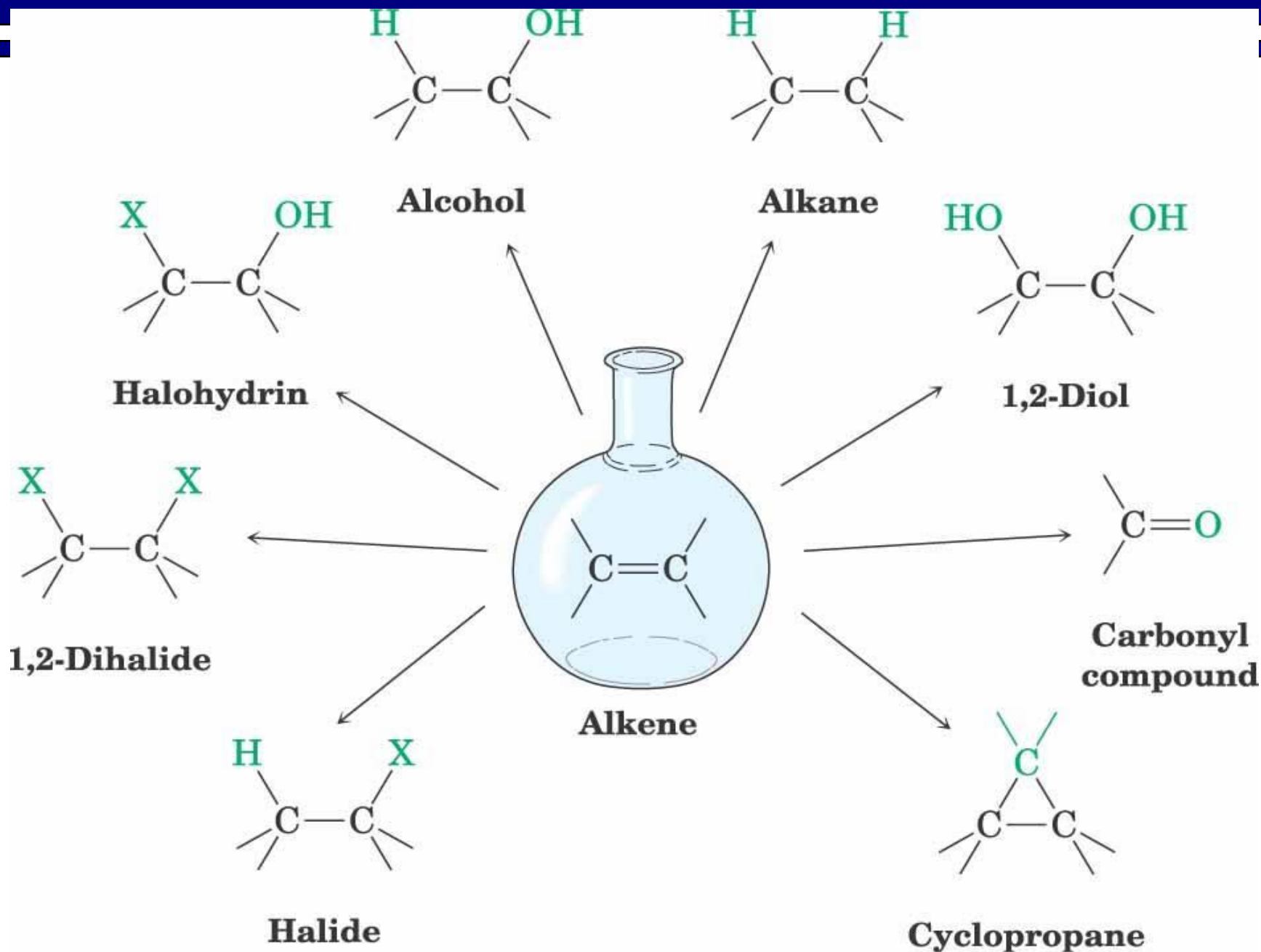


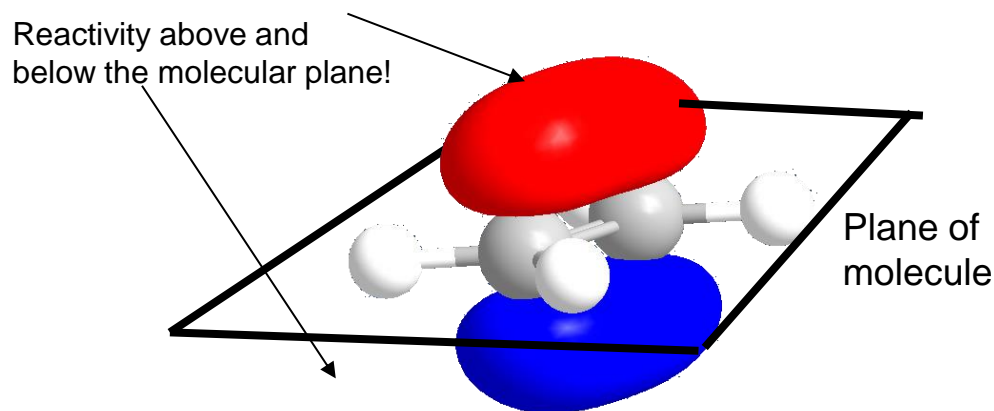
limoneno
(encontrado no óleo da laranja)

Reações de Adição Eletrofílica



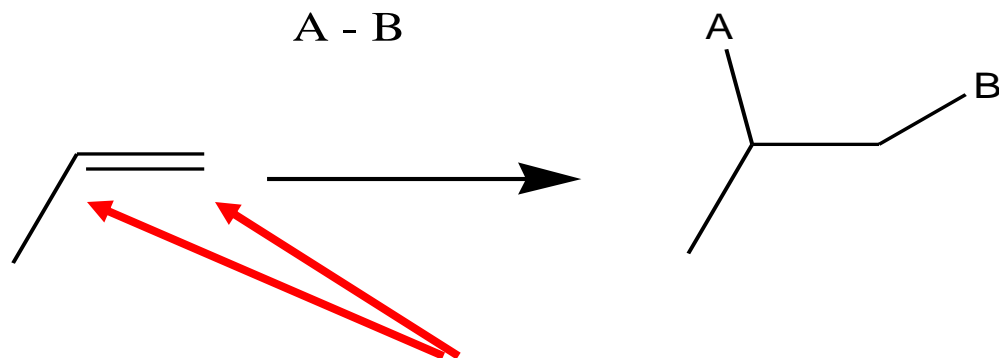
Reactivity of C=C

- u **Electrons in π -bond are loosely held.**



- u **Electrophiles are attracted to the π electrons.**
- u **Carbocation intermediate forms.**
- u **Nucleophile adds to the carbocation.**
- u **Net result is addition to the double bond.**

Addition Reactions



Important characteristics of addition reactions

Orientation (Regioselectivity)

If the doubly bonded carbons are not equivalent which one gets the A and which gets the B.

Stereochemistry: geometry of the addition.

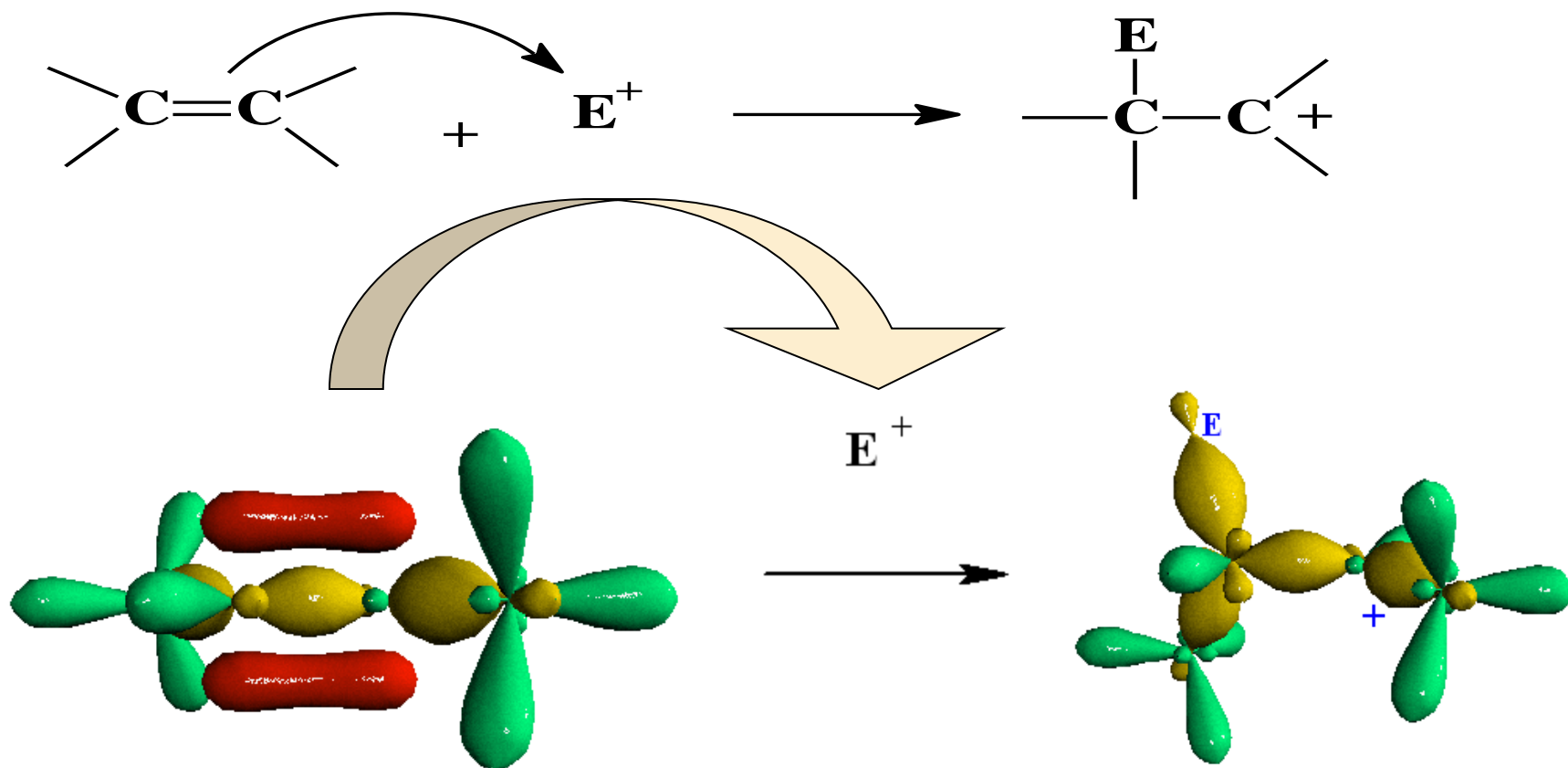
Syn addition: Both A and B come in from the same side of the alkene. Both from the top or both from the bottom.

Anti Addition: A and B come in from opposite sides (anti addition).

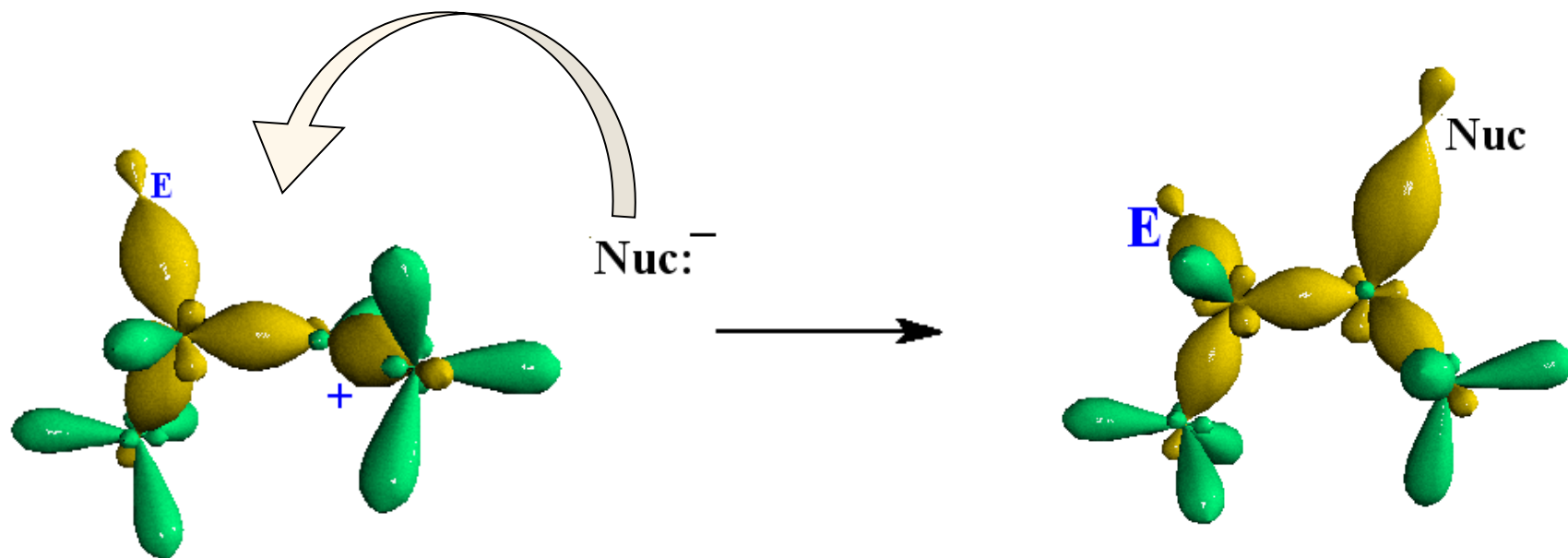
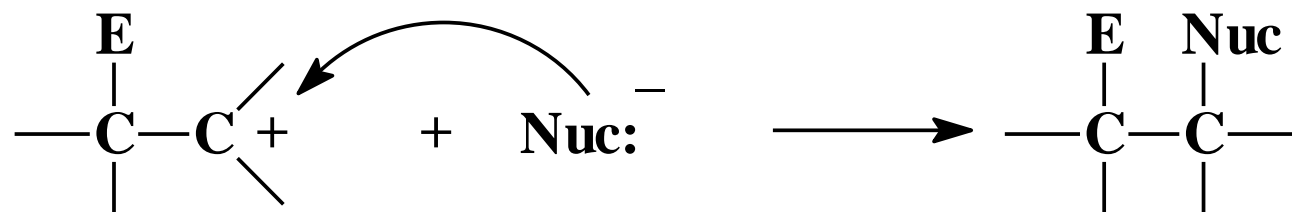
No preference.

Electrophilic Addition

Step 1: π electrons attack the electrophile.

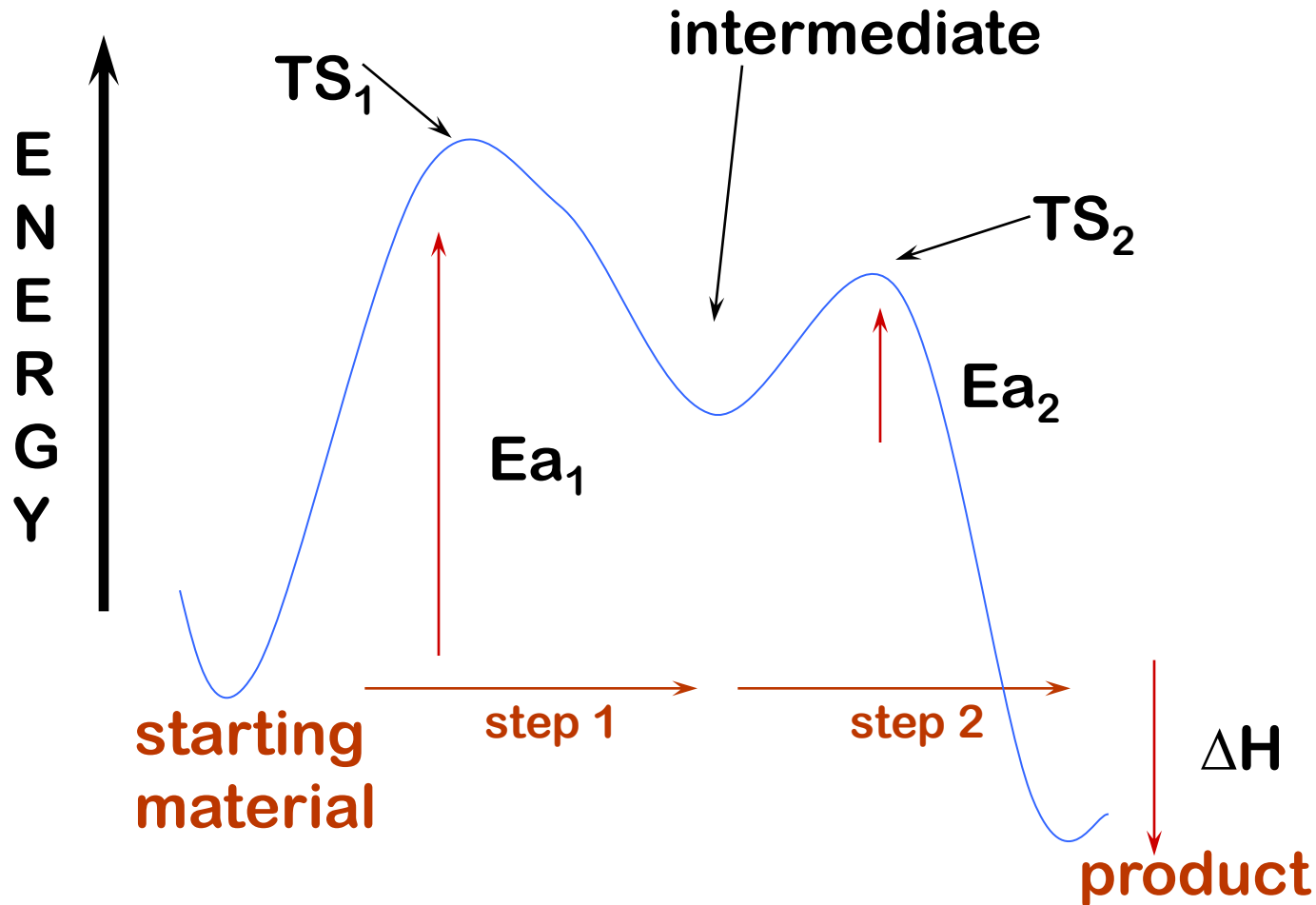


Step 2: Nucleophile attacks the carbocation.



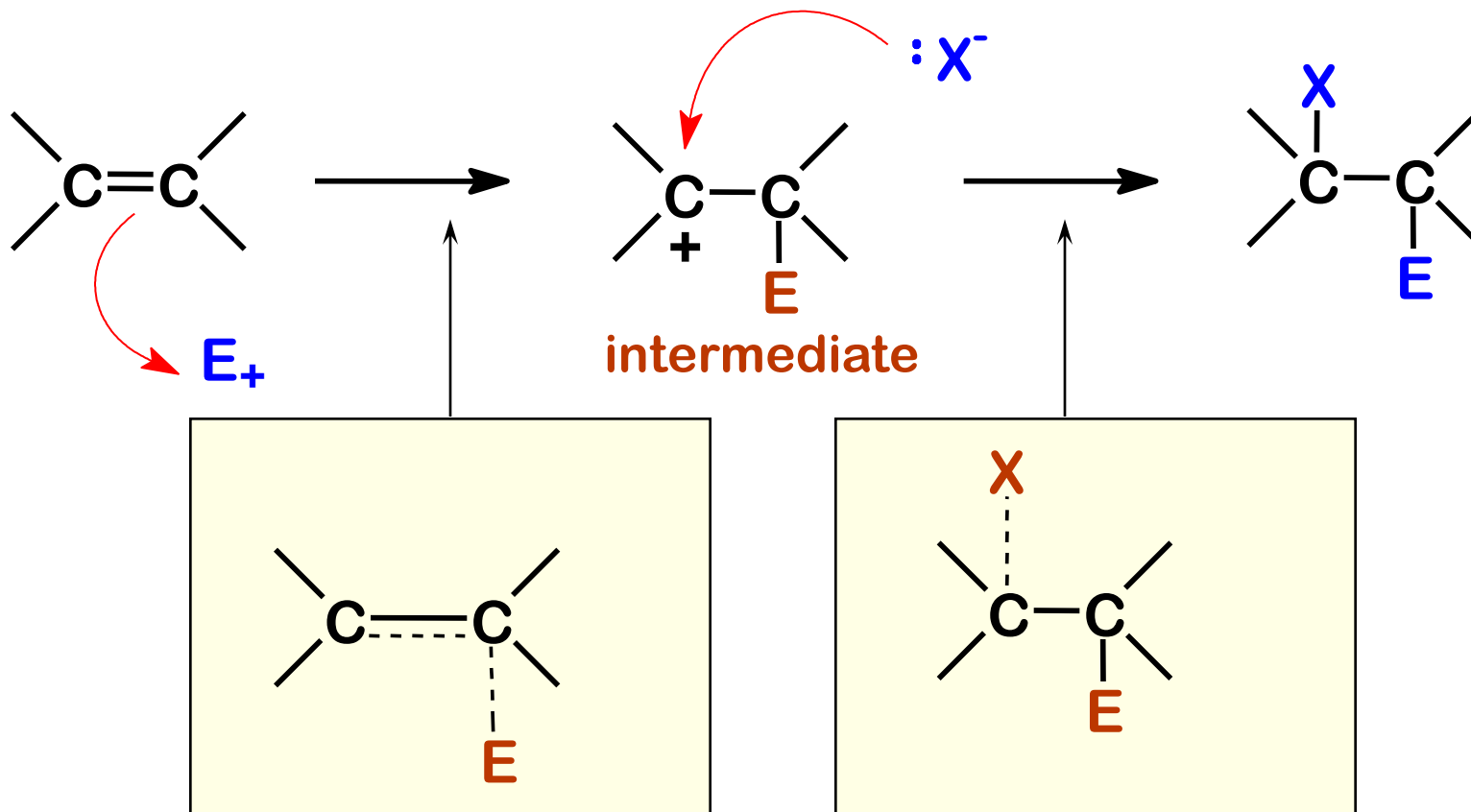
ENERGY PROFILE

two step reaction



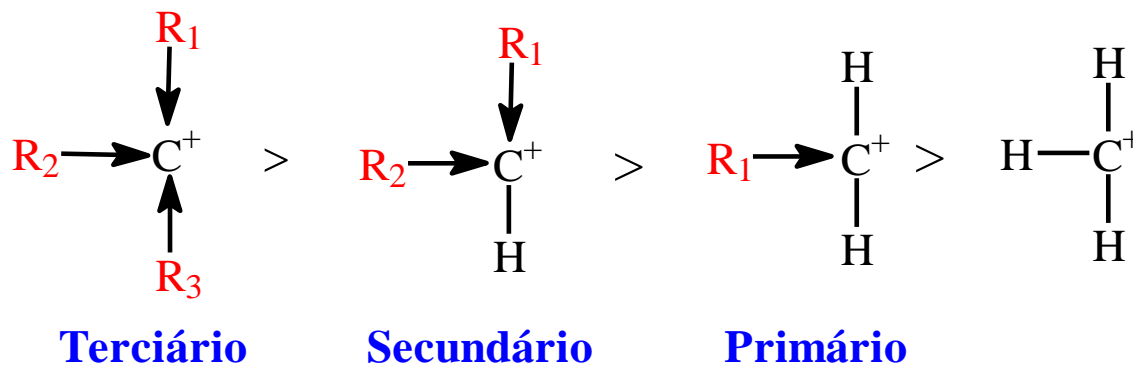
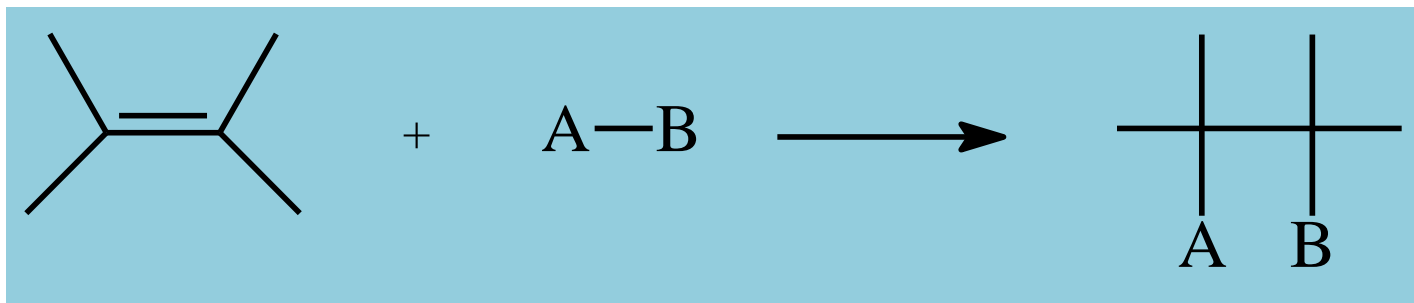
ACTIVATED COMPLEXES

correspond to transition states for each step



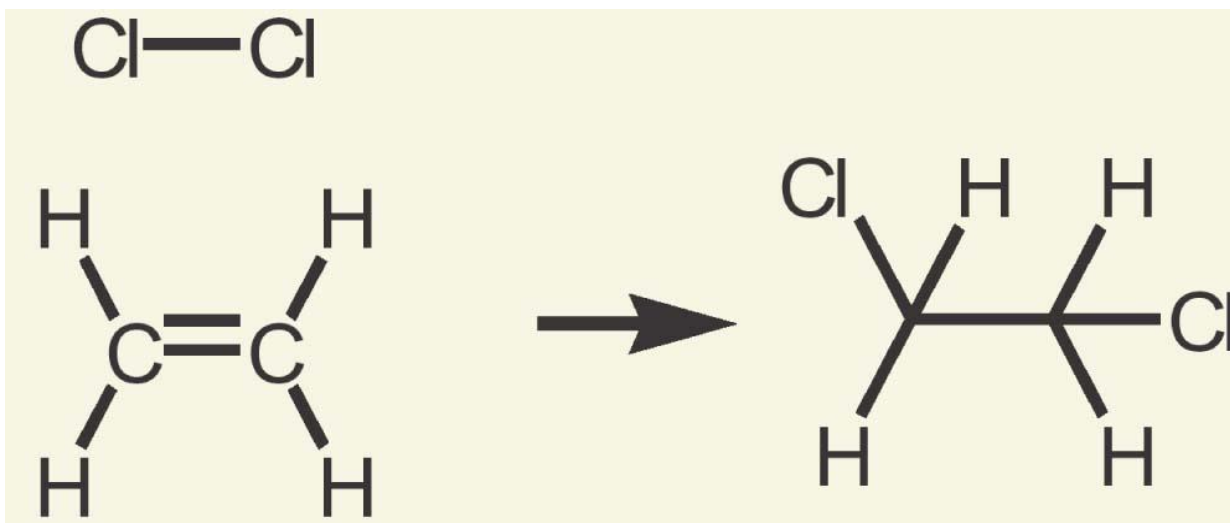
**ACTIVATED
COMPLEXES**

show bonds in the process of breaking or forming
(bonds are half formed or half broken)



Addition of Halogens to Alkenes

- u Bromine and chlorine add to alkenes to give 1,2-dihalides, an industrially important process
 - F_2 is too reactive and I_2 does not add
- u Cl_2 reacts as $Cl^+ Cl^-$
 - Br_2 is similar



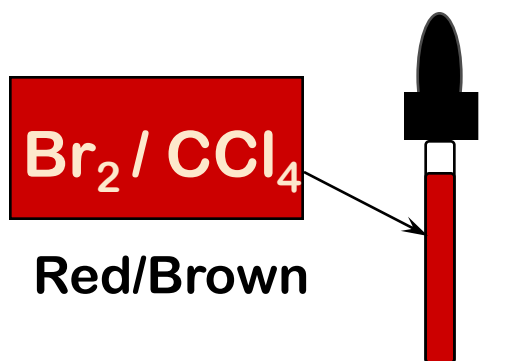
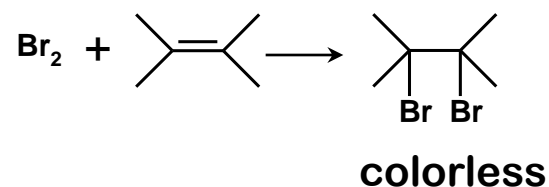
Adição de Cl_2 e Br_2

- u Utilizam-se os reagentes puros ou em um solvente inerte como CCl_4 ou CH_2Cl_2
- u A adição é estereosseletiva
- u **Reação estereosseletiva:** reação na qual um estereoisômero é formado ou destruído preferencialmente em relação aos outros que poderiam ser formados ou destruídos.

