Química Orgânica I

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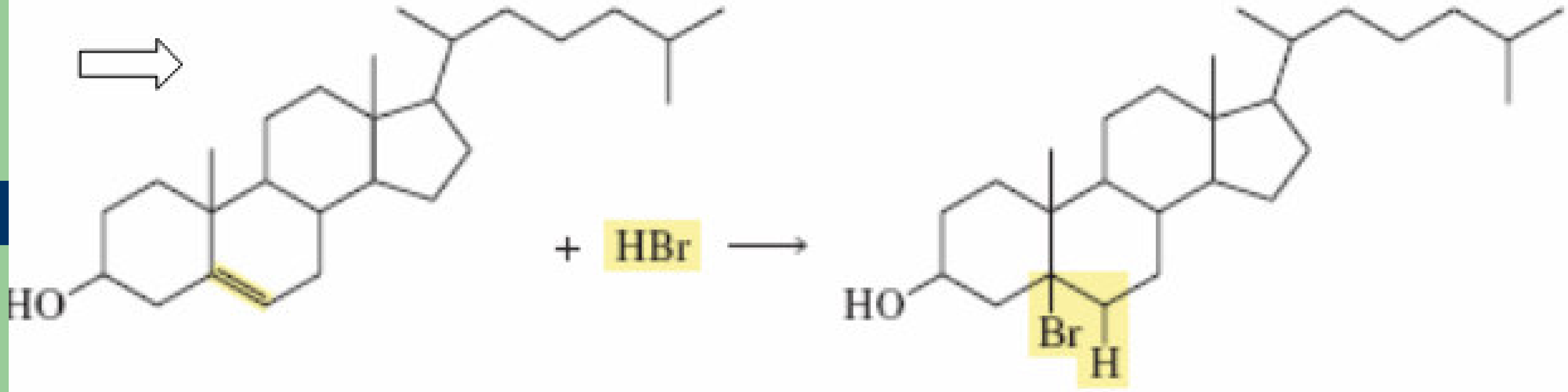
Profa. Dra. Tania Márcia do Sacramento Melo

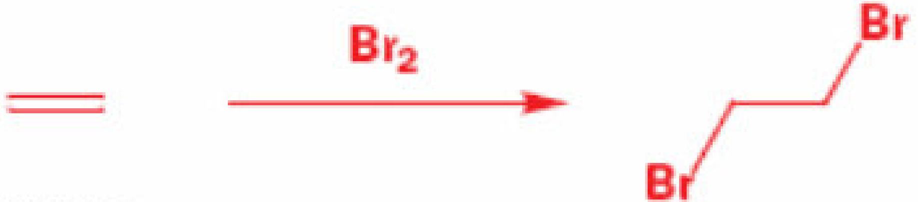
Adição Eletrofilica a C=C

Aula nº 12

Como os alcenos reagem?

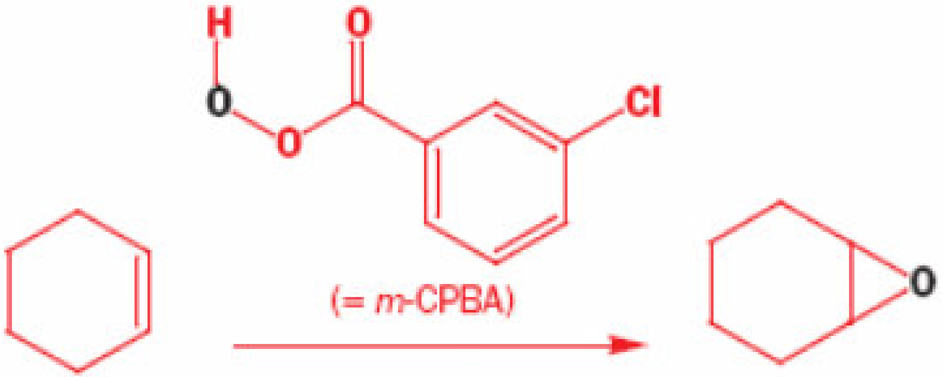


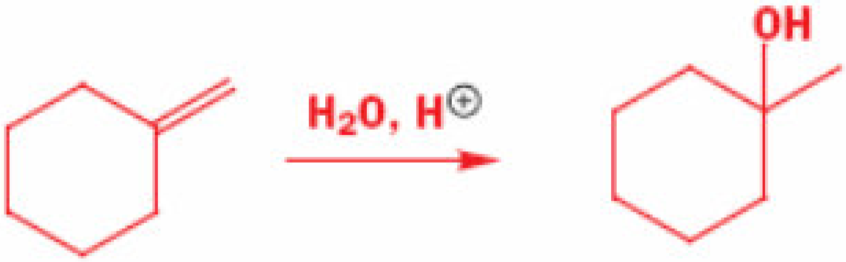
cholesterol

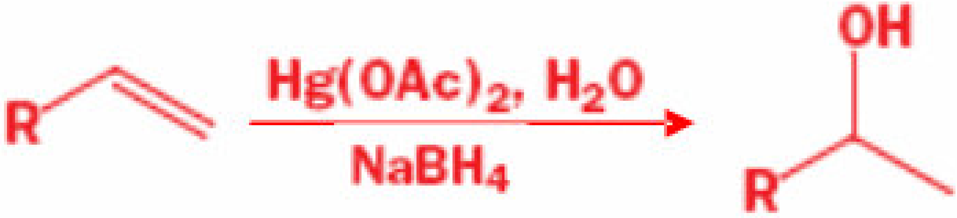


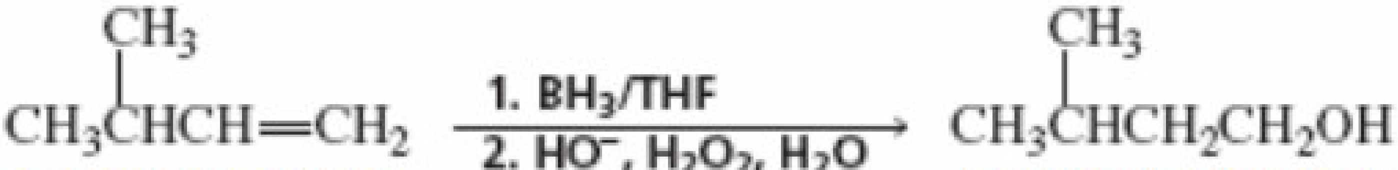
ethylene
(ethene)

1,2-dibromoethylene









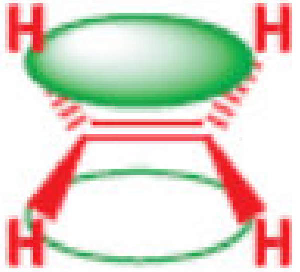
$$\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CH_2} \xrightarrow[\text{2. HO}^-\text{, } H_2O_2\text{, } H_2O]{\text{1. } BH_3/THF} \mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2OH}$$

3-methyl-1-butene

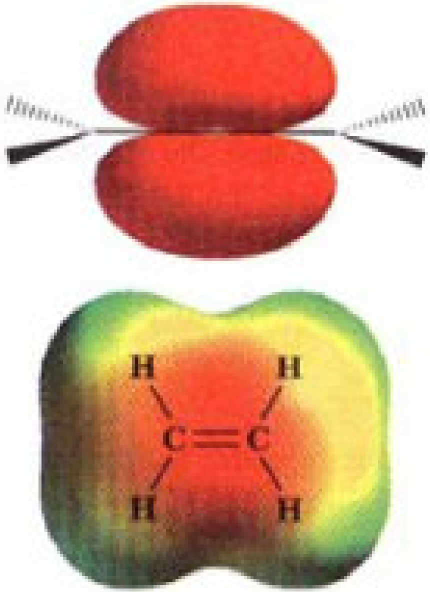
3-methyl-1-butanol

Adição eletrofílica de bromo

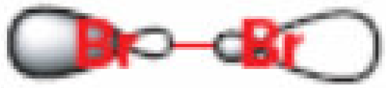
alkene = nucleophile



HOMO = filled π orbital



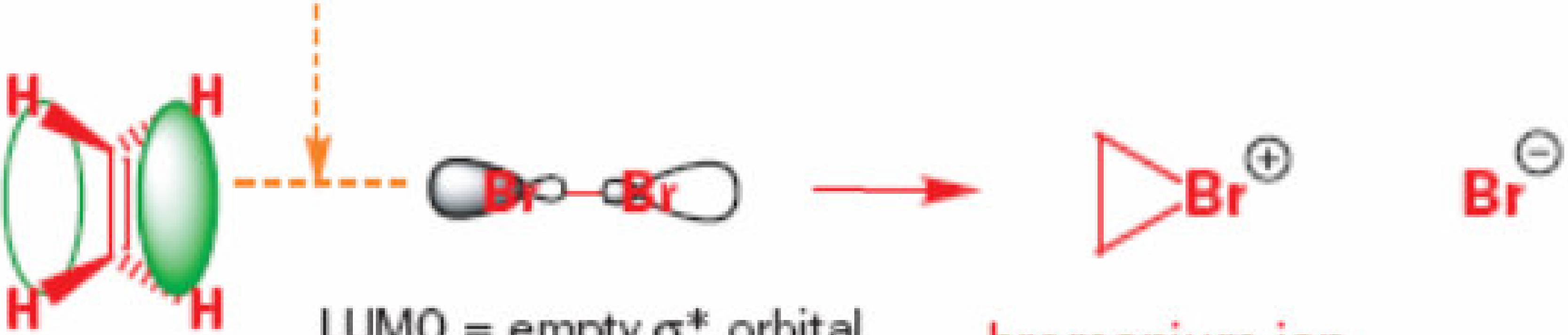
Br_2 = electrophile



LUMO = empty σ* orbital

electrophilic attack by Br_2 on ethylene

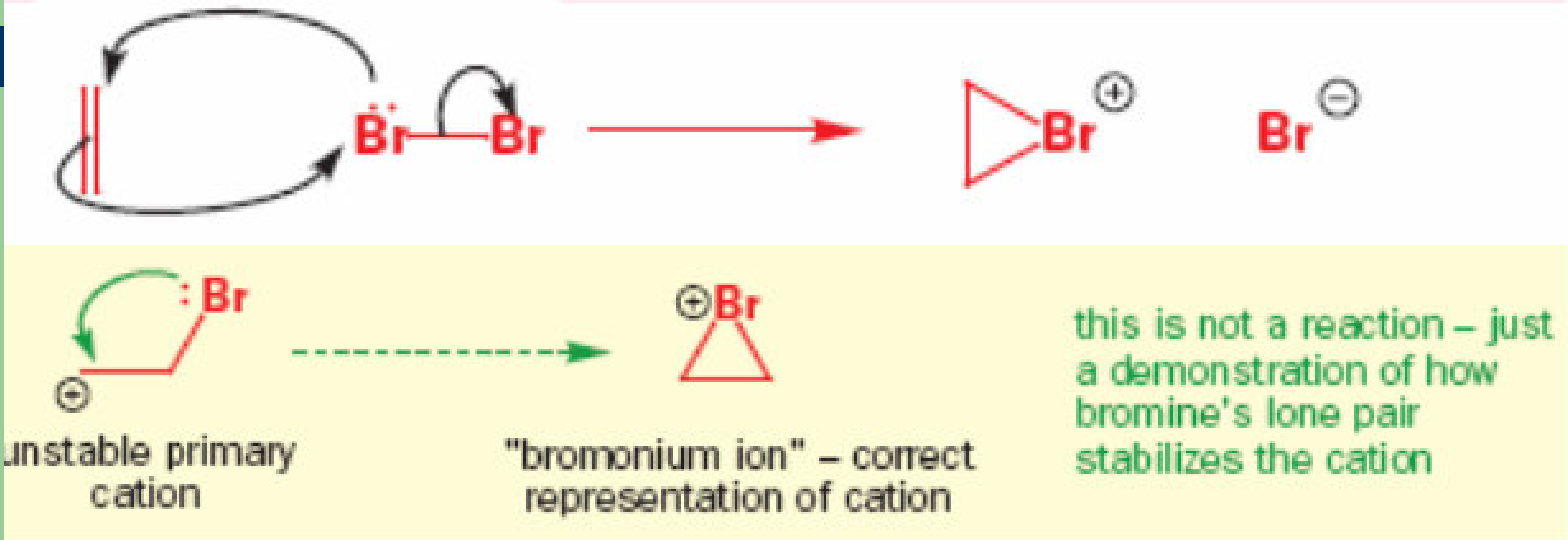
bonding interaction



HOMO = filled π orbital

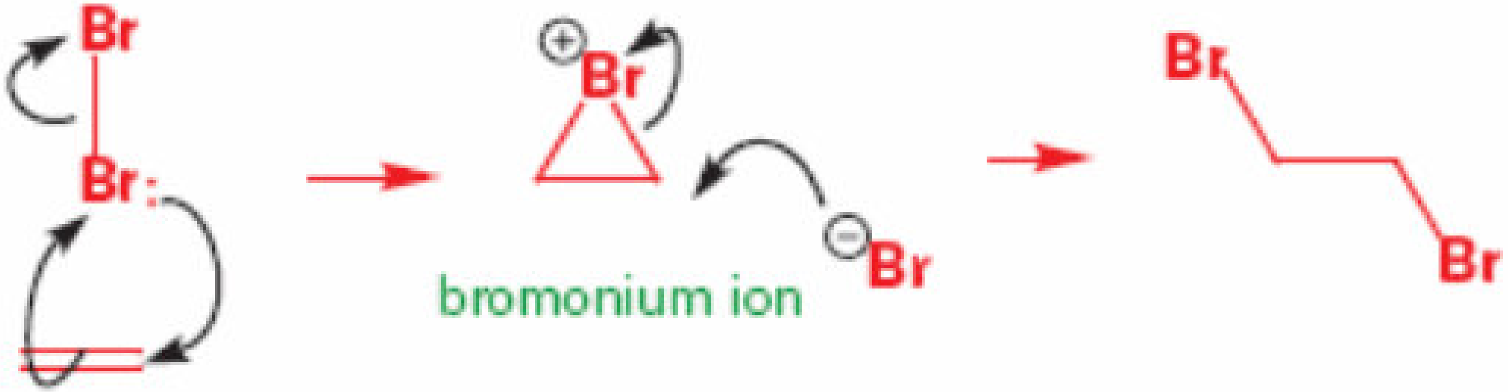
LUMO = empty σ* orbital

bromonium ion

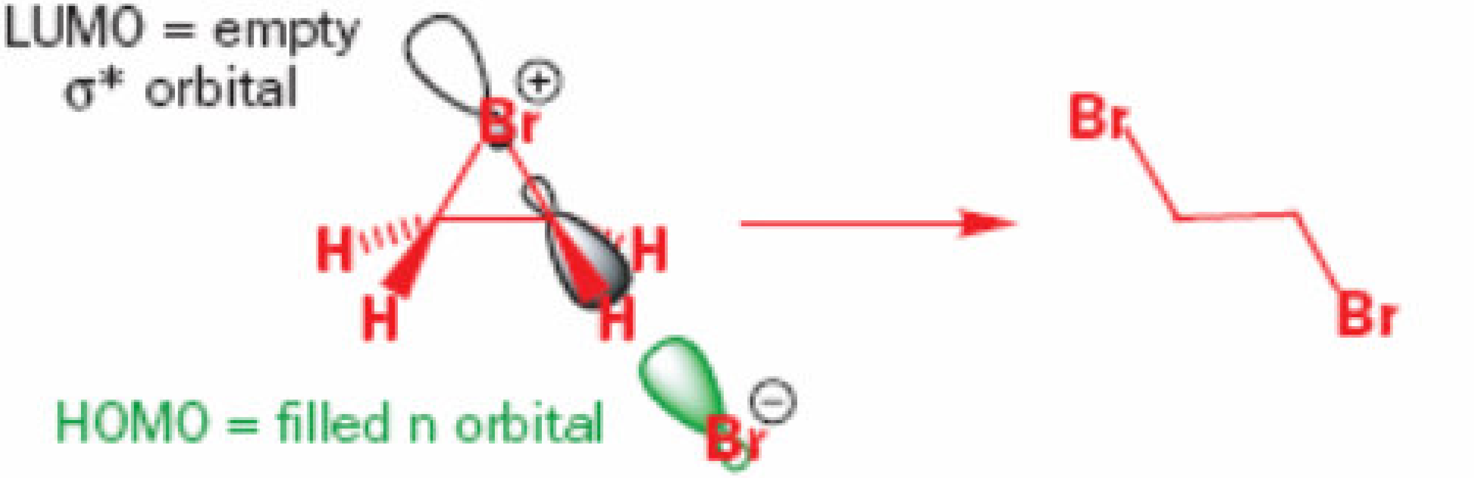


this is not a reaction – just a demonstration of how bromine's lone pair stabilizes the cation

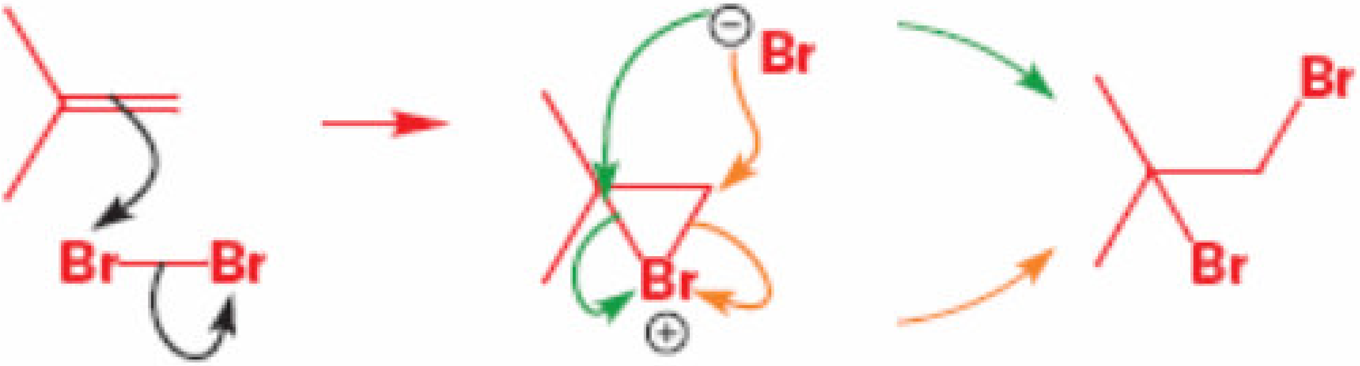
Adição eletrofílica de bromo



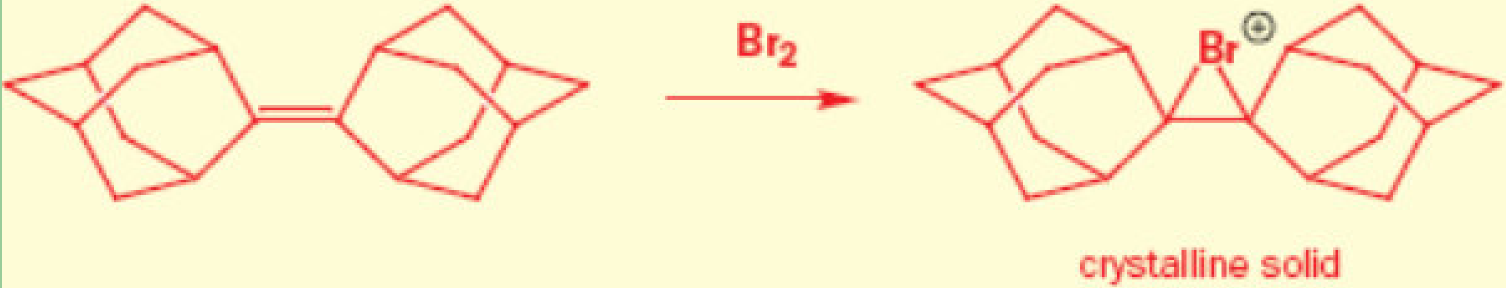
orbitals involved in the opening of the bromonium ion



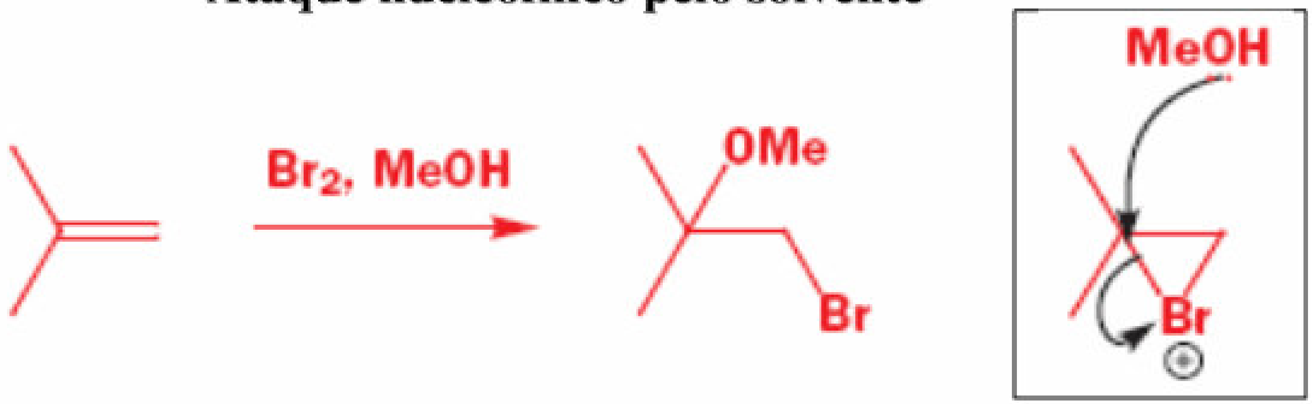
Íon bromônio assimétrico abre regiosseletivamente



