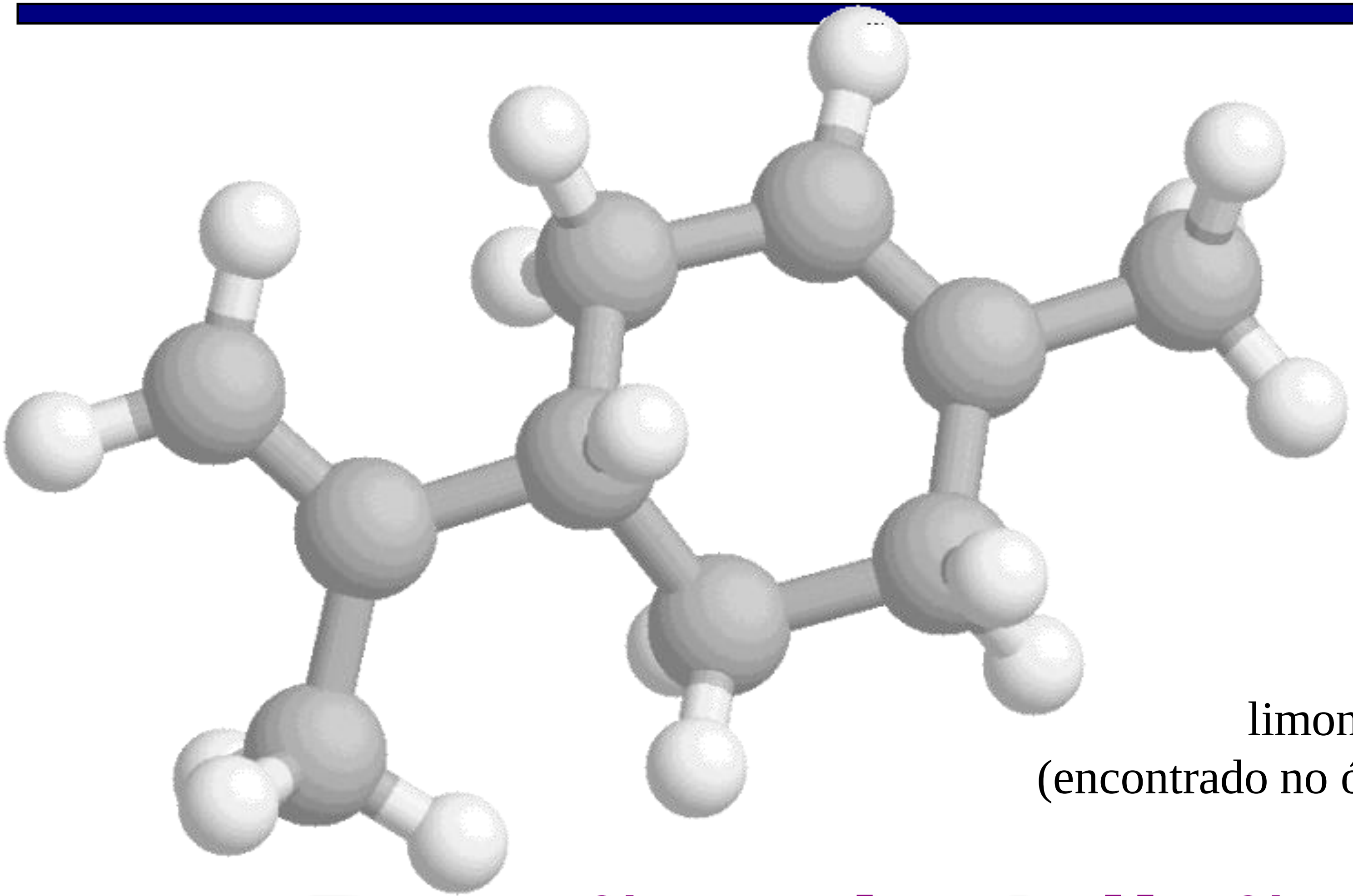


limoneno
(encontrado no óleo da laranja)

Reações de Adição Eletrofílica

Tipos de Reações Orgânicas

- Geralmente, observar o que acontece na transformação e tentar entender como ela ocorre.

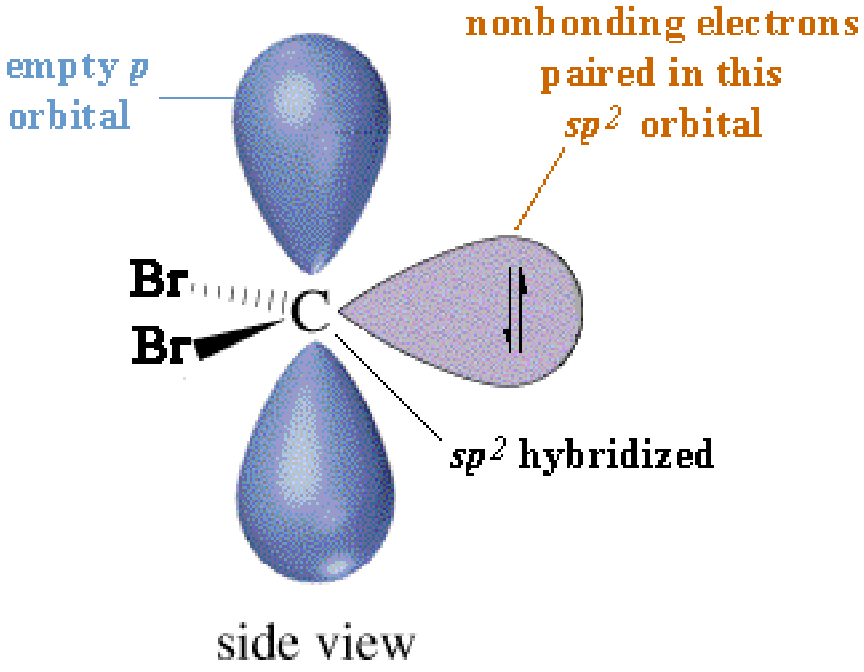
- Atributos comuns descrevem as mudanças
  - **Reações de :**
  - **Adição** – duas moléculas se combinam
  - **Eliminação** – uma molécula quebra em duas
  - **Substituição** – partes de duas moléculas trocam
  - **Rearranjo** – a molécula sofre mudanças no modo como seus átomos são conectados.

Intermediários Reativos de Carbono mais Comuns

- Carbocátions
- Radicais Livres
- Carbânions
- Carbenos

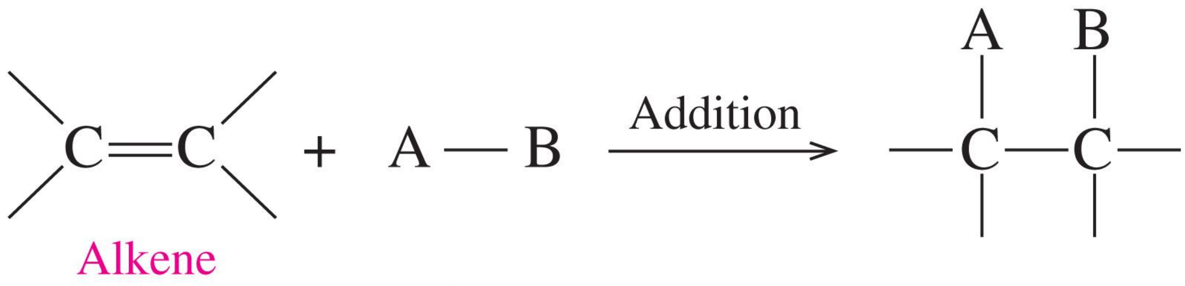
Carbenos

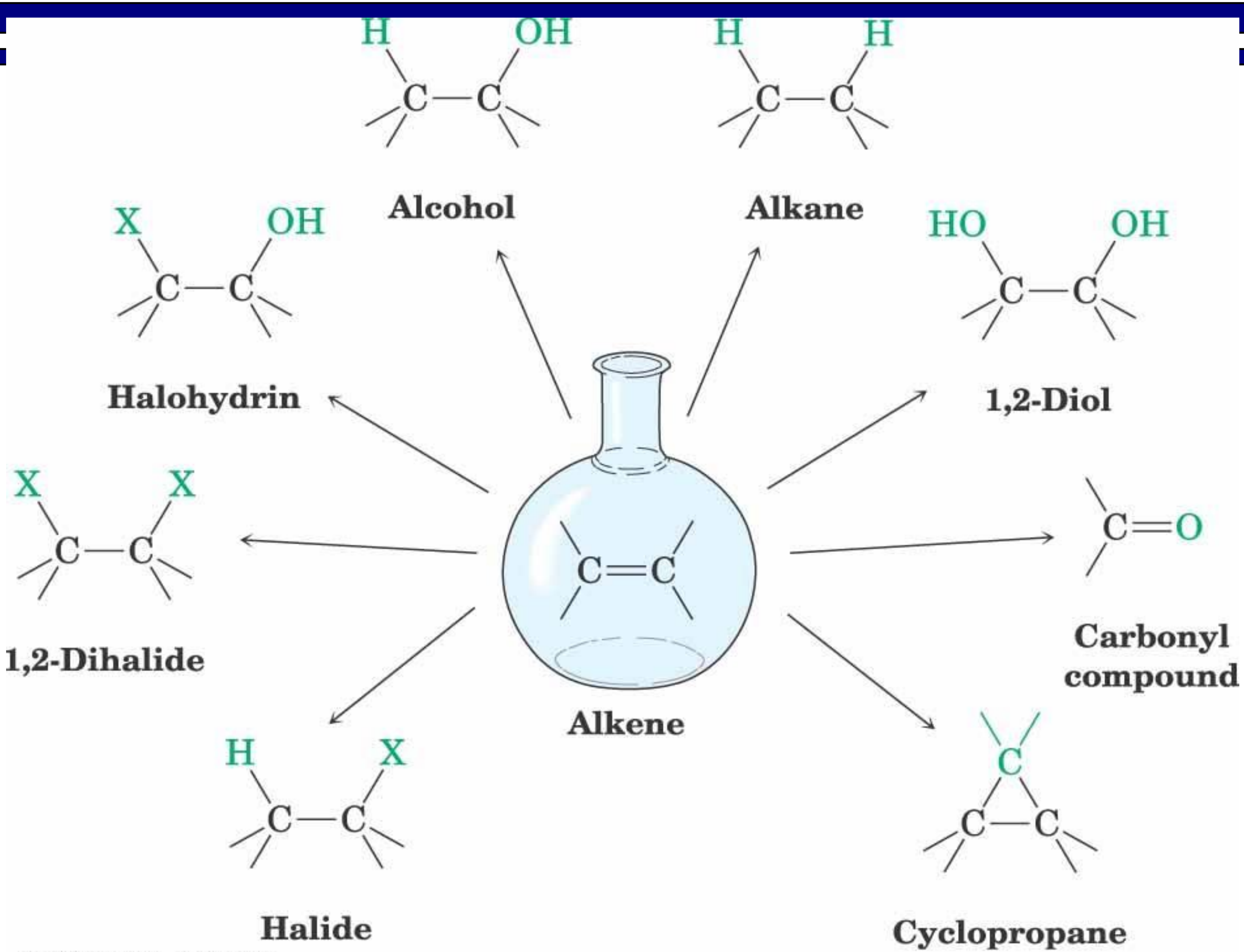
- O Carbono é neutro.
- Orbital *p* vazio, confere caráter eletrofílico.
- Um par de elétrons isolados, confere caráter nucleofílico.



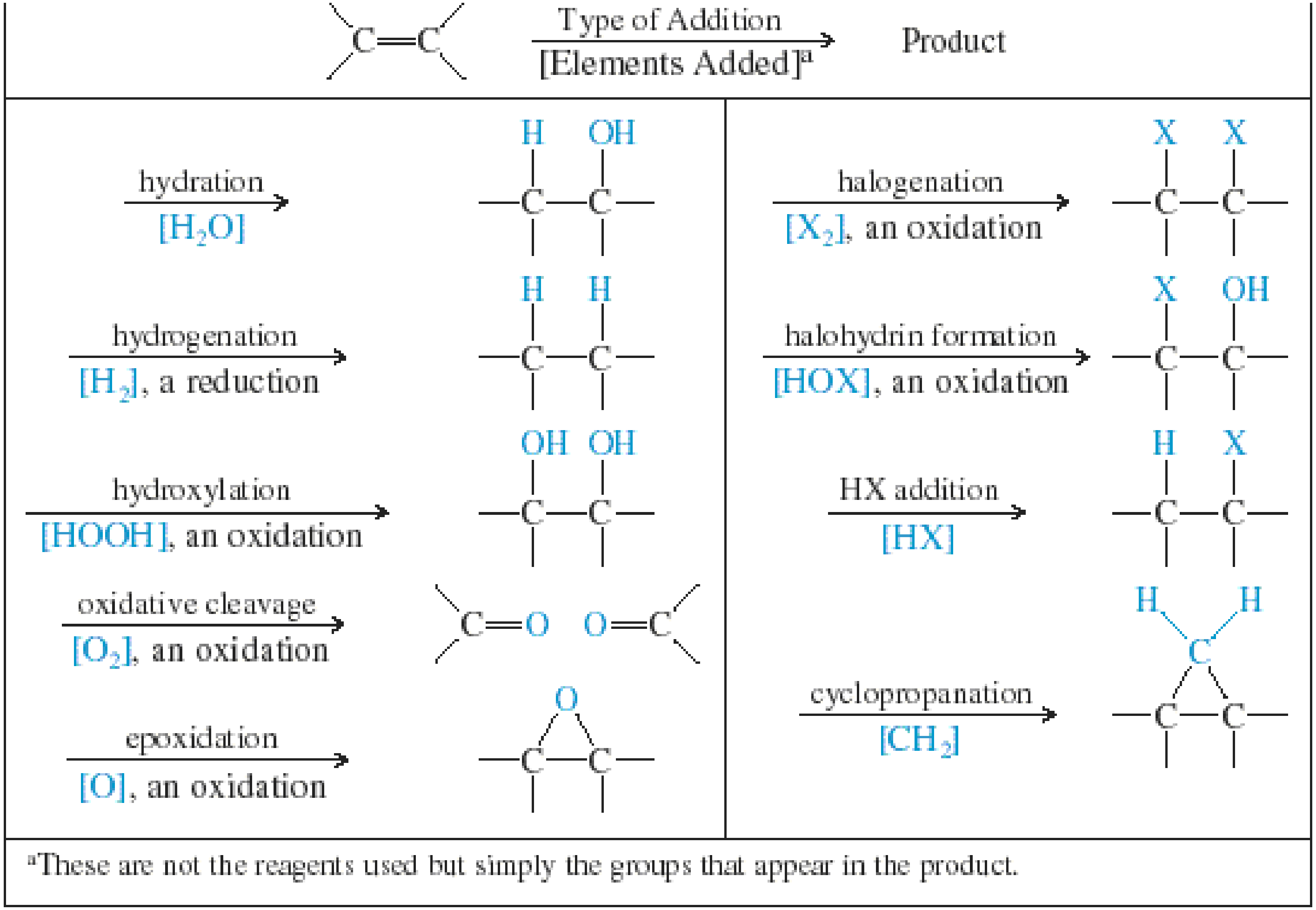
Reações de adição

- Nas reações de adição:
  - os reagentes se adicionam aos átomos de carbono das ligações duplas ou triplas
  - uma ligação dupla ou tripla é facilmente quebrada, o que os torna muito reativos




Alcohol
Alkane
Halohydrin
1,2-Diol
1,2-Dihalide
Carbonyl compound
Alkene
Halide
Cyclopropane

Types of Additions

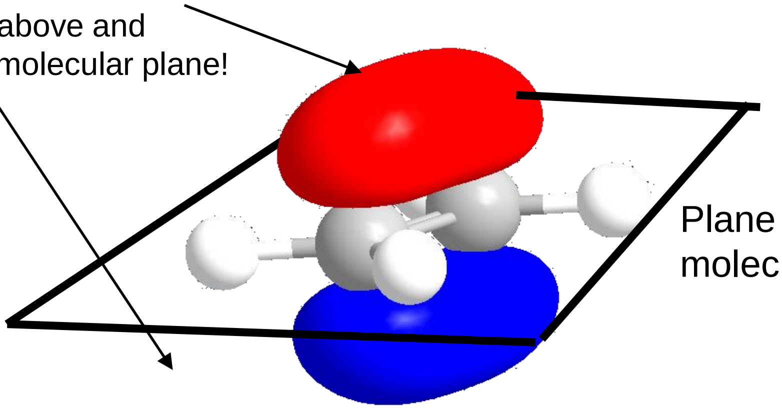


Type of Addition	[Elements Added][a]	Product
hydration	$[H_2O]$	H OH
hydrogenation	$[H_2]$, a reduction	H H
hydroxylation	[HOOH], an oxidation	OH OH
oxidative cleavage	$[O_2]$, an oxidation	C=O O=C
epoxidation	[O], an oxidation	O
halogenation	$[X_2]$, an oxidation	X X
halohydrin formation	[HOX], an oxidation	X OH
HX addition	[HX]	H X
cyclopropanation	$[CH_2]$	H H C

[a] These are not the reagents used but simply the groups that appear in the product.

Reactivity of C=C

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

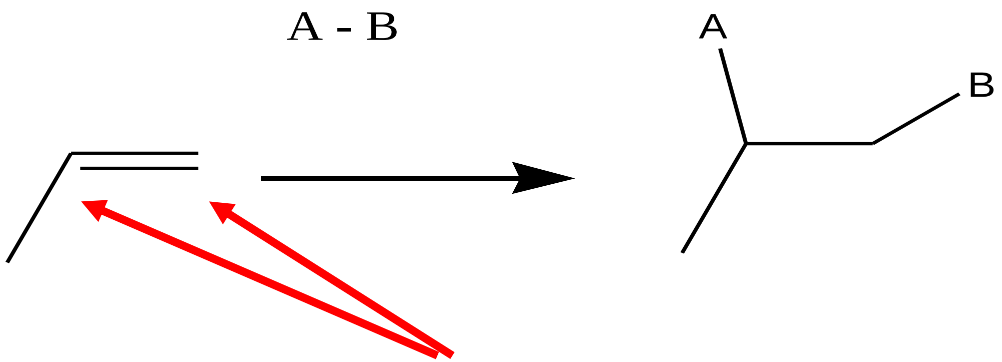


Reactivity above and below the molecular plane!

Plane of molecule

- **Electrophiles are attracted to the π electrons.**
- **Carbocation intermediate forms.**
- **Nucleophile adds to the carbocation.**
- **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 get the A and which gets the B.

Stereochemistry: geometry of the addition.

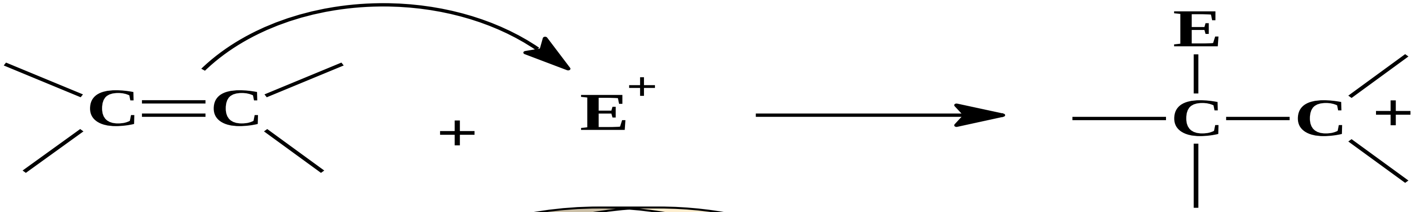
Syn addition: Both A and B come in from the same side of the alkene. Both from the top or both from the bottom.

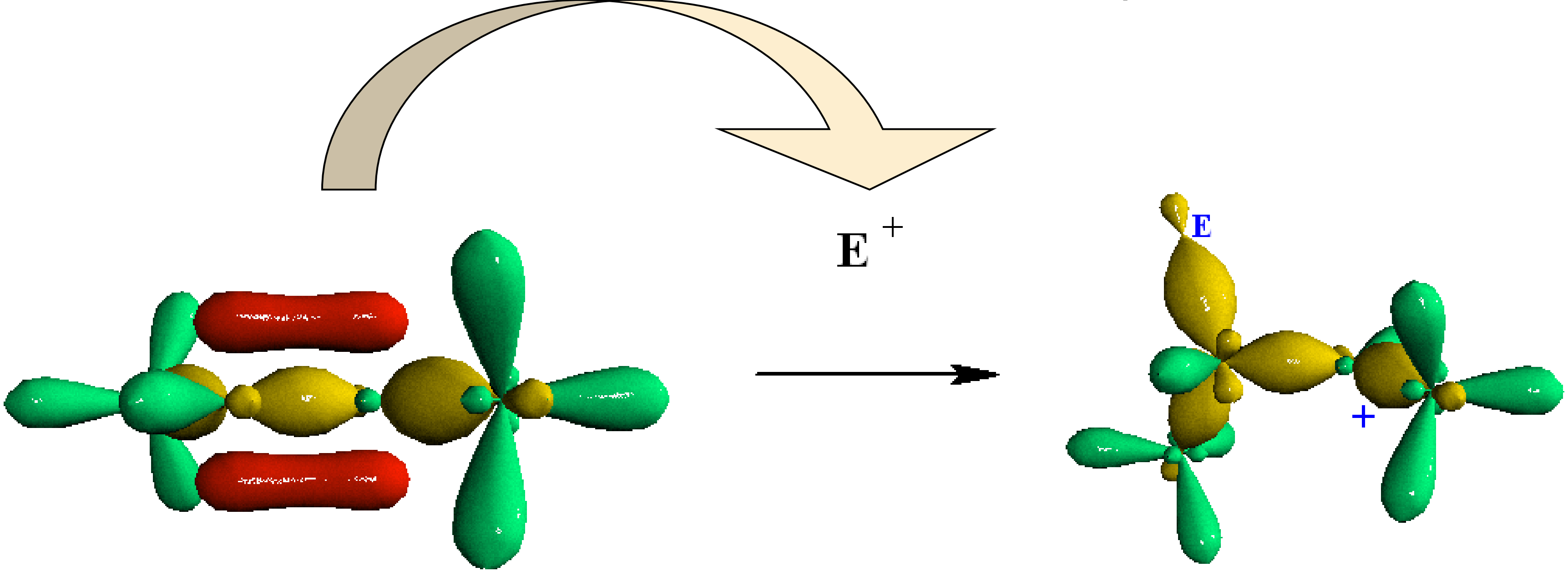
Anti Addition: A and B come in from opposite sides (anti addition).

No preference.

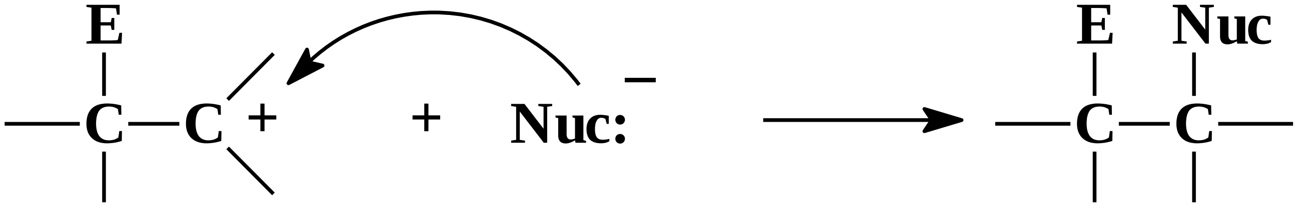
Electrophilic Addition

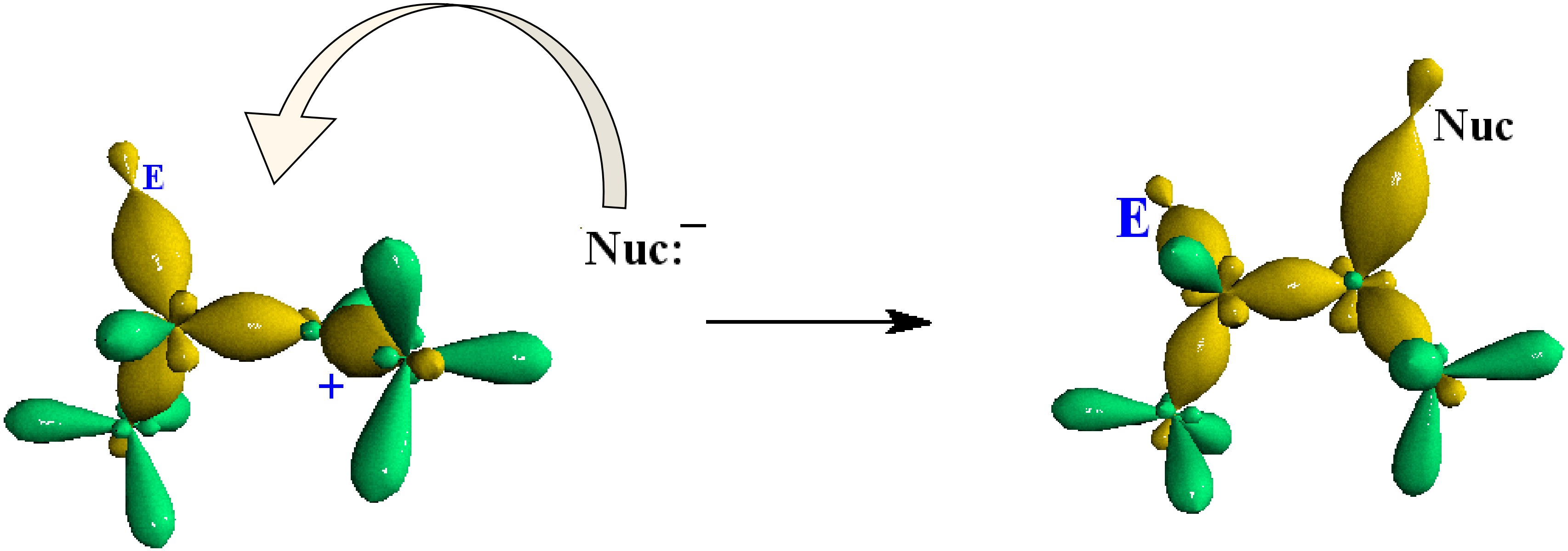
Step 1: π electrons attack the electrophile.





