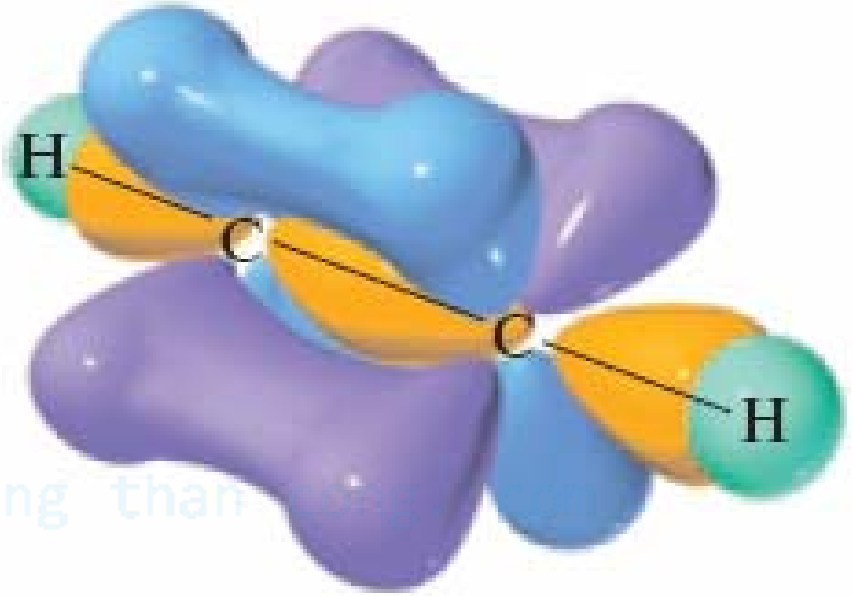
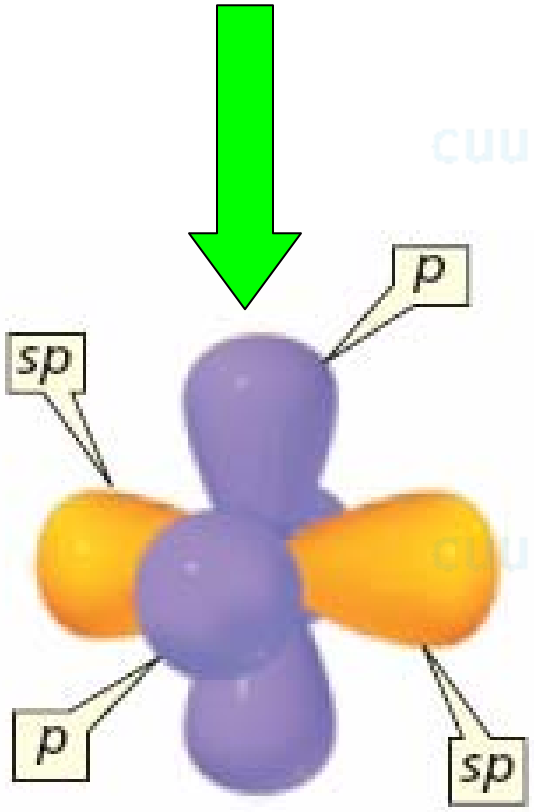
ORGANIC CHEMISTRY

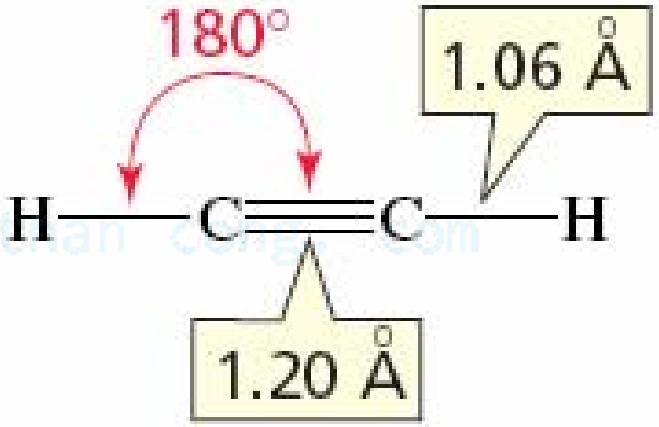
Dr Nam T. S. Phan
Faculty of Chemical Engineering
HCMC University of Technology
Office: room 211, B2 Building
Phone: 38647256 ext. 5681
Email: ptsnam@hcmut.edu.vn