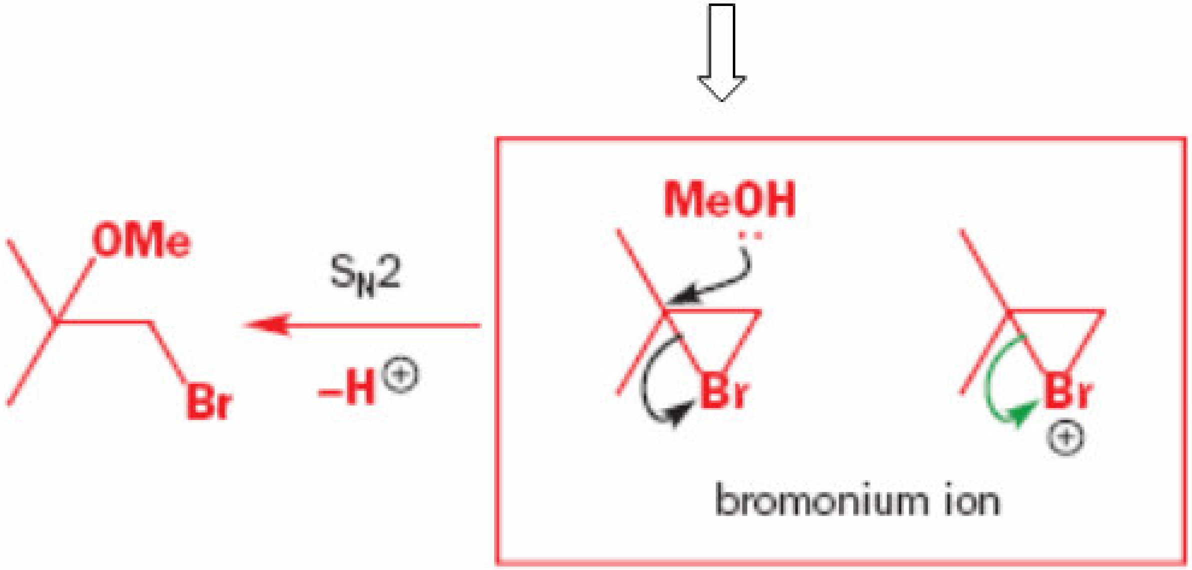
Ambos os ataques formam o mesmo produto

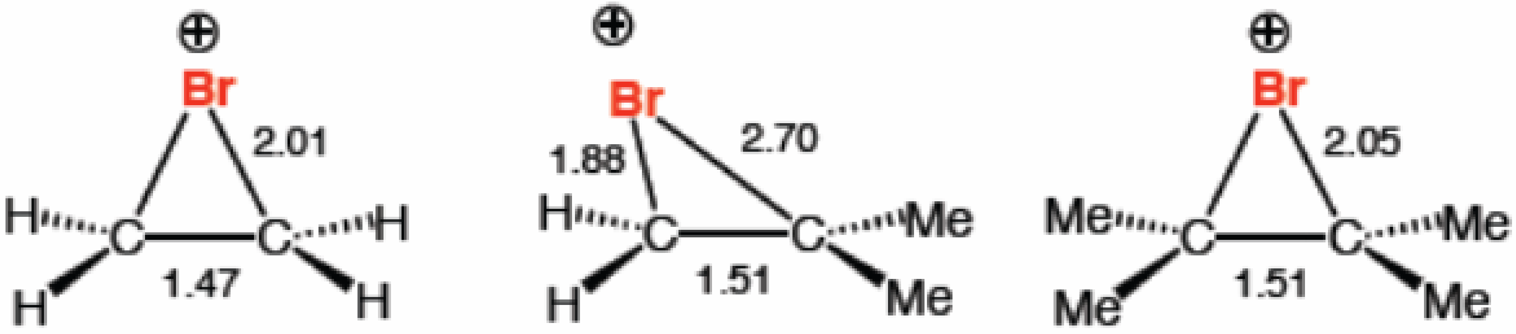


Ataque nucleofílico pelo solvente



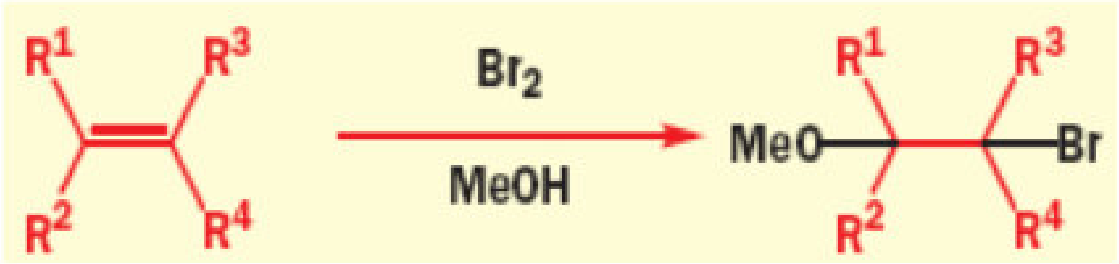
O solvente ataca o carbono mais substituído





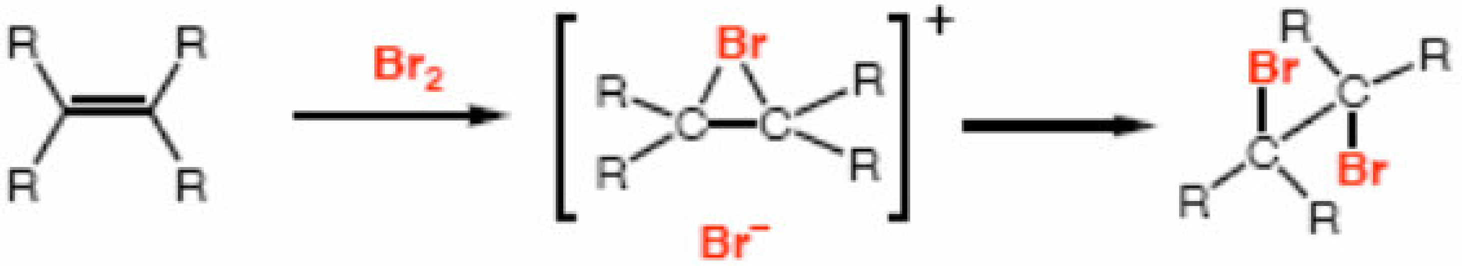
Note; the C–Br bond lengths in previous X-ray structure are 2.116 Å.

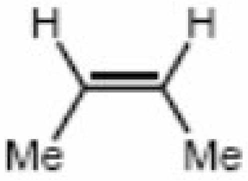
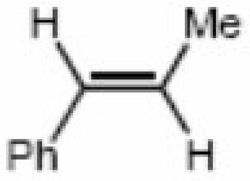
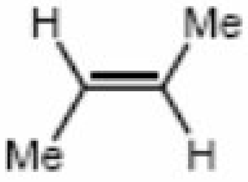
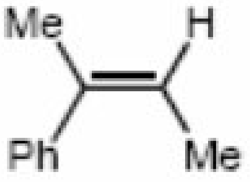
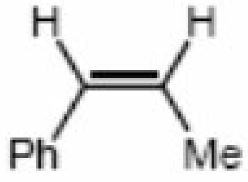
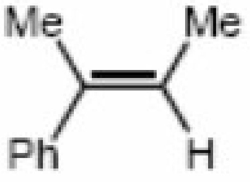
Velocidade relativa dos alcenos

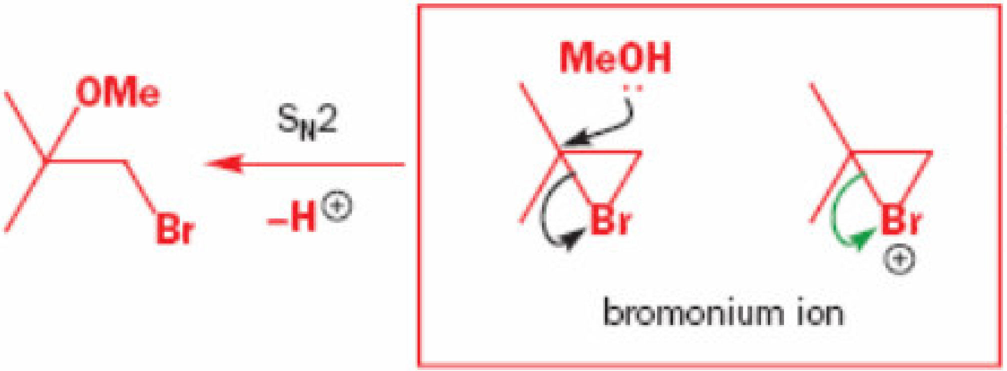


Alkene	k_{rel}
$CH_2{=}CH_2$	1
$CH_3CH{=}CH_2$	61
n-$PrCH{=}CH_2$	70
i-$PrCH{=}CH_2$	57
t-$BuCH{=}CH_2$	27
$(CH_3)_2C{=}CH_2$	5470
cis-$CH_3CH{=}CHCH_3$	2620
trans-$CH_3CH{=}CHCH_3$	1700
$(CH_3)_2C{=}CHCH_3$	130,000
$(CH_3)_2C{=}C(CH_3)_2$	1,800,000

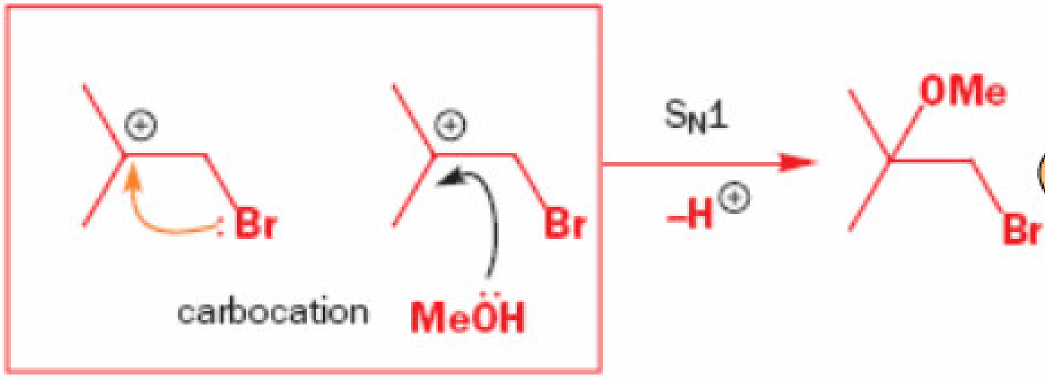
Estereoquímica X Estrutura do alceno na adição de bromo



Alkene	% anti addition	Alkene	% anti addition
	100%		83%
	100%		63%
	73%		68%

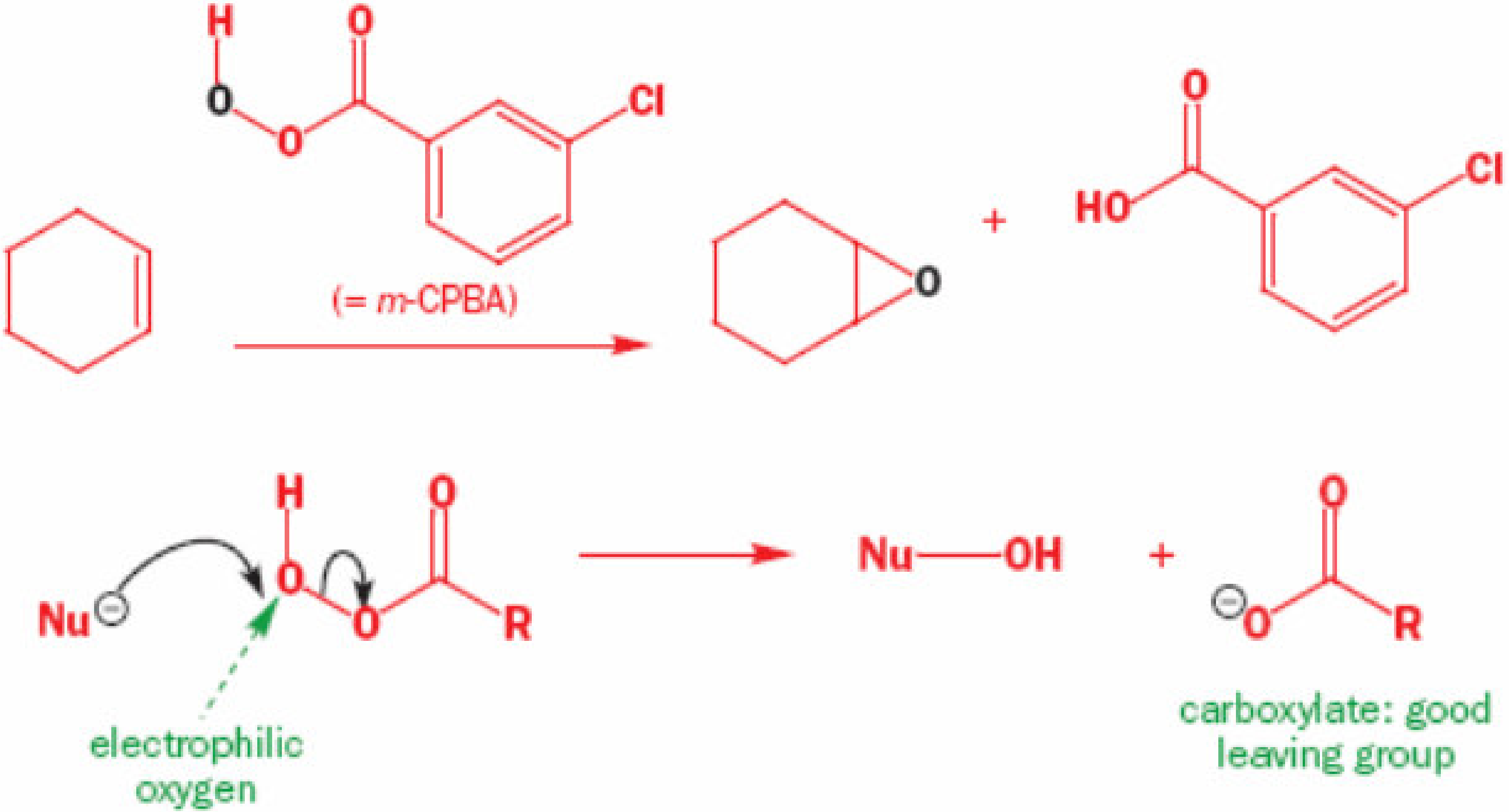


Adição anti



Adição anti e syn

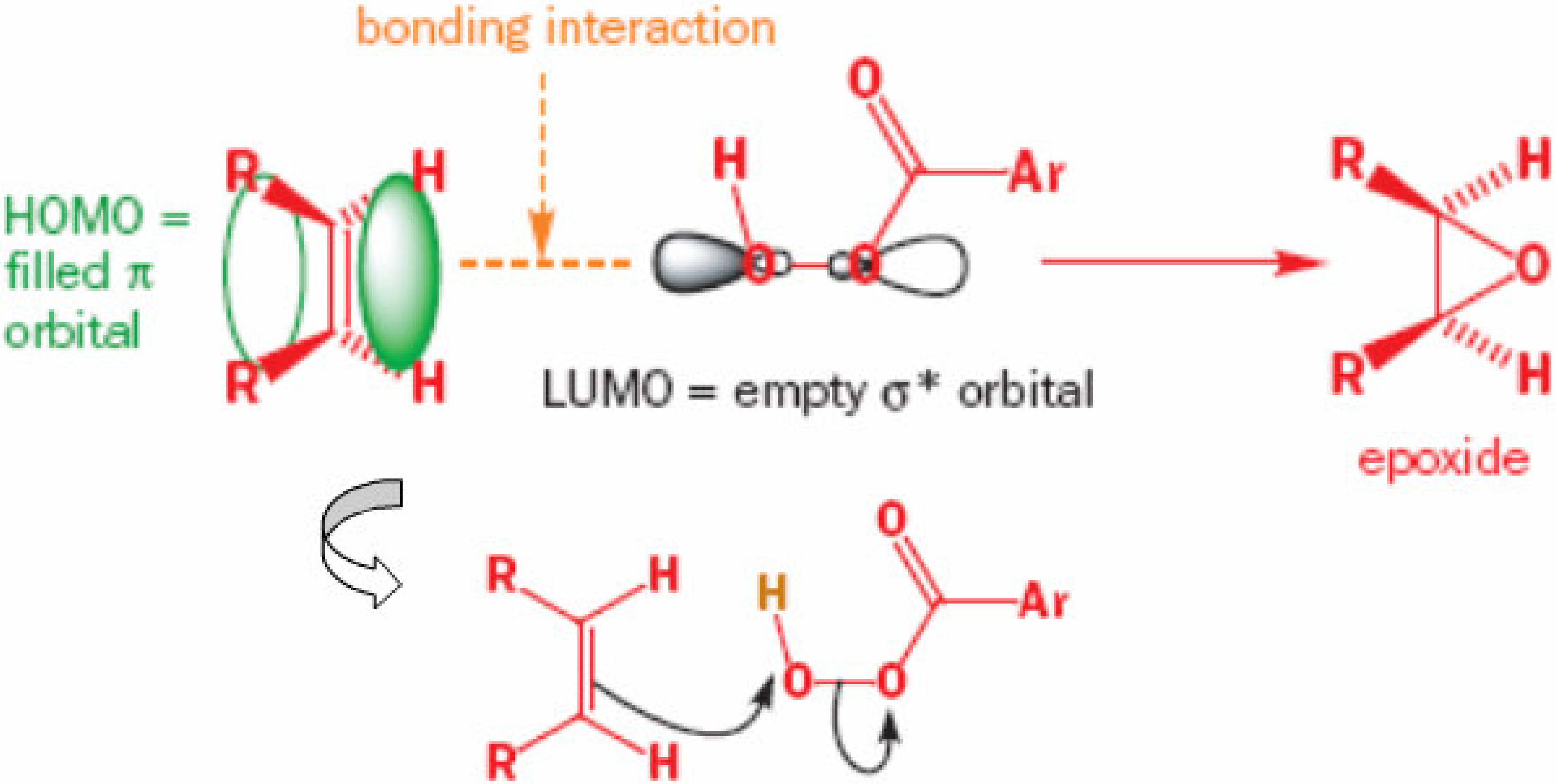
Oxidação de alcenos para formar epóxidos



