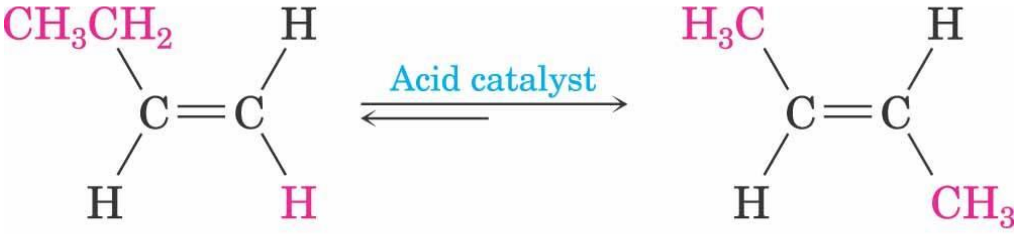
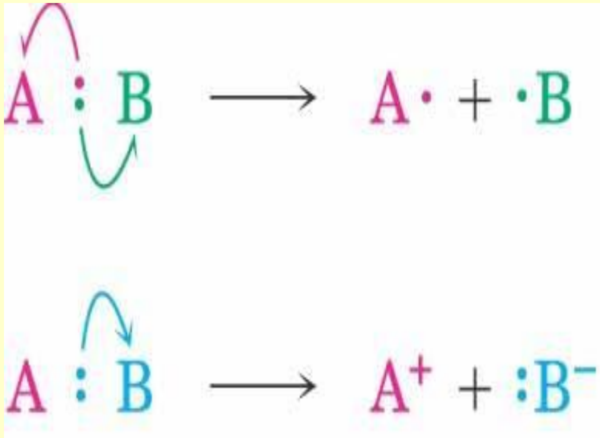
$Ag^{+}_{(aq)}$ + $Cl^{-}_{(aq)}$ $\longrightarrow$ AgCl(s)



1-Butene

2-Butene

Quebra de Ligações Covalentes



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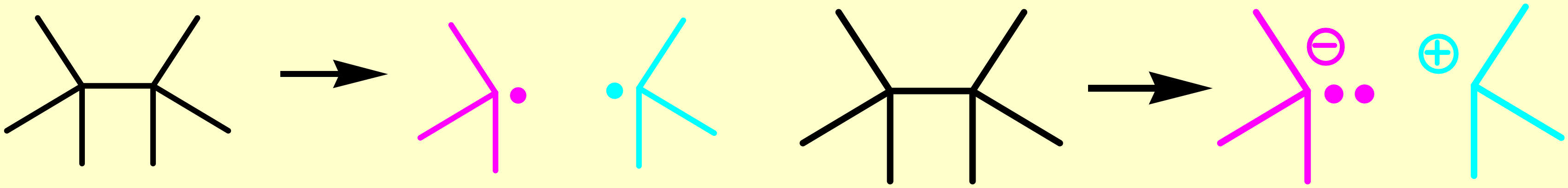
Quebra homolítca (Radical)

[um elétron permanece em cada fragmento]

Quebra heterolítca (Polar)
[dois elétrons permanecem com um dos fragmentos]



Formação de Ligações Covalentes

Formação homogênica (Radical)

[um elétron proveniente de cada fragmento]

Formação heterogênica (Polar)
[dois elétrons provenientes de um dos fragmentos]

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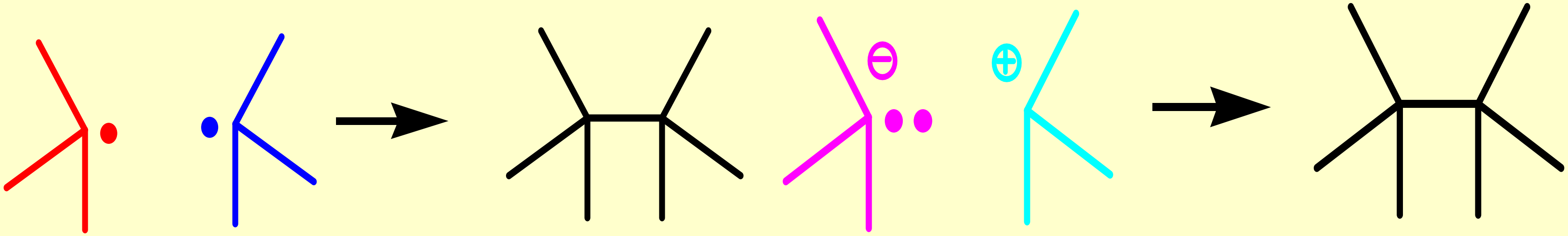
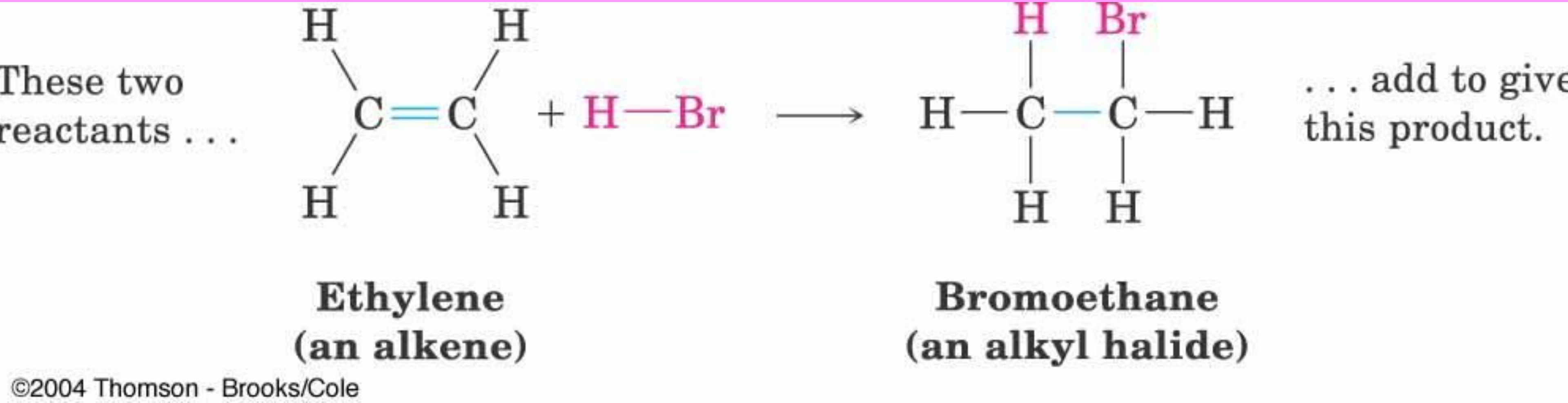


Tipos de Reações Orgânicas

- 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.

Adição



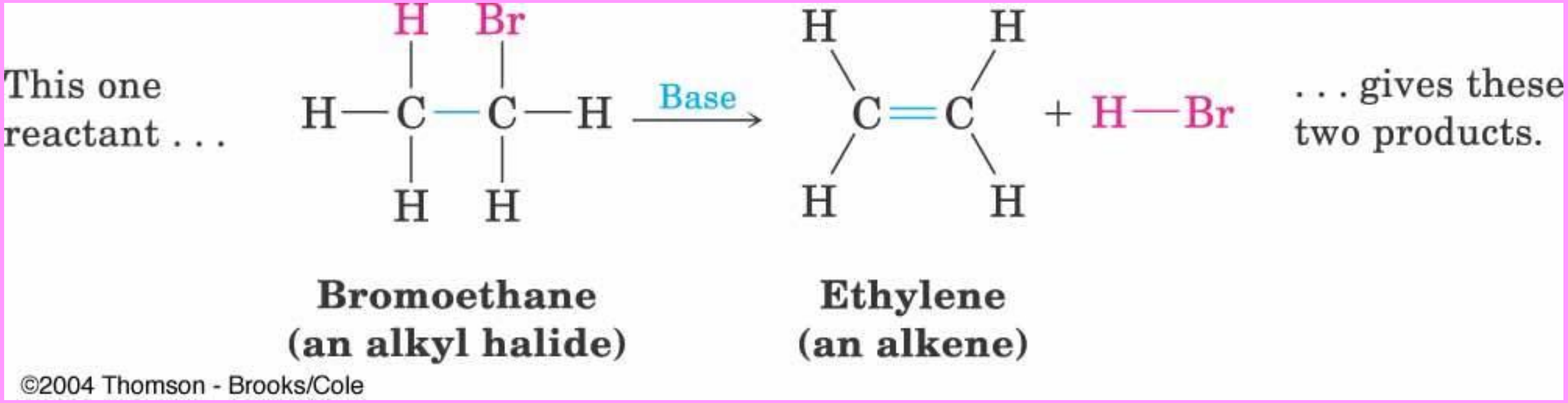
These two reactants . . .

. . . add to give this product.

Ethylene
(an alkene)

Bromoethane
(an alkyl halide)

Eliminação



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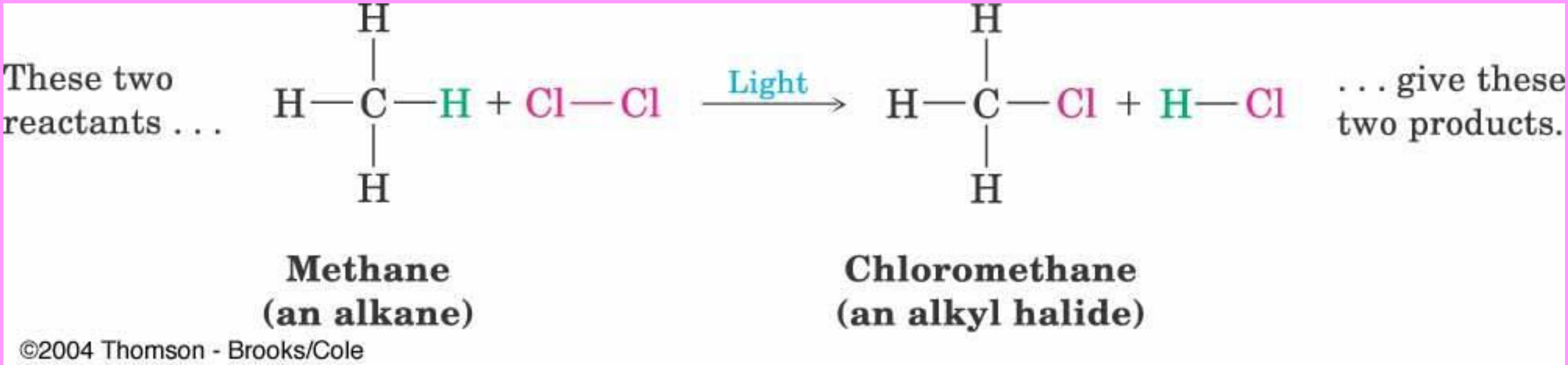
Substituição



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H + Cl-Cl \xrightarrow{\text{Light}} H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Cl + H-Cl$$

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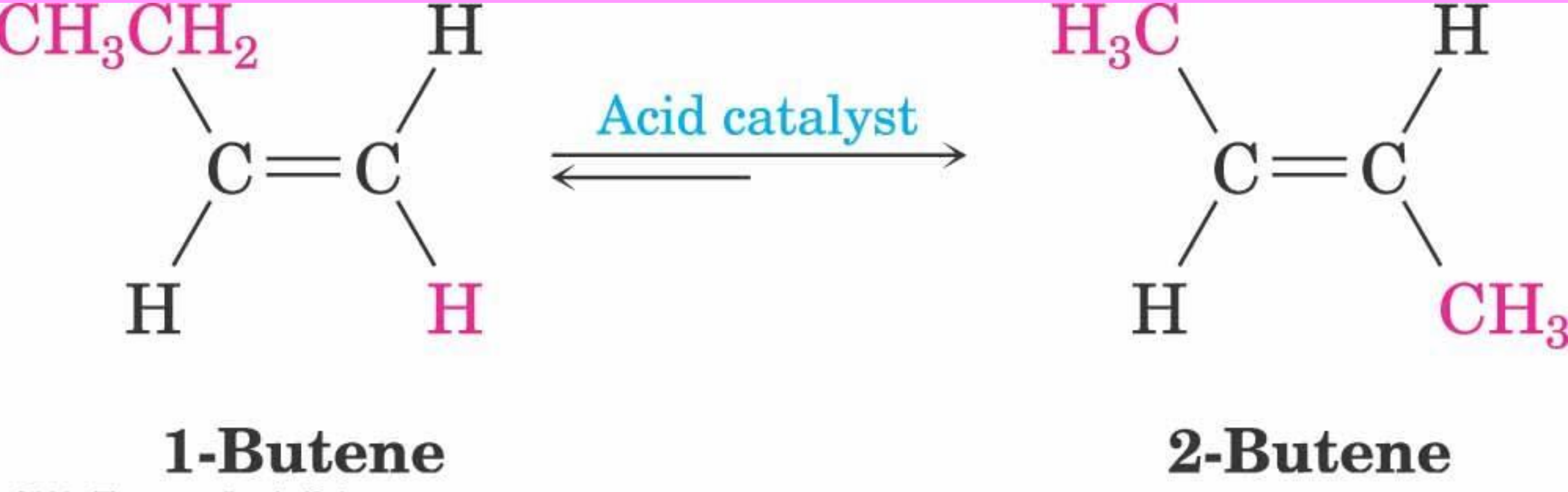
Rearranjo

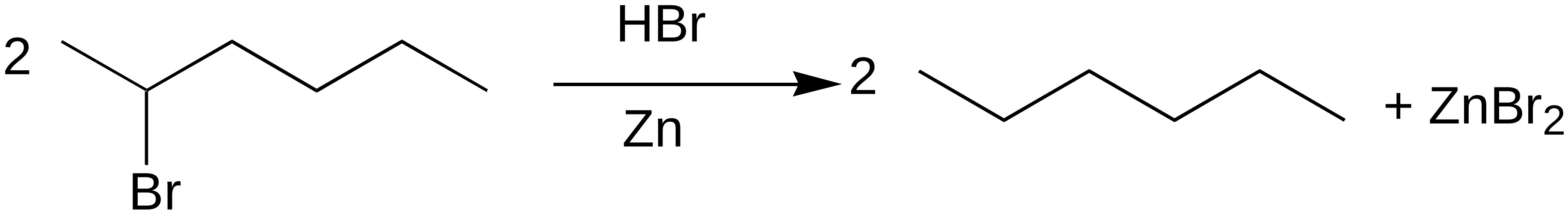


1-Butene

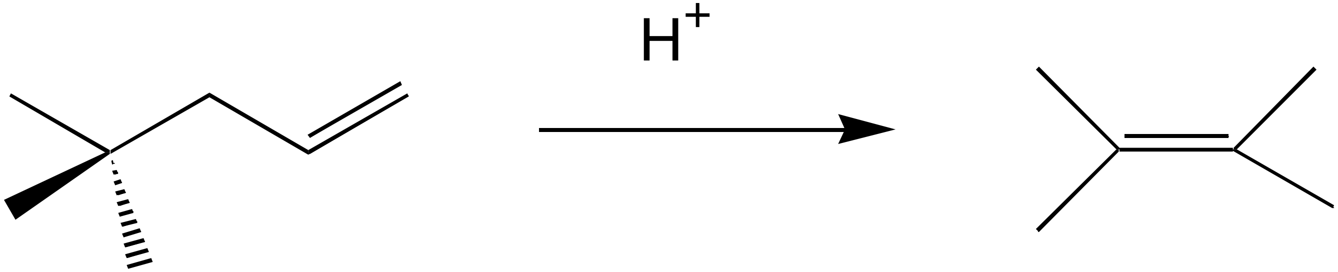
2-Butene

Equações para serem classificadas:

1)



2)



Problema:

- O estudo de reações químicas e sua aplicação constituem o cerne da química orgânica.

- Devido ao grande número de reagentes que podem ser empregados, a memorização da vasta gama de reações possíveis é uma tarefa inviável.

Caminho:

- Como se descrevem os caminhos das reações orgânicas?

- Que fatores devem ser considerados?

- As reações orgânicas podem ser agrupadas considerando seus **mecanismos** e os intermediários envolvidos.

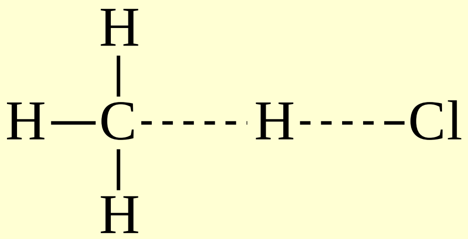
Mecanismo:

- uma rota passo a passo que conduz dos reagentes aos produtos, mostrando quais ligações são quebradas, quais se formam e a ordem desses eventos.

- inclui estruturas de todos reagentes, intermediários e produtos, além de flechas curvas mostrando o movimento dos elétrons.

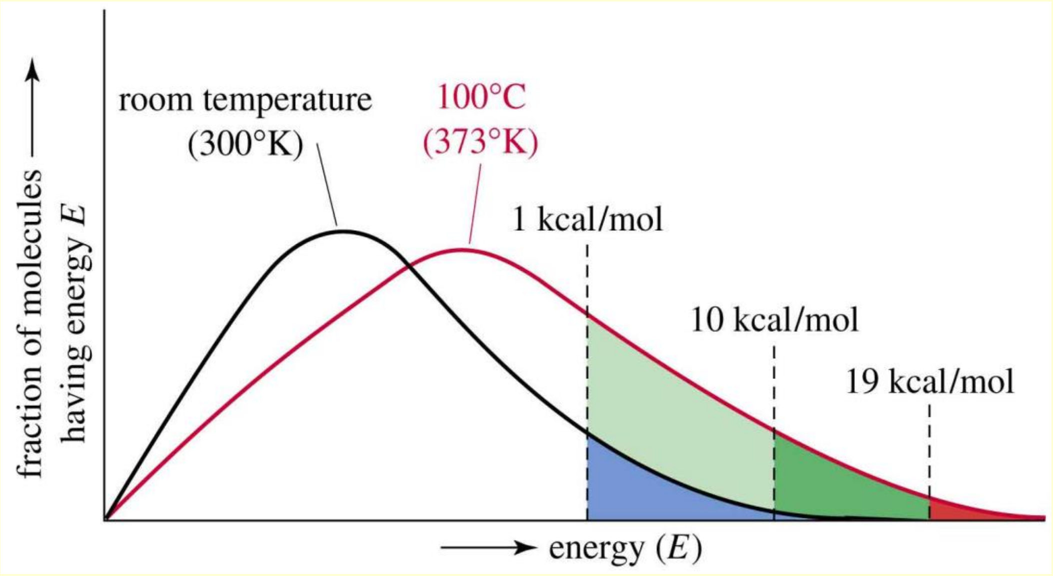
Energia de Ativação

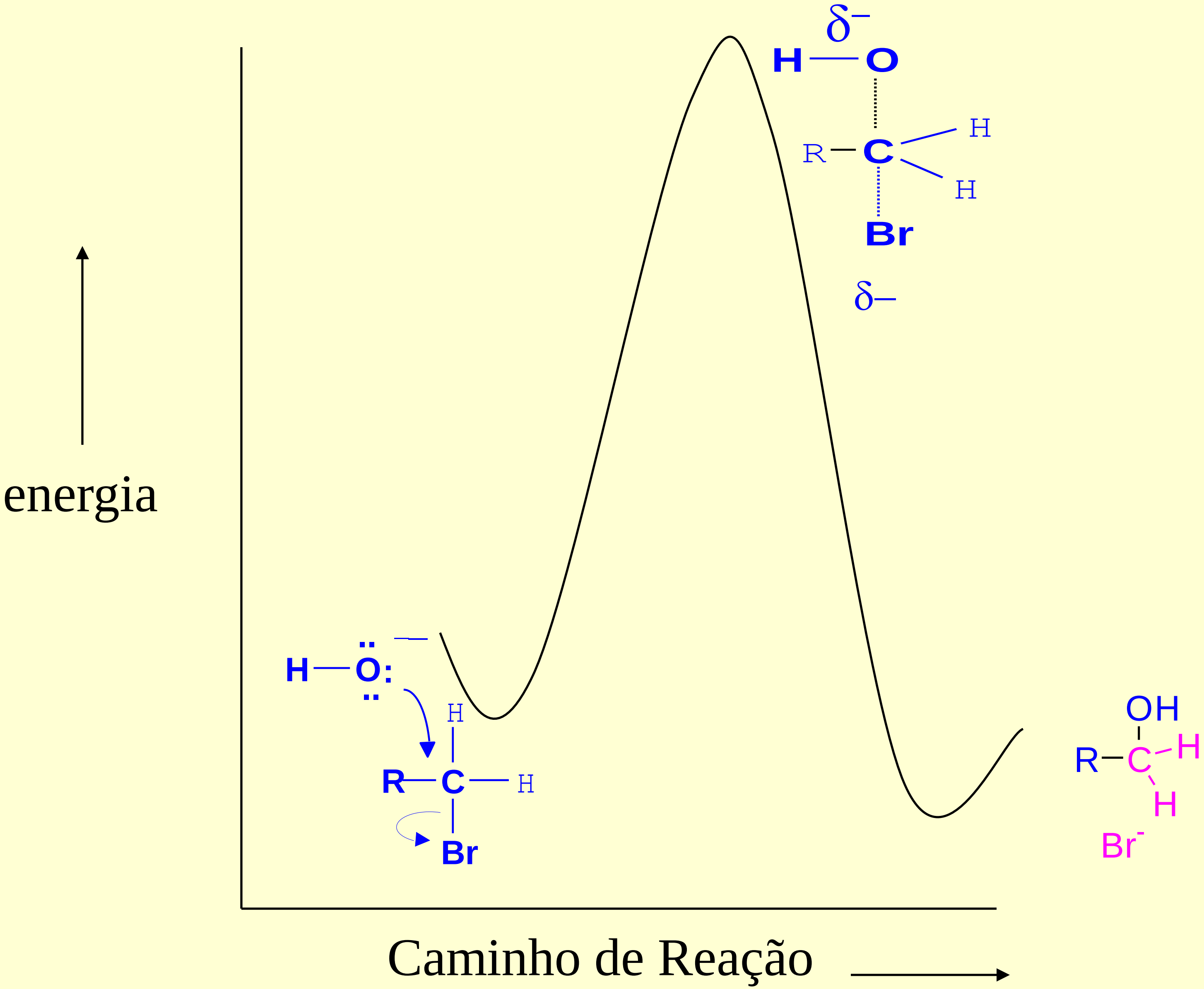
- Energia mínima requerida para atingir o estado de transição

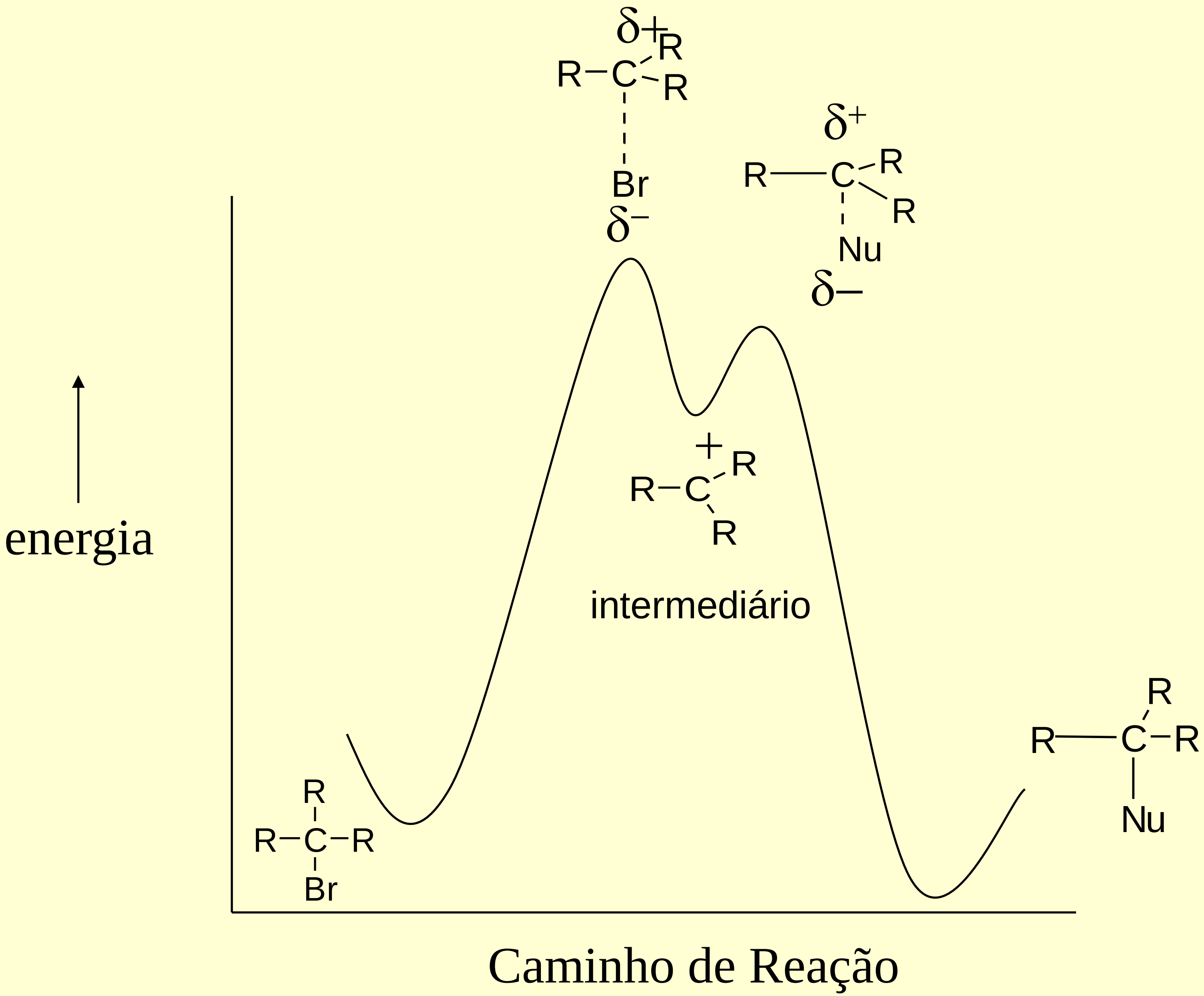


$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{-----}H\text{-----}Cl}$$

- A temperaturas elevadas, um número maior de moléculas adquirem a energia requerida.




energia
Caminho de Reação
H—Ö:⁻
R—C—H
H
Br
δ−
H—O
R—C
H
H
Br
δ−
OH
R—C—H
H
Br⁻



intermediário

energia

Caminho de Reação

Intermediários Reativos de Carbono mais Comuns

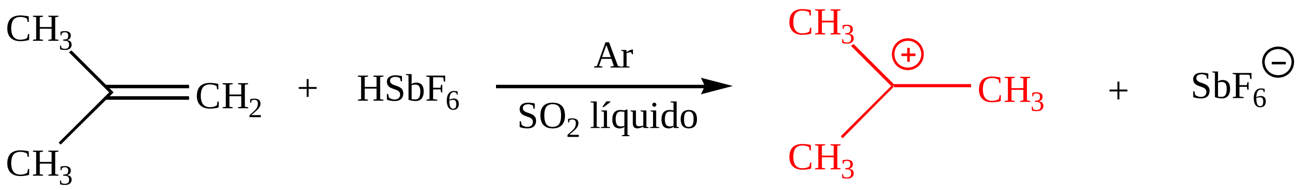
- Carbocátions
- Radicais Livres
- Carbânions
- Carbenos

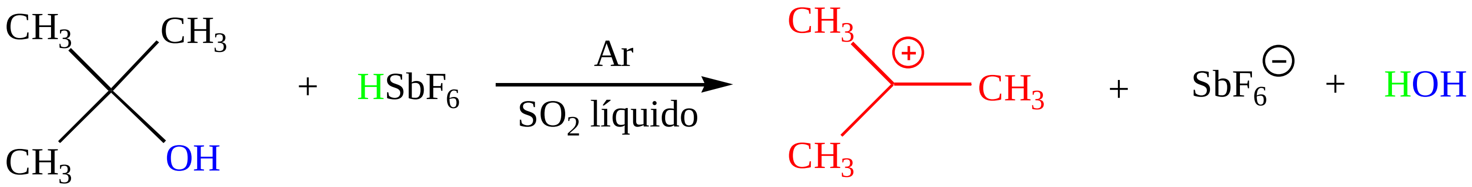
$$HF + HF \xrightarrow[\text{SO}_2\text{ líquido}]{\text{Ar}} H^{\oplus} + F{-}H\cdots F^{\ominus}$$

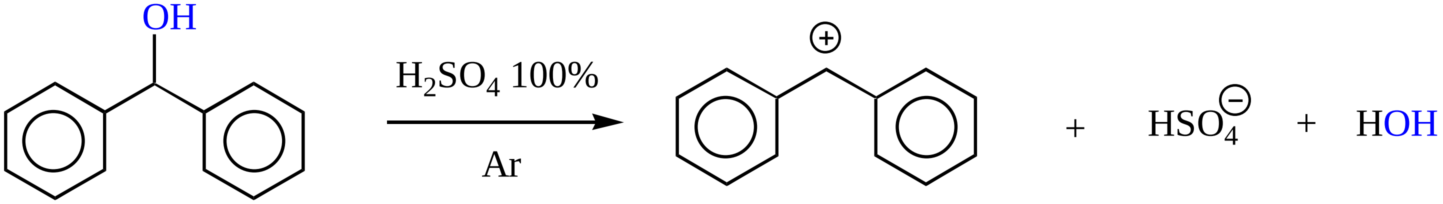
$$HF + SbF_5 \xrightarrow[\text{SO}_2\text{ líquido}]{\text{Ar}} H^{\oplus} + SbF_6^{\ominus}$$

Ácido Hexafluoroestíbico
(um Superácido)

George A. Olah Nobel 1994

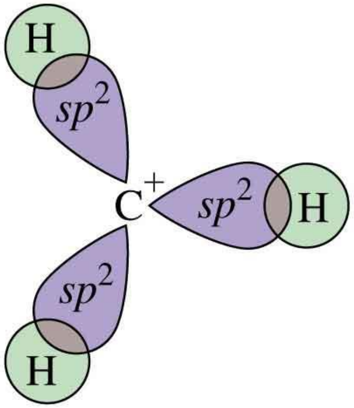




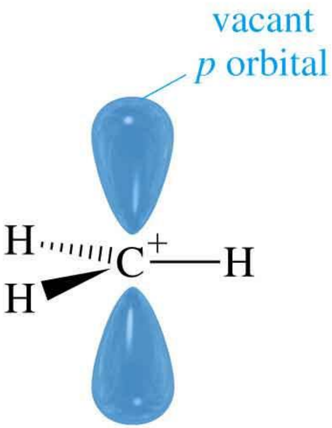


Estrutura do Carbocátion

- O Carbono tem 6 elétrons, carga positiva.
- O Carbon encontra-se hibridizado *sp*^{2} com um orbital *p* livre.



top view



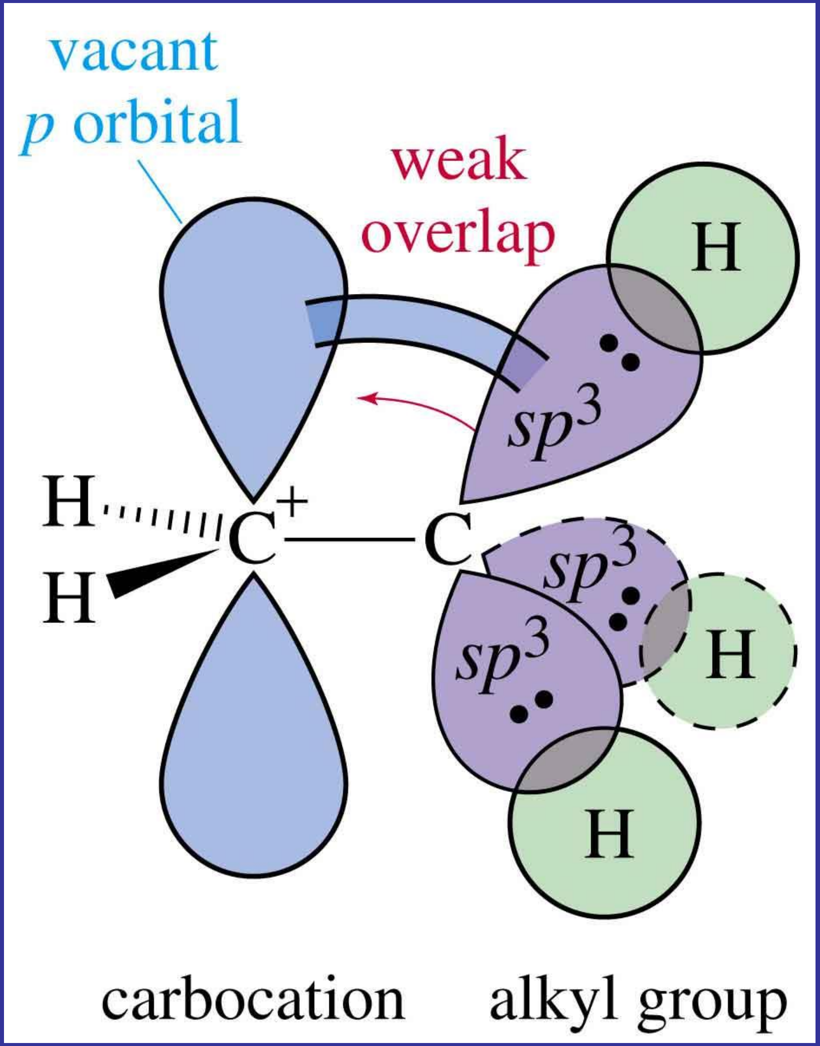
side view

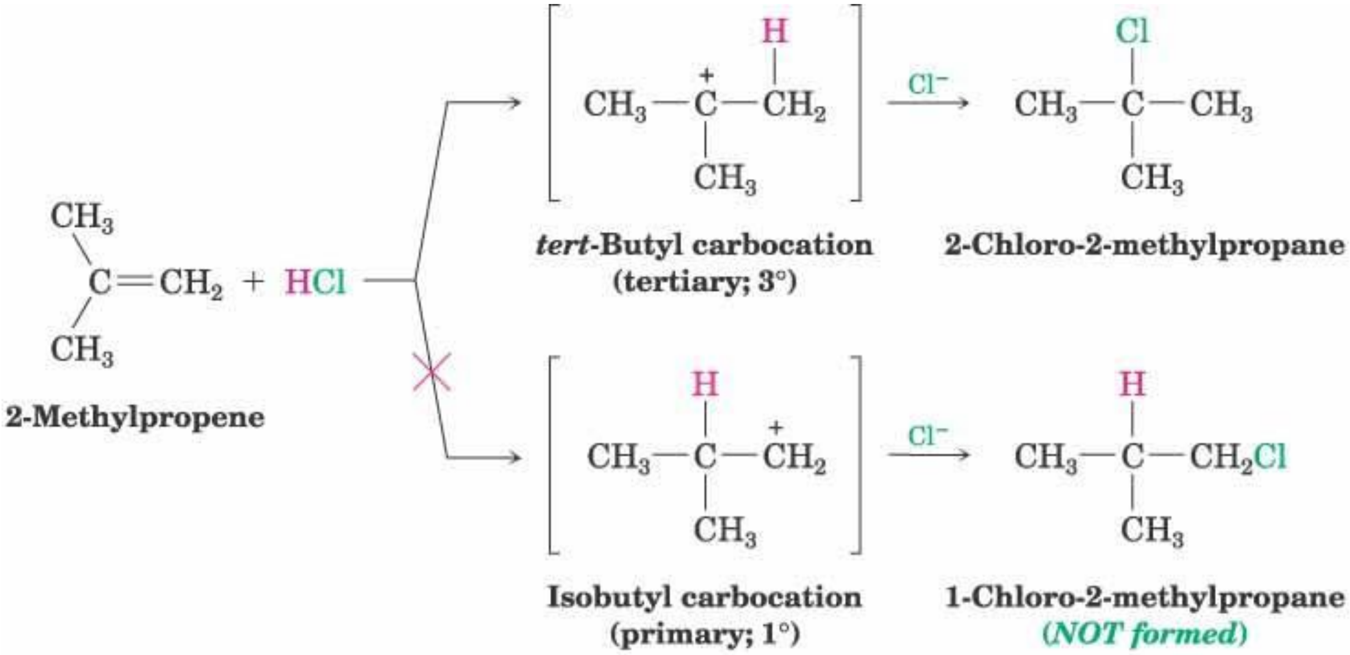
Estabilidade do Carbocátion

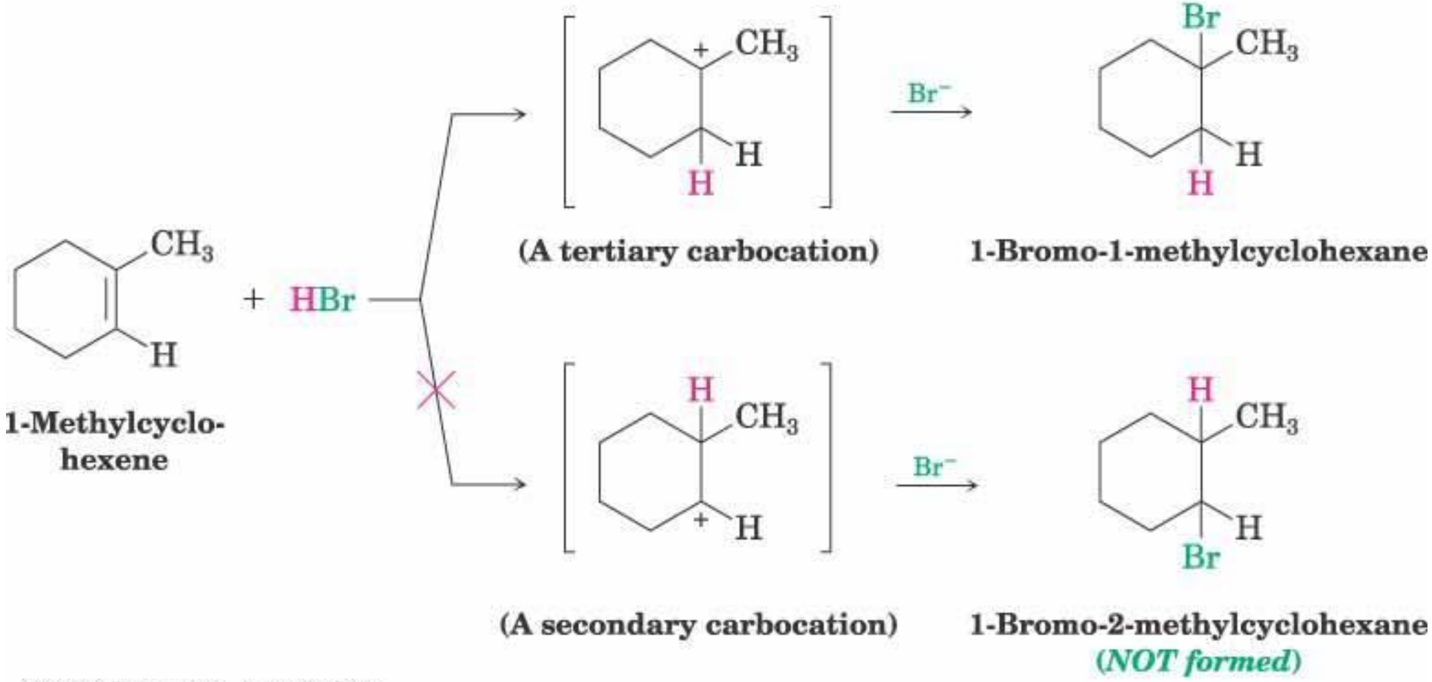
- Estabilizado pelos substituintes de 2 maneiras:

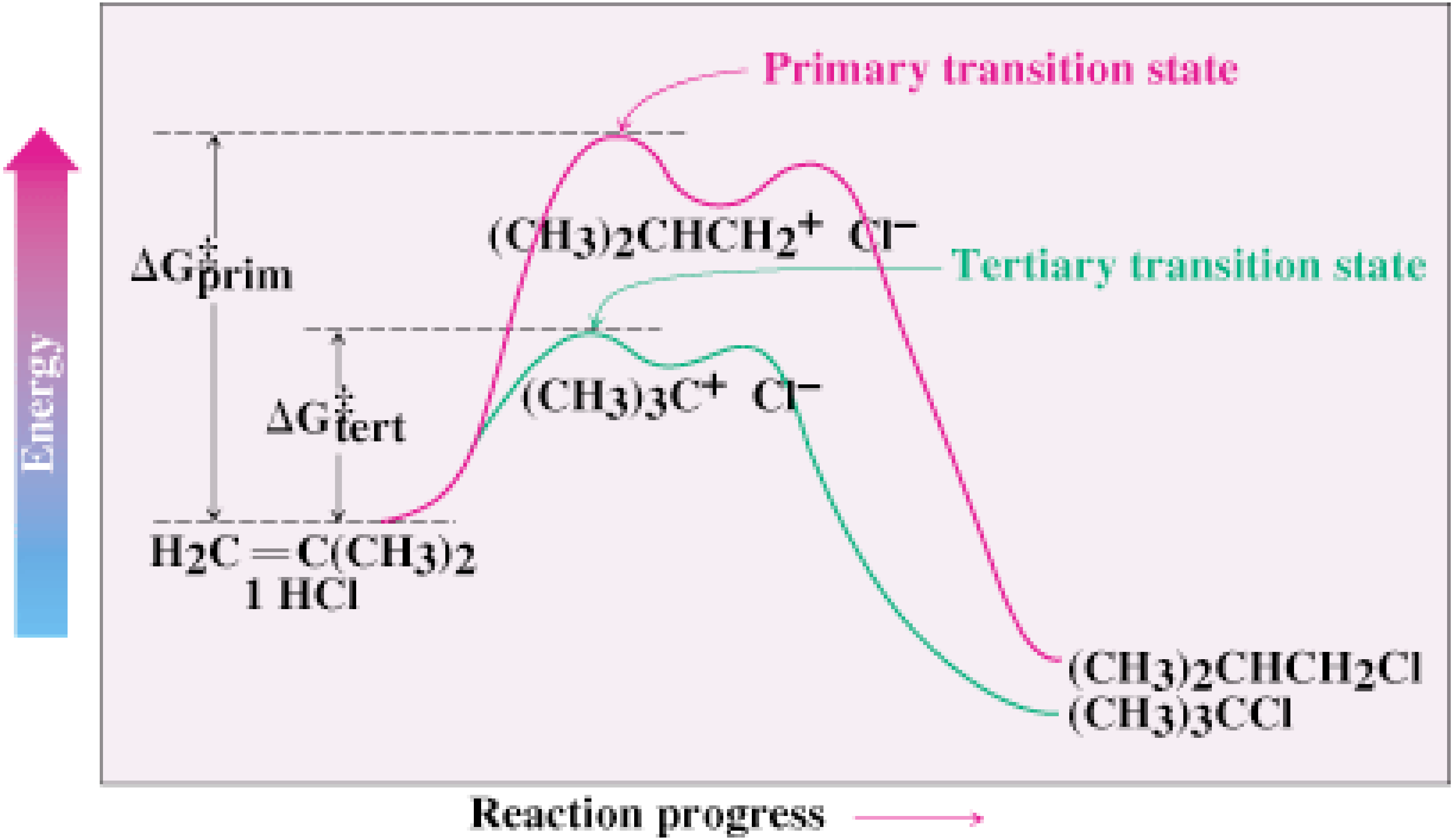
- (1) Efeito Indutivo: doação de densidade eletrônica através das ligações sigma.

- (2) Hiperconjugação: sobreposição de um orbital de uma ligação sigma com o orbital *p* orbital vazio.



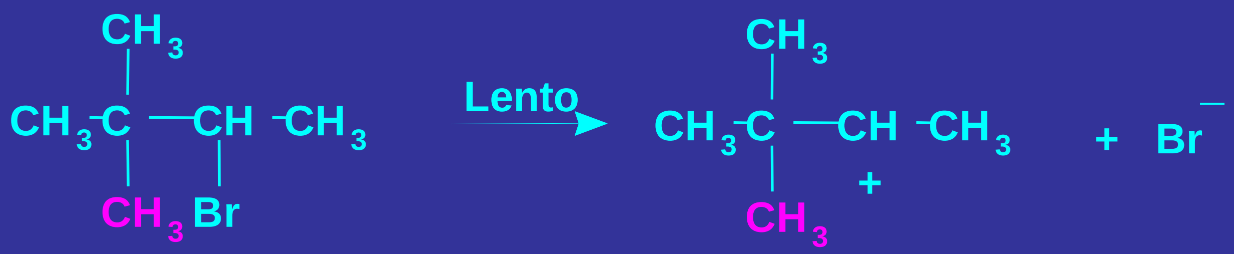

2-Methylpropene
HCl
Cl⁻
tert-Butyl carbocation (tertiary; 3°)
2-Chloro-2-methylpropane
Isobutyl carbocation (primary; 1°)
1-Chloro-2-methylpropane (NOT formed)


1-Methylcyclohexene
HBr
Br⁻
(A tertiary carbocation)
1-Bromo-1-methylcyclohexane
(A secondary carbocation)
1-Bromo-2-methylcyclohexane (NOT formed)


Primary transition state
Energy
ΔG‡prim
(CH3)2CHCH2+ Cl−
Tertiary transition state
ΔG‡tert
(CH3)3C+ Cl−
H2C = C(CH3)2
1 HCl
(CH3)2CHCH2Cl
(CH3)3CCl
Reaction progress

Rearranjo de Carbocátions

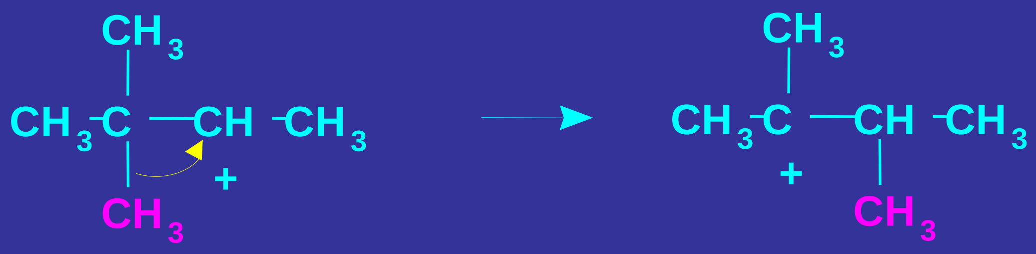
1)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 \xrightarrow{\text{Lento}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{CH}-CH_3 + Br^-$$

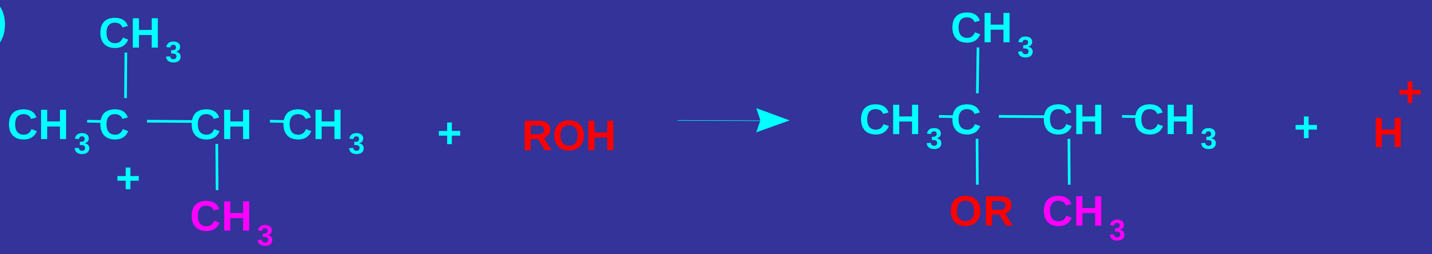
Um carbocátion

2)



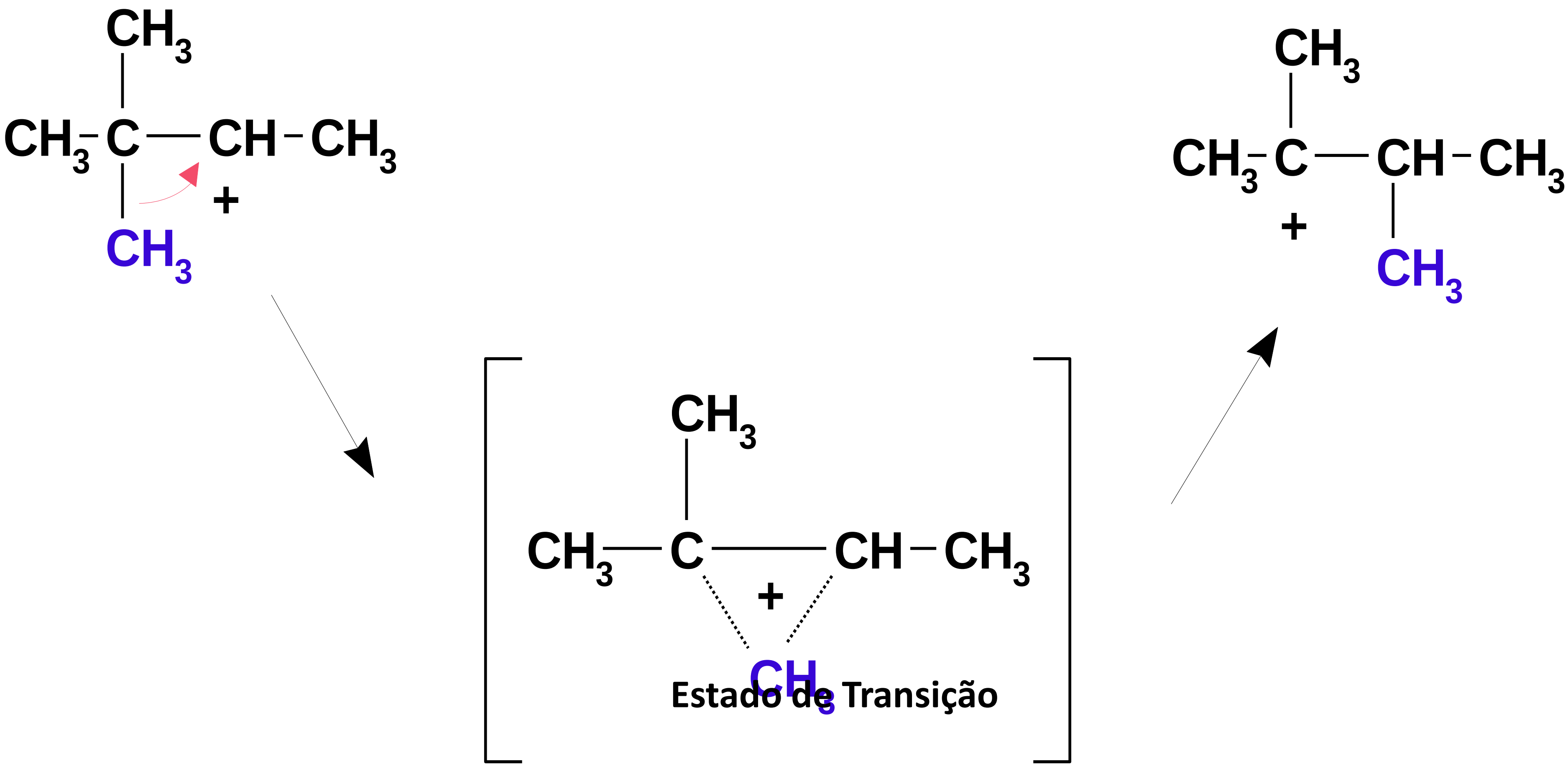
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{CH}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3$$

3)



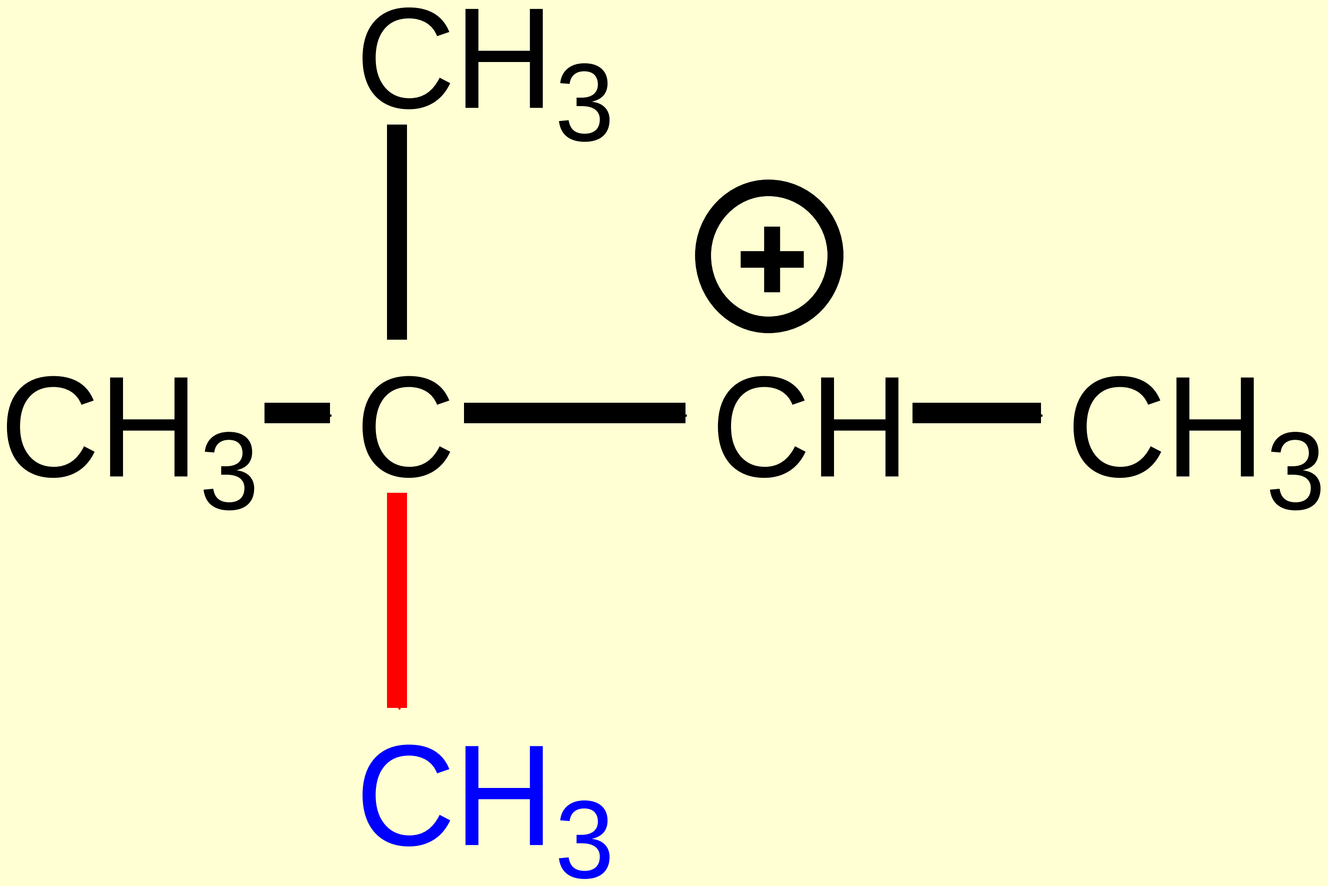
$$CH_3-\underset{+}{\overset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3 + ROH \longrightarrow CH_3-\underset{OR}{\overset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3 + H^+$$

Uma visão mais detalhada...



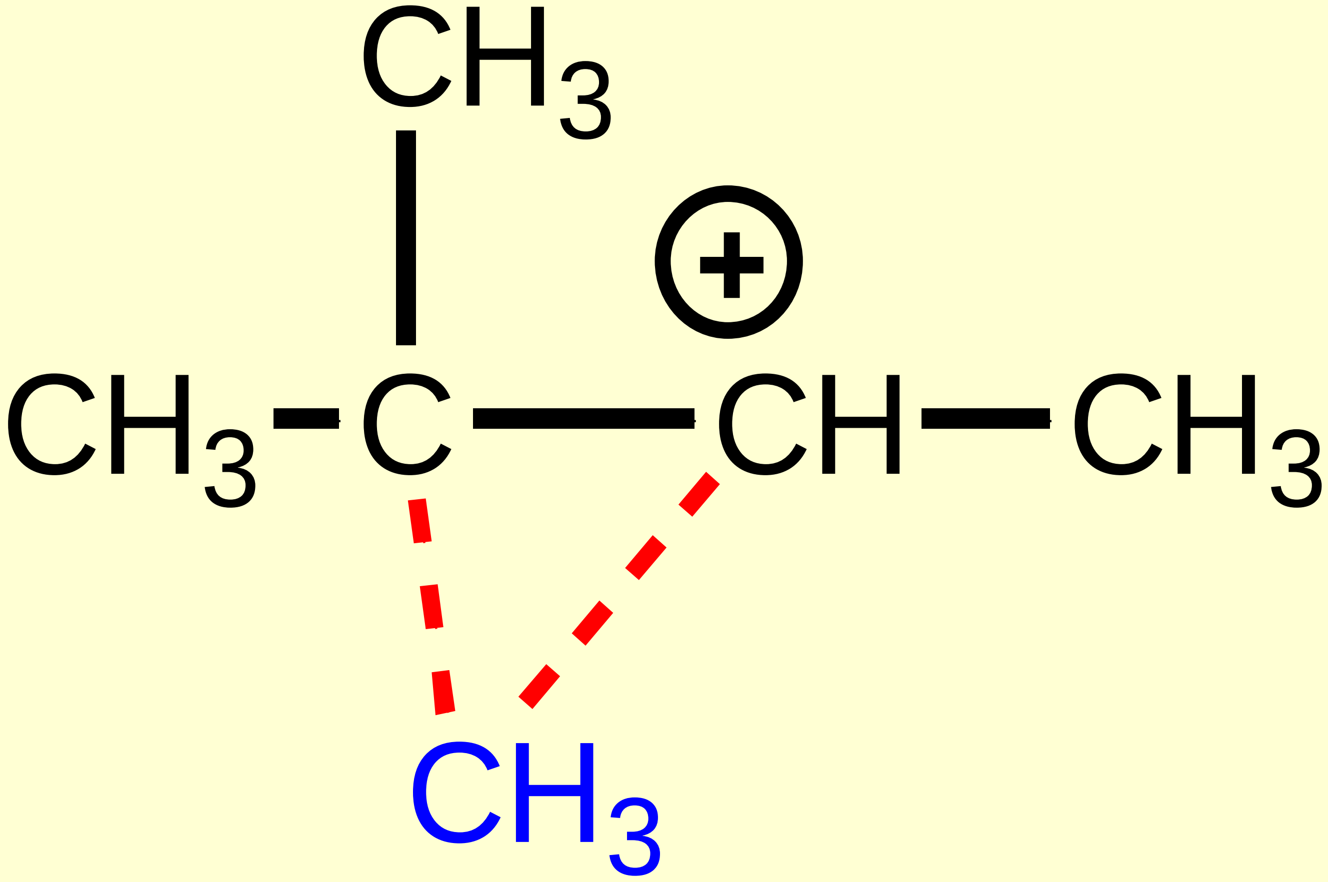
Estado de Transição

Rearranjo do Carbocátion



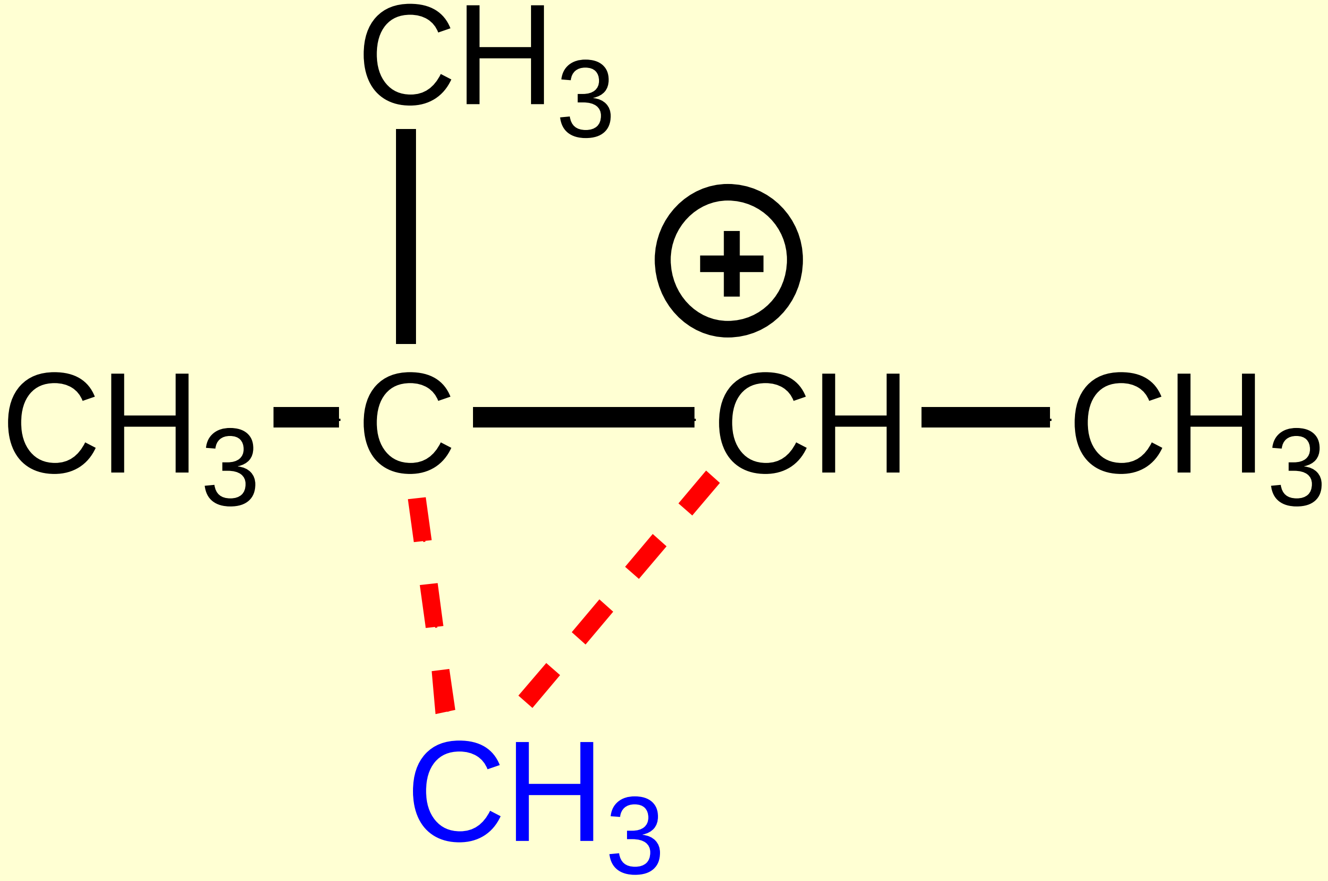
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{CH}-CH_3$$

Rearranjo do Carbocátion



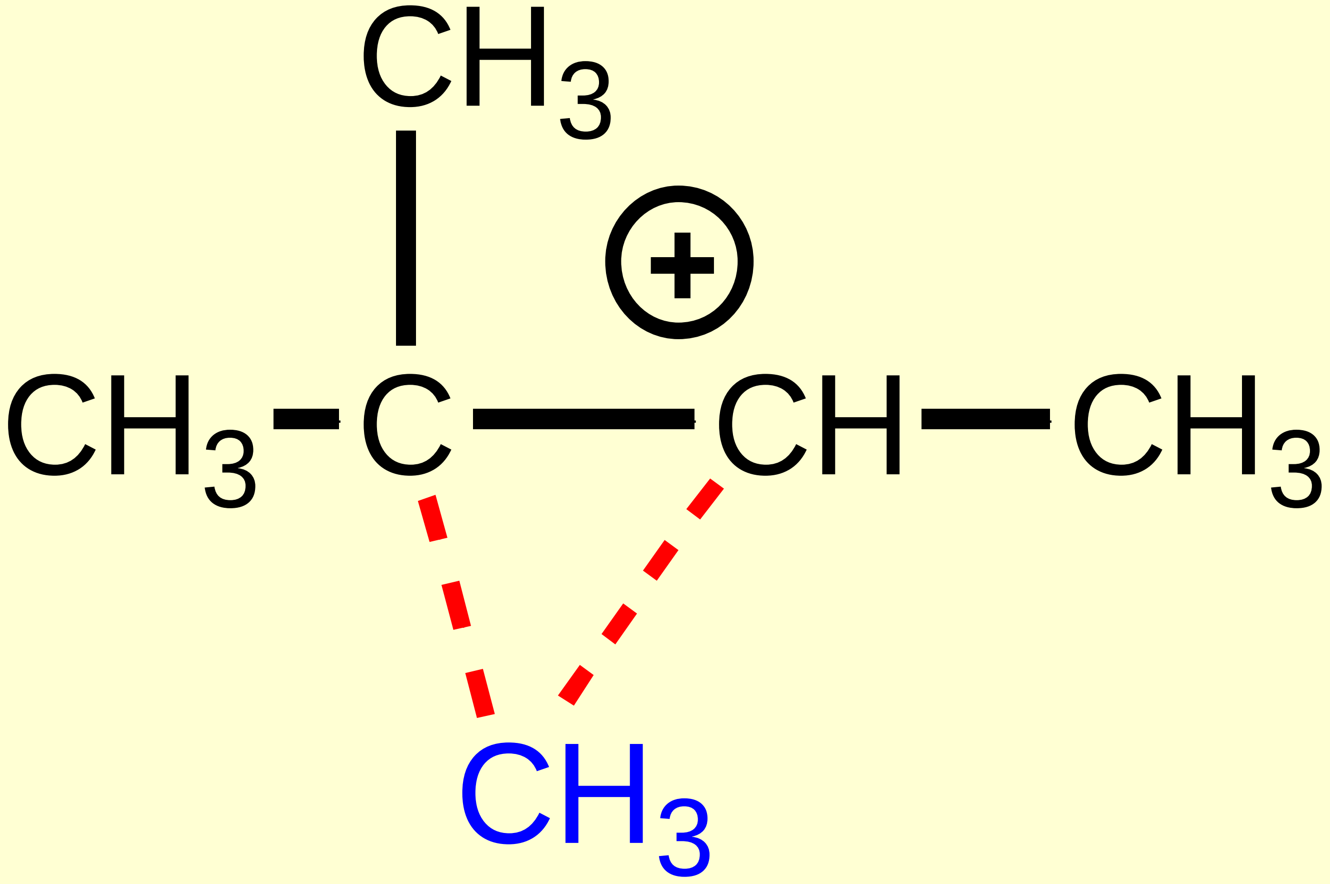
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H-CH_3$$

Rearranjo do Carbocátion

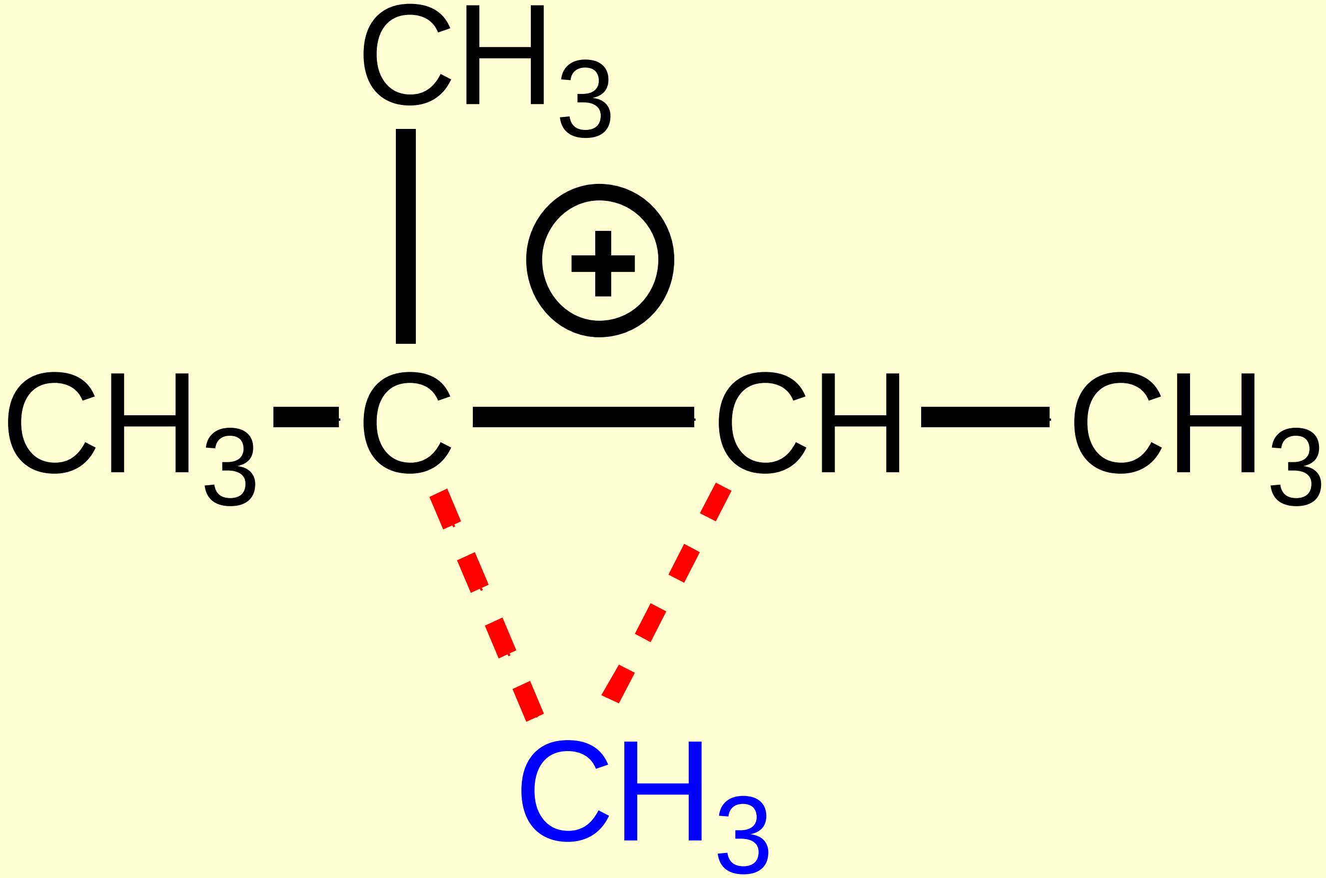


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{C}H-CH_3$$