Chapter 7: ALKYNES

An sp hybridized carbon



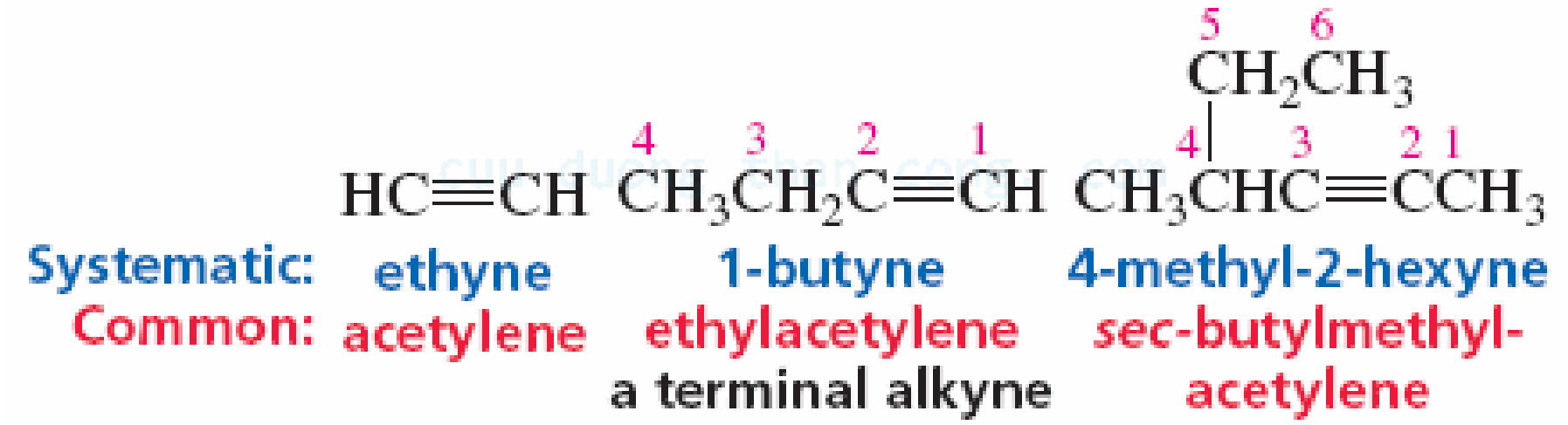




a triple bond consists of one σ bond and two π bonds

NOMENCLATURE OF ALKYNES

The IUPAC name of an alkyne is obtained by replacing the "ane" ending of the corresponding alkane with "yne"



In common nomenclature, alkynes are named as 'substituted acetylenes'

Both ethyne & acetylene are acceptable names for C_2H_2

Lowest possible number, regardless of which functional group gets the lower number