electrophilic oxygen

carboxylate: good leaving group

electrophilic attack by a peroxy-acid on an alkene

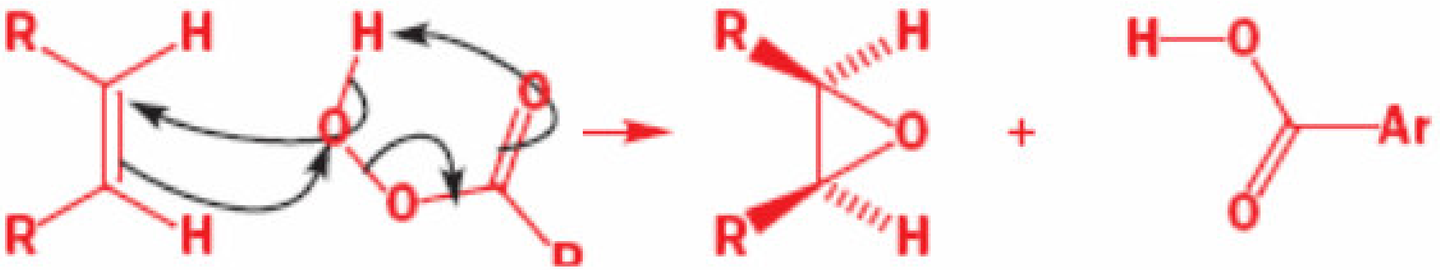


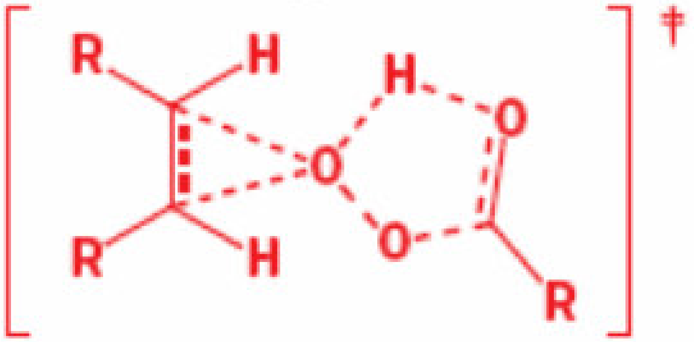
bonding interaction

HOMO = filled π orbital

LUMO = empty σ* orbital

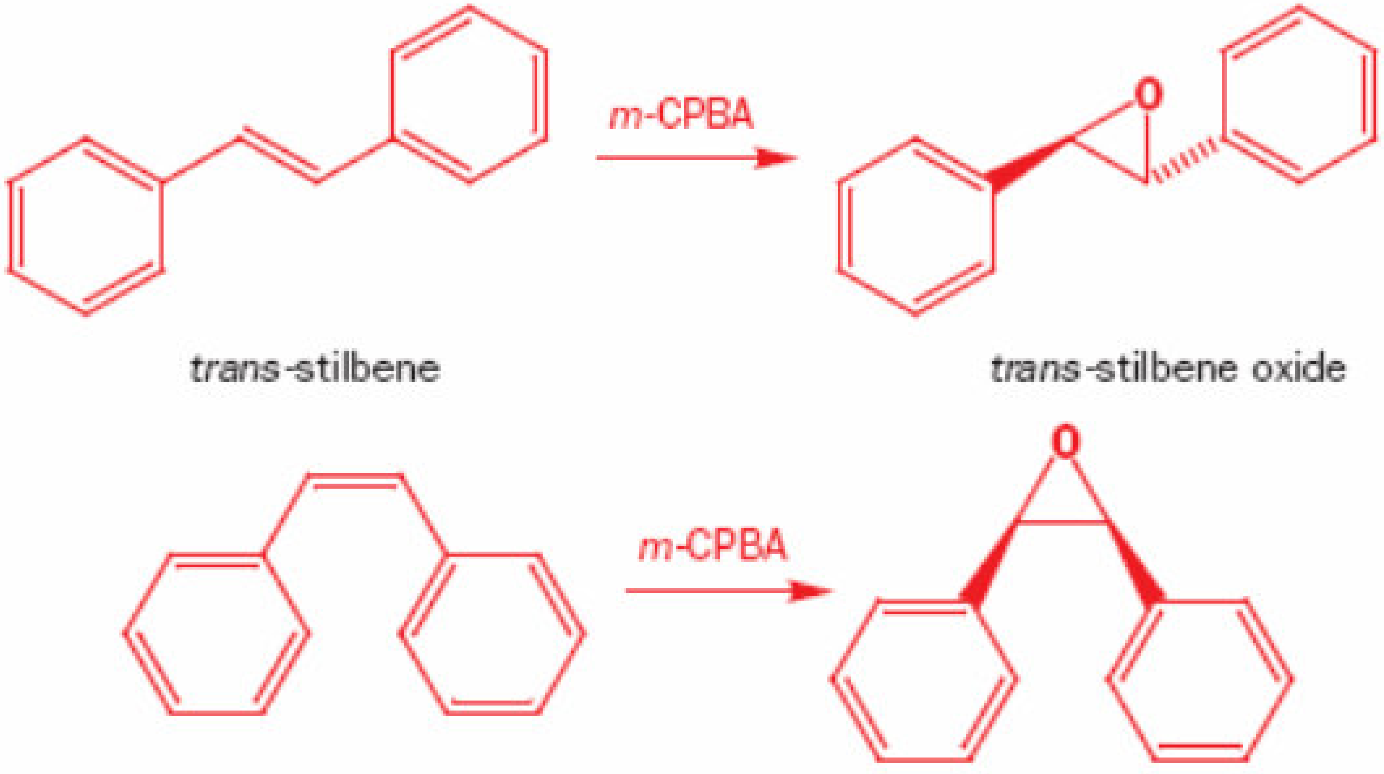
epoxide





transition state for epoxidation

A epoxidação é estereoespecífica – adição syn



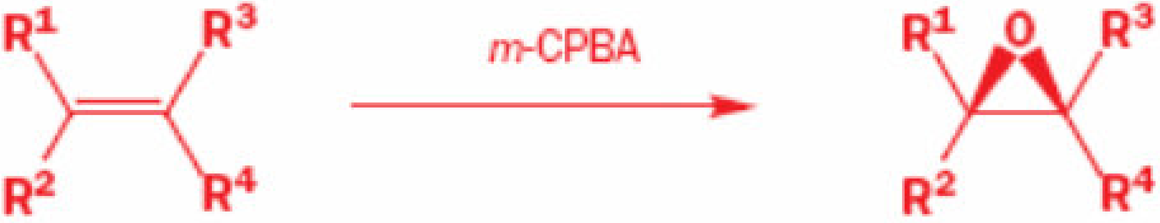
trans-stilbene

trans-stilbene oxide

cis-stilbene

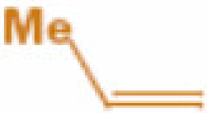
cis

Velocidade relativa de epoxidação



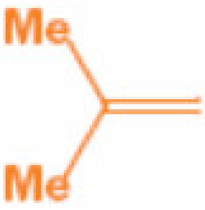
$H_2C{=}CH_2$

1

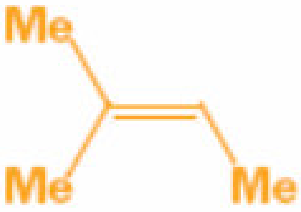


24

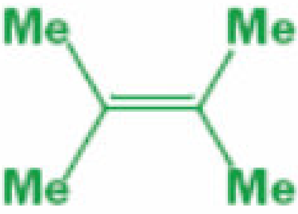
500



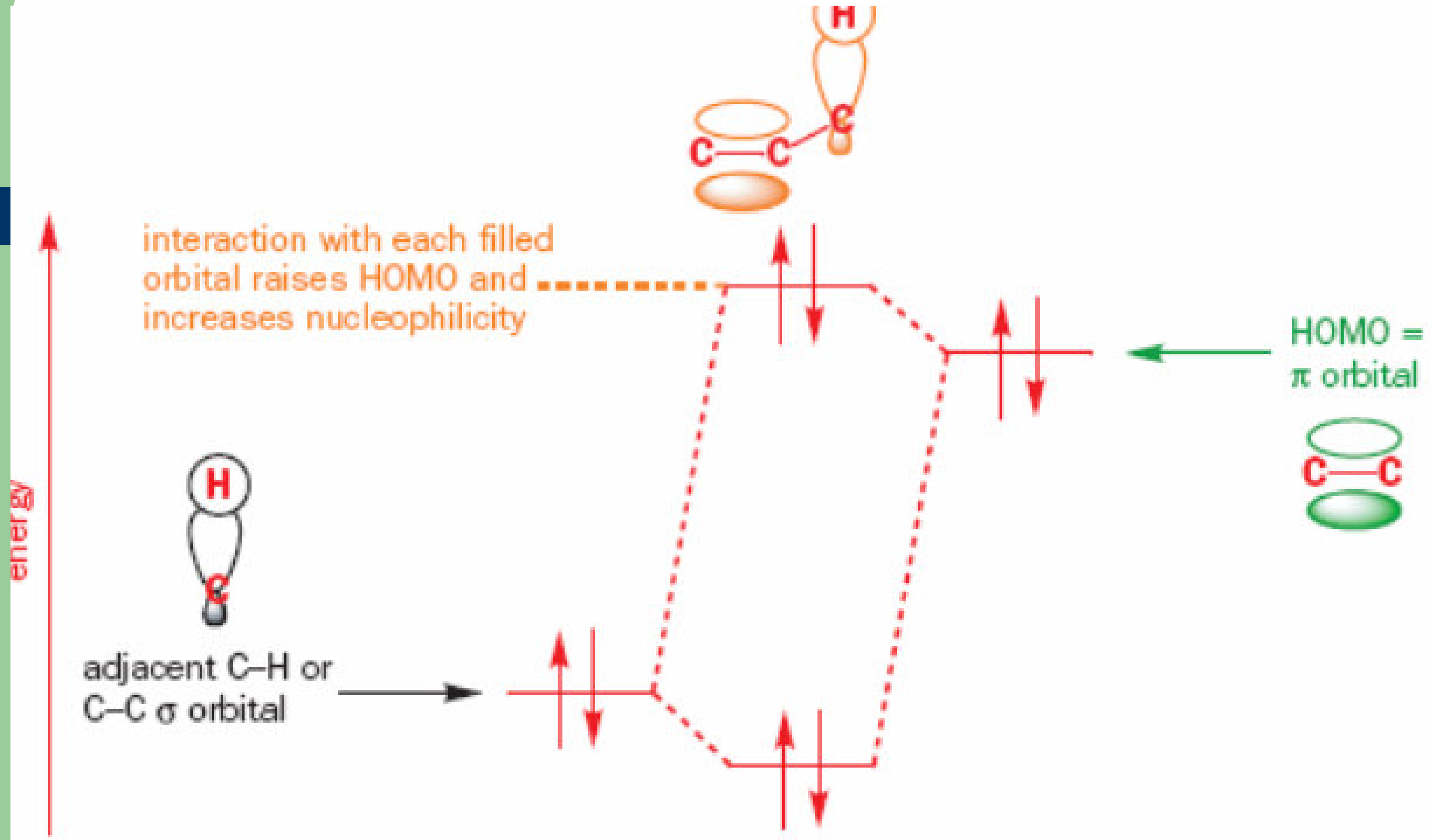
500



6500

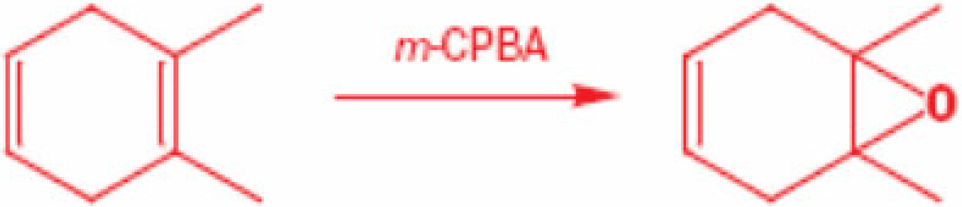


>6500

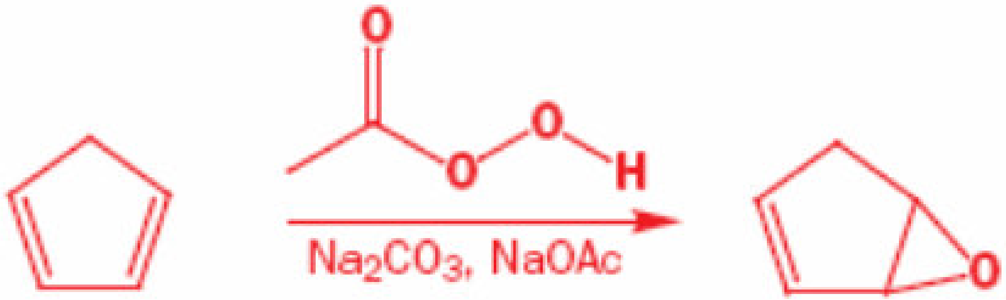


Aumento da nucleofilicidade da dupla ligação deve-se a interação C=C com a C-H adjacente.

Exemplos



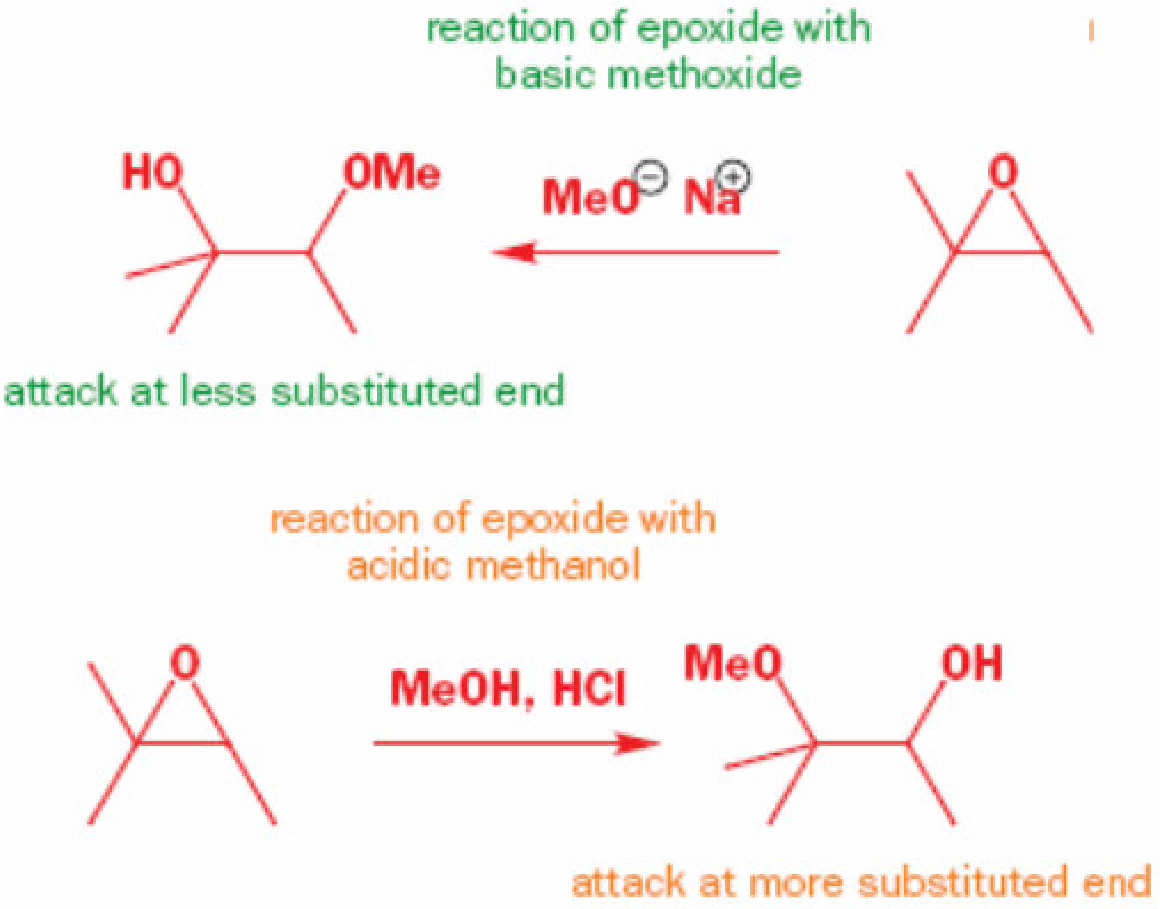
Dupla ligação mais substituída reage mais rapidamente



A epoxidação diminui a nucleofilicidade da outra dupla ligação

Por que preparar epóxidos?

Abertura do epóxido pode ser regiosseletiva



reaction of epoxide with
basic methoxide

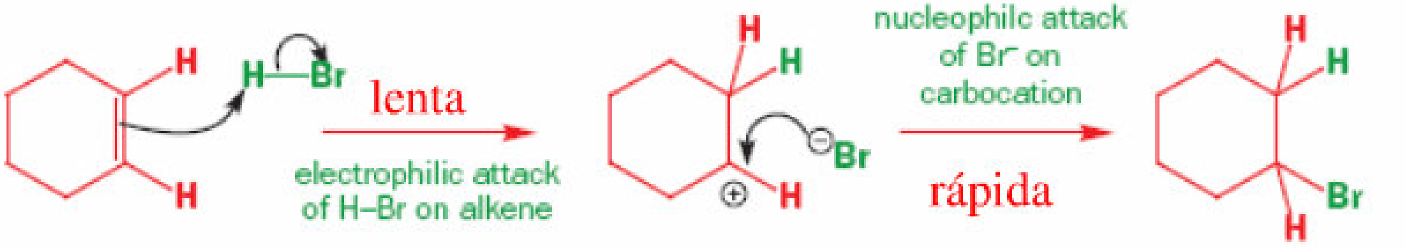
attack at less substituted end

reaction of epoxide with
acidic methanol

attack at more substituted end

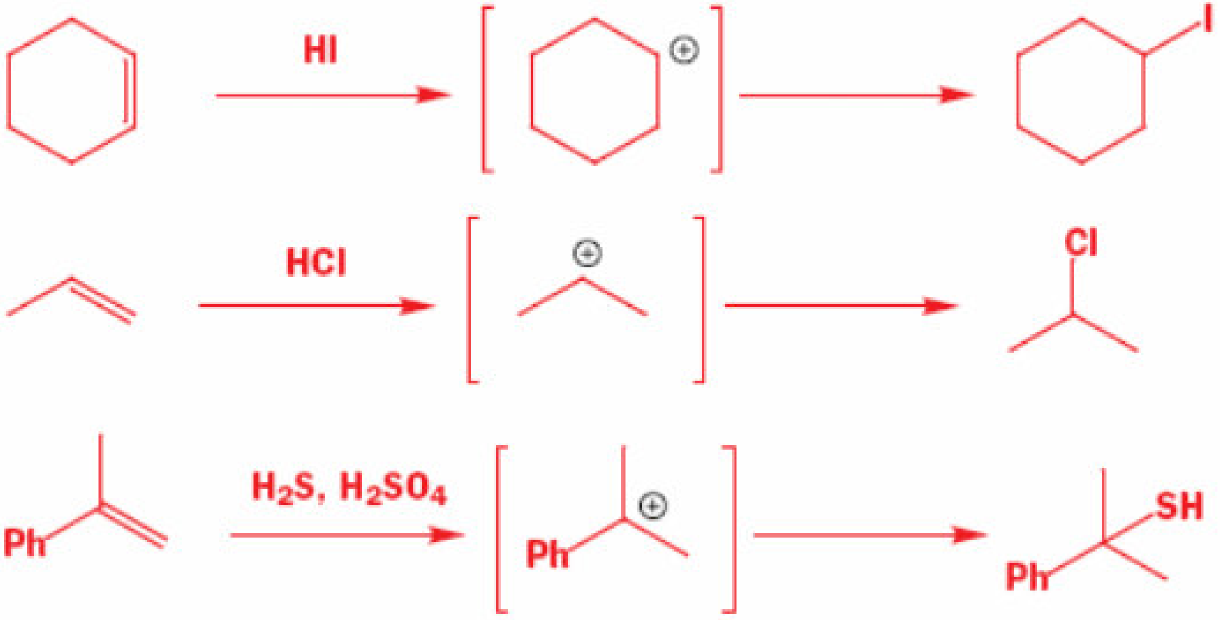
Adição eletrofílica de H-X (X=halogênio) -

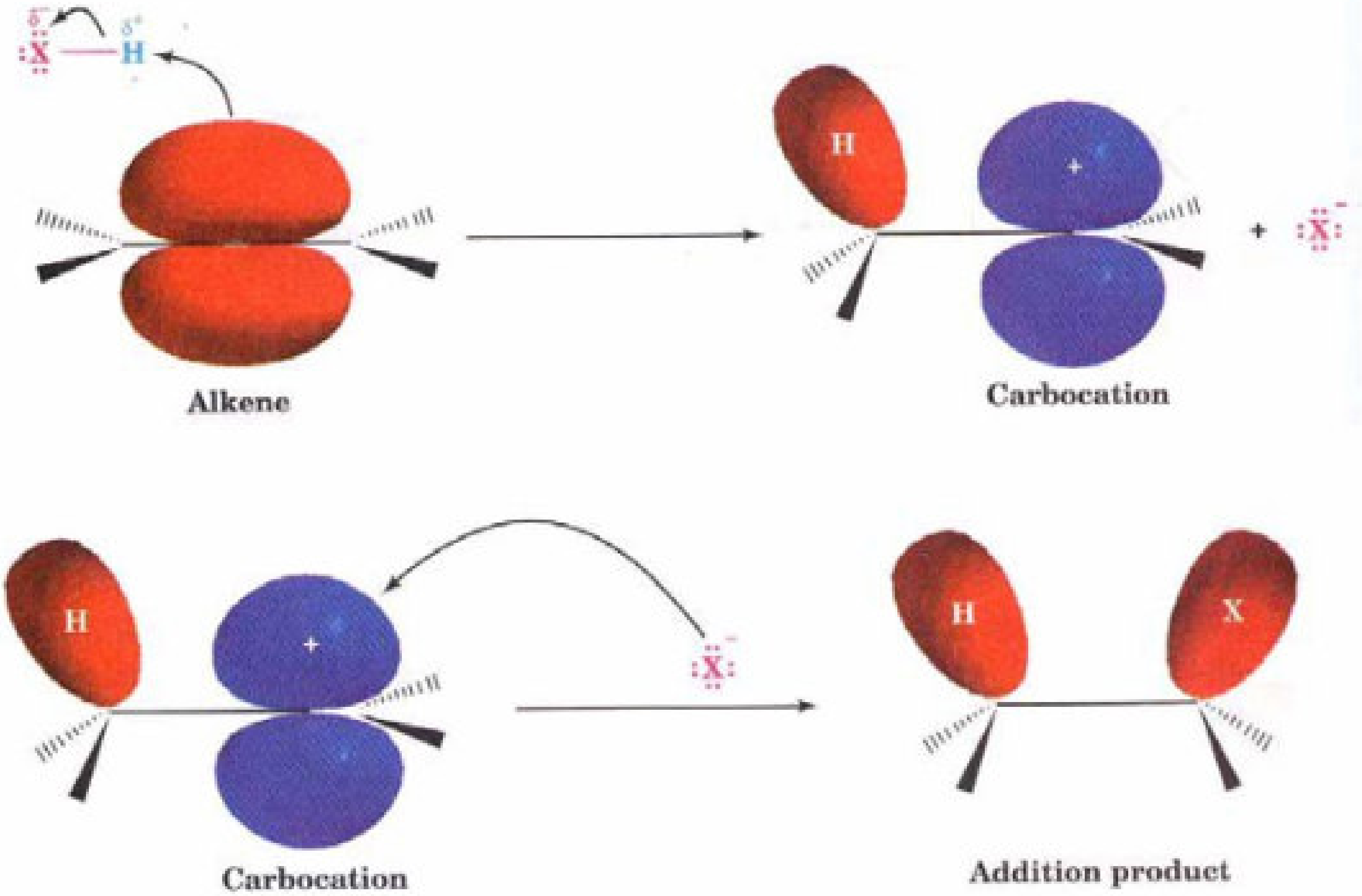
electrophilic addition of HBr to cyclohexene

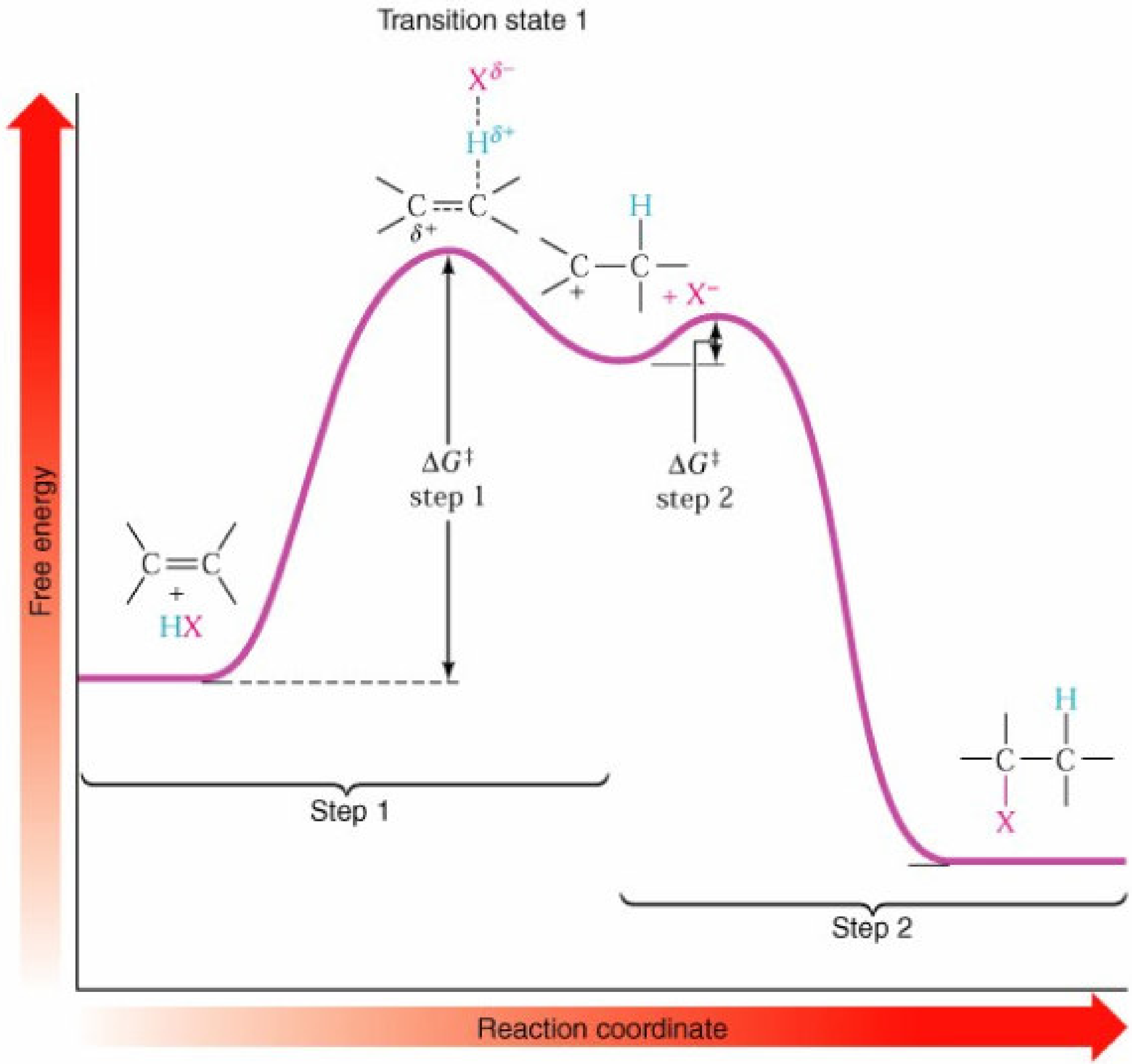


cyclohexene

cyclohexyl bromide

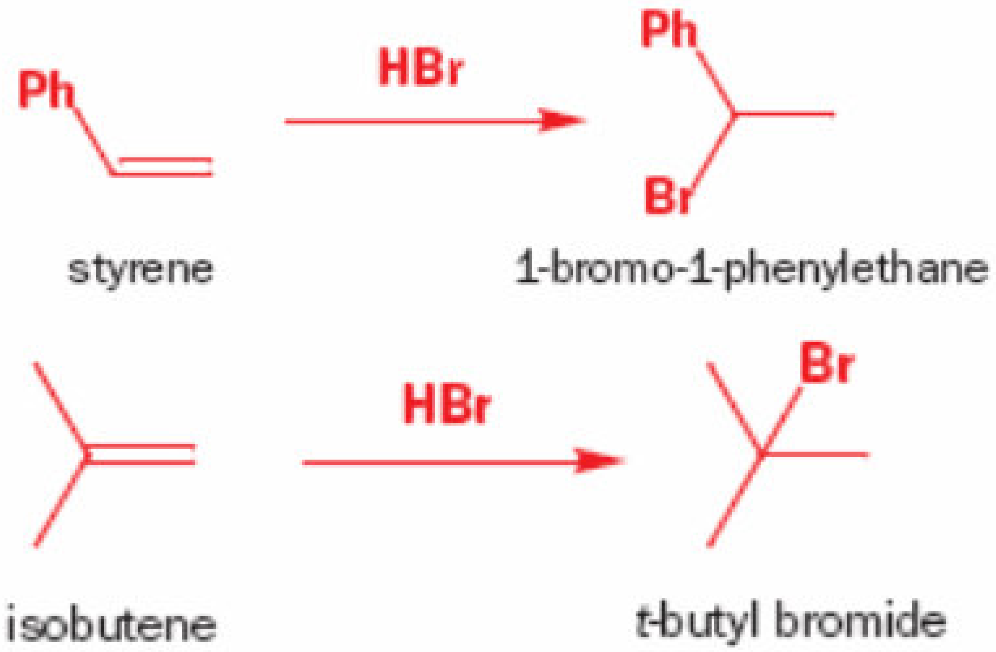



δ⁻
δ⁺
:X — H
Alkene
H
+
+ :X:⁻
Carbocation
H
+
:X:⁻
Carbocation
H
X
Addition product


