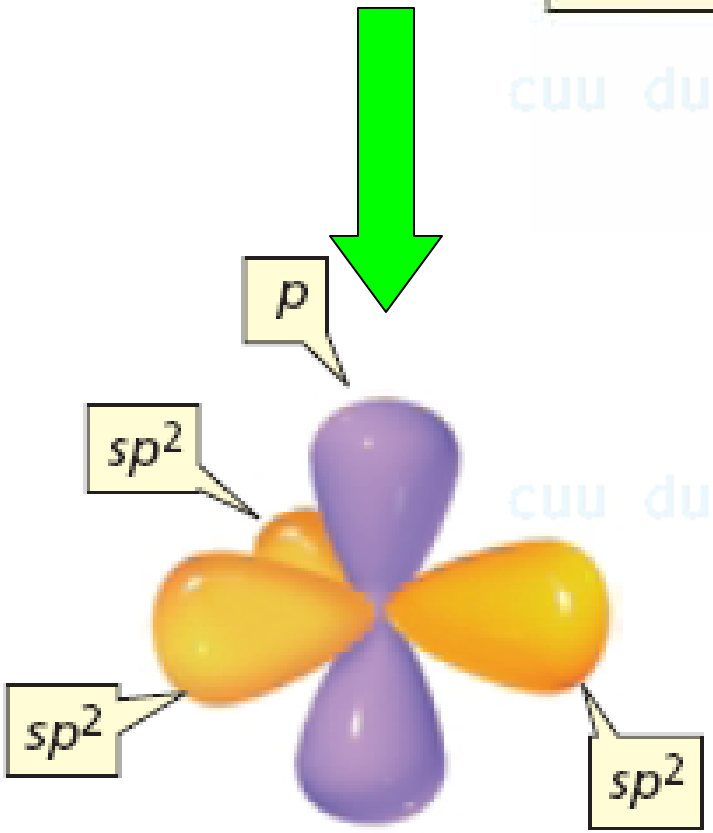
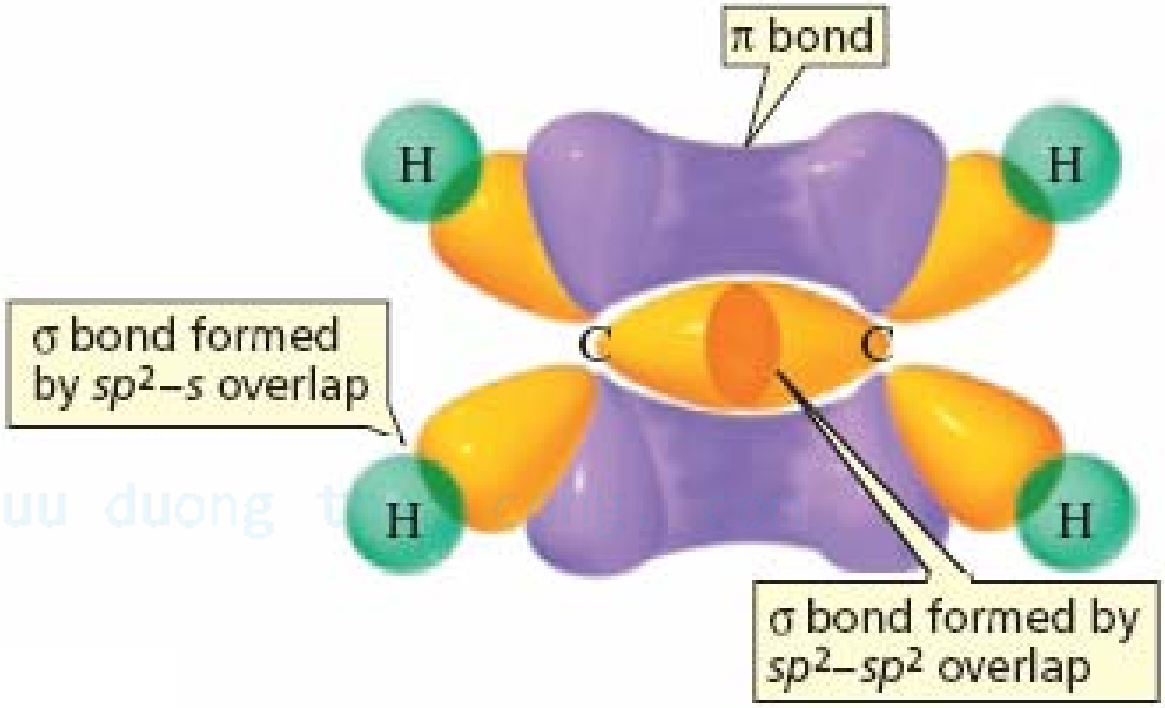
ORGANIC CHEMISTRY

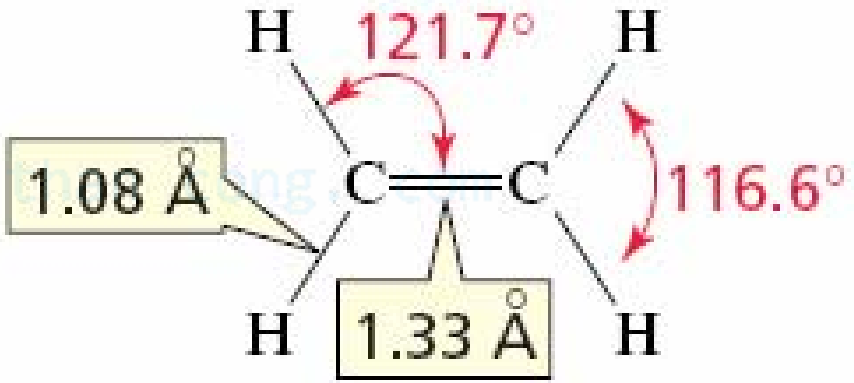
Dr Nam T. S. Phan
Faculty of Chemical Engineering
HCMC University of Technology
Office: room 211, B2 Building
Phone: 38647256 ext. 5681
Email: ptsnam@hcmut.edu.vn

Chapter 5: ALKENES

An sp^2 hybridized carbon



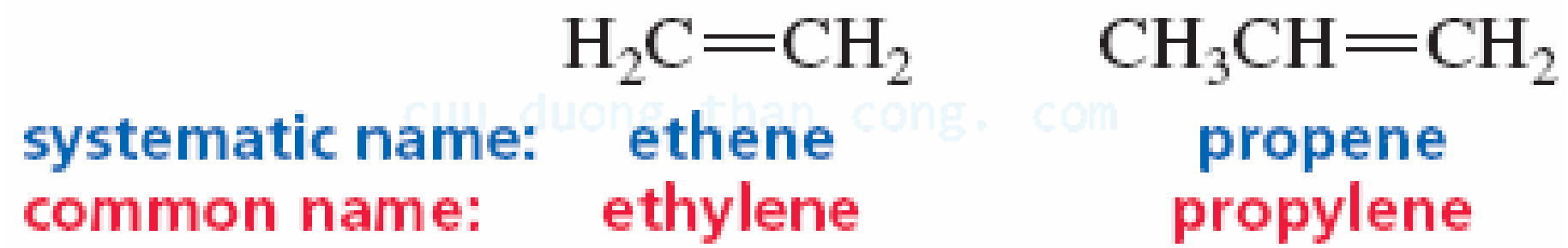




a double bond consists of one σ bond and one π bond

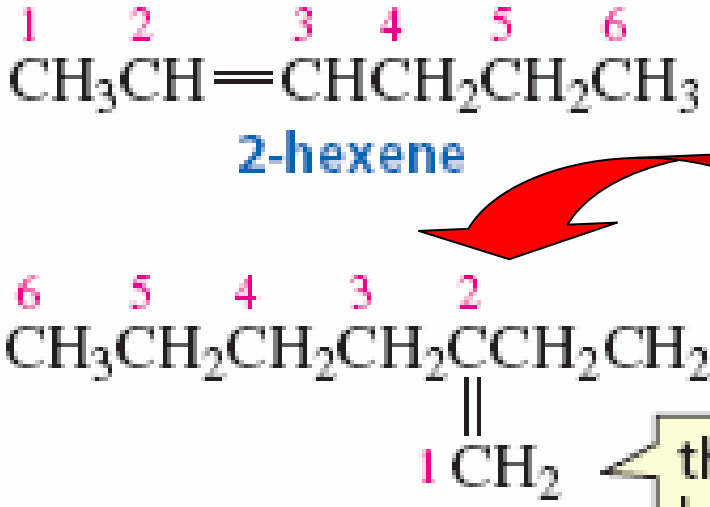
NOMENCLATURE OF ALKENES

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

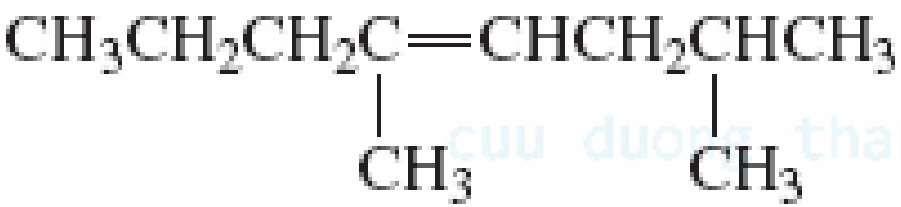


- ***Ethylene*** **is an acceptable synonym for ethene in the IUPAC system**
- ***Propylene, isobutylene*** **and other common names ending in "*ylene*" are NOT acceptable IUPAC names**

Determine the parent hydrocarbon – *the longest continuous carbon chain <u>containing the C=C</u>*



the longest continuous chain has eight carbons but the longest continuous chain containing the functional group has six carbons, so the parent name of the compound is hexene

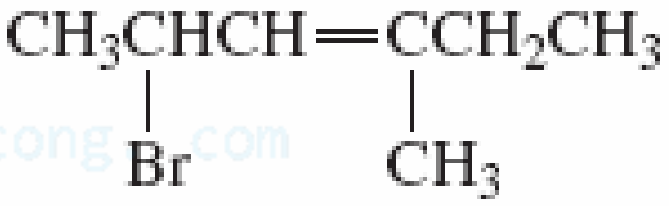


2,5-dimethyl-4-octene

not

4,7-dimethyl-4-octene

because 2 < 4



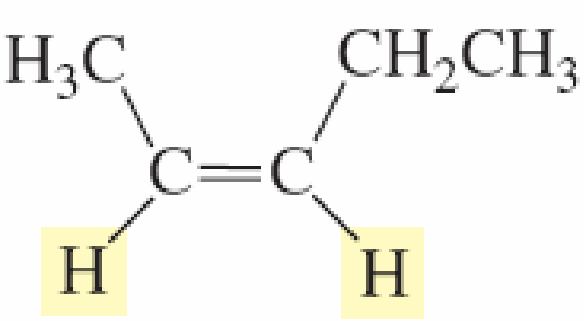
2-bromo-4-methyl-3-hexene

not

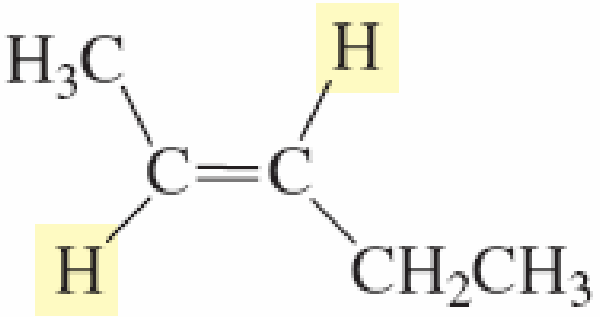
5-bromo-3-methyl-3-hexene

because 2 < 3

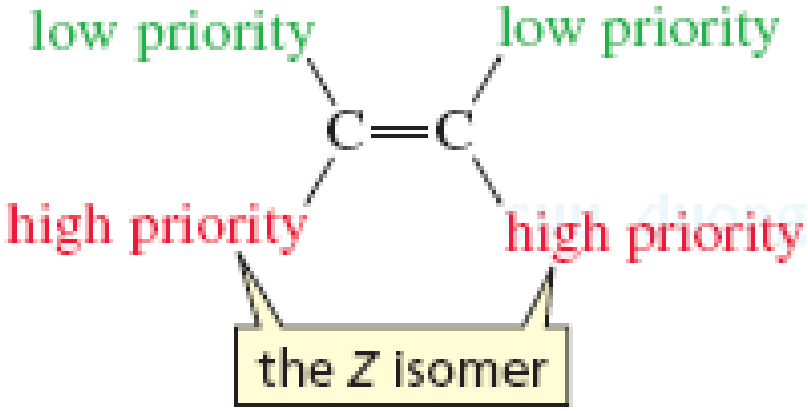
Note: Alkenes can have geometric isomers