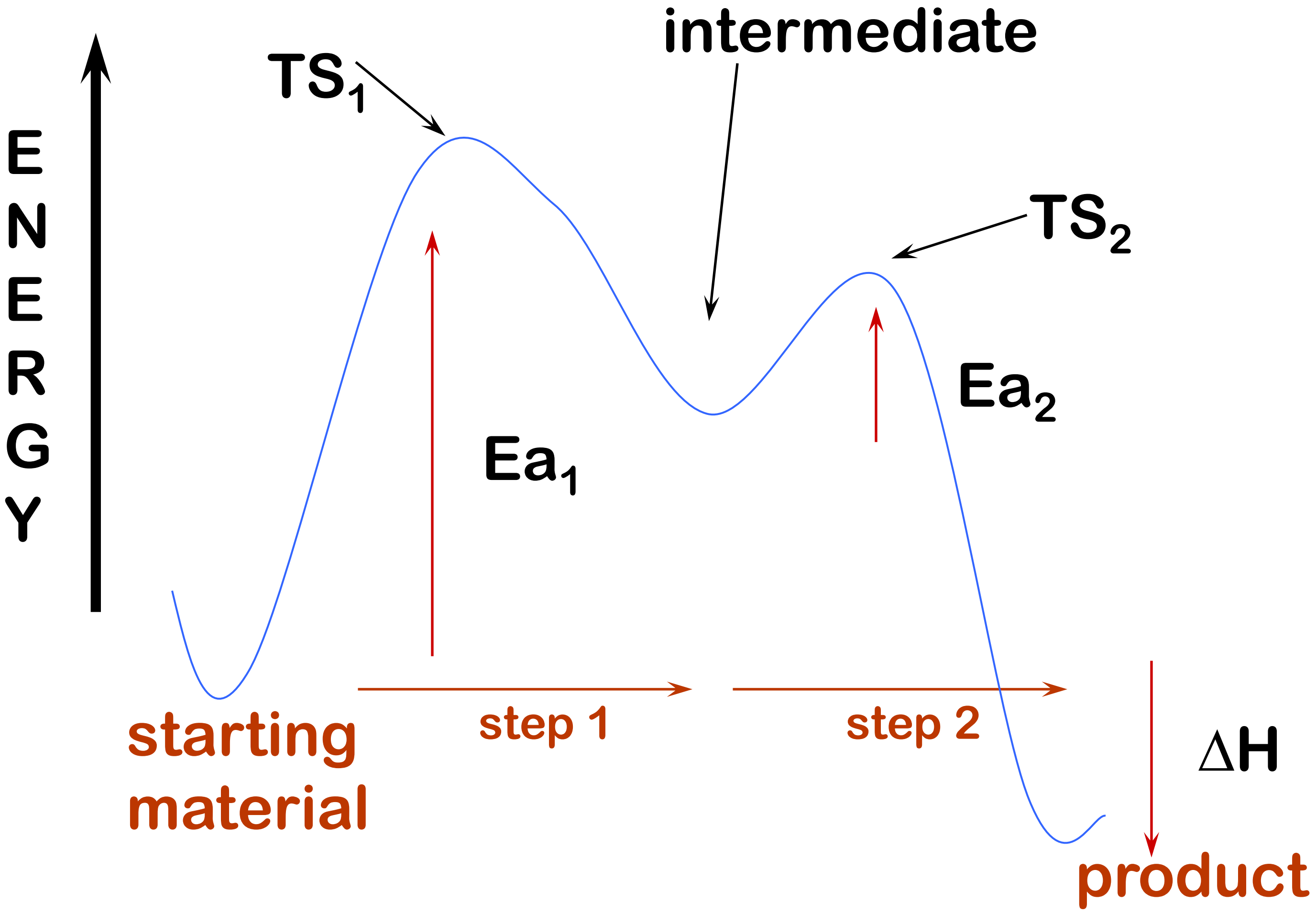
Step 2: Nucleophile attacks the carbocation.





ENERGY PROFILE

two step reaction



intermediate

TS_1

TS_2

ENERGY

Ea_1

Ea_2

starting material

step 1

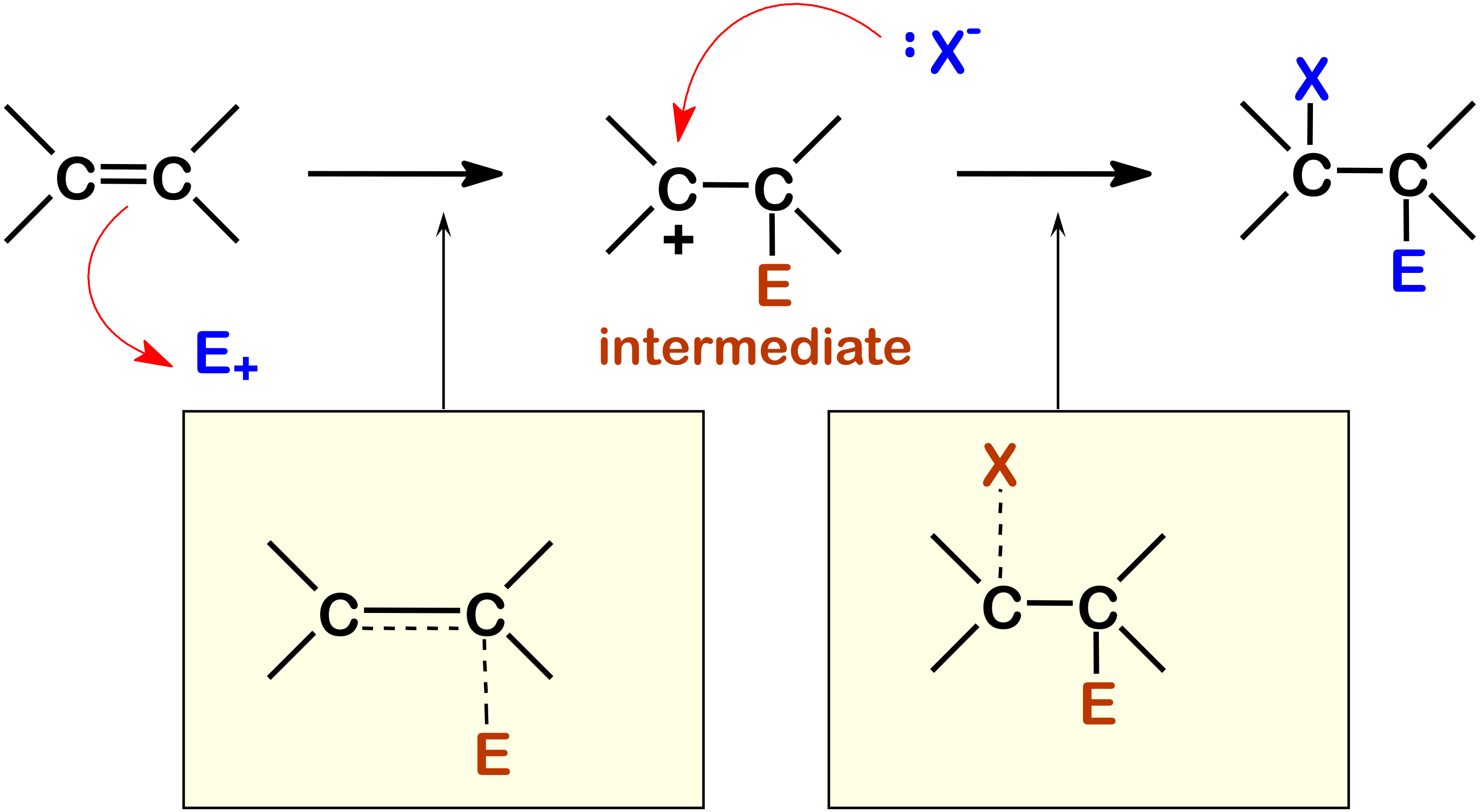
step 2

ΔH

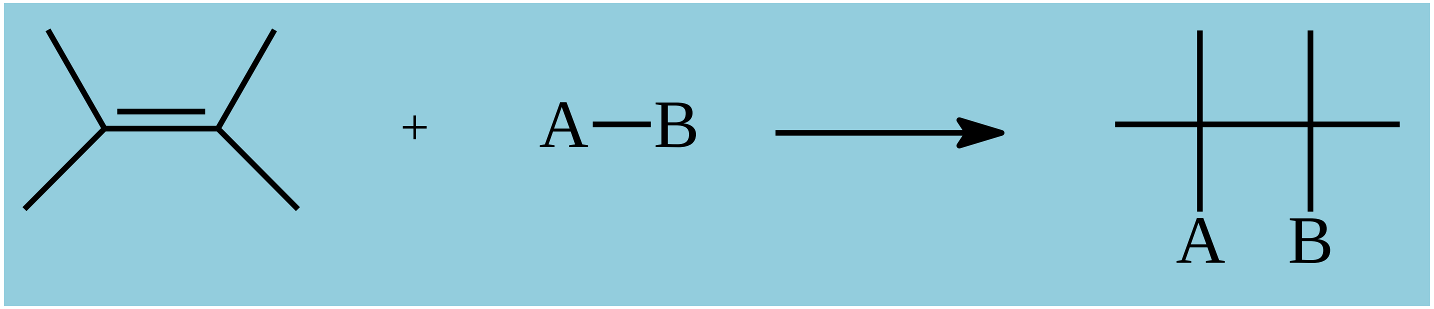
product

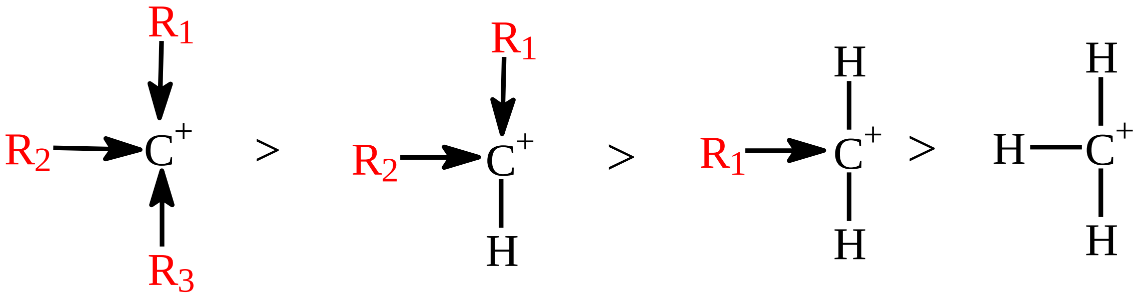
ACTIVATED COMPLEXES

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)

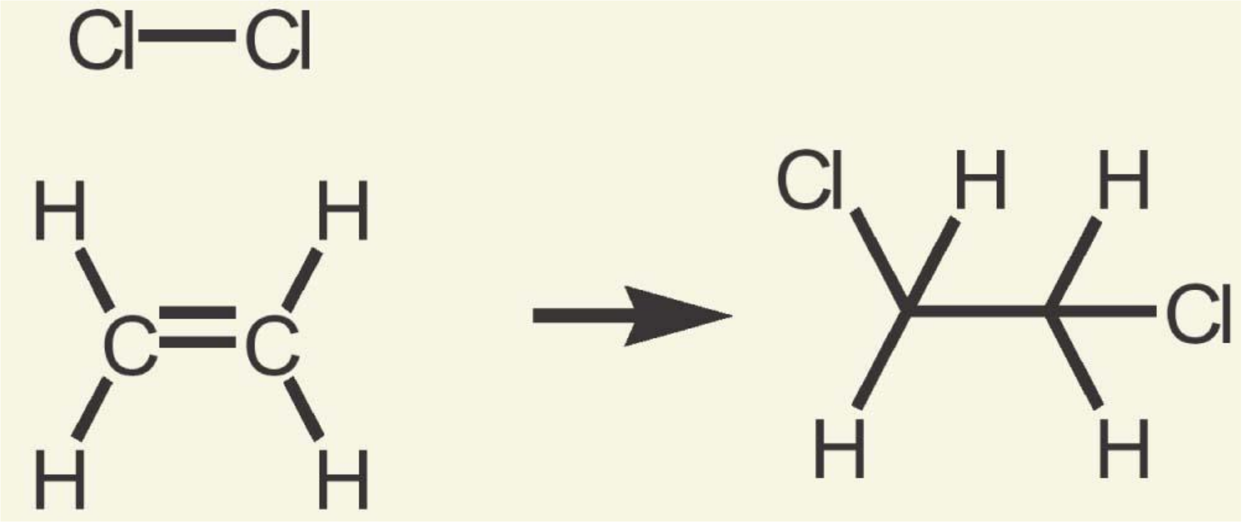




Terciário **Secundário** **Primário**

Addition of Halogens to Alkenes

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



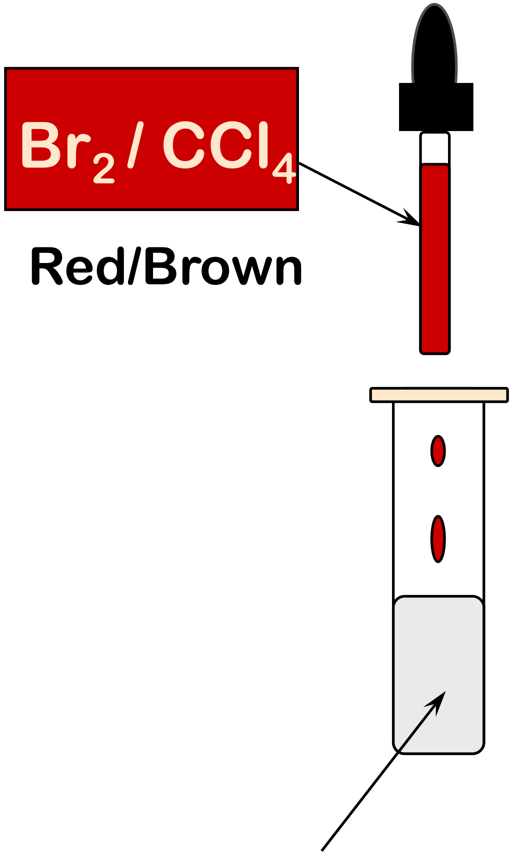
Adição de Cl_2 e Br_2

- **Utilizam-se os reagentes puros ou em um solvente inerte como CCl_4 ou CH_2Cl_2**

- **A adição é estereosseletiva**

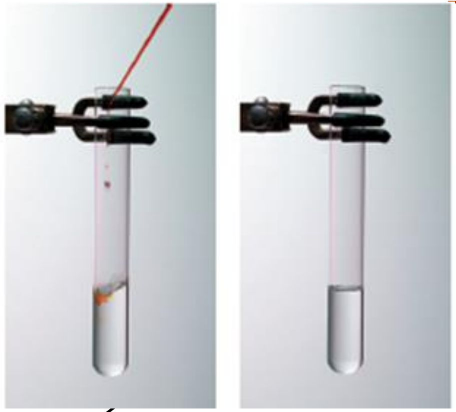
- **Reação estereosseletiva: reação na qual um estereoisômero é formado ou destruído preferencialmente em relação aos outros que poderiam ser formados ou destruídos.**

BROMINE TEST FOR A C=C DOUBLE BOND



compound with a suspected double bond

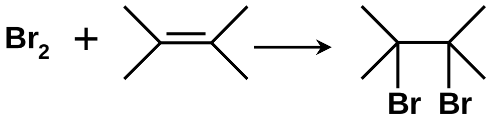
(+)



POSITIVE TEST

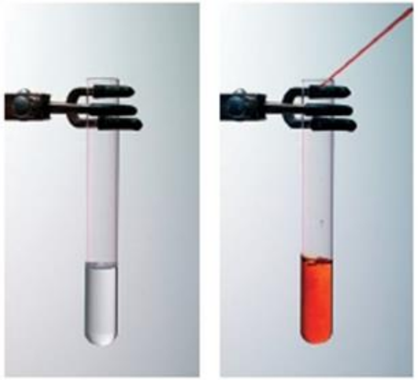
Br_2 reacts

implies the presence of a double bond



colorless

(-)

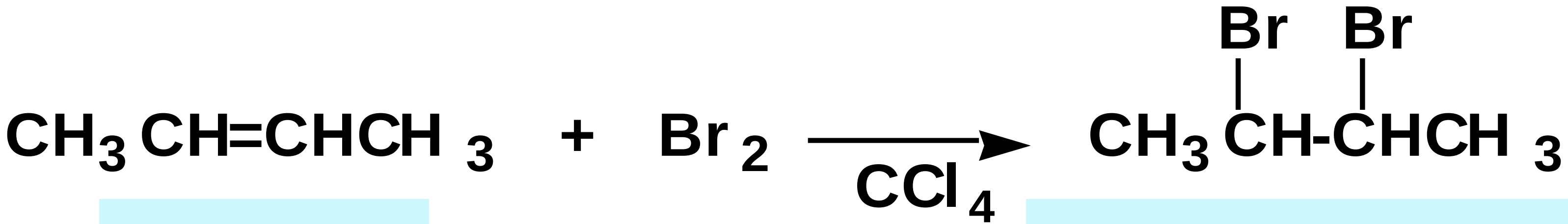


NEGATIVE TEST

Br_2 is not decolorized (does not react)

implies that a double bond is not present

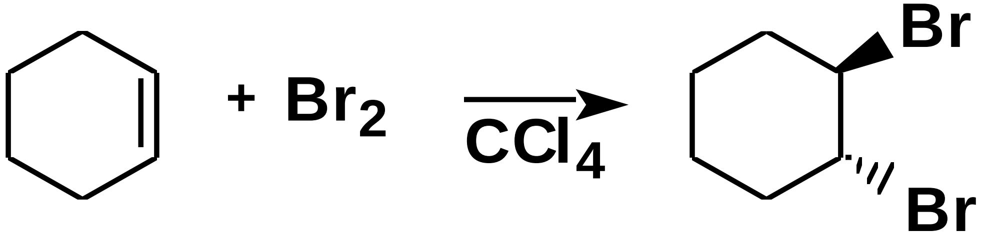
Adição de Cl_2 e Br_2



$$CH_3CH{=}CHCH_3 + Br_2 \xrightarrow[CCl_4]{} CH_3\overset{Br}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}HCH_3$$

2-Buteno

2,3-Dibromobutano



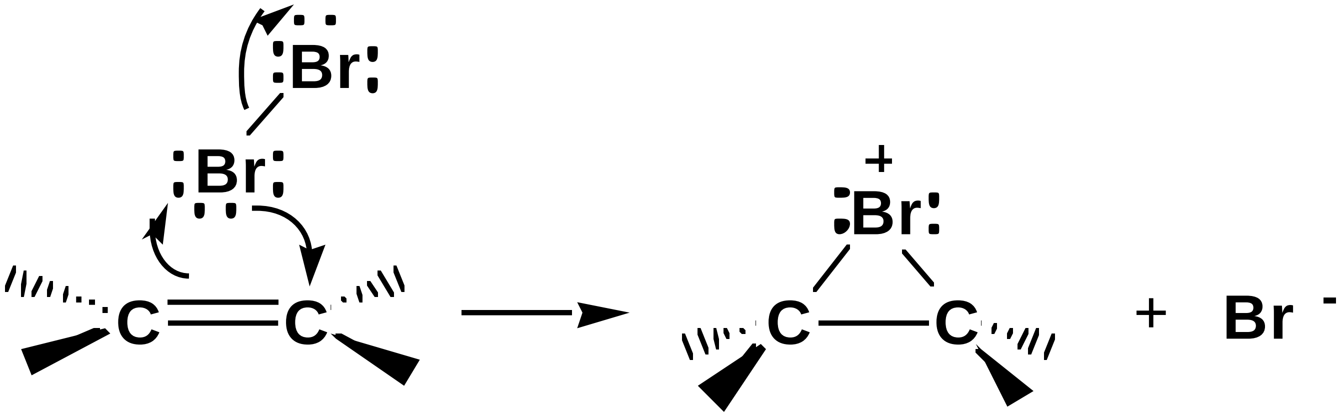
Ciclo-hexeno

trans-1,2-Dibromo-ciclo-hexano

Adição de Cl_2 e Br_2

- A adição envolve um mecanismo de duas etapas

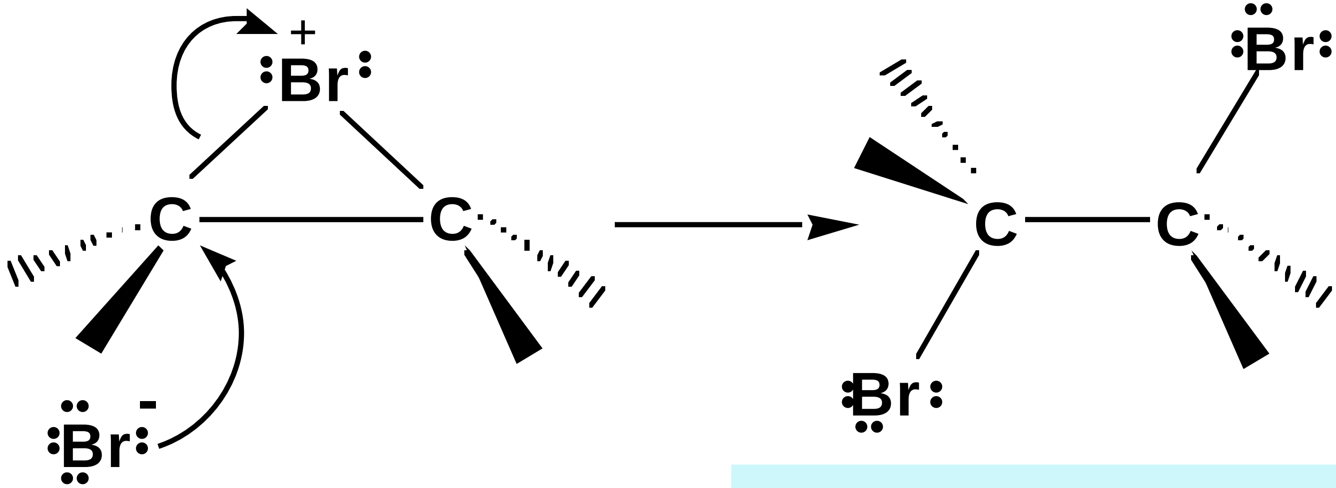
  Etapa 1: formação de um íon bromônio cíclico, intermediário



Íon bromônio cíclico

Adição de Cl_2 e Br_2

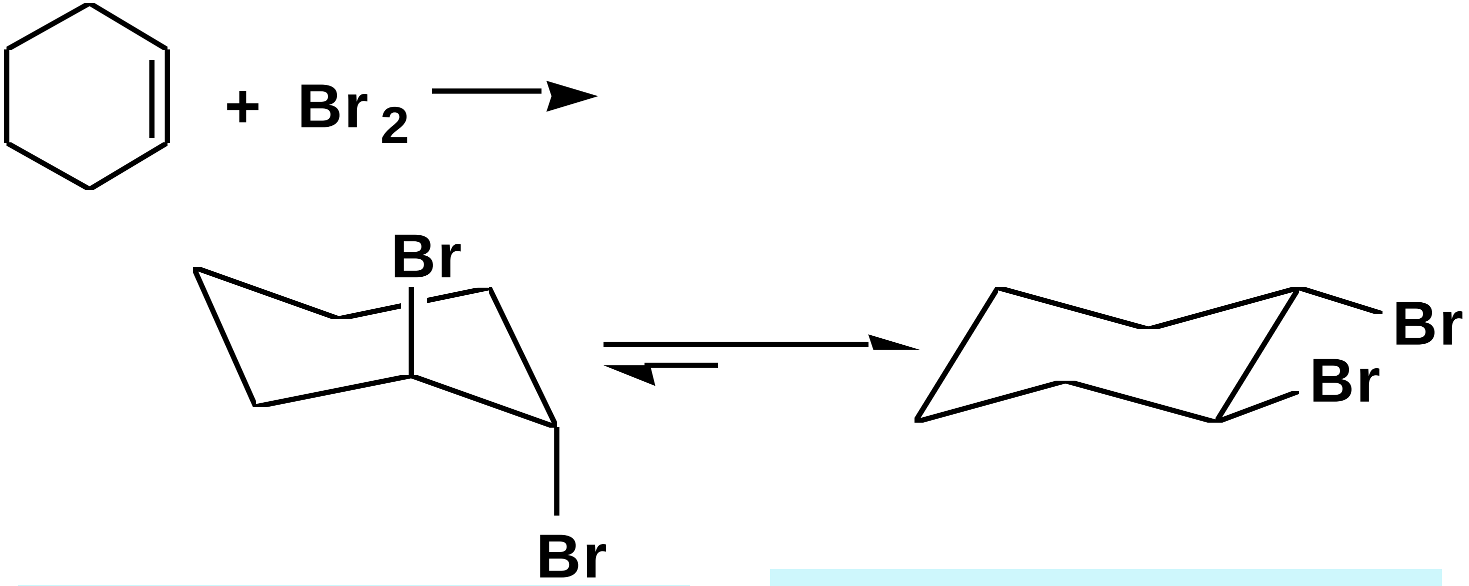
Etapa 2: Ataque do íon haleto pelo lado oposto do anel de três membros



Adição anti

Adição de Cl_2 e Br_2

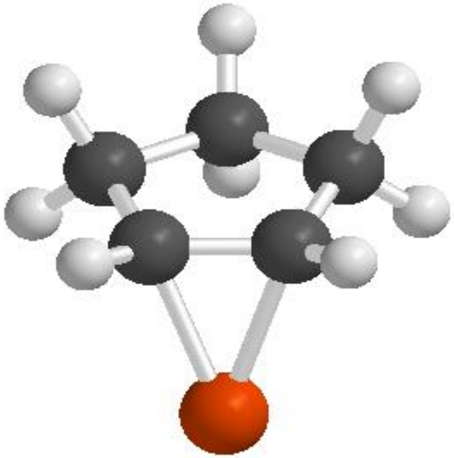
- **Para o ciclo-hexeno, a adição anti coplanar corresponde a uma adição *trans*-diaxial**

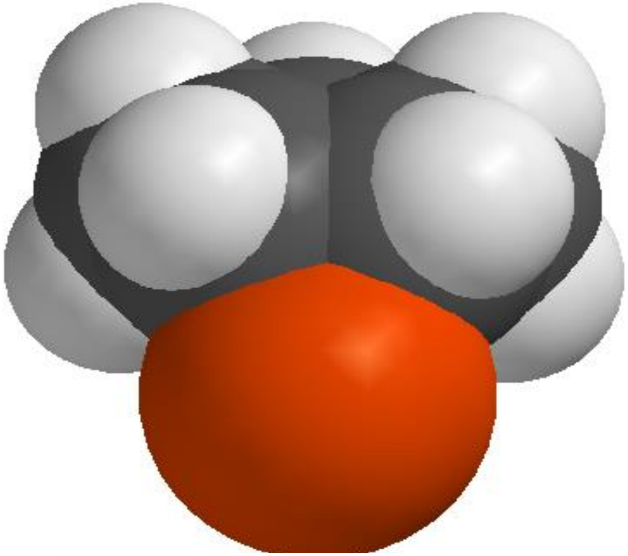


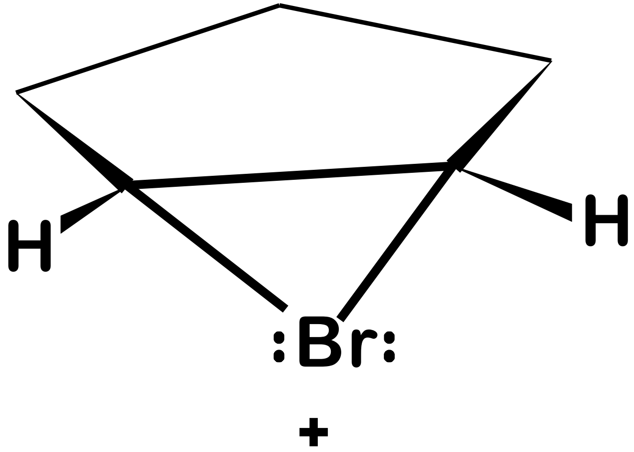
trans-Diaxial
(menos estável)

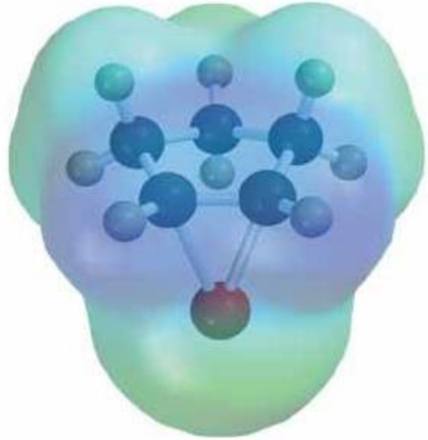
trans-Diequatorial
(mais estável)