Transition state 1
$X^{\delta-}$
$H^{\delta+}$
C=C
δ^{+}
H
C—C
+
+ X^{-}
$\Delta G^{\ddagger}$ step 1
$\Delta G^{\ddagger}$ step 2
C=C
+
HX
H
—C—C—
X
Step 1
Step 2
Free energy
Reaction coordinate

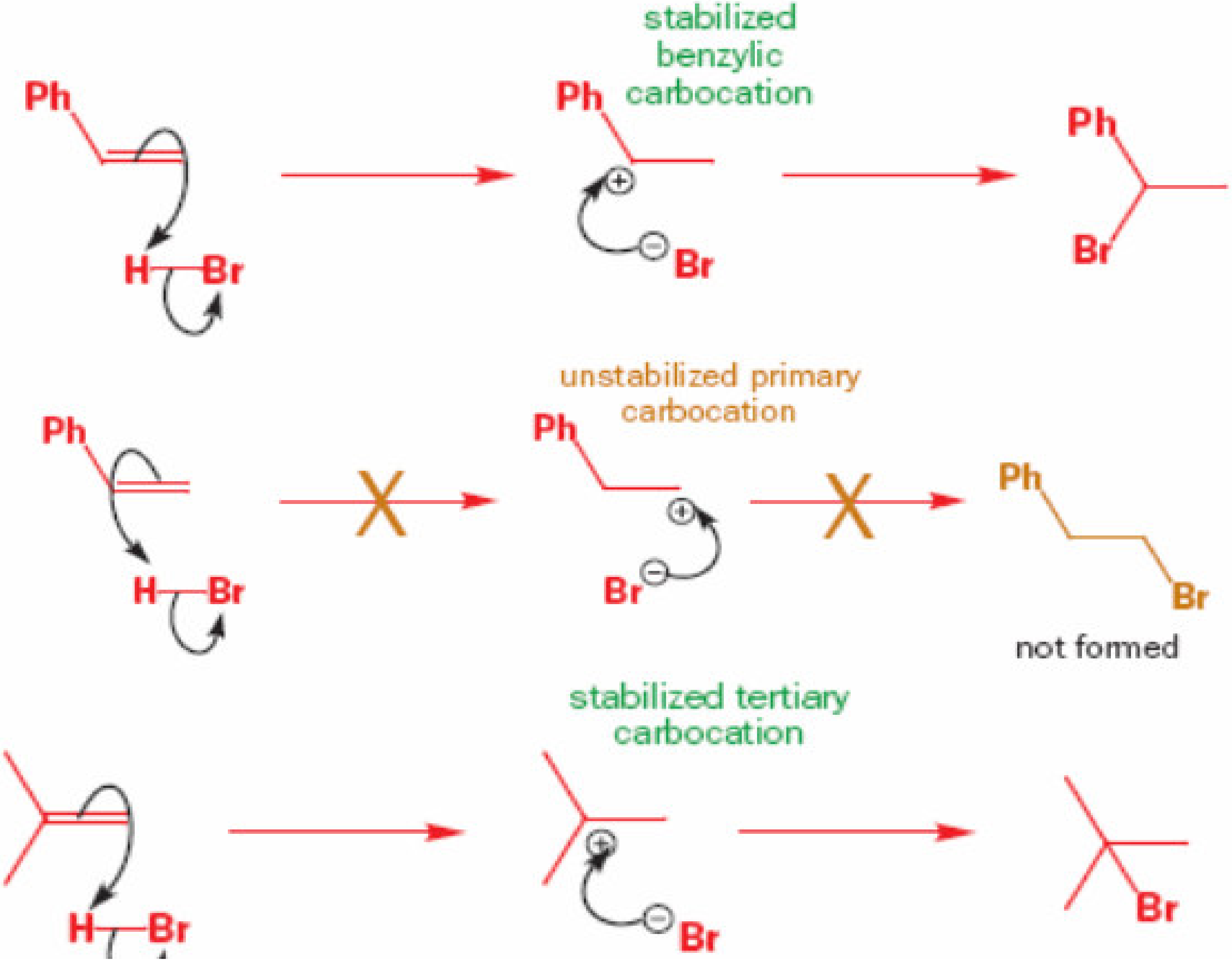
Alcenos assimétricos– Regra de Markovnikov

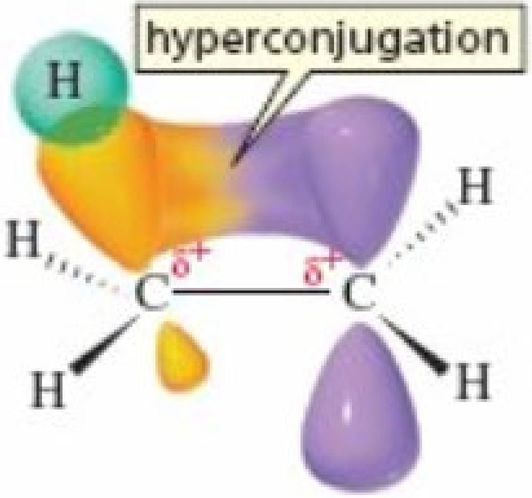
Regiosseletividade



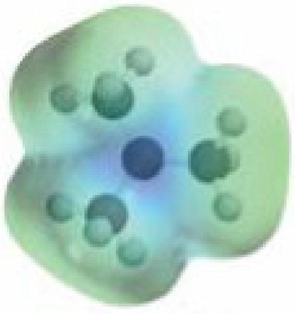
Alcenos assimétricos– Regra de Markovnikov

Regiosseletividade

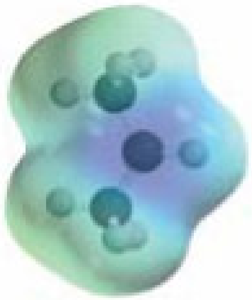




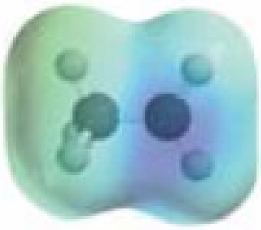
$CH_3CH_2^+$
ethyl cation



electrostatic
potential map
for the *tert*-butyl cation

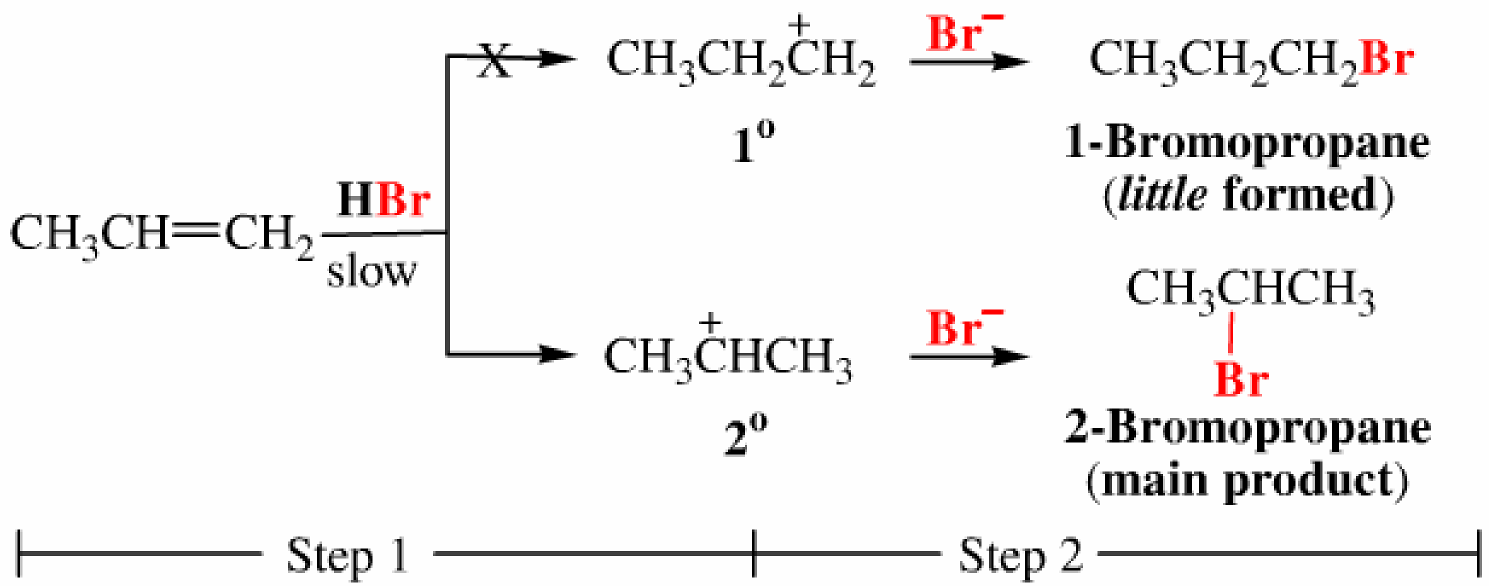


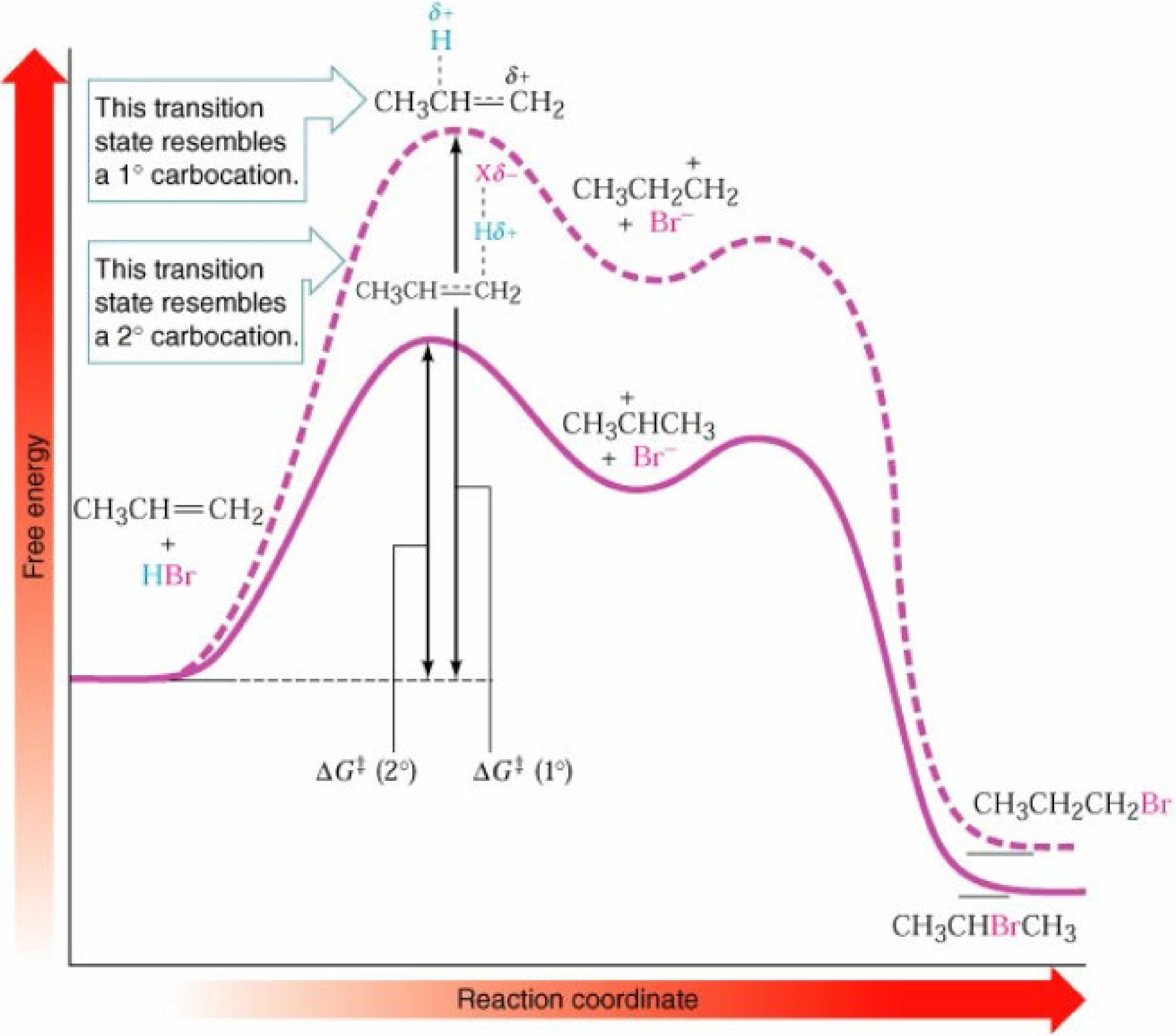
electrostatic
potential map
for the isopropyl cation



electrostatic
potential map
for the ethyl cation

electrostatic
potential map
for the methyl cation


$CH_3CH{=}CH_2 \xrightarrow[\text{slow}]{HBr}$
$\not\longrightarrow CH_3CH_2\overset{+}{C}H_2 \xrightarrow{Br^-} CH_3CH_2CH_2Br$
1°
1-Bromopropane
(*little* formed)
$\longrightarrow CH_3\overset{+}{C}HCH_3 \xrightarrow{Br^-} CH_3\underset{\underset{Br}{|}}{C}HCH_3$
2°
2-Bromopropane
(main product)
Step 1
Step 2

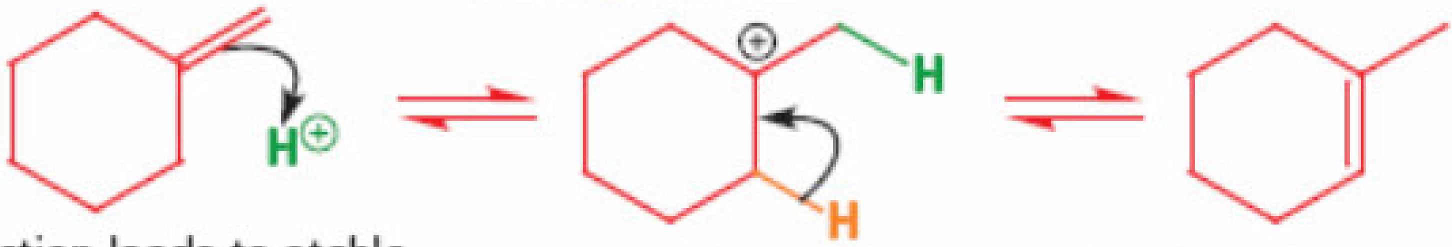


This transition state resembles a 1° carbocation.

This transition state resembles a 2° carbocation.

Isomerização de um Alceno em meio ácido

isomerization of an alkene in acid



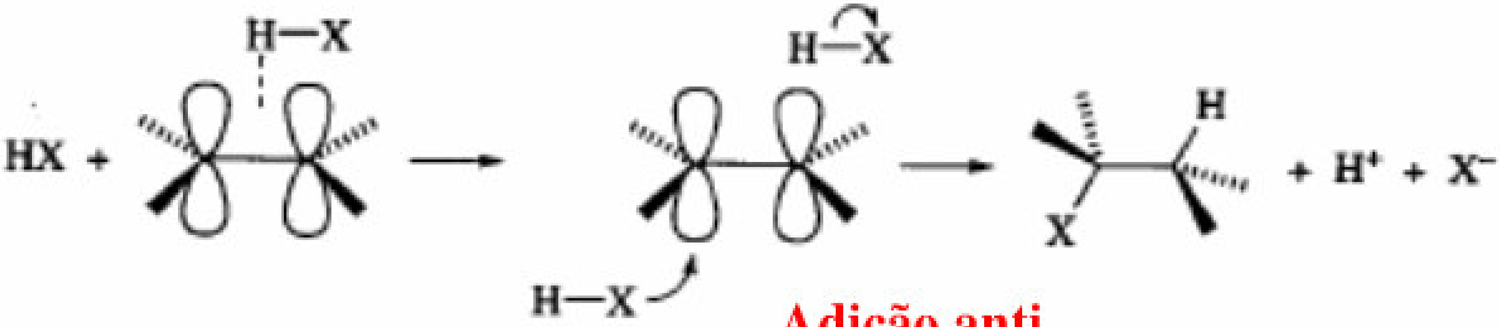
loss of green proton gives back starting material

protonation leads to stable, tertiary carbocation

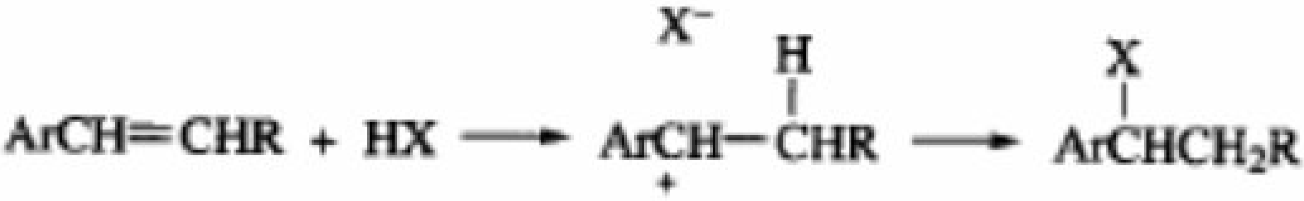
loss of orange proton leads to more stable trisubstituted double bond

E$_1$ e isomerização – controle termodinâmico

Estereoquímica



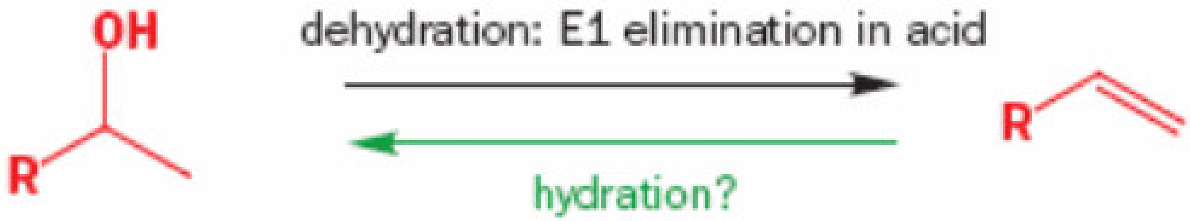
Adição anti



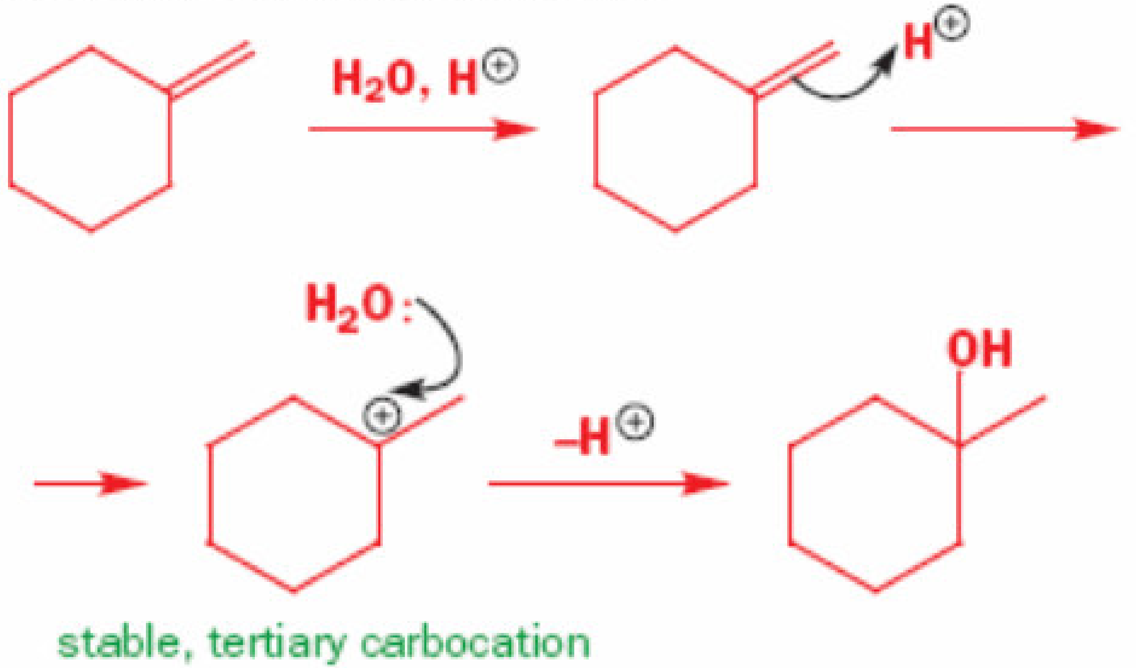
$$\mathrm{ArCH{=}CHR} + \mathrm{HX} \longrightarrow \overset{X^-}{} \ \underset{+}{\mathrm{ArCH}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\mathrm{HR} \longrightarrow \mathrm{Ar}\overset{\mathrm{X}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2R}$$

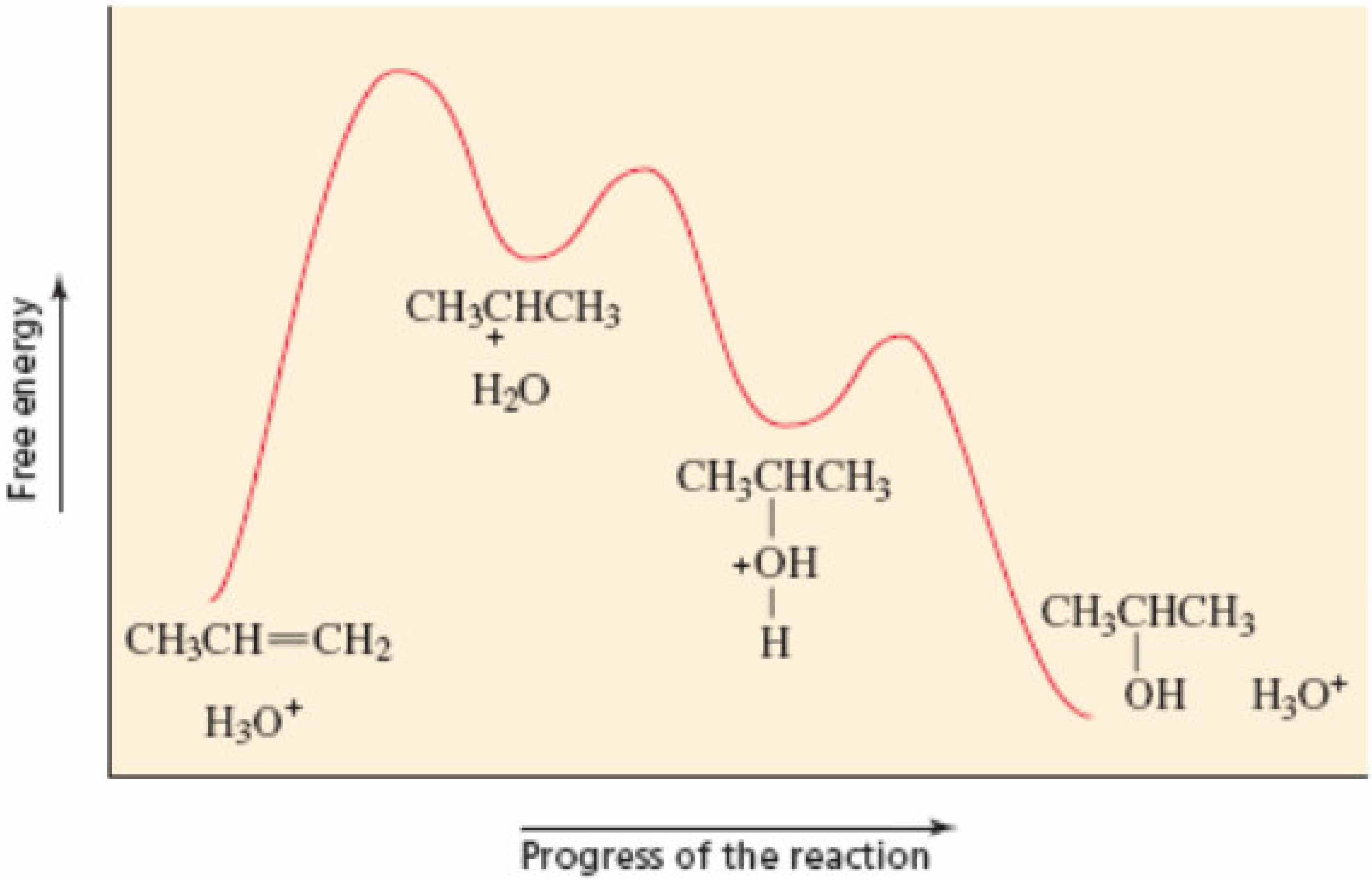
Carbocátion estável – adição syn via par iônico