BROMINE TEST FOR A C=C DOUBLE BOND

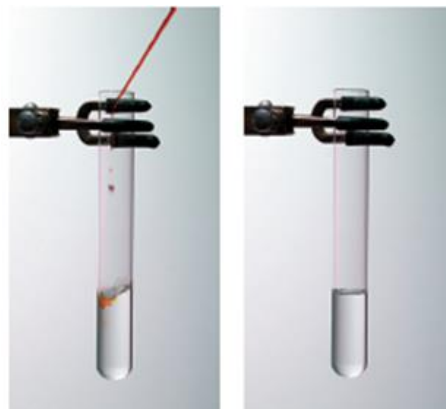
POSITIVE TEST

Br₂ reacts
implies the presence
of a double bond

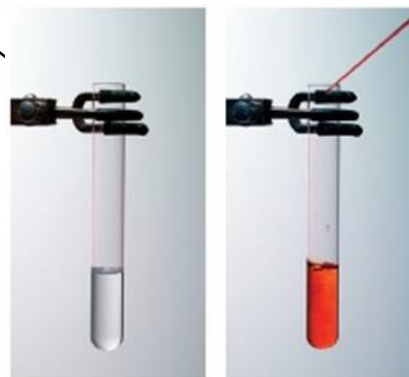


Red/Brown

(+)



(-)



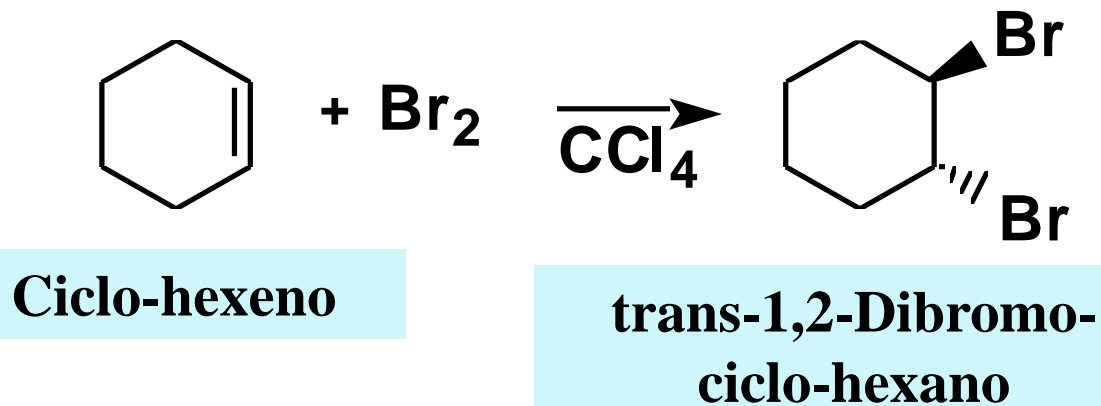
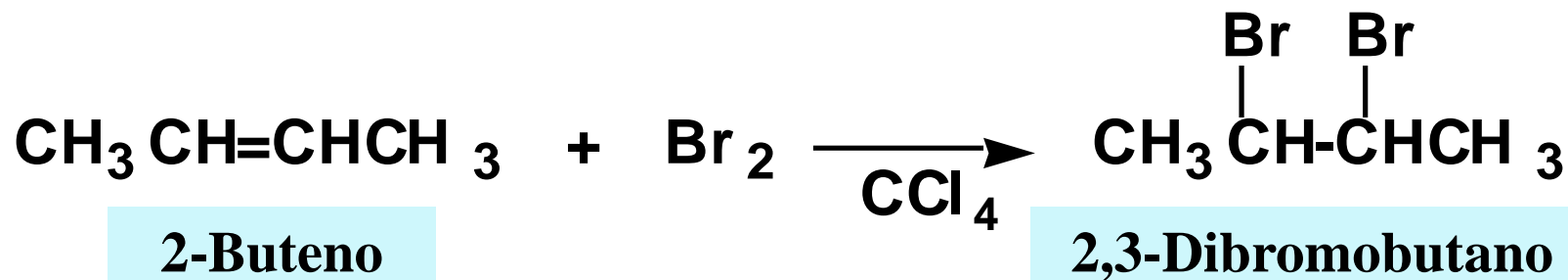
NEGATIVE TEST

Br₂ is not decolorized
(does not react)

implies that a double
bond is not present

compound with a
suspected double bond

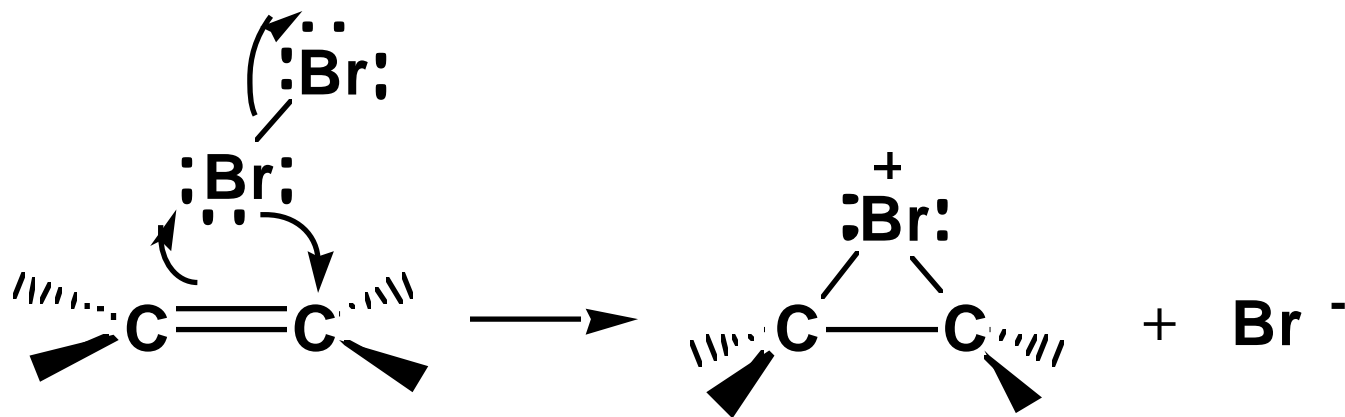
Adição de Cl_2 e Br_2



Adição de Cl_2 e Br_2

u A adição envolve um mecanismo de duas etapas

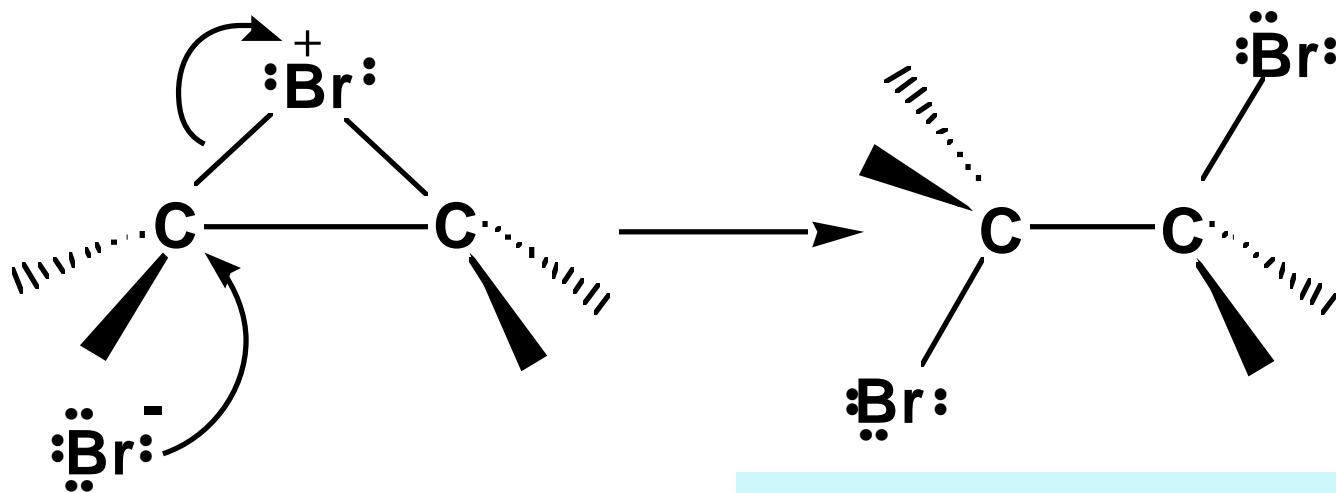
Etapa 1: formação de um íon bromônio cíclico, intermediário



Íon bromônio cíclico

Adição de Cl_2 e Br_2

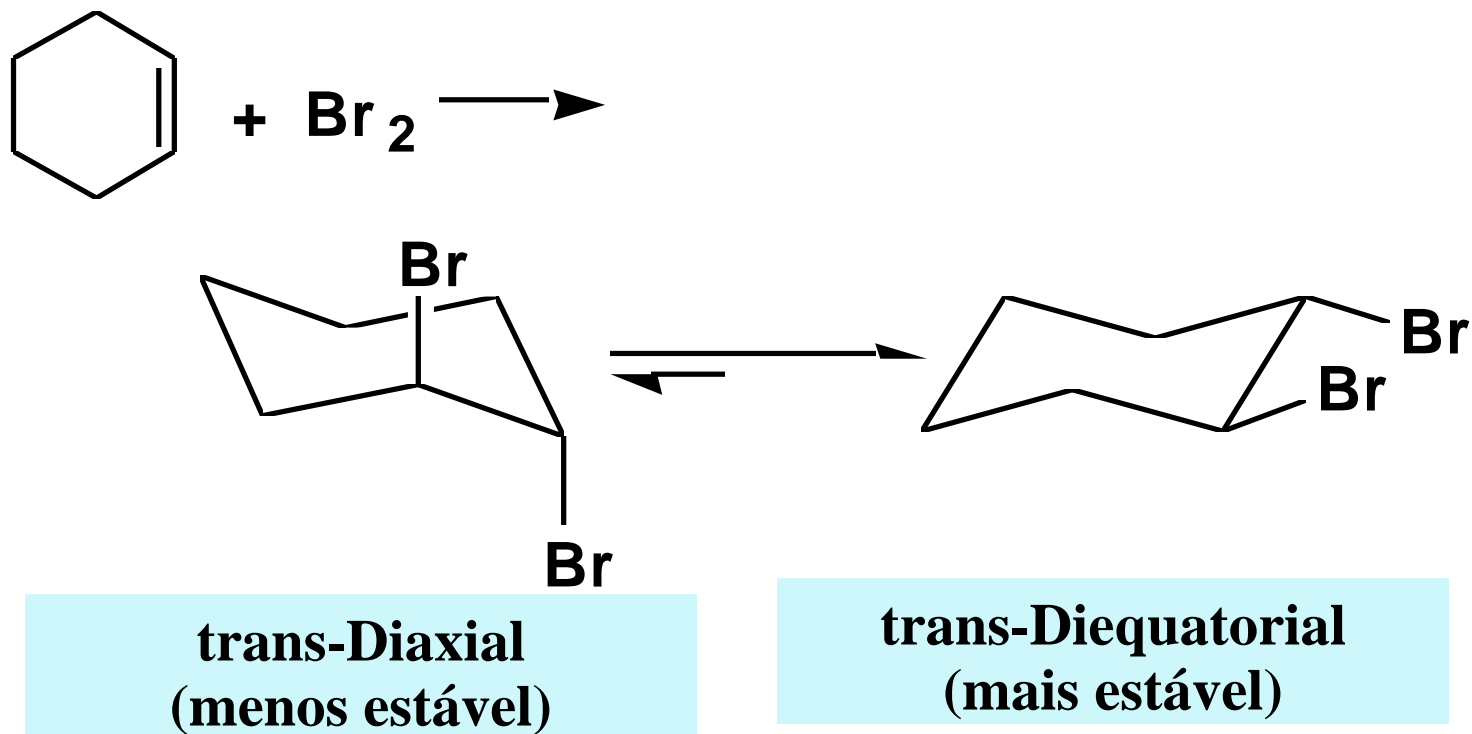
Etapa 2: Ataque do íon haleto pelo lado oposto do anel de três membros



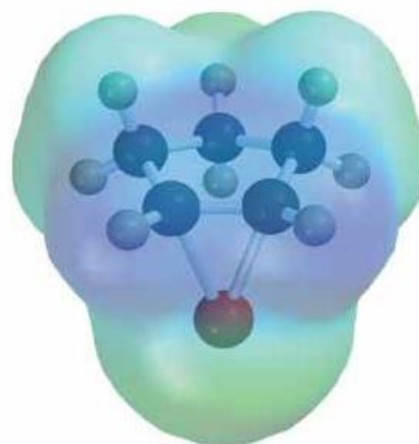
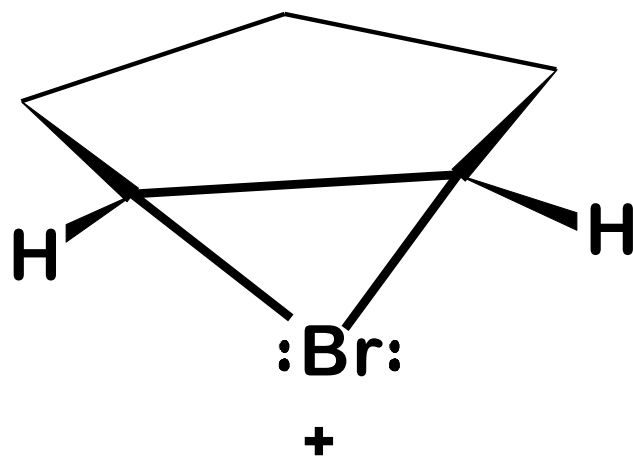
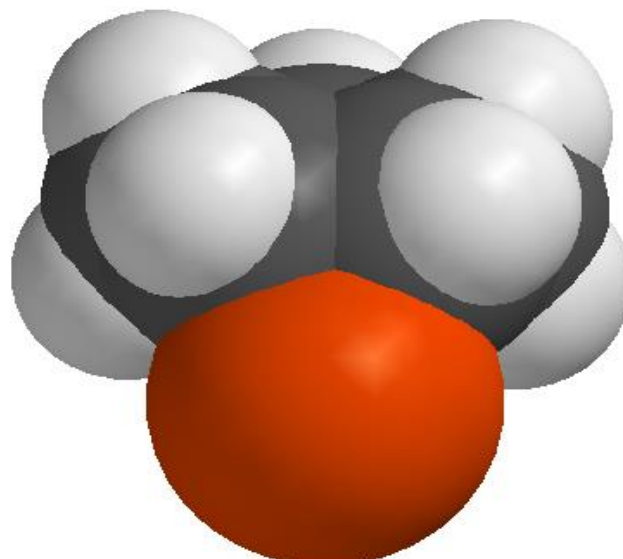
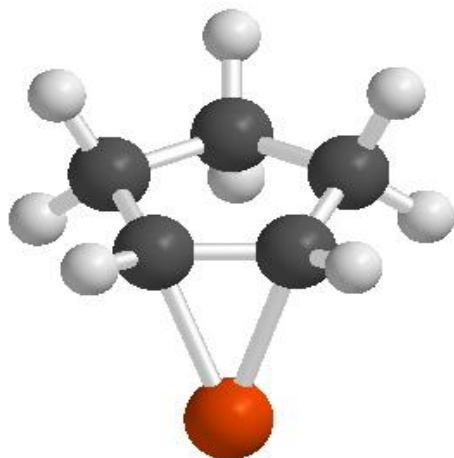
Adição anti

Adição de Cl_2 e Br_2

- u Para o ciclo-hexeno, a adição anti coplanar corresponde a uma adição *trans*-diaxial

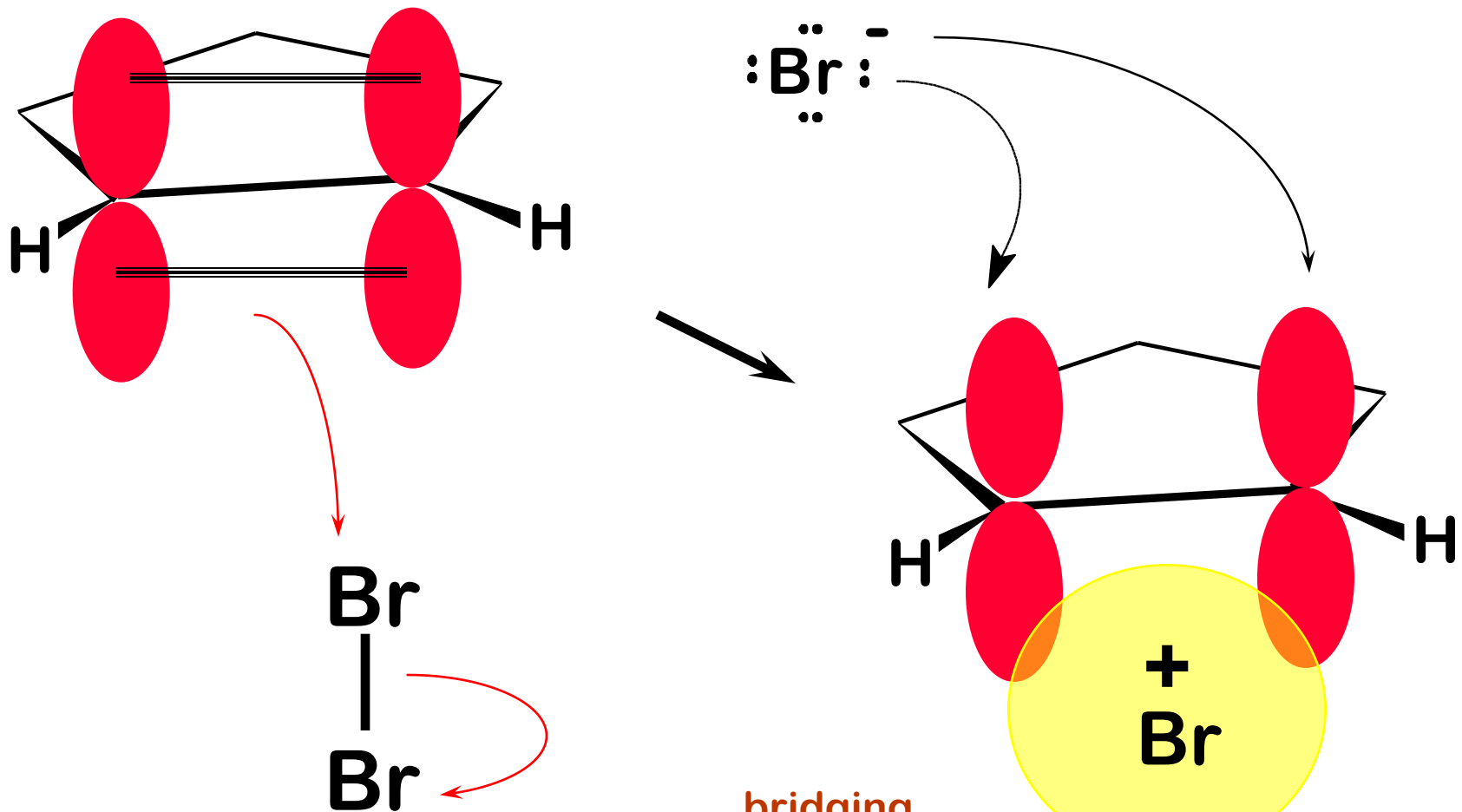


CYCLIC BROMONIUM ION



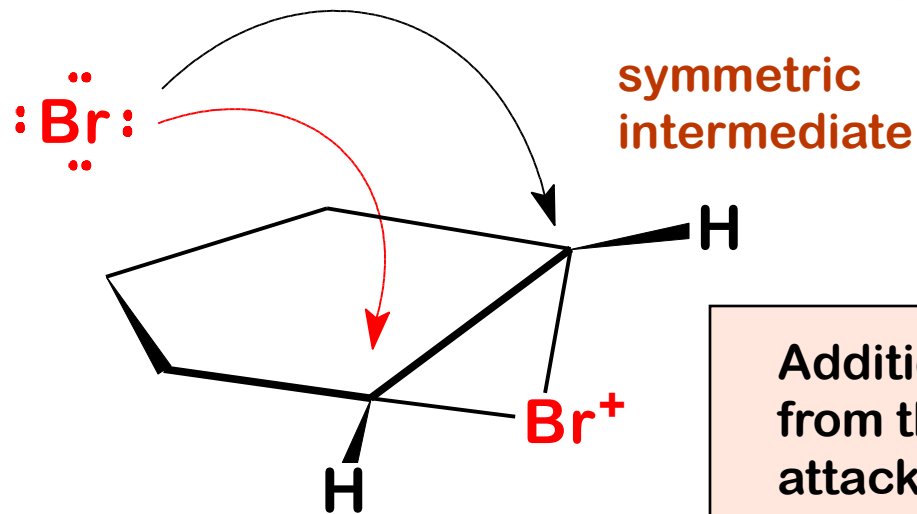
note size of
bromine

BRIDGED BROMONIUM ION

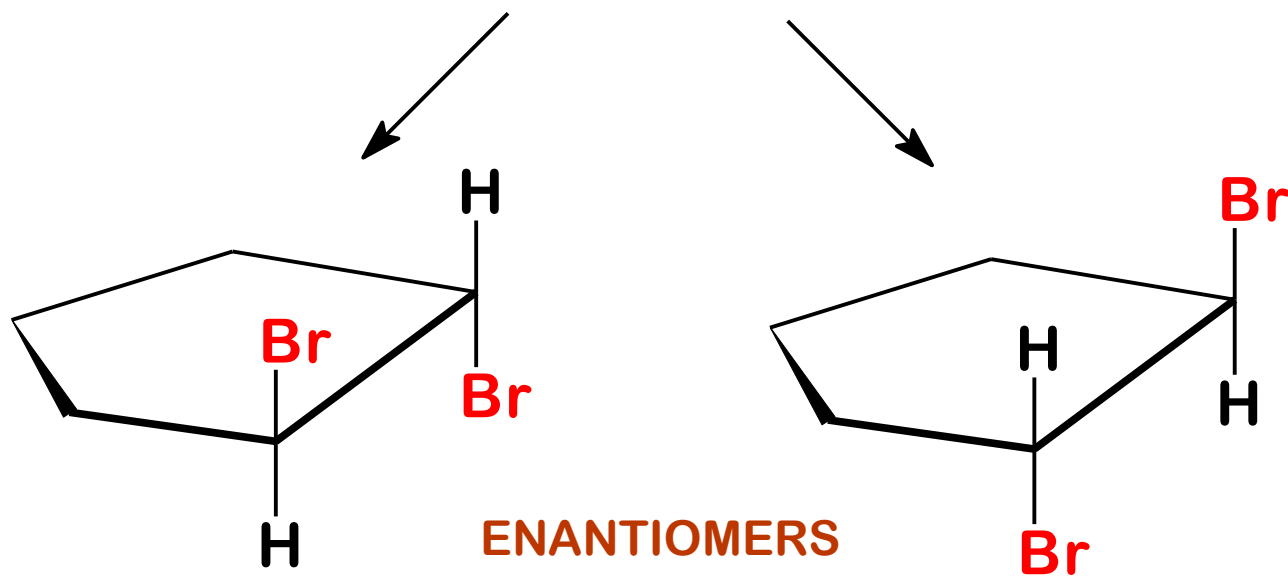


bridging
blocks approach
from this side

FORMATION OF ENANTIOMERS

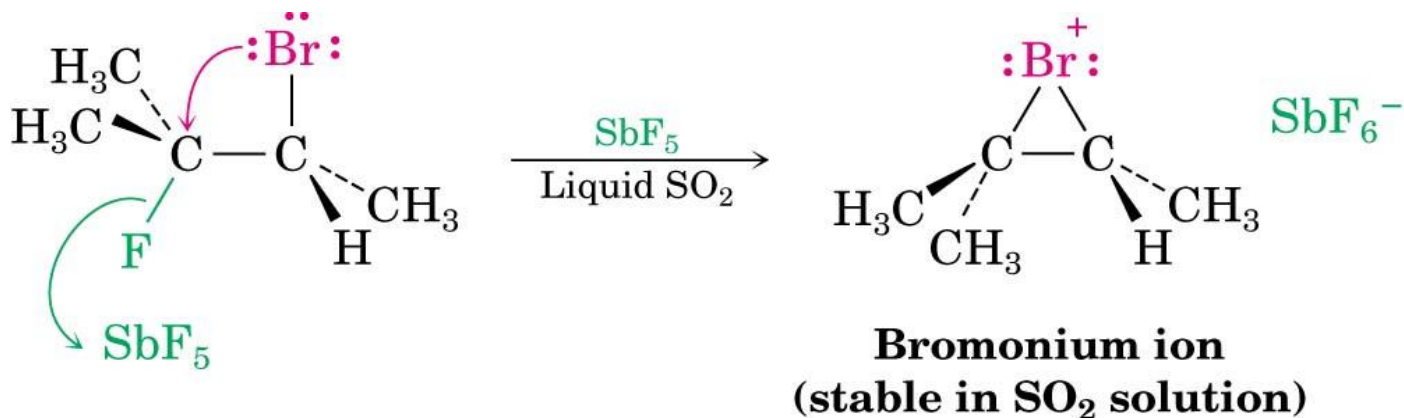


Addition could also start from the top with bromide attacking the bottom.