CYCLIC BROMONIUM ION



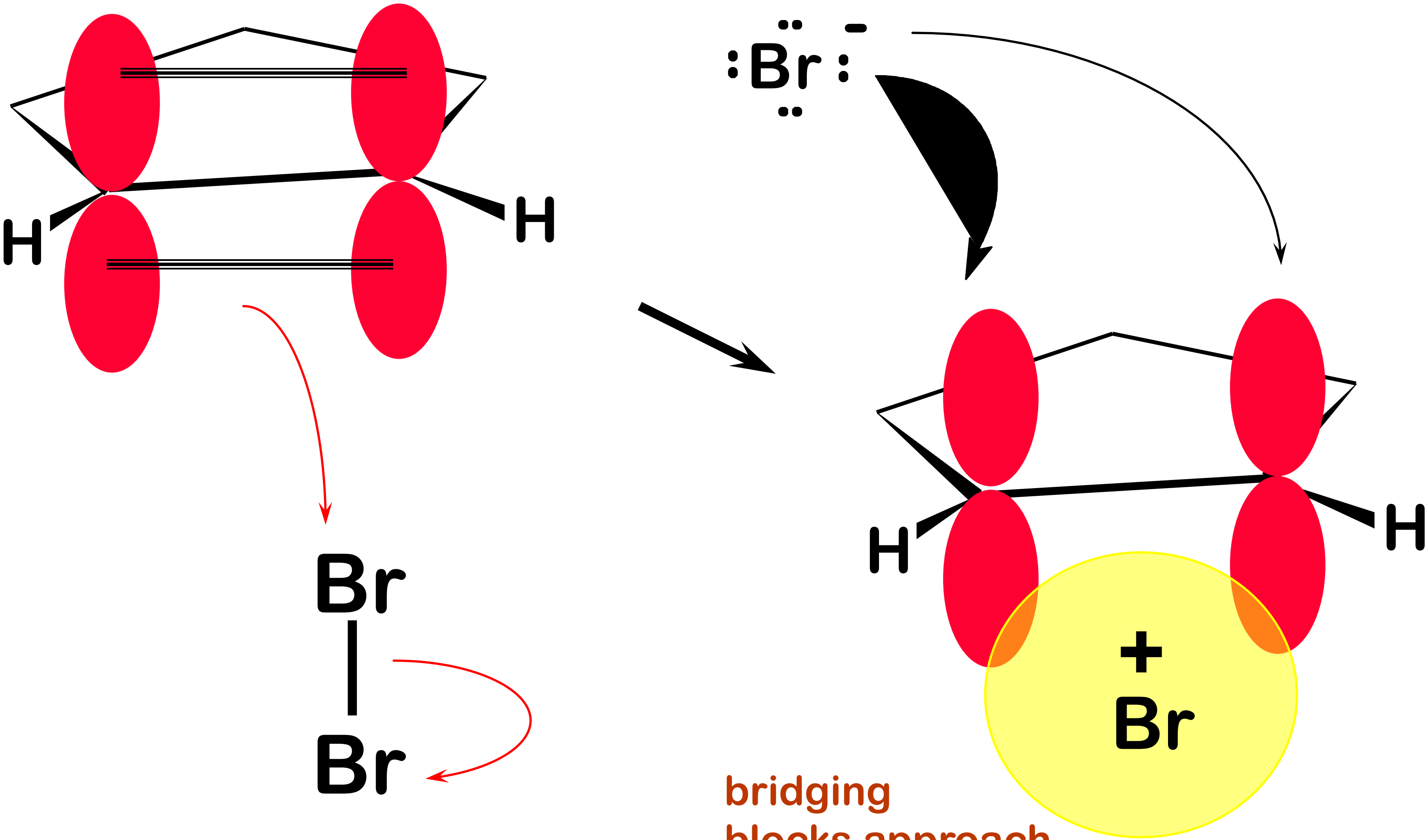






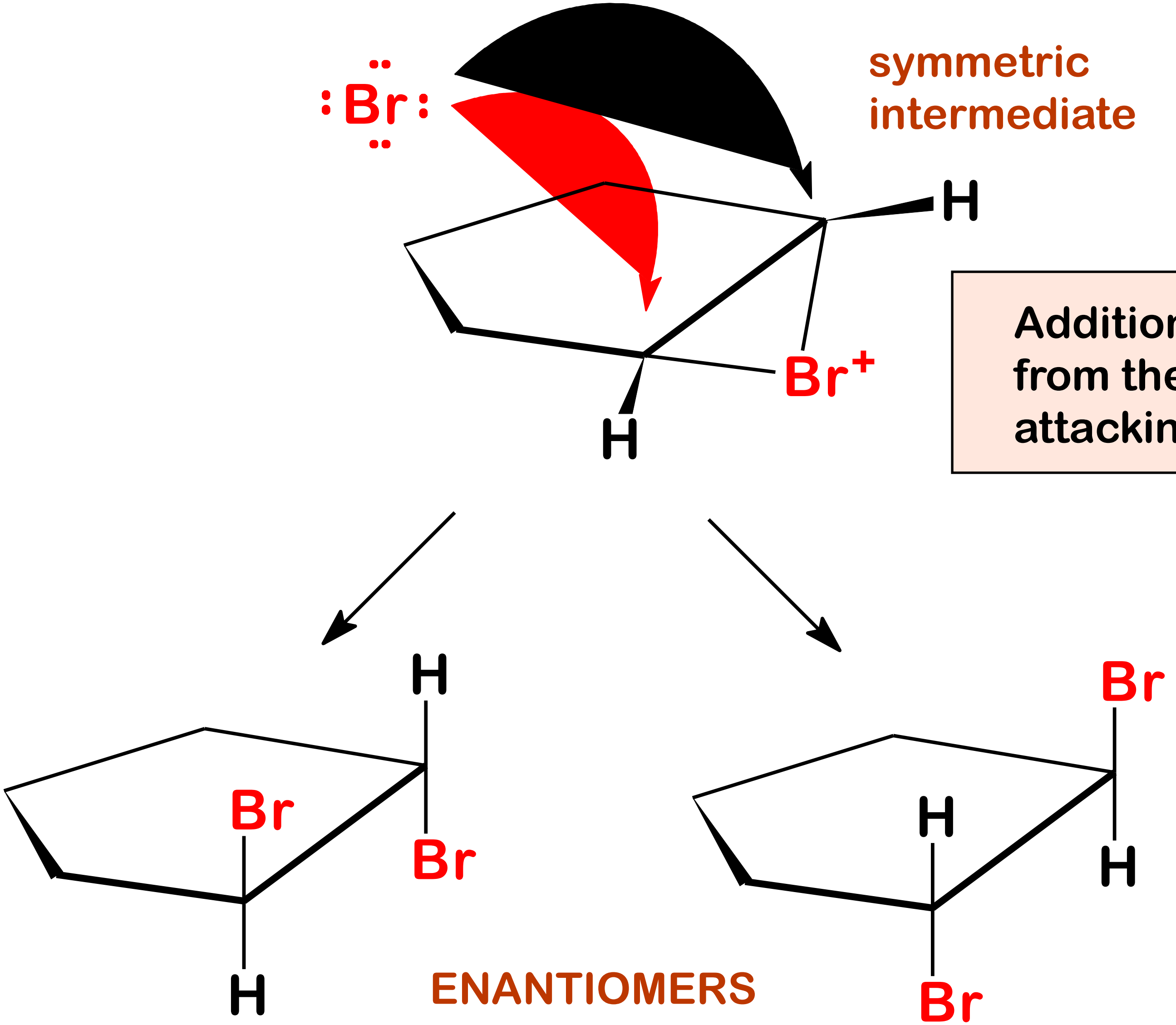
note size of bromine

BRIDGED BROMONIUM ION



bridging
blocks approach
from this side

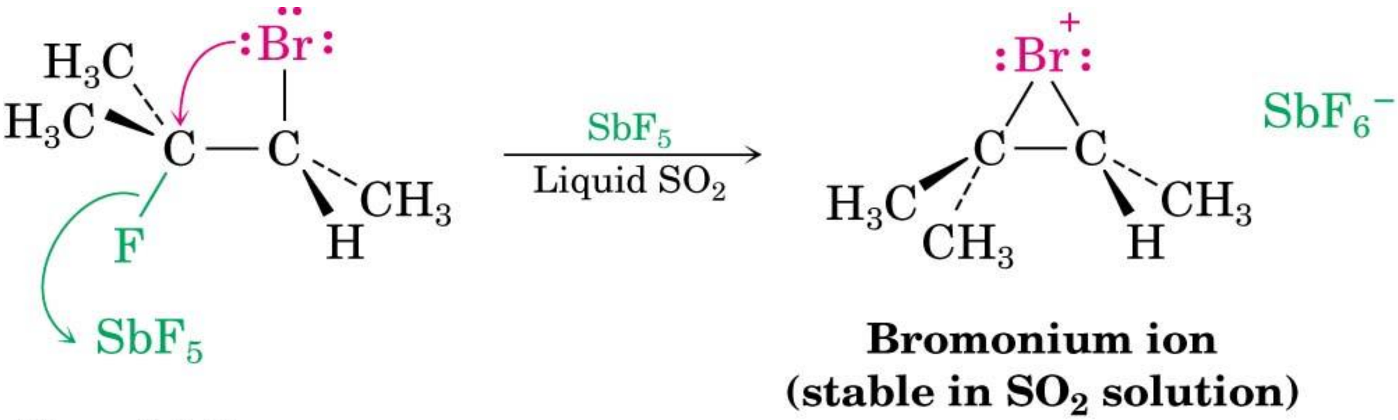
FORMATION OF ENANTIOMERS



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

The Reality of Bromonium Ions

- **Bromonium 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 SO_2 with SbF_5 and can be studied directly**

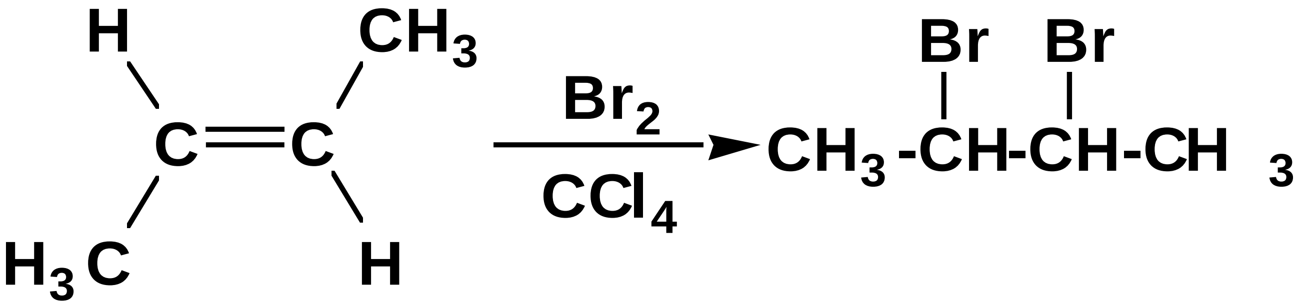


© Thomson - Brooks Cole

Roberts, Irving; Kimball, George E. (1937). "The Halogenation of Ethylenes". J. Am. Chem. Soc. 59 (5): 947. doi:10.1021/ja01284a507

Estereoquímica de Reação

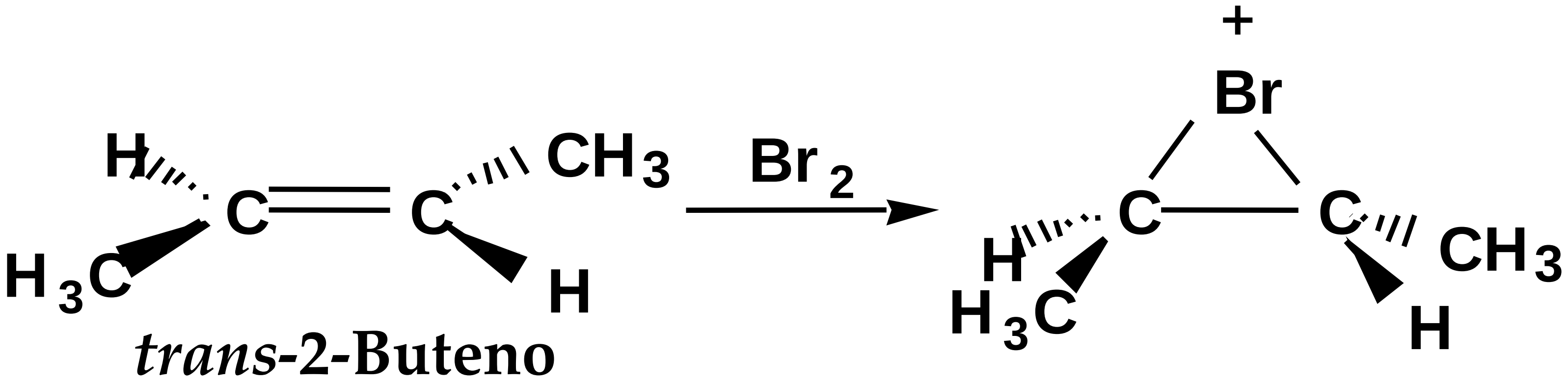
- **Quais dos três estereoisômeros possíveis para o 2,3-dibromobutano são formados na adição de bromo a trans-2-buteno?**



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

Estereoquímica de Reação

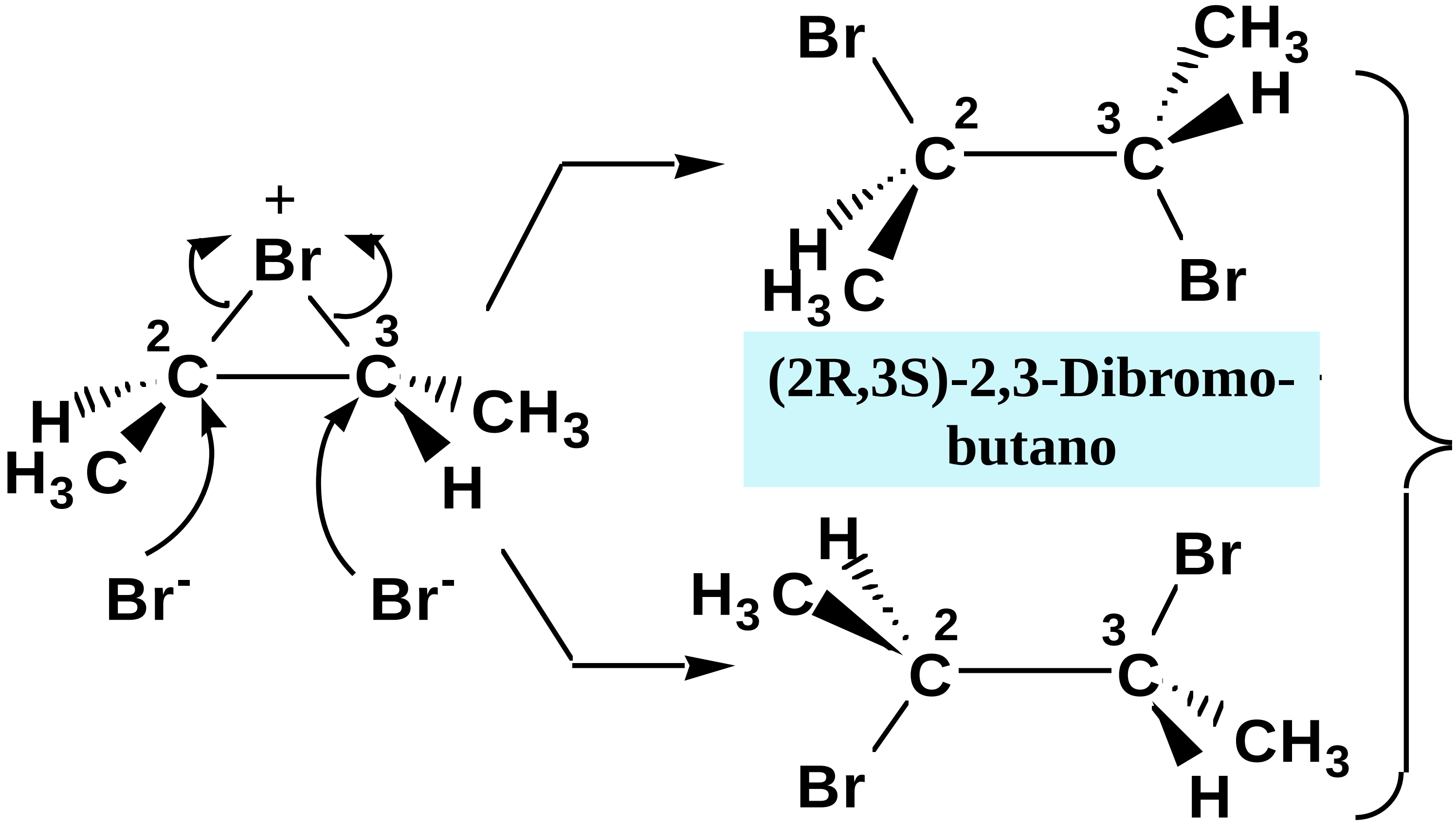
- A reação de bromo com o alceno forma um íon bromônio cíclico como intermediário



trans-2-Buteno
(aquiral)

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

Estereoquímica de Reação



(2R,3S)-2,3-Dibromo-butano

(2S,3R)-2,3-Dibromo-butano

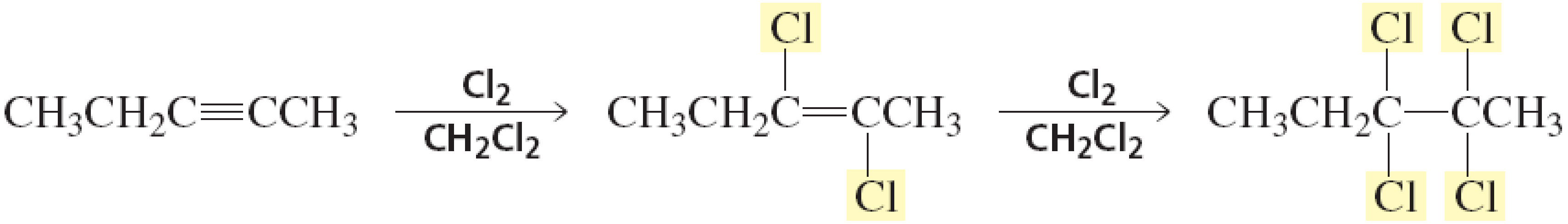
Idênticos; composto meso

Estereoquímica de Reação

- **Produtos enantiomericamente puros nunca poderão ser formados a partir de materiais de partida e reagentes aquirais**

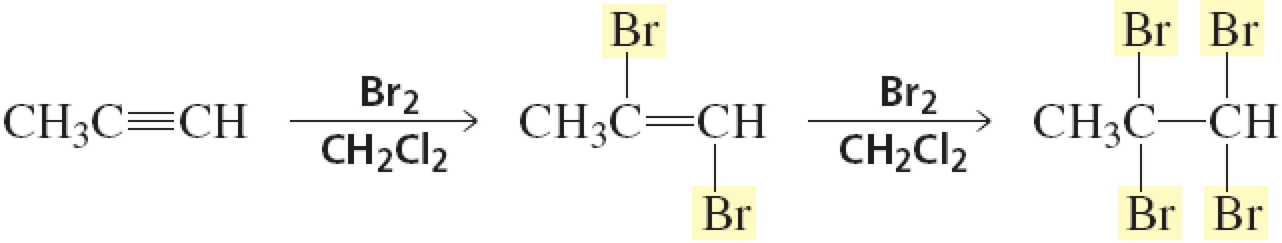
- **Um produto enantiomericamente puro poderá ser gerado numa reação se ao menos um dos reagentes for enantiomericamente puro, ou se a reação for conduzida em um ambiente quiral**

Adição de bromo e cloro



$$CH_3CH_2C\equiv CCH_3 \xrightarrow[CH_2Cl_2]{Cl_2} CH_3CH_2\overset{Cl}{\overset{|}{C}}=\underset{\underset{Cl}{|}}{C}CH_3 \xrightarrow[CH_2Cl_2]{Cl_2} CH_3CH_2\overset{Cl}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-\overset{Cl}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}CH_3$$

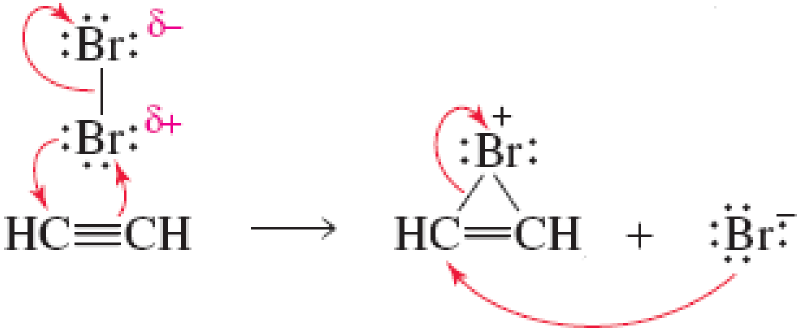
adição anti coplanar



$$CH_3C\equiv CH \xrightarrow[CH_2Cl_2]{Br_2} CH_3\overset{Br}{\overset{|}{C}}=\underset{\underset{Br}{|}}{C}H \xrightarrow[CH_2Cl_2]{Br_2} CH_3\overset{Br}{\overset{|}{\underset{\underset{Br}{|}}{C}}}-\overset{Br}{\overset{|}{\underset{\underset{Br}{|}}{C}}}H$$

adição anti coplanar

Mecanismo via anel de três membros contendo haleto positivo



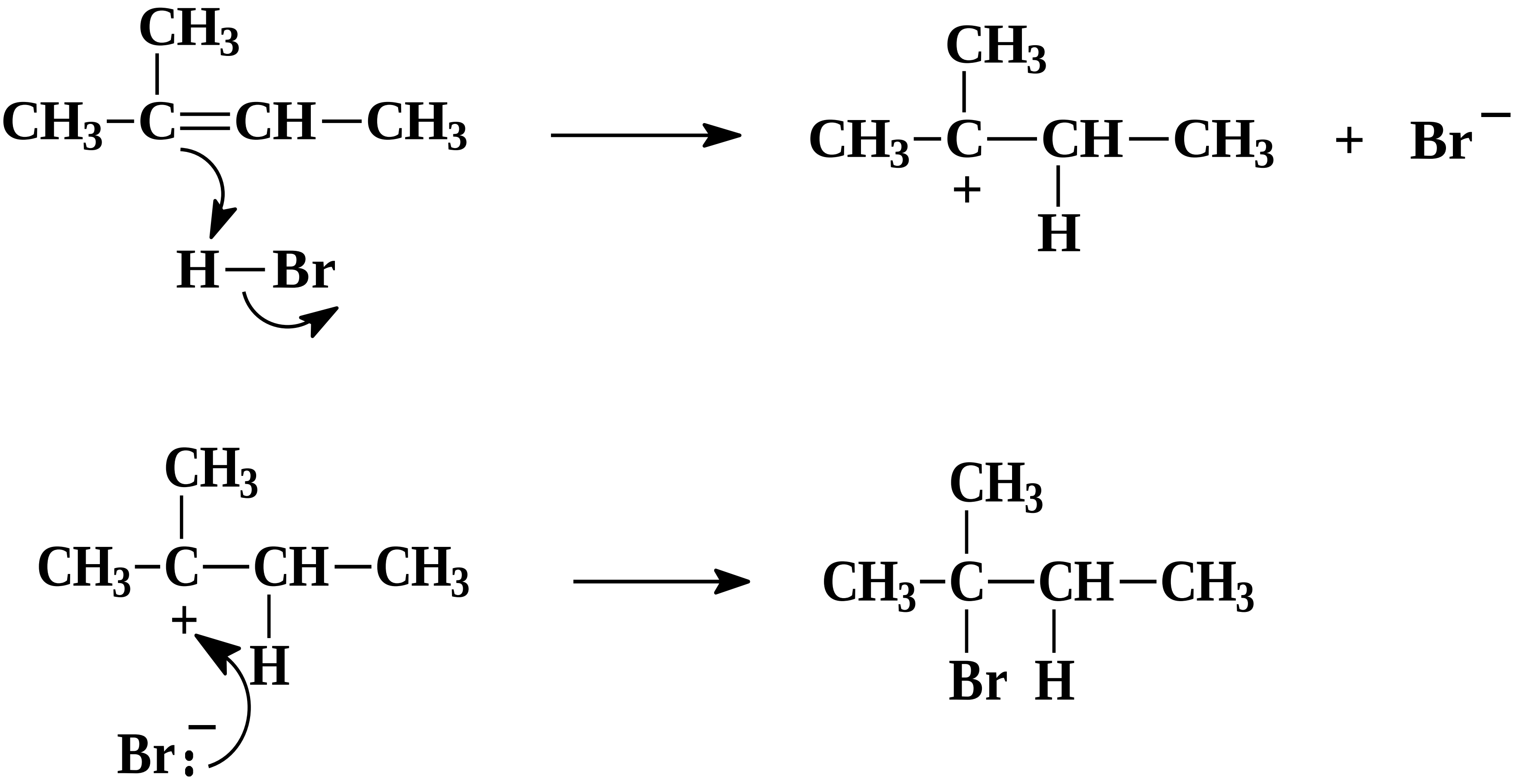
Adição de HX

- **Executada com reagentes puros ou em solventes polares - ex.: ácido acético**

- **A reação é regiosseletiva**

- **Reação regiosseletiva: reação na qual há formação ou quebra de ligações preferenciais.**