5-hepten-1-yne

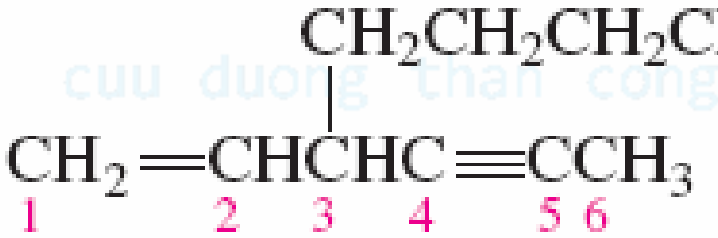
not 2-hepten-6-yne

because 1 < 2

1-hepten-5-yne

not 6-hepten-2-yne

because 1 < 2



3-butyl-1-hexen-4-yne

2-hexen-4-yne

not 4-hexen-2-yne

1-hexen-5-yne

not 5-hexen-1-yne

The same low number for both directions, lower number for C=C

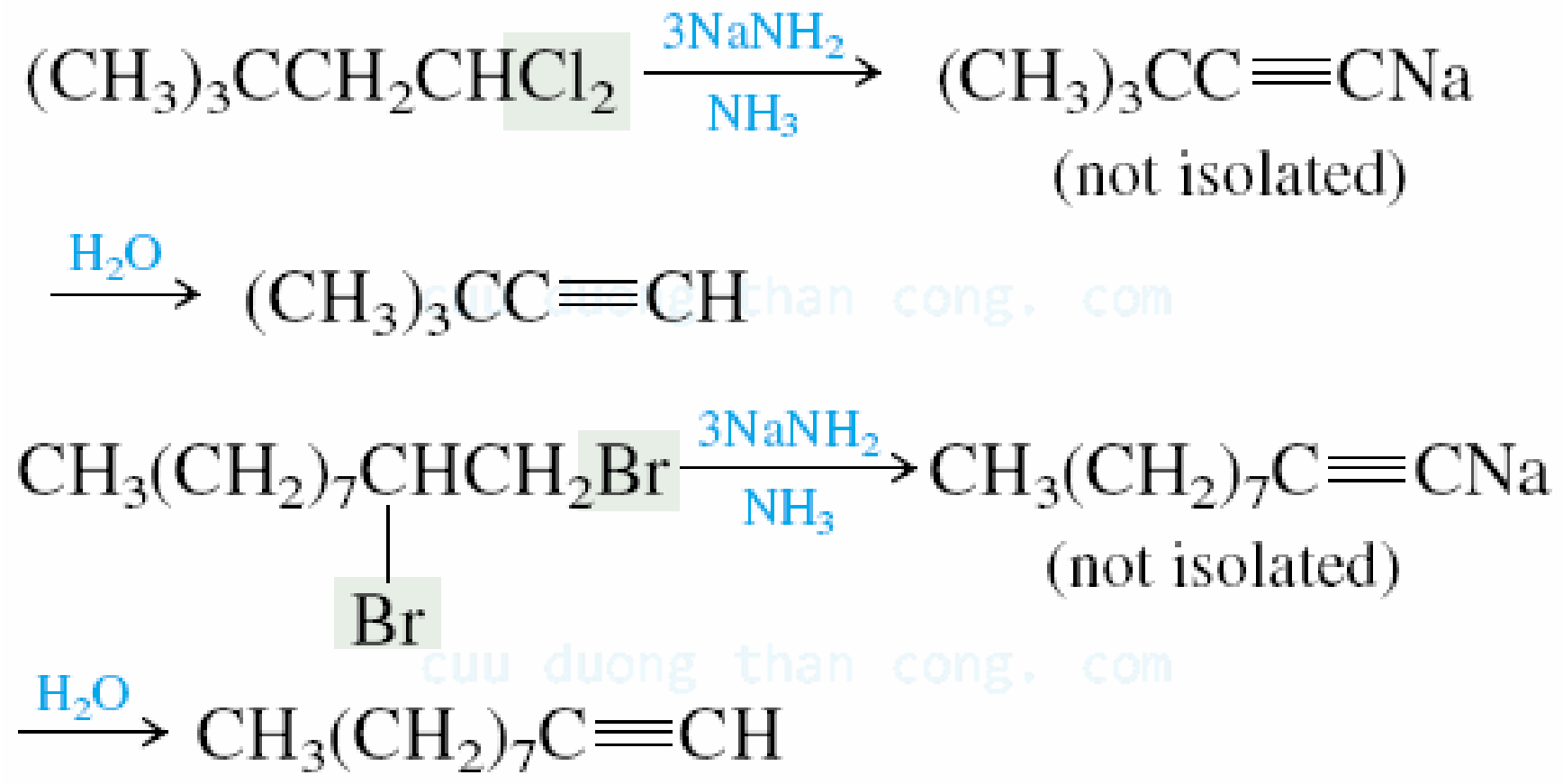
PREPARATION OF ALKYNES

Sources of acetylene

$$\underset{\substack{\text{Calcium oxide}\\\text{(from limestone)}}}{CaO} + \underset{\substack{\text{Carbon}\\\text{(from coke)}}}{3C} \xrightarrow{1800\text{–}2100^{\circ}C} \underset{\text{Calcium carbide}}{CaC_2} + CO$$

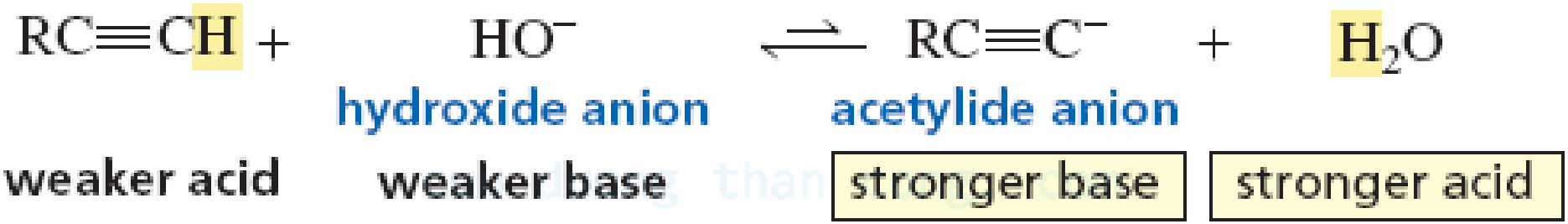
$$\underset{\text{Calcium carbide}}{Ca^{2+}\left[:C\equiv C:\right]^{2-}} + 2H_2O \longrightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Acetylene}}{HC\equiv CH}$$