Adição eletrofílica de água - hidratação

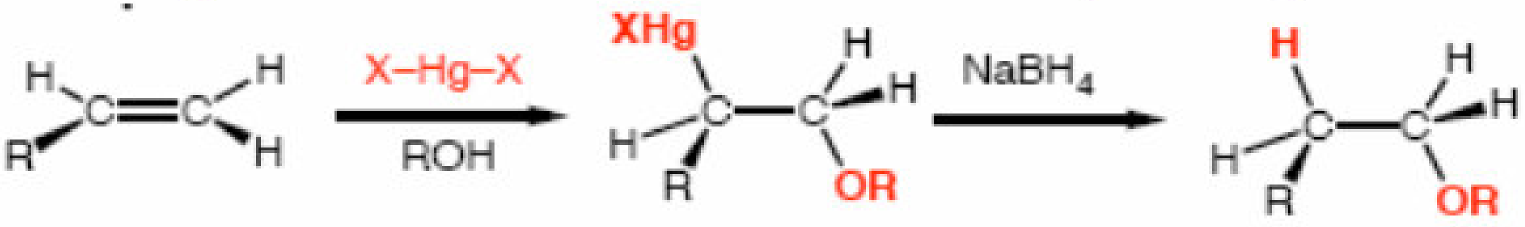


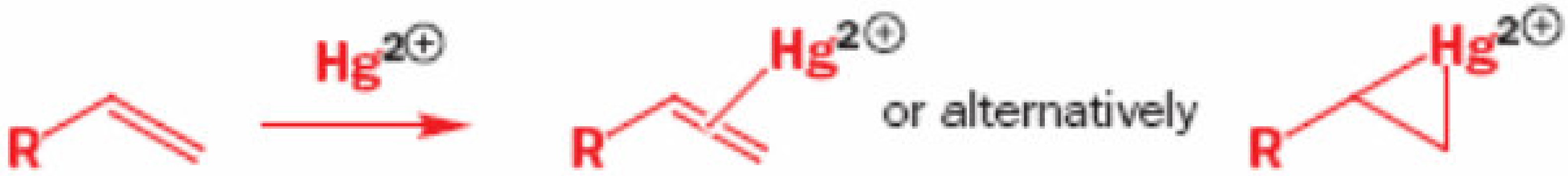
acid-catalysed hydration of an alkene

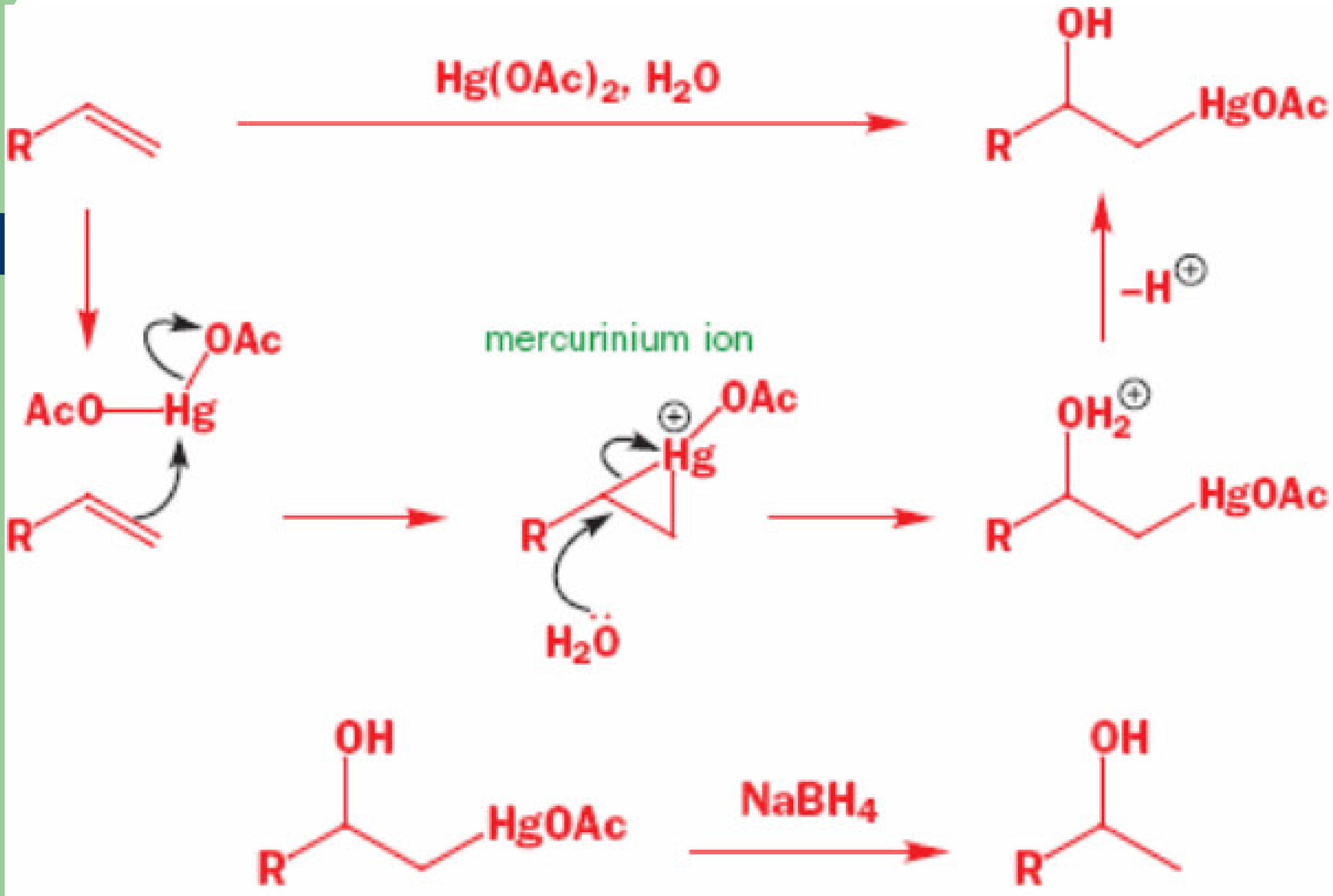



Free energy
$CH_3\overset{+}{C}HCH_3$
H_2O
$CH_3CH=CH_2$
H_3O^+
CH_3CHCH_3
$+OH$
H
CH_3CHCH_3
OH
H_3O^+
Progress of the reaction

Adição eletrofílica de água – oximercuração/redução

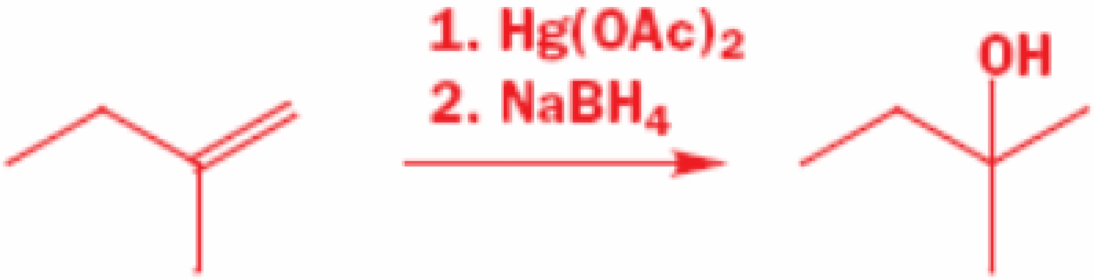






Hg(OAc)$_2$, H$_2$O
R
OH
HgOAc
R
-H$^{\oplus}$
OAc
AcO—Hg
R
mercurinium ion
⊕
OAc
Hg
R
H$_2$Ö
OH$_2^{\oplus}$
HgOAc
R
OH
HgOAc
R
NaBH$_4$
OH
R

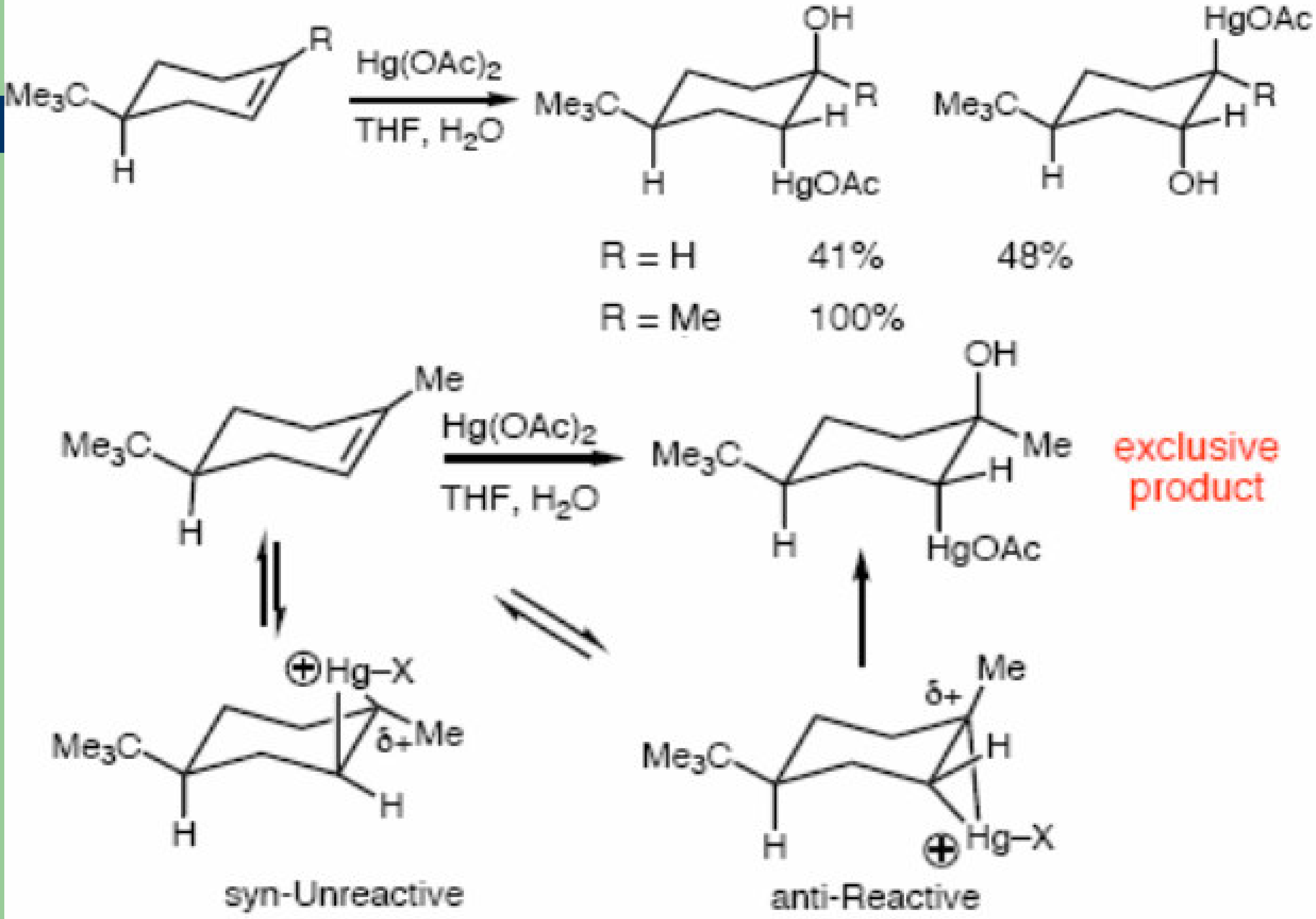
- **Exemplo**



Adição anti – estereoespecífica

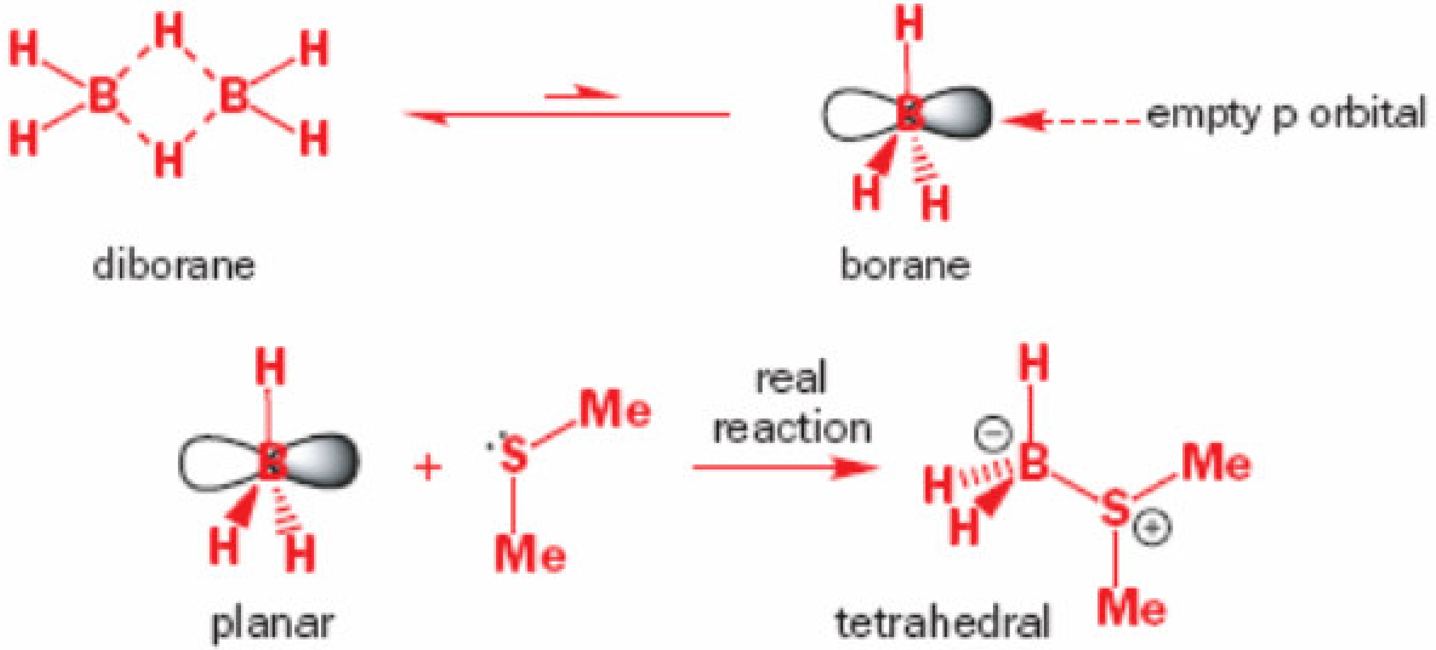
Segue a regra de Markovnikov - Regioespecífica

