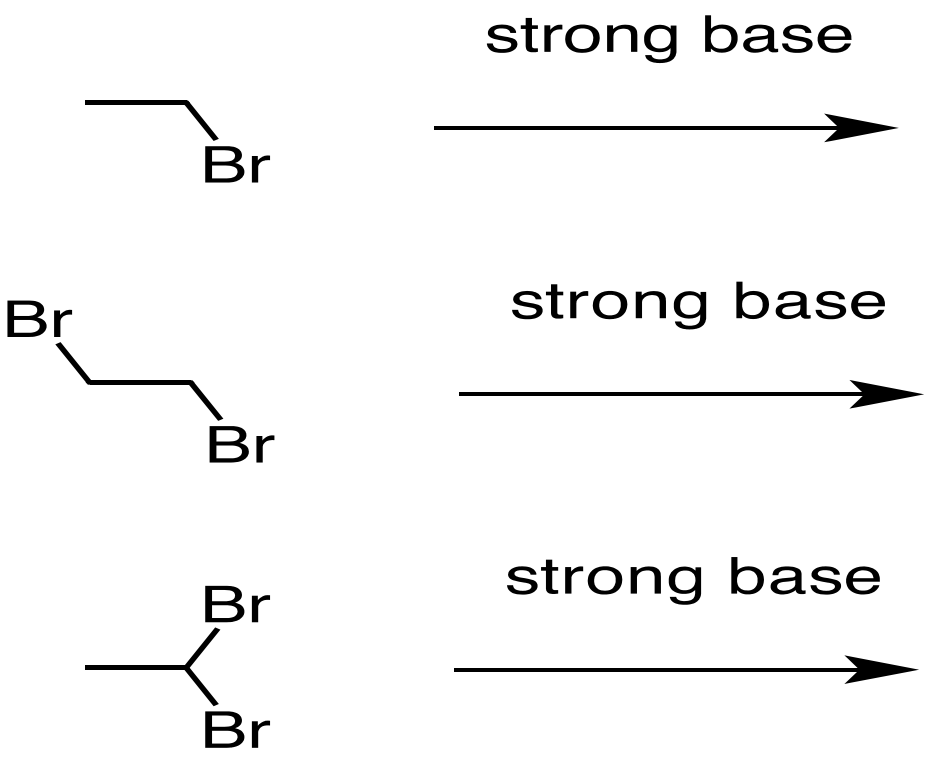


Vicinal dihalide = X on adjacent C

Geminal ("*twins*") dihalide = X on same C

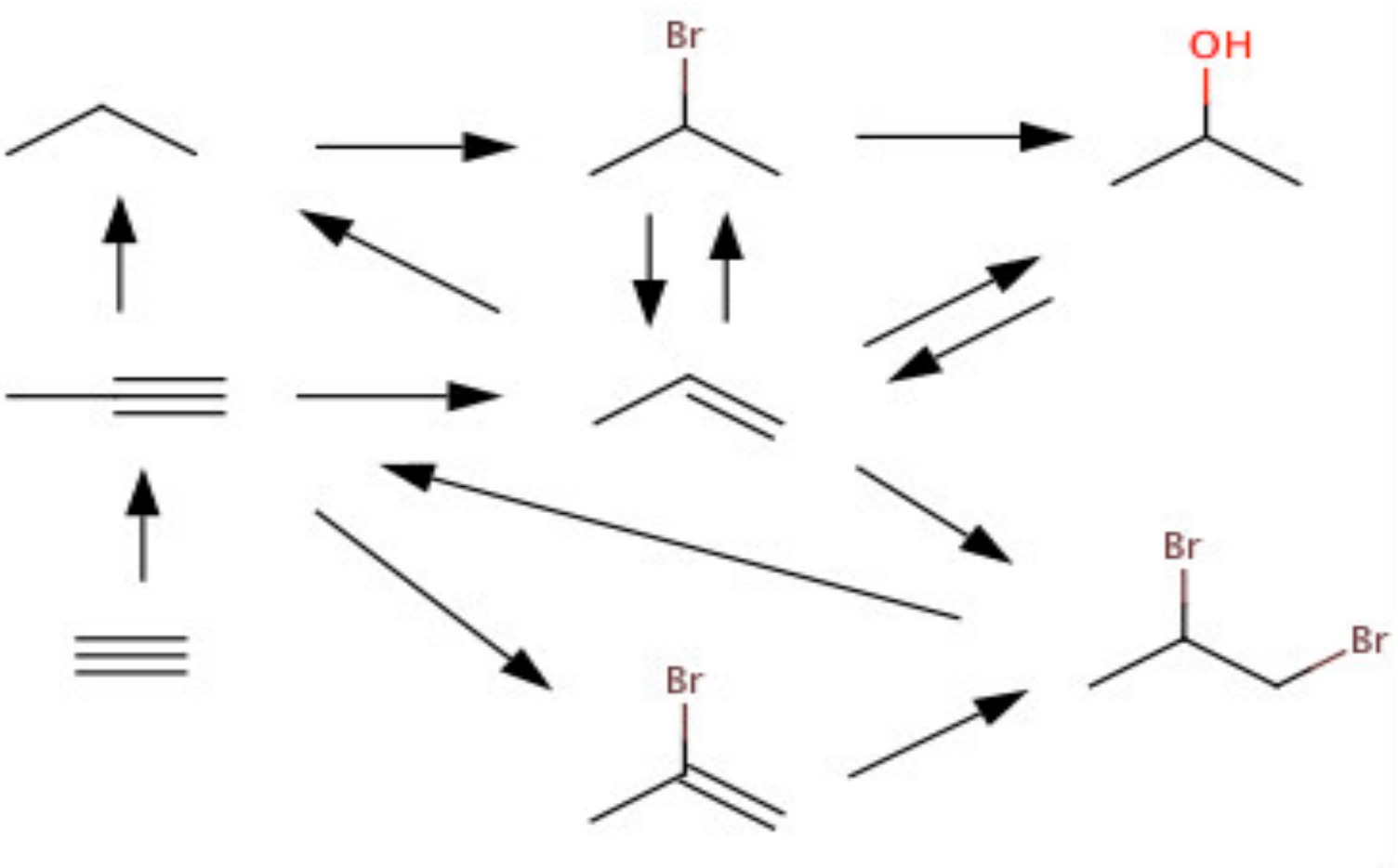
Carey, "Organic Chemistry", 8th ed., #9.22a, 29b and c

Which method does **not** work to make acetylene?



Add Alkyne Reactions to your Organic Reaction Map

Note: ***Alkenes are the "hub" to make different groups***



Klein, 1st ed., #10.40 and 41 and 46 and 52

Carey, 8th ed., #9.21, 22b, 23c, 24, 31, 33, 34, 36