Alkynes by elimination reactions



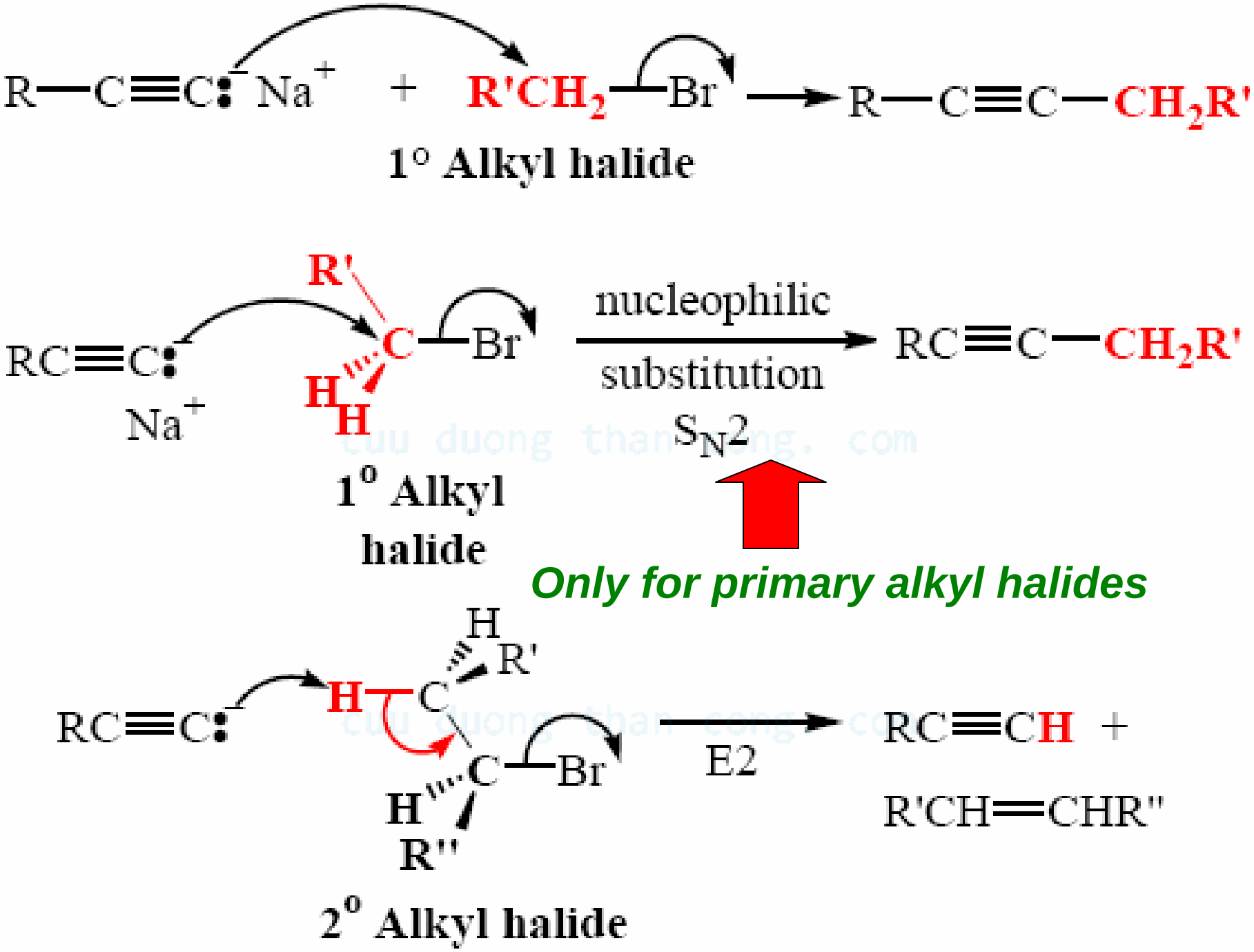
REACTIONS OF ALKYNES

Acidic hydrogen

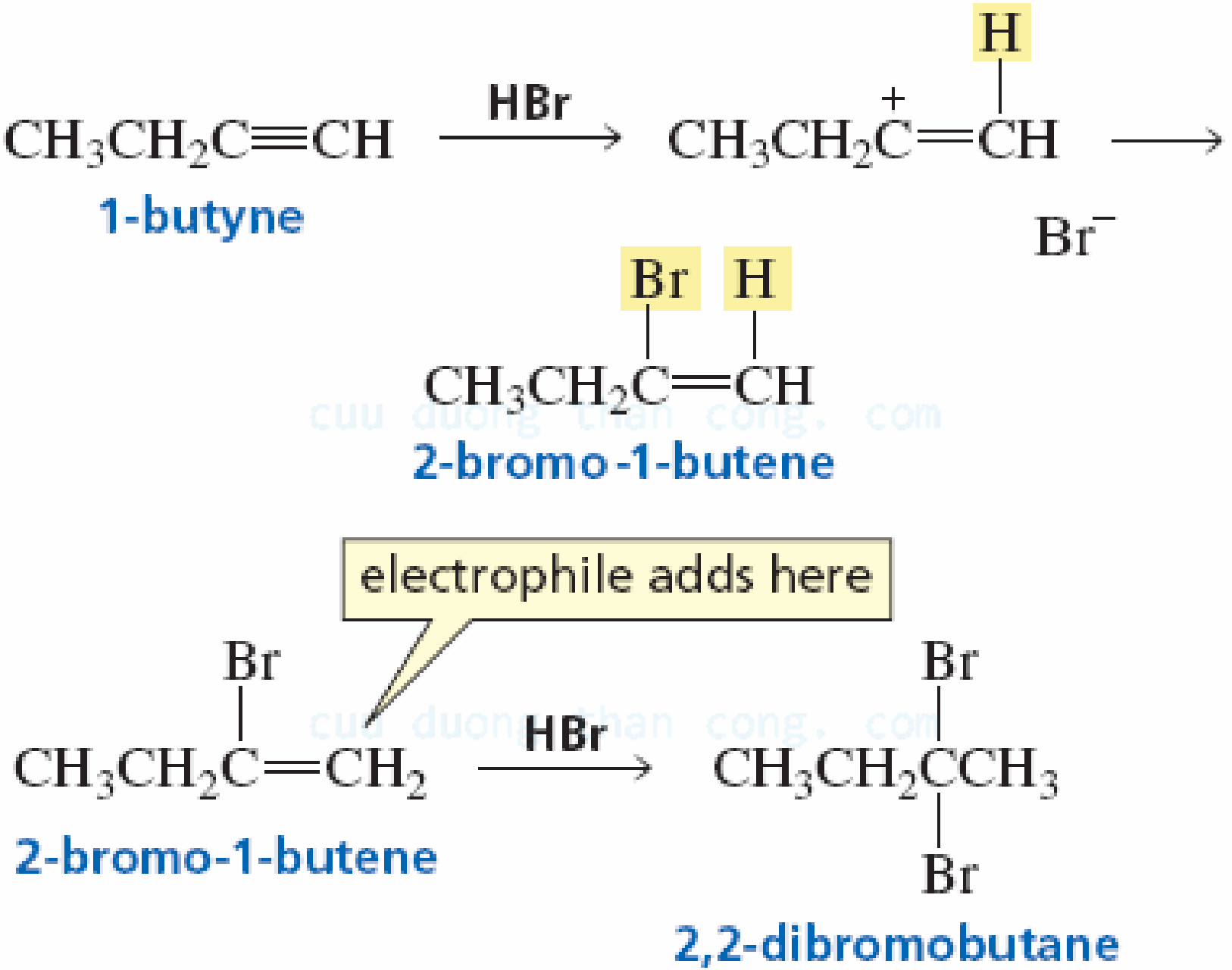


strongest base

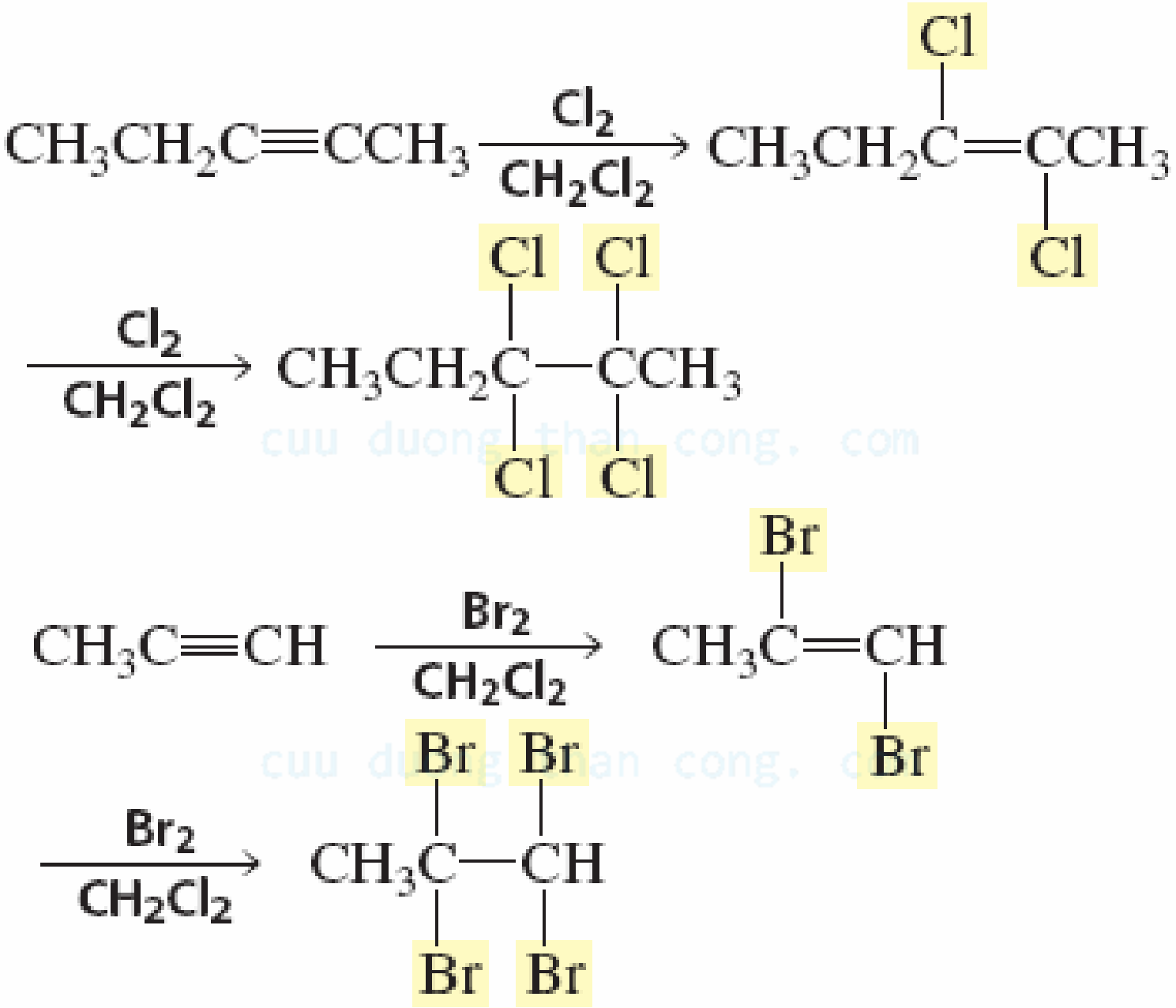
$$CH_3CH_2^- > H_2C{=}CH^- > H_2N^- > HC{\equiv}C^- > HO^- > F^-$$


R—C≡C: Na+ + R'CH2—Br → R—C≡C—CH2R'
1° Alkyl halide
R'
RC≡C:
Na+
C
Br
H
H
nucleophilic
substitution
SN2
RC≡C—CH2R'
1° Alkyl
halide
Only for primary alkyl halides
H
R'
RC≡C:
H
C
C
Br
H
R''
E2
RC≡CH +
R'CH=CHR''
2° Alkyl halide