Oximercuração X Halogenação – mesmo caminho reacional

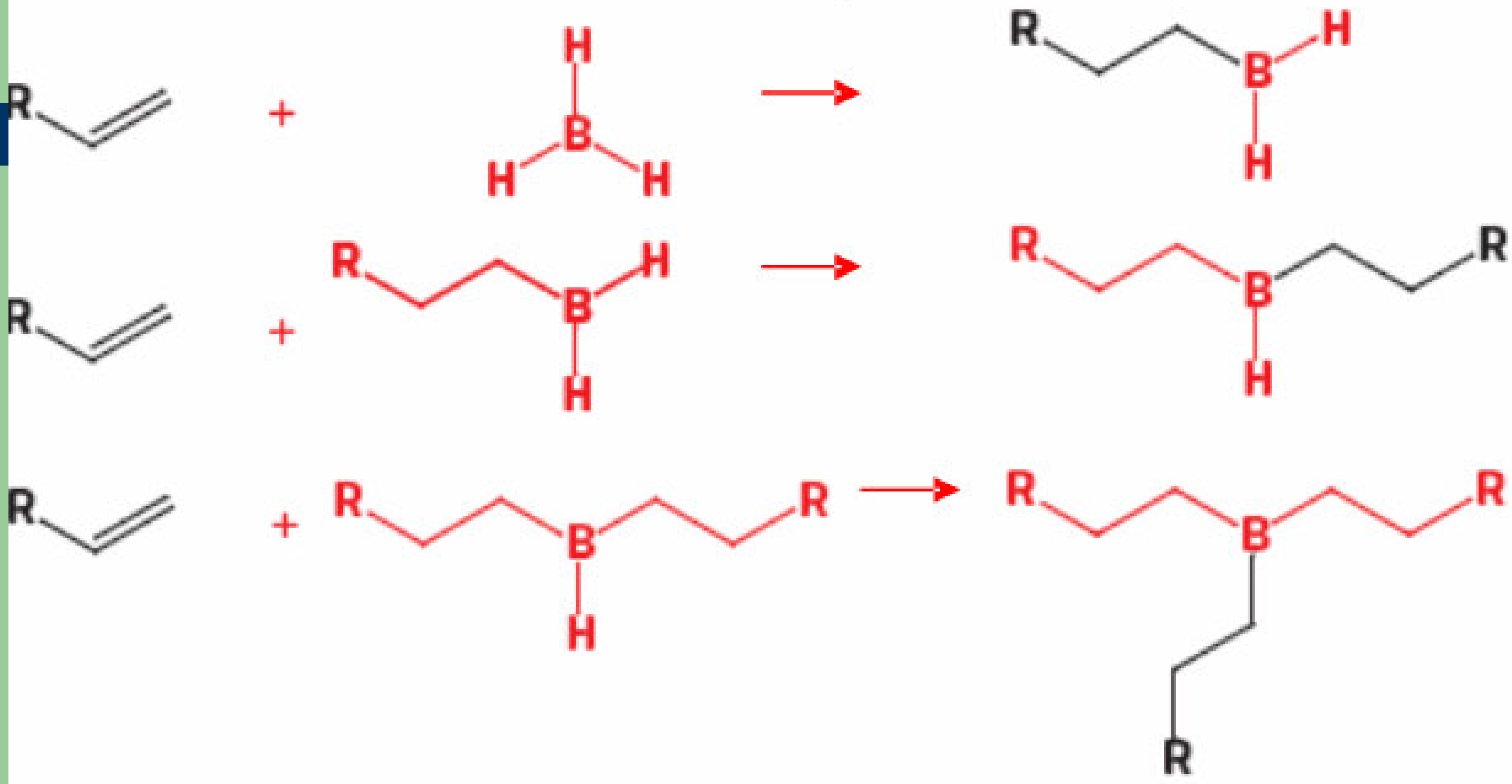


Reação de adição de boro – hidroboração

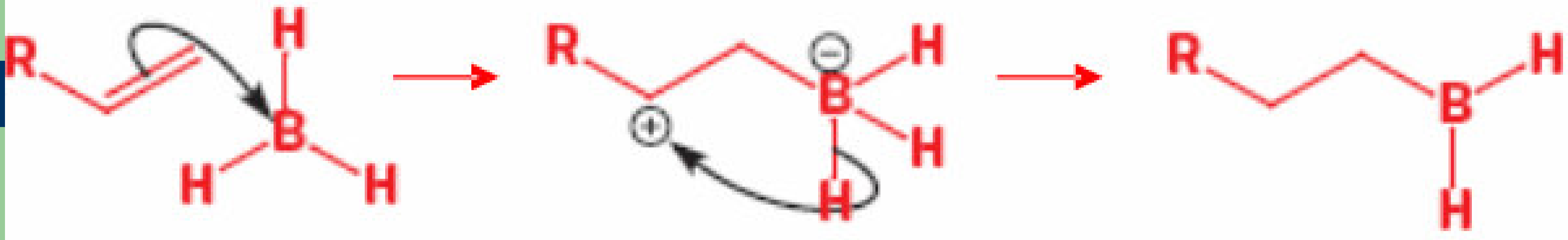
Boro



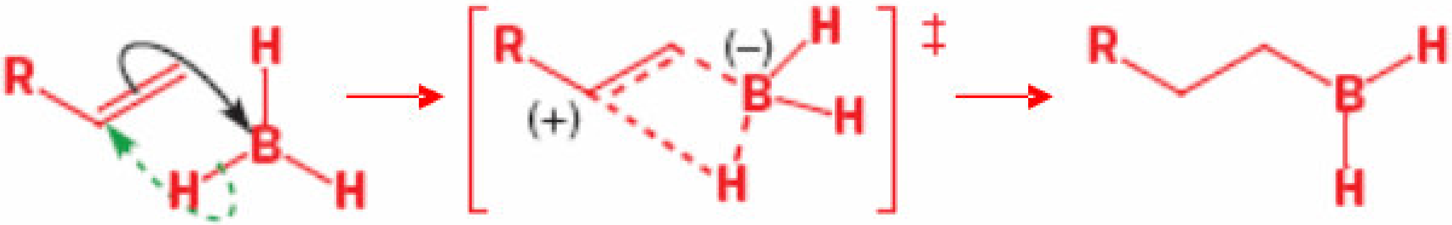
Hidroboração



Mecanismo parcial

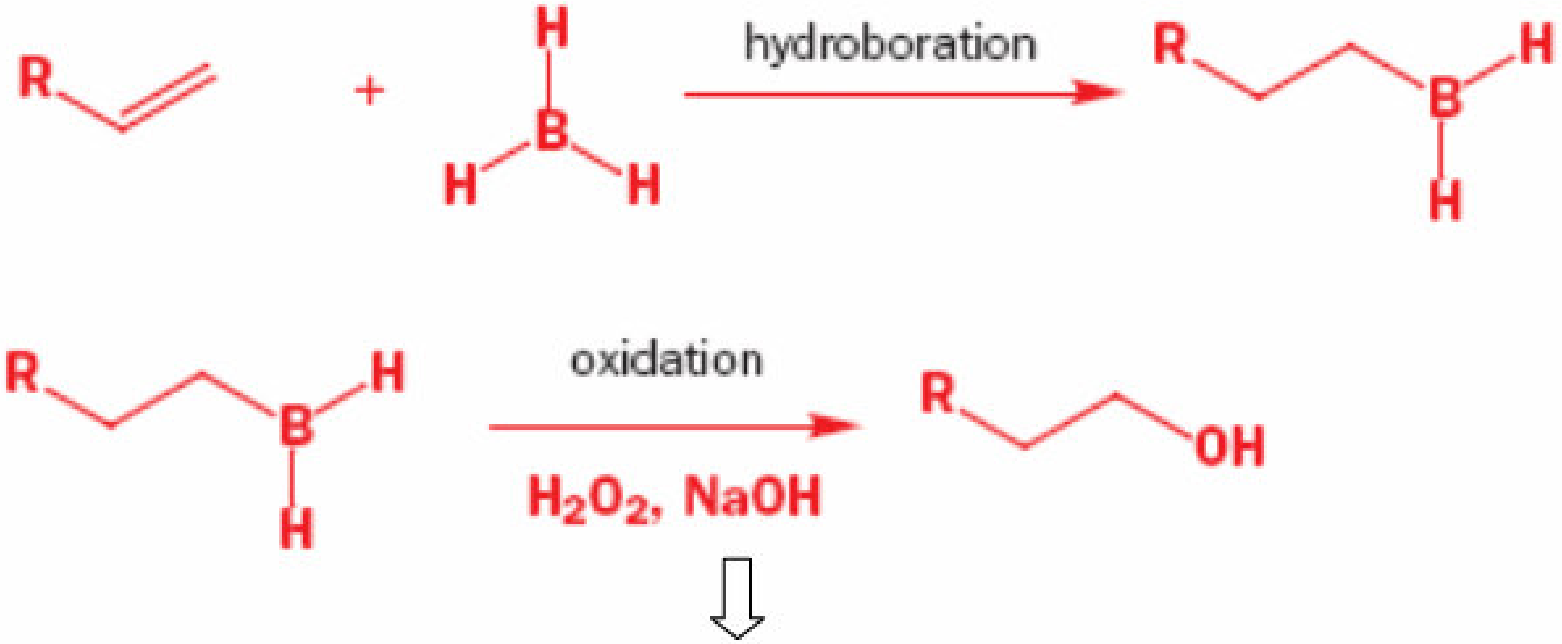


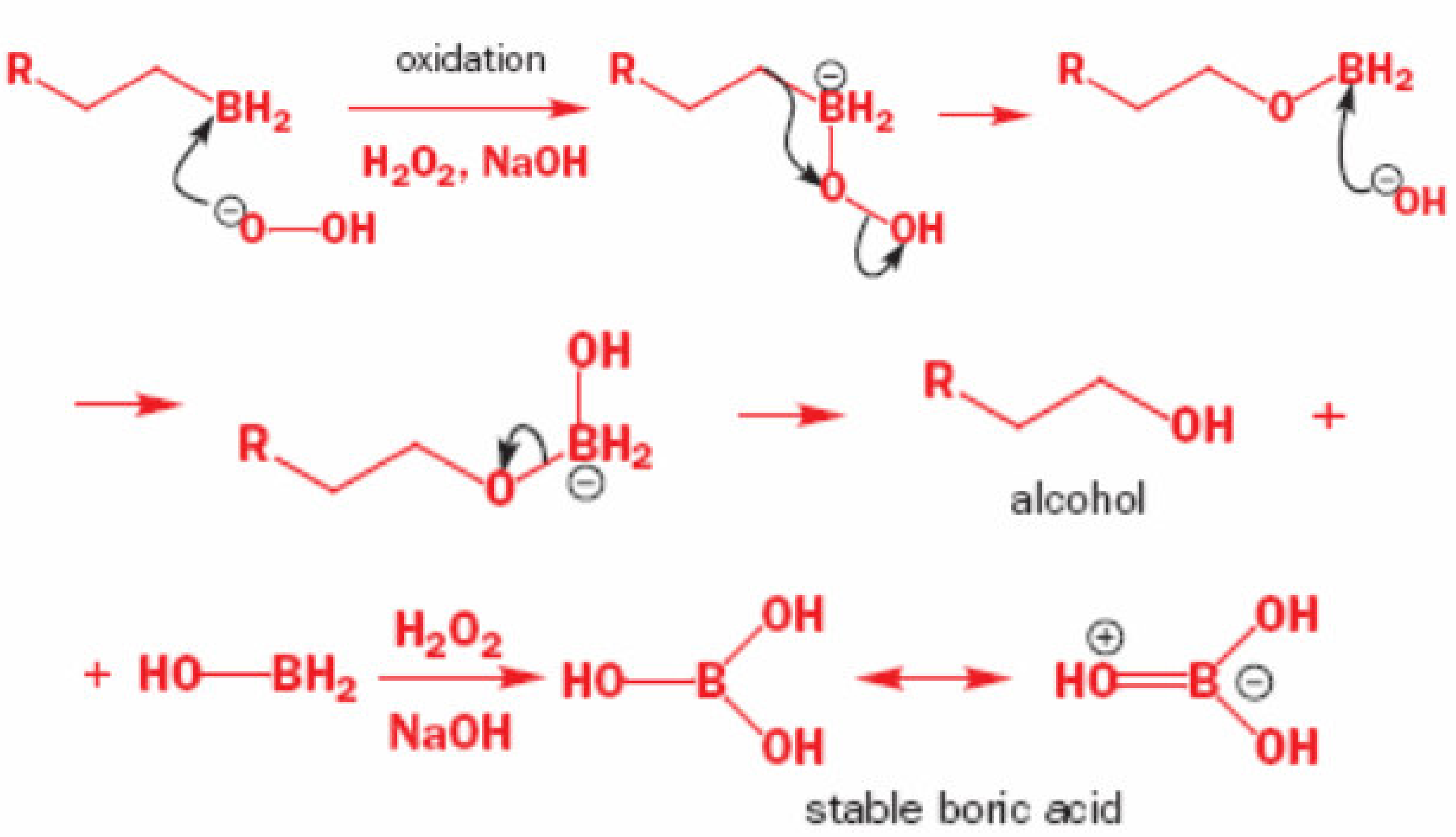
Estado de transição - estereoespecífico

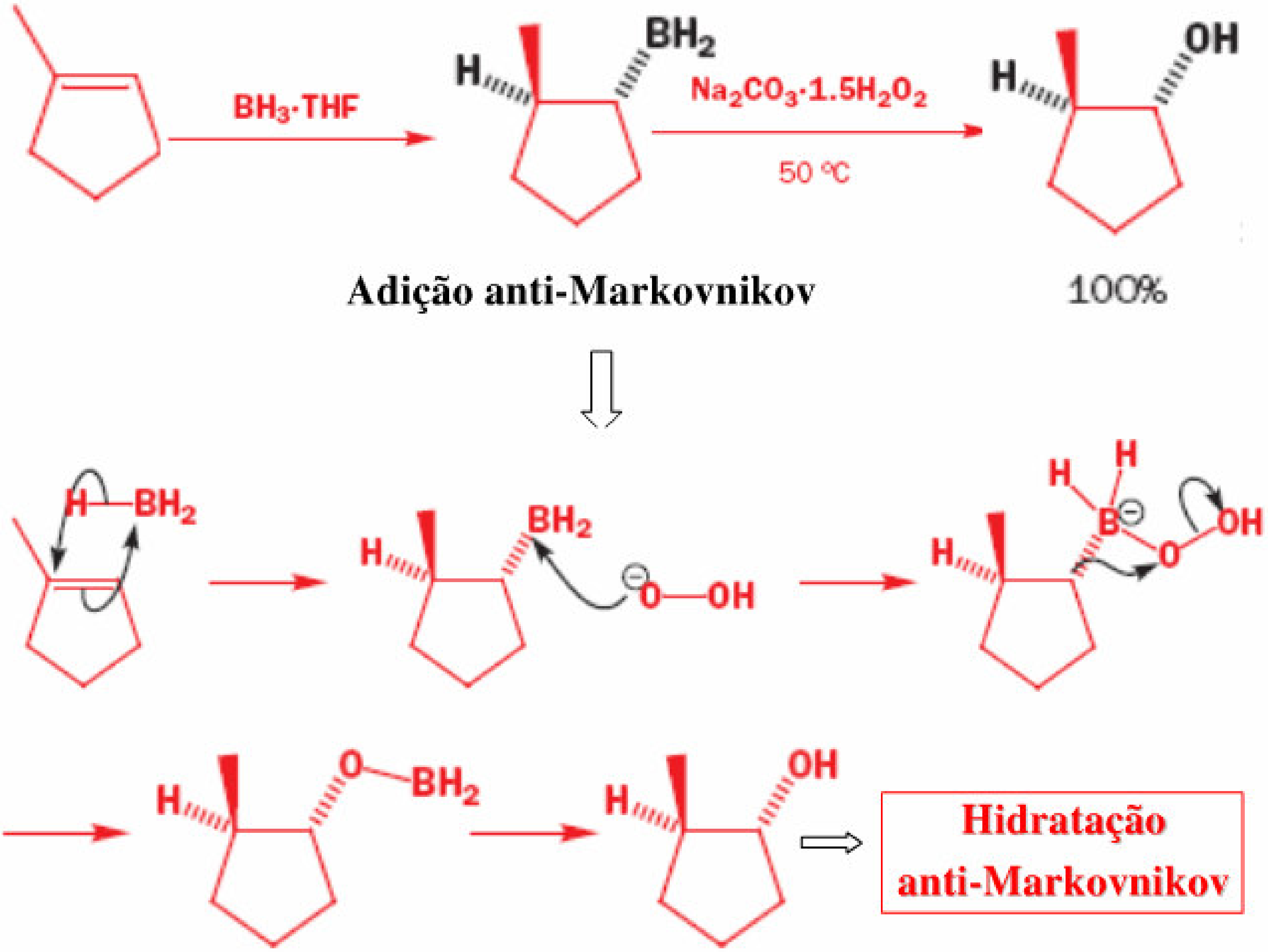


Adição cis

Hidroboração / Oxidação



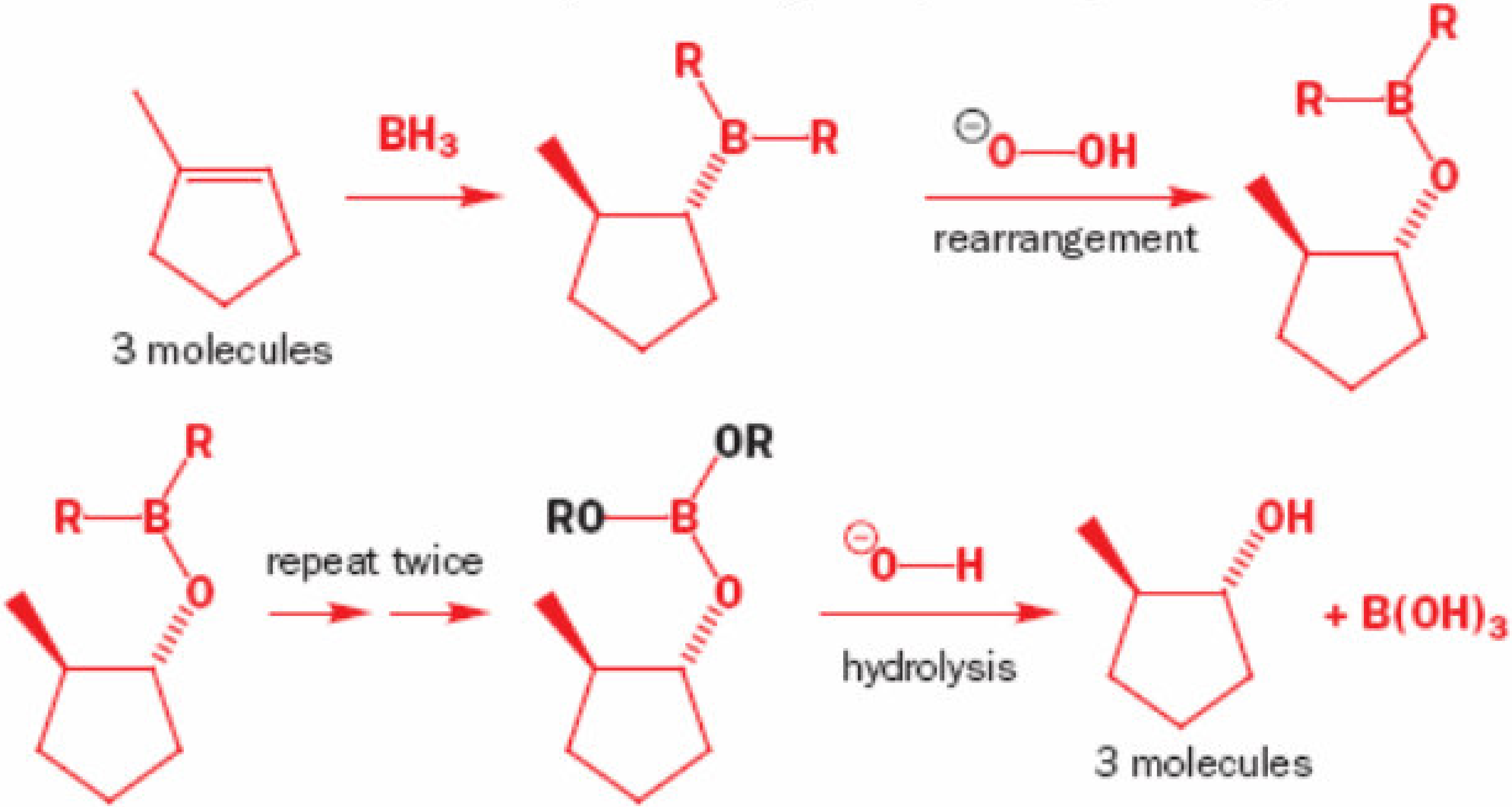

oxidation
H_2O_2, NaOH
alcohol
H_2O_2
NaOH
stable boric acid



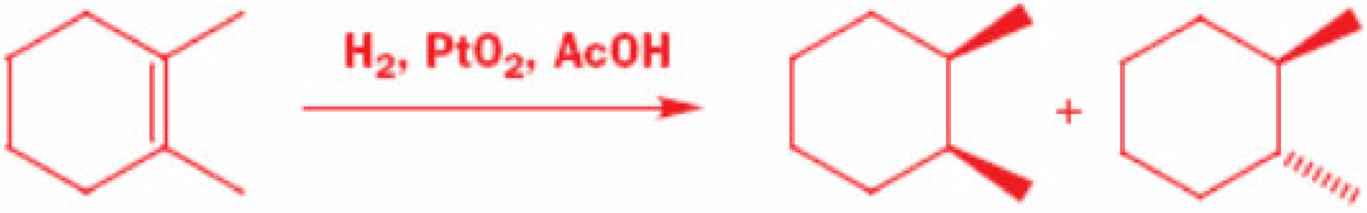
Adição anti-Markovnikov

Hidratação anti-Markovnikov

A hidroboração/Oxidação ocorre três vezes

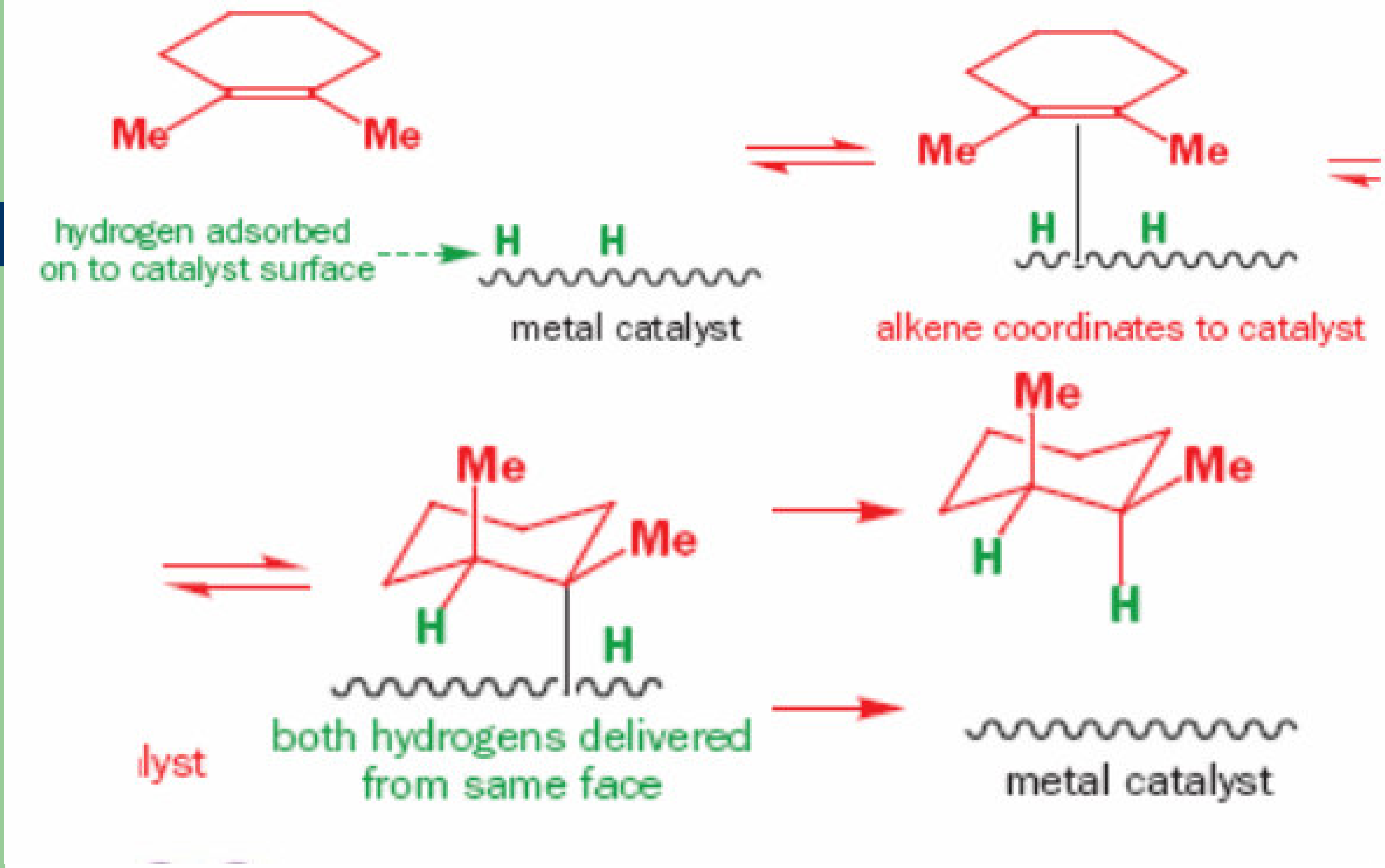


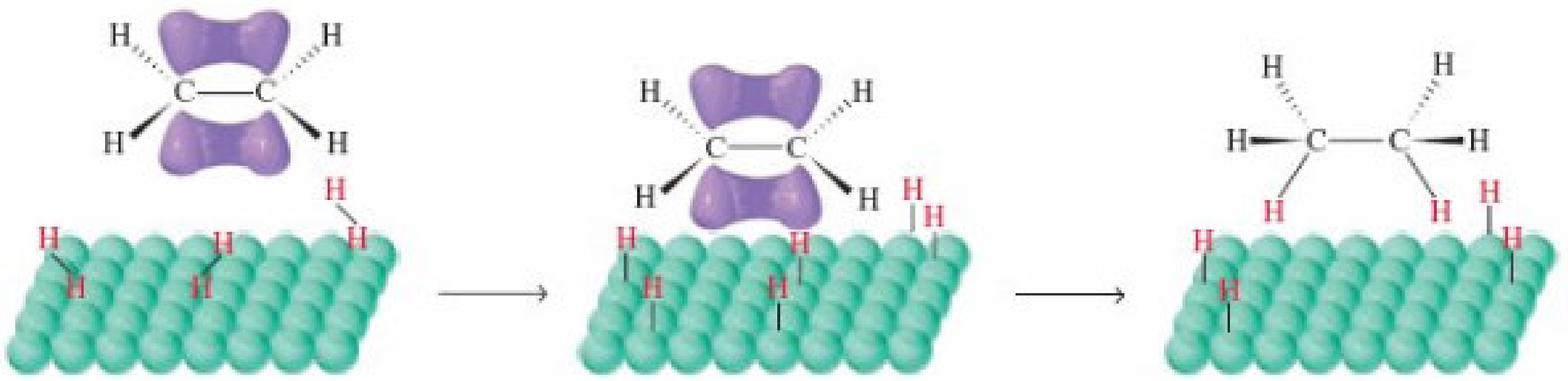
Hidrogenação catalítica



82% *cis* 18% *trans*

Substrate	Usual choice of metal
benzyl amine or ether	Pd
alkene	Pd, Pt, or Ni
aromatic ring	Pt or Rh, or Ni under high pressure

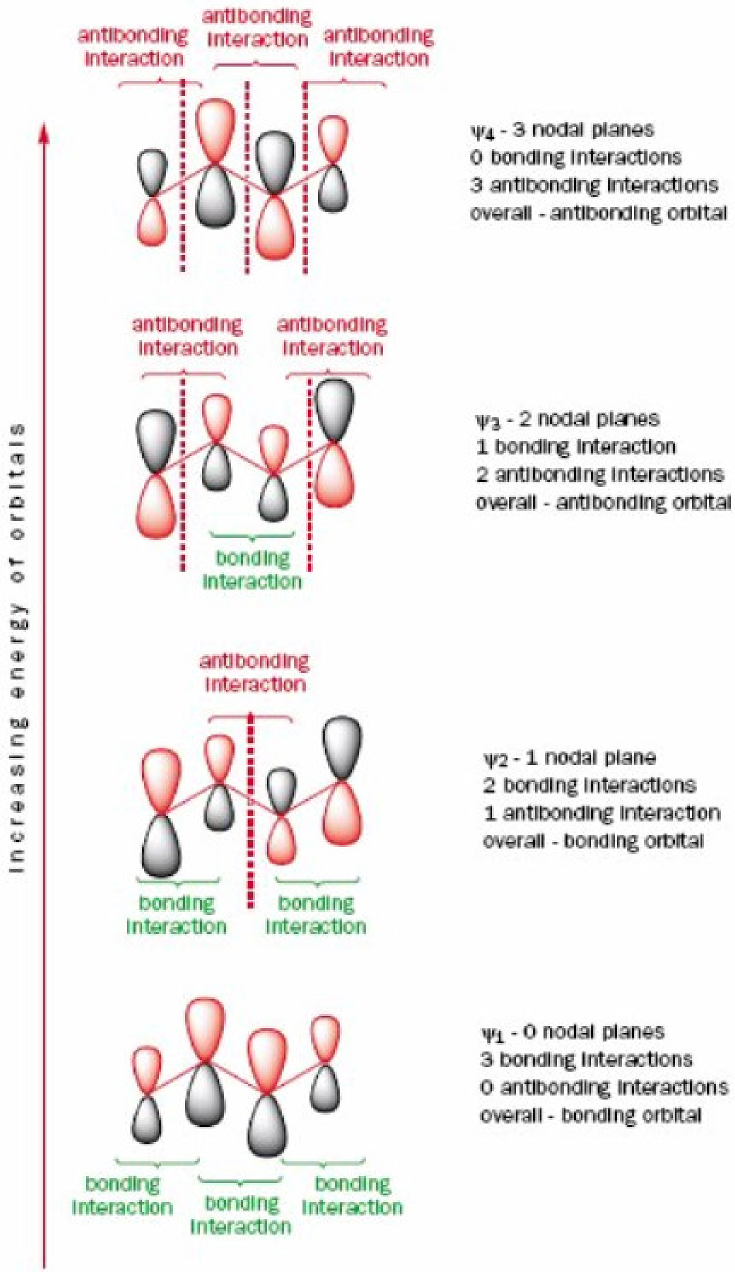

Me
Me
hydrogen adsorbed on to catalyst surface
H H
metal catalyst
Me
Me
H H
alkene coordinates to catalyst
lyst
Me
Me
H
H
both hydrogens delivered from same face
Me
Me
H
H
metal catalyst