The Reality of Bromonium Ions

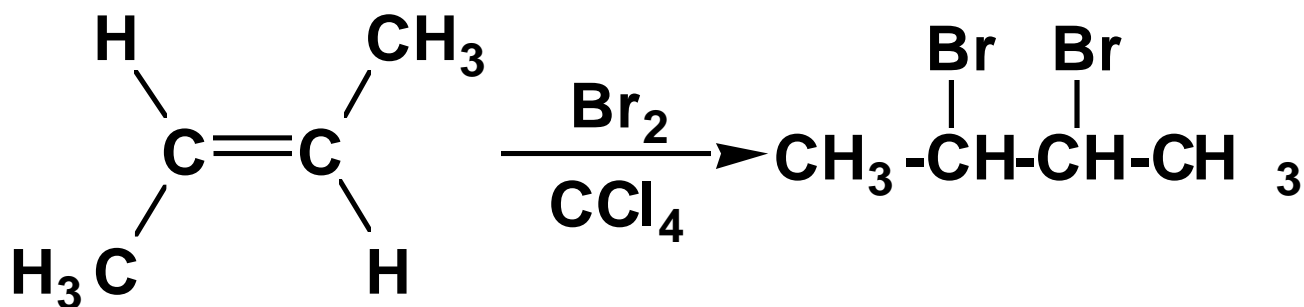
- Bromonium ions were postulated by Roberts and Kimball in 1937 to explain the stereochemical course of the addition (to give the *trans*-dibromide from a cyclic alkene)
- Olah (1970) showed that bromonium ions are stable in liquid SO₂ with SbF₅ and can be studied directly



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Estereoquímica de Reação

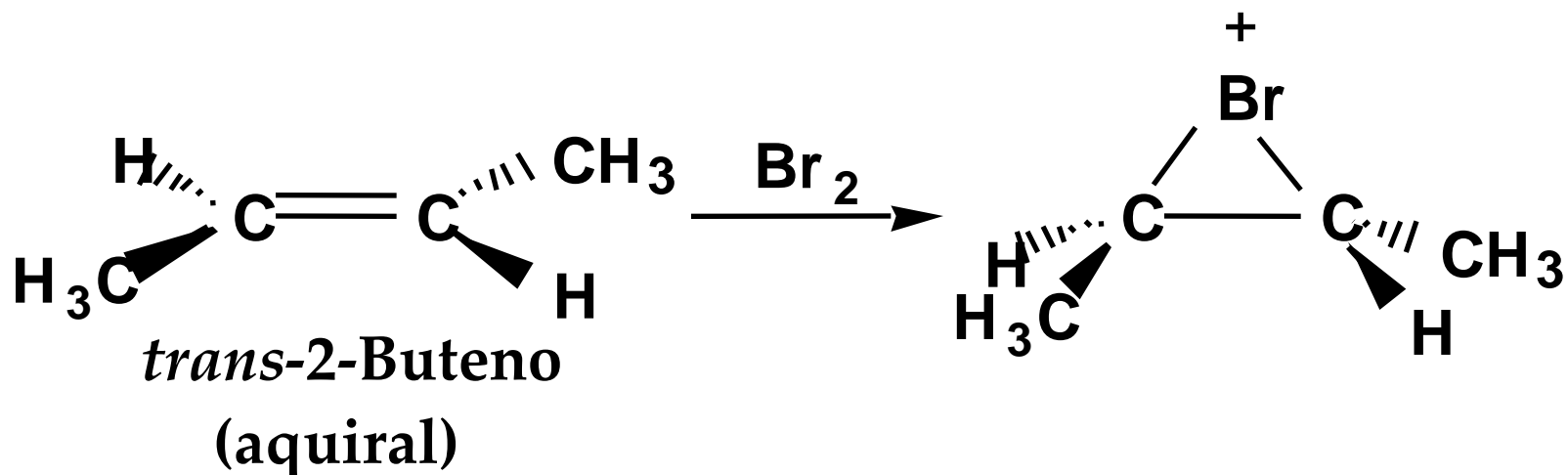
- u Quais dos três estereoisômeros possíveis para o 2,3-dibromobutano são formados na adição de bromo a trans-2-buteno?



- os três estereoisômeros possíveis para este composto são um par de enantiômeros e um composto meso

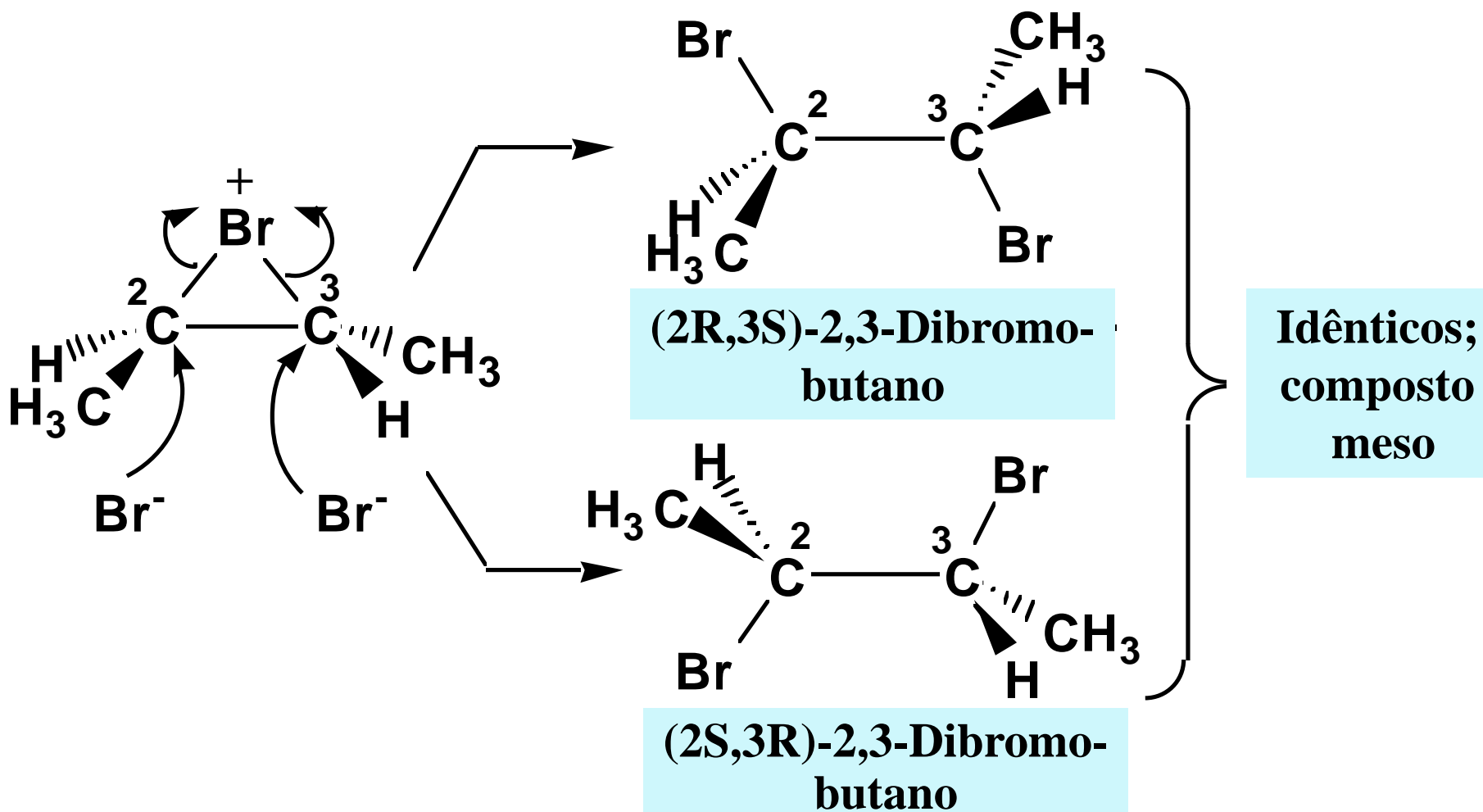
Estereoquímica de Reação

- u A reação de bromo com o alceno forma um íon bromônio cíclico como intermediário



- u o qual é então atacado pelo íon brometo no lado oposto ao do anel contendo o bromo

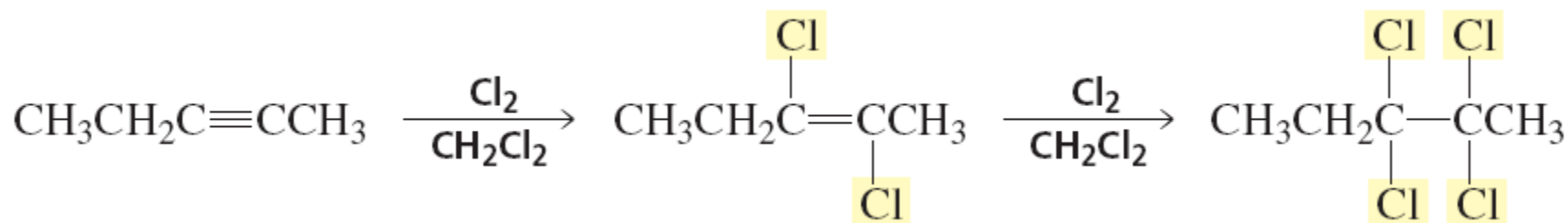
Estereoquímica de Reação



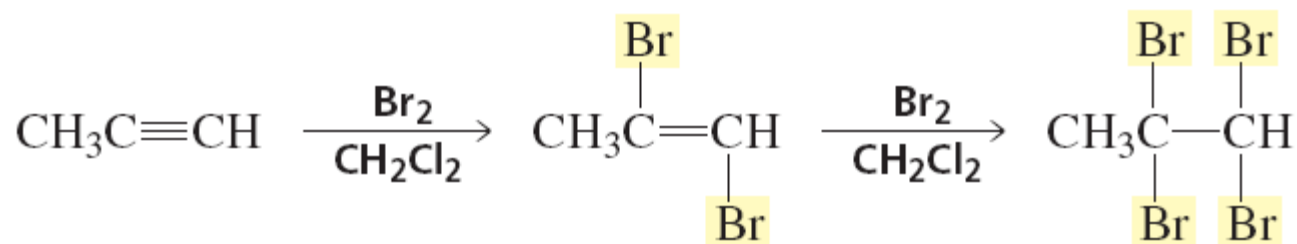
Estereoquímica de Reação

- u **Produtos enantiomericamente puros nunca poderão ser formados a partir de materiais de partida e reagentes aquirais**
- u **Um produto enantiomericamente puro poderá ser gerado numa reação se ao menos um dos reagentes for enantiomericamente puro, ou se a reação for conduzida em um ambiente quiral**

Adição de bromo e cloro

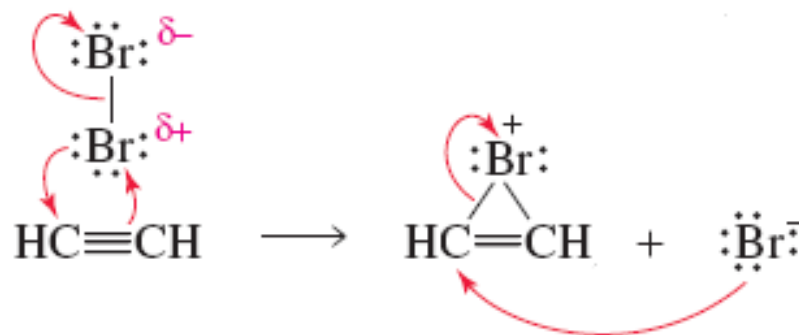


adição anti coplanar



adição anti coplanar

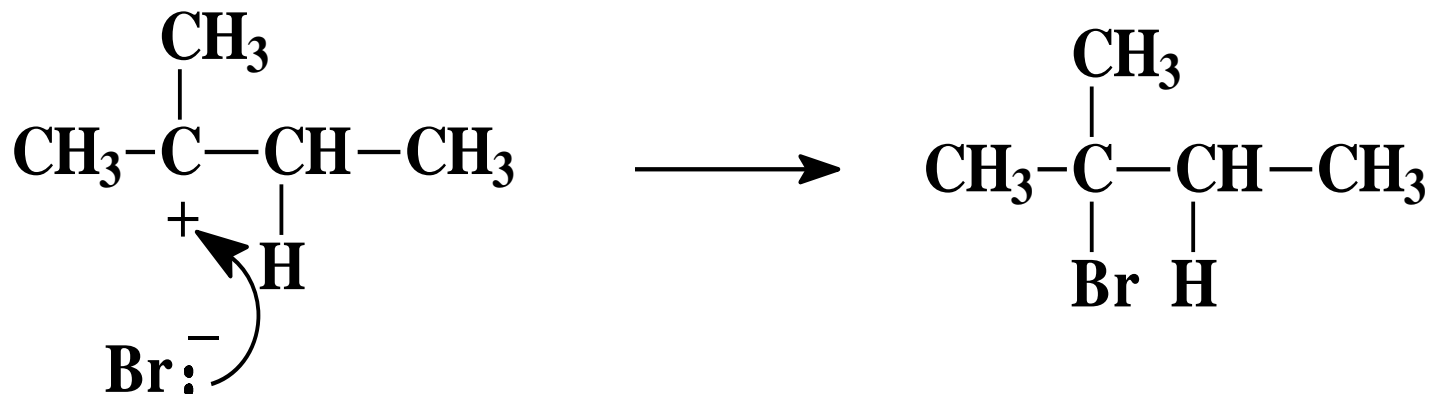
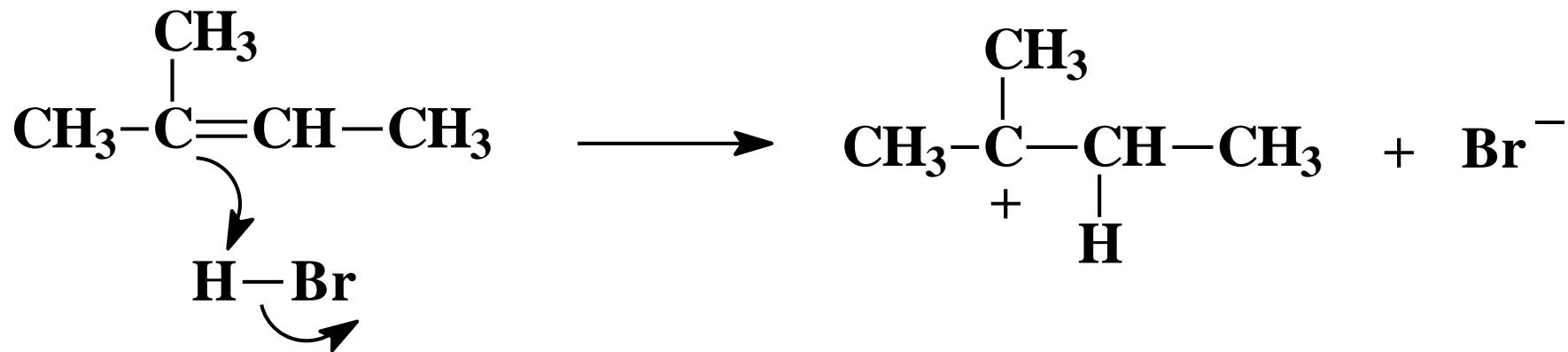
Mecanismo via anel de três membros contendo haleto positivo



Adição de HX

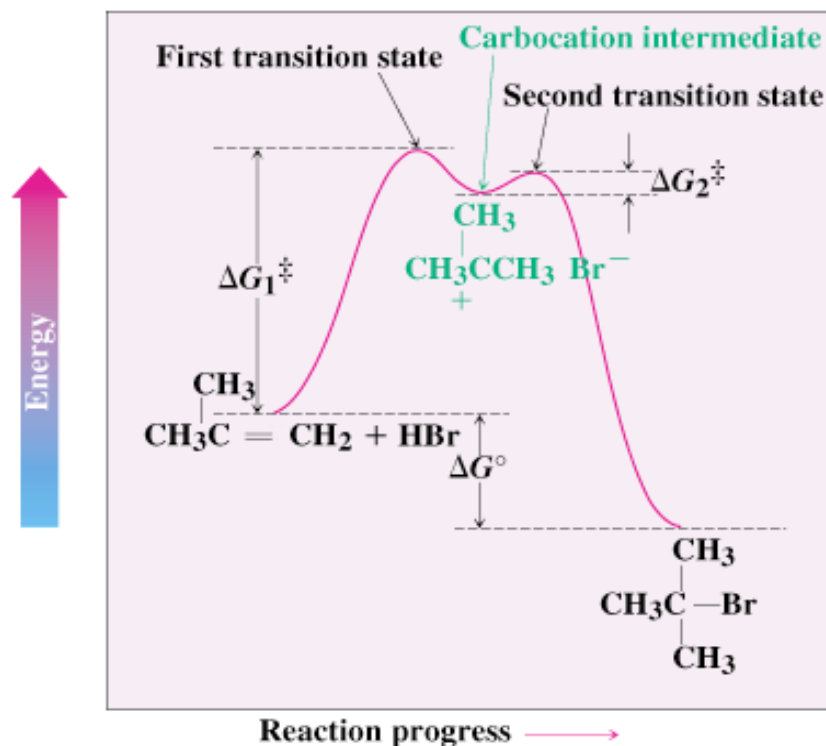
- u Executada com reagentes puros ou em solventes polares - ex.: ácido acético
- u A reação é regiosseletiva
- u **Reação regiosseletiva:** reação na qual há formação ou quebra de ligações preferenciais.

Adição de HX

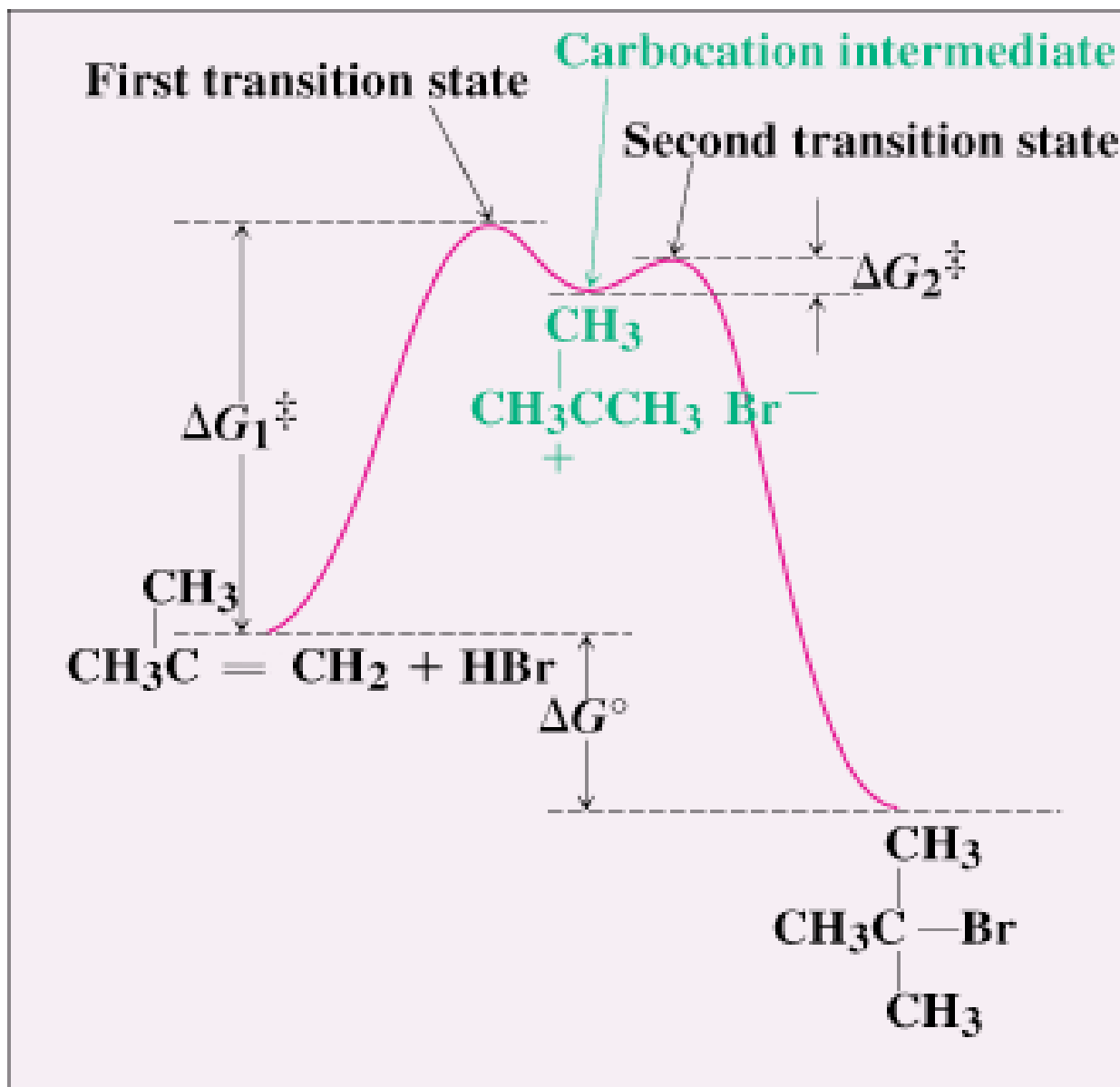


Electrophilic Addition Energy Path

- u Two step process
- u First transition state is high energy point



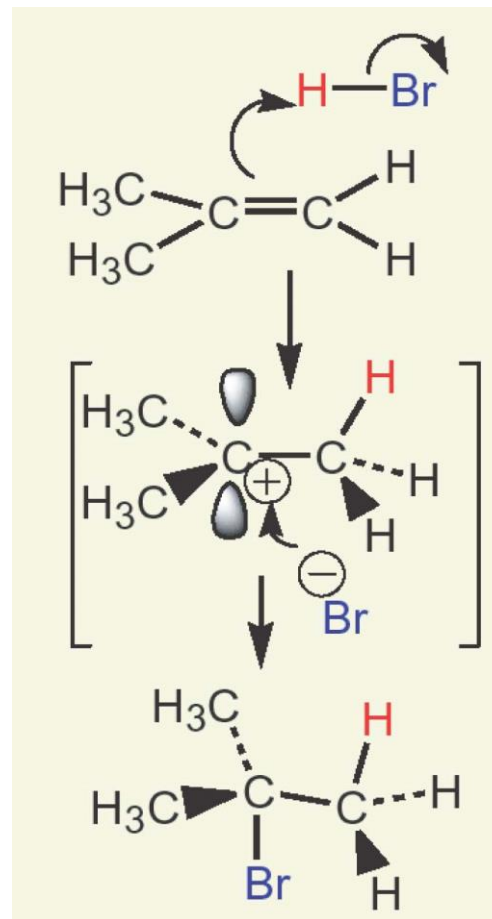
Energy ↑



Reaction progress →

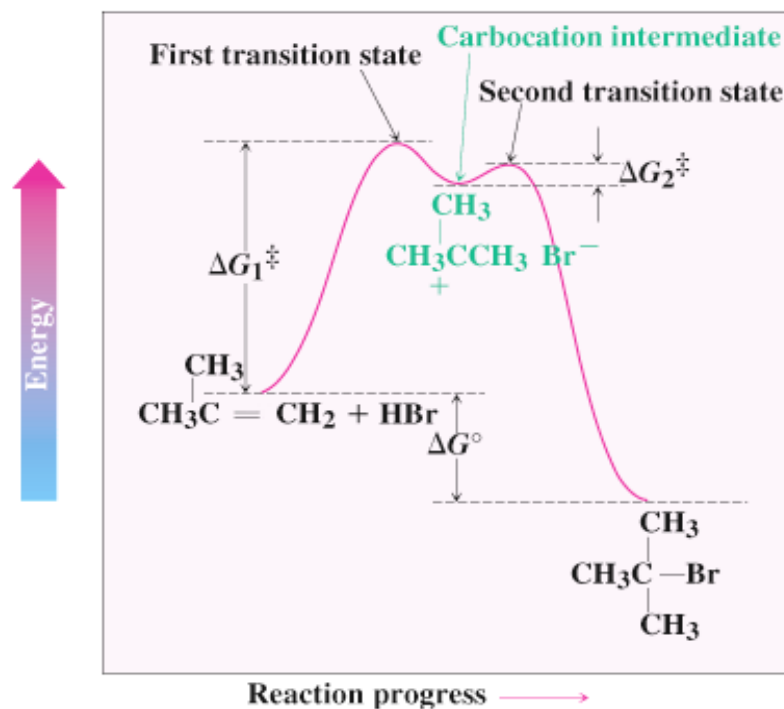
Example of Electrophilic Addition

- u Addition of hydrogen bromide to 2-Methyl-propene
- u H-Br transfers proton to C=C
- u Forms carbocation intermediate
 - More stable cation forms
- u Bromide adds to carbocation