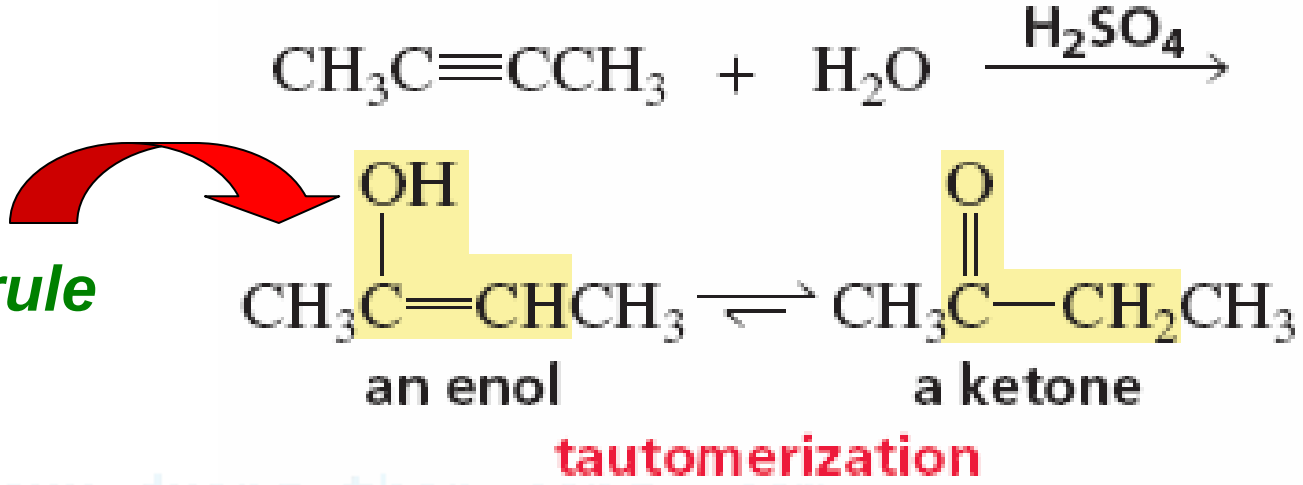
Additions of hydrogen halides (A_E)



Additions of halogens (A_E)