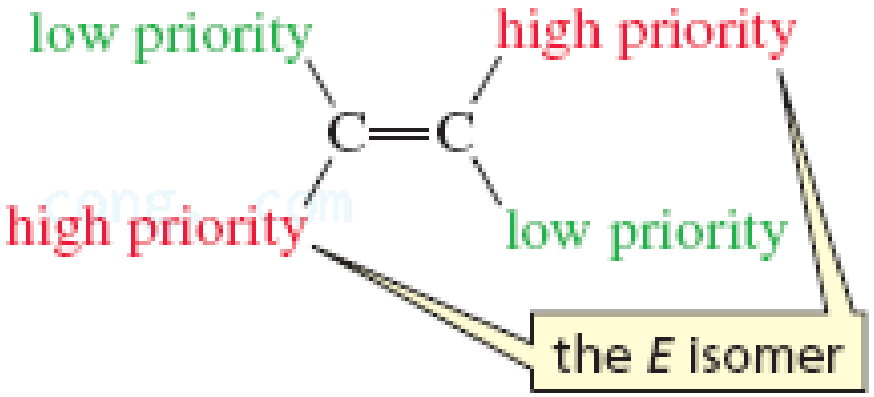


cis-2-pentene



trans-2-pentene

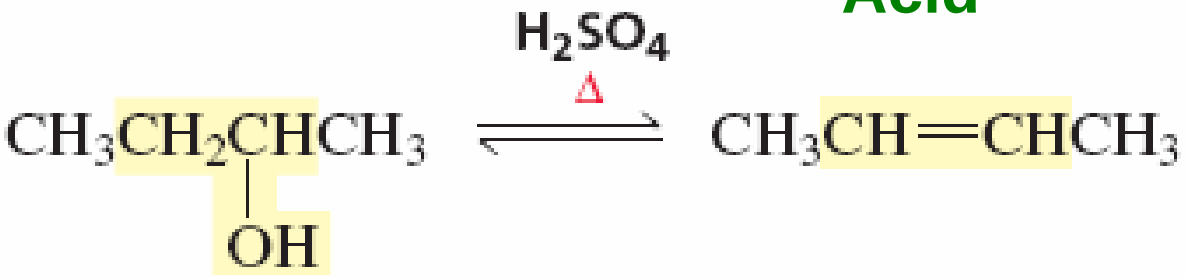


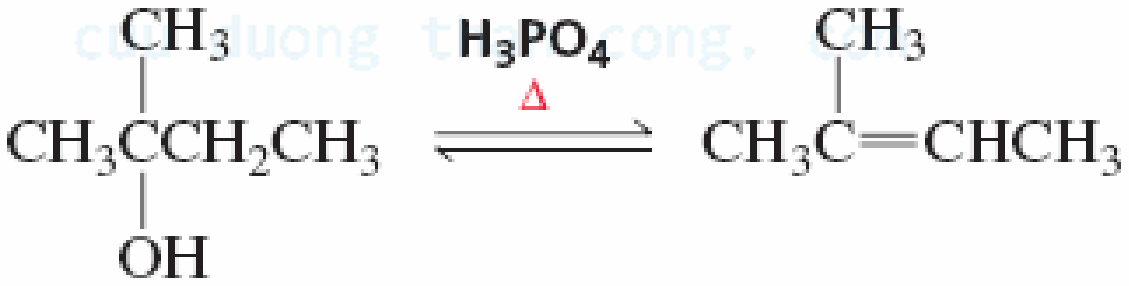


PREPARATION OF ALKENES

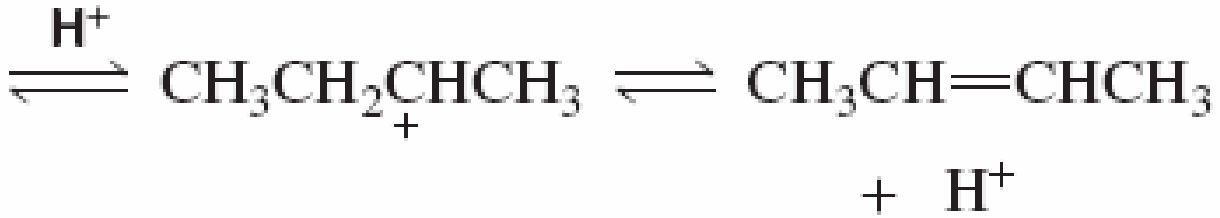
Dehydrations of alcohols

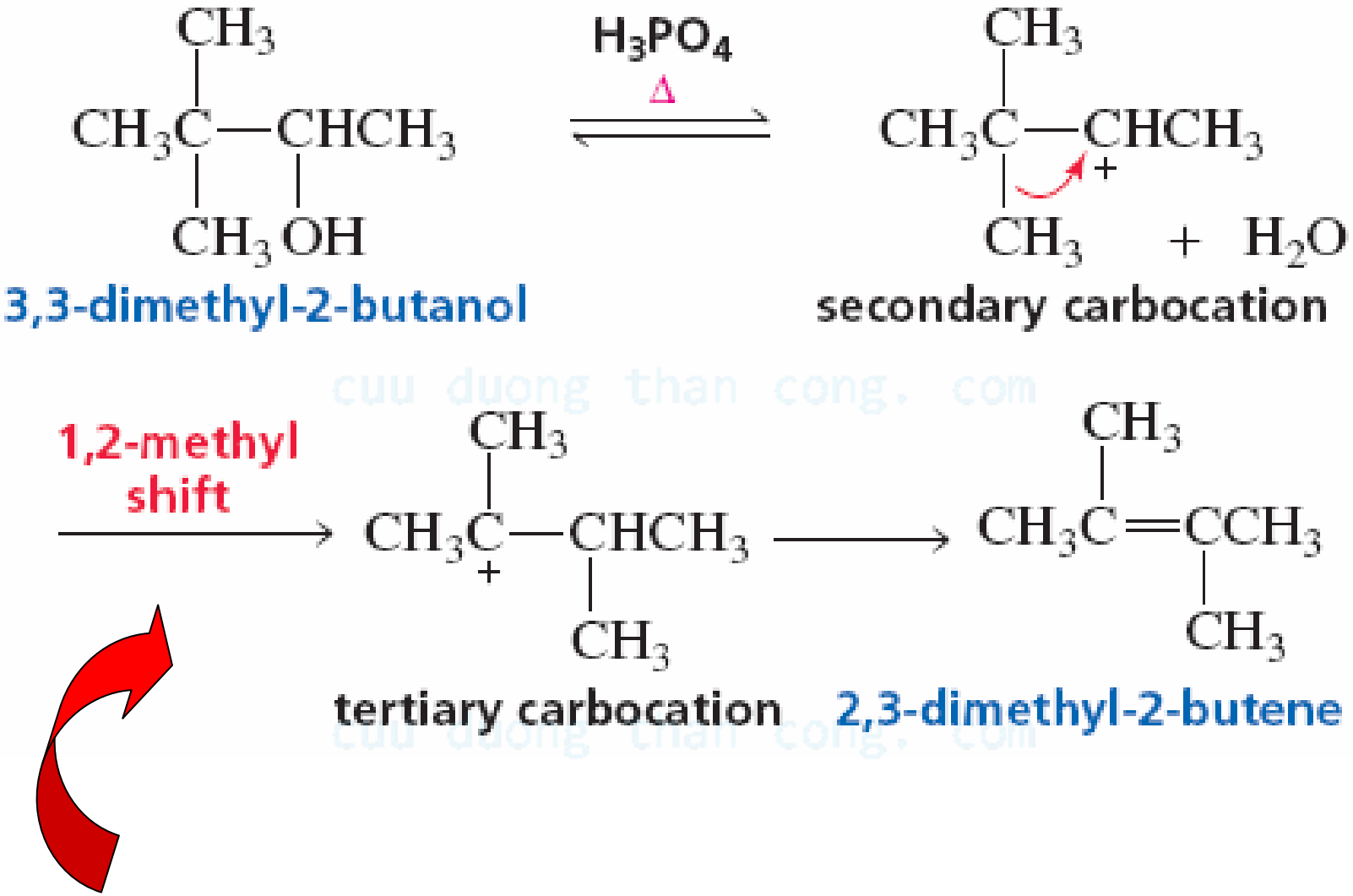
Acid



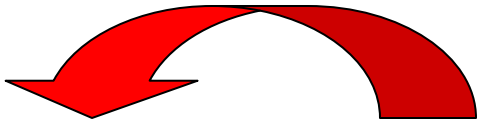


isomerization

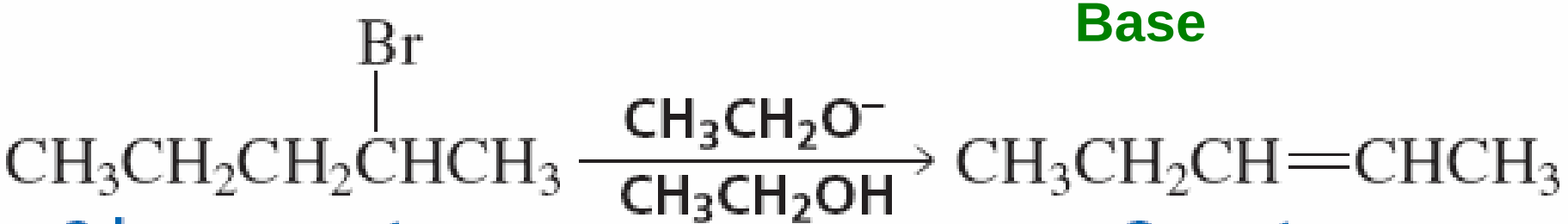




Eliminations of alkyl halides

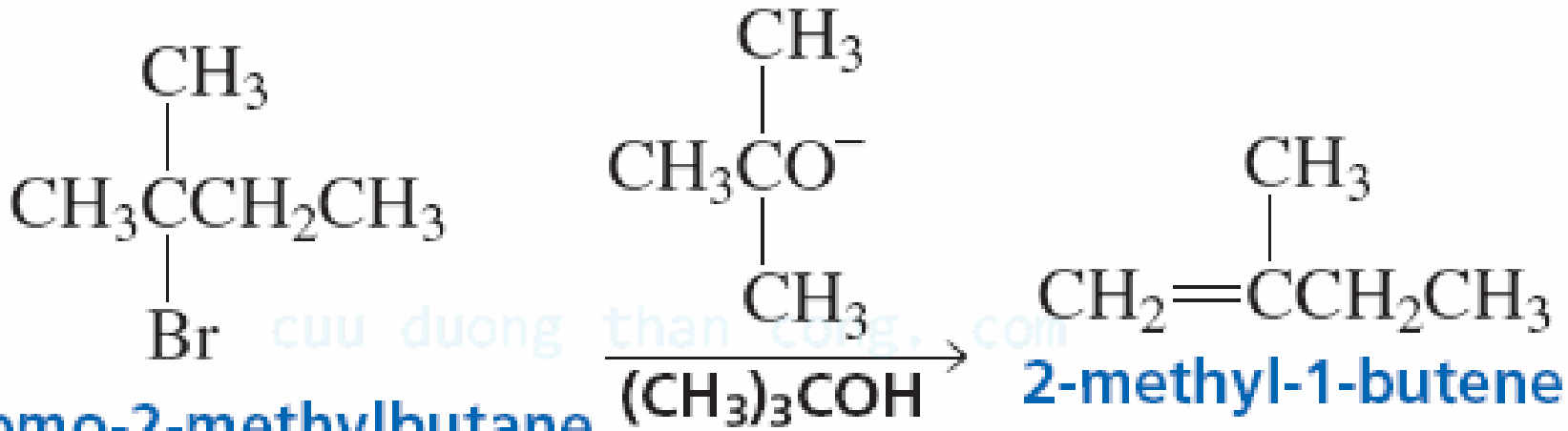


Base



2-bromopentane

2-pentene

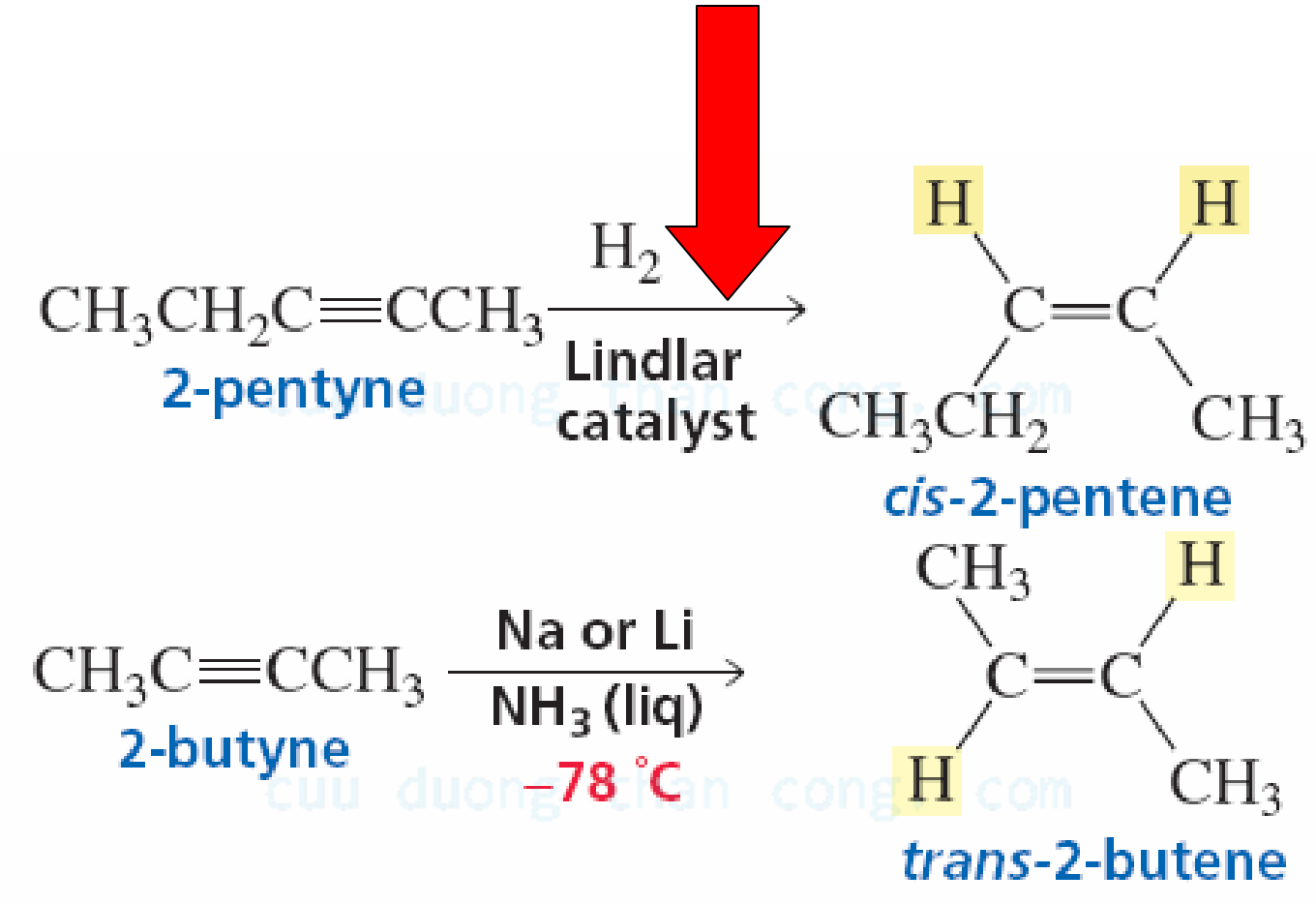


2-bromo-2-methylbutane

2-methyl-1-butene

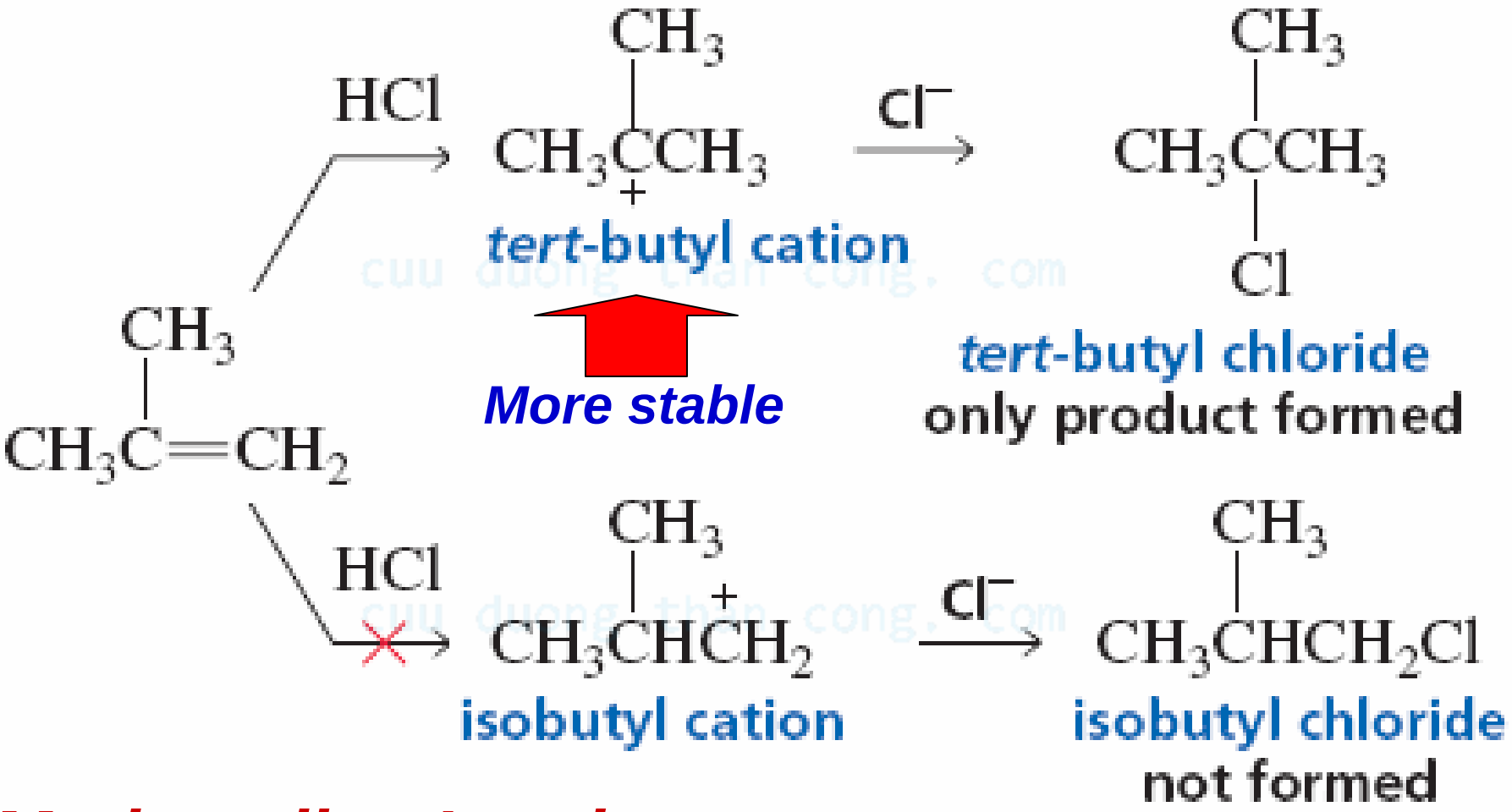
Alkyne hydrogenations

$Pd/CaCO_3$ + $Pb(OAc)_2$ / quinoline



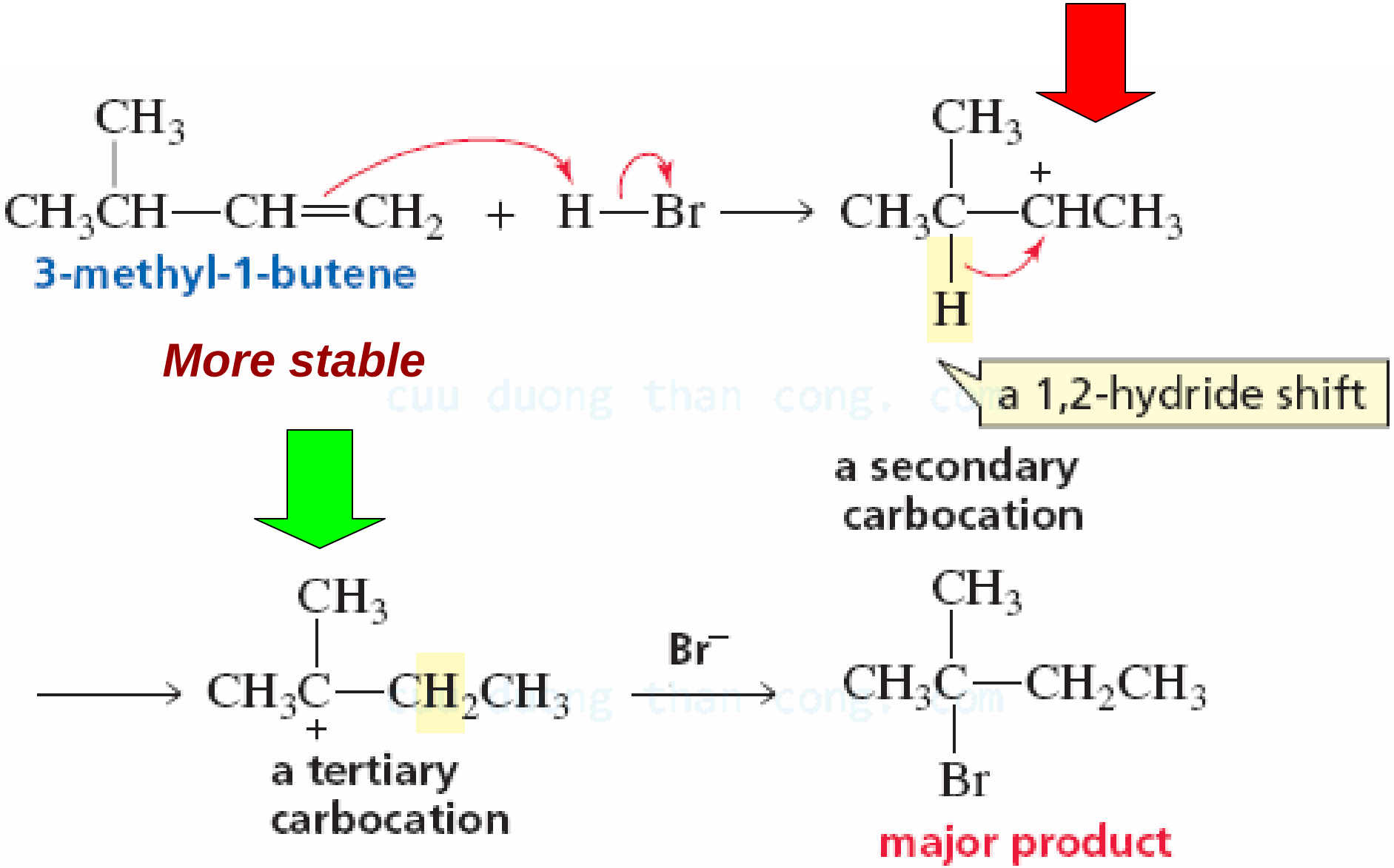
REACTIONS OF ALKENES

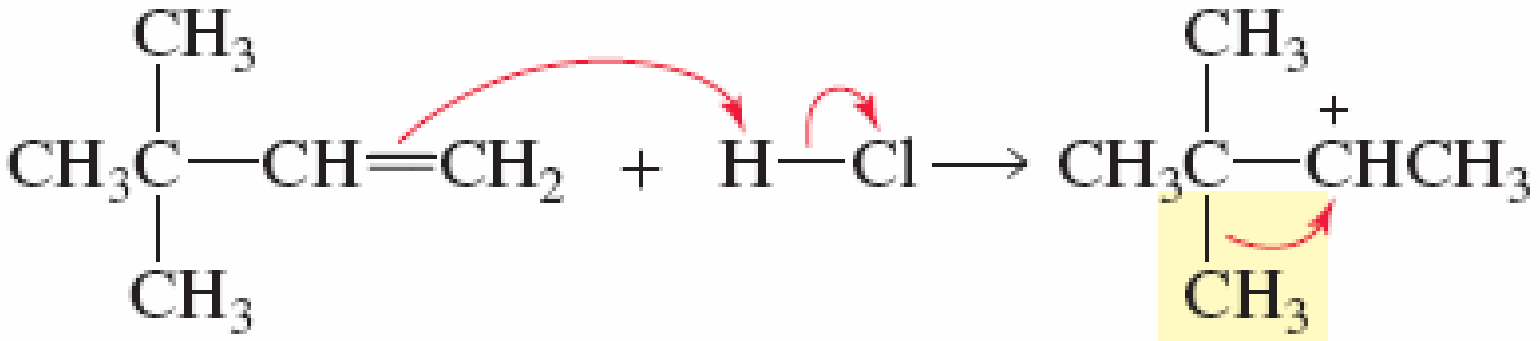
Additions of hydrogen halides (A_E)