Adição de HX

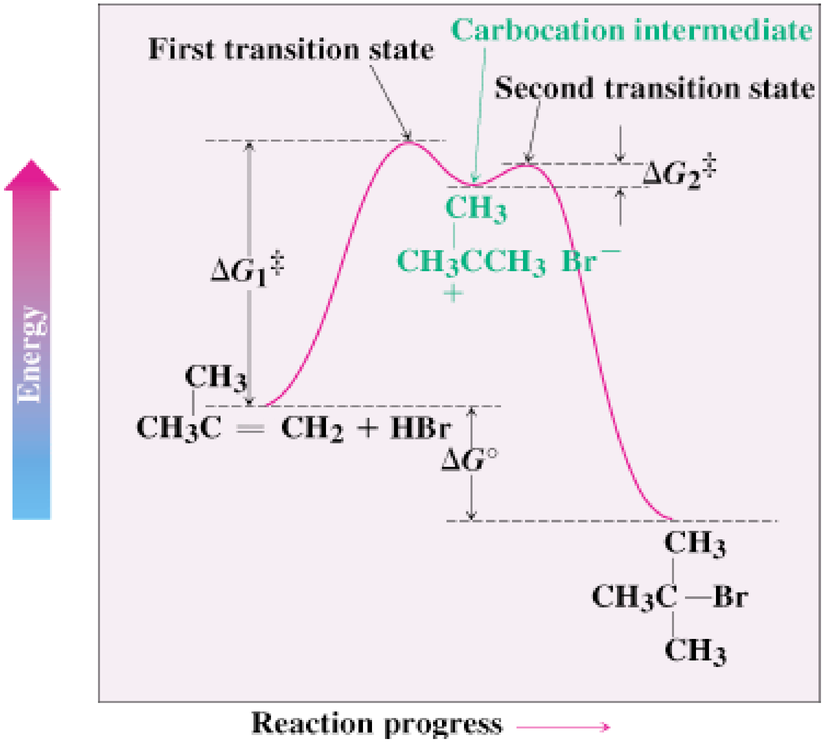


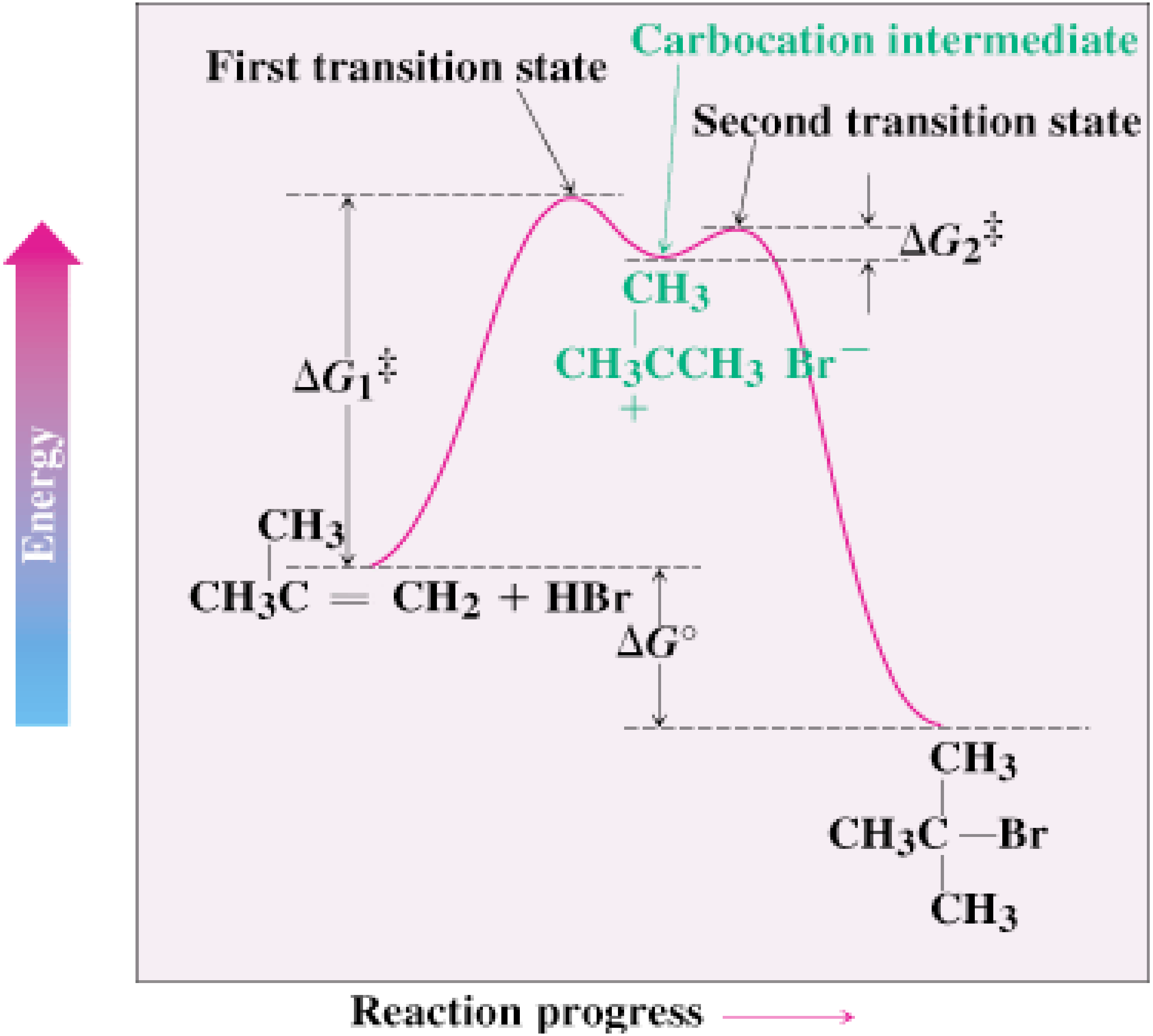
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \quad H-Br \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-\underset{\underset{H}{|}}{CH}-CH_3 + Br^-$$

$$CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-\underset{\underset{H}{|}}{CH}-CH_3 \quad Br:^- \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{Br}{|}}{C}}}-\underset{\underset{H}{|}}{CH}-CH_3$$

Electrophilic Addition Energy Path

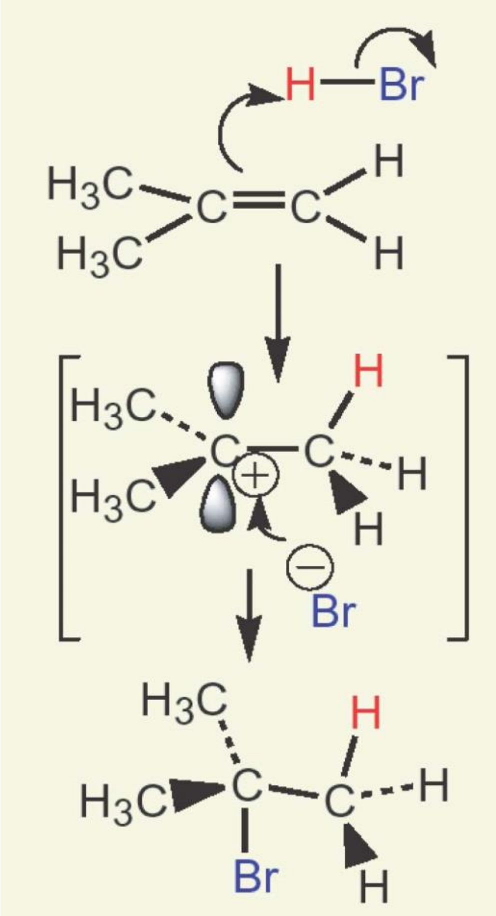
- Two step process
- First transition state is high energy point




First transition state
Carbocation intermediate
Second transition state
$\Delta G_1^\ddagger$
$\Delta G_2^\ddagger$
CH_3
$CH_3\overset{+}{C}CH_3$ Br^-
CH_3
$CH_3C=CH_2 + HBr$
ΔG°
CH_3
CH_3C-Br
CH_3
Energy
Reaction progress

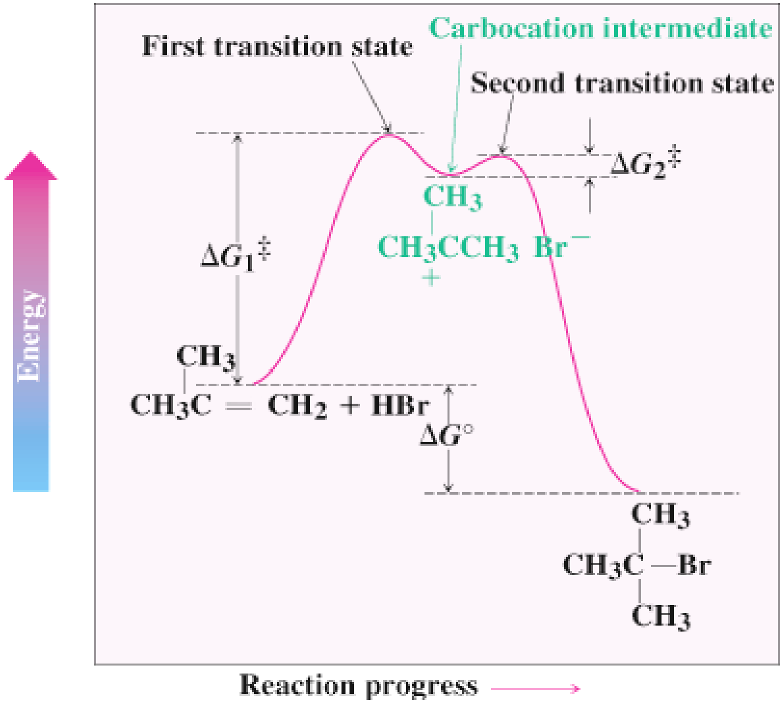
Example of Electrophilic Addition

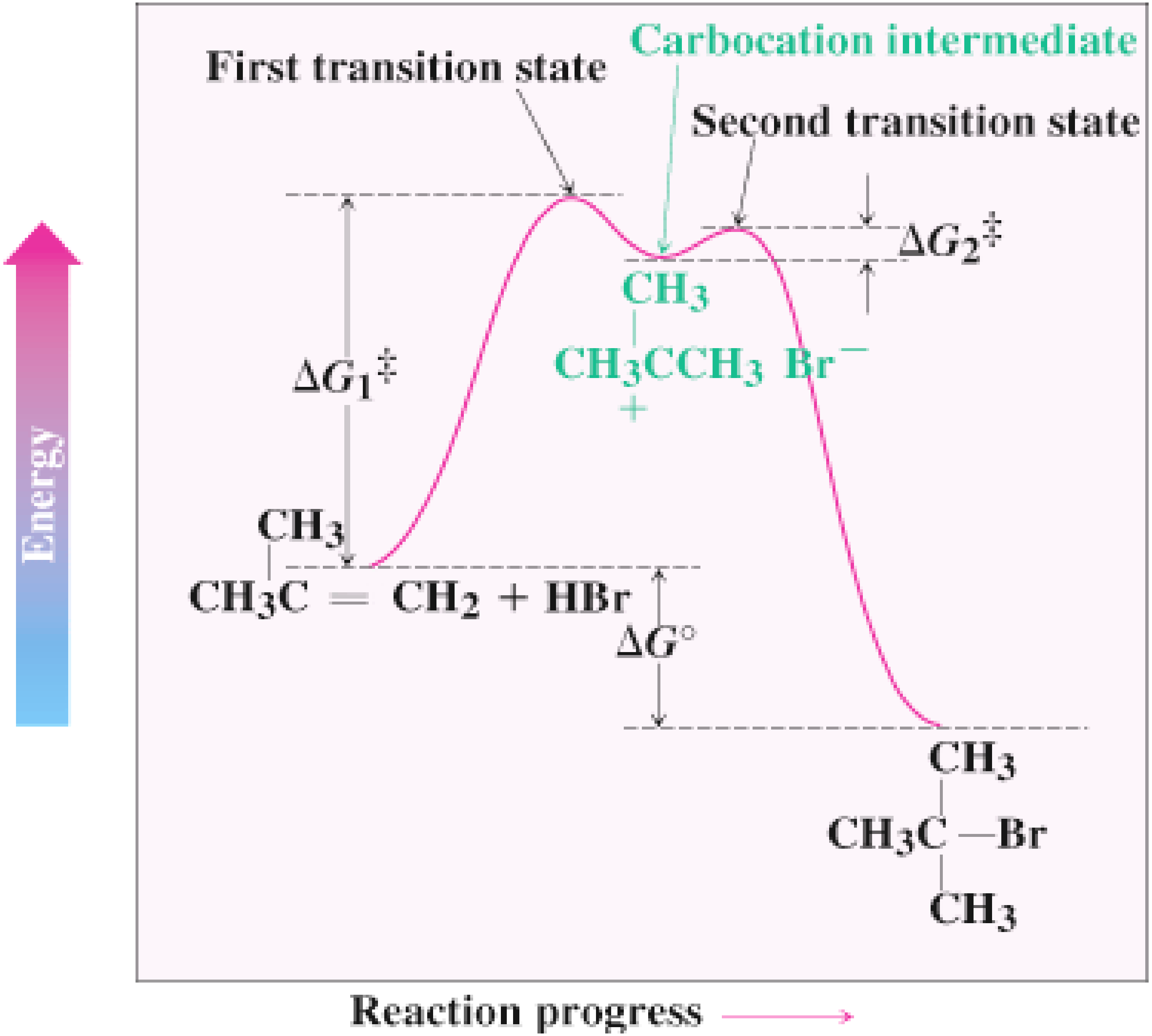
- **Addition of hydrogen bromide to 2-Methyl-propene**
- **H-Br transfers proton to C=C**
- **Forms carbocation intermediate**
  - **More stable cation forms**
- **Bromide adds to carbocation**



Energy Diagram for Electrophilic Addition

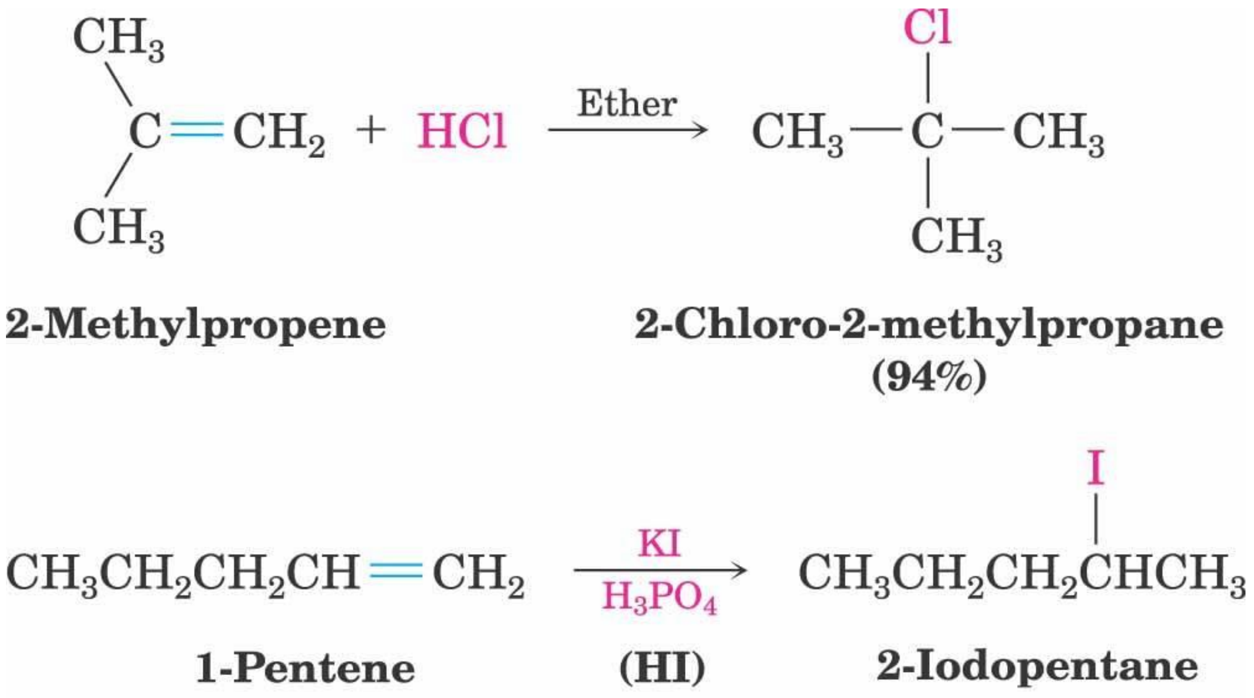
- Rate determining (slowest) step has highest energy transition state
  - Independent of direction
  - In this case it is the first step in forward direction
  - “rate” is not the same as “rate constant”




First transition state
Carbocation intermediate
Second transition state
$\Delta G_2^{\ddagger}$
$\Delta G_1^{\ddagger}$
CH_3
$CH_3\overset{+}{C}CH_3$ Br^-
Energy
CH_3
$CH_3C=CH_2 + HBr$
ΔG°
CH_3
CH_3C-Br
CH_3
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**

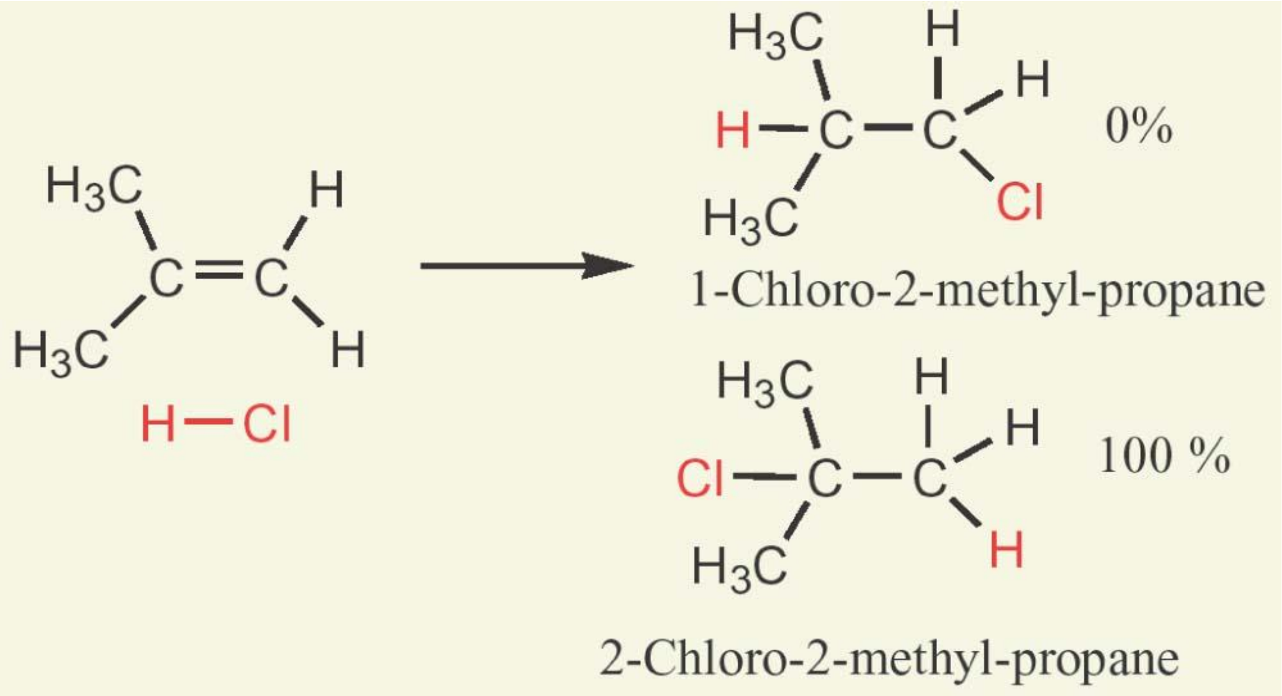


Orientation of Electrophilic Addition:

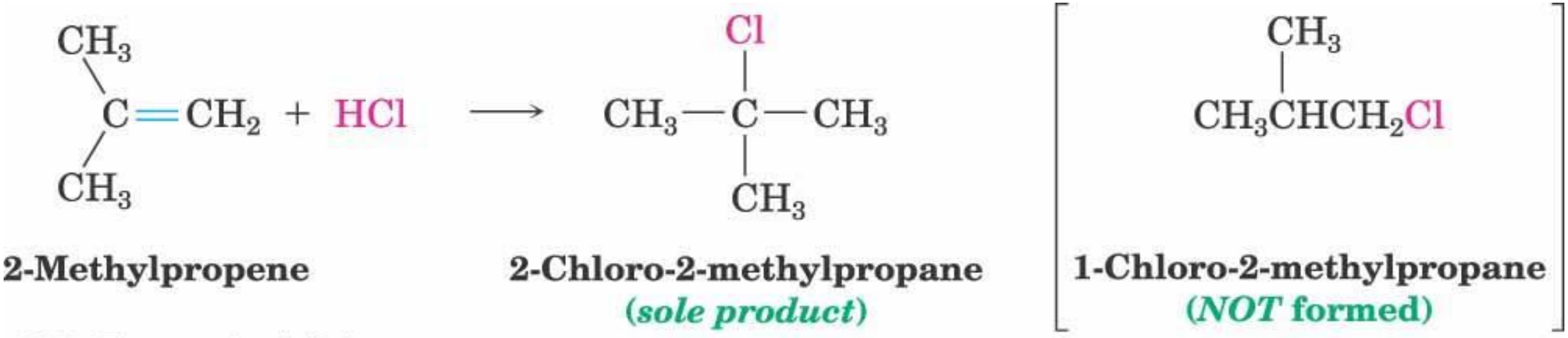
- **In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other**
- **If one orientation predominates, the reaction is** *regiospecific*
- **The reaction will always occur favoring the formation of the most stable carbocation**

Example of Regiospecific reactions

- Addition of HCl to 2-methylpropene
- Regiospecific – one product forms where two are possible
- 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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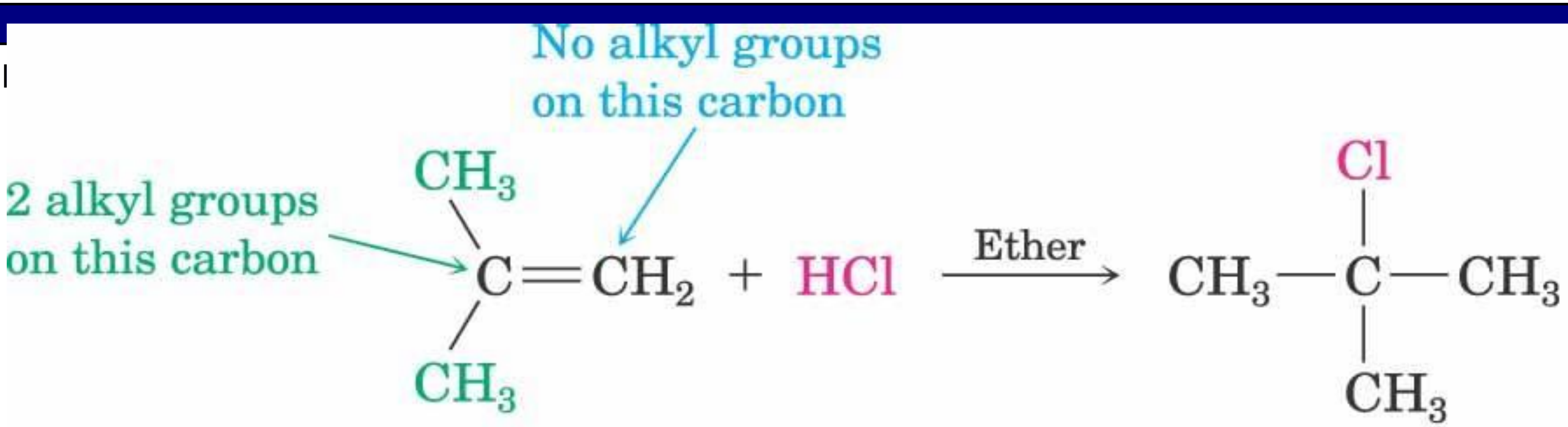
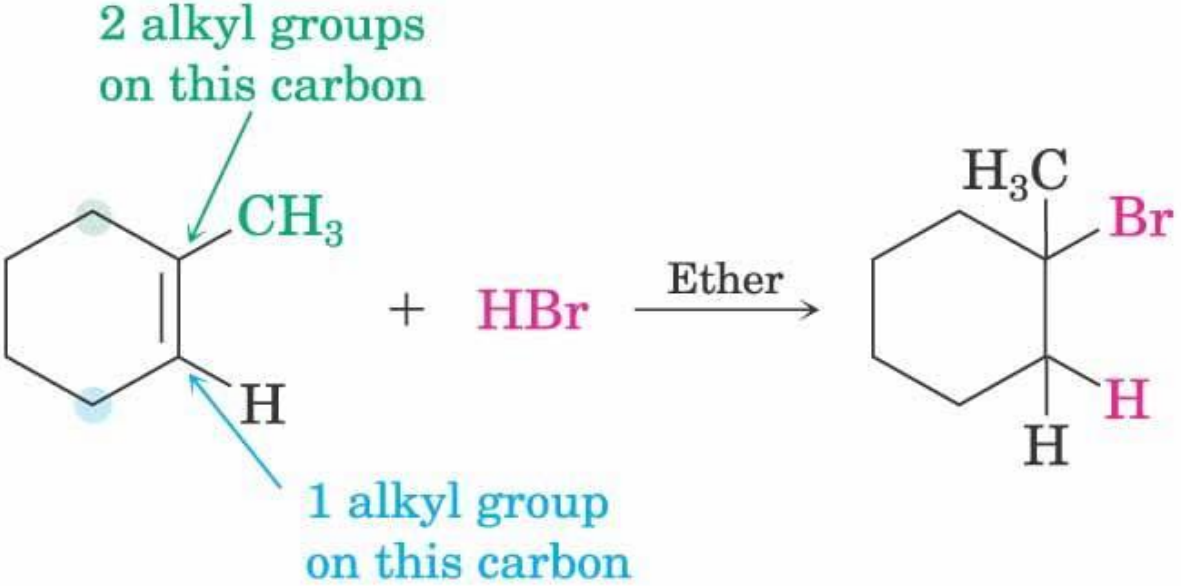

No alkyl groups on this carbon

2 alkyl groups on this carbon

2-Methylpropene

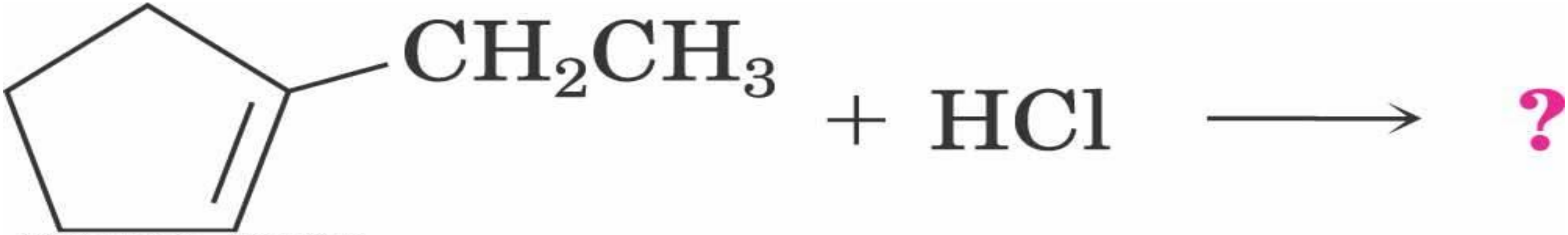
2-Chloro-2-methylpropane

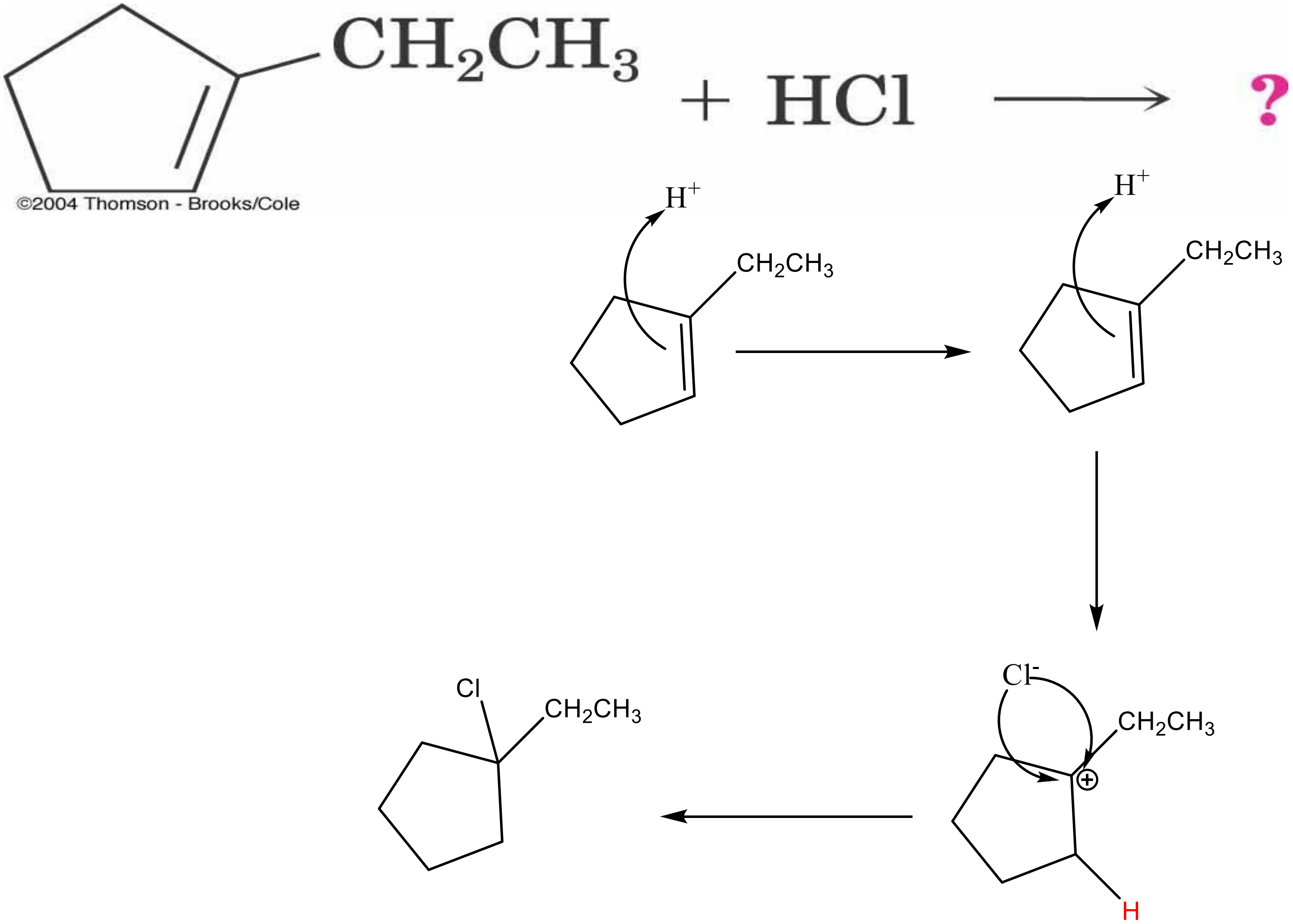

2 alkyl groups on this carbon

1 alkyl group on this carbon

1-Methylcyclohexene

1-Bromo-1-methylcyclohexane


CH_2CH_3
+ HCl
?