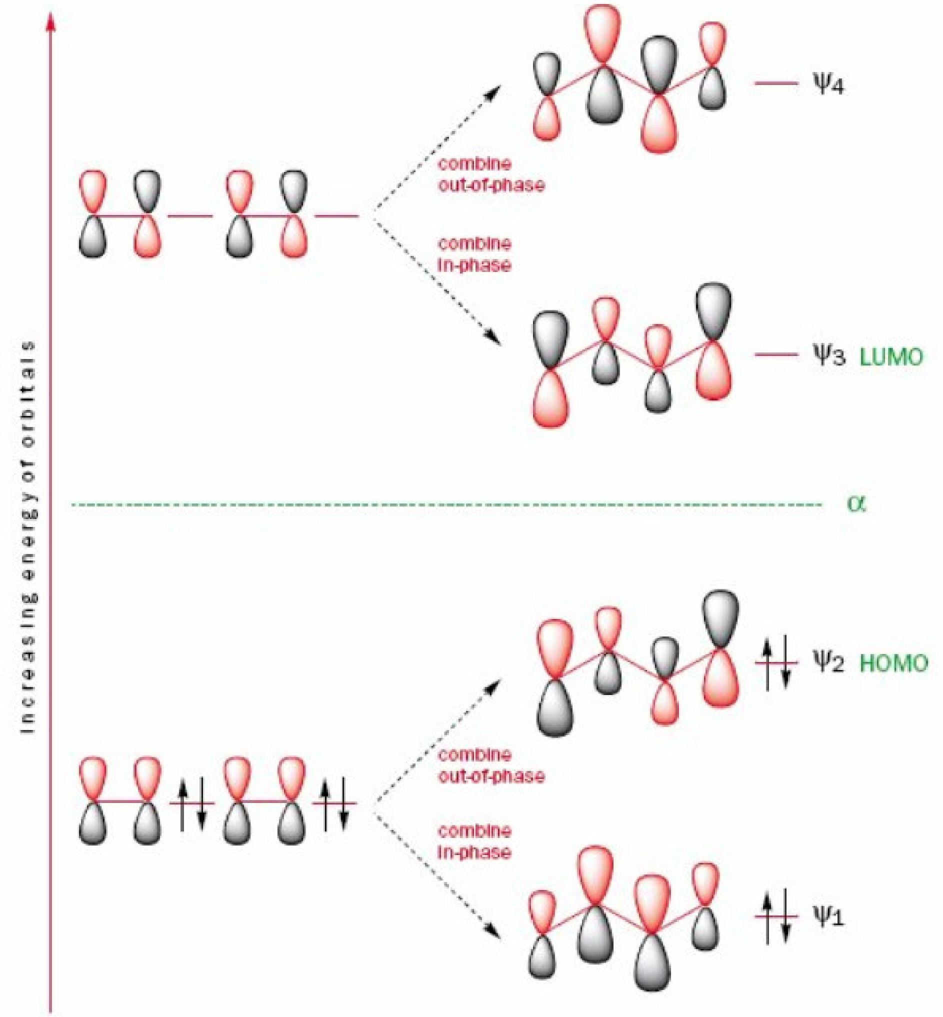


H
C
C
H
H
H
H
H
H
H
H
H

Adição eletrofílica a alcadienos

butadiene

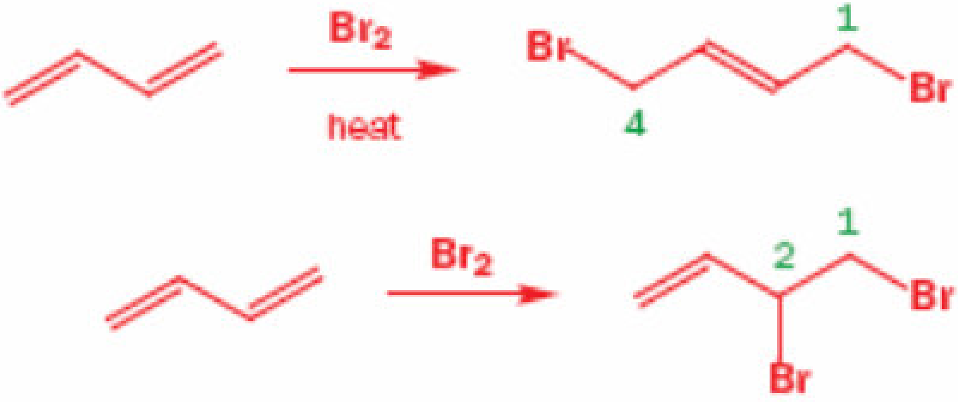




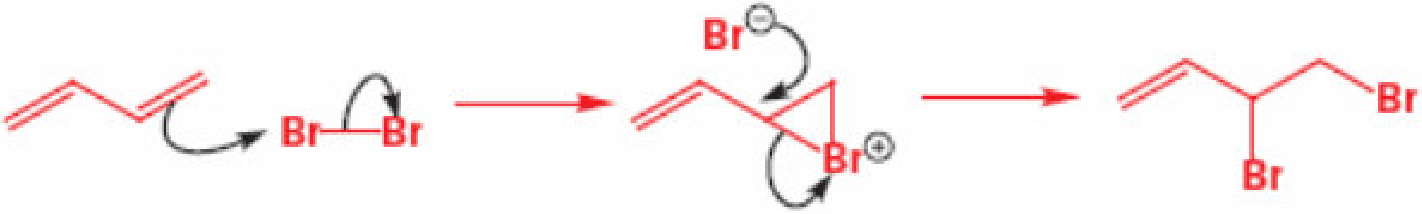
- O HOMO do alcadieno possui maior energia do que o HOMO do eteno, portanto o alcadieno é mais reativo frente a eletrófilos;

- O LUMO do butadieno possui menor energia do que o LUMO do eteno, consequentemente o butadieno é mais reativo frente a nucleófilos.

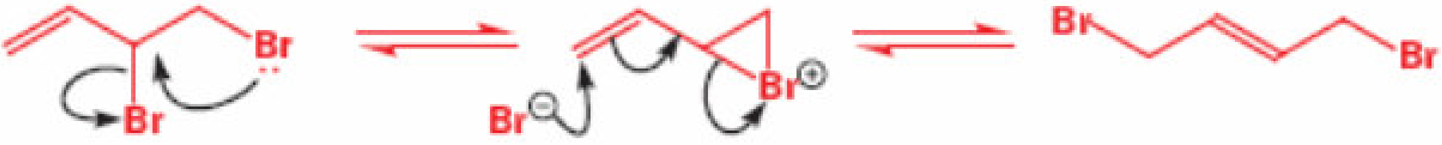
Adição eletrofílica de Br_2 a alcadienos



Adição 1,4 X Adição 1,2



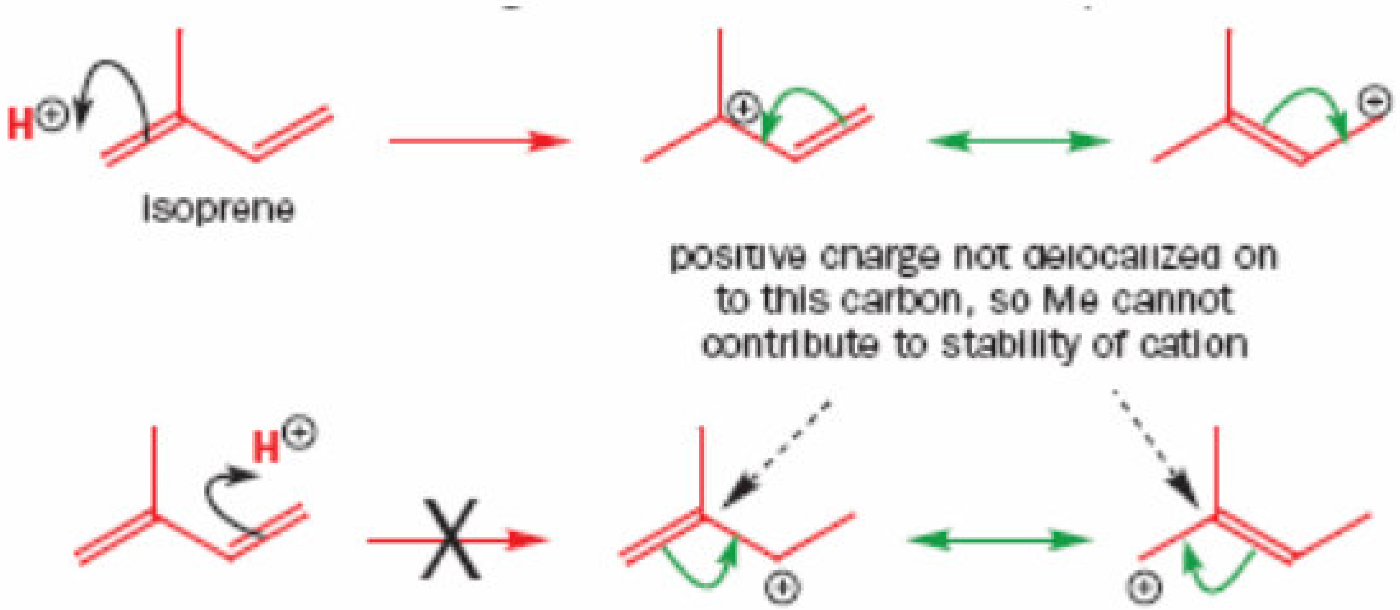
Adição 1,2 – controle cinético



Equilíbrio químico para formar o produto de adição 1,4

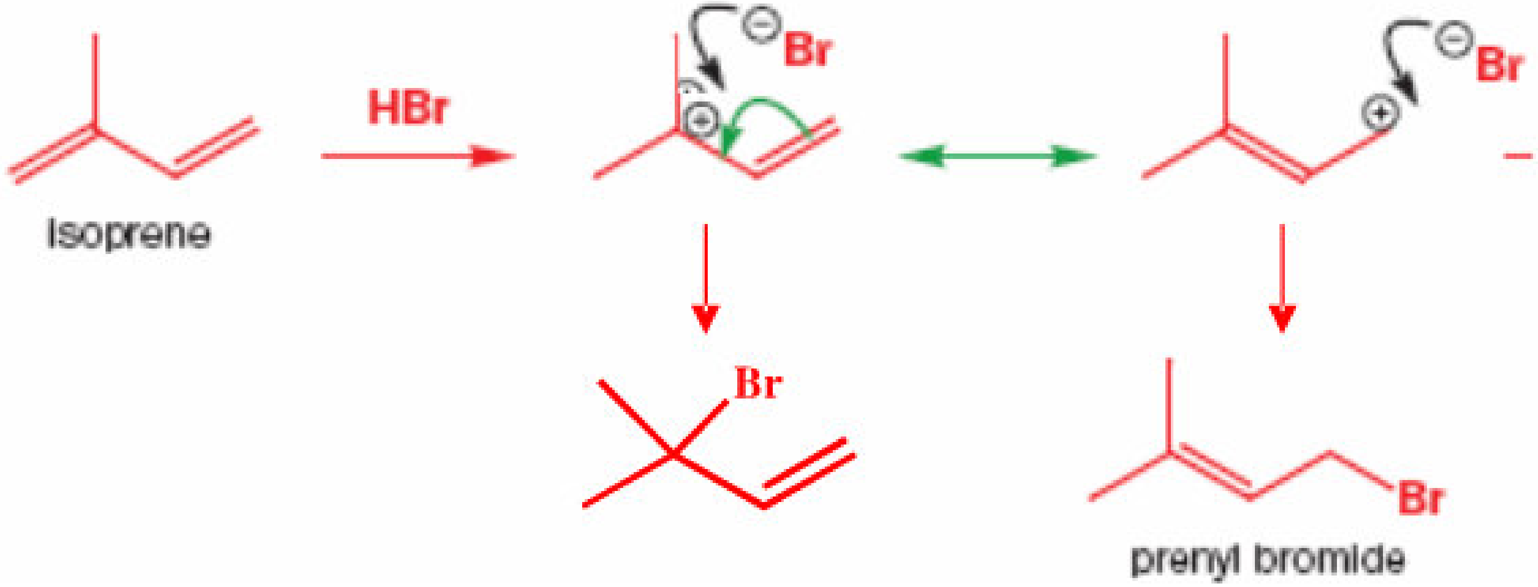
Adição eletrofílica de H-X a alcadienos

Regiosseletividade

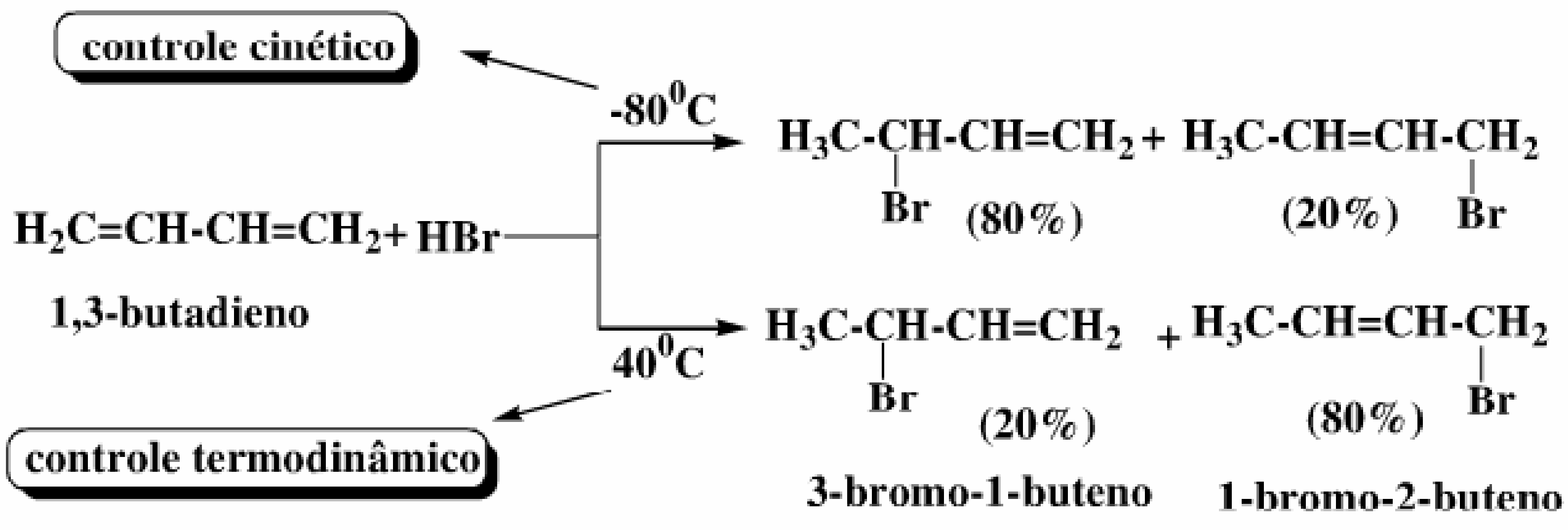


positive charge not delocalized on to this carbon, so Me cannot contribute to stability of cation

Carbocátions menos estáveis



HBr
Isoprene
Br
Br
Br
Br
prenyl bromide



controle cinético

controle termodinâmico

$H_2C{=}CH{-}CH{=}CH_2 + HBr$

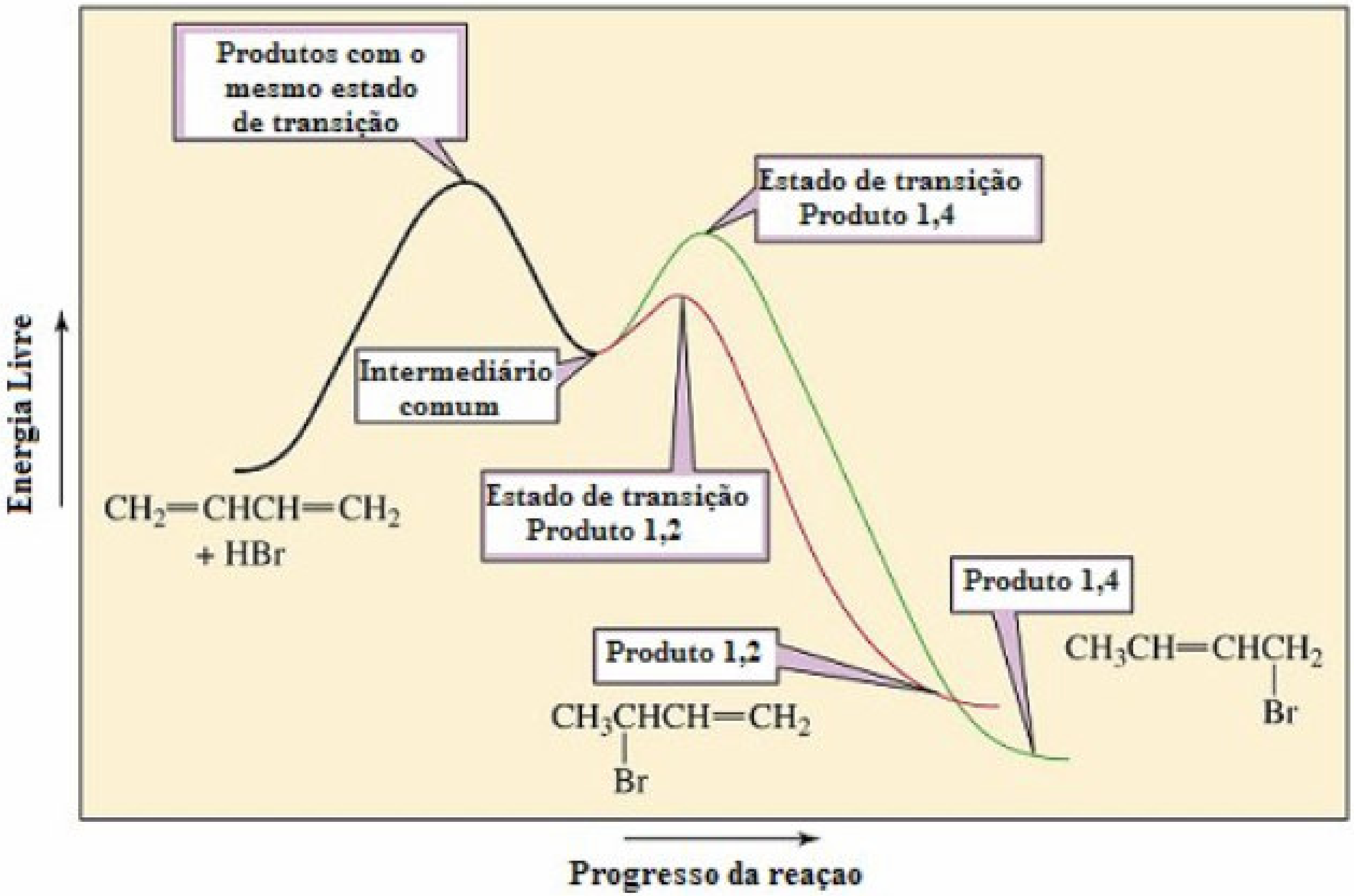
1,3-butadieno

$\xrightarrow{-80^0C}$ $H_3C{-}\underset{\displaystyle Br}{\underset{|}{C}}H{-}CH{=}CH_2$ (80%) + $H_3C{-}CH{=}CH{-}\underset{\displaystyle Br}{\underset{|}{C}}H_2$ (20%)

$\xrightarrow{40^0C}$ $H_3C{-}\underset{\displaystyle Br}{\underset{|}{C}}H{-}CH{=}CH_2$ (20%) + $H_3C{-}CH{=}CH{-}\underset{\displaystyle Br}{\underset{|}{C}}H_2$ (80%)

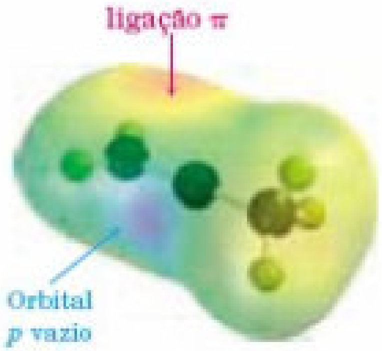
3-bromo-1-buteno

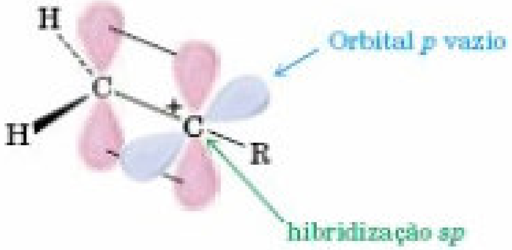
1-bromo-2-buteno


Produtos com o mesmo estado de transição
Estado de transição Produto 1,4
Intermediário comum
Estado de transição Produto 1,2
Produto 1,4
Produto 1,2
$CH_2{=}CHCH{=}CH_2$ + HBr
$CH_3CHCH{=}CH_2$ Br
$CH_3CH{=}CHCH_2$ Br
Energia Livre
Progresso da reaçao