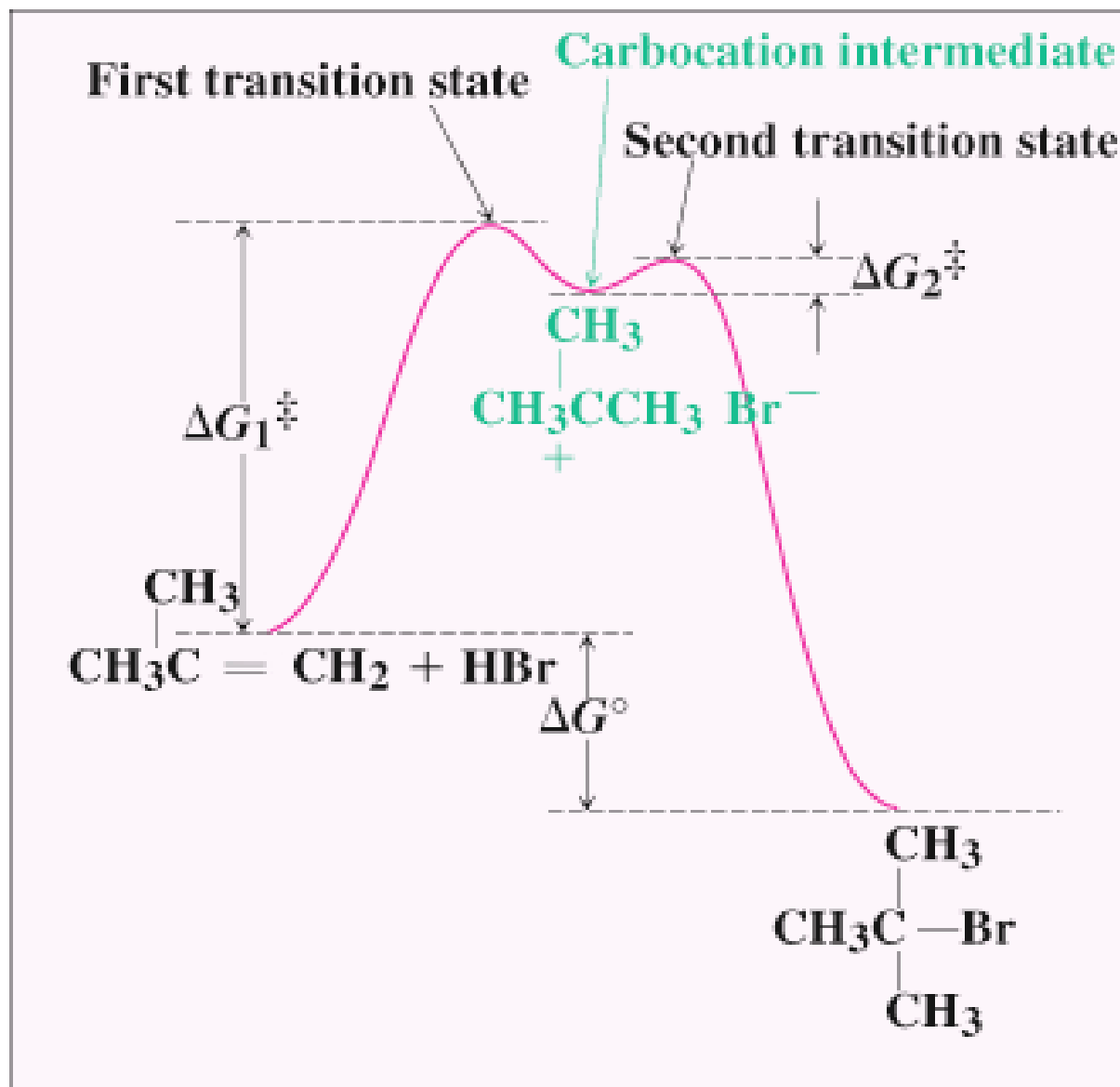


Energy Diagram for Electrophilic Addition

- u Rate determining (slowest) step has highest energy transition state
- Independent of direction
 - In this case it is the first step in forward direction
 - “rate” is not the same as “rate constant”



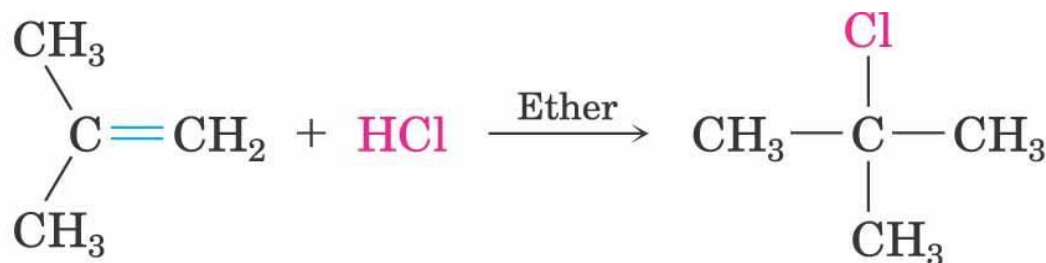
Energy ↑



Reaction progress →

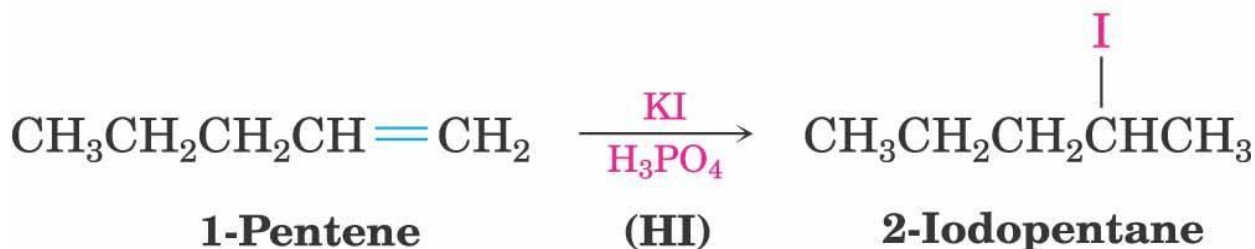
Electrophilic Addition for Syntheses

- The reaction is successful with HCl and with HI as well as HBr. Note that HI is generated from KI and phosphoric acid



2-Methylpropene

2-Chloro-2-methylpropane
(94%)



1-Pentene

(HI)

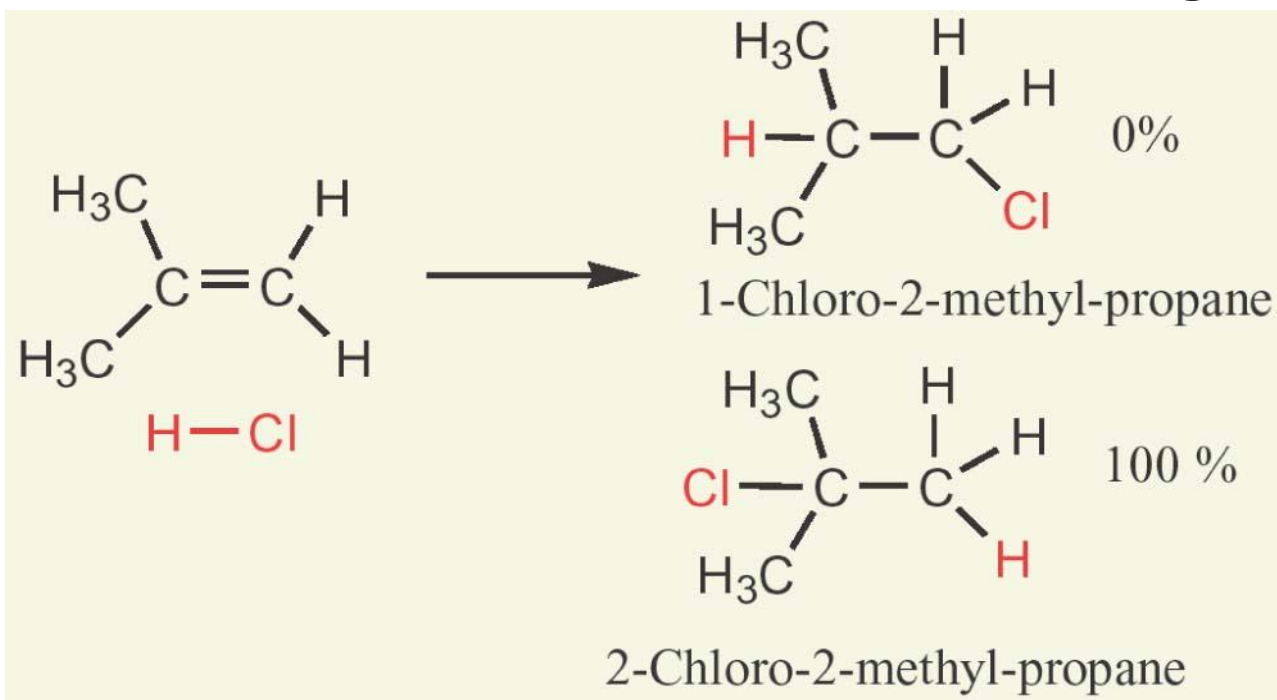
2-Iodopentane

Orientation of Electrophilic Addition:

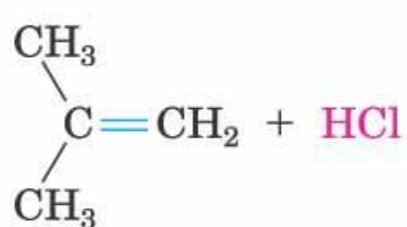
- u In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other
- u If one orientation predominates, the reaction is *regiospecific*
- u The reaction will always occur favoring the formation of the most stable carbocation

Example of Regiospecific reactions

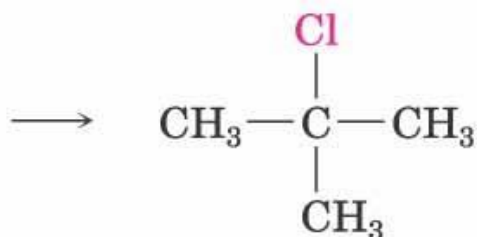
- u Addition of HCl to 2-methylpropene
- u Regiospecific – one product forms where two are possible
- u If both ends have similar substitution, then not regiospecific



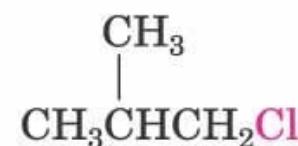
Same example:



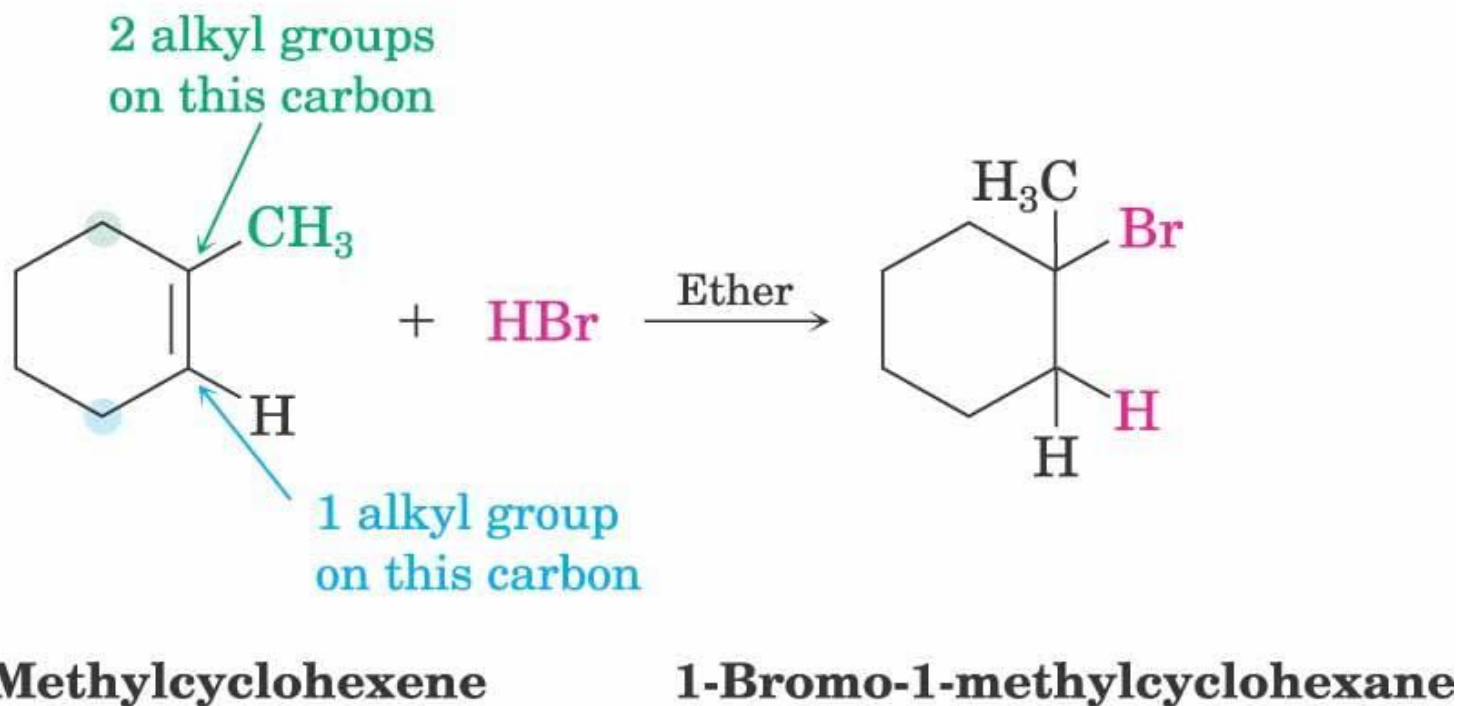
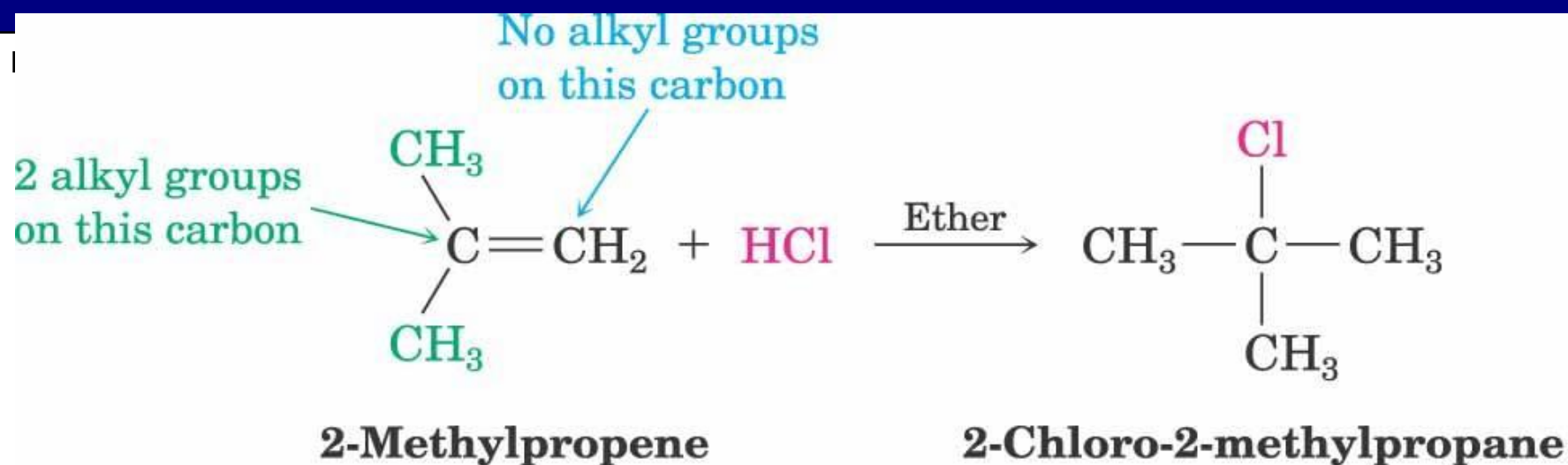
2-Methylpropene

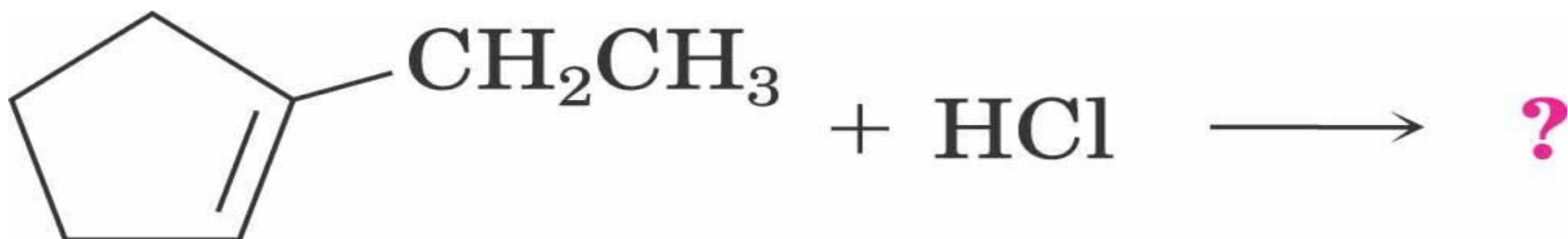


2-Chloro-2-methylpropane
(sole product)

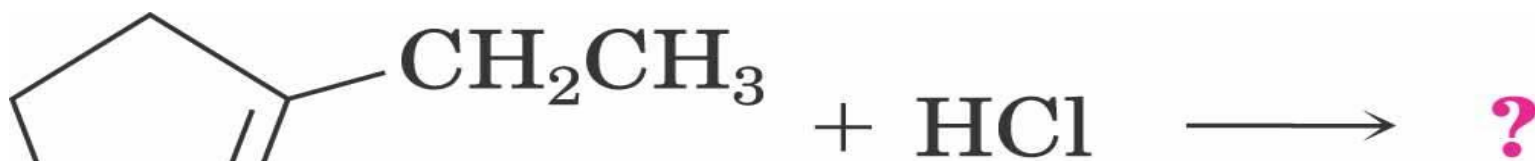


1-Chloro-2-methylpropane
(NOT formed)

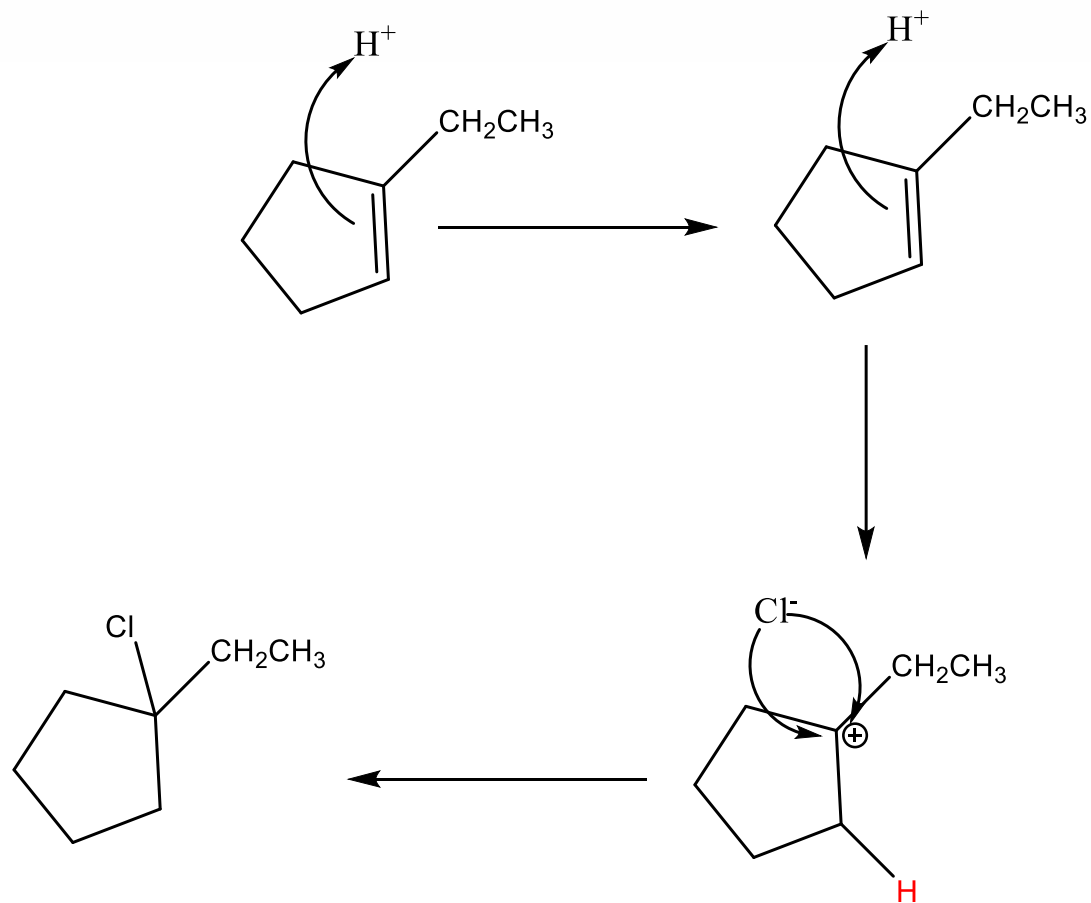




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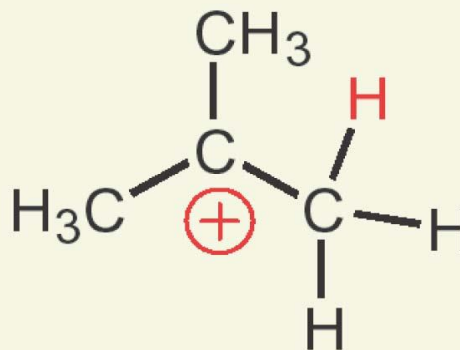


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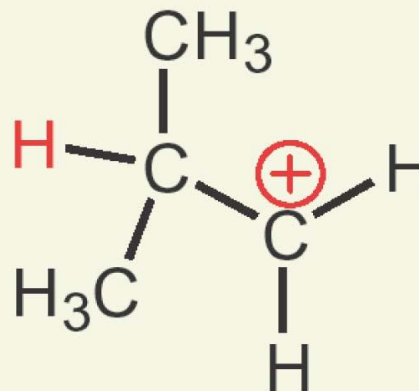


Mechanistic Source of Regiospecificity in Addition Reactions

- u If addition involves a carbocation intermediate
- and there are two possible ways to add
 - the route producing the more alkyl substituted cationic center is lower in energy
 - alkyl groups stabilize carbocation