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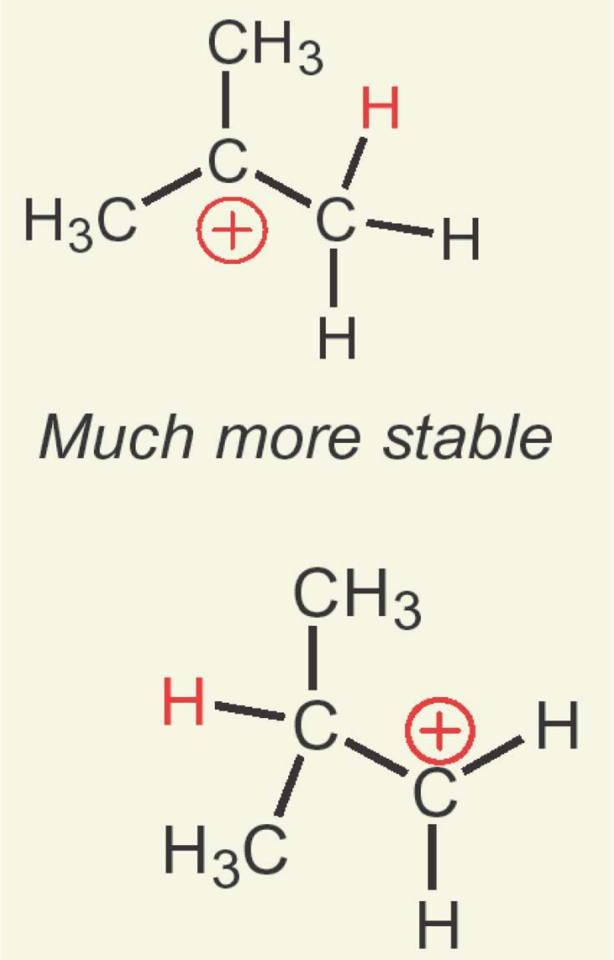
Mechanistic Source of Regiospecificity in Addition Reactions

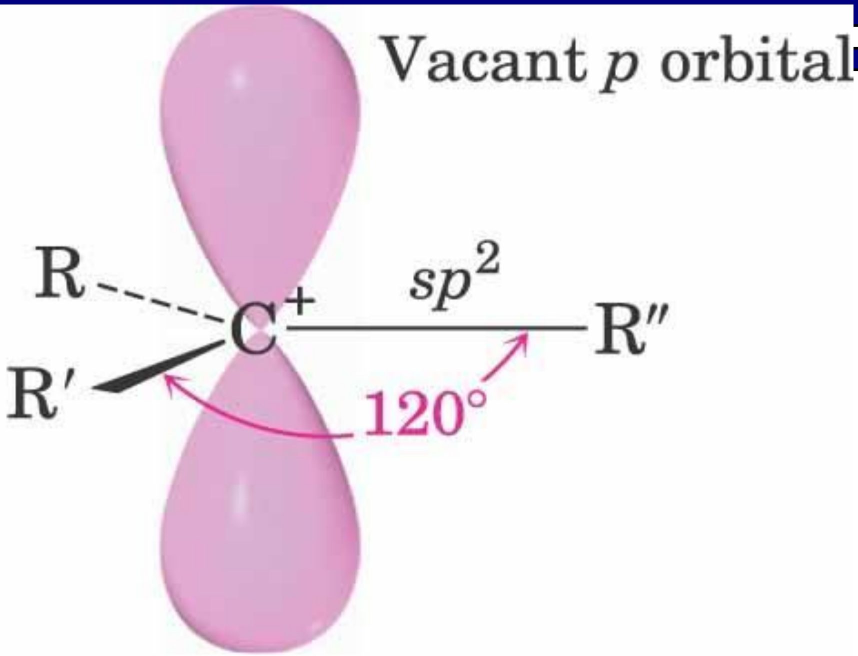
- **If addition involves a carbocation intermediate**
  - **and there are two possible ways to add**
  - **the route producing the more alkyl substituted cationic center is lower in energy**
  - **alkyl groups stabilize carbocation**

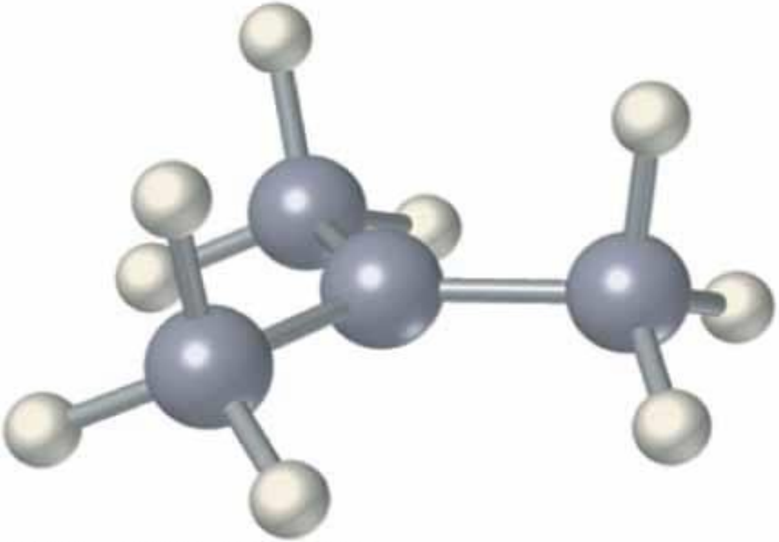


Much more stable

Carbocation Structure and Stability

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

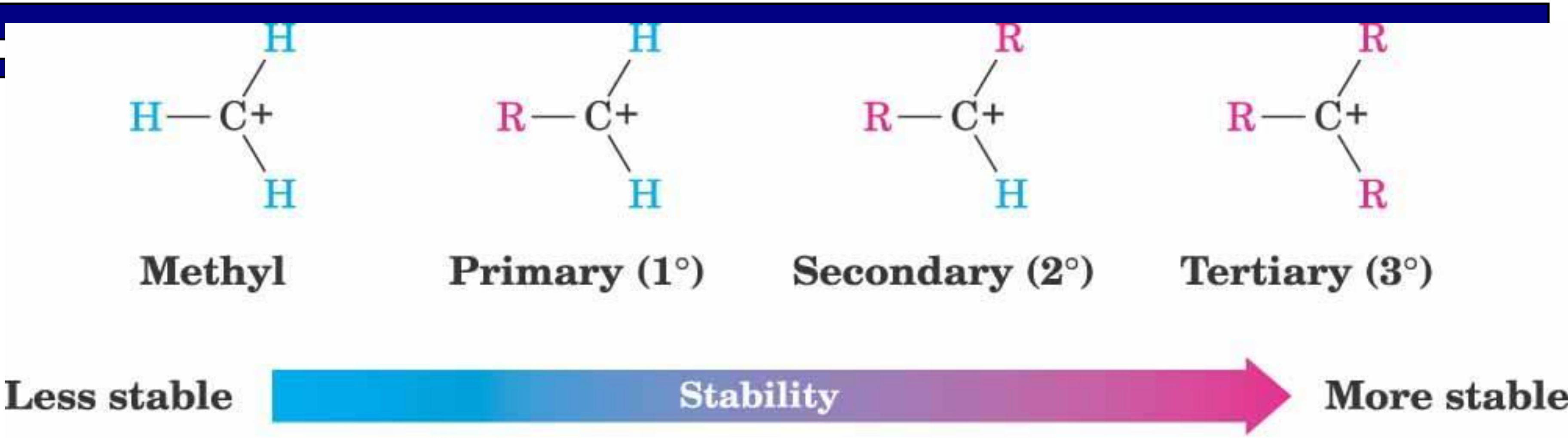

Vacant *p* orbital
R
R′
C+
sp^2
R″
120°



Carbocation Structure and Stability

- The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents
- Therefore stability of carbocations:

$$3^{o} > 2^{o} > 1^{o} > {}^{+}CH_3$$



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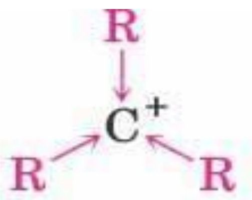
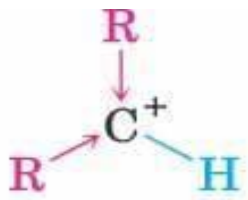


3°: Three alkyl groups donating electrons



2°: Two alkyl groups donating electrons

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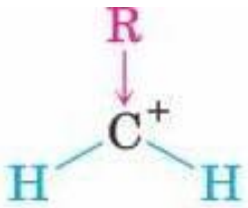
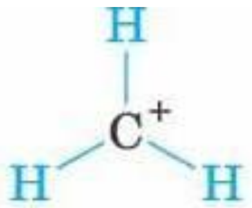
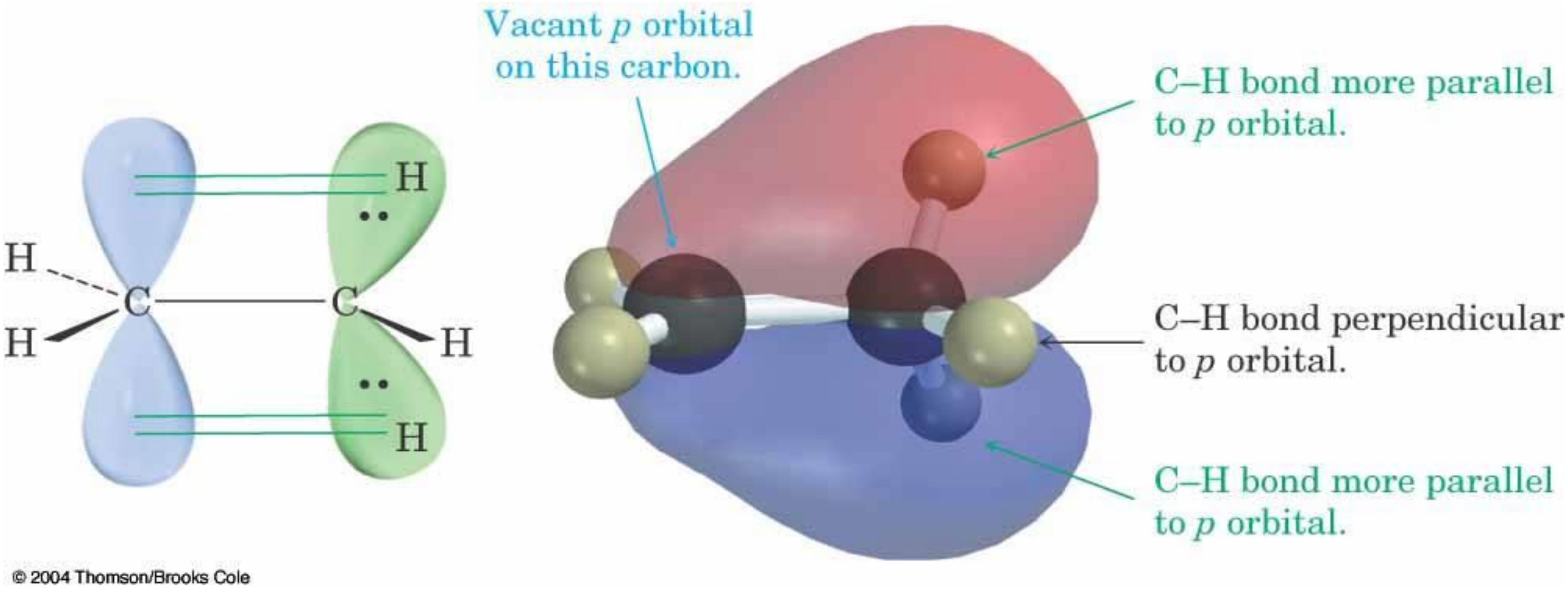


1°: One alkyl group donating electrons



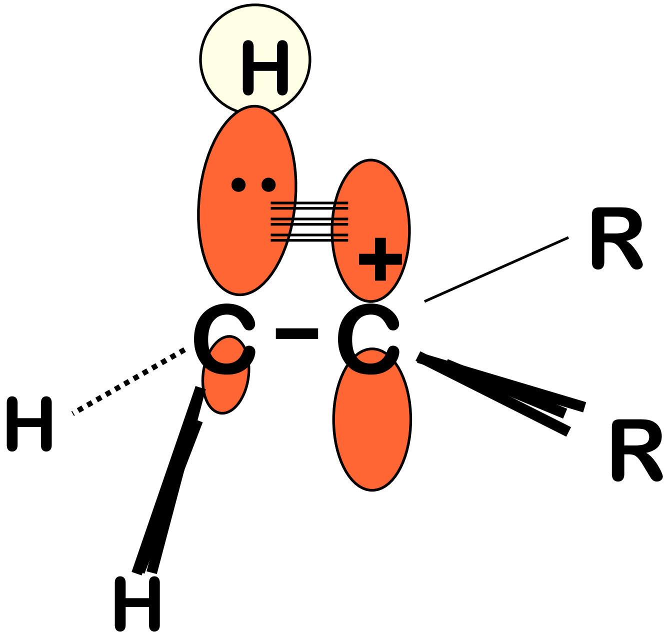
Methyl: No alkyl groups donating electrons

Stabilizing Carbocations:



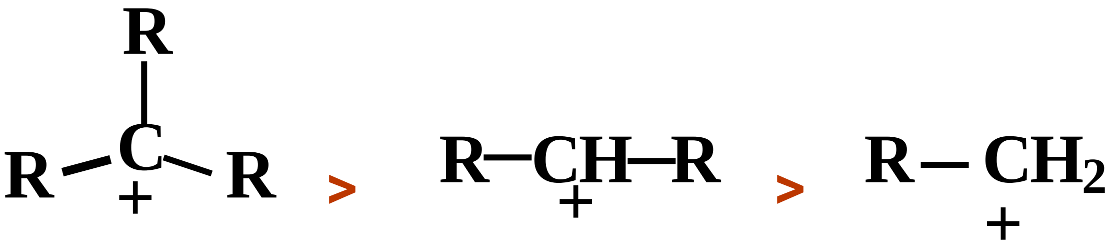
CARBOCATION STABILITY

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

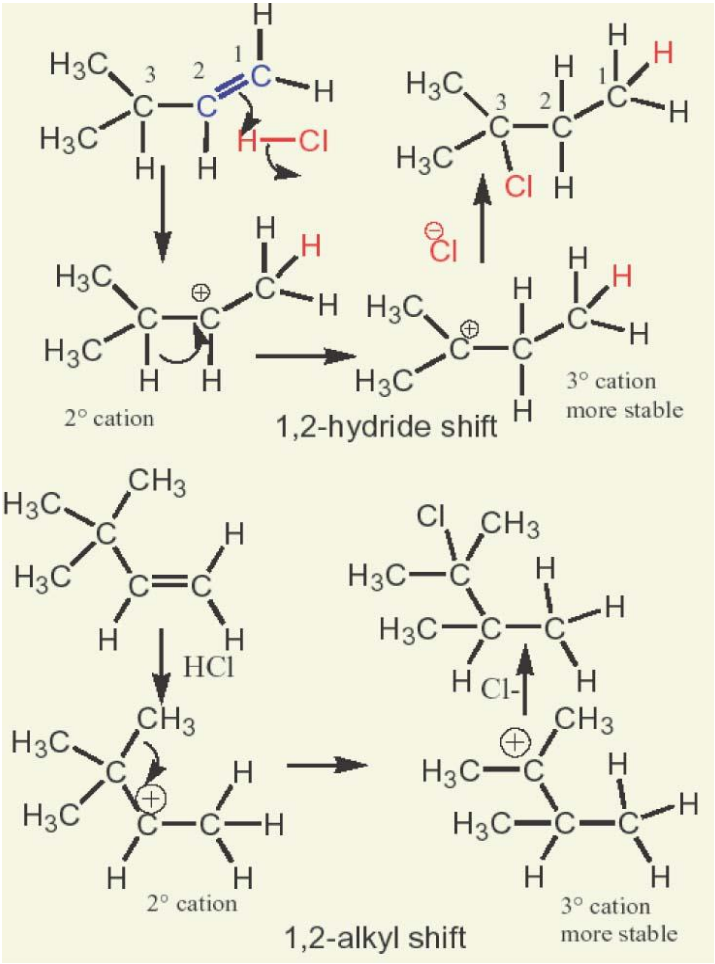
Markovnikov's Rule

- **Markovnikov observed in the 19th century that in the addition of HX to alkene, the H attaches to the carbon with the most H's and X attaches to the other end (to the one with the most alkyl substituents)**
  - **This is** Markovnikov's rule

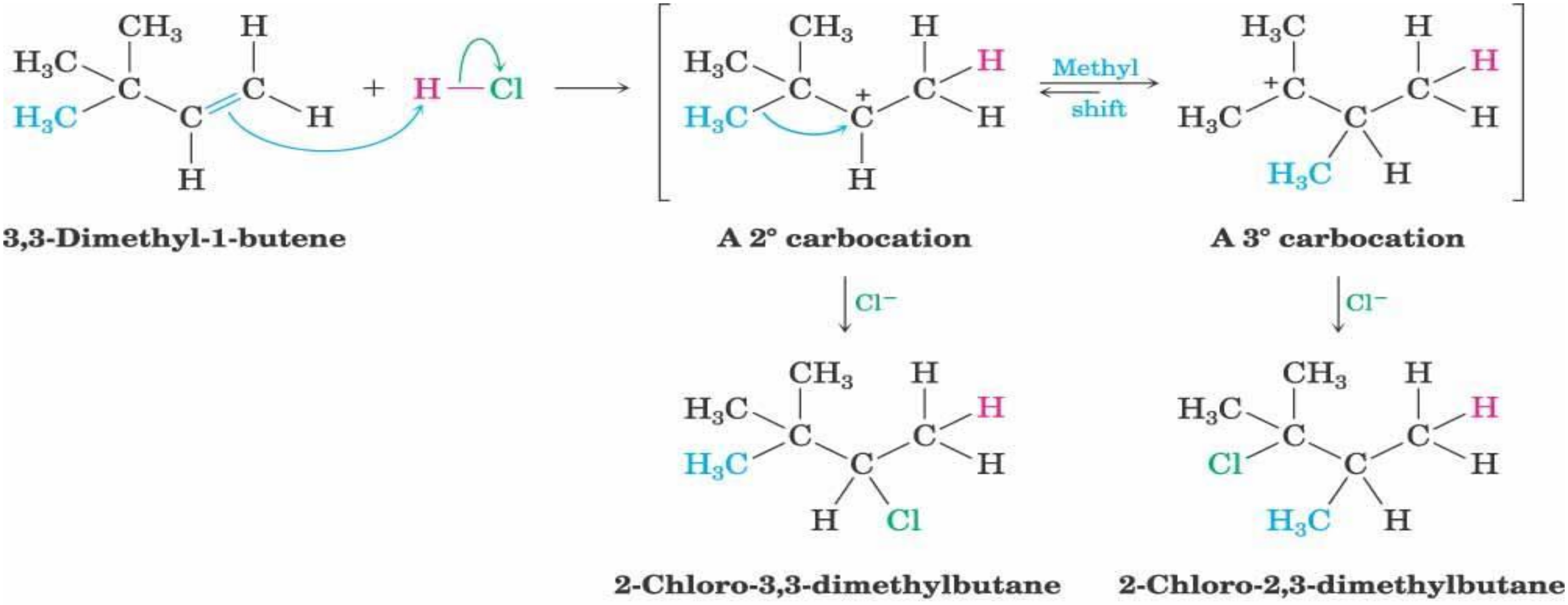
This was an experimental observation before the mechanism was established.

Mechanism of Electrophilic Addition: Rearrangements of Carbocations

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



Hydride Shifts



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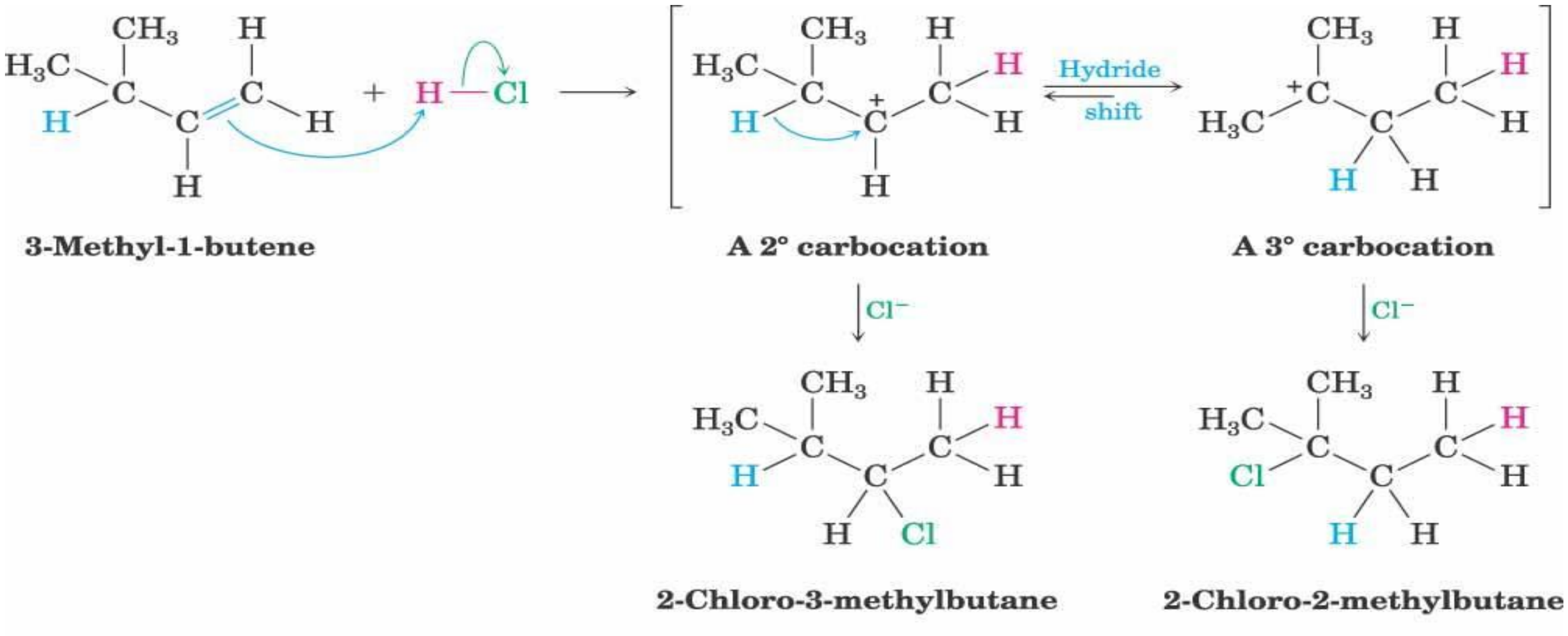
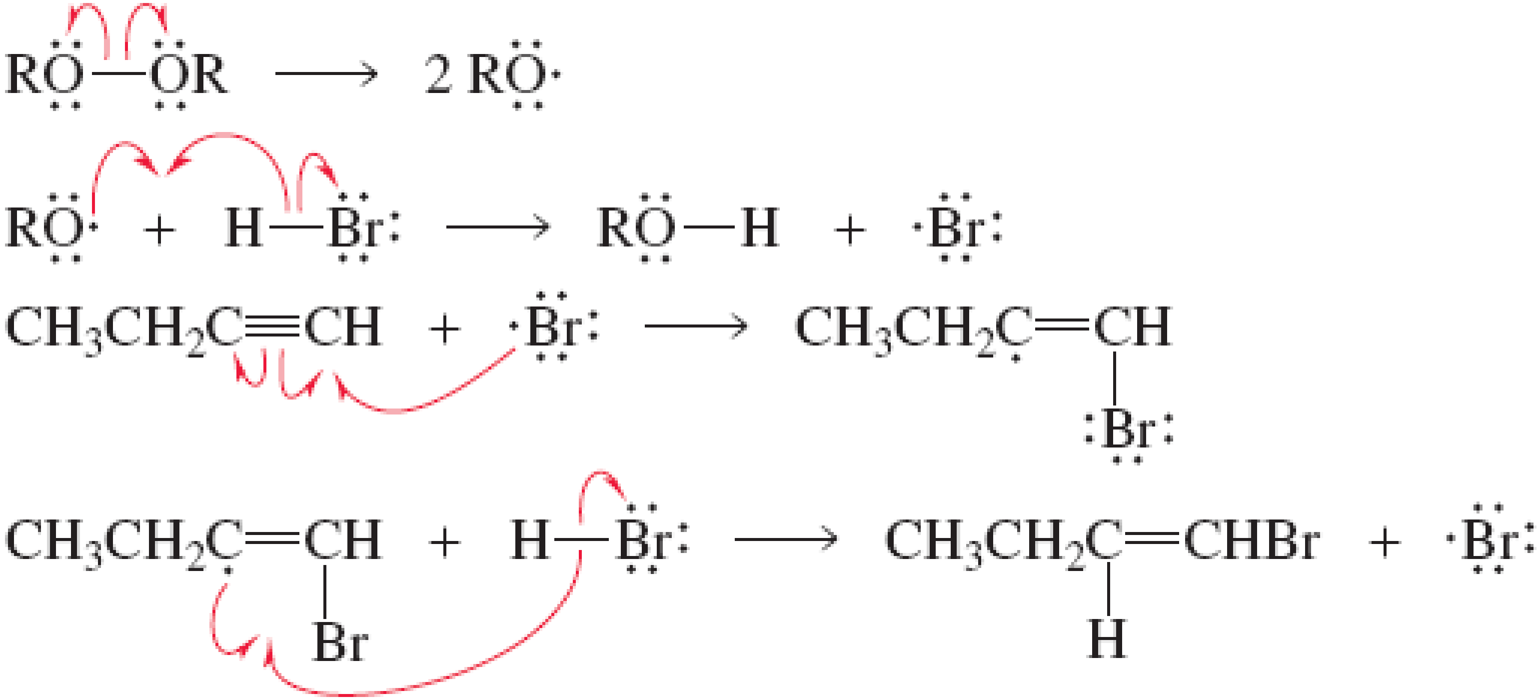
Alkyl (methyl) shifts