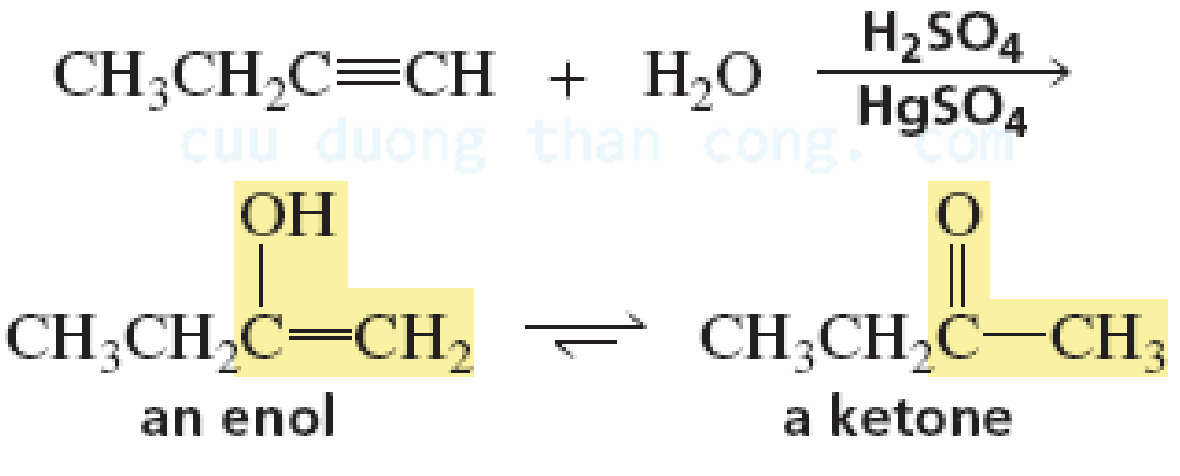


Additions of water – hydration reactions

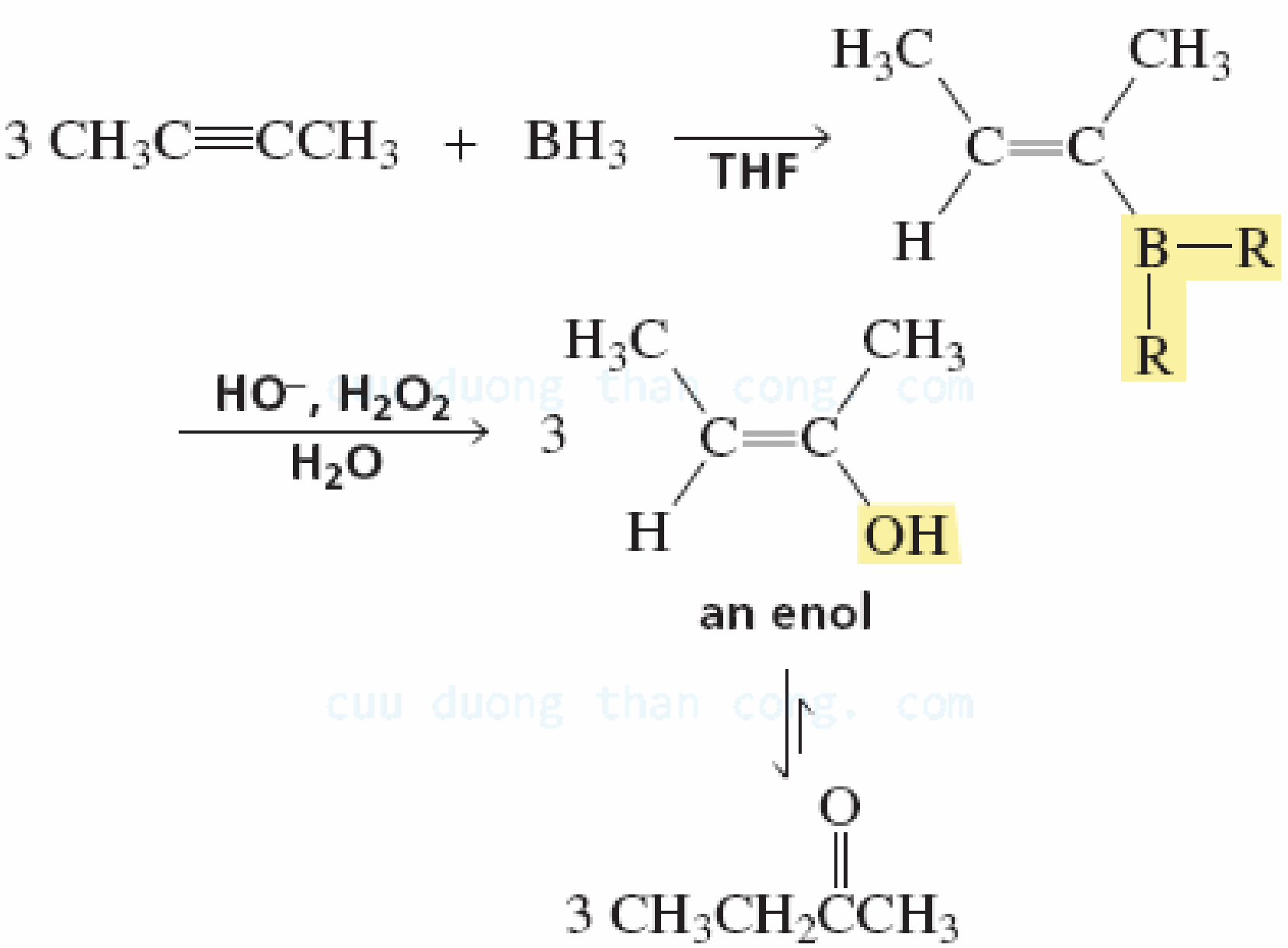


Markovnikov's rule

Terminal alkynes are less reactive than internal alkynes, need Hg^{2+} as a catalyst