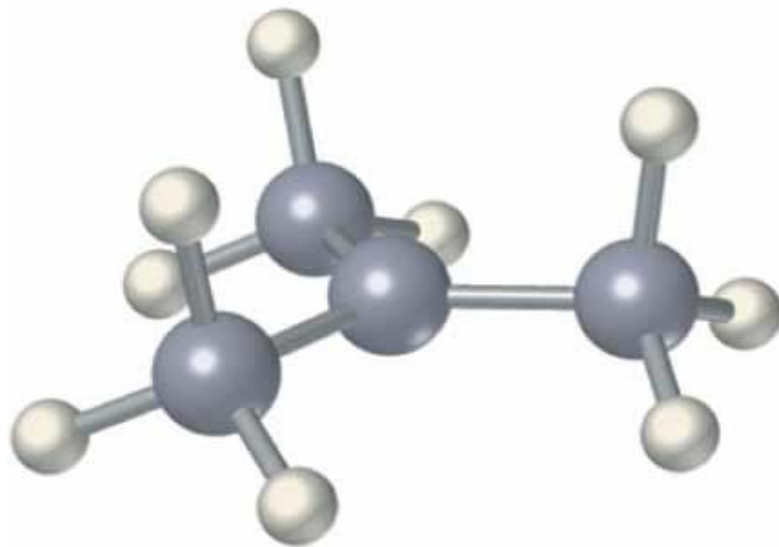
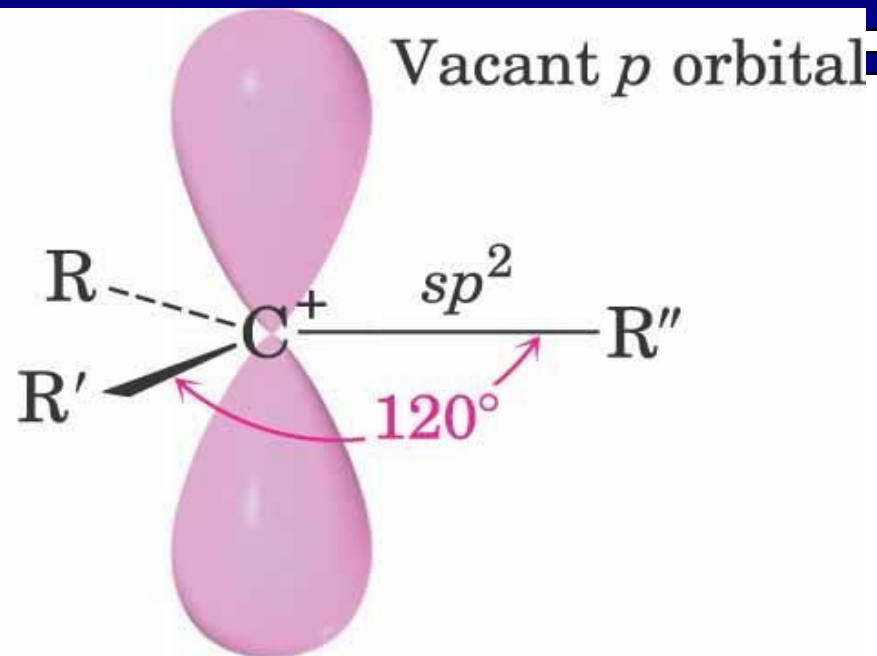


Much more stable



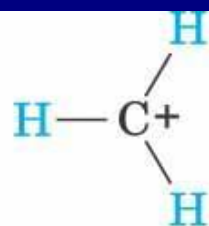
Carbocation Structure and Stability

- u Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in sp^2 orbitals
- u The fourth orbital on carbon is a vacant p -orbital

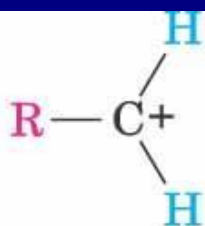


Carbocation Structure and Stability

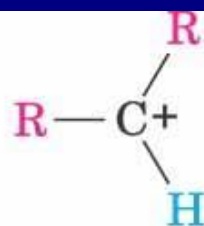
- u The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents
- u Therefore stability of carbocations:
$$3^\circ > 2^\circ > 1^\circ > ^+\text{CH}_3$$



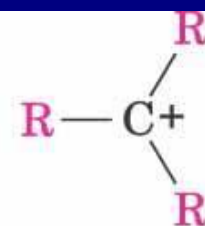
Methyl



Primary (1°)



Secondary (2°)



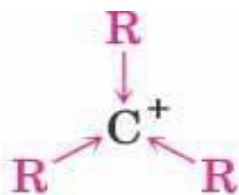
Tertiary (3°)

Less stable



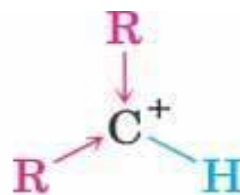
More stable

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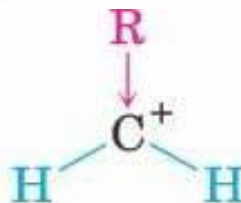


3°: Three alkyl groups donating electrons

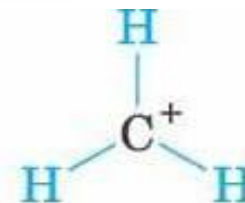
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2°: Two alkyl groups donating electrons

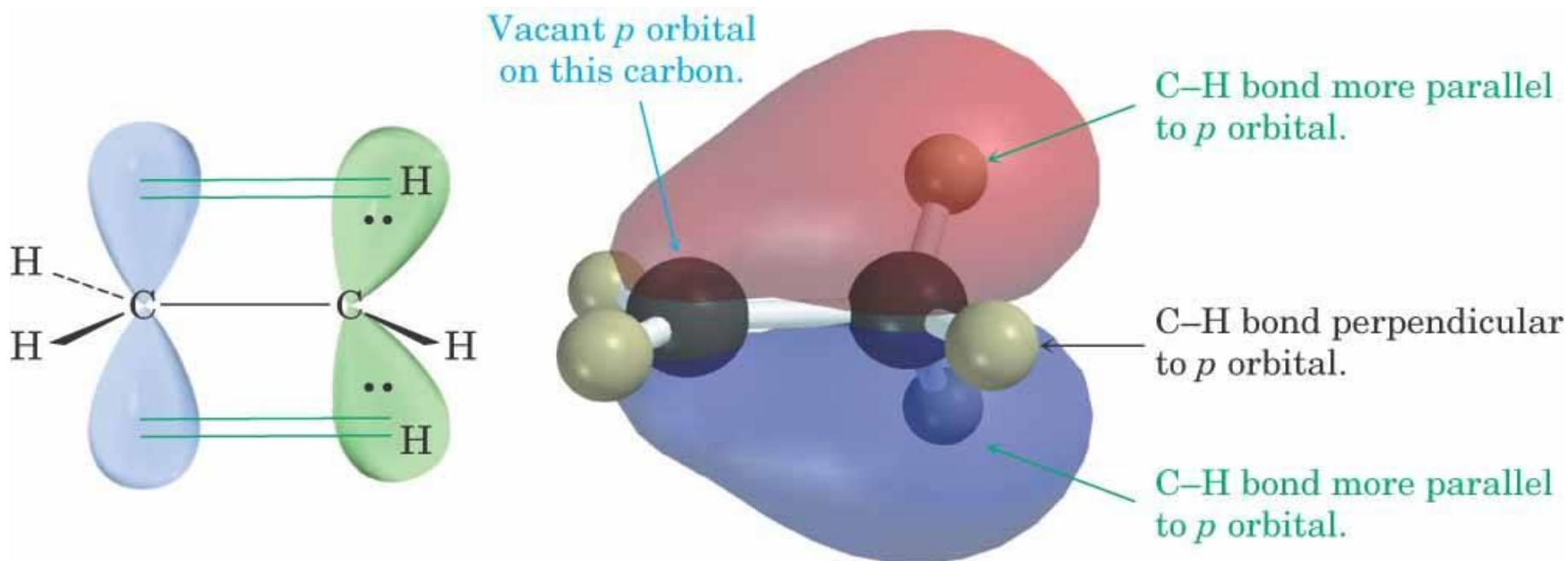


1°: One alkyl group donating electrons



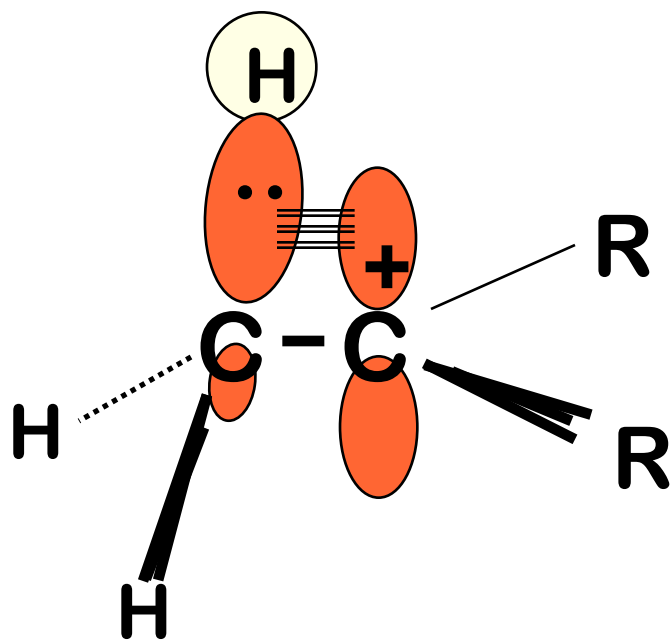
Methyl: No alkyl groups donating electrons

Stabilizing Carbocations:



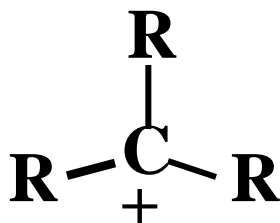
CARBOCATION STABILITY

HYPERCONJUGATION



electrons in an adjacent C-H σ bond help to stabilize the positive charge of the carbocation by proximity (overlap)

Most
stable



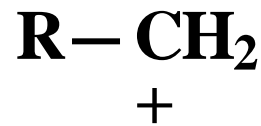
tertiary

>



secondary

>

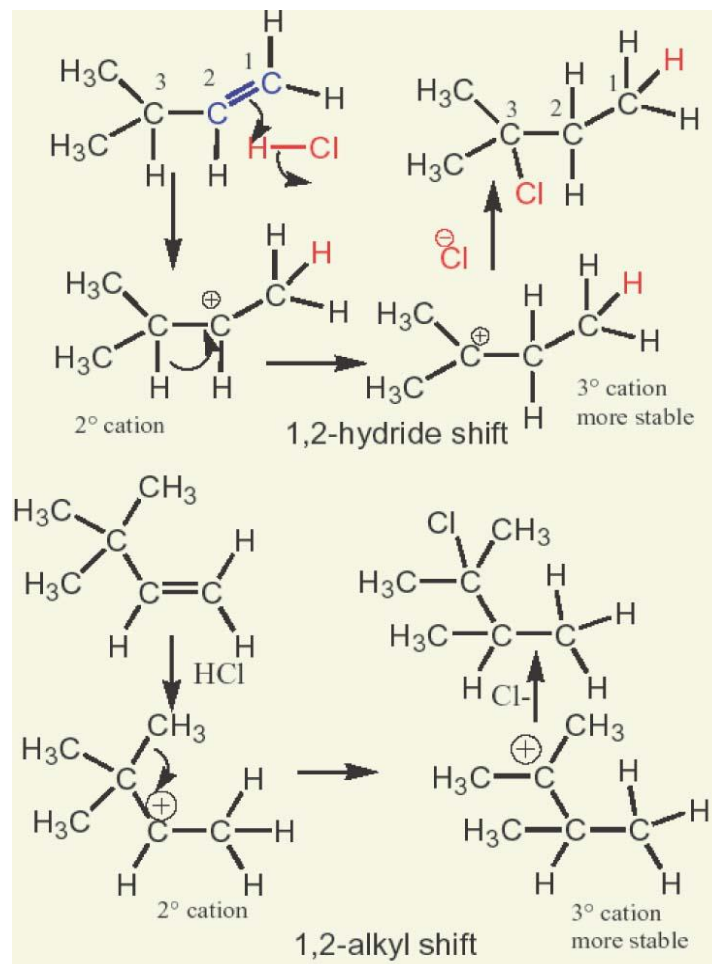


primary

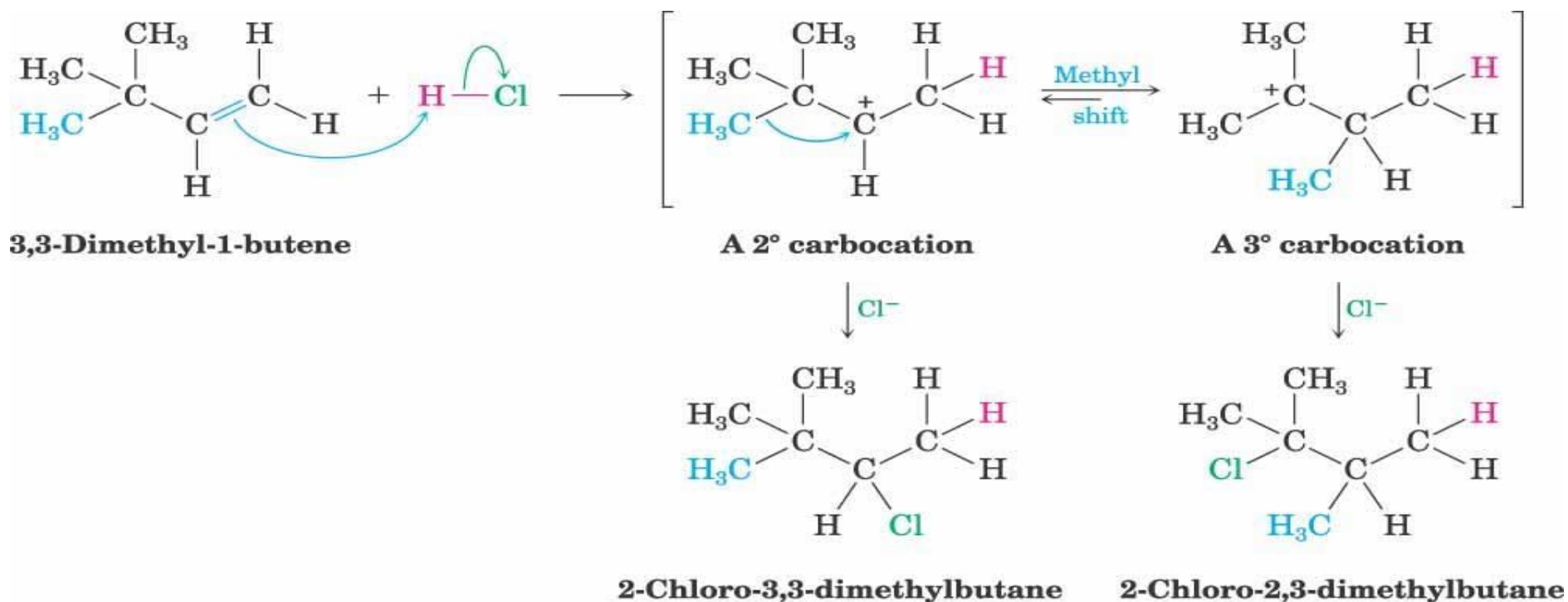
Least
stable

Mechanism of Electrophilic Addition: Rearrangements of Carbocations

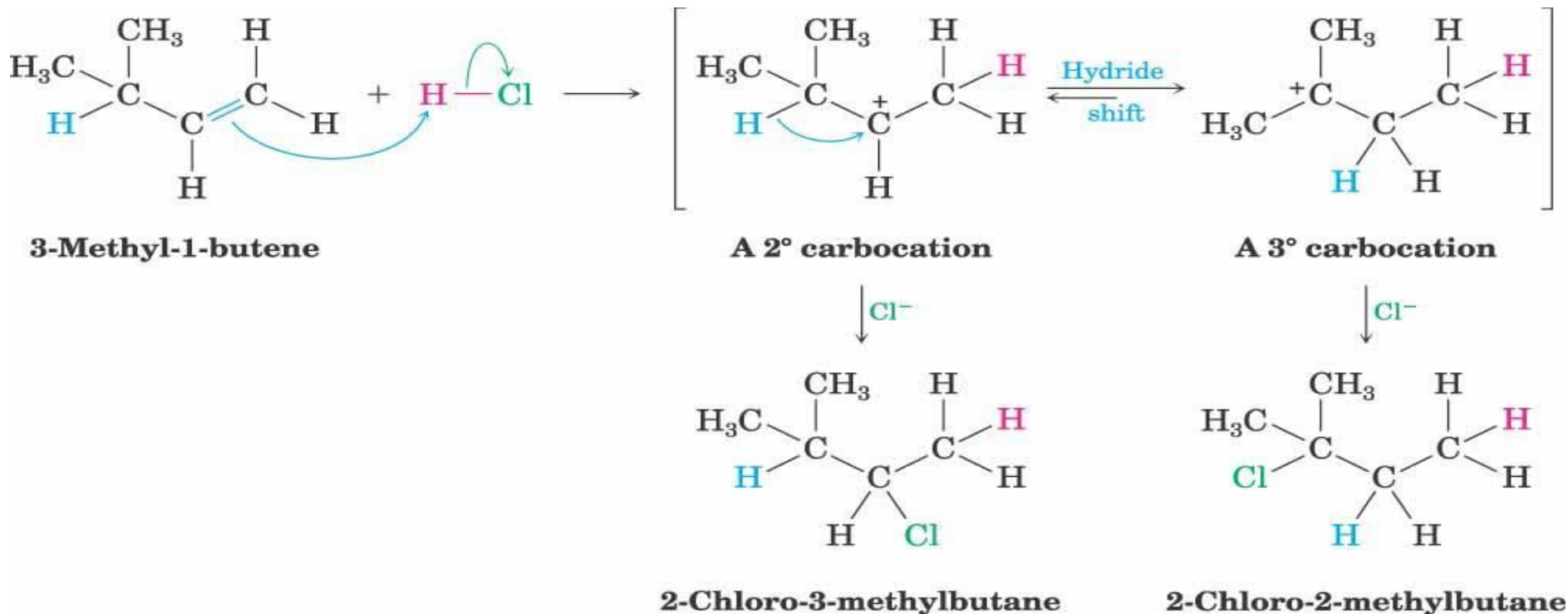
- u Carbocations undergo structural rearrangements following set patterns
- u 1,2-H and 1,2-alkyl shifts occur
- u Goes to give more stable carbocation
- u Can go through less stable ions as intermediates



Hydride Shifts



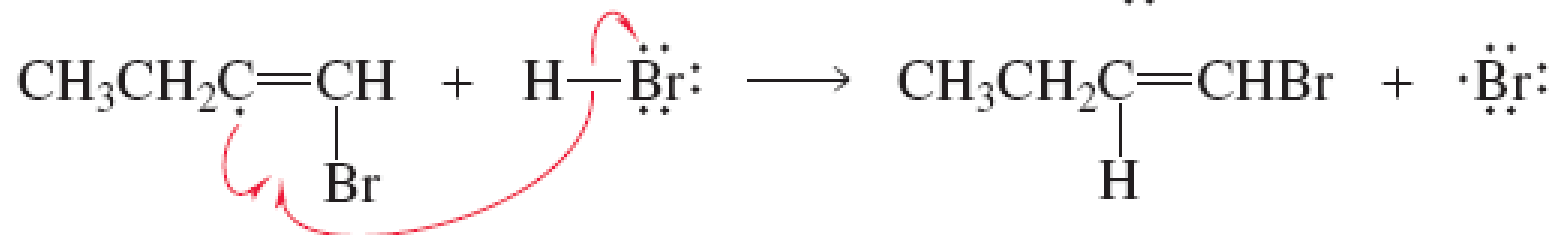
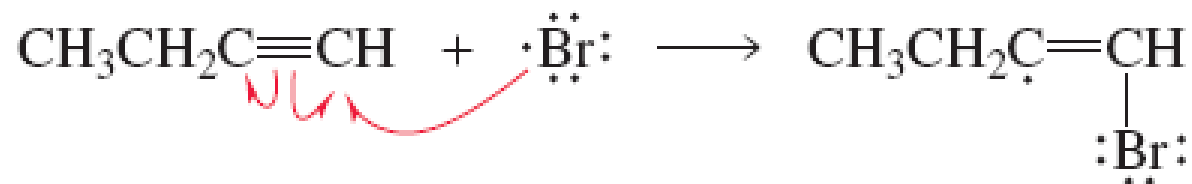
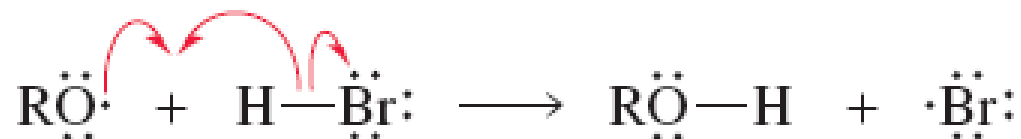
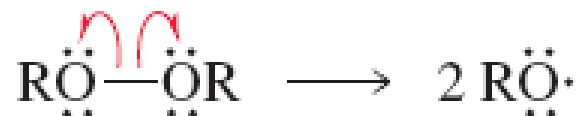
Alkyl (methyl) shifts



Adição de brometo de hidrogênio

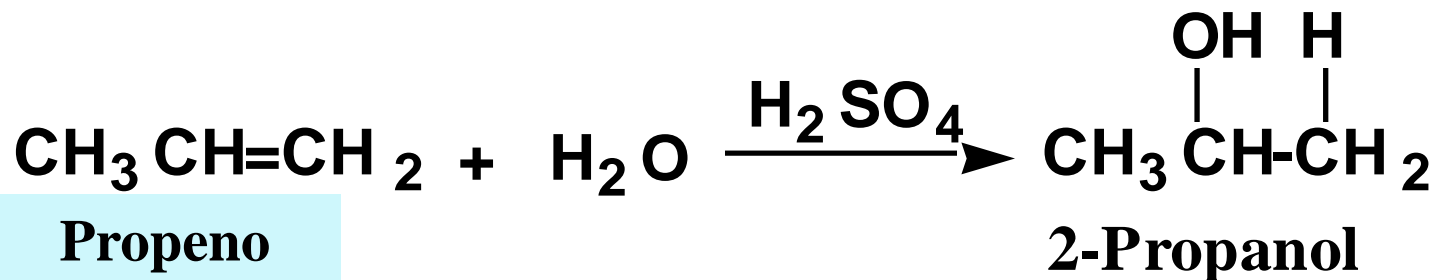


Mecanismo radicalar

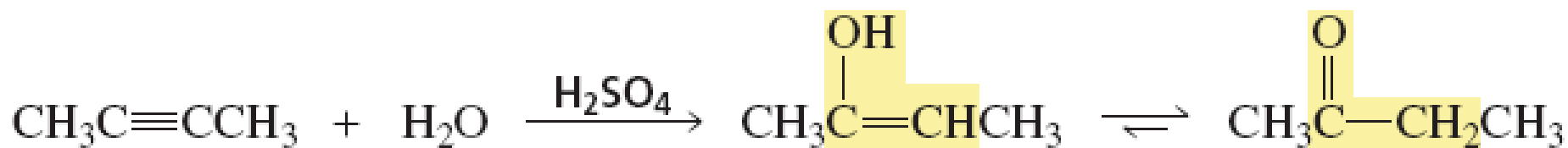


Adição de H₂O

- u A adição de água denomina-se hidratação
- u A hidratação de um alceno catalisada por ácido é regiosseletiva - o hidrogênio adiciona-se ao carbono menos substituído da dupla ligação



Adição de água



tautômero enol

tautômero ceto

tautomerismo ceto-enólico

Indirect Hydration

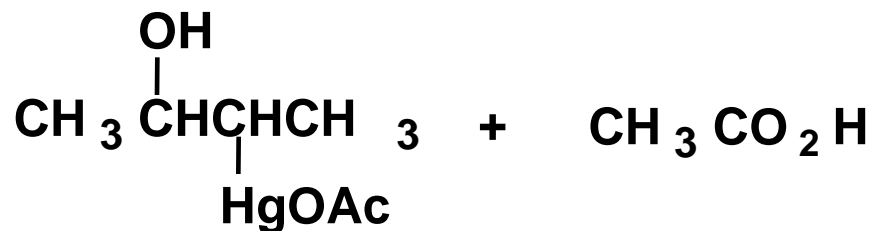
- u **Oxymercuration-Demercuration**
 - Anti addition of H-OH
 - No rearrangements
- u **Hydroboration**
 - Syn addition of H-OH

Oximercuração/Redução

- Oximercuração:** a um dos C da dupla ligação há adição de Hg(II) e, ao outro, do oxigênio da água. No final o mercúrio é eliminado por redução gerando um álcool.

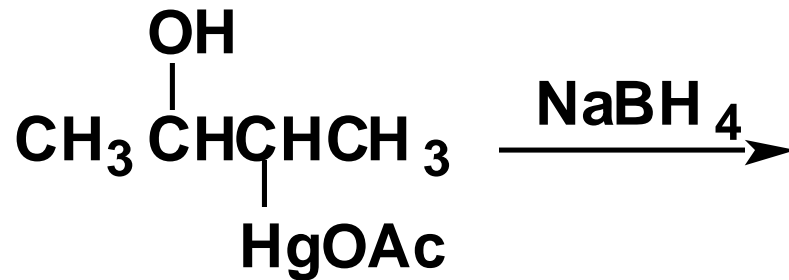


2-Buteno

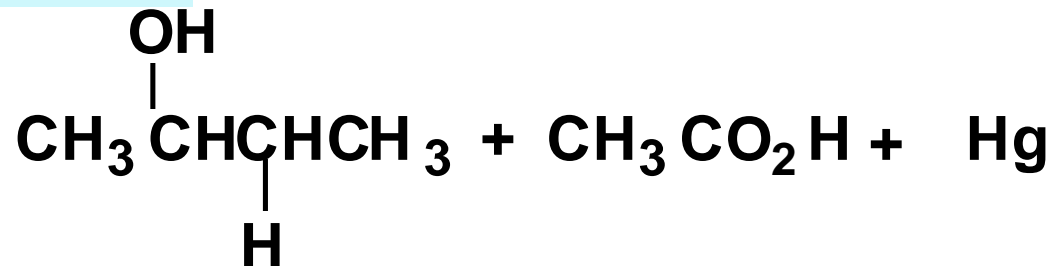


Oximercuração/Redução

- u A redução com NaBH_4 substitui o Hg por H



Composto
organomercúrio

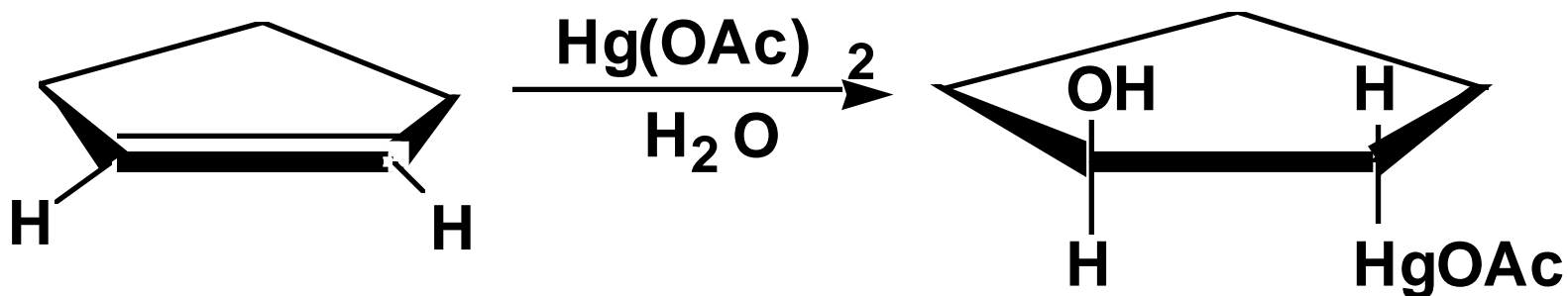


2-Butanol

Ácido acético

Oximercuração/Redução

- u A adição de Hg(II) e oxigênio tem estereoseletividade anticoplanar



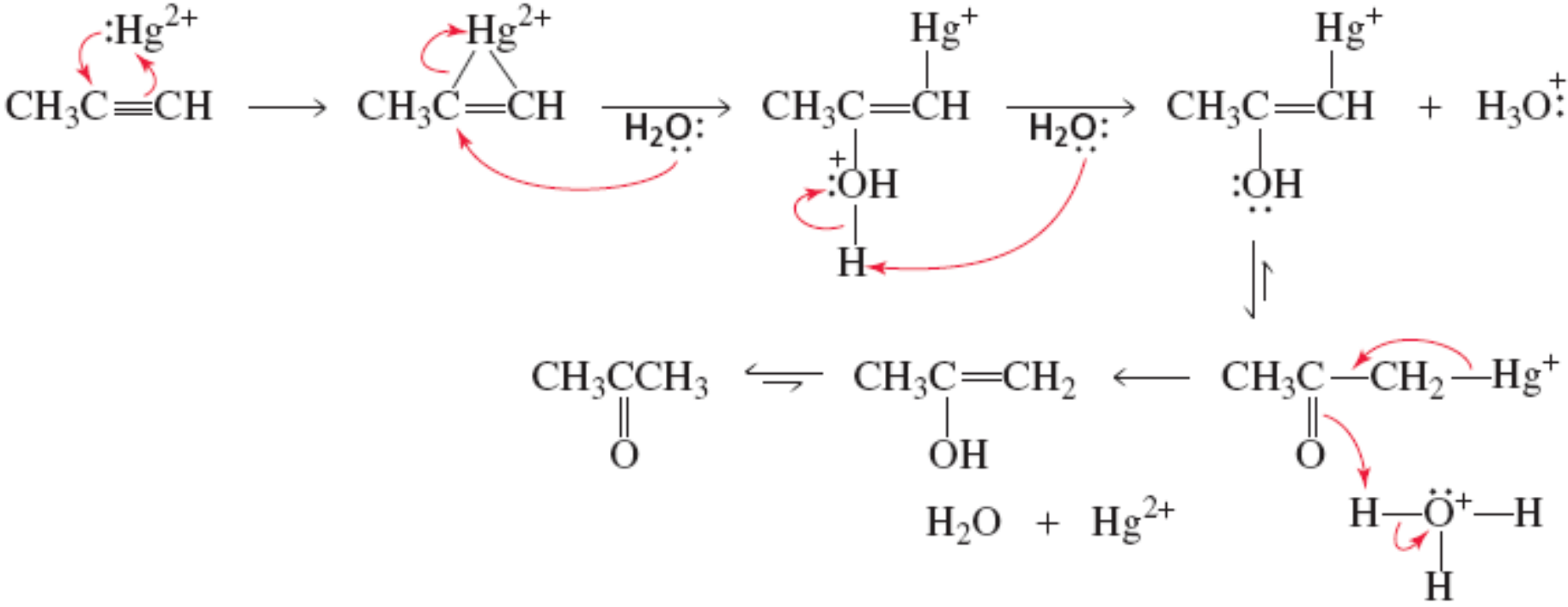
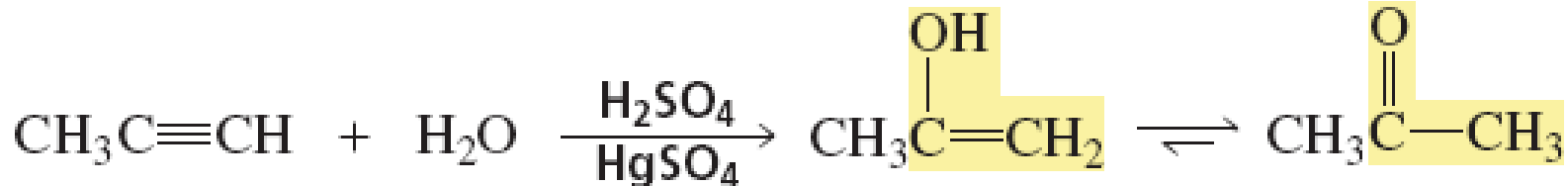
Ciclopenteno

(adição anti de -
OH e -HgOAc)

Oximercuração/Redução

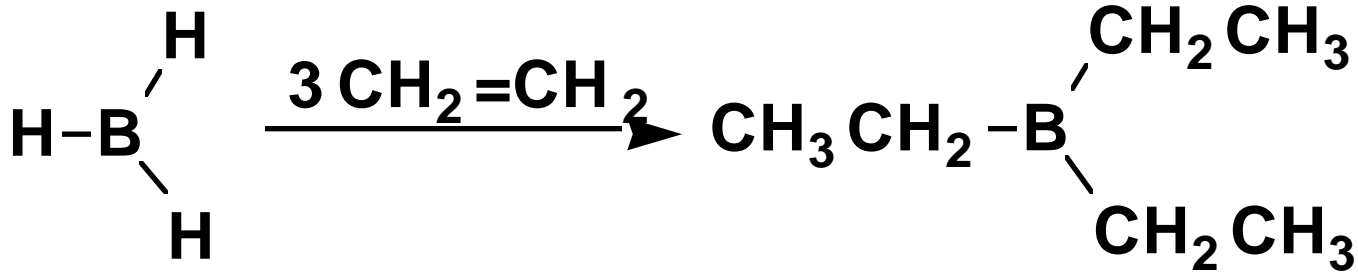
- u A regioseletividade é explicada devido à existência de um certo caráter de carbocátion no intermediário cíclico
- u A estereosseletividade é explicada devido ao ataque anti ao intermediário cíclico

Hidratação de alcinos terminais catalisada por sulfato de mercúrio



Hidroboração/Oxidação

- u **Hidroboração:** adição de borano, BH_3 , a um alceno, formando um trialquilborano

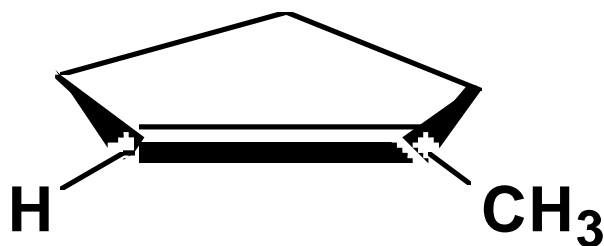


Borano

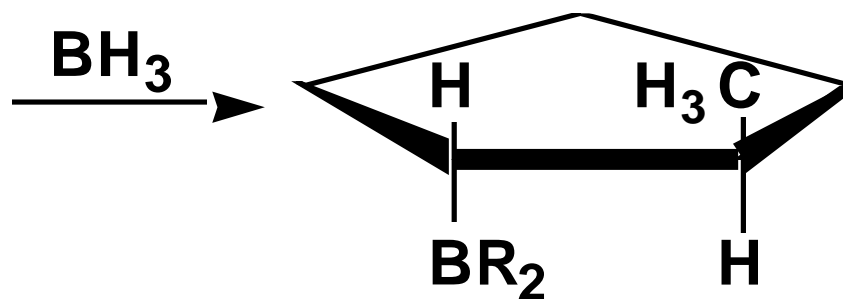
Trialquilborano

Hidroboração/Oxidação

- u A hidroboração é tanto regioseletiva (boro adiciona no carbono menos impedido) como estereosseletiva (adição syn)



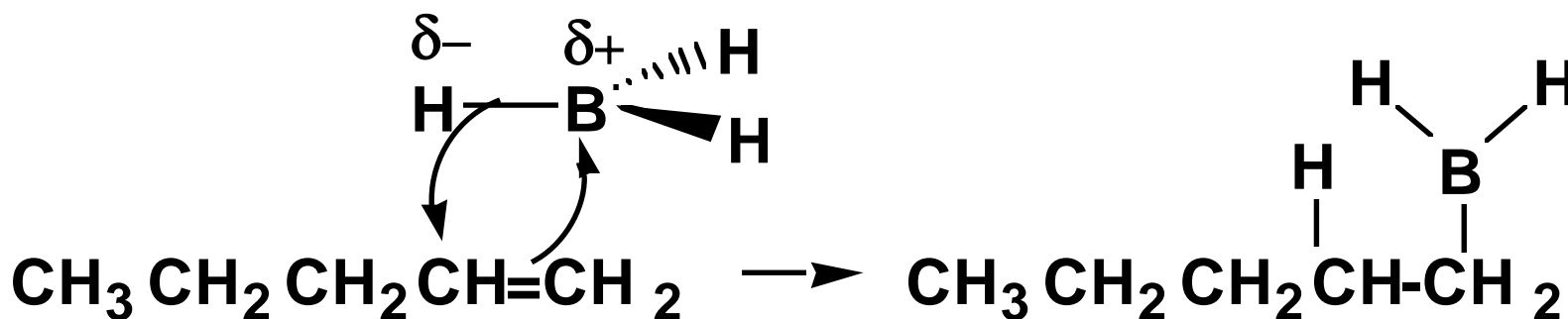
1-Metilciclopenteno



(adição sin ao BH_3)
($\text{R} = 2\text{-metilciclopentila}$)

Hidroboração/Oxidação

- u O mecanismo envolve uma adição simultânea (concertada) regioseletiva e estereosseletiva, de B e H à dupla ligação carbono-carbono



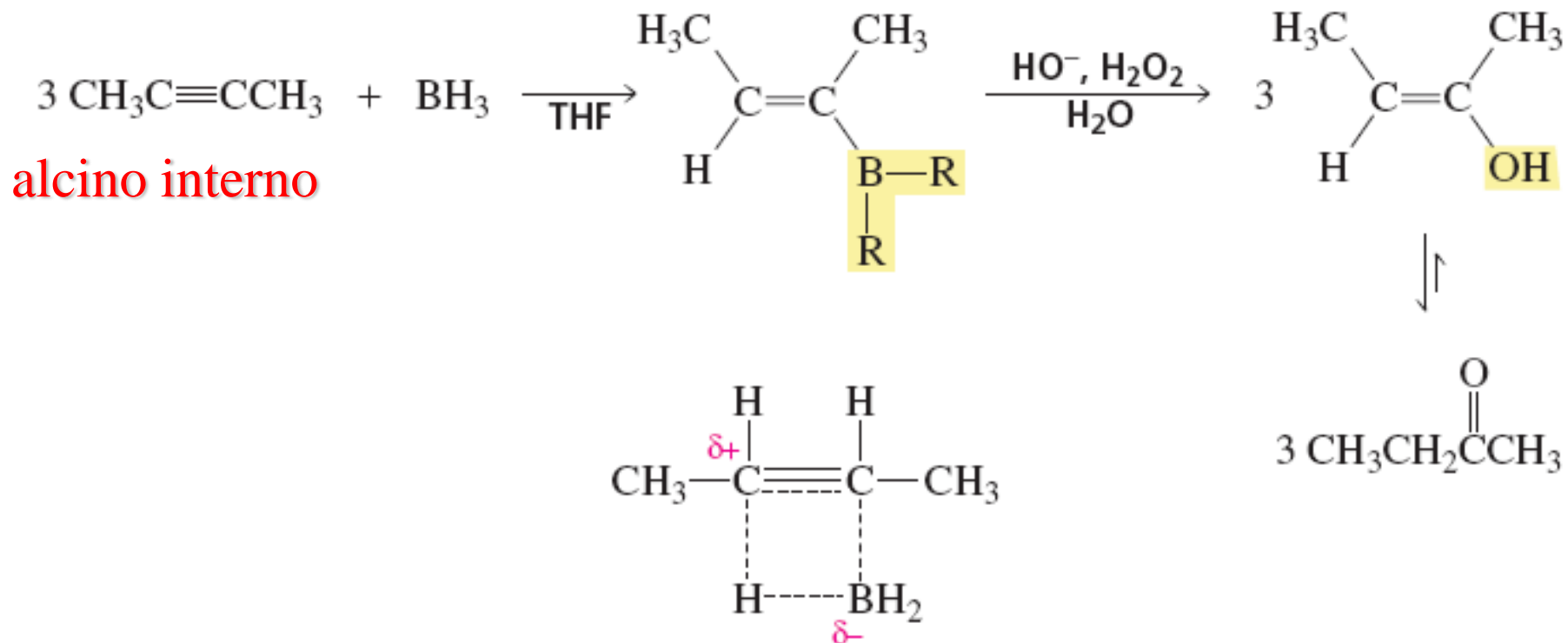
A quebra e formação das ligações ocorre simultaneamente

O boro adiciona-se ao carbono menos substituído da dupla ligação

Hidroboração/Oxidação

- u O resultado da hidroboração/oxidação é a hidratação regio e estereoseletiva de uma dupla ligação carbono-carbono

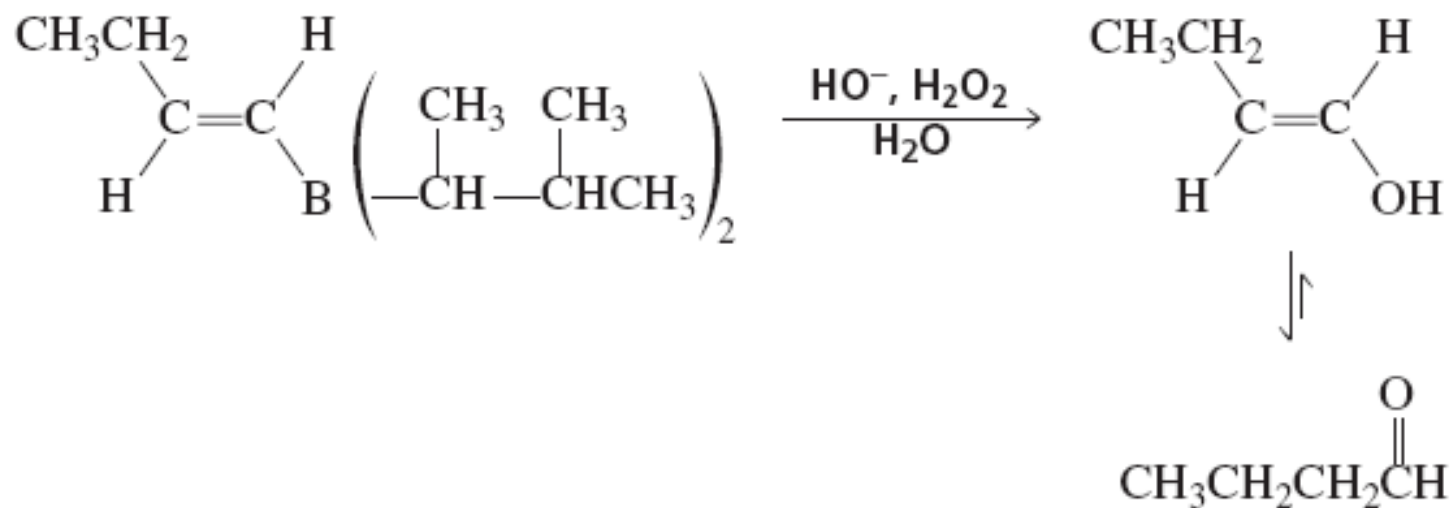
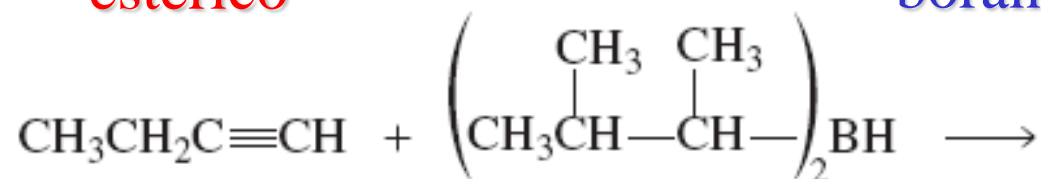
Hidroboração-oxidação



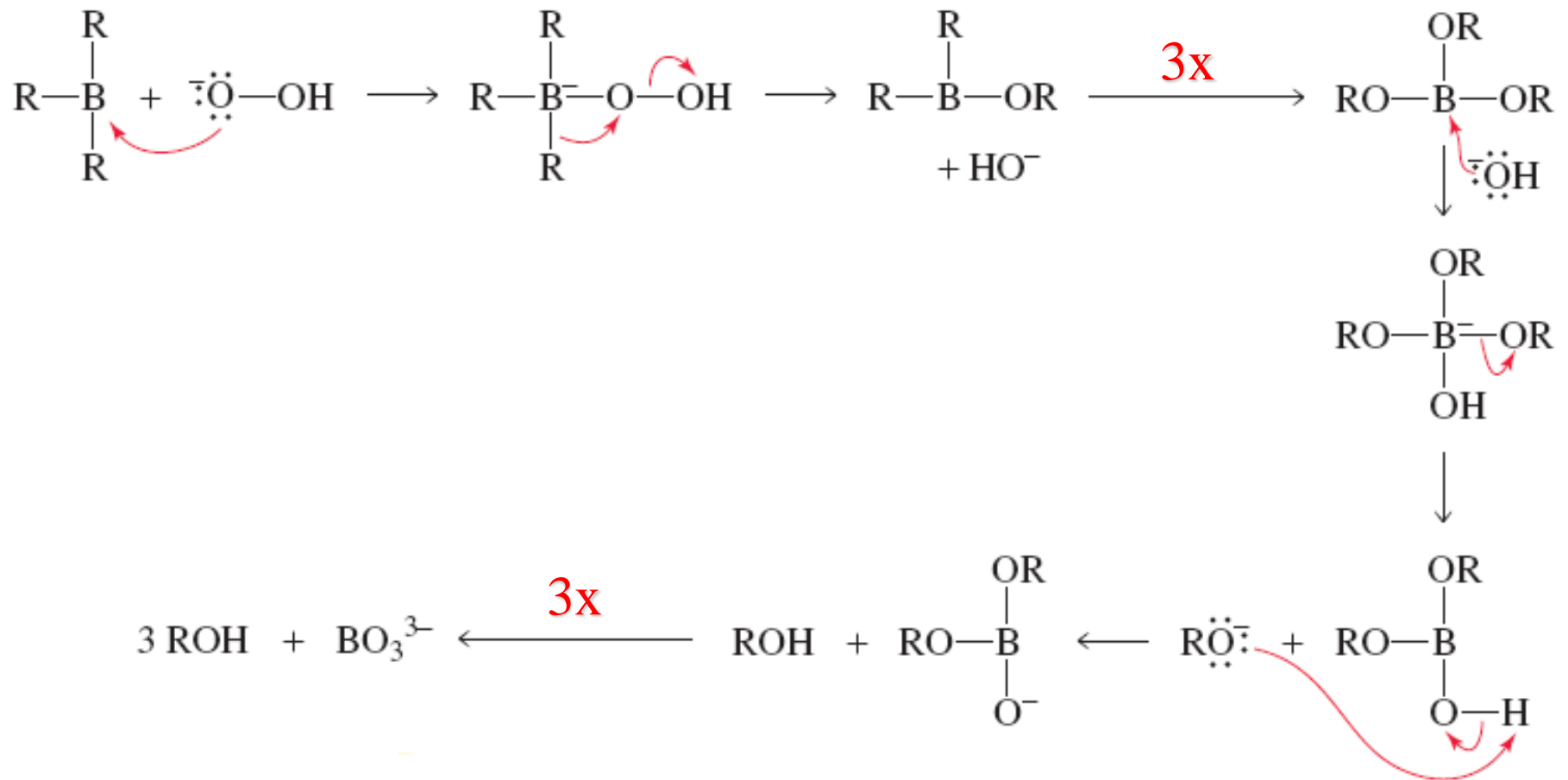
Mecanismo via estado de transição de anel de quatro membros

alcino terminal
sem impedimento
estérico

bis(1,2,-dimetilpropil)-
borana



Mecanismo de oxidação da borana



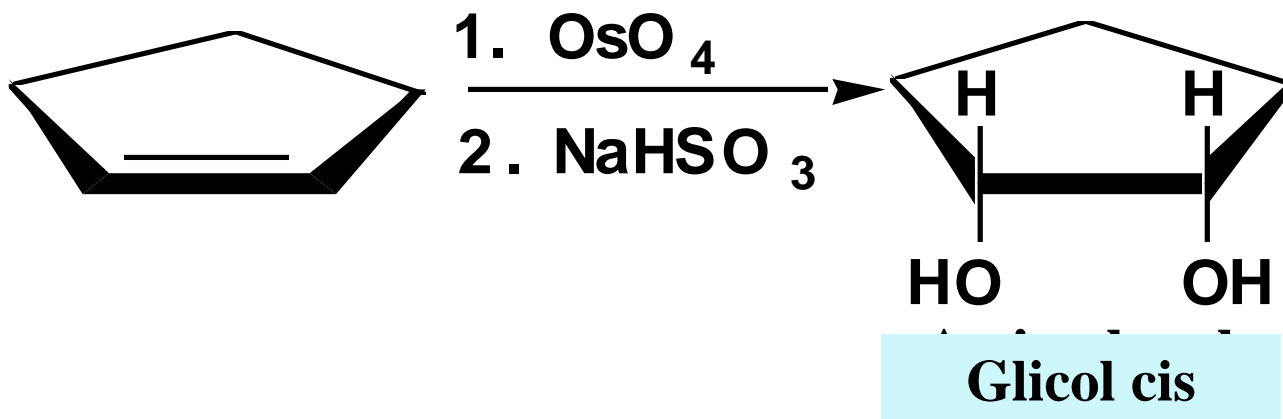
Oxidação/Redução

- u **Oxidação:** perda de elétrons
- u **Redução:** ganho de elétrons

- u **Determinável usando-se uma semi-reação balanceada**
 1. Escreve-se uma semi-reação mostrando um dos reagentes e seu(s) produto(s)
 2. Faz-se um balanço material. Usa-se H_2O e H^+ em solução ácida; H_2O e OH^- em solução básica
 3. Faz-se um balanço de carga, usando elétrons, e^-

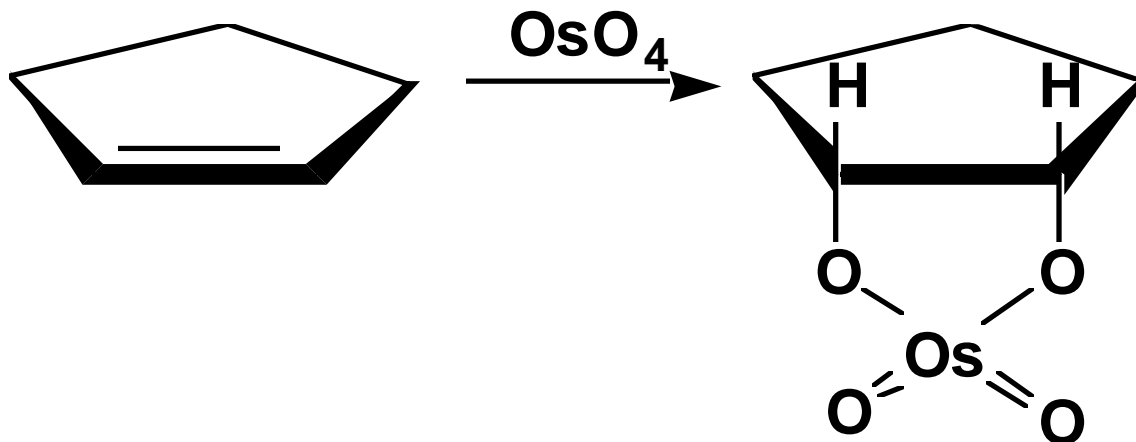
Oxidação com OsO_4

- u A oxidação por OsO_4 converte um alceno em um glicol, um composto com grupos $-\text{OH}$ em dois carbonos adjacentes
 - a oxidação é sin e estereoseletiva