Adição de brometo de hidrogênio anti-Markovnikov

$$CH_3CH_2C{\equiv}CH + HBr \xrightarrow{ROOR} CH_3CH_2CH{=}CHBr$$

Mecanismo radicalar



$$R\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}R \longrightarrow 2\,R\ddot{\underset{..}{O}}\cdot$$

$$R\ddot{\underset{..}{O}}\cdot + H-\ddot{\underset{..}{Br}}: \longrightarrow R\ddot{\underset{..}{O}}-H + \cdot\ddot{\underset{..}{Br}}:$$

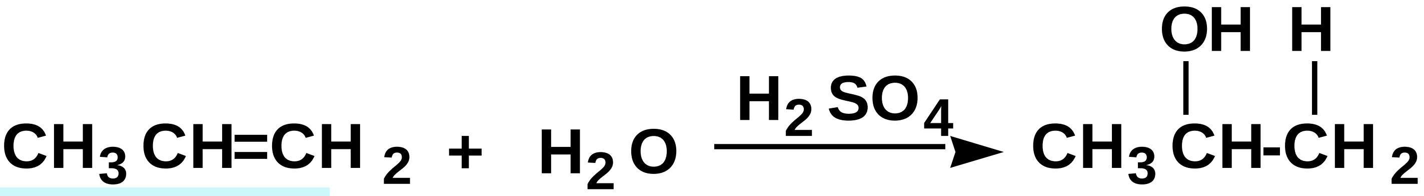
$$CH_3CH_2C{\equiv}CH + \cdot\ddot{\underset{..}{Br}}: \longrightarrow CH_3CH_2\dot{C}{=}CH(:\ddot{\underset{..}{Br}}:)$$

$$CH_3CH_2\dot{C}{=}CH(Br) + H-\ddot{\underset{..}{Br}}: \longrightarrow CH_3CH_2C(H){=}CHBr + \cdot\ddot{\underset{..}{Br}}:$$

Adição de H_2O

- A adição de água denomina-se hidratação

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



$$\mathrm{CH_3CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{OH}{|}}{CH}-\overset{\overset{H}{|}}{CH_2}}$$

Propeno

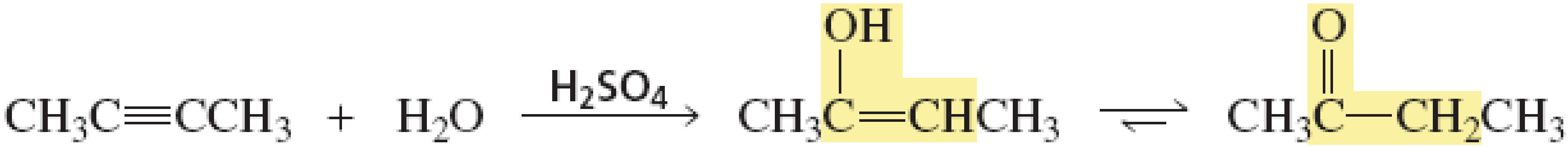
2-Propanol

Indirect Hydration

- Oxymercuration-Demercuration
  - Markovnikov product formed
  - Anti addition of H-OH
  - No rearrangements

- Hydroboration
  - Anti-Markovnikov product formed
  - Syn addition of H-OH

Adição de água



$$CH_3C\equiv CCH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{OH}{\overset{|}{C}}=CHCH_3 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

tautômero enol

tautômero ceto

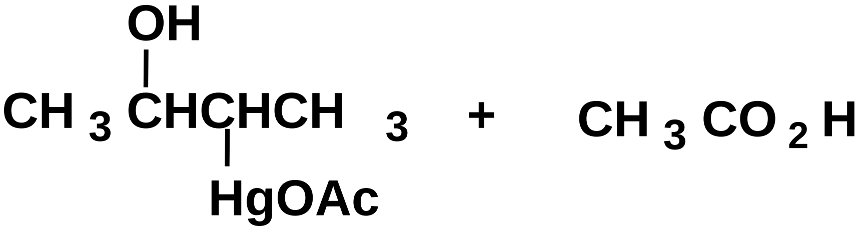
tautomerismo ceto-enólico

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.

$$CH_3CH{=}CHCH_3 + Hg(OAc)_2 + H_2O \longrightarrow$$

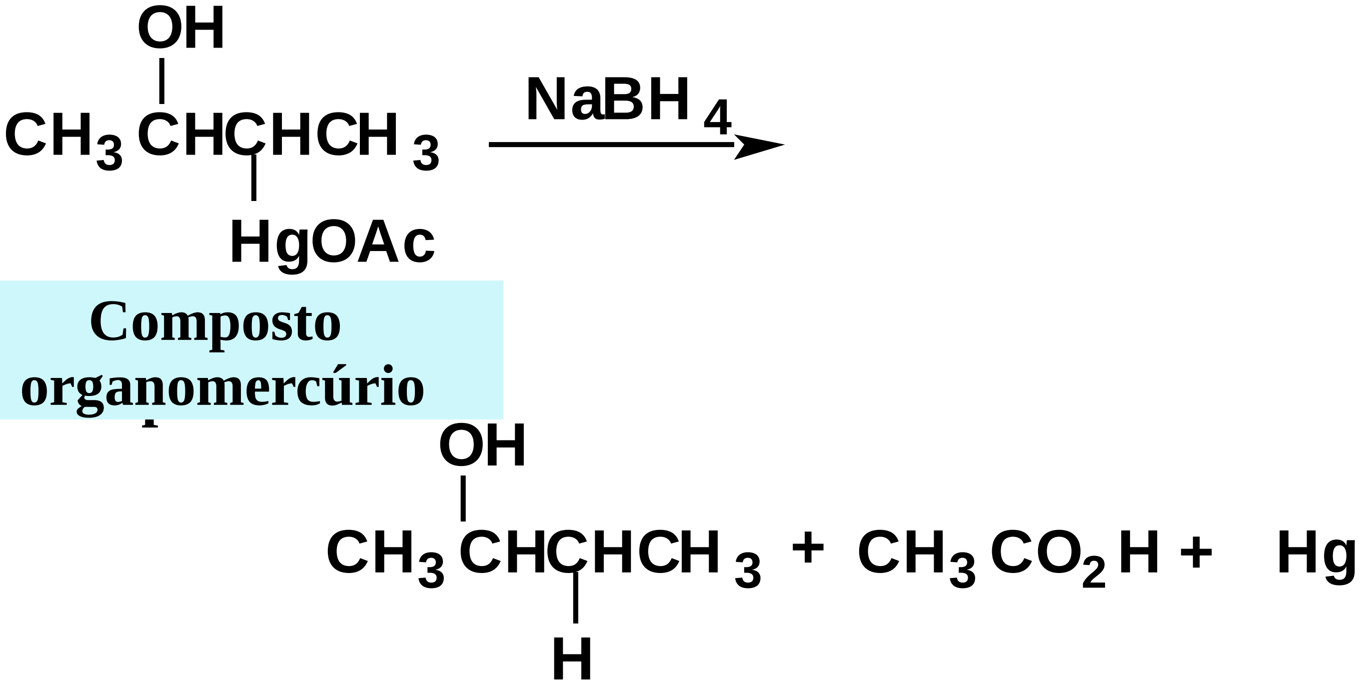
2-Buteno



$$CH_3\underset{\displaystyle HgOAc}{\overset{\displaystyle OH}{CH}}CHCH_3 + CH_3CO_2H$$

Oximercuração/Redução

- A redução com $NaBH_4$ substitui o Hg por H



$$CH_3\overset{OH}{C}H\underset{HgOAc}{C}HCH_3 \xrightarrow{NaBH_4}$$

$$CH_3\overset{OH}{C}H\underset{H}{C}HCH_3 + CH_3CO_2H + Hg$$

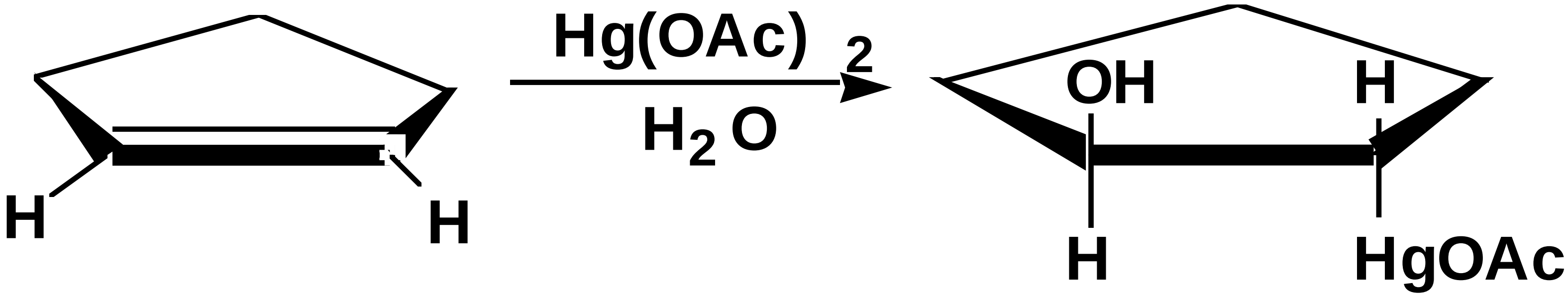
Composto organomercúrio

2-Butanol

Ácido acético

Oximercuração/Redução

- A adição de Hg(II) e oxigênio tem estereo-seletividade anticoplanar



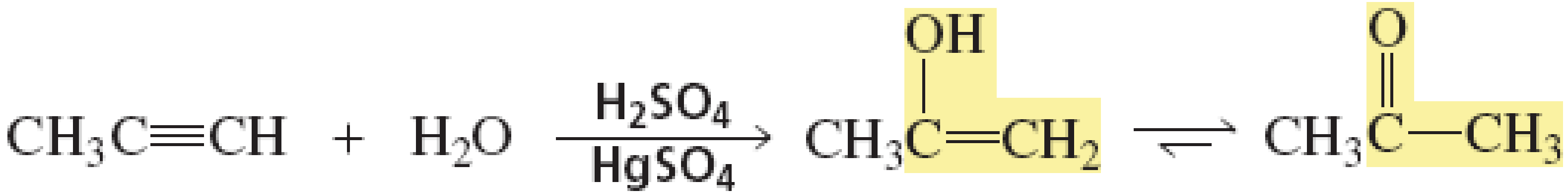
Ciclopenteno

(adição anti de -OH e -HgOAc

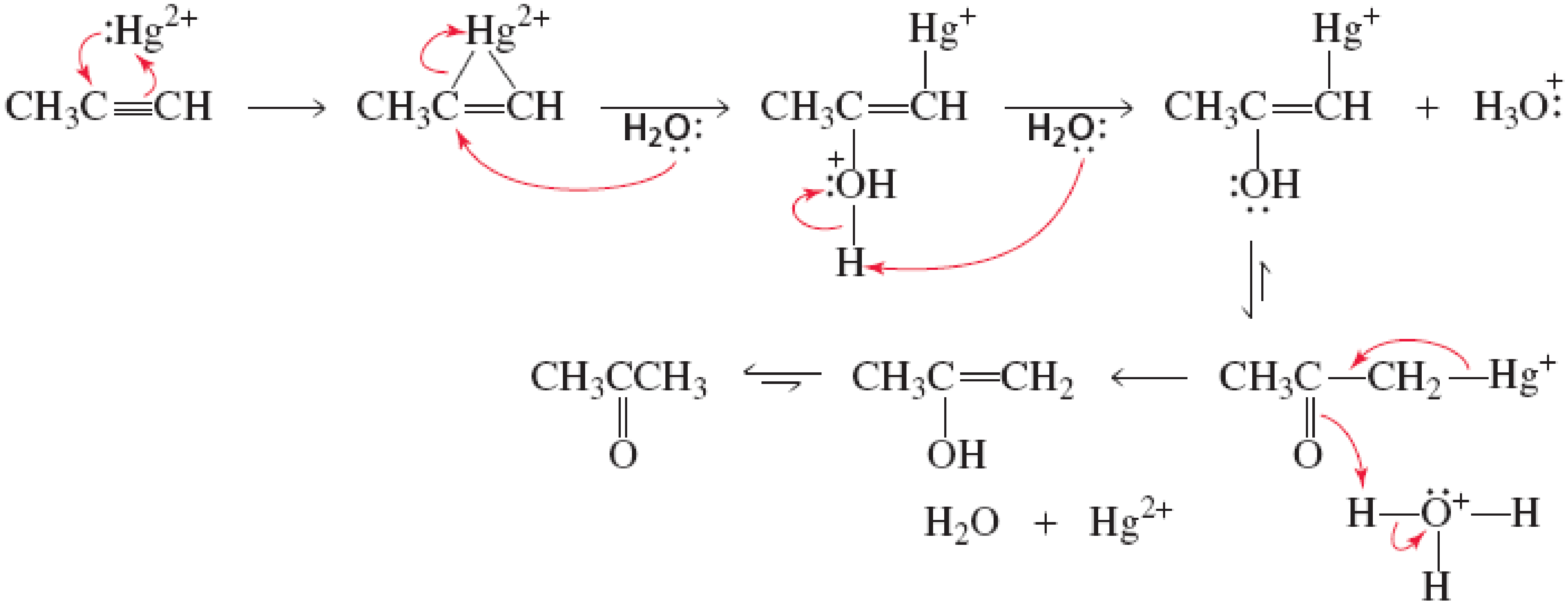
Oximercuração/Redução

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

Hidratação de alcinos terminais catalisada por sulfato de mercúrio

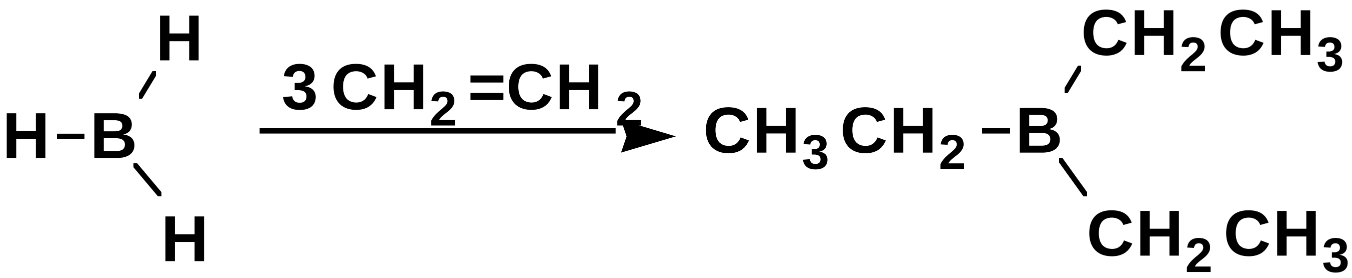


$$CH_3C\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3\overset{OH}{\overset{|}{C}}=CH_2 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-CH_3$$



Hidroboração/Oxidação

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

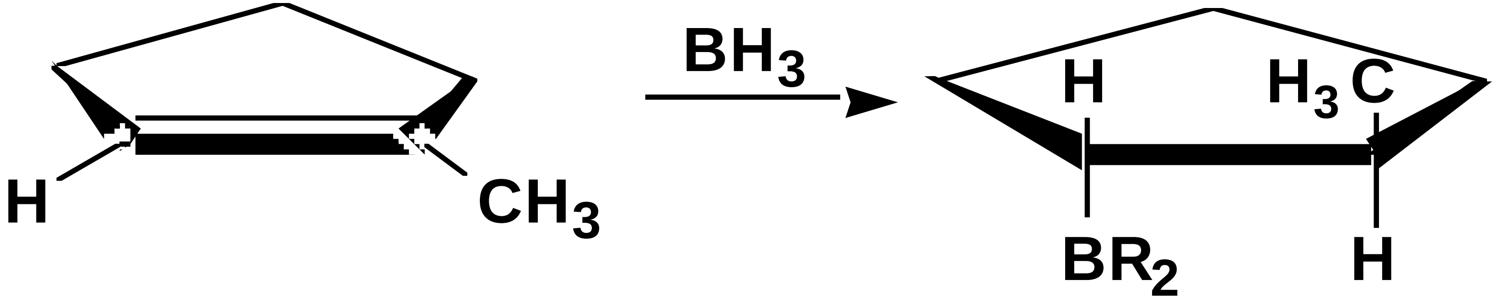


Borano

Trialquilborano

Hidroboração/Oxidação

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

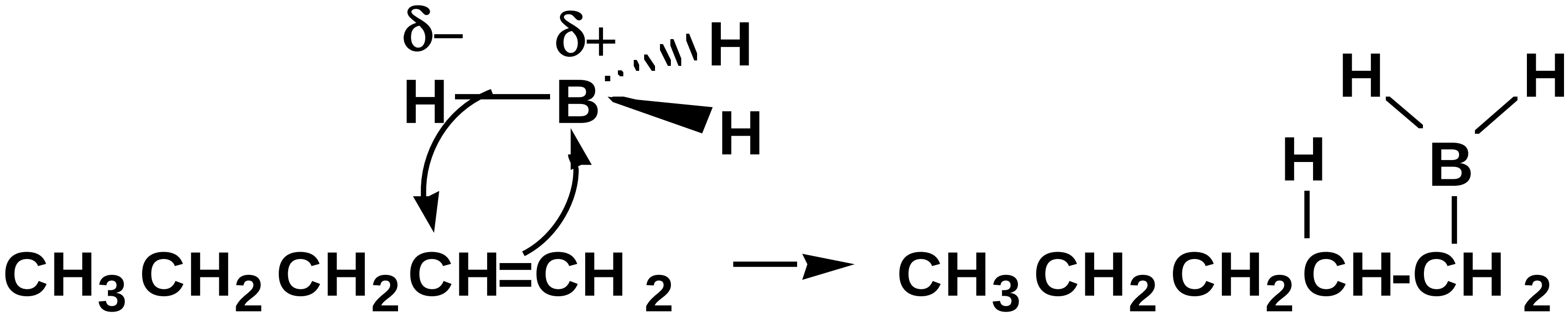


1-Metilciclopenteno

(adição sin ao BH_3)
(R = 2-metilciclopentila)

Hidroboração/Oxidação

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



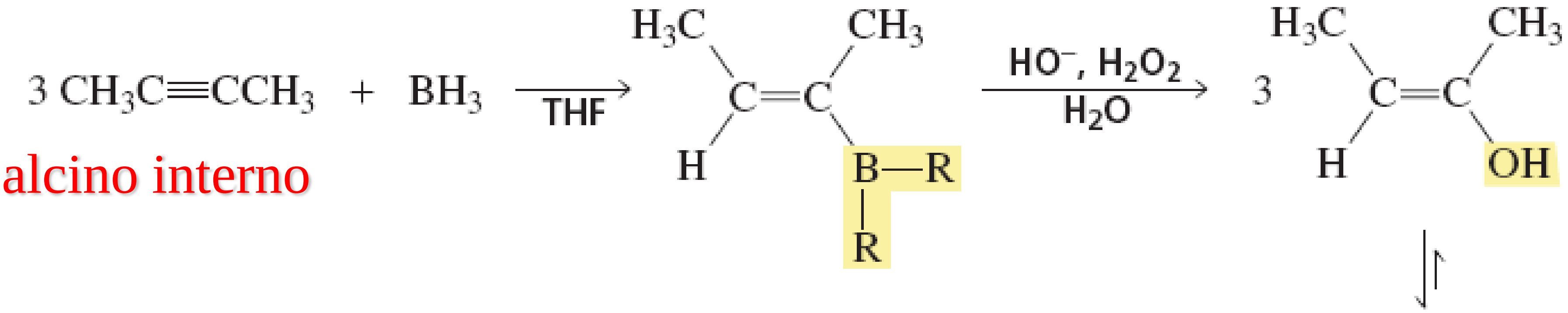
A quebra e formação das ligações ocorre simultaneamente

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

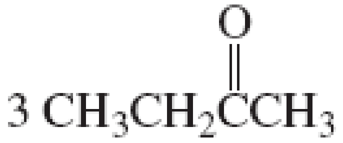
Hidroboração/Oxidação

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

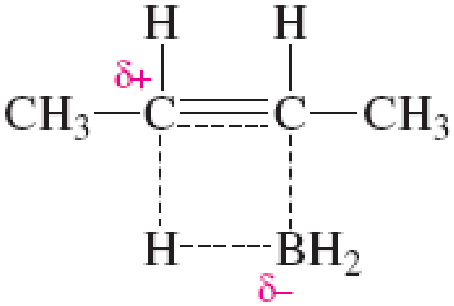
Hidroboração-oxidação



alcino interno



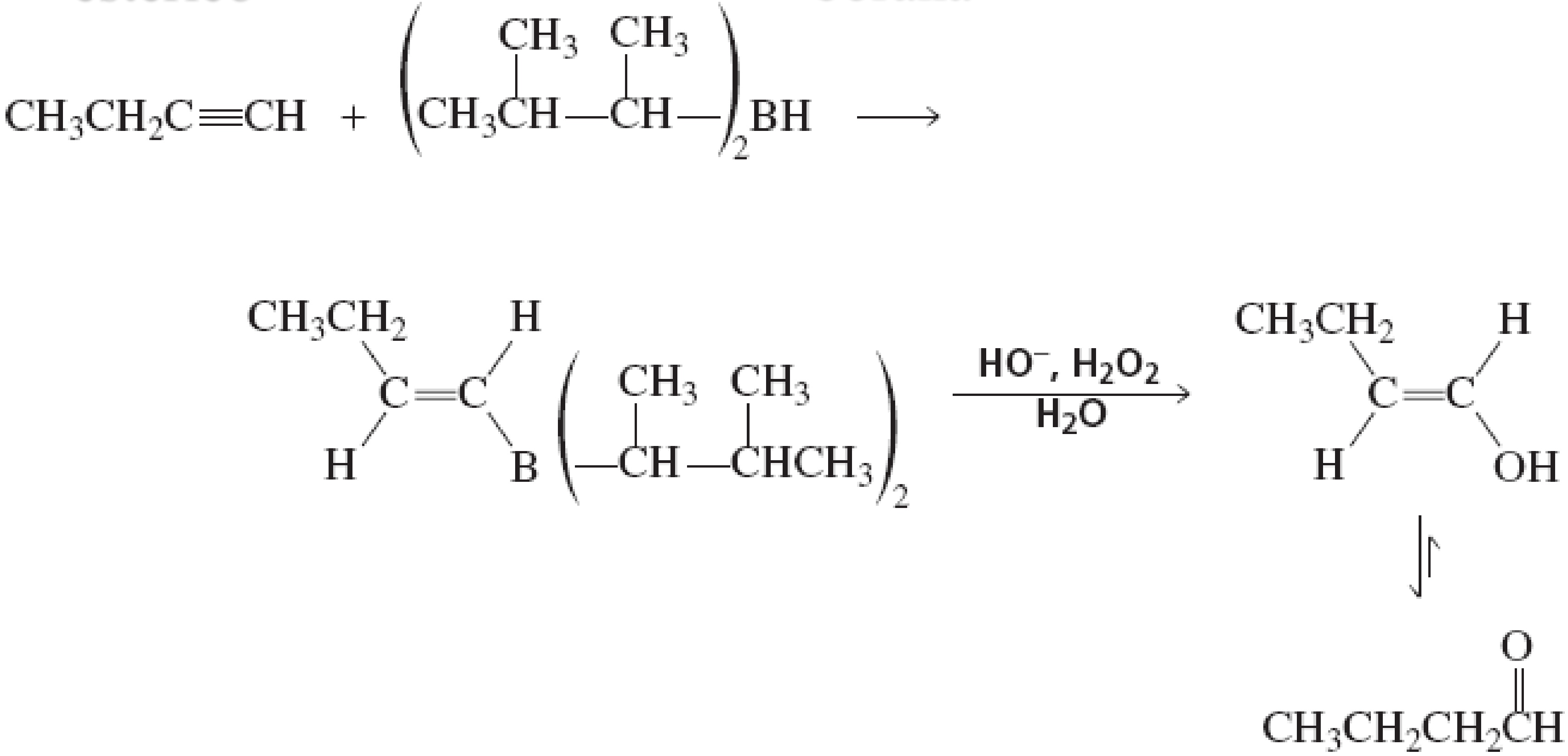
$$3\ CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$