Markovnikov's rule

Carbocation rearrangement

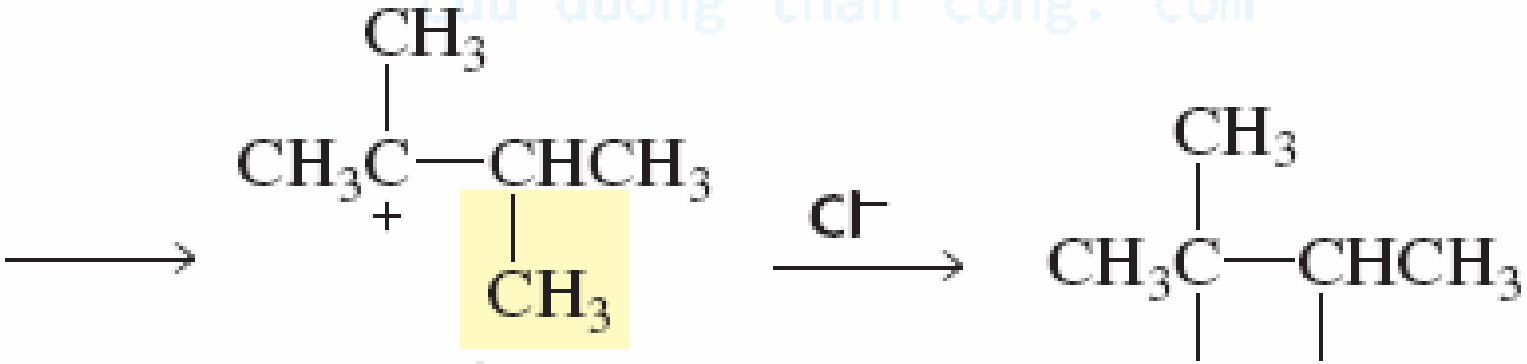




3,3-dimethyl-1-butene

a 1,2-methyl shift

a secondary carbocation

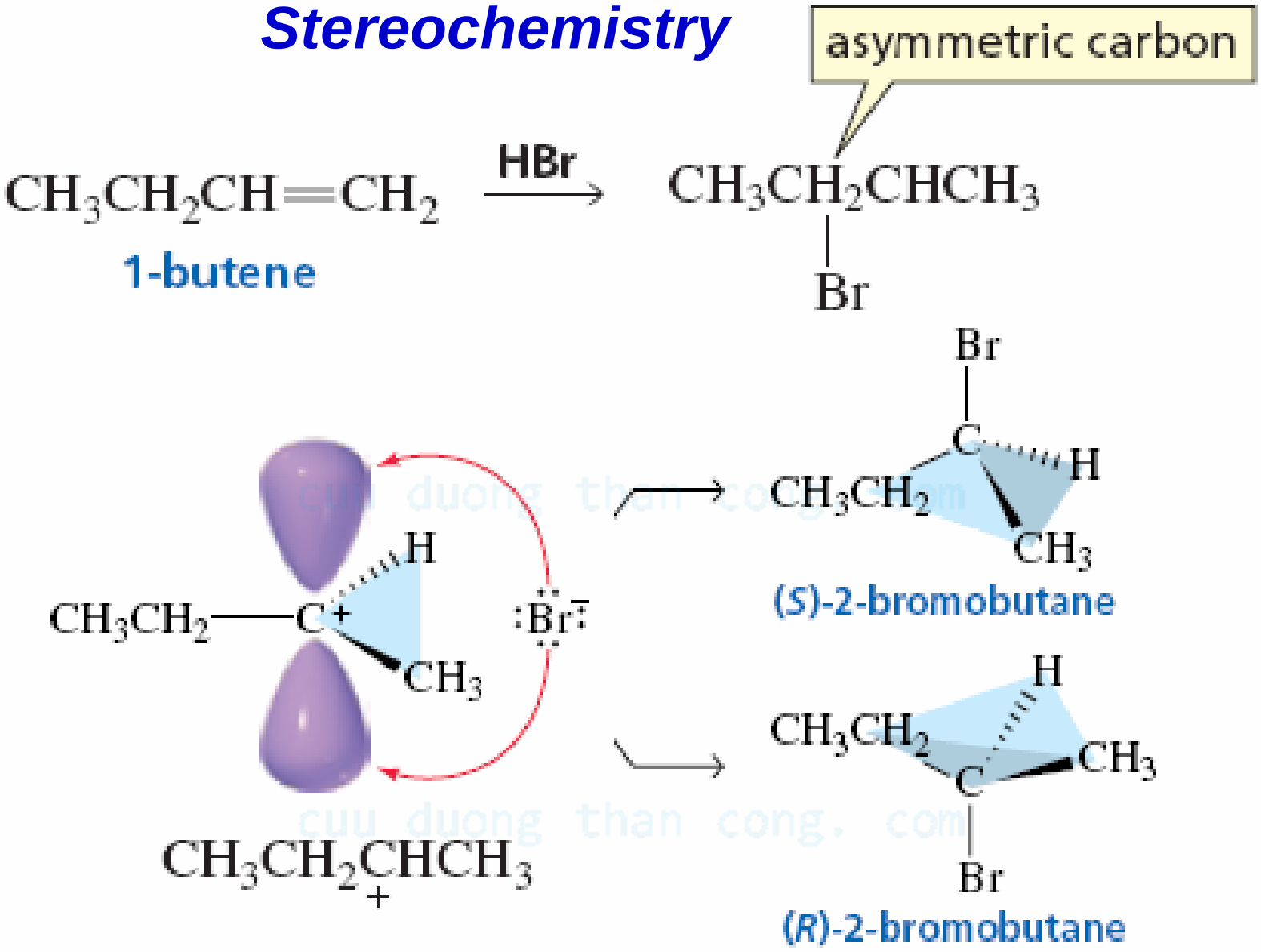


a tertiary carbocation

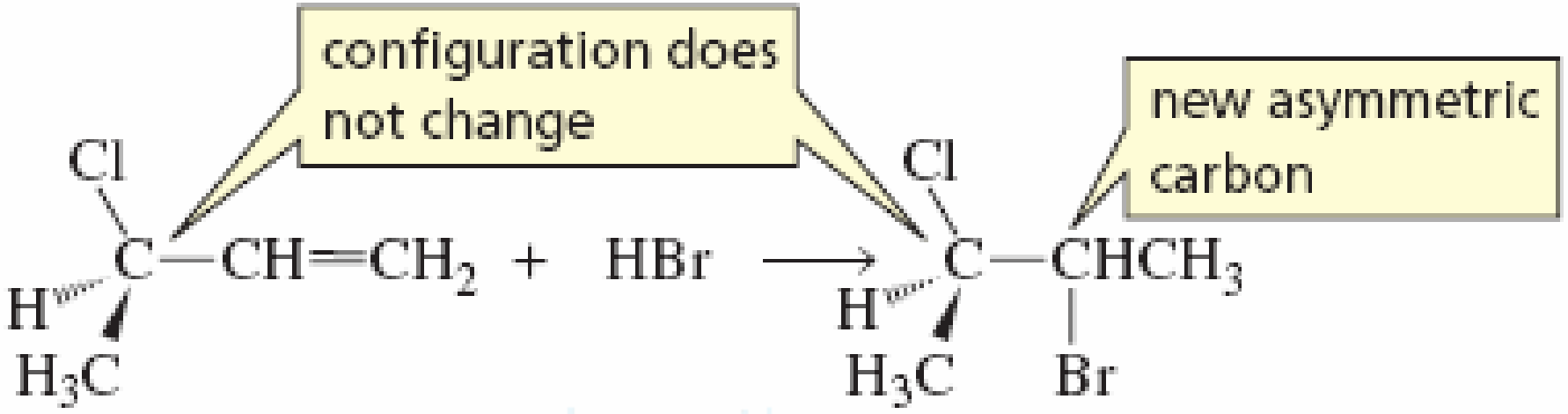
major product

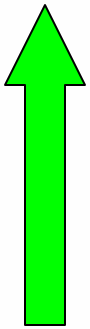
More stable

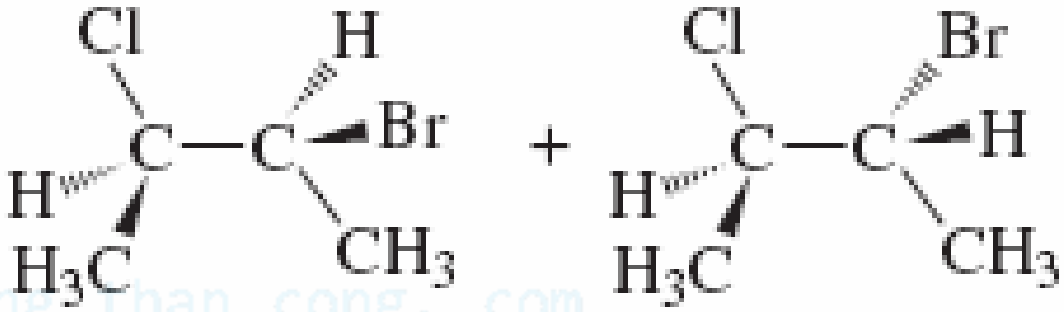
Stereochemistry



Racemic mixture



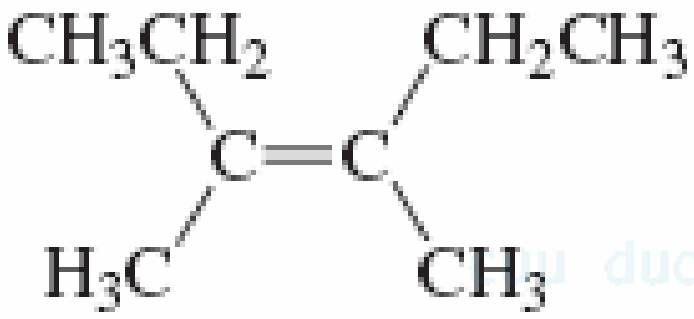




Already has 1 asymmetric carbon

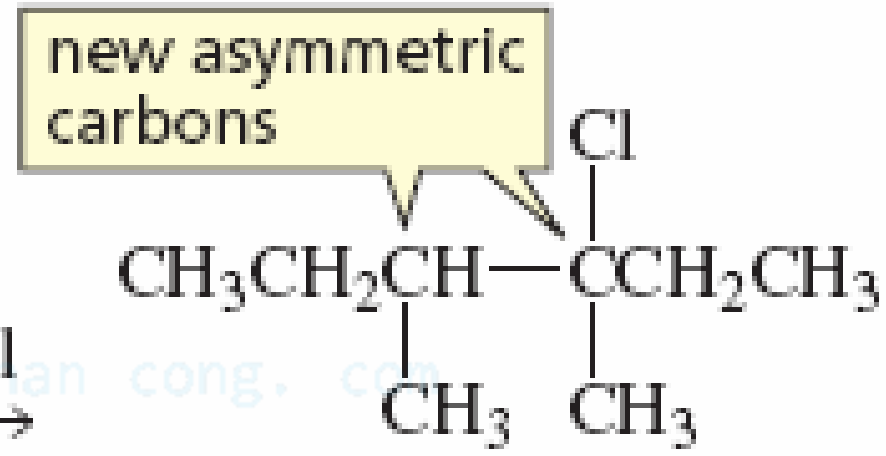
diastereomers

2 asymmetric carbons are created

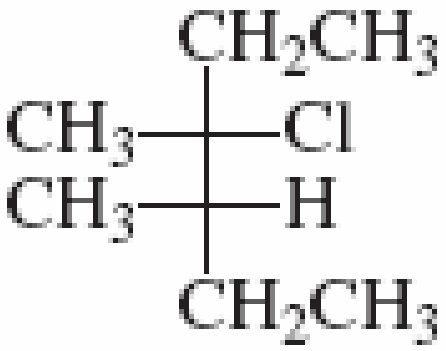


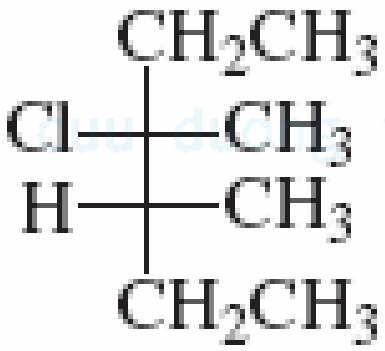
cis-3,4-dimethyl-3-hexene

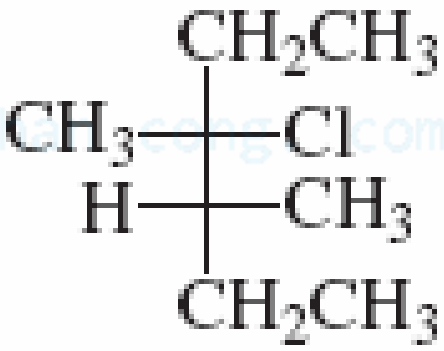
HCl

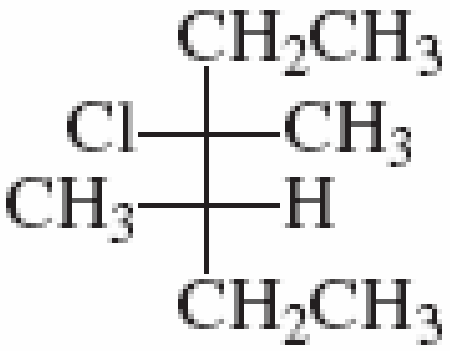


3-chloro-3,4-dimethylhexane



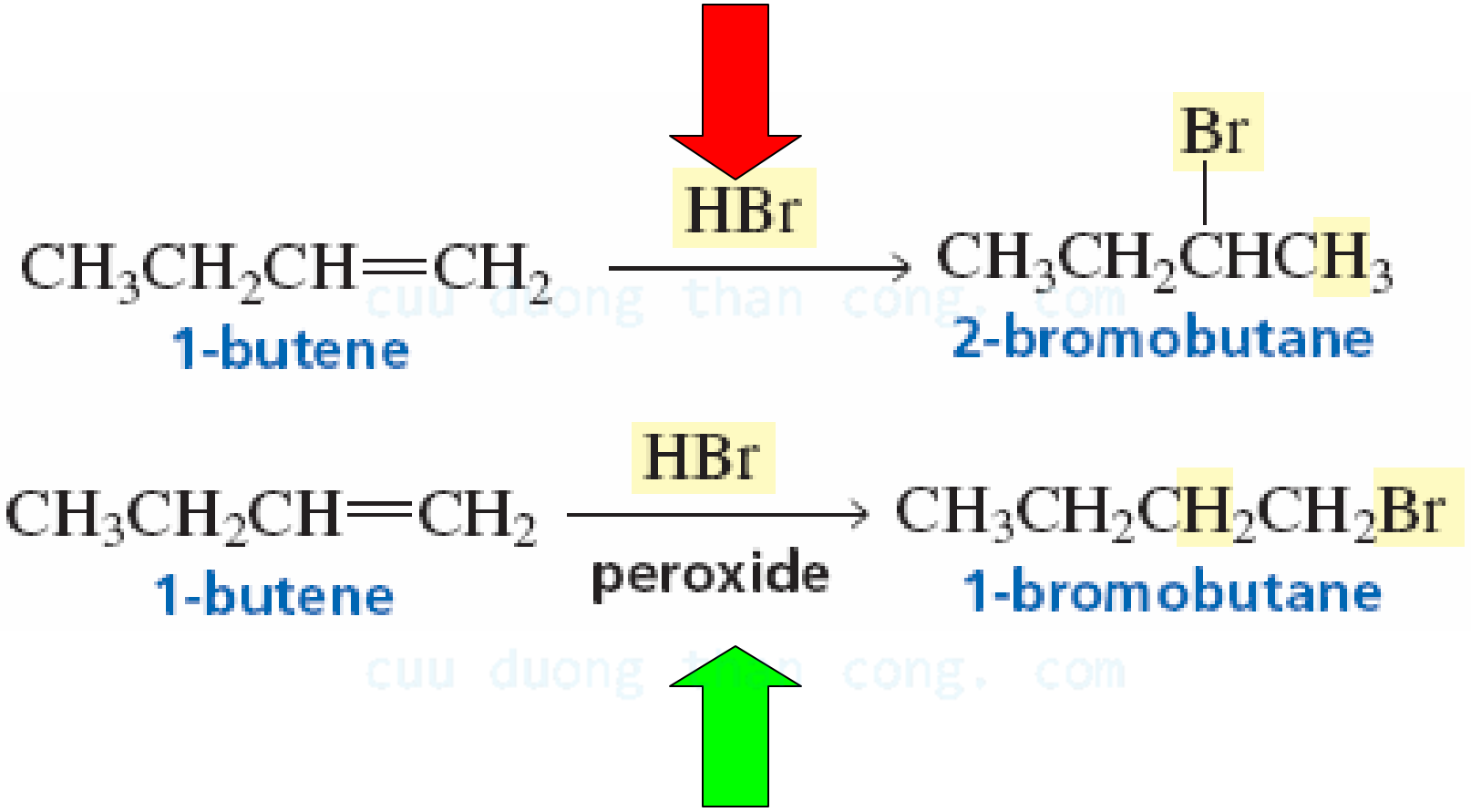






Additions of hydrogen bromide (A_R)

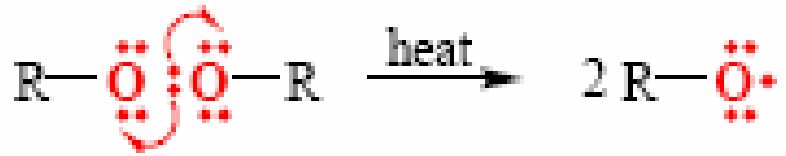
Electrophilic addition (A_E)



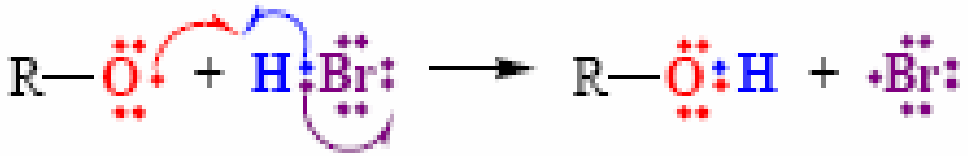
Radical addition (A_R) – <u>only for HBr</u>

Reaction mechanism:

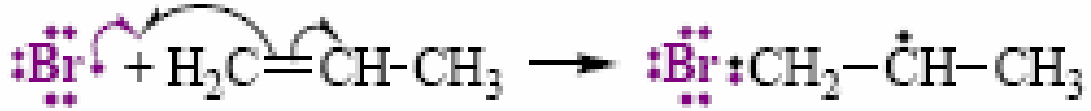
Chain Initiation

Step 1 

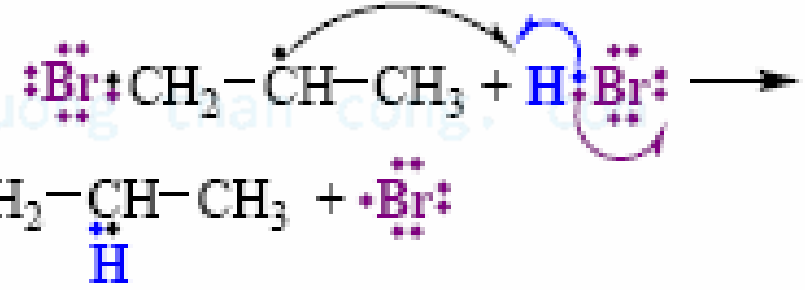
Heat brings about homolytic cleavage of the weak oxygen-oxygen bond.