Oxidação com OsO_4

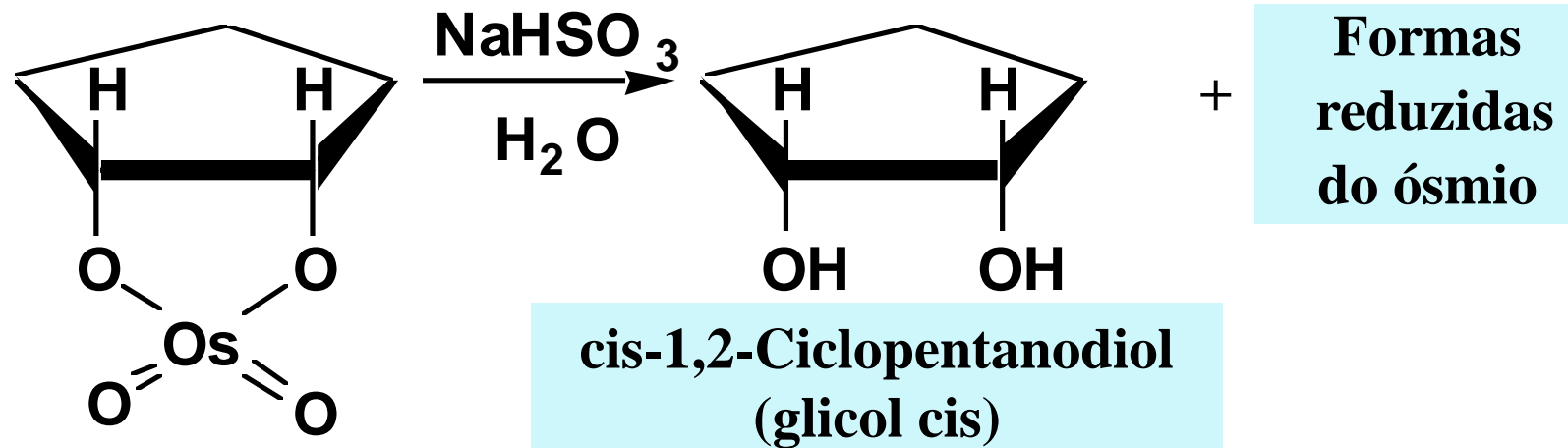
- u O intermediário é um éster de ósmio cíclico, contendo um anel de 5 membros



Um osmato cíclico
(éster cíclico do ósmio)

Oxidação com OsO₄

- u A redução do éster de ósmio com NaHSO₃ resulta em um glicol e em formas reduzidas (menor número de oxidação) do ósmio

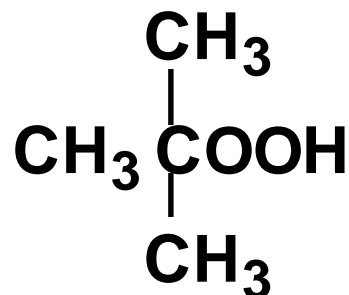


Oxidação com OsO₄

- u O OsO₄ é caro e altamente tóxico
- u Ele é utilizado em quantidades catalíticas, na presença de outros agentes oxidantes que reoxidam suas formas reduzidas e, assim, reciclam o OsO₄



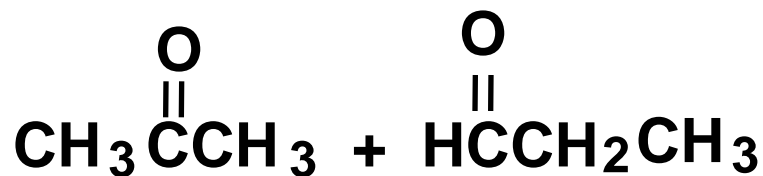
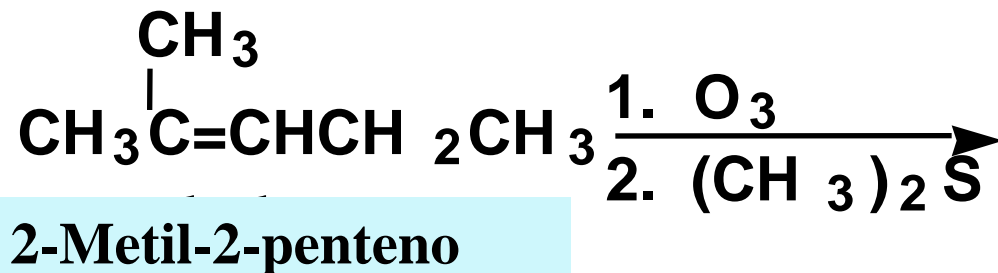
Peróxido de
hidrogênio



Hidroperóxido de *terc*-butila
(t-BuOOH)

Oxidação com O₃

- u O tratamento de um alceno com ozônio, seguido por um agente redutor fraco, cliva a ligação C=C, formando dois grupos carbonila em seu lugar

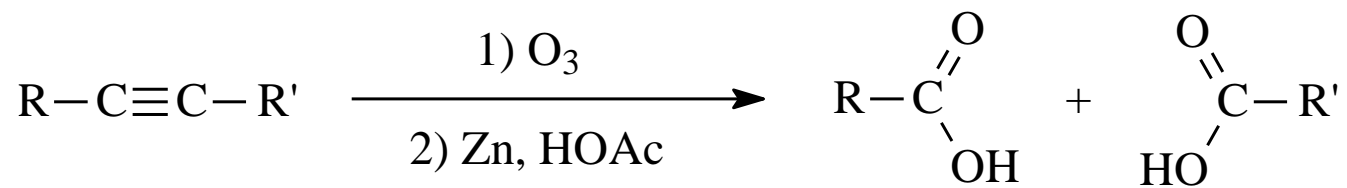


Propanona
(cetona)

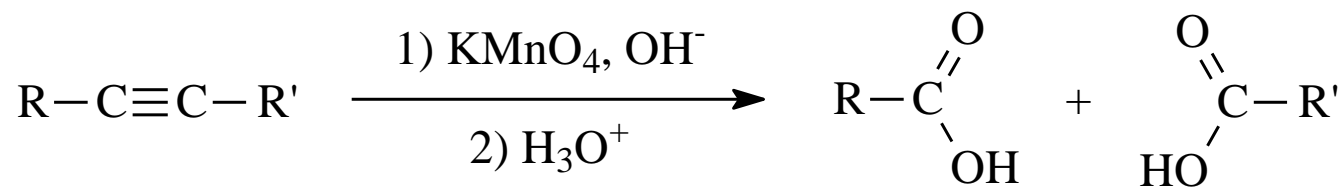
Propanal
(aldeído)

Quebra oxidativa

Reação de ozonólise

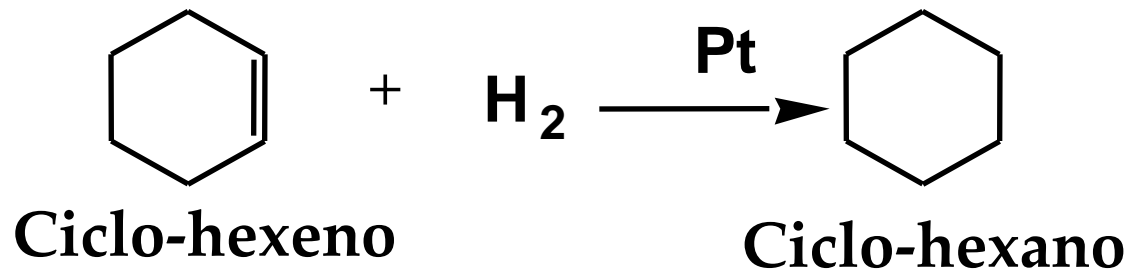


Reação com permanganato de potássio em meio alcalino



Redução de Alcenos

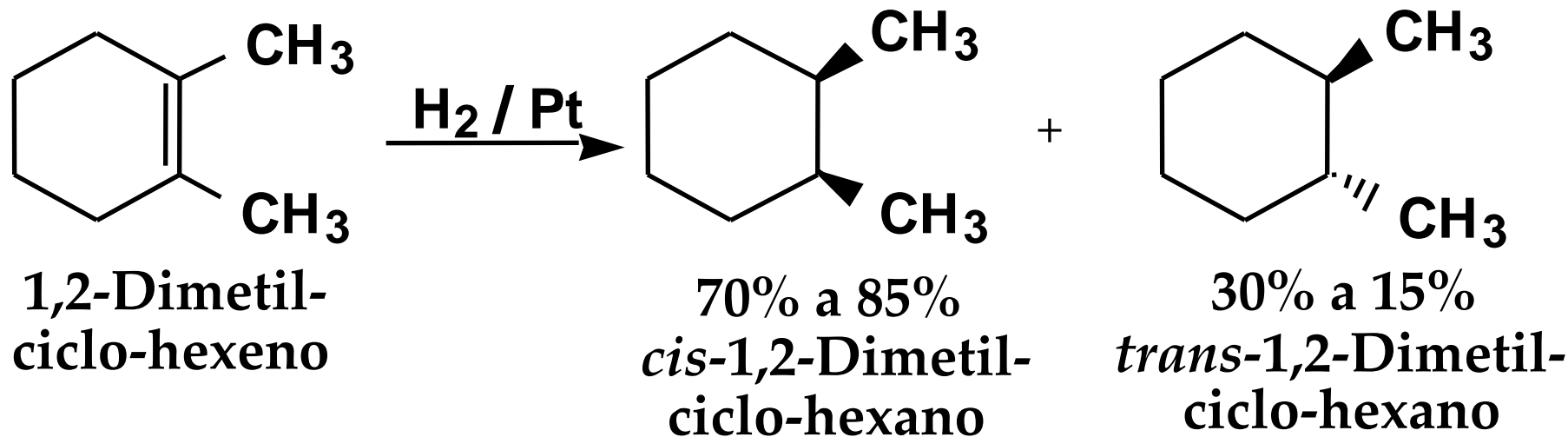
- u A maior parte dos alcenos reage com H_2 na presença de catalisadores de metais de transição, resultando em alcanos



- os catalisadores mais usados são Pt, Pd, Ru, e Ni
- u O processo é denominado redução catalítica ou, alternativamente, hidrogenação catalítica

Redução de Alcenos

- u O padrão de estereoseletividade mais comum é tipo sin



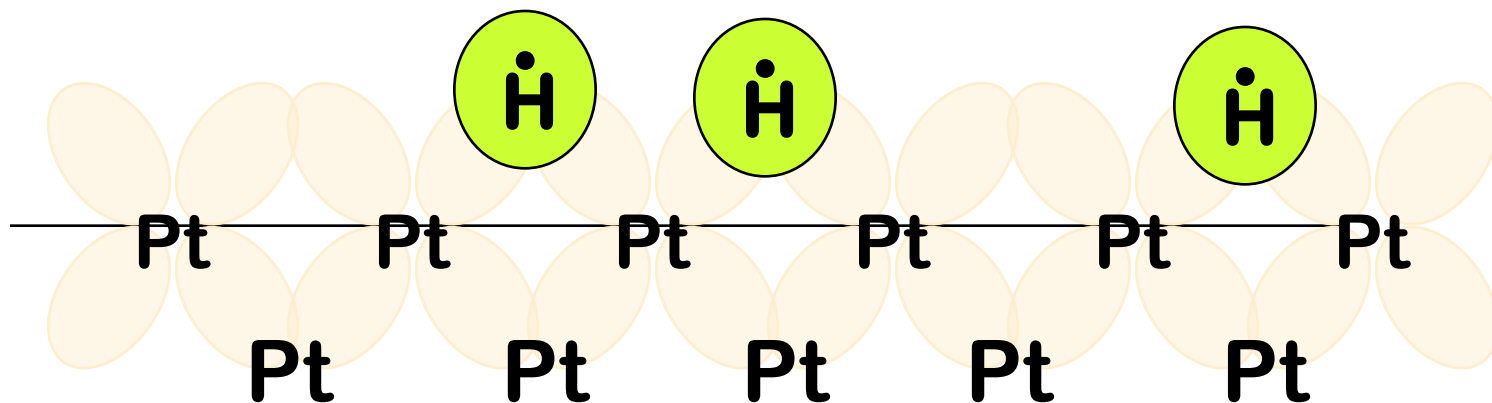
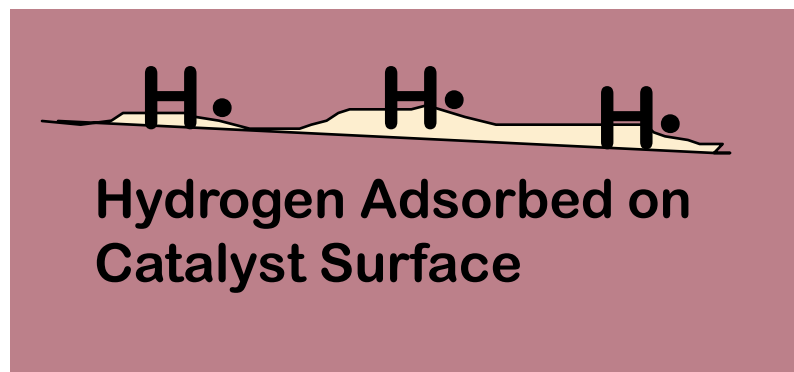
Redução de Alcenos

- u **Mecanismo da hidrogenação catalítica**
 - o H_2 é absorvido na superfície do metal, com a formação de ligações metal-hidrogênio
 - o alceno também é absorvido com a formação de ligações metal-carbono
 - um átomo de hidrogênio é transferido para o alceno, formando uma nova ligação C-H
 - um segundo átomo de hidrogênio é transferido, formando a segunda ligação C-H

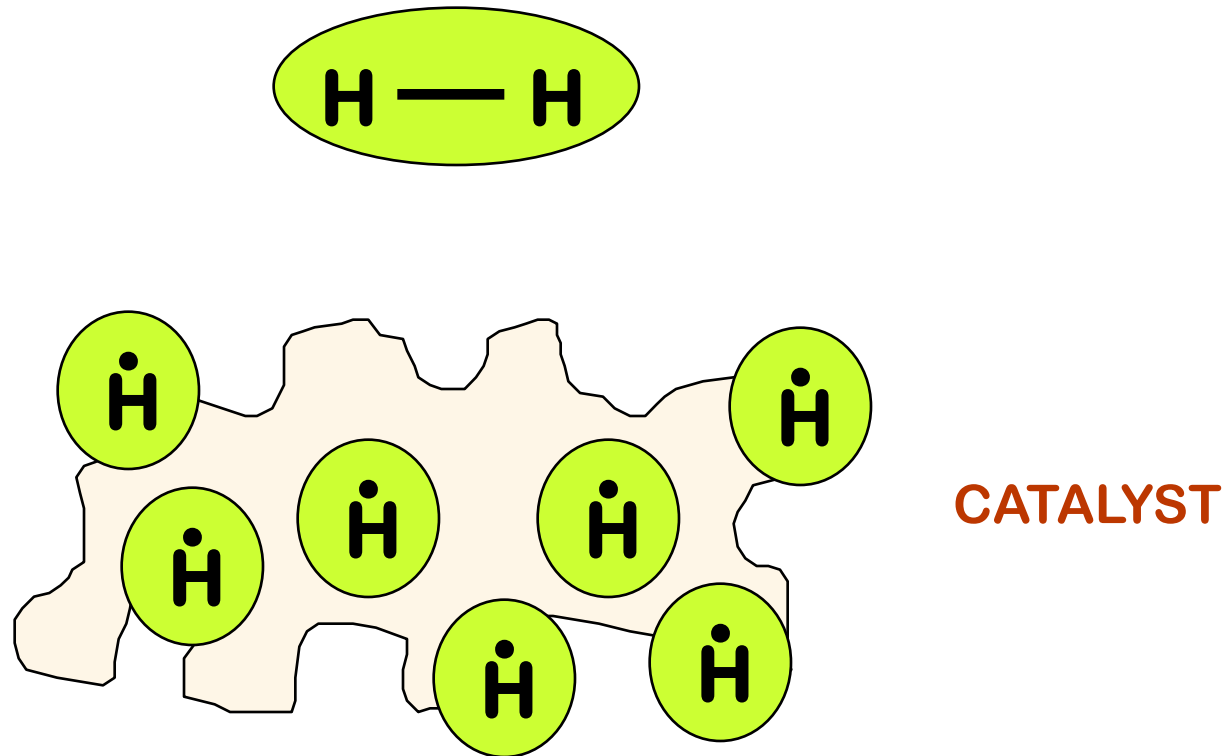
HYDROGEN ADSORBS ON THE SURFACE OF THE CATALYST



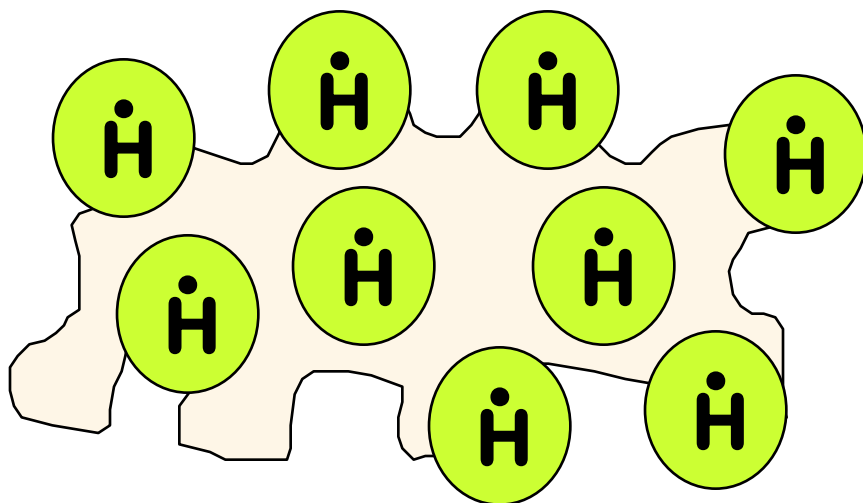
finely-divided
particles
dispersed in
solution



MECHANISM OF HYDROGENATION

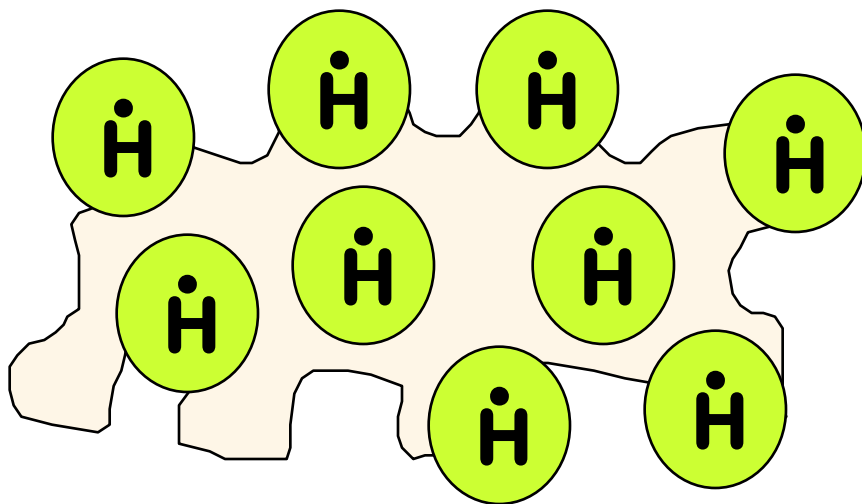
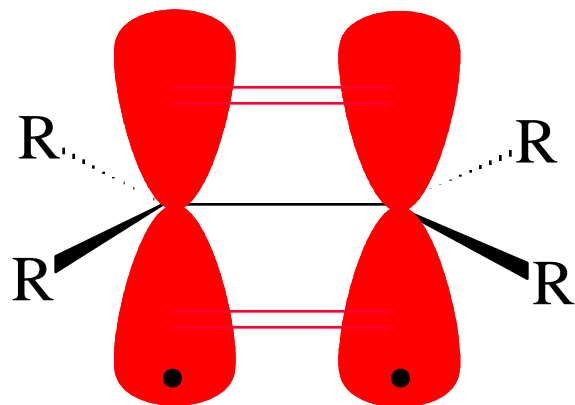


MECHANISM OF HYDROGENATION



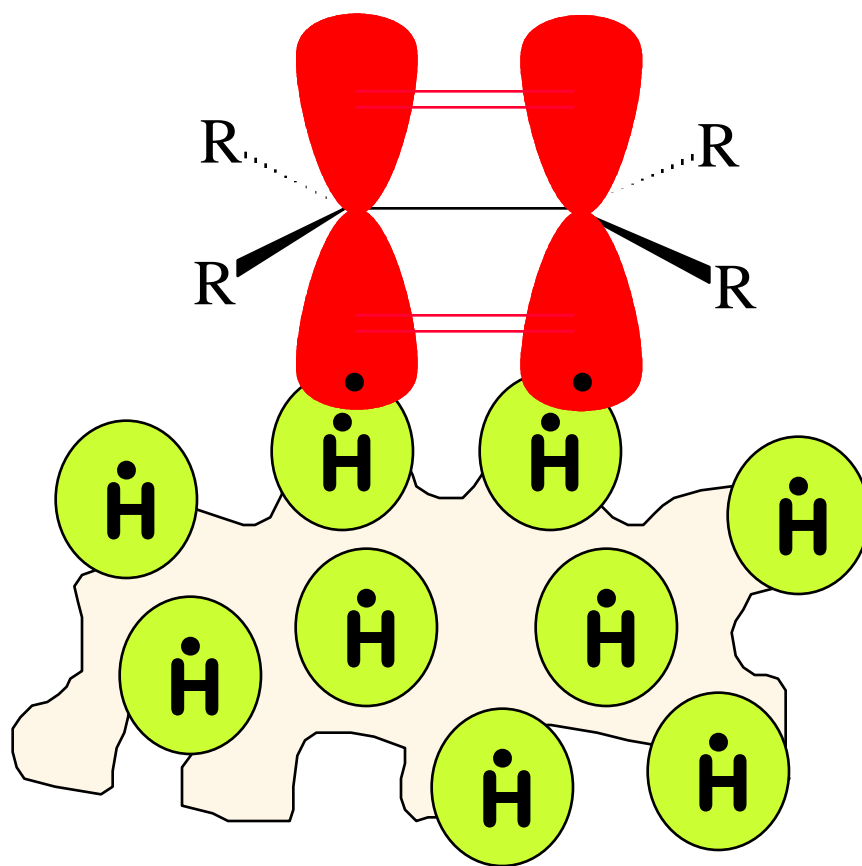
HYDROGEN
ADSORBS

MECHANISM OF HYDROGENATION



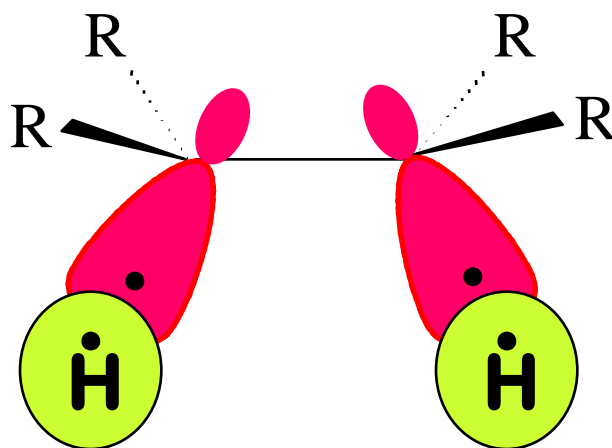
ALKENE
APPROACHES

MECHANISM OF HYDROGENATION

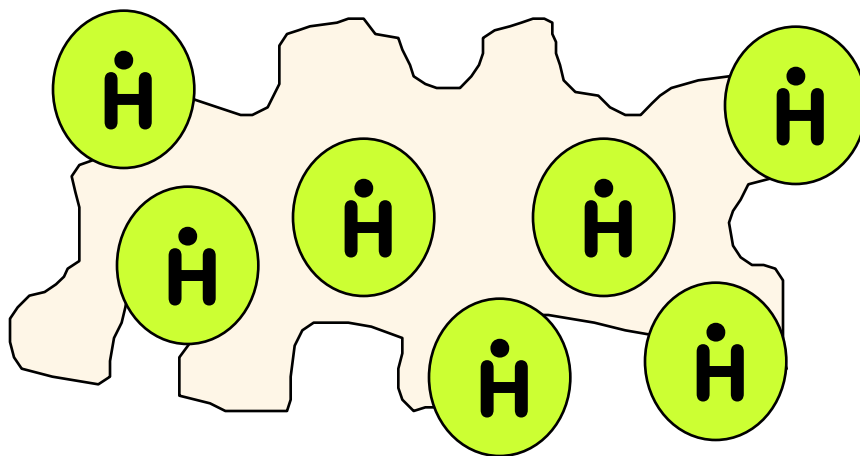


ALKENE PICKS UP
TWO HYDROGENS

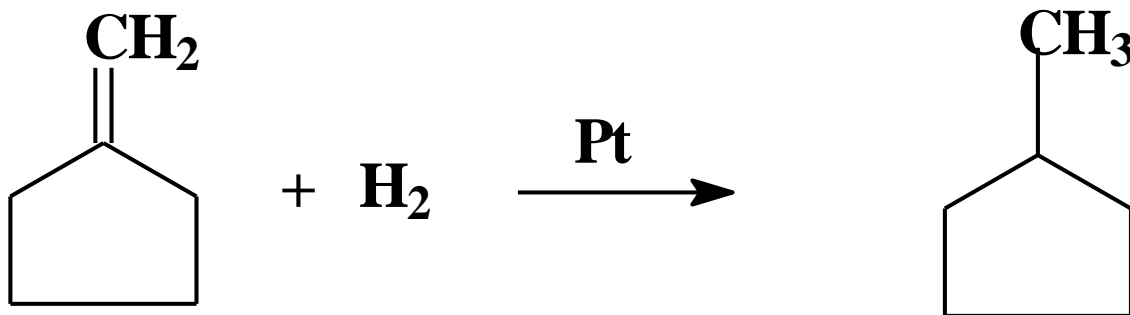
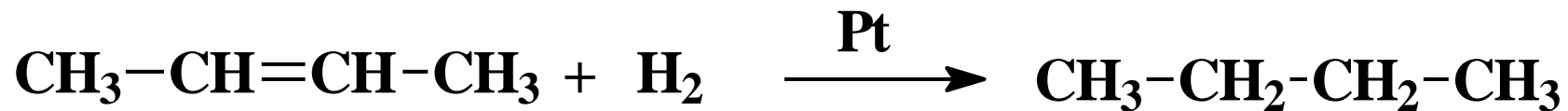
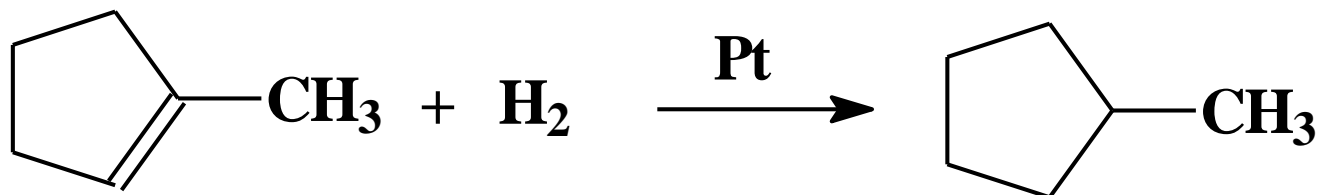
MECHANISM OF HYDROGENATION



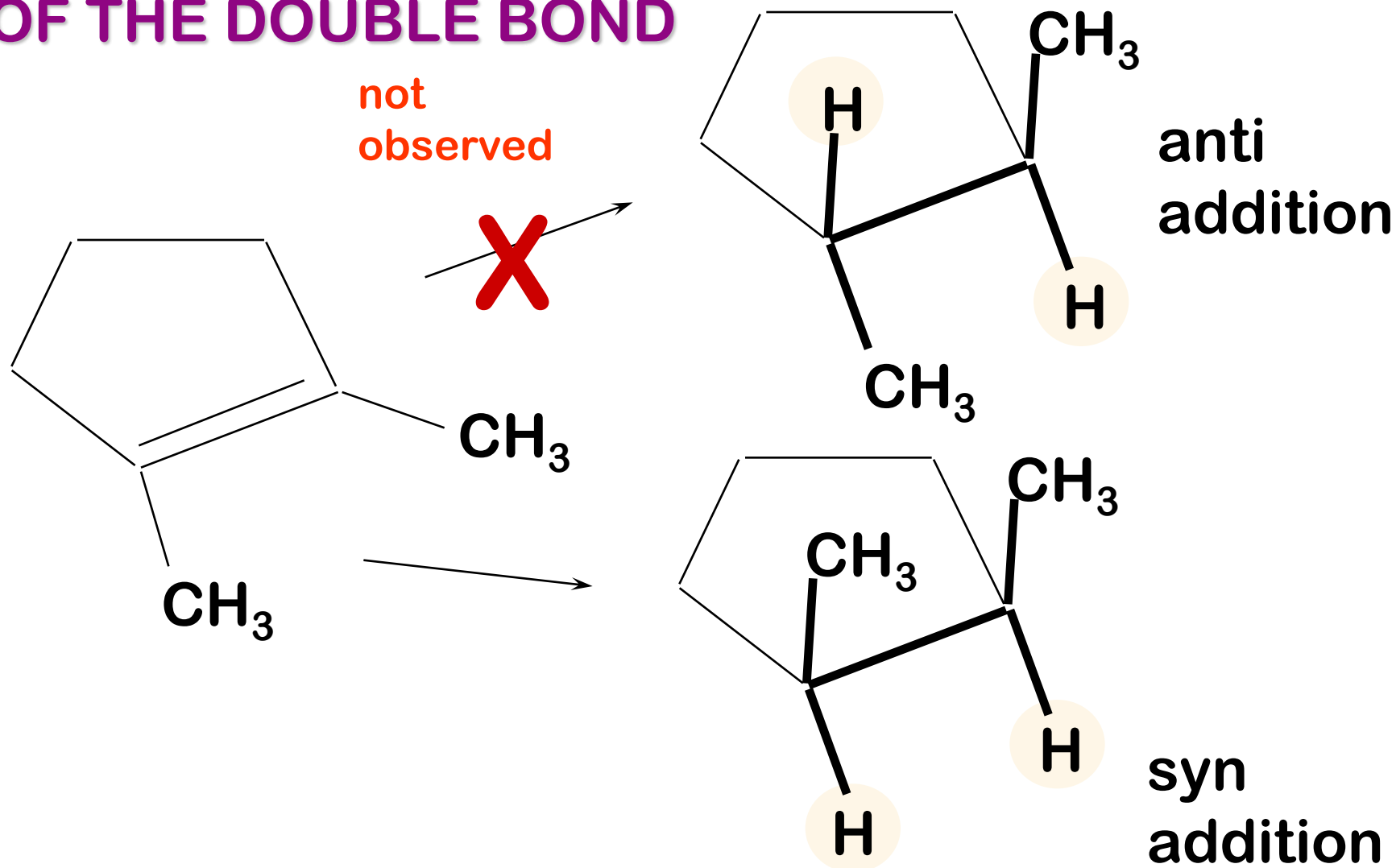
ALKANE IS
FORMED



EXAMPLES

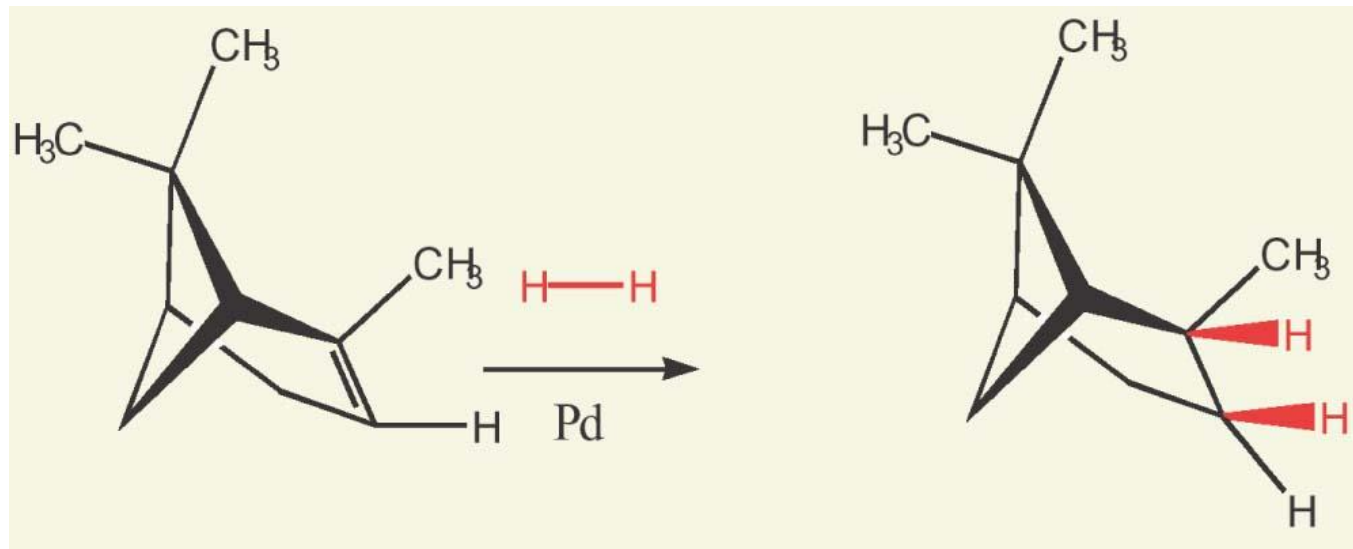


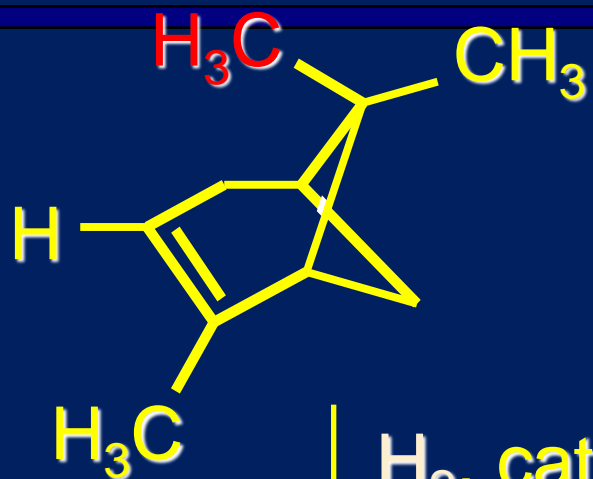
BOTH HYDROGENS ADD TO THE SAME SIDE OF THE DOUBLE BOND



Selectivity in Hydrogen Addition

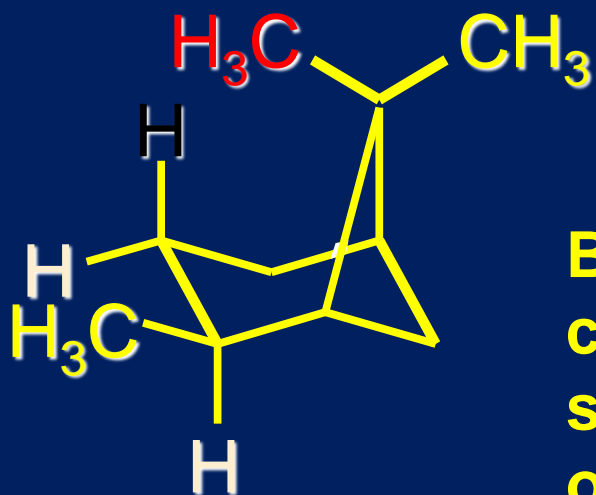
- **Selective for C=C.** No reaction with C=O, C=N
- **Polyunsaturated liquid oils become solids**
- **If one side is blocked, hydrogen adds to other**



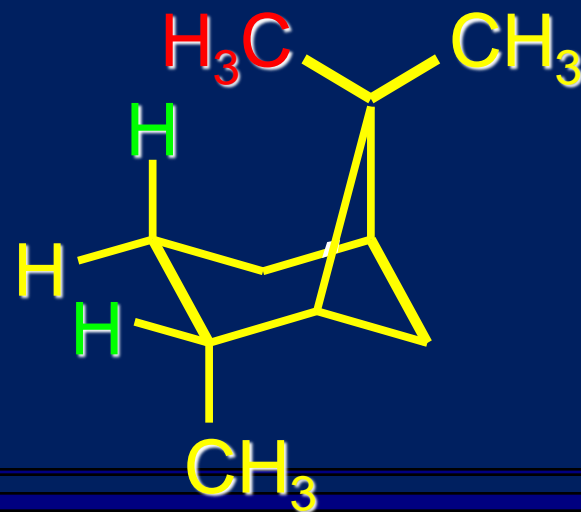


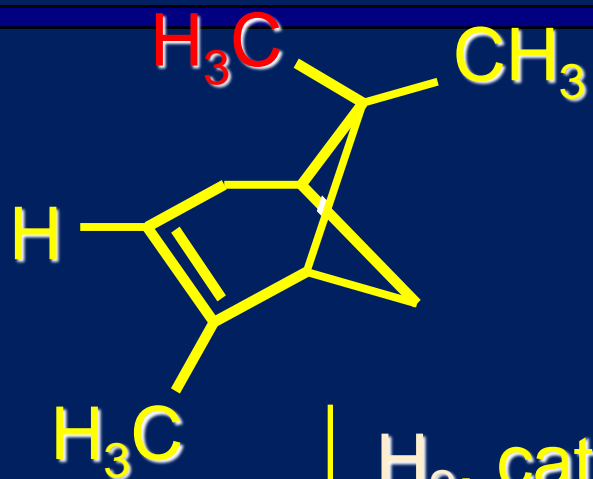
*Example of
stereoselective reaction*

H_2 , cat



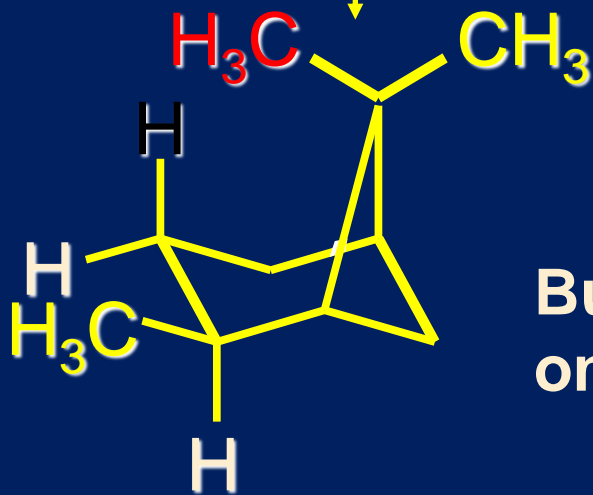
Both products
correspond to
syn addition
of H_2 .



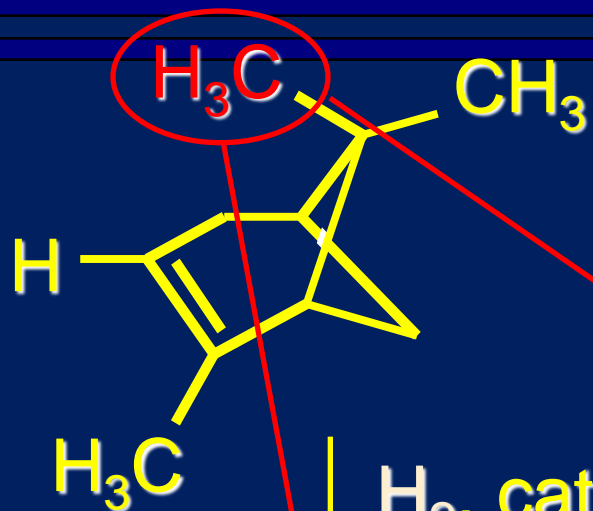


*Example of
stereoselective reaction*

H_2 , cat



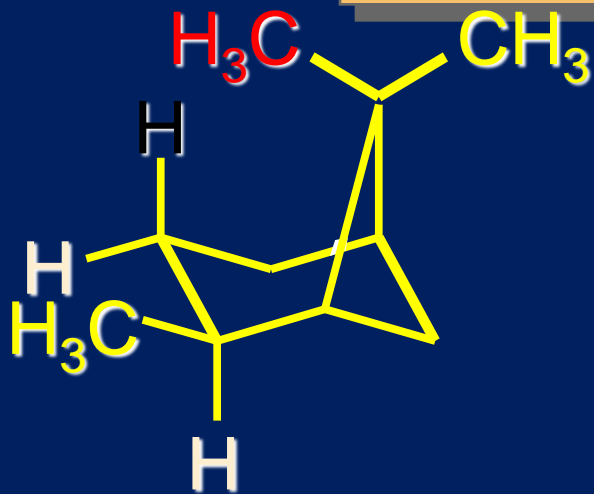
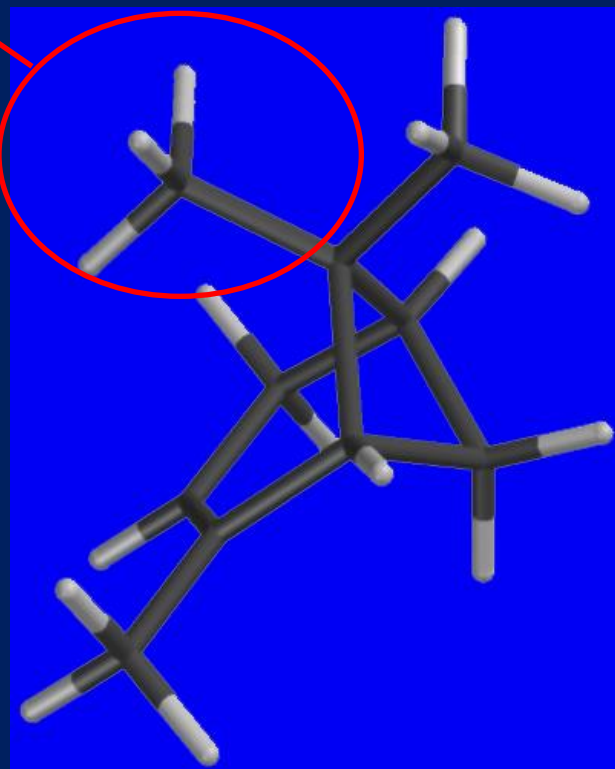
But only this
one is formed.



Example of stereoselective reaction

H_2 , cat

Top face of double bond blocked by this methyl group



ΔH° de Hidrogenação

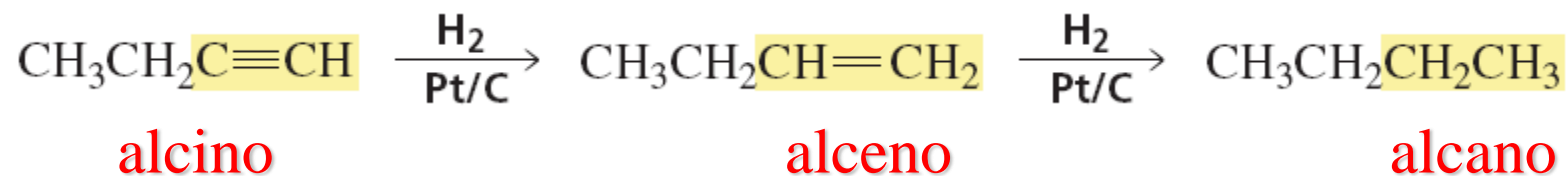
- Na hidrogenação catalítica, há a conversão líquida de uma ligação pi em uma ligação sigma
- A hidrogenação catalítica de um alceno é exotérmica
- Os calores de hidrogenação dependem do grau de substituição da ligação dupla carbono-carbono

ΔH° de Hidrogenação

- Quanto maior o grau de substituição da dupla ligação, menor seu calor de hidrogenação
 - quanto maior o grau de substituição, mais estável é a dupla ligação
- O calor de hidrogenação de um alceno *trans* é menor que o de seu isômero *cis*.
 - um alceno *trans* é mais estável que seu isômero *cis*. A diferença deve-se a interações estéricas desfavoráveis no alceno *cis*

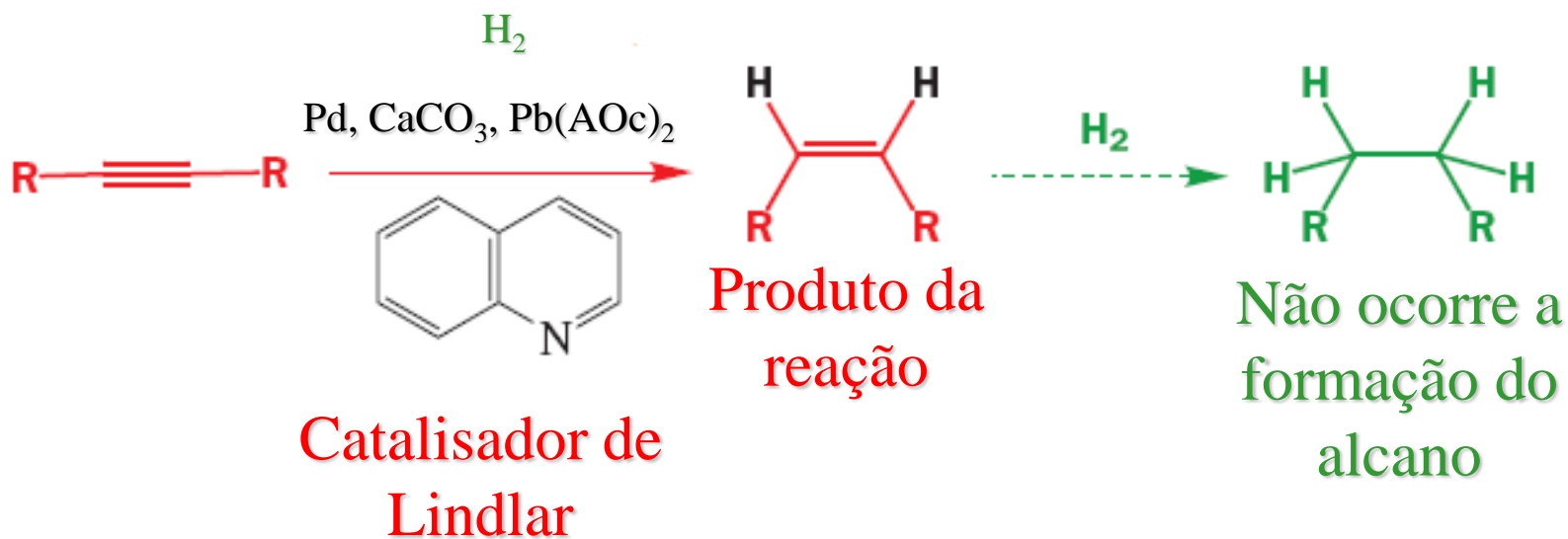
Hidrogenação

Na presença de Pt, Pd e Ni



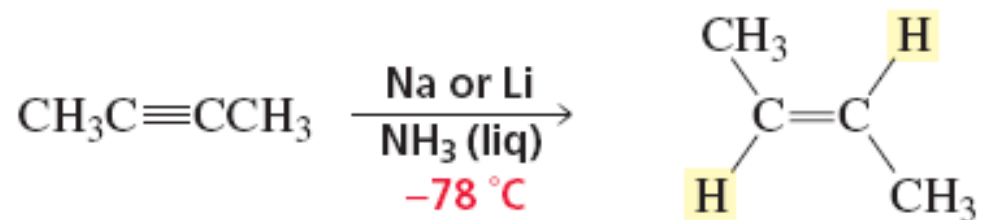
A reação de hidrogenação ocorre na superfície do catalisador heterogêneo.

Adição sin de hidrogênio (síntese de alcenos *cis*)

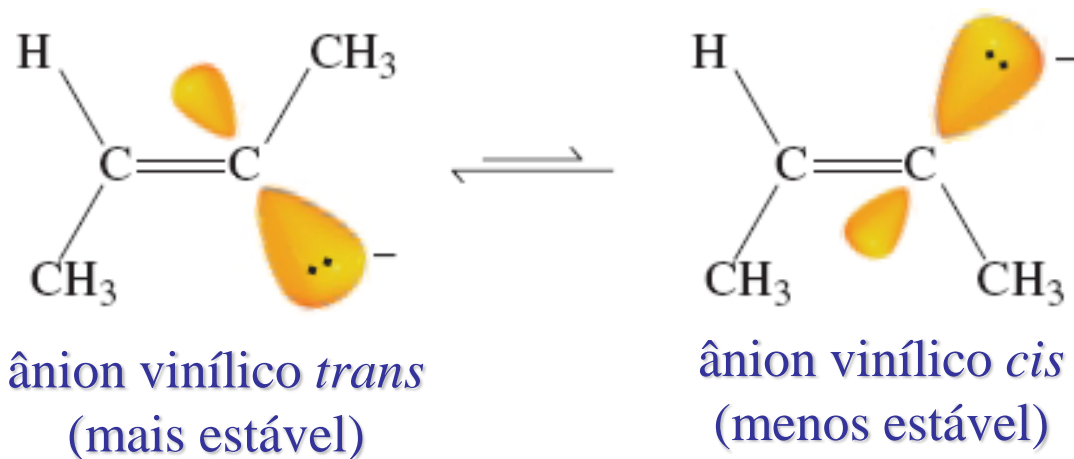
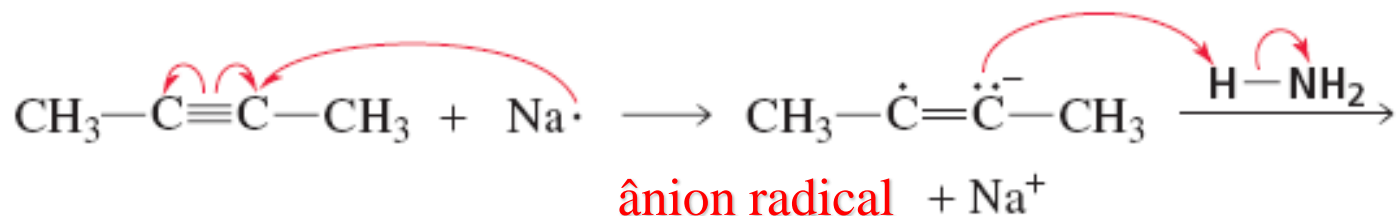


A adição sin de hidrogênio ocorre na superfície do catalisador heterogêneo.

Adição anti de hidrogênio (síntese de alcenos *trans*)



Mecanismo para adição anti de hidrogênio



Types of Additions

	$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} = \begin{array}{c} \diagdown \\ \text{C} \\ \diagup \end{array}$	Type of Addition [Elements Added] ^a	Product
hydration $\xrightarrow{[\text{H}_2\text{O}]}$	$\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$		
hydrogenation $\xrightarrow{[\text{H}_2], \text{ a reduction}}$	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$		
hydroxylation $\xrightarrow{[\text{HOOH}], \text{ an oxidation}}$	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$		
oxidative cleavage $\xrightarrow{[\text{O}_2], \text{ an oxidation}}$	$\begin{array}{c} \diagup \quad \quad \quad \diagdown \\ \text{C}=\text{O} \quad \quad \quad \text{O}=\text{C} \\ \diagdown \quad \quad \quad \diagup \end{array}$		
epoxidation $\xrightarrow{[\text{O}], \text{ an oxidation}}$	$\begin{array}{c} \quad \quad \text{O} \\ \quad \quad / \quad \backslash \\ -\text{C} \quad \quad \text{C}- \\ \quad \quad \end{array}$		
		halogenation $\xrightarrow{[\text{X}_2], \text{ an oxidation}}$	$\begin{array}{c} \text{X} \quad \text{X} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$
		halohydrin formation $\xrightarrow{[\text{HOX}], \text{ an oxidation}}$	$\begin{array}{c} \text{X} \quad \text{OH} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$
		HX addition $\xrightarrow{[\text{HX}]}$	$\begin{array}{c} \text{H} \quad \text{X} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$
		cyclopropanation $\xrightarrow{[\text{CH}_2]}$	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \quad \quad \backslash \quad / \\ \quad \quad \text{C} \\ \quad \quad / \quad \backslash \\ -\text{C} \quad \quad \text{C}- \\ \quad \quad \end{array}$

^aThese are not the reagents used but simply the groups that appear in the product.