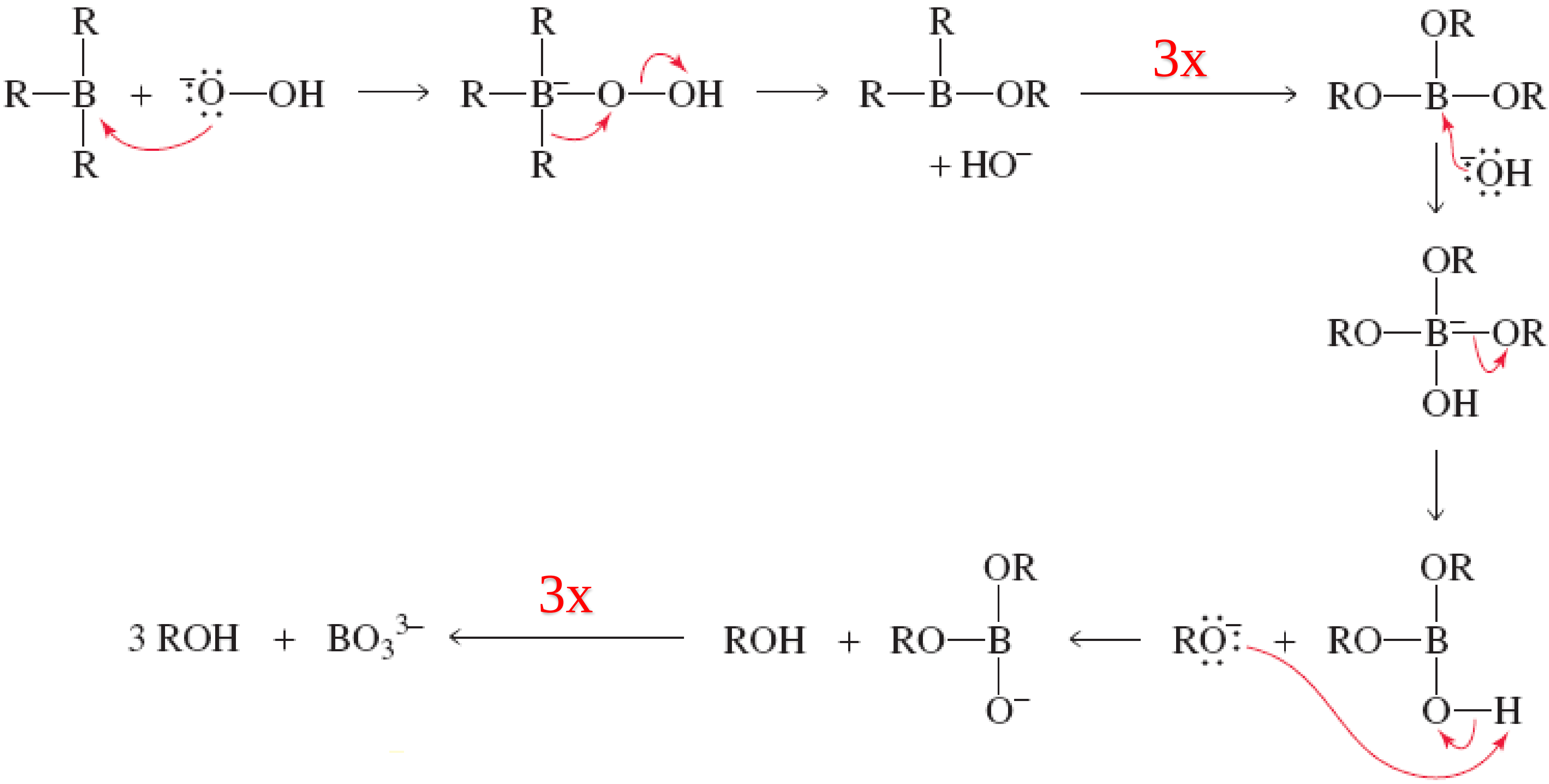
Mecanismo via estado de transição de anel de quatro membros

alcino terminal
sem impedimento
estérico

bis(1,2,-dimetilpropil)-
borana



Mecanismo de oxidação da borana



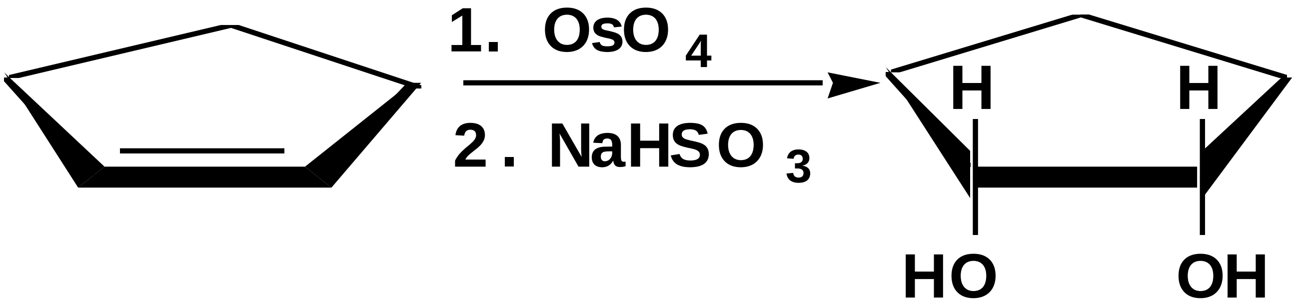
Oxidação/Redução

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

- 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

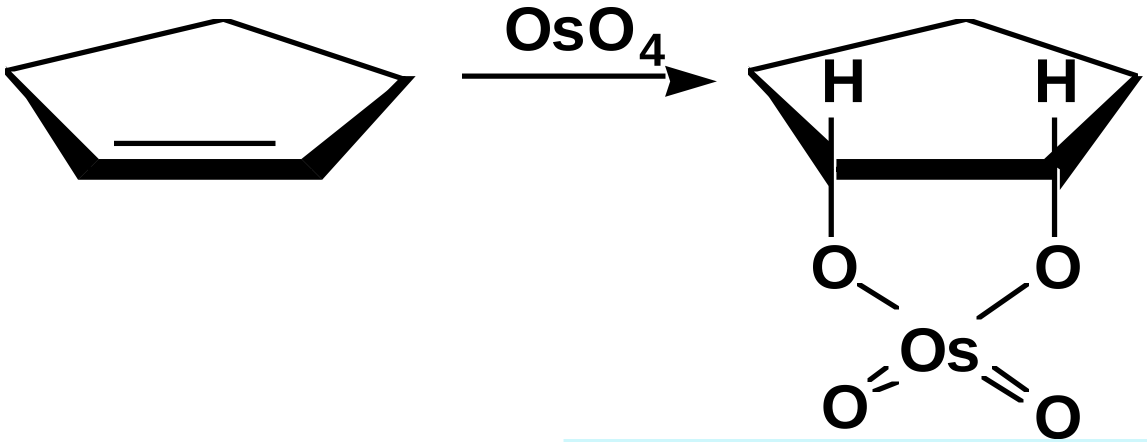
- A oxidação por OsO_4 converte um alceno em um glicol, um composto com grupos -OH em dois carbonos adjacentes
  - a oxidação é sin e estereoseletiva



Glicol cis

Oxidação com OsO_4

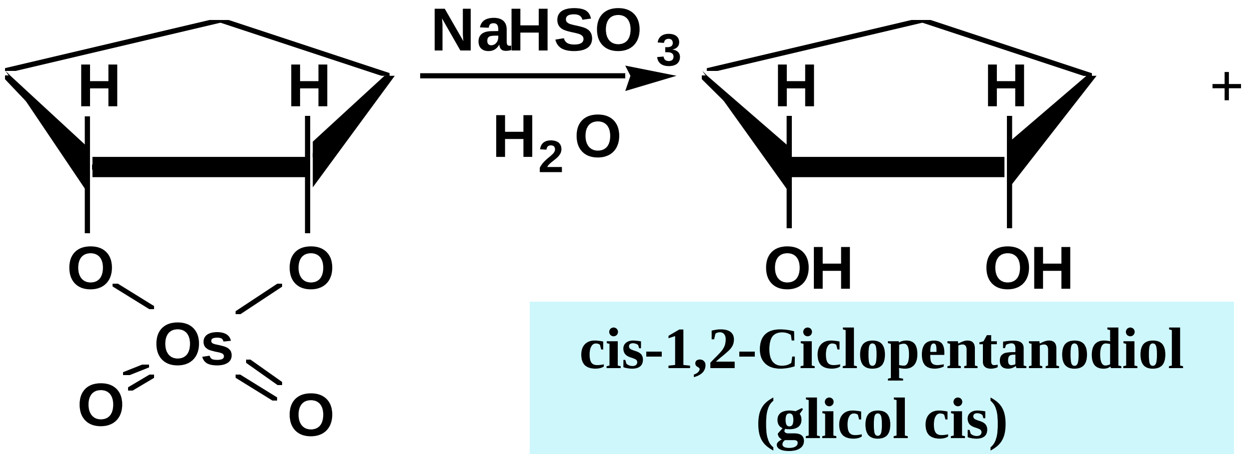
- O intermediário é um éster de ósmio cíclico, contendo um anel de 5 membros



Um osmato cíclico
(éster cíclico do ósmio)

Oxidação com OsO_4

- A redução do éster de ósmio com $NaHSO_3$ resulta em um glicol e em formas reduzidas (menor número de oxidação) do ósmio



Formas reduzidas do ósmio

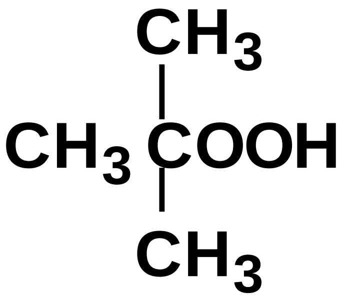
cis-1,2-Ciclopentanodiol
(glicol cis)

Oxidação com OsO_4

- O OsO_4 é caro e altamente tóxico
- Ele é utilizado em quantidades catalíticas, na presença de outros agentes oxidantes que reoxidam suas formas reduzidas e, assim, reciclam o OsO_4

HOOH

Peróxido de hidrogênio

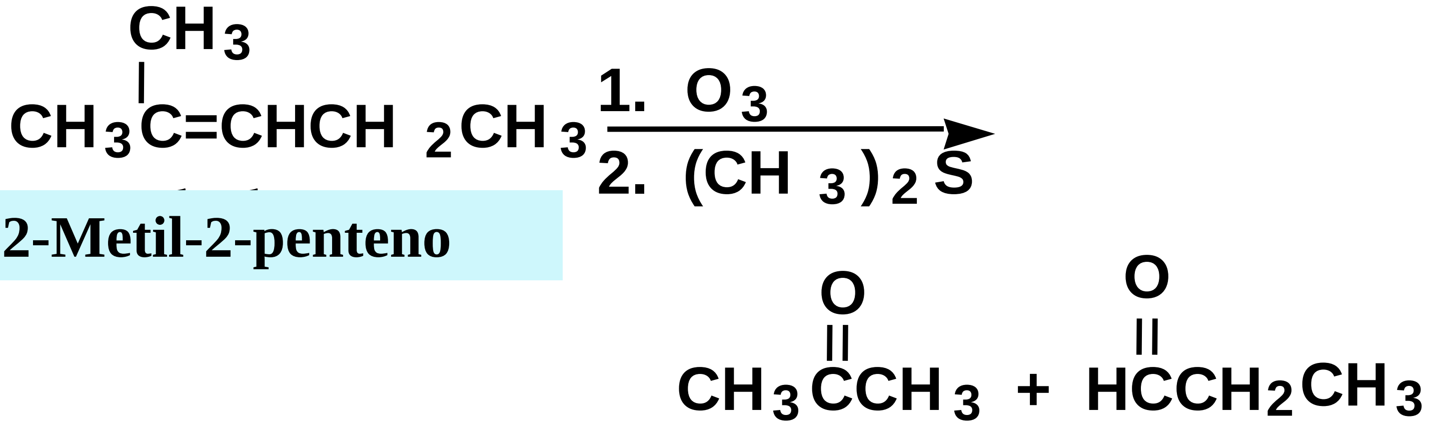


$$\begin{array}{c} CH_3 \\ | \\ CH_3\,\text{—}\,C\,\text{—}\,OOH \\ | \\ CH_3 \end{array}$$

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

Oxidação com O_3

- 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



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_3 \xrightarrow[2.\ (CH_3)_2S]{1.\ O_3} CH_3\overset{O}{\overset{||}{C}}CH_3 + H\overset{O}{\overset{||}{C}}CH_2CH_3$$

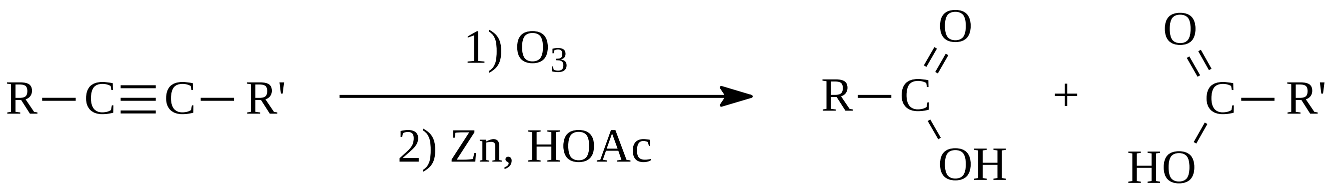
2-Metil-2-penteno

Propanona
(cetona)

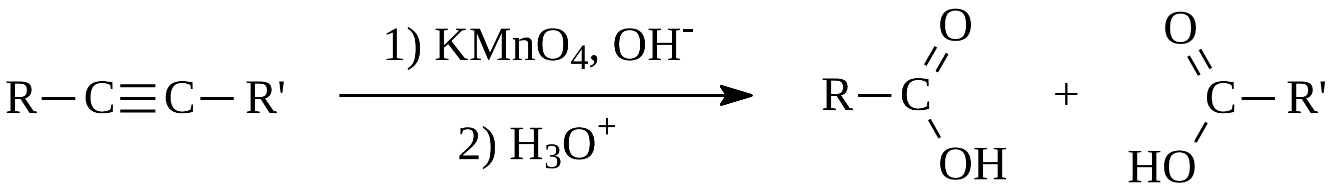
Propanal
(aldeído)

Quebra oxidativa

Reação de ozonólise

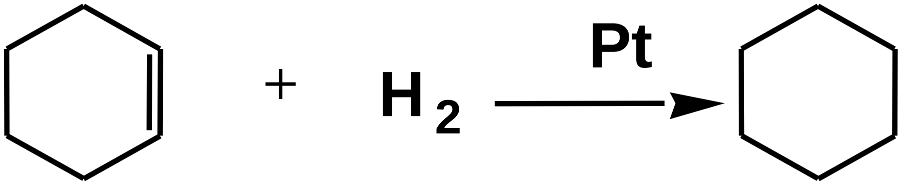


Reação com permanganato de potássio em meio alcalino



Redução de Alcenos

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



Ciclo-hexeno

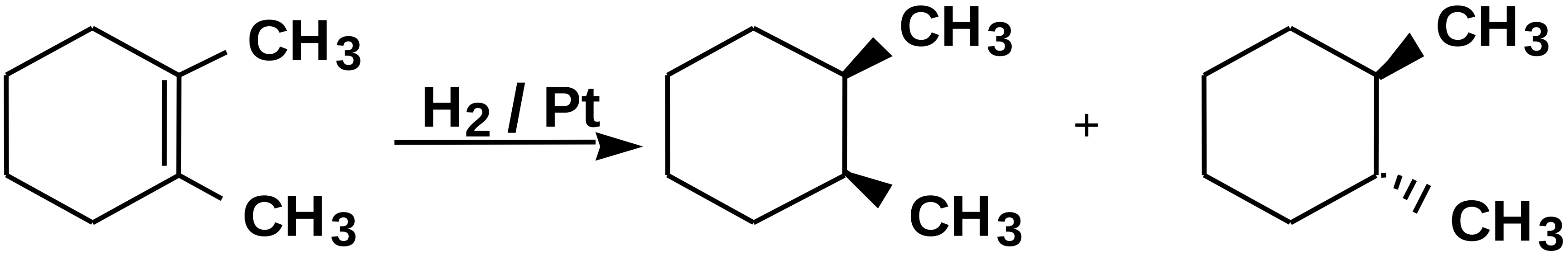
Ciclo-hexano

  - os catalisadores mais usados são Pt, Pd, Ru, e Ni

- O processo é denominado redução catalítica ou, alternativamente, hidrogenação catalítica

Redução de Alcenos

- O padrão de estereoseletividade mais comum é tipo sin



1,2-Dimetil-
ciclo-hexeno

70% a 85%
cis-1,2-Dimetil-
ciclo-hexano

30% a 15%
trans-1,2-Dimetil-
ciclo-hexano

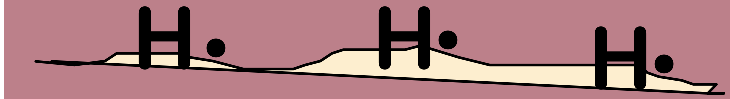
Redução de Alcenos

- 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

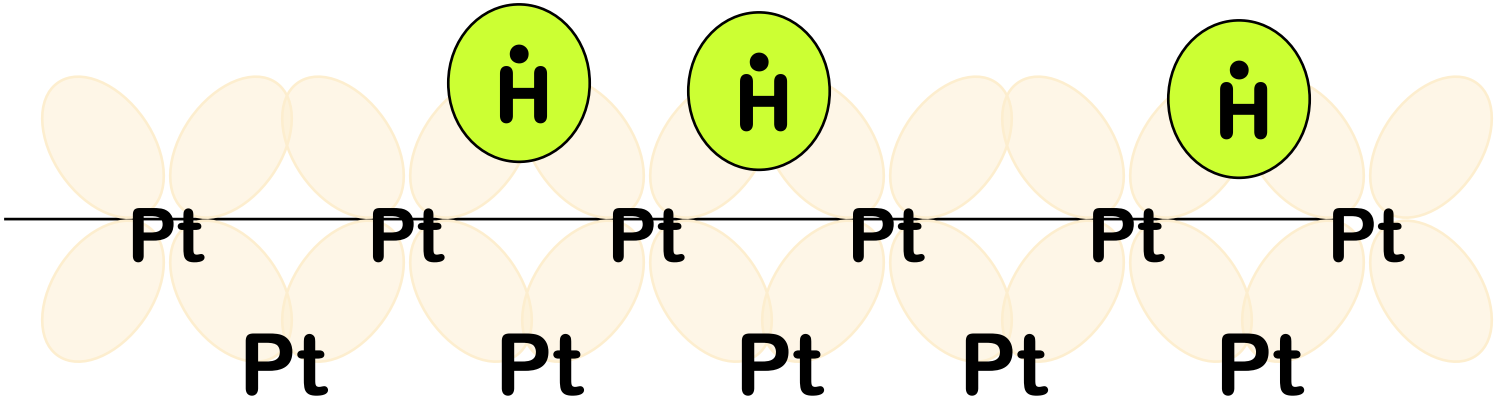
HYDROGEN ADSORBS ON THE SURFACE OF THE CATALYST

$$n\ H_2 \quad + \quad Pt \quad \longrightarrow \quad Pt(H\cdot)_{2n}$$

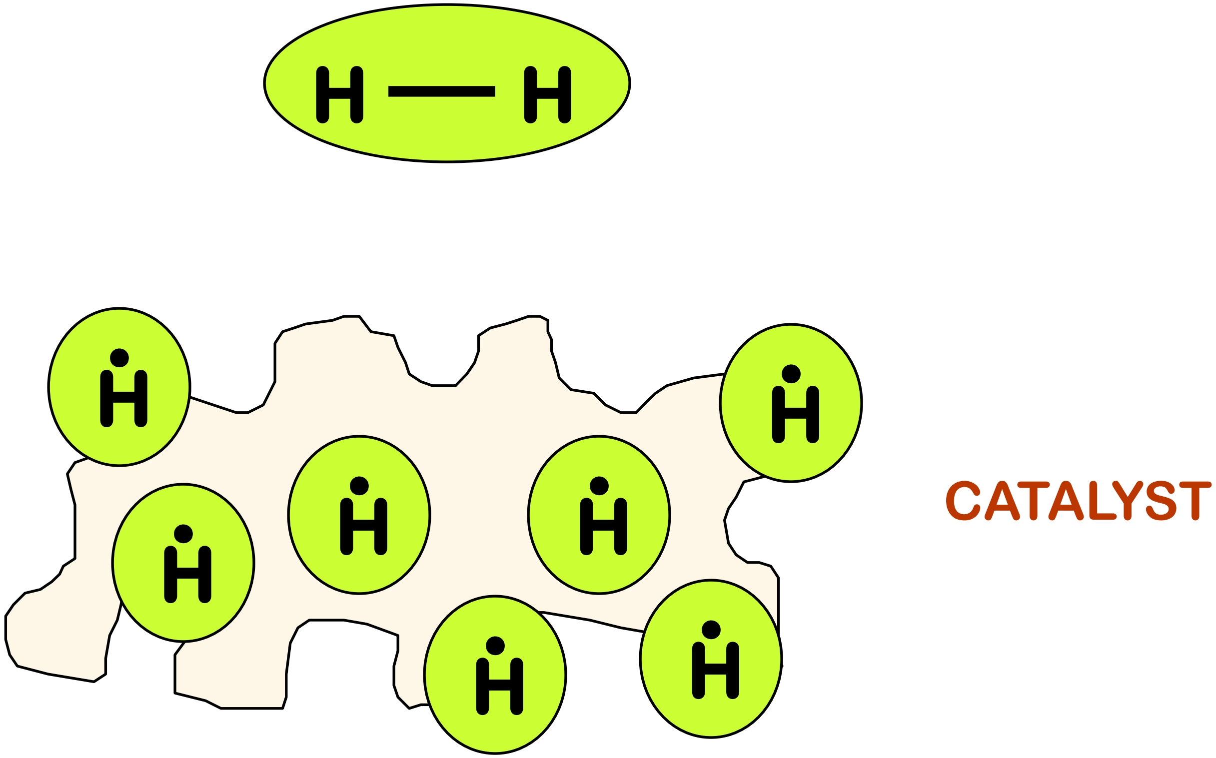
finely-divided particles dispersed in solution