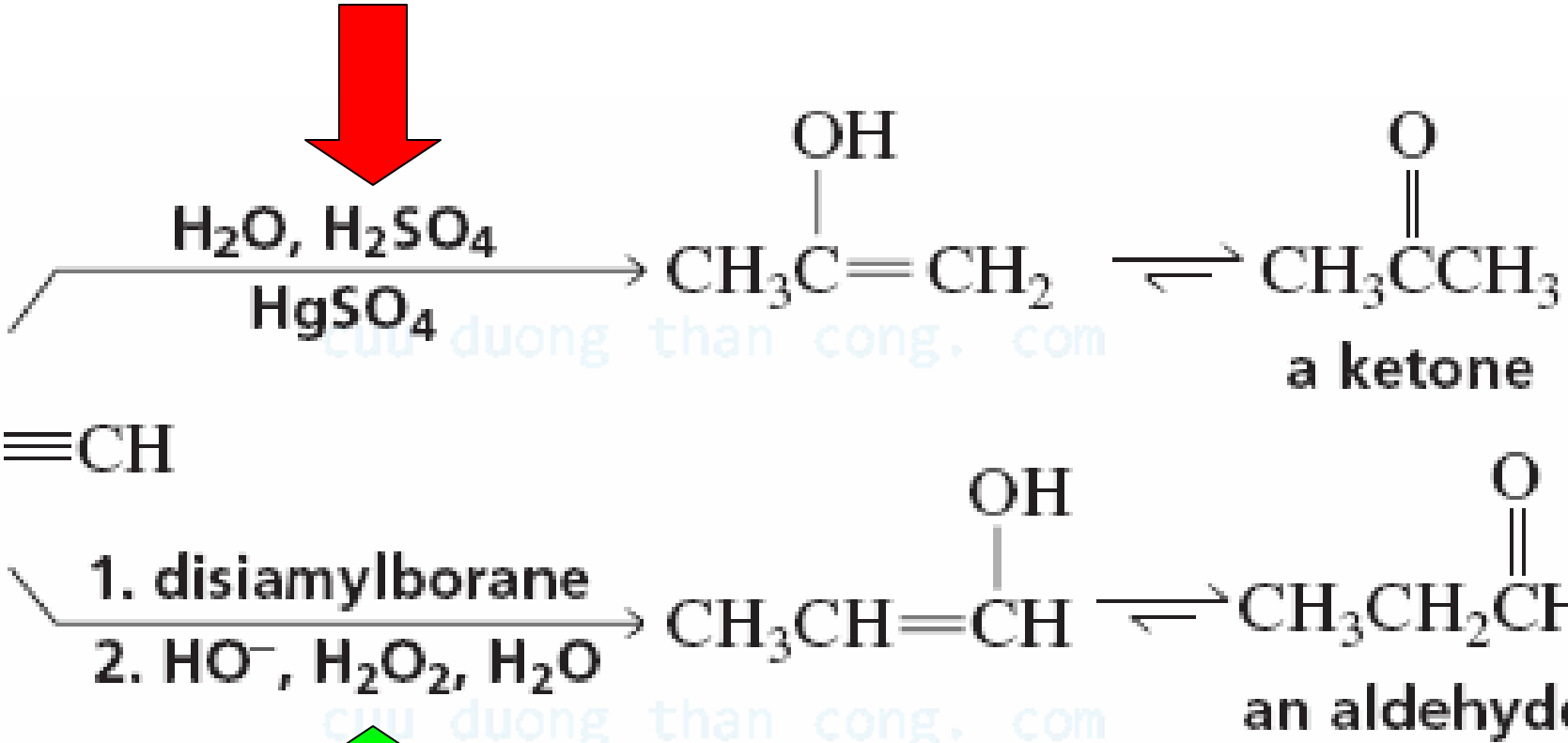


Additions of boran – hydroboration & oxidation



Regioselectivity

Markovnikov's rule



Anti-Markovnikov

Additions of hydrogen – hydrogenation

Product is alkane

$CH_3CH_2C{\equiv}CH \xrightarrow[Pt/C]{H_2} CH_3CH_2CH{=}CH_2$

alkyne → alkene

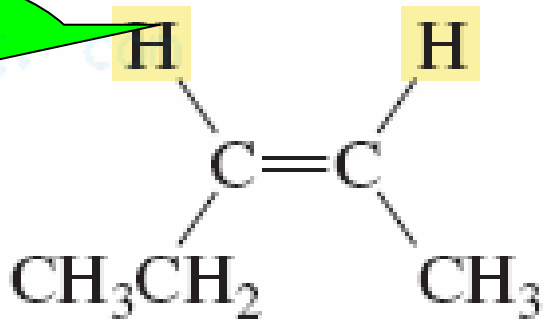
$\xrightarrow[Pt/C]{H_2} CH_3CH_2CH_2CH_3$

alkane

Product is alkene

$CH_3CH_2C{\equiv}CCH_3 \xrightarrow[\text{Lindlar catalyst}]{H_2}$

2-pentyne

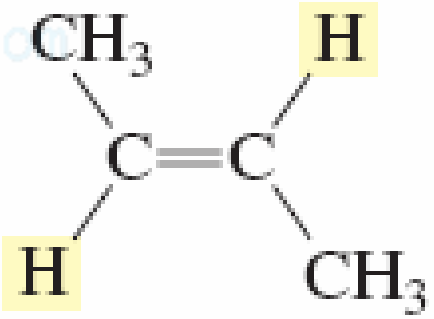


cis-2-pentene

$CH_3C{\equiv}CCH_3 \xrightarrow[NH_3\,(liq)]{\text{Na or Li}}$

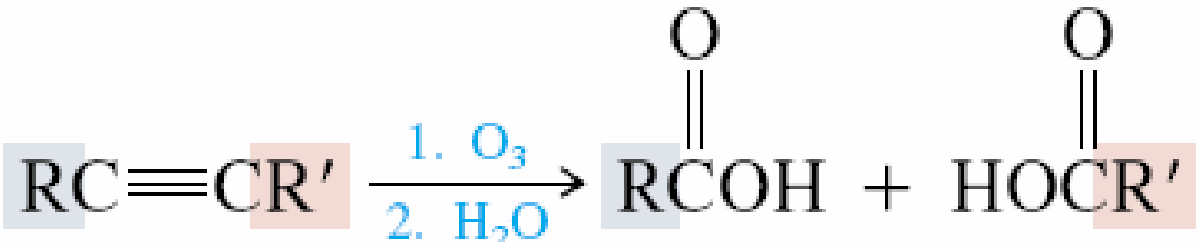
2-butyne

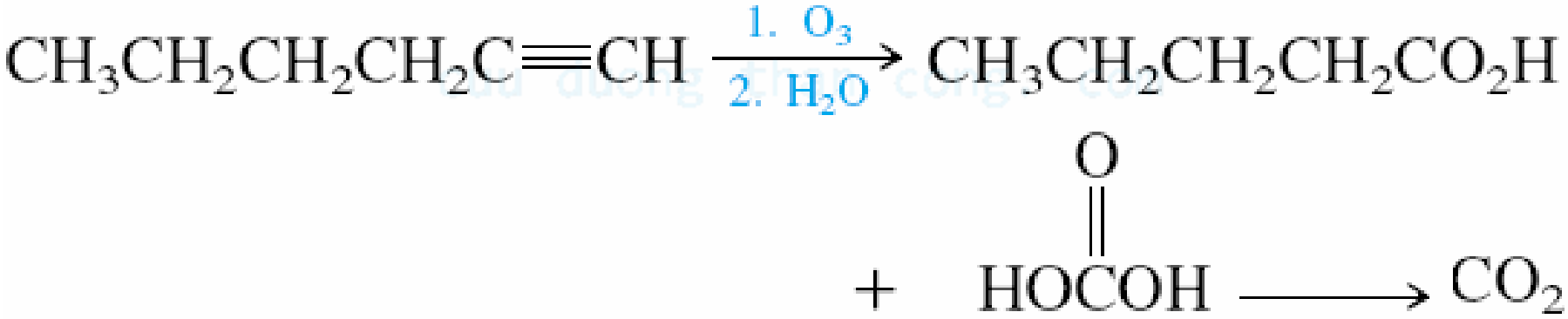
–78 °C



trans-2-butene

Ozonolysis of alkynes





Ozonolysis used to be employed in structure determination, but has been superseded by spectroscopic methods

Polymerizations