Adição eletrofílica a alcinos

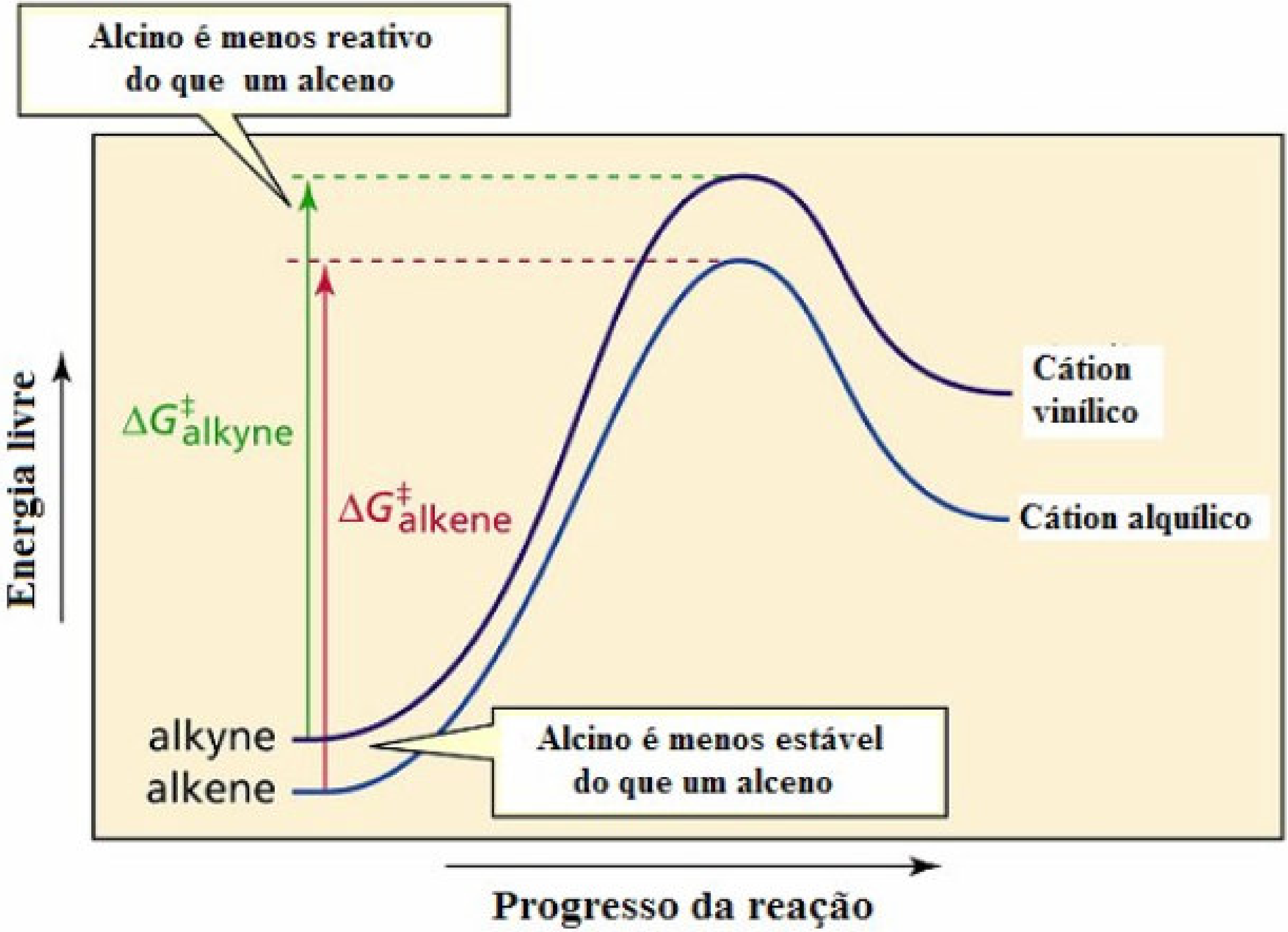
Reatividade





Um carbocátion vinila secundário

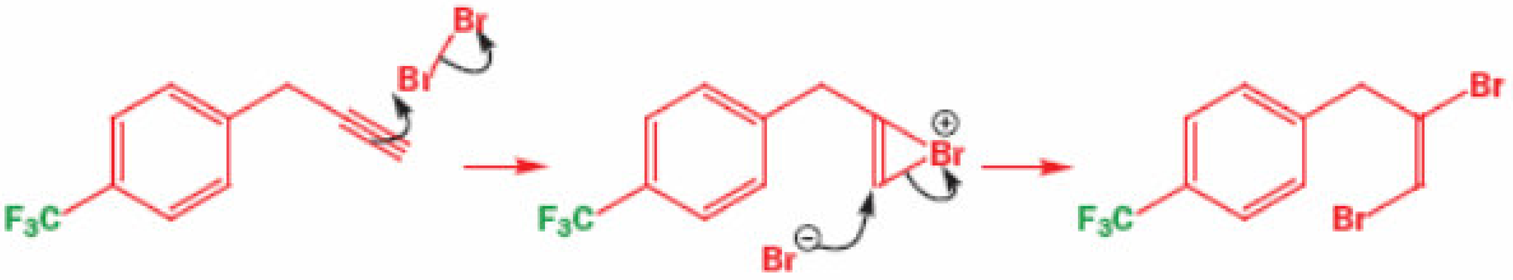
Um carbocátion alquila secundário



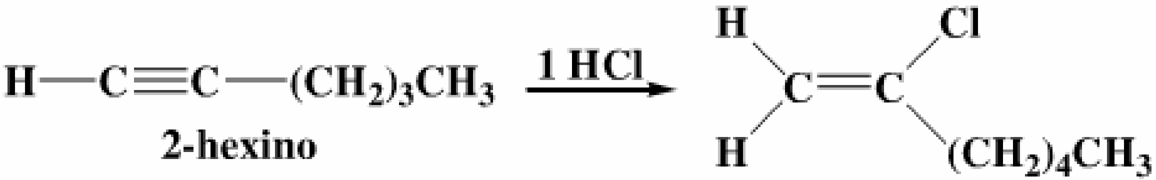
Alcino é menos reativo do que um alceno

Alcino é menos estável do que um alceno

Adição eletrofílica de halogênio

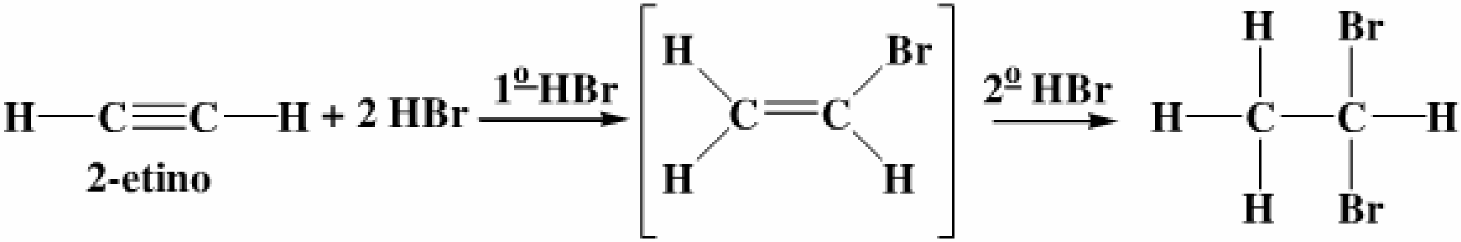


Adição eletrofílica de H-X



2-hexino

produto de Markownikoff



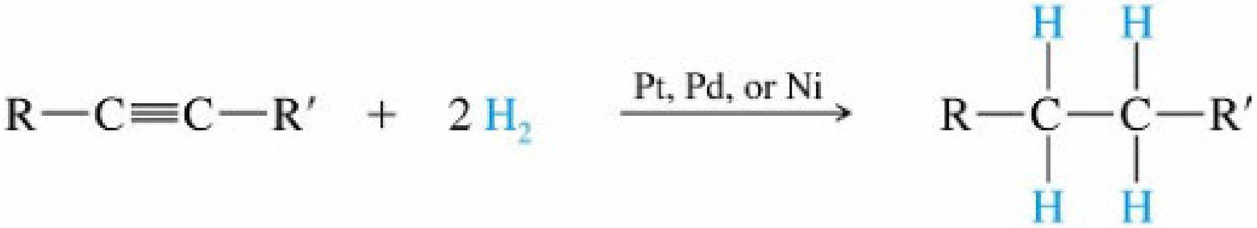
2-etino

produto de Markownikoff

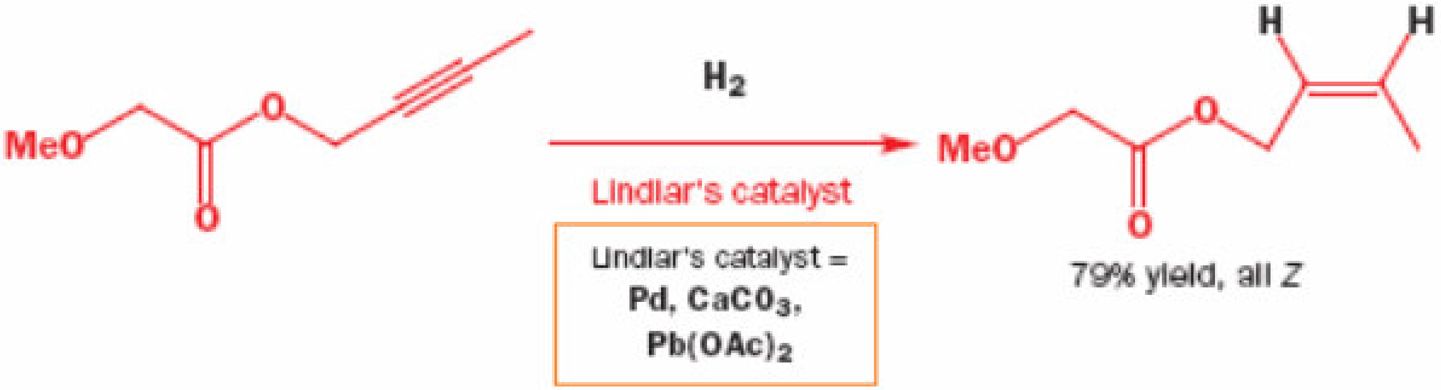
Em alcinos simétricos, somente a segunda adição segue a regra de Markownikoff

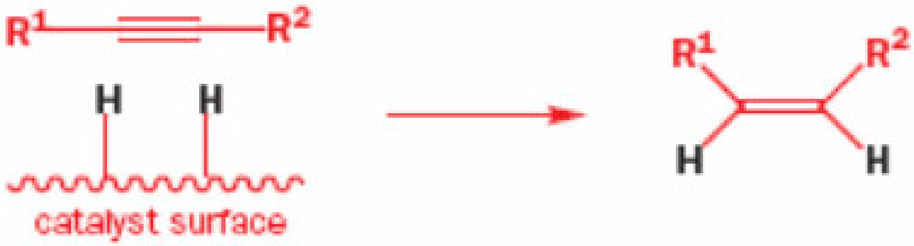
Hidrogenação catalítica – redução Z-seletiva

Hidrogenação catalítica – redução Z-seletiva

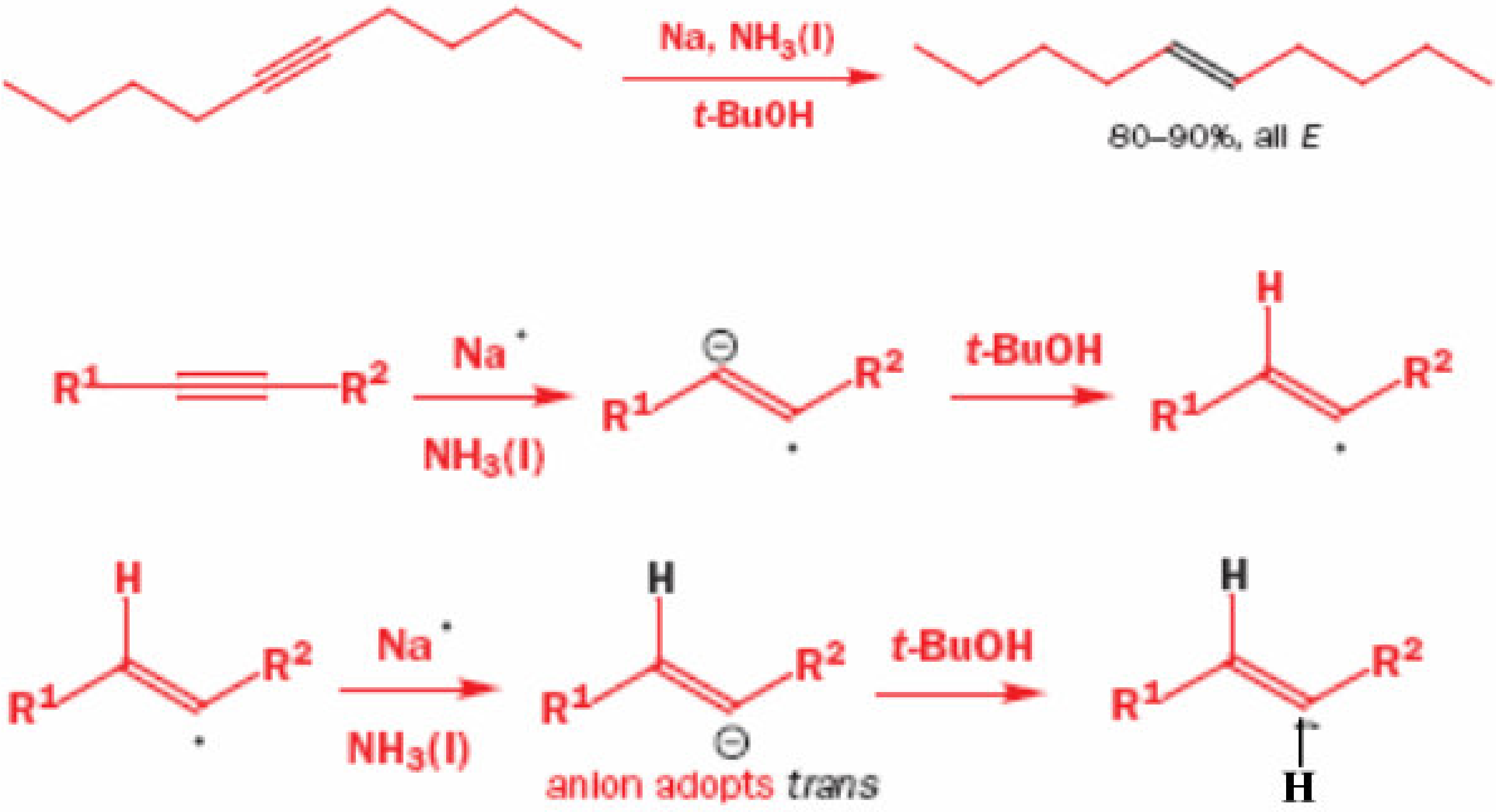


$$R-C\equiv C-R' + 2\,H_2 \xrightarrow{\text{Pt, Pd, or Ni}} R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-R'$$

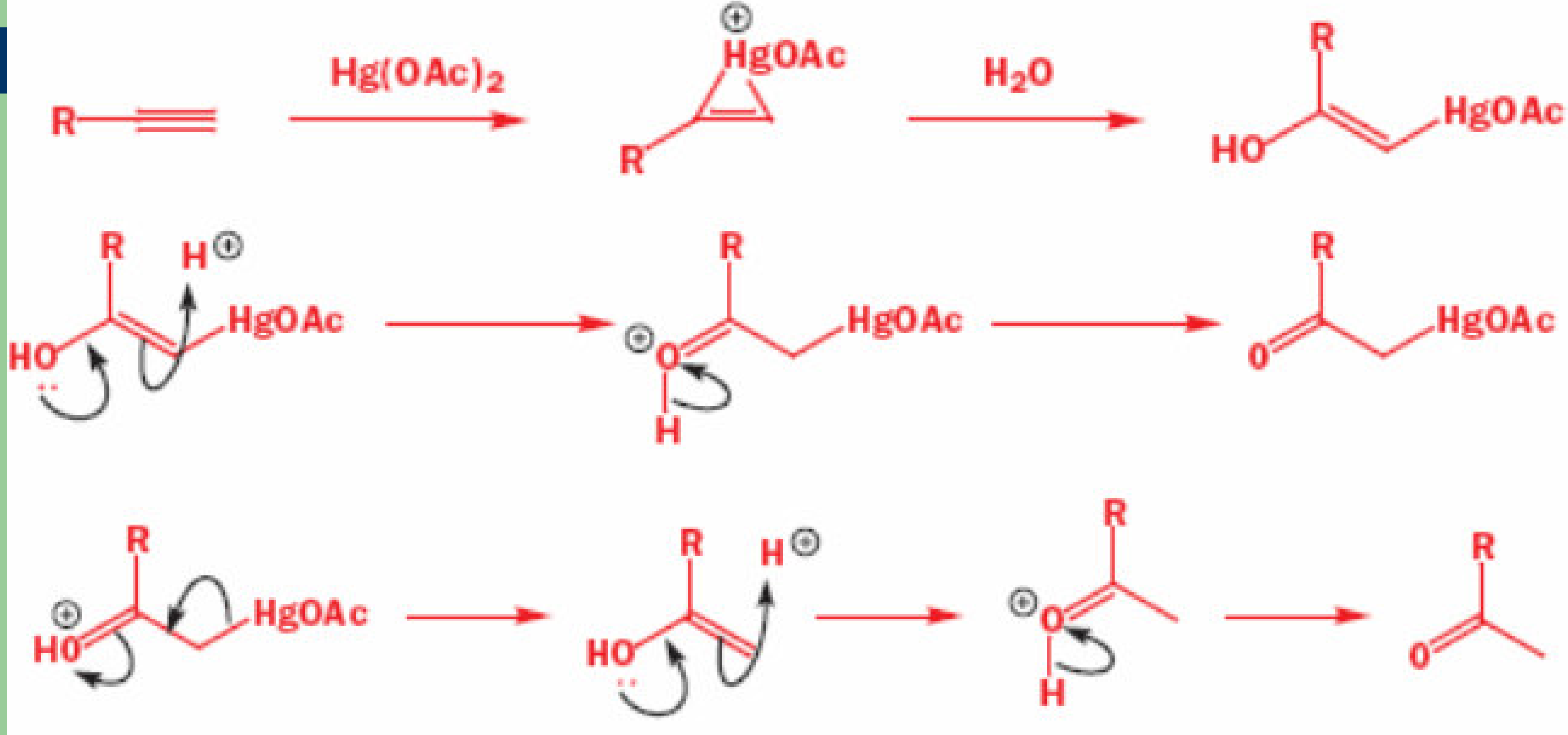




Hidrogenação via ânion radical – E - seletiva

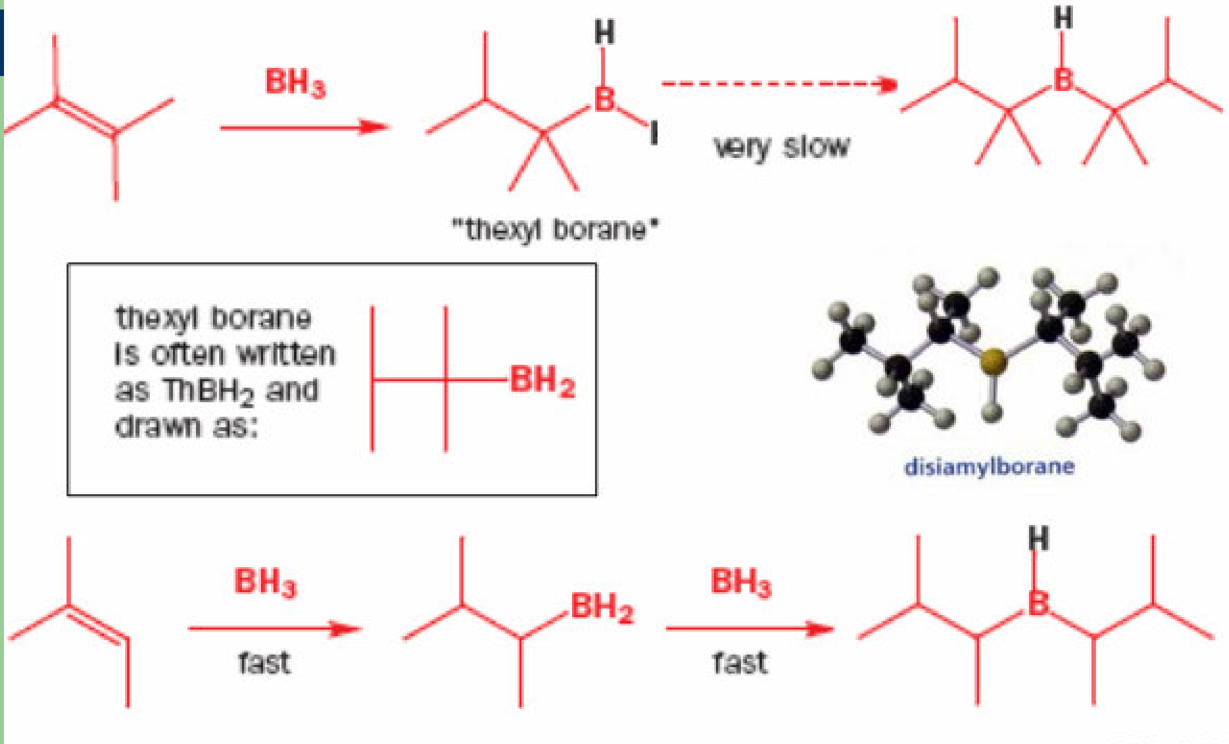


Hidratação



A hidratação de um alcino forma uma cetona

Hiboração de alquinos



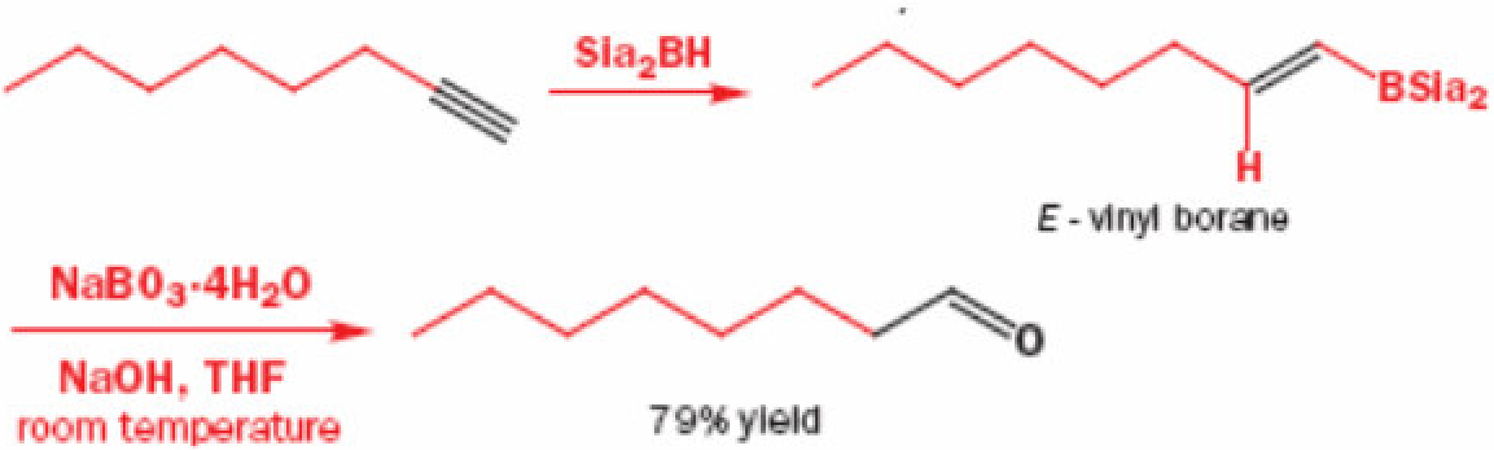
thexyl borane is often written as $ThBH_2$ and drawn as:

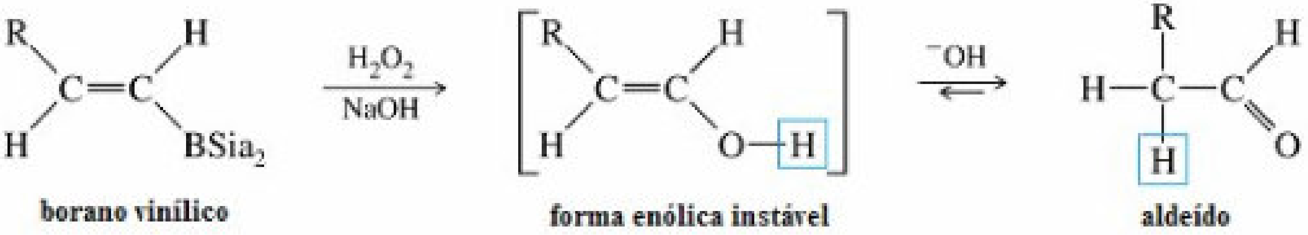
disiamylborane or Sia_2BH

lento ↓

R_3B

Boranos volumosos permitem uma única hidroboração em alcinos terminais





Equilíbrio ceto-enólico