Step 2 

The alkoxyl radical abstracts a H-atom from HBr, producing a Br-atom.

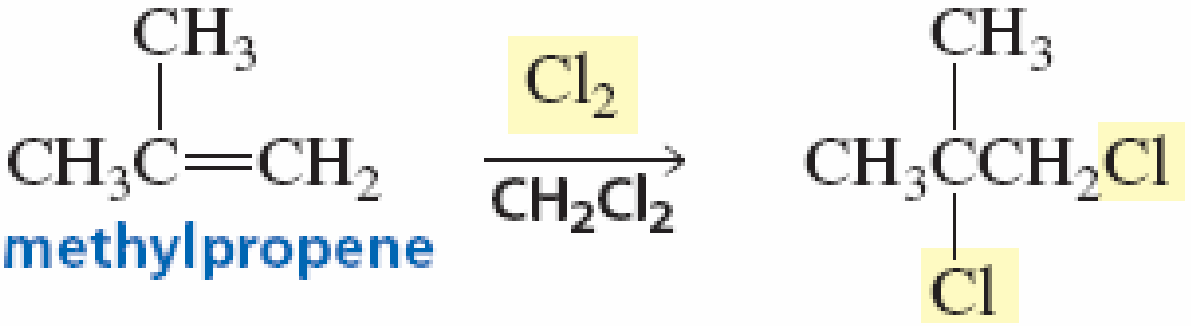
Step 3 

A Br-atom adds to the double bond to produce the more stable 2° radical.

Step 4 

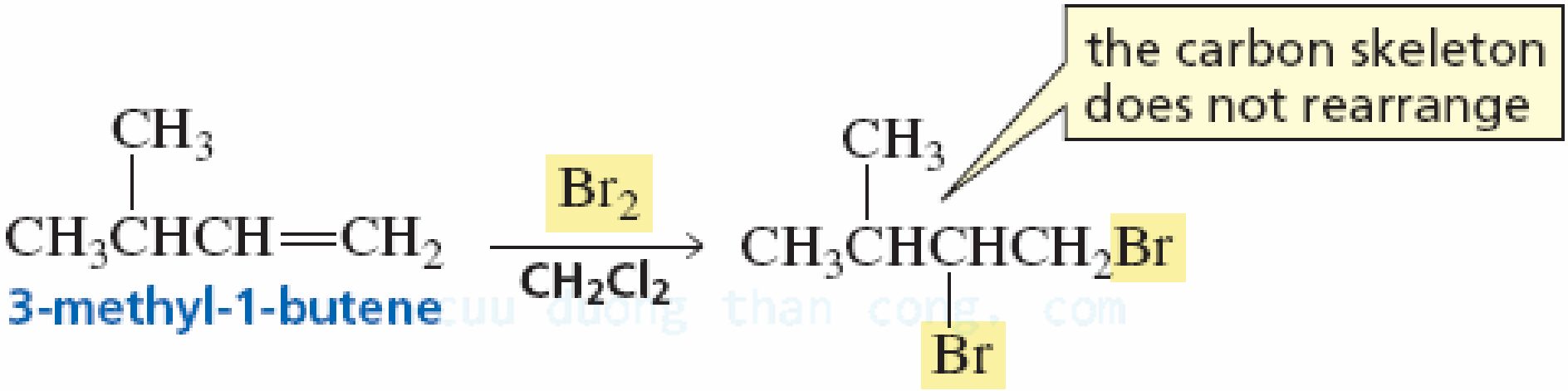
The 2° radical abstracts a H-atom from HBr. This leads to the product and regenerates a Br-atom.

Additions of halogens



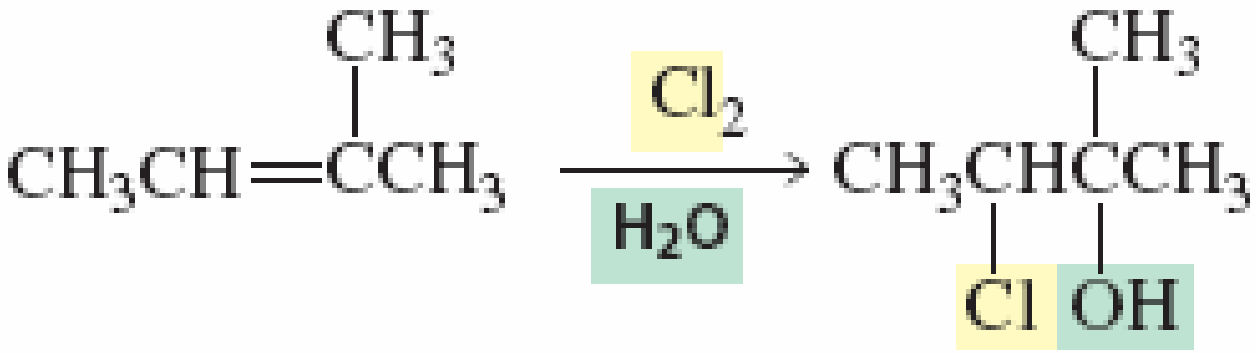
2-methylpropene

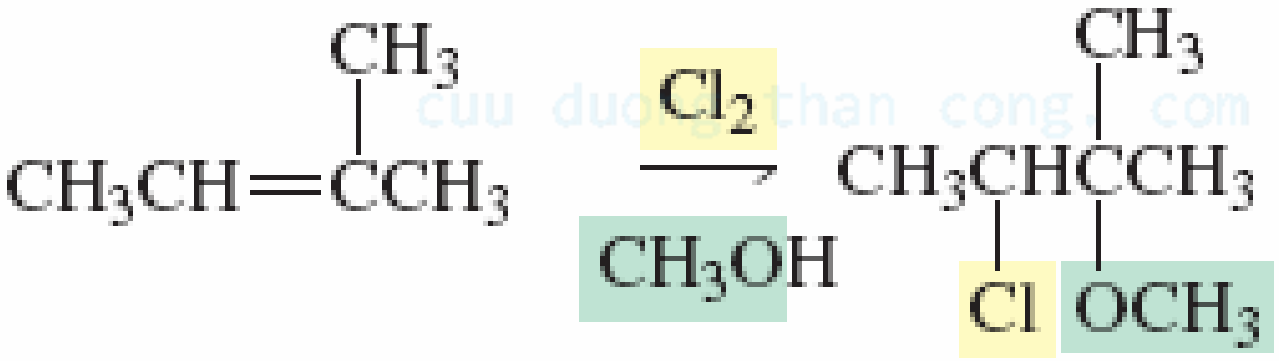
1,2-dichloro-2-methylpropane

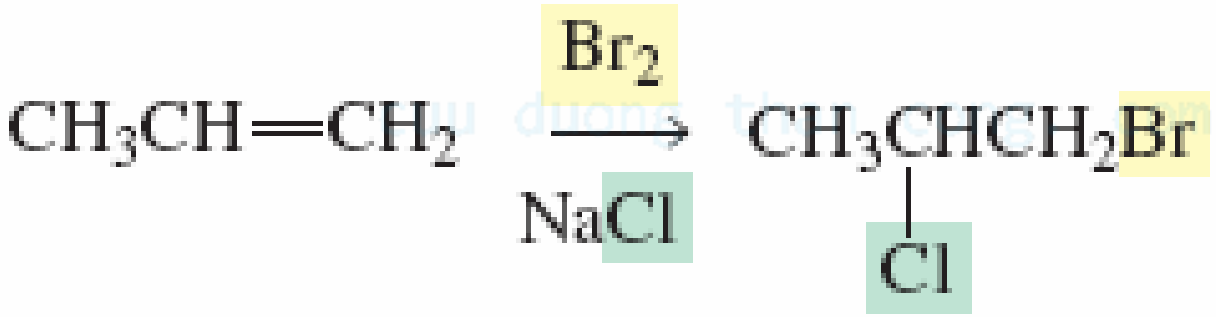


3-methyl-1-butene

1,2-dibromo-3-methylbutane

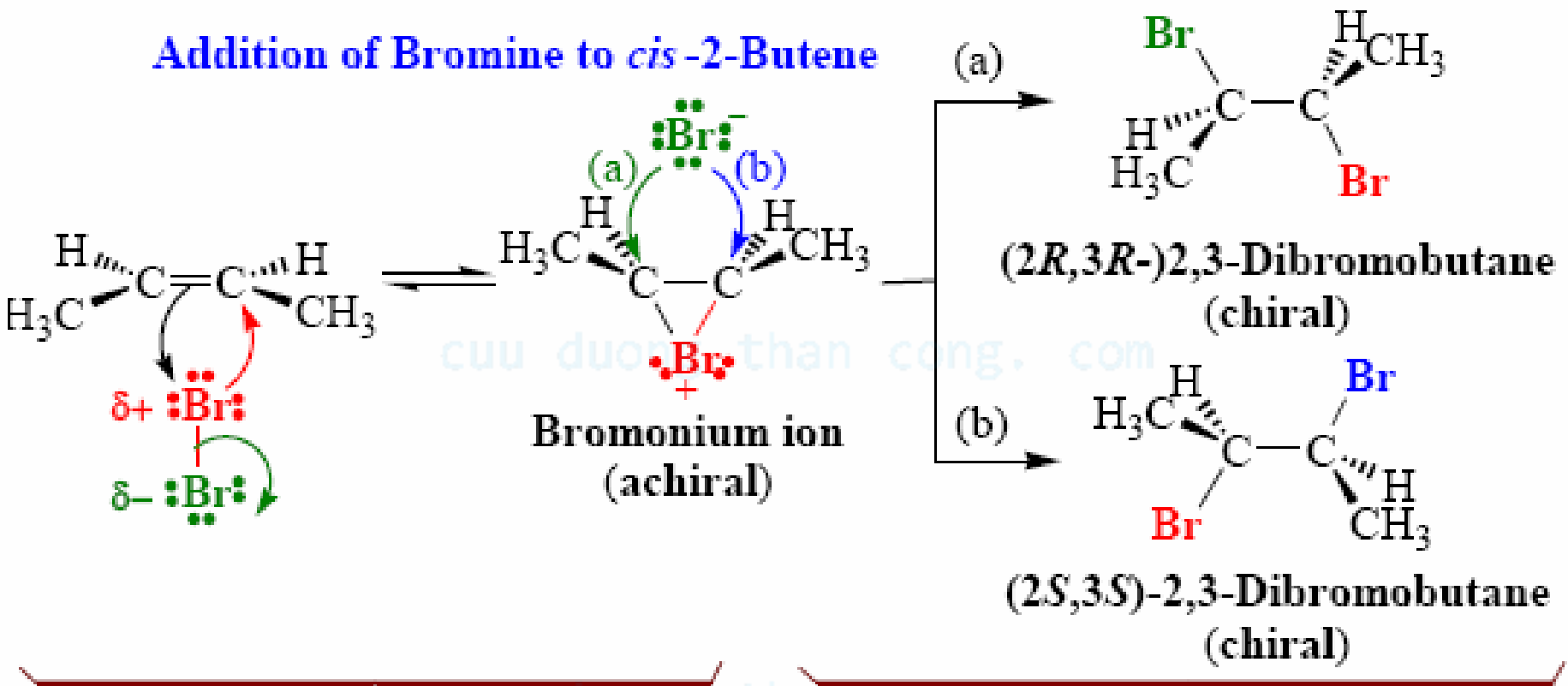






Major addition product – NOT a dihalide

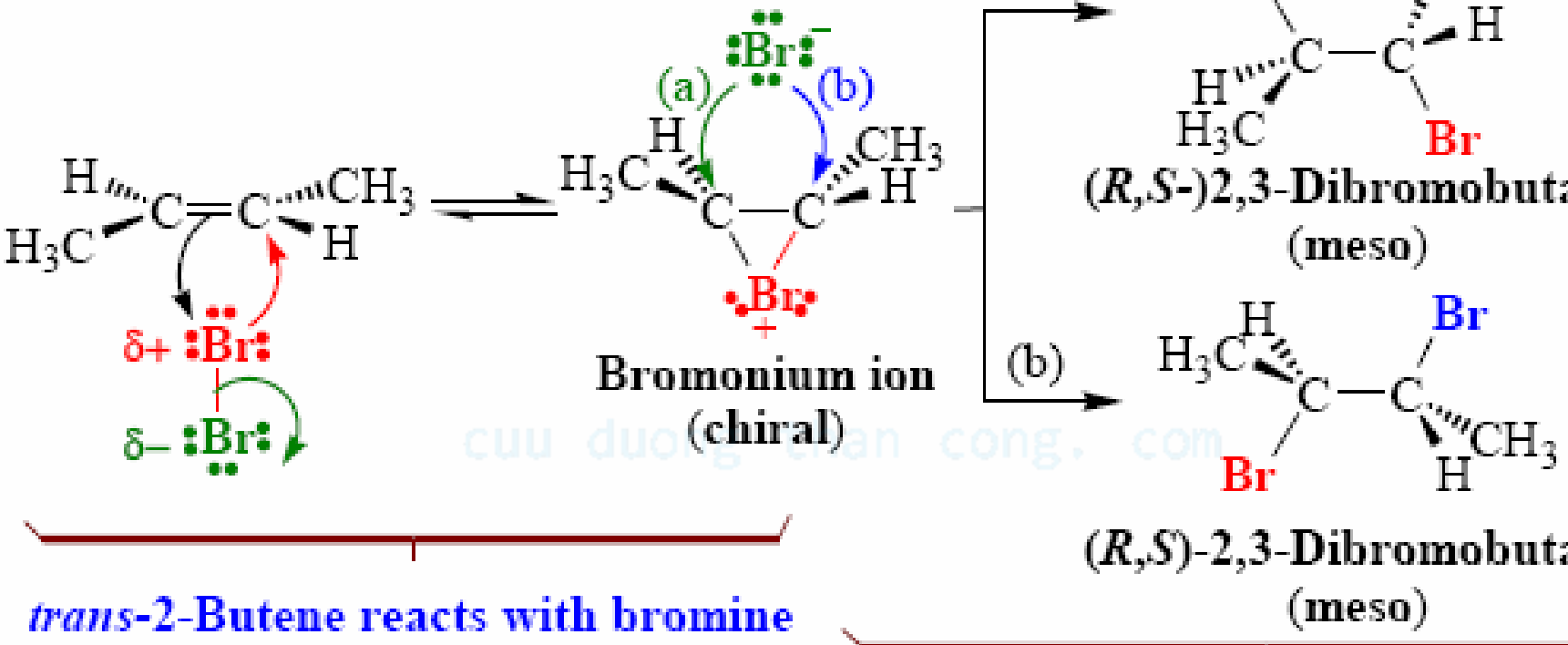
Stereochemistry



cis-2-butene reacts with bromine to yield an achiral bromonium ion and a bromide ion. [Reaction at the other face of the alkene (top) would yield the same bromonium ion.]

The bromonium ion reacts with the bromide ions at equal rates by paths (a) and (b) to yield the two enantiomers in equal amounts (i.e., as the racemic form).

Addition of Bromine to *trans*-2-Butene

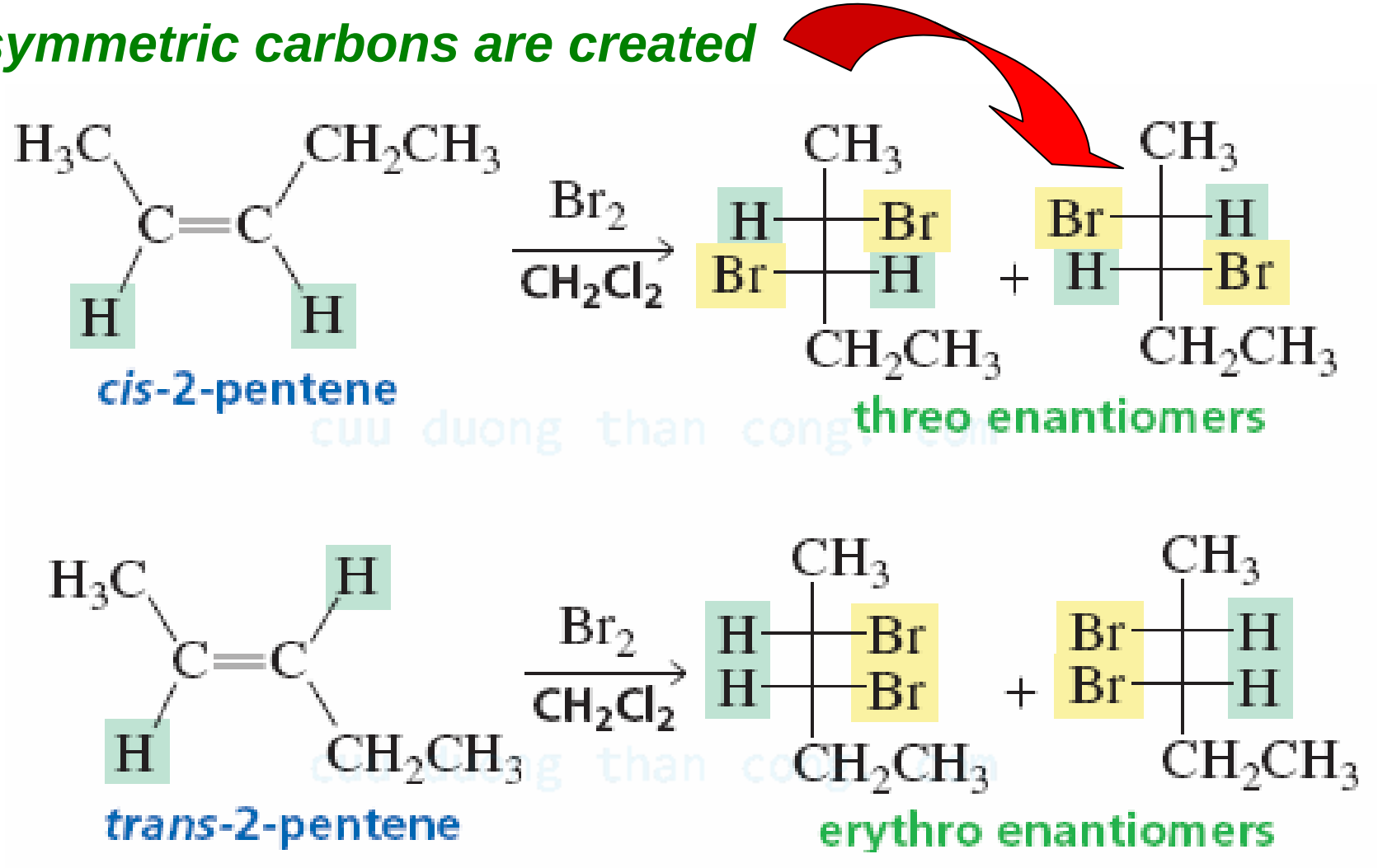


trans-2-Butene reacts with bromine yo yield chiral bromonium ions and bromide ions. [Reaction at the other face (top) would yield the enantiomer of the bromonium ion as shown here.]

When the bromonium ions react by either path (a) or path (b), they yield the same achiral meso compound. [Reaction of the enantiomer of the intermediate bromonium ion would produce the same result.]

Stereochemistry

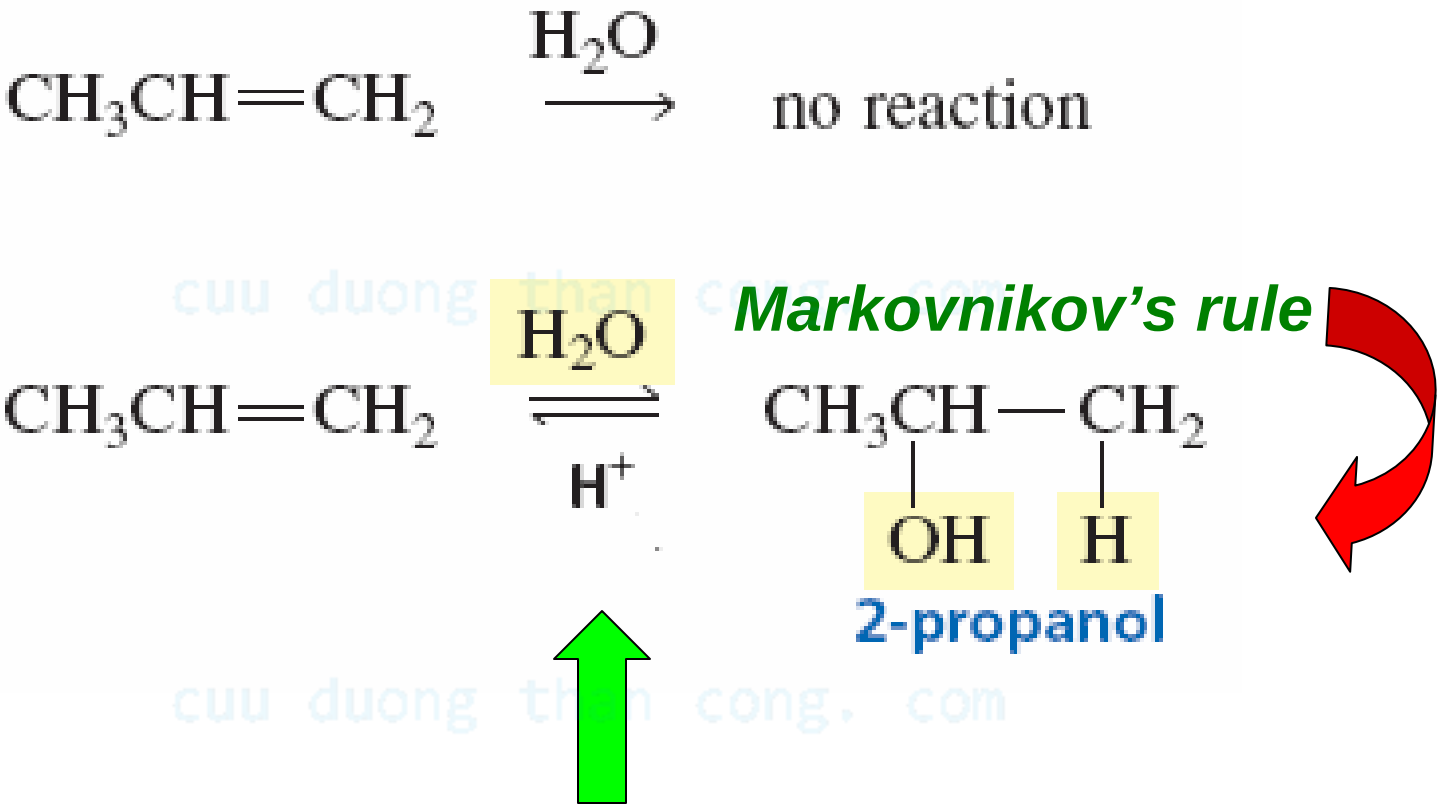
2 asymmetric carbons are created



***Trans*-2-butene → *meso* compound**

Additions of water – hydration reactions

Water is too weakly acidic to allow the hydrogen to act as an electrophile

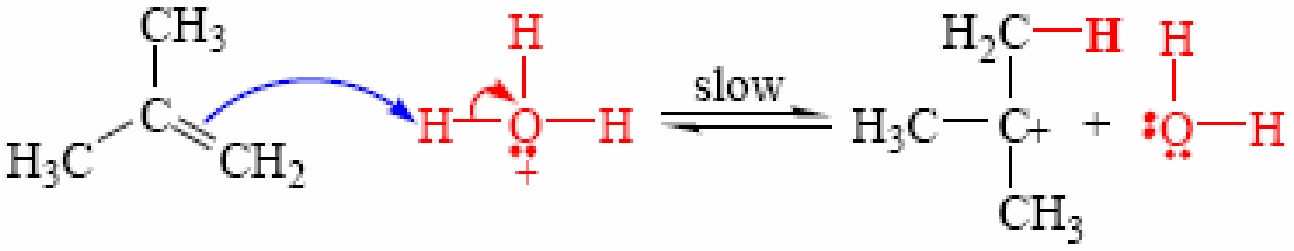


H_2SO_4, H_3PO_4…

Reaction mechanism:

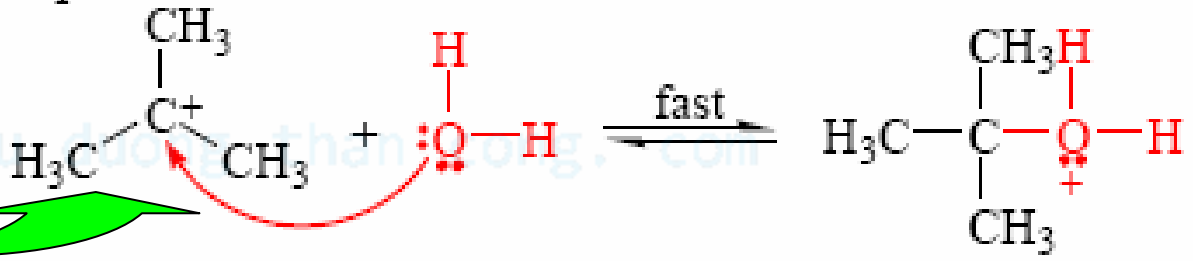
Carbocation rearrangement might occur

Step 1



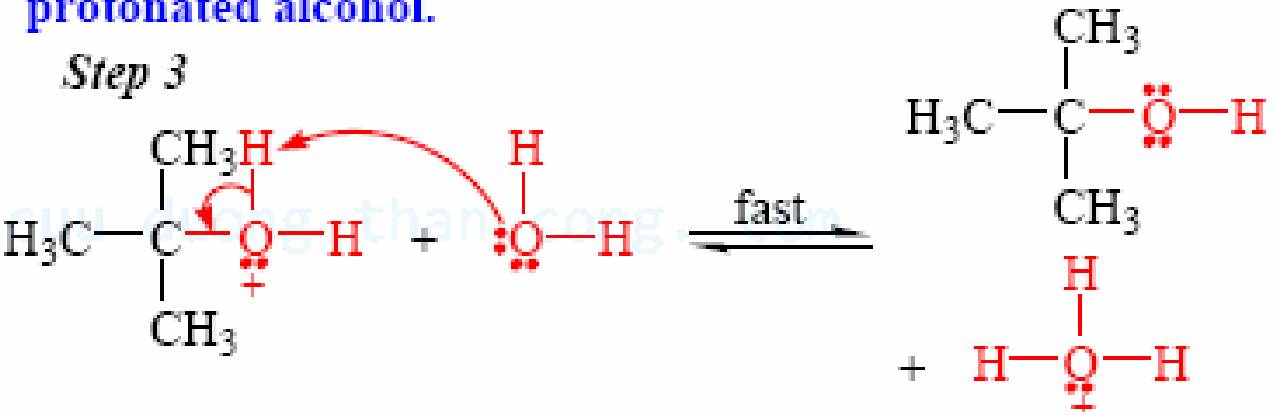
The alkene accepts a proton to form the more stable 3° carbocation.

Step 2



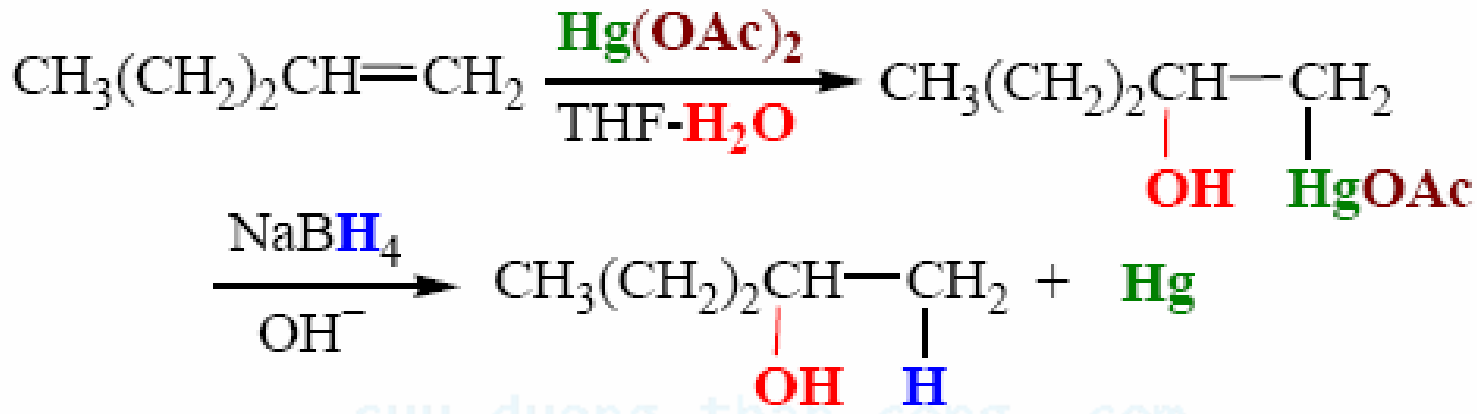
The carbocation reacts with a molucule of water to form a protonated alcohol.

Step 3



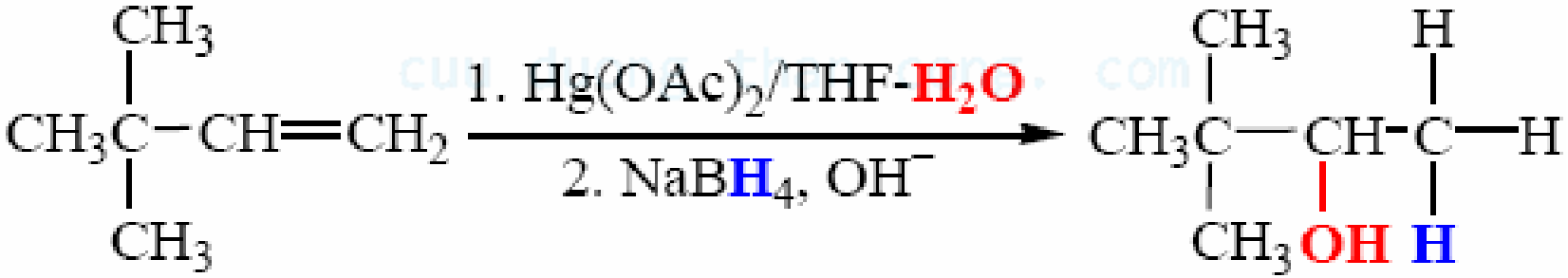
A transfer of a proton to a molecule of water leads to the product.

Alcohols by oxymercuration-reduction

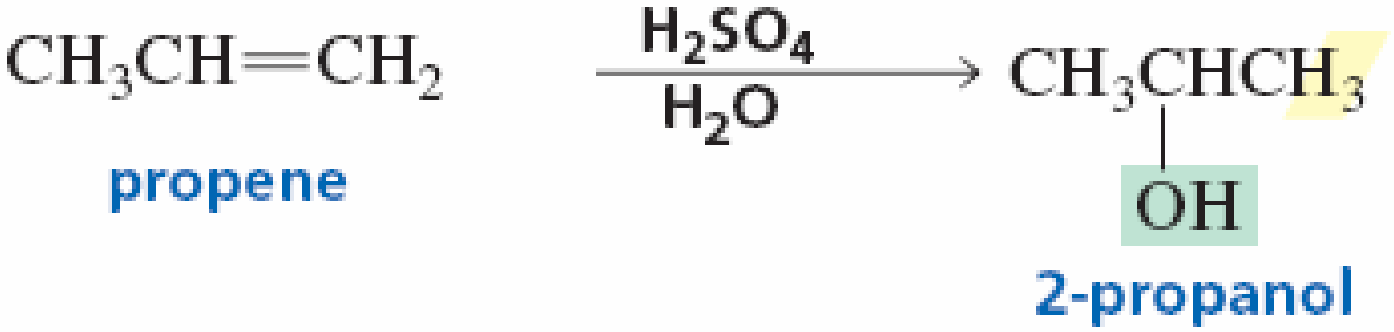


Markovnikov's rule

No carbocation formation, no rearrangement

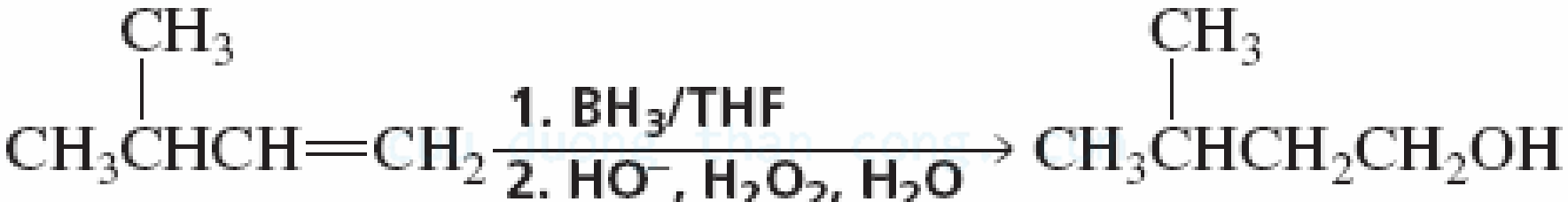


Additions of borane: hydroboration-oxidation



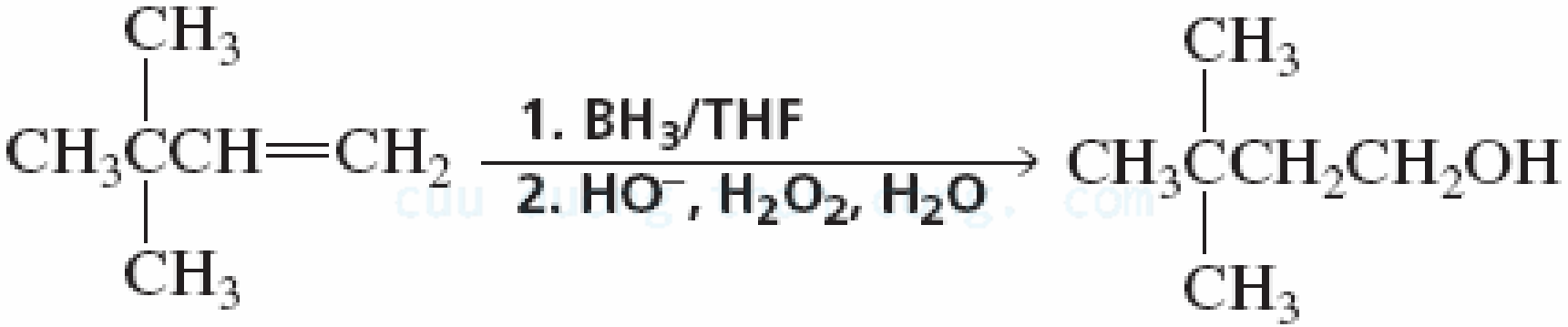
propene

2-propanol



3-methyl-1-butene

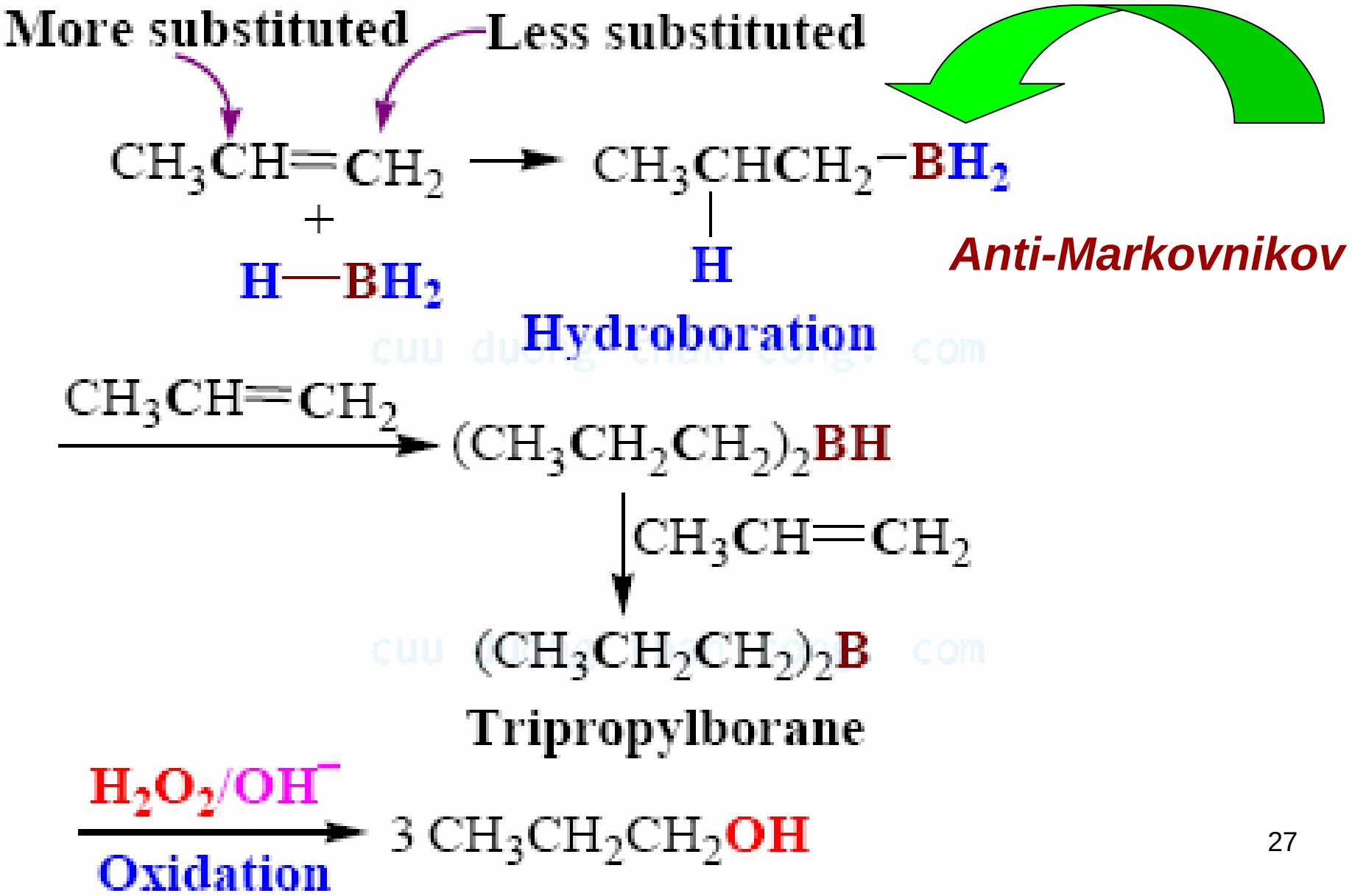
3-methyl-1-butanol



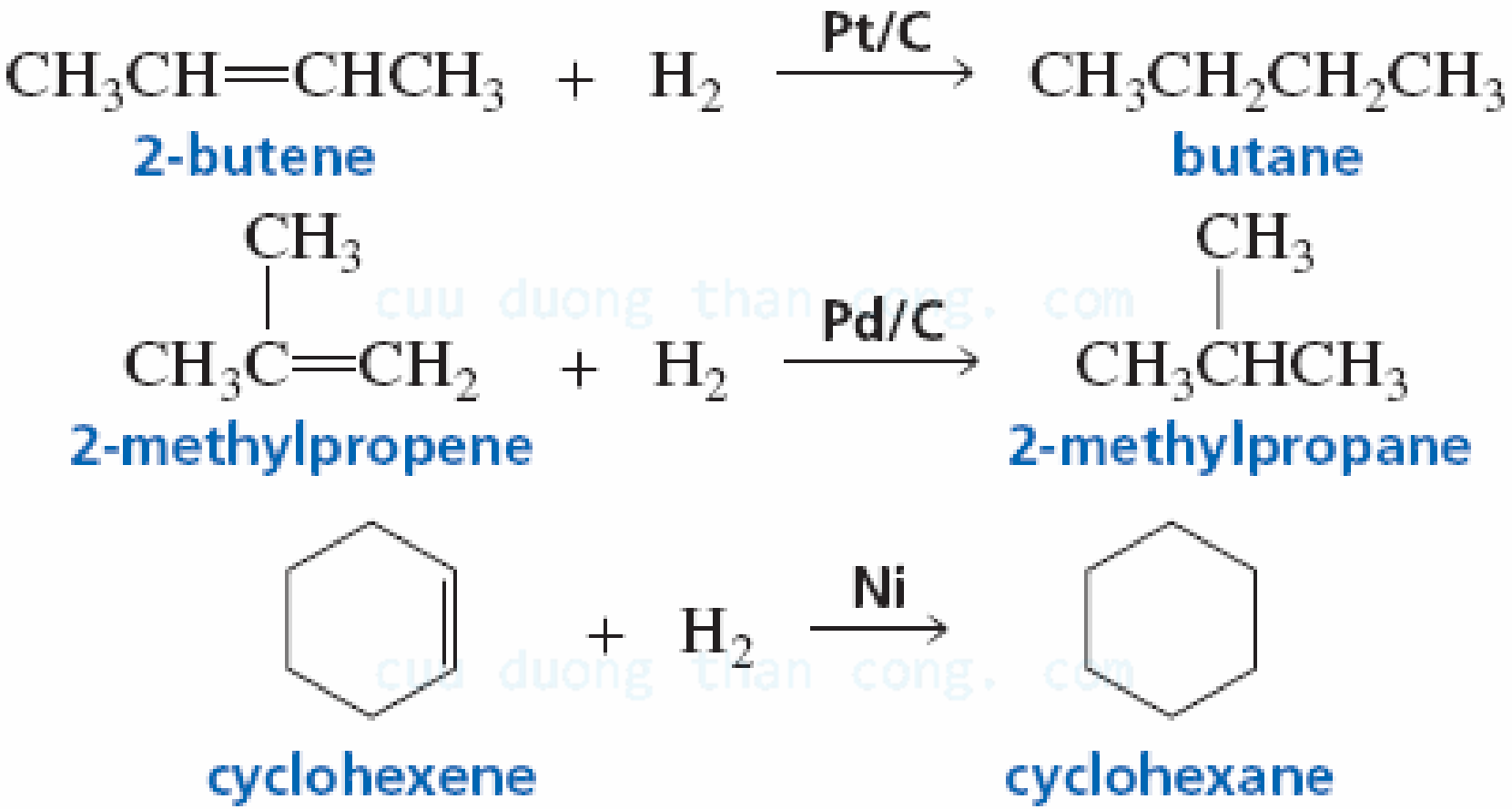
3,3-dimethyl-1-butene

3,3-dimethyl-1-butanol

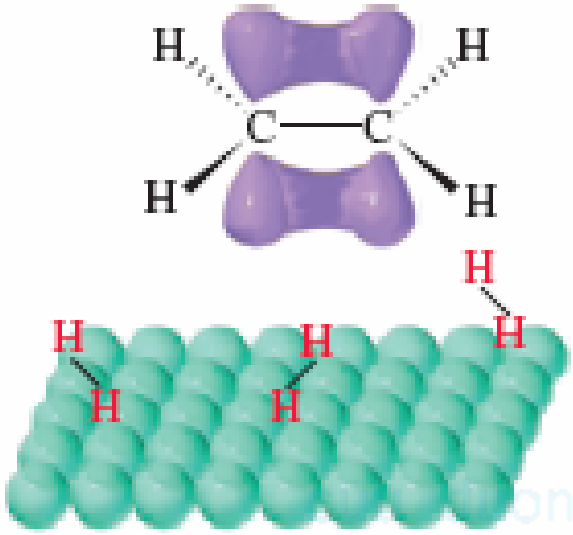
Regioselectivity:



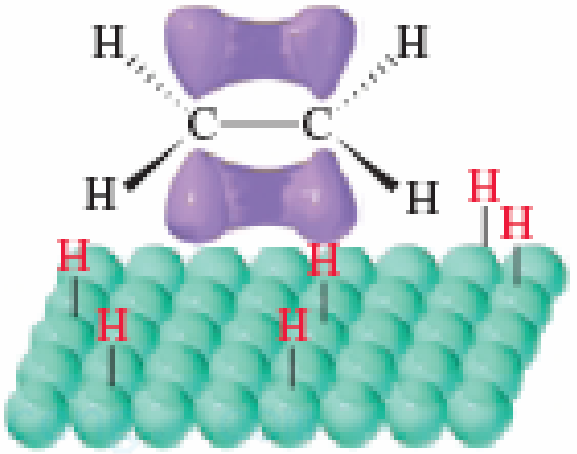
Additions of hydrogen – hydrogenation



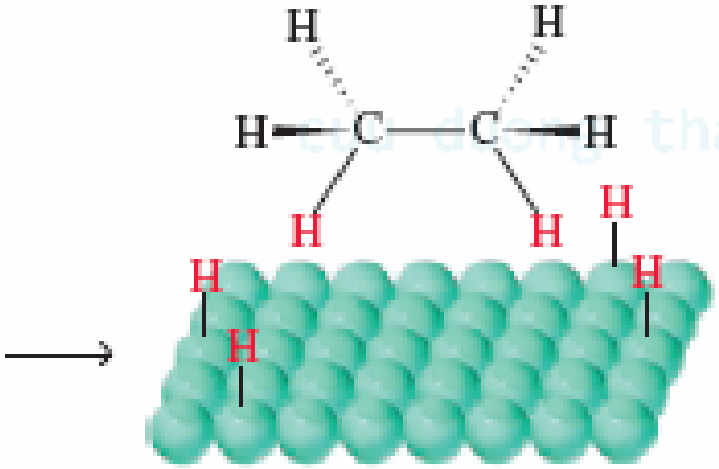
Reaction mechanism:



hydrogen molecules settle on the surface of the catalyst and react with the metal atoms



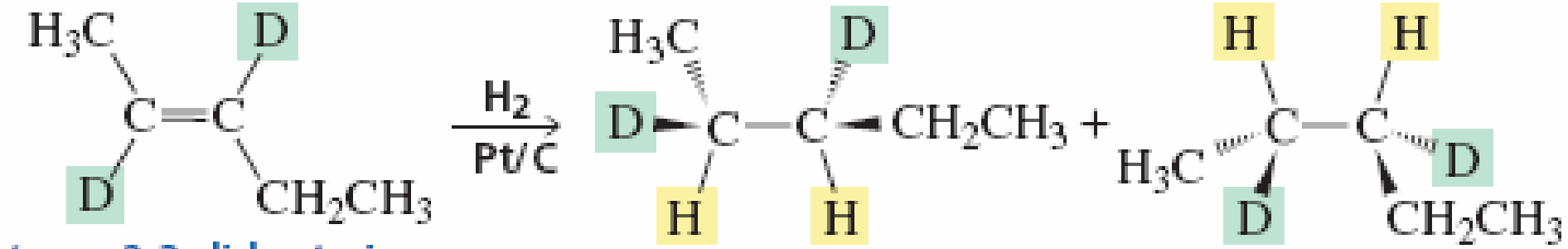
the alkene approaches the surface of the catalyst



Syn addition

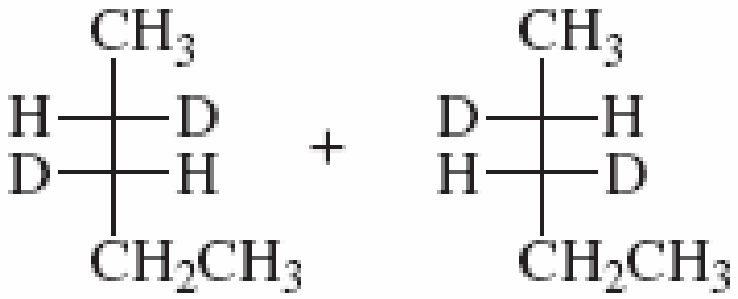
the π bond between the two carbons is replaced by two C—H σ bonds

Stereochemistry

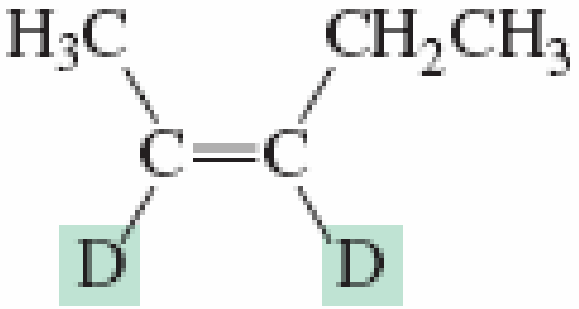


trans-2,3-dideuterio-2-pentene

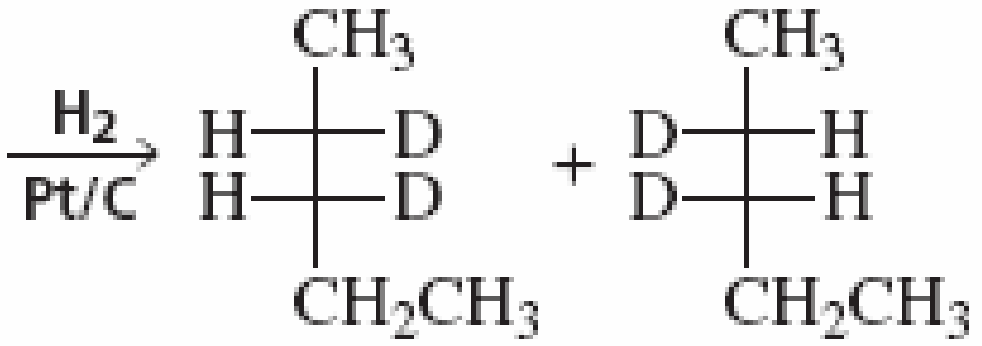
threo enantiomers



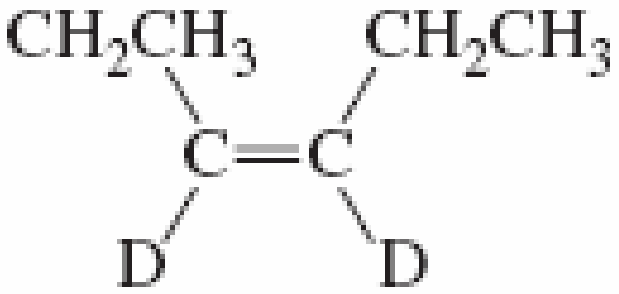
threo enantiomers



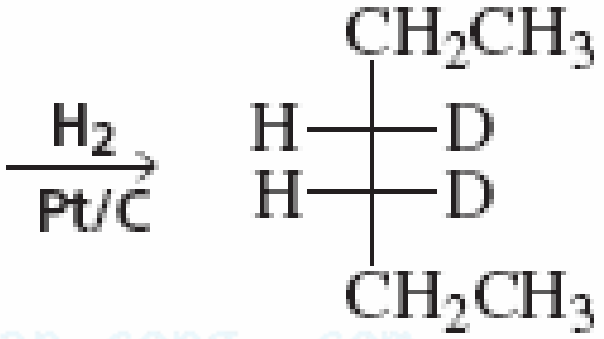
cis-2,3-dideuterio-2-pentene



erythro enantiomers

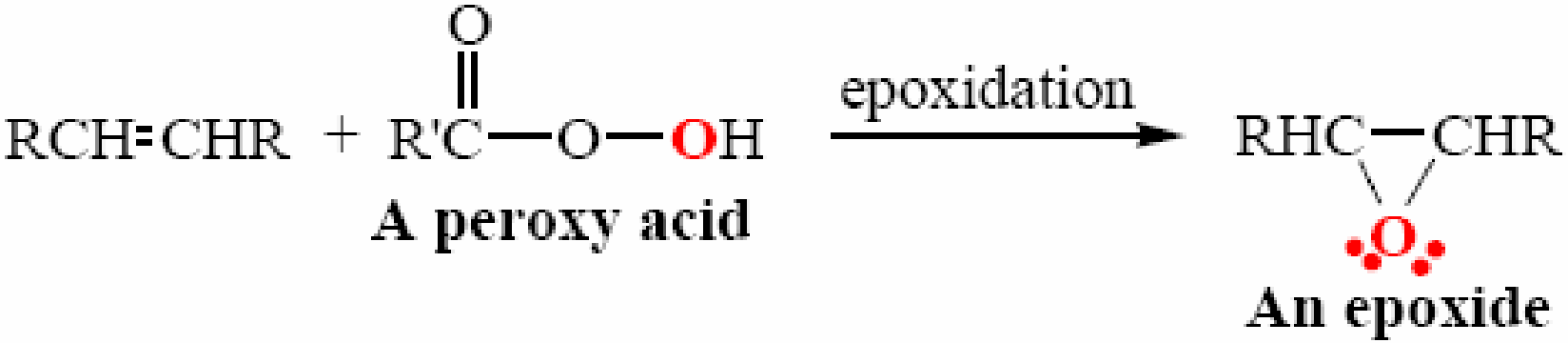


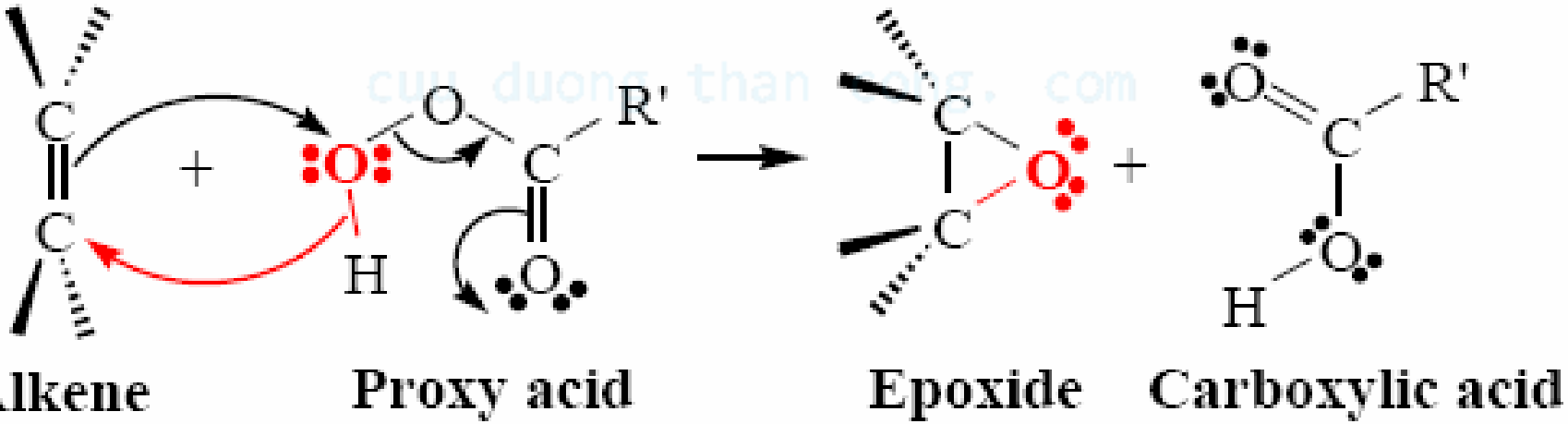
cis-2,3-dideuterio-2-pentene



meso compound

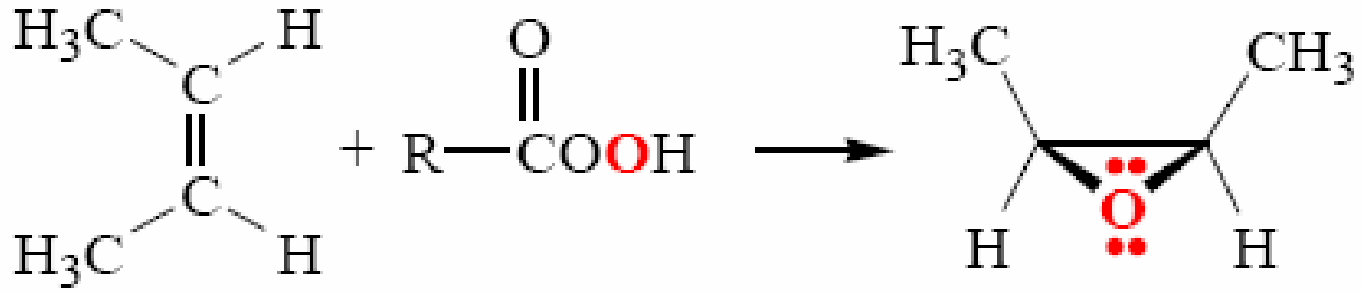
Alkene epoxidations – *Anti* hydroxylations





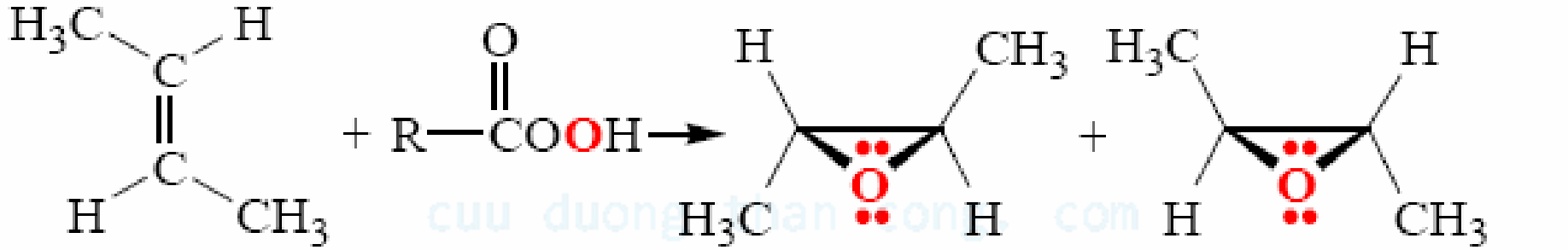
The peroxy acid transfers an oxygen atom to the alkene in a cyclic, single-step mechanism. The result is the syn addition of the oxygen to the alkene, with formation of an epoxide and a carboxylic acid.

Stereochemistry



cis-2-Butene

cis-2,3-Dimethyloxirane
(a meso compound)

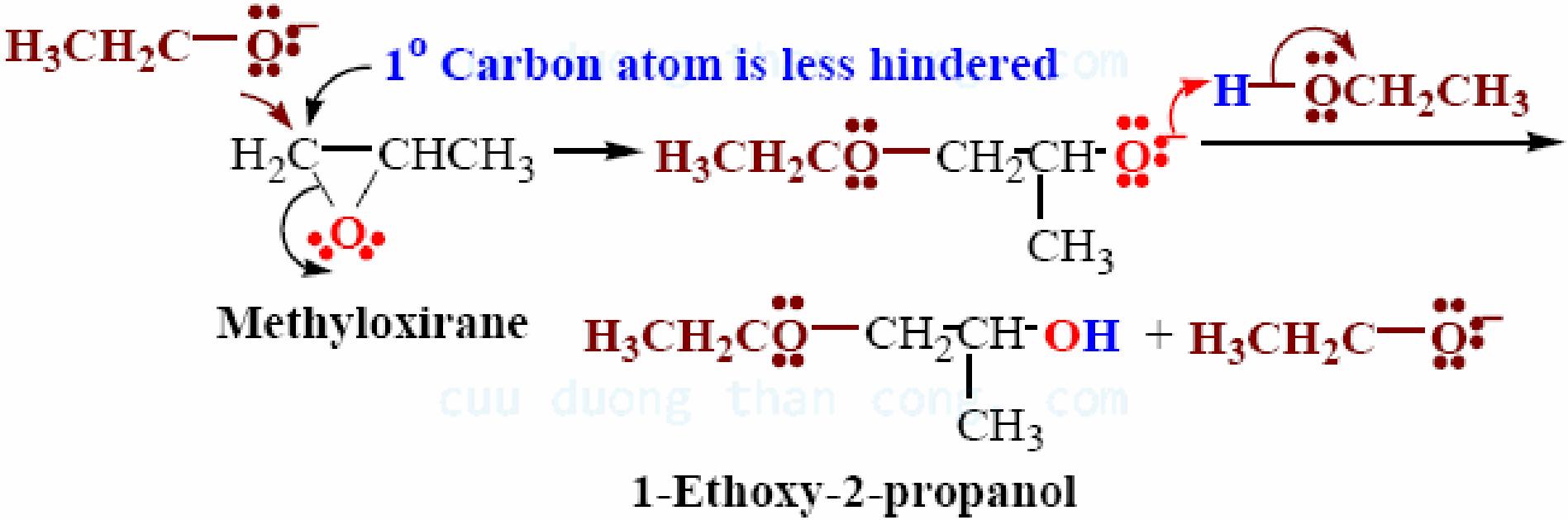


trans-2-Butene

Enantiomeric *trans*-2,3-dimethyloxiranes

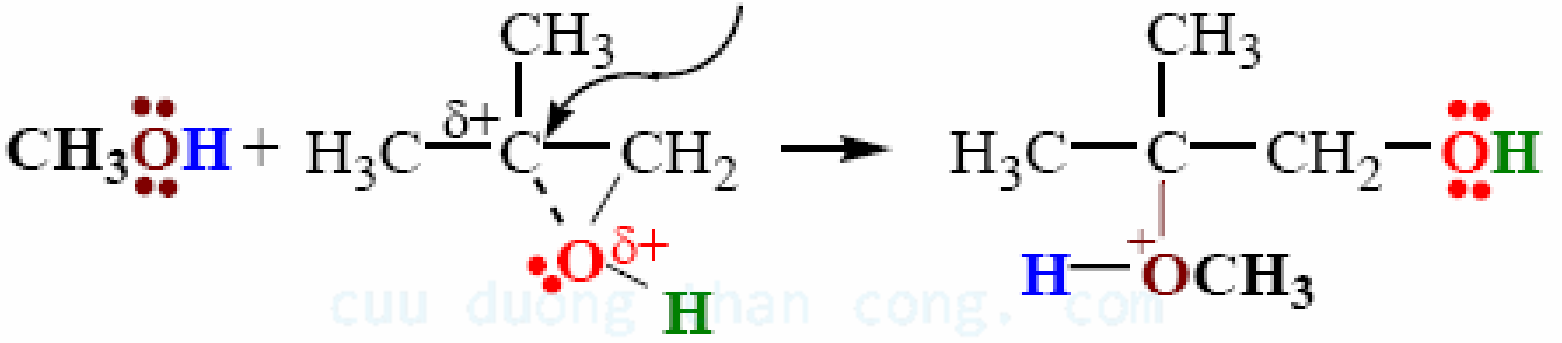
Reactions of epoxides

If the epoxide is unsymmetrical, the **nucleophile** attacks primarily at ***the less substituted carbon atom*** in **base-catalyzed ring opening**.

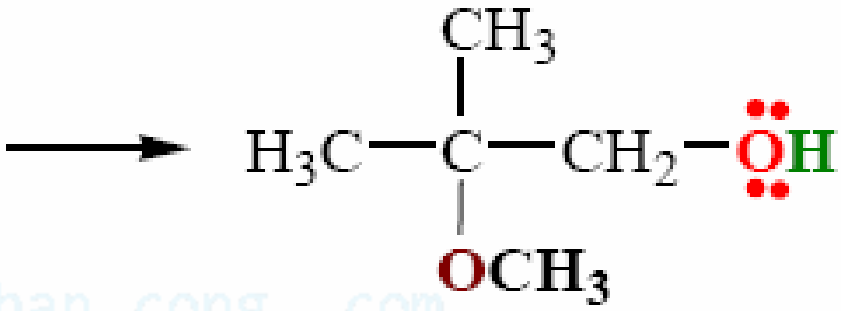


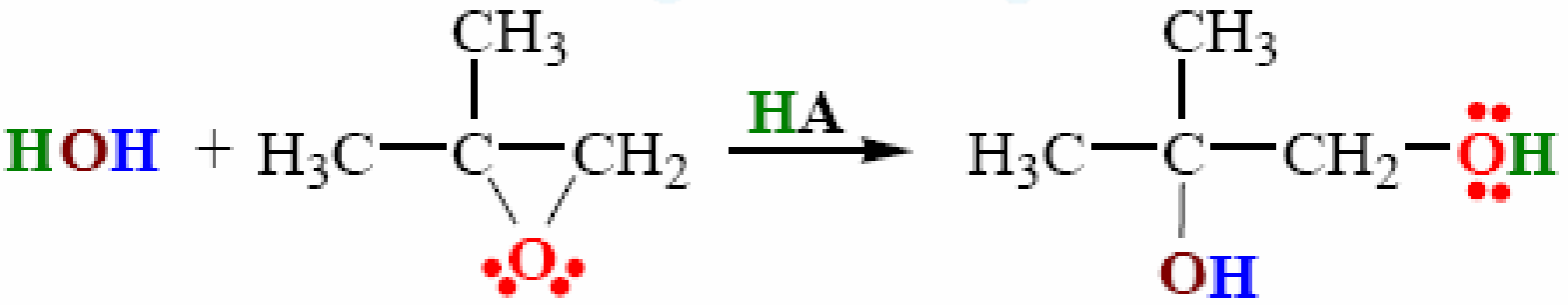
If the epoxide is unsymmetrical, the **nucleophile** attacks primarily at ***the more substituted carbon atom*** in **acid-catalyzed ring opening**.

This carbon resembles a 3° carbocation

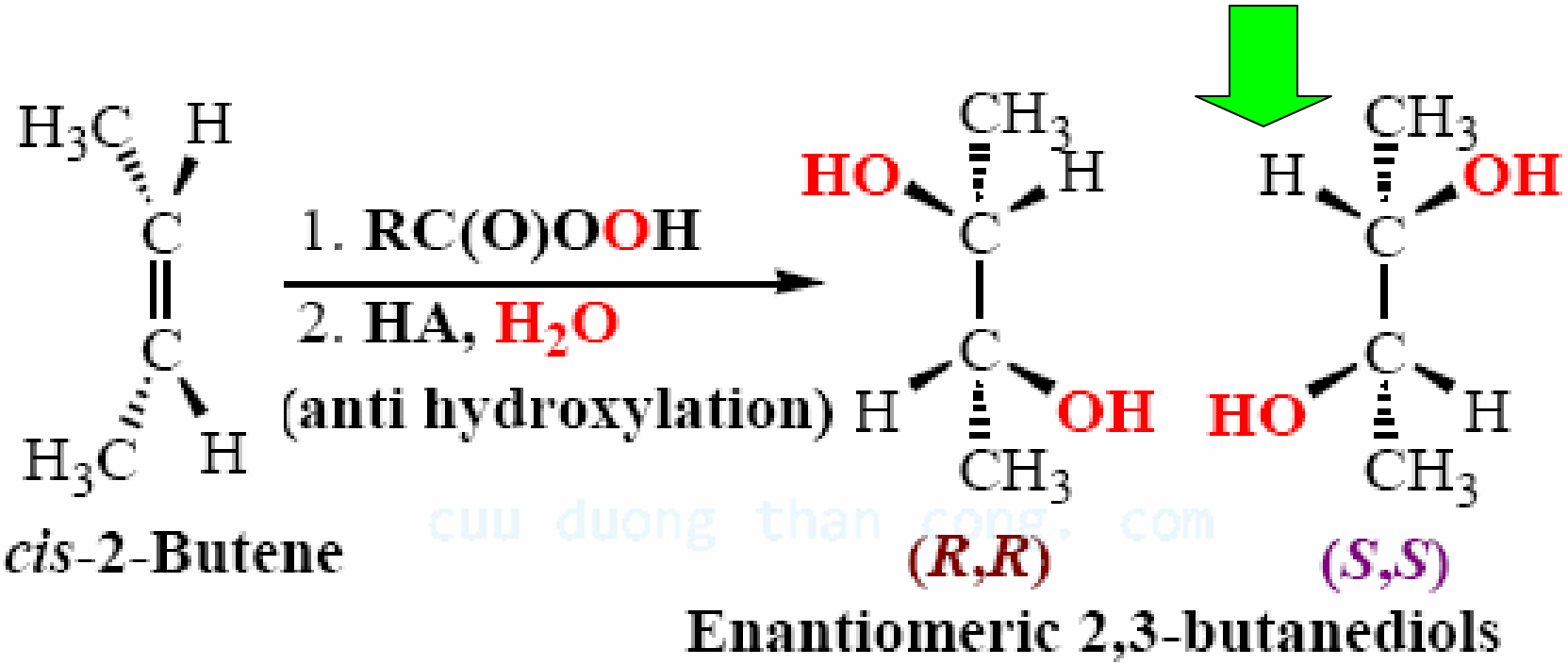


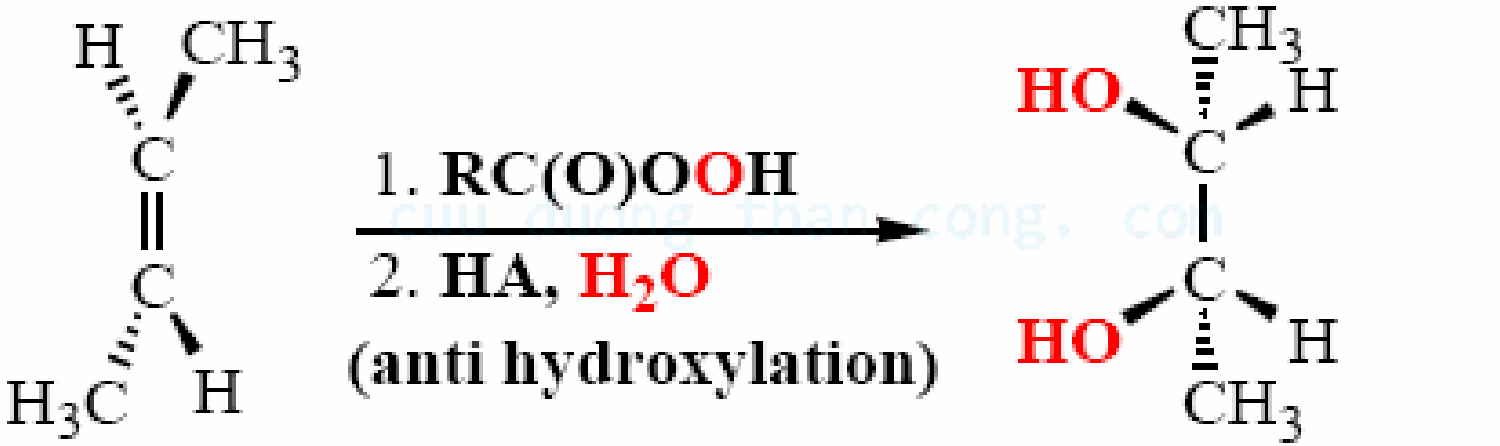
Protonated epoxide



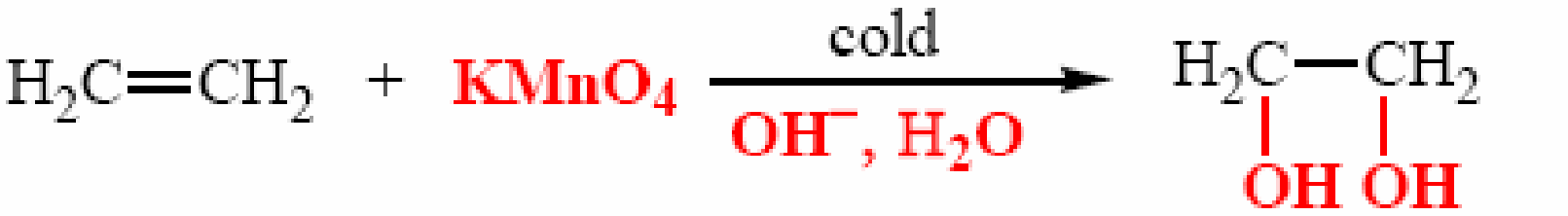


Stereochemistry — *Anti* additions



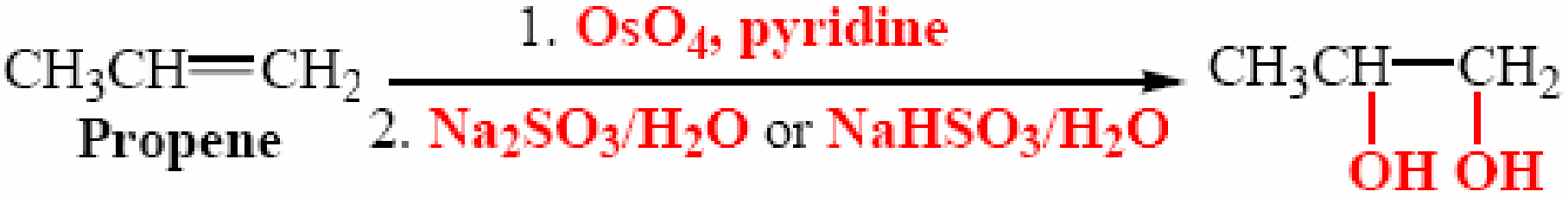


Syn hydroxylations of alkenes



Ethene

1,2-Ethanediol
(ethylene glycol)

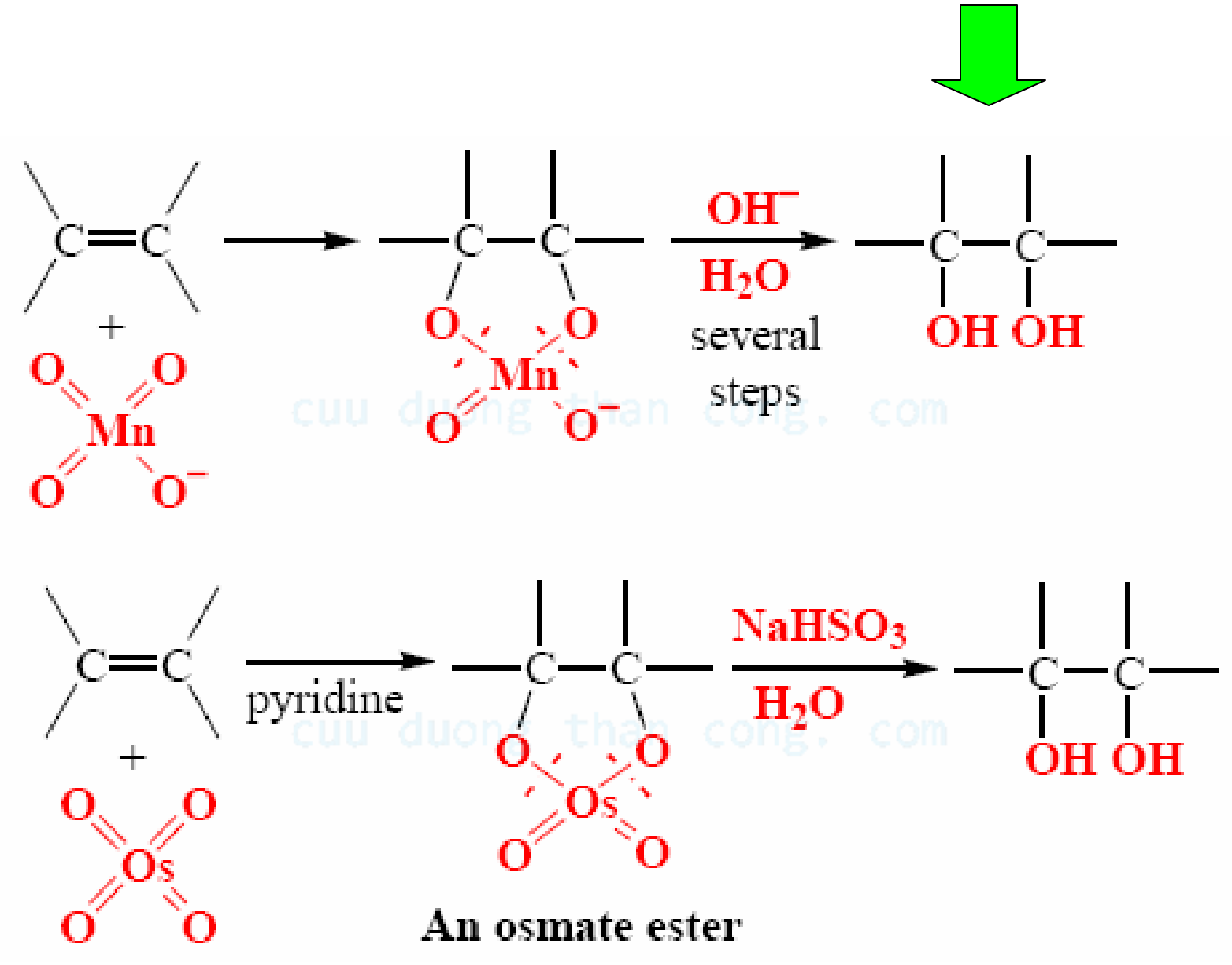


Propene

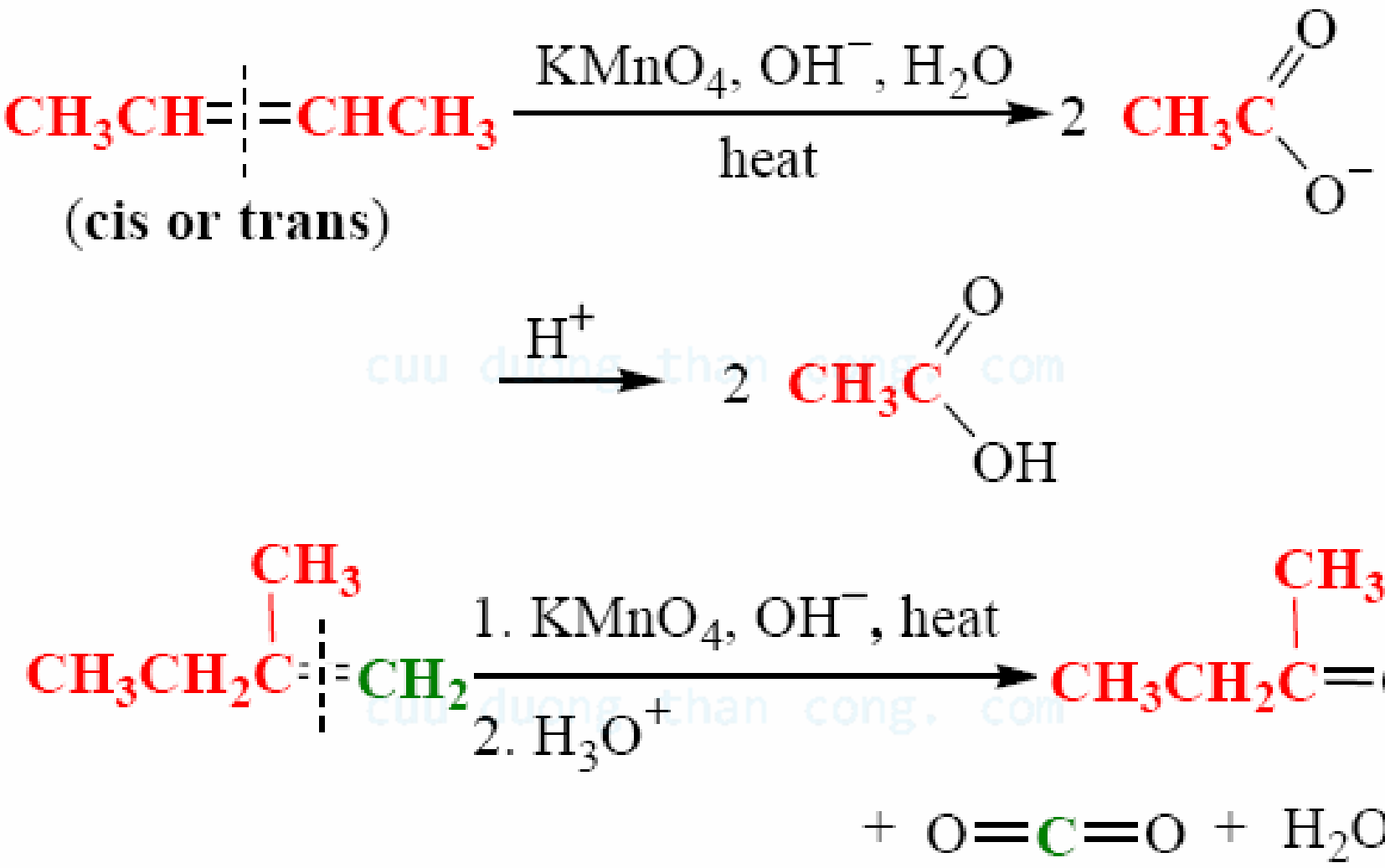
1,2-Propanediol
(propylene glycol)

Reaction mechanism:

Syn additions

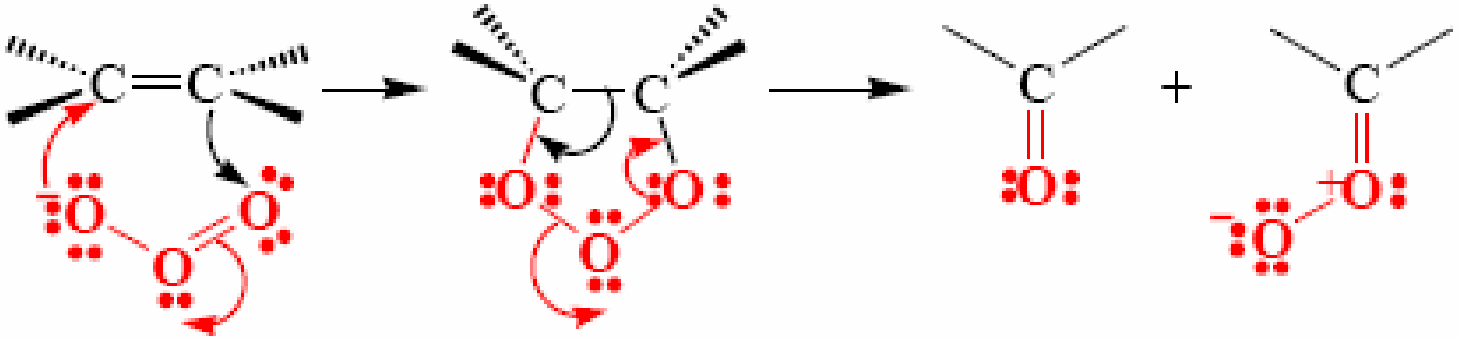


Permanganate cleavage of alkenes



Ozonolysis of alkenes

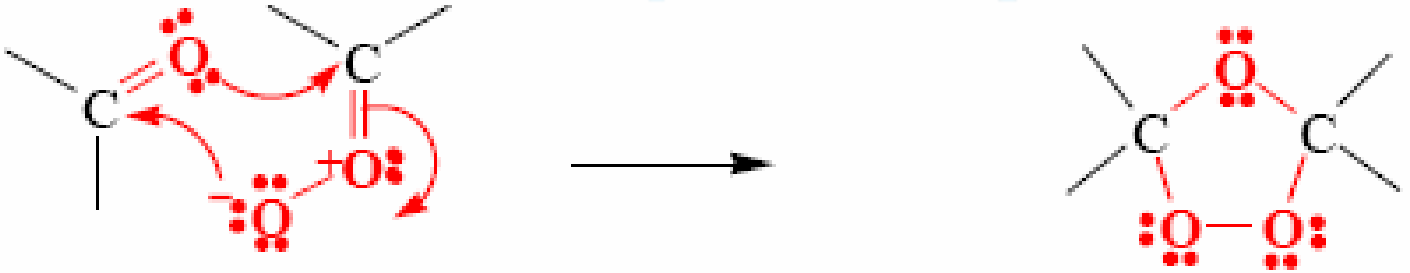
Ozonide Formation from an Alkene



Ozone adds to the alkene to form an initial ozonide.

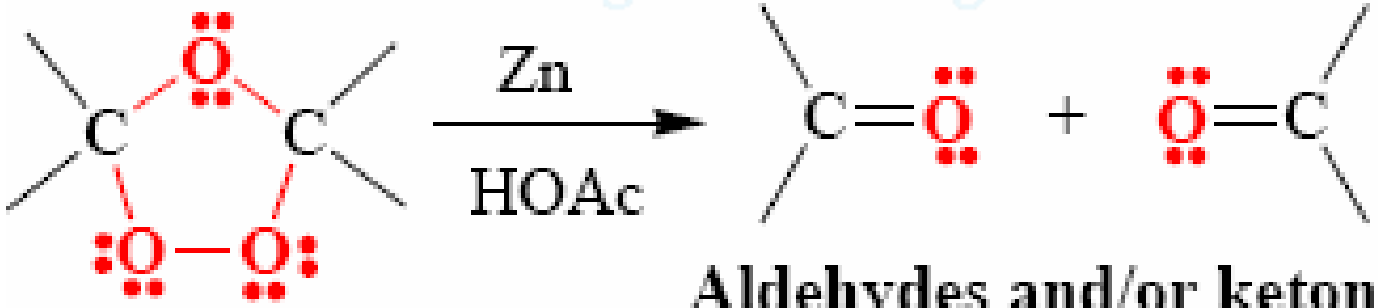
Initial ozonide

The initial ozonide fragments.

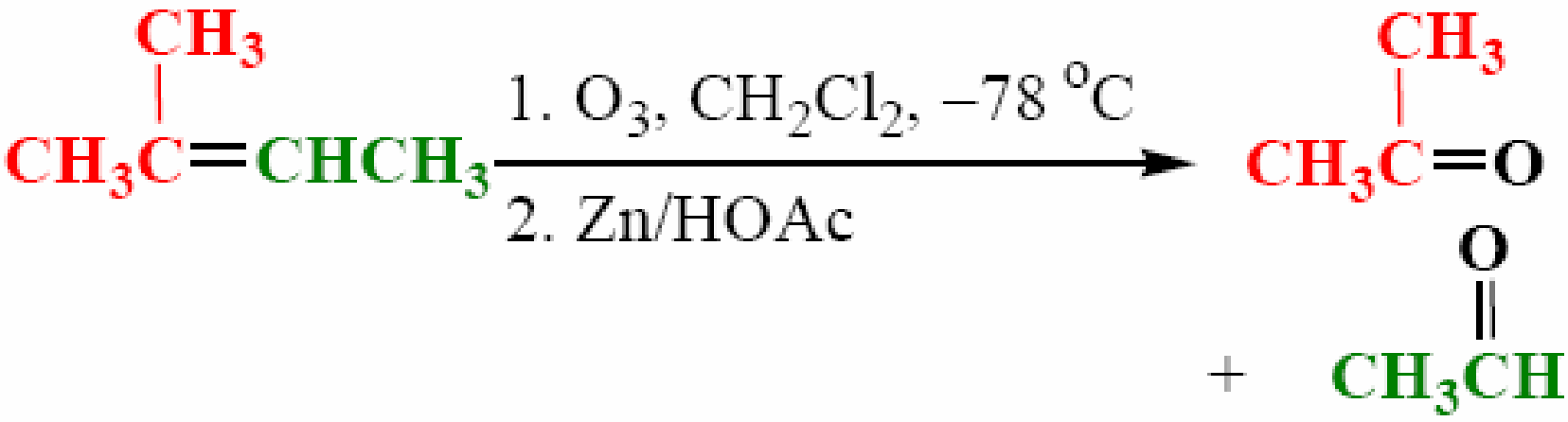


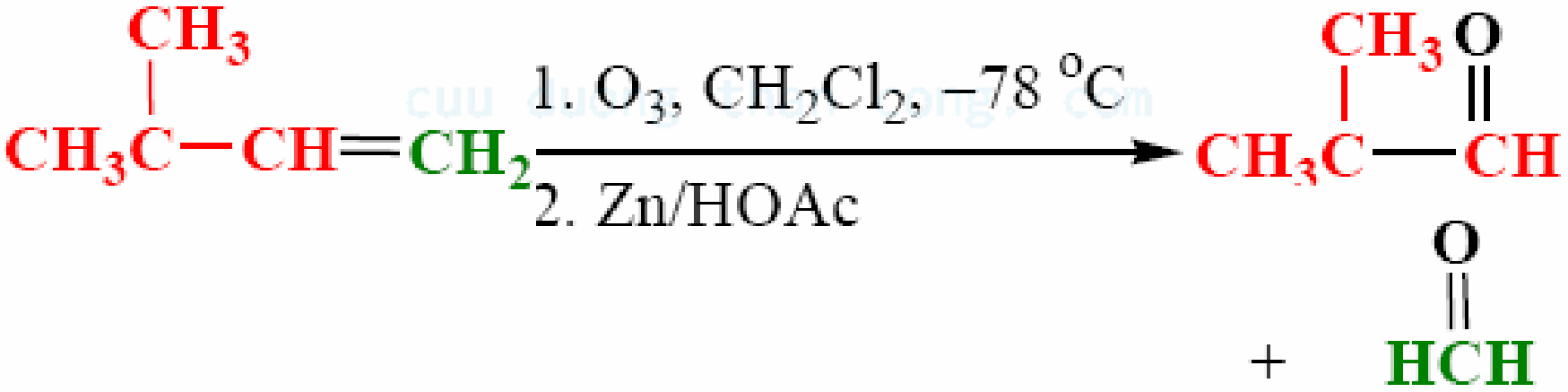
The fragments recombine to form the ozonide.

Ozonide



Aldehydes and/or ketones

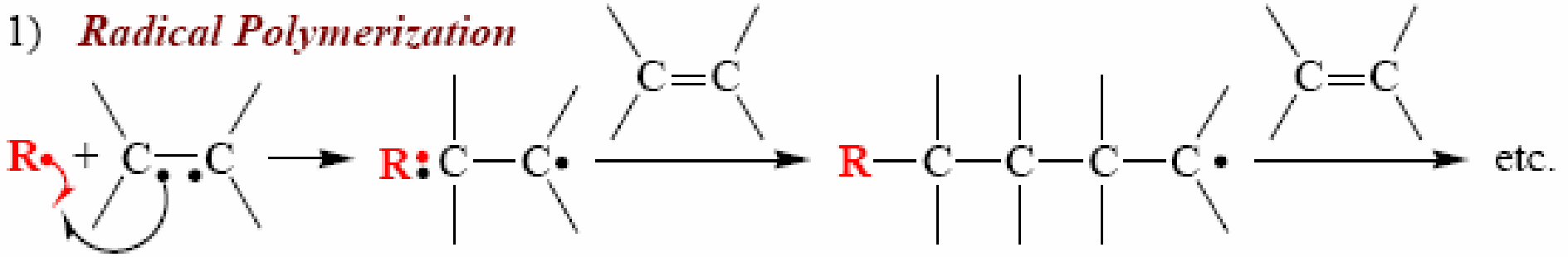




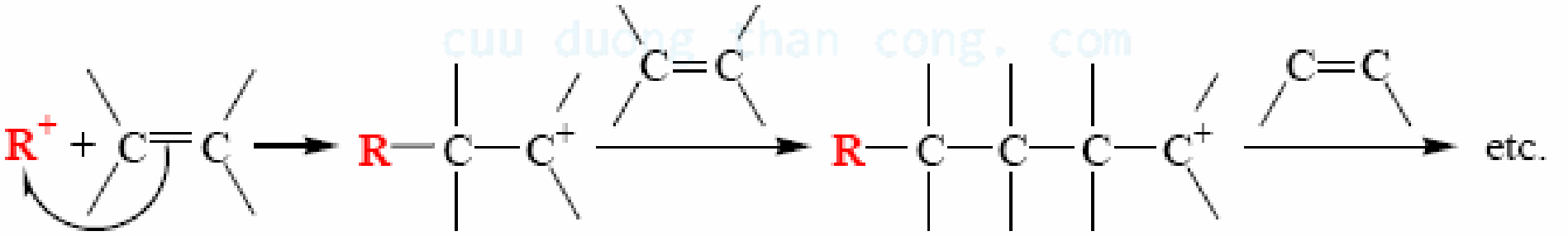
In the presence of an *oxidizing agent*, the products will be ketones / carboxylic acids

Polymerizations

1) *Radical Polymerization*



2) *Cationic Polymerization*



3) *Anionic Polymerization*