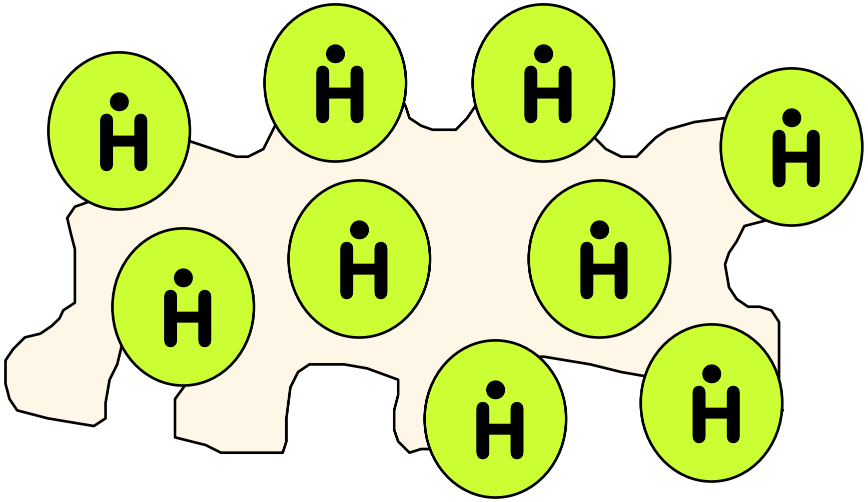
Hydrogen Adsorbed on Catalyst Surface



MECHANISM OF HYDROGENATION

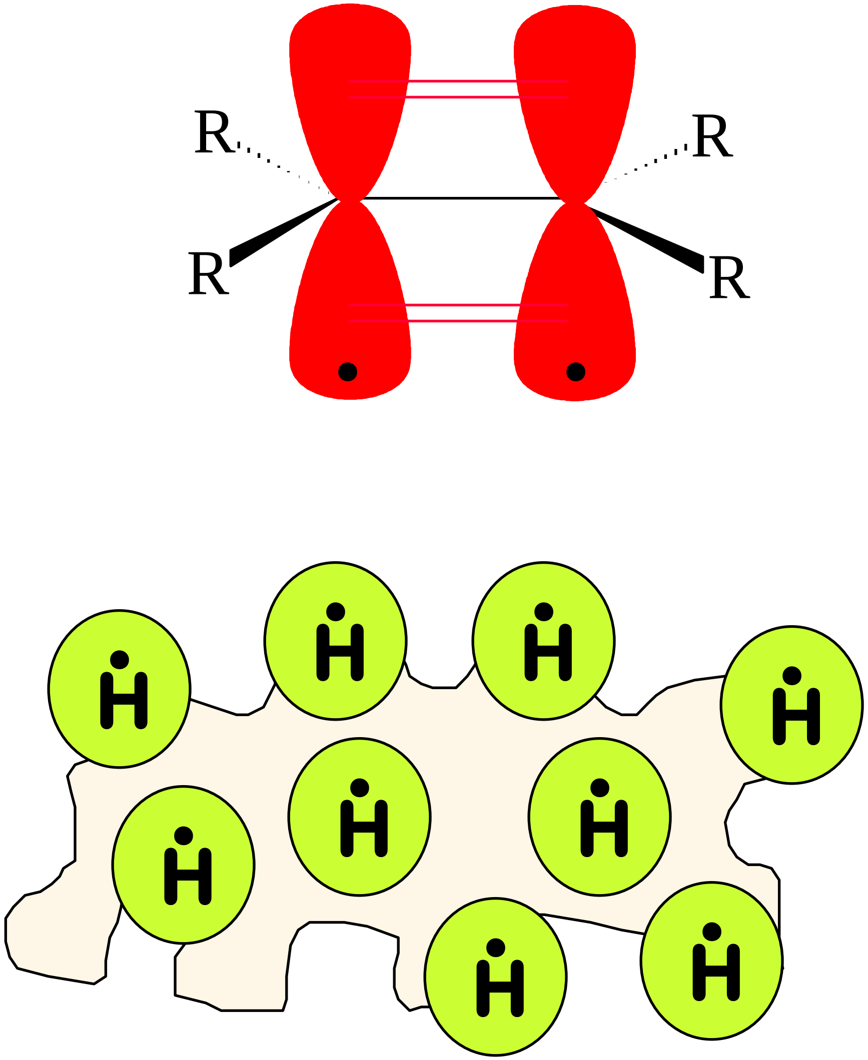


MECHANISM OF HYDROGENATION



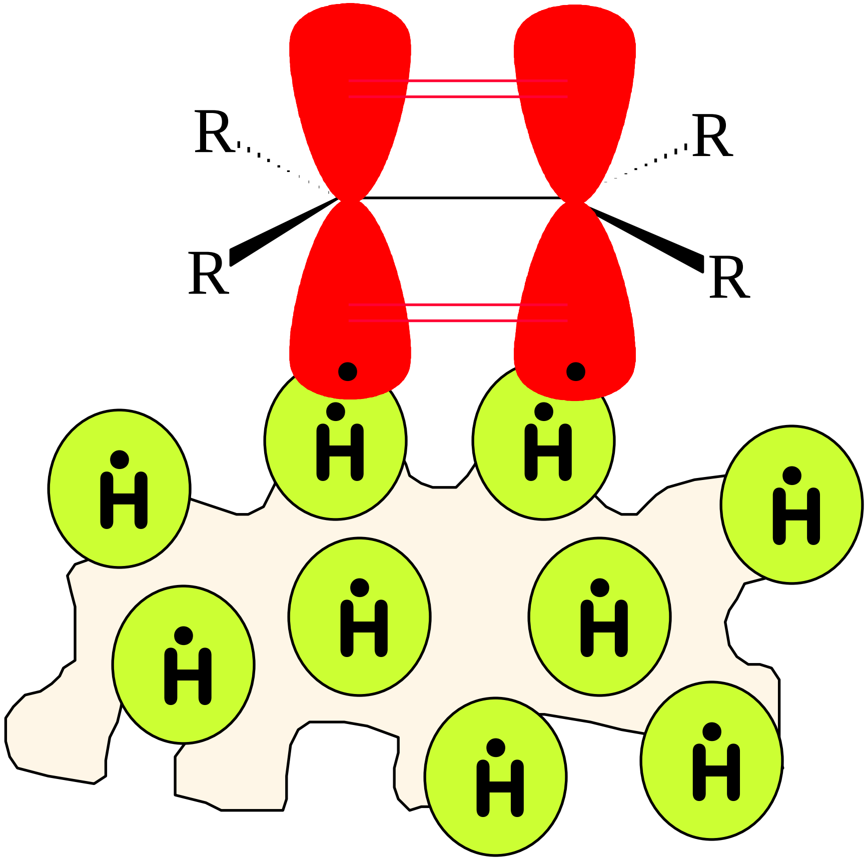
HYDROGEN
ADSORBS

MECHANISM OF HYDROGENATION



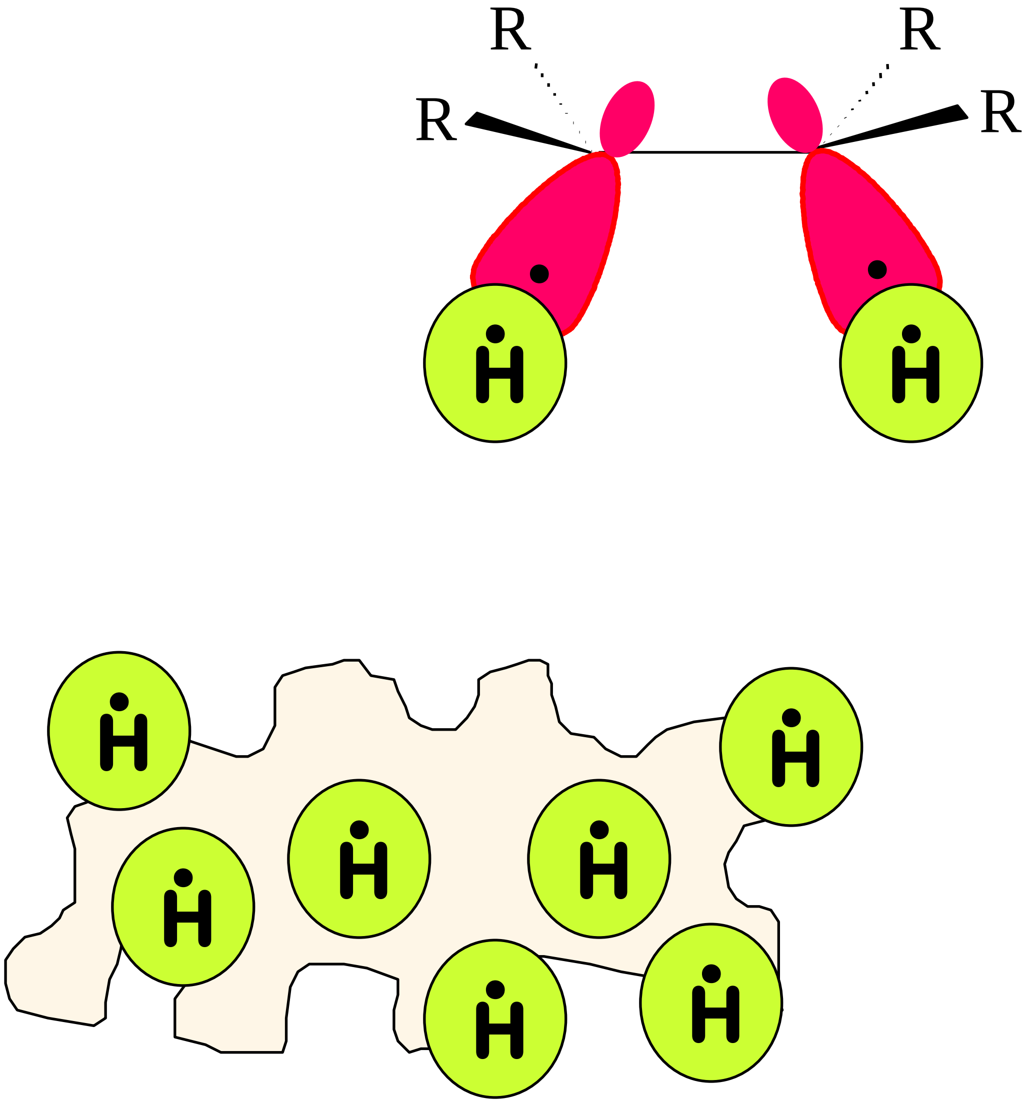
ALKENE
APPROACHES

MECHANISM OF HYDROGENATION



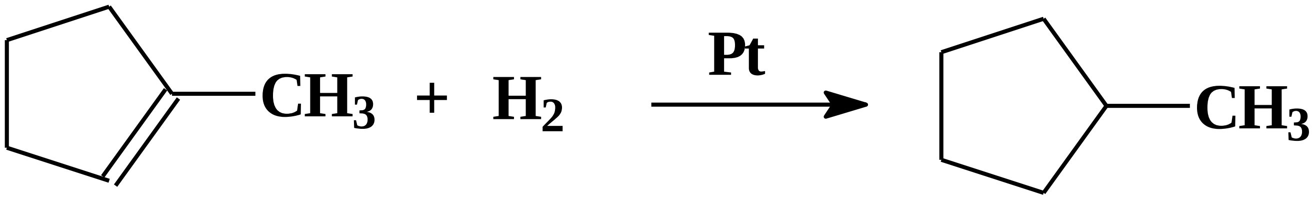
ALKENE PICKS UP
TWO HYDROGENS

MECHANISM OF HYDROGENATION

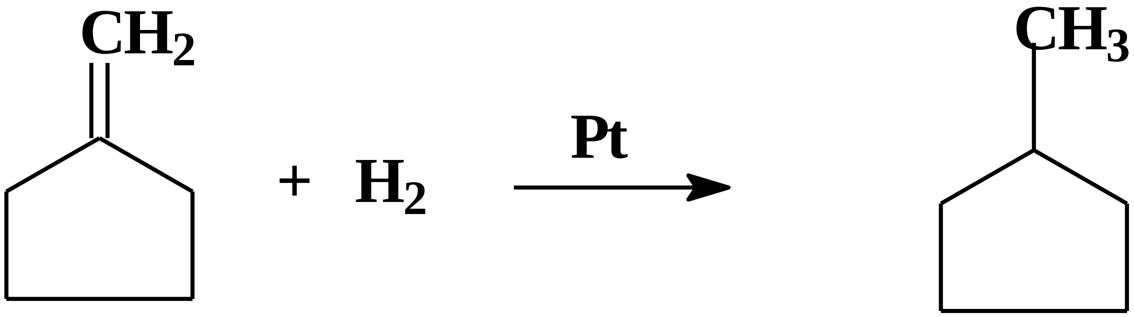


ALKANE IS FORMED

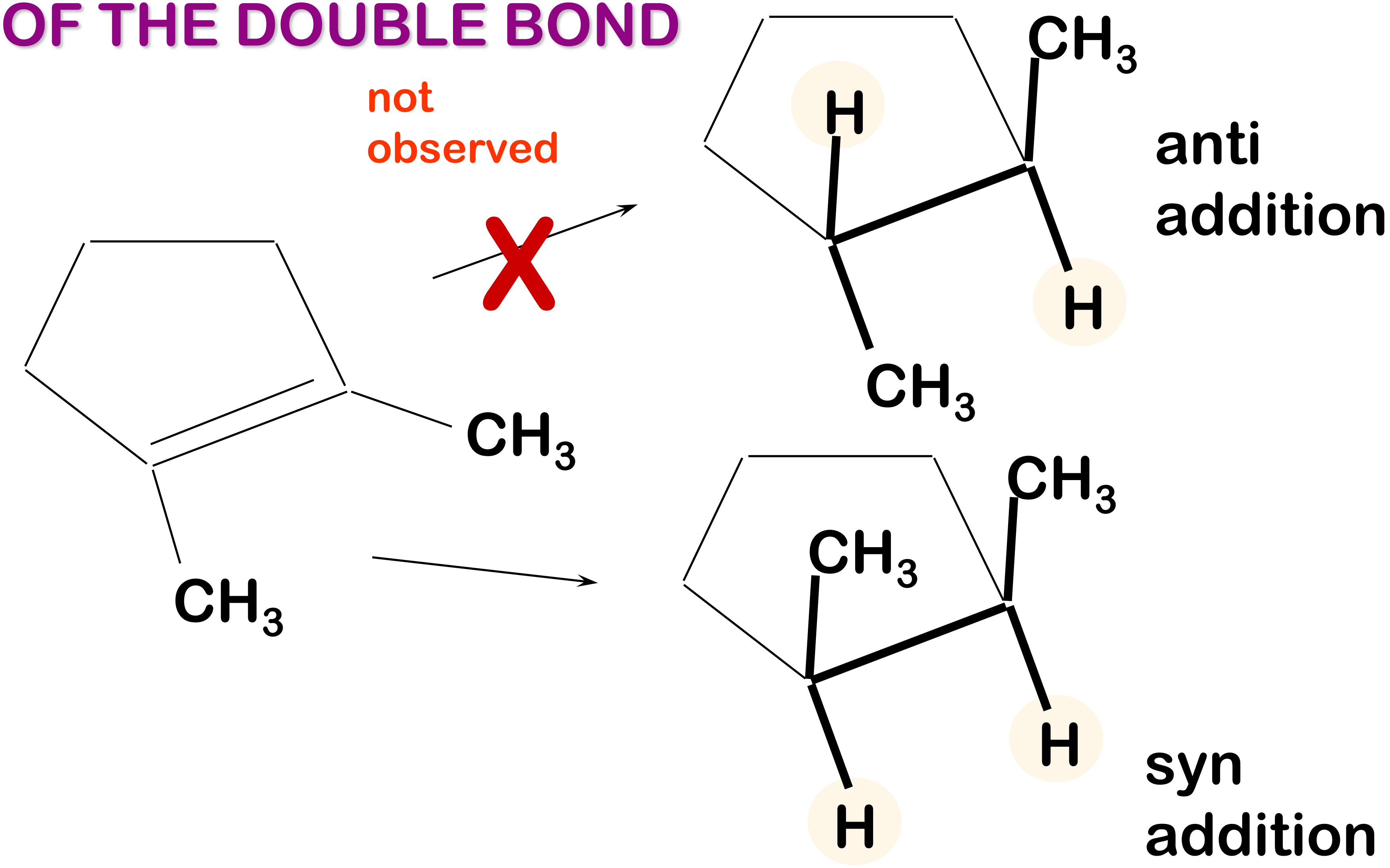
EXAMPLES



$$CH_3-CH=CH-CH_3 + H_2 \xrightarrow{Pt} CH_3-CH_2-CH_2-CH_3$$



BOTH HYDROGENS ADD TO THE SAME SIDE OF THE DOUBLE BOND



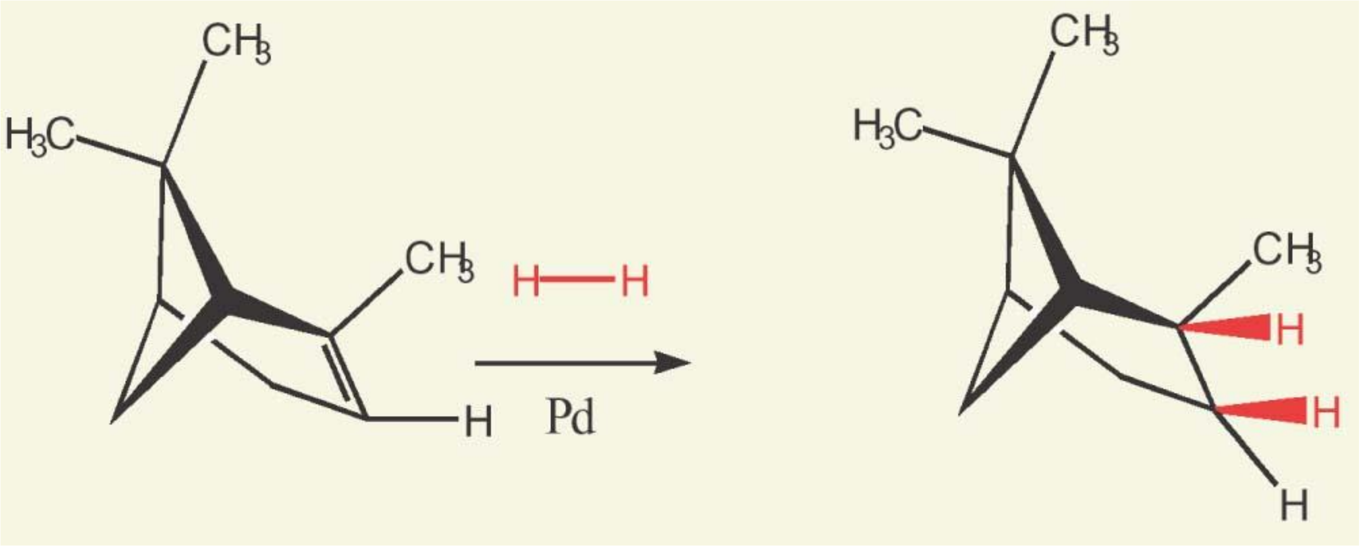
not observed

anti addition

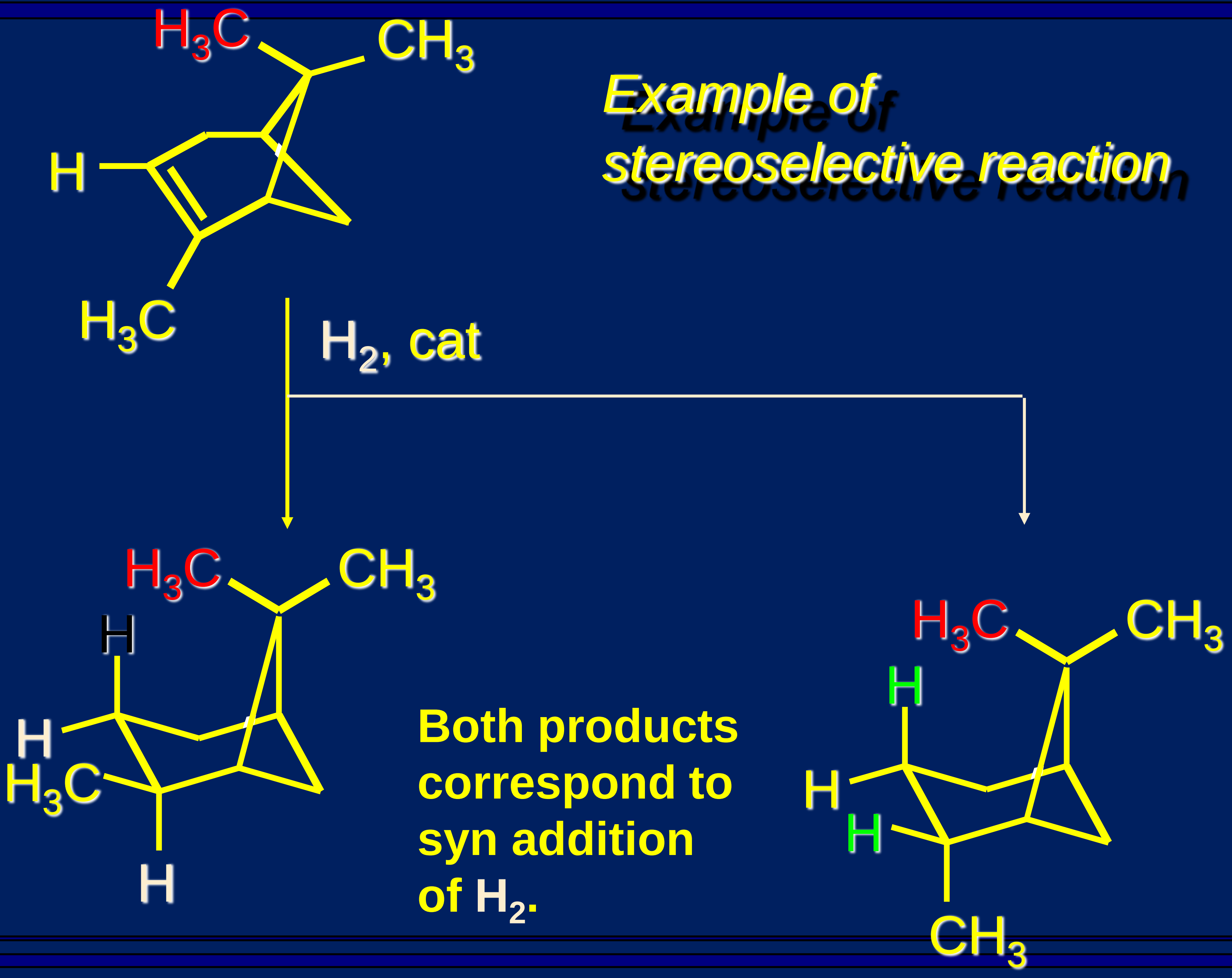
syn addition

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

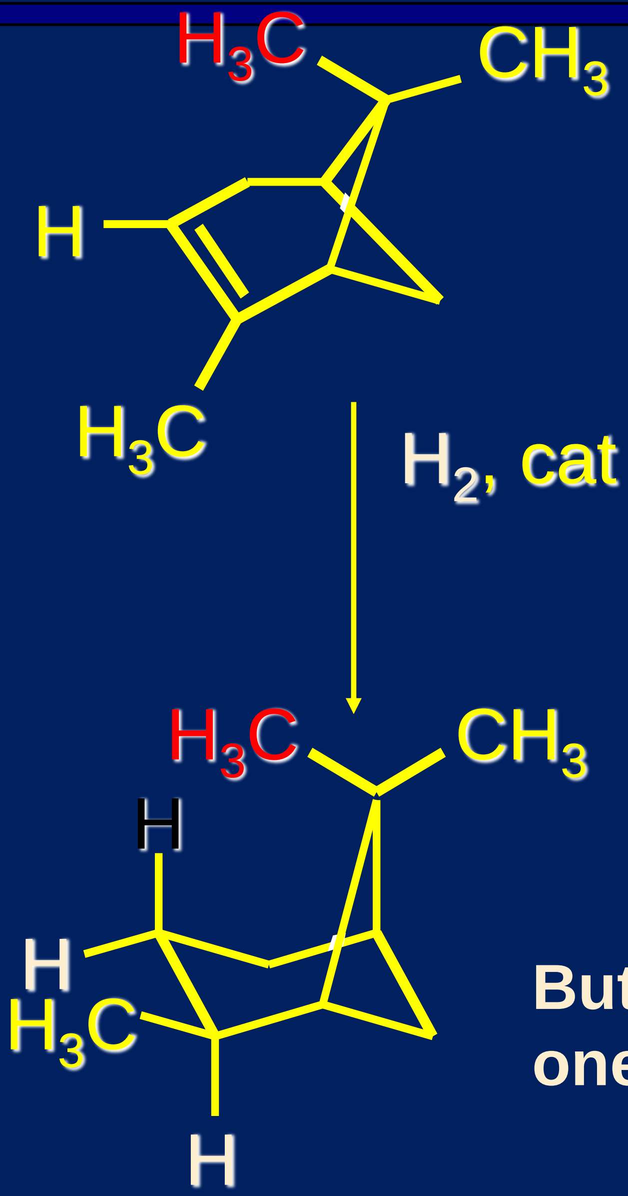


Example of stereoselective reaction



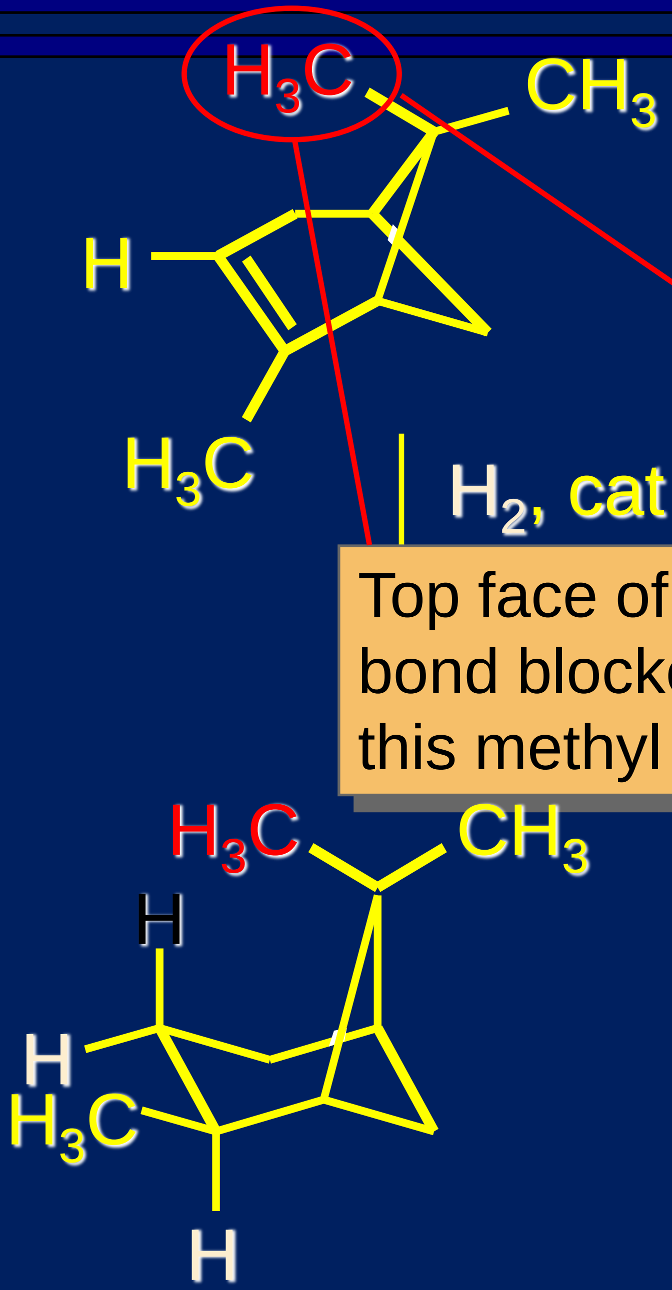
Both products correspond to syn addition of H_2.

Example of stereoselective reaction

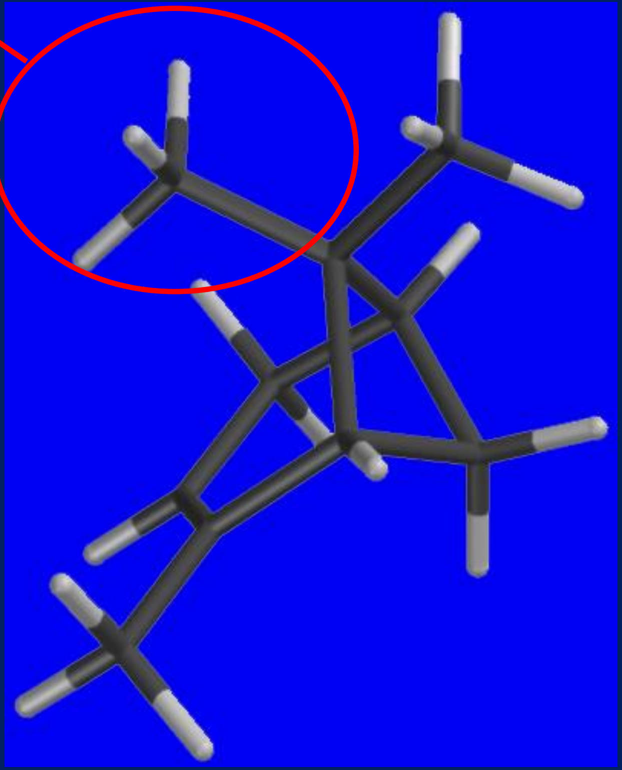


But only this one is formed.

Example of stereoselective reaction



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

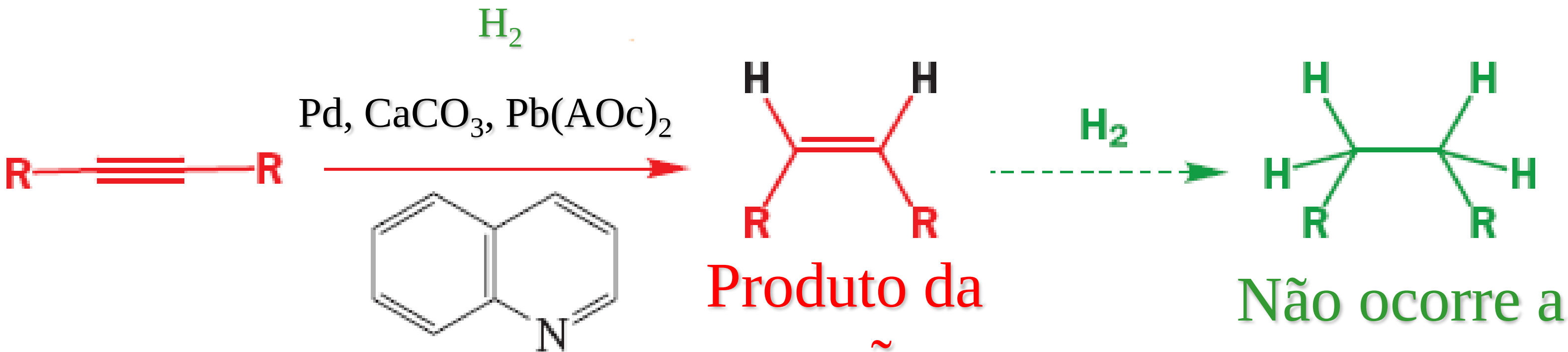
Na presença de Pt, Pd e Ni

$$CH_3CH_2C{\equiv}CH \xrightarrow[Pt/C]{H_2} CH_3CH_2CH{=}CH_2 \xrightarrow[Pt/C]{H_2} CH_3CH_2CH_2CH_3$$

alcino alceno alcano

A reação de hidrogenação ocorre na superfície do catalisador heterogêneo.

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



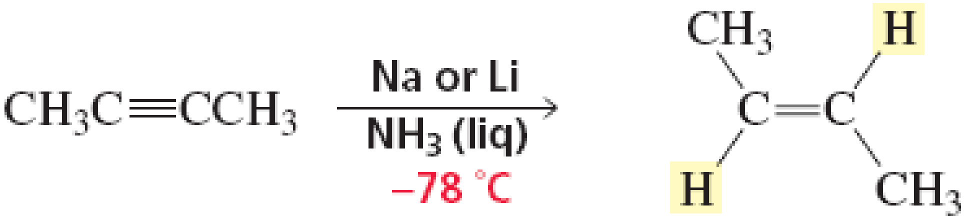
Catalisador de Lindlar

Produto da reação

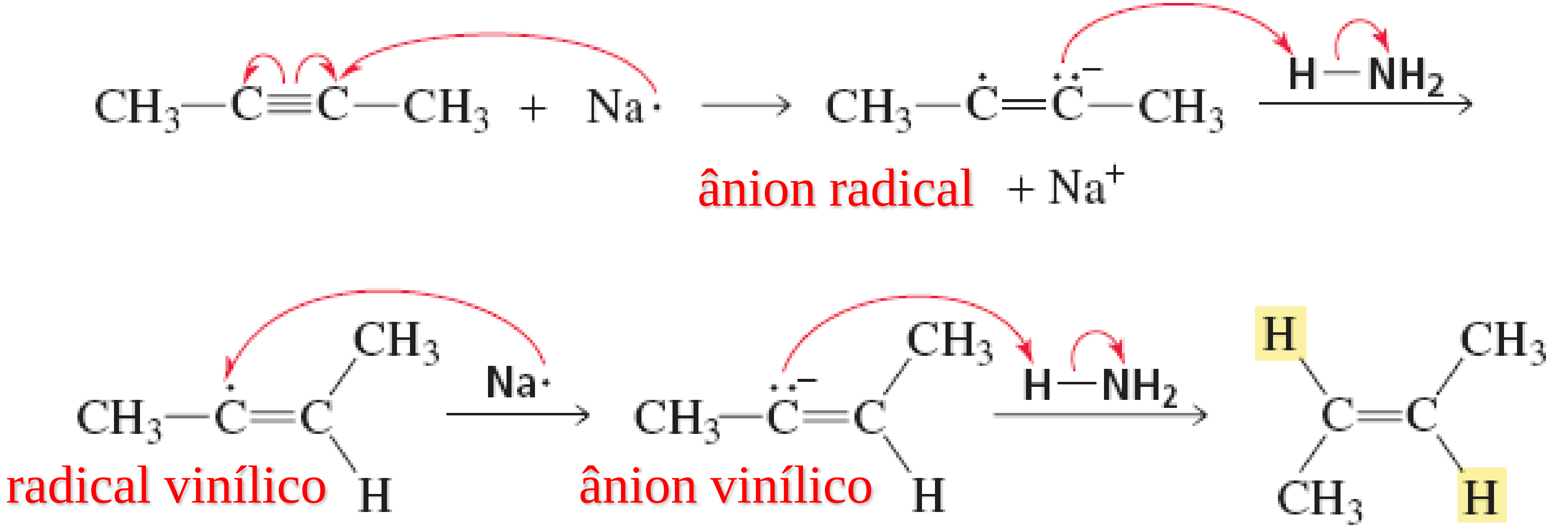
Não ocorre a formação do alcano

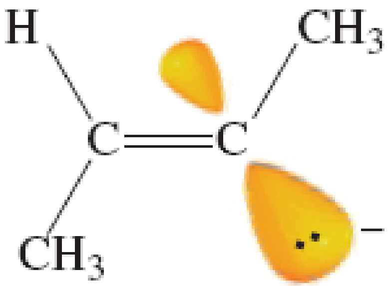
A adição sin de hidrogênio ocorre na superfície do catalisador heterogêneo.

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

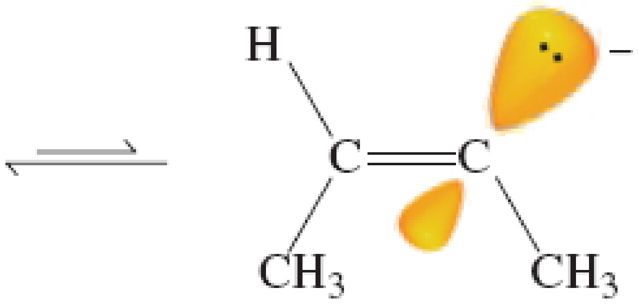


Mecanismo para adição anti de hidrogênio





ânion vinílico *trans*
(mais estável)



ânion vinílico *cis*
(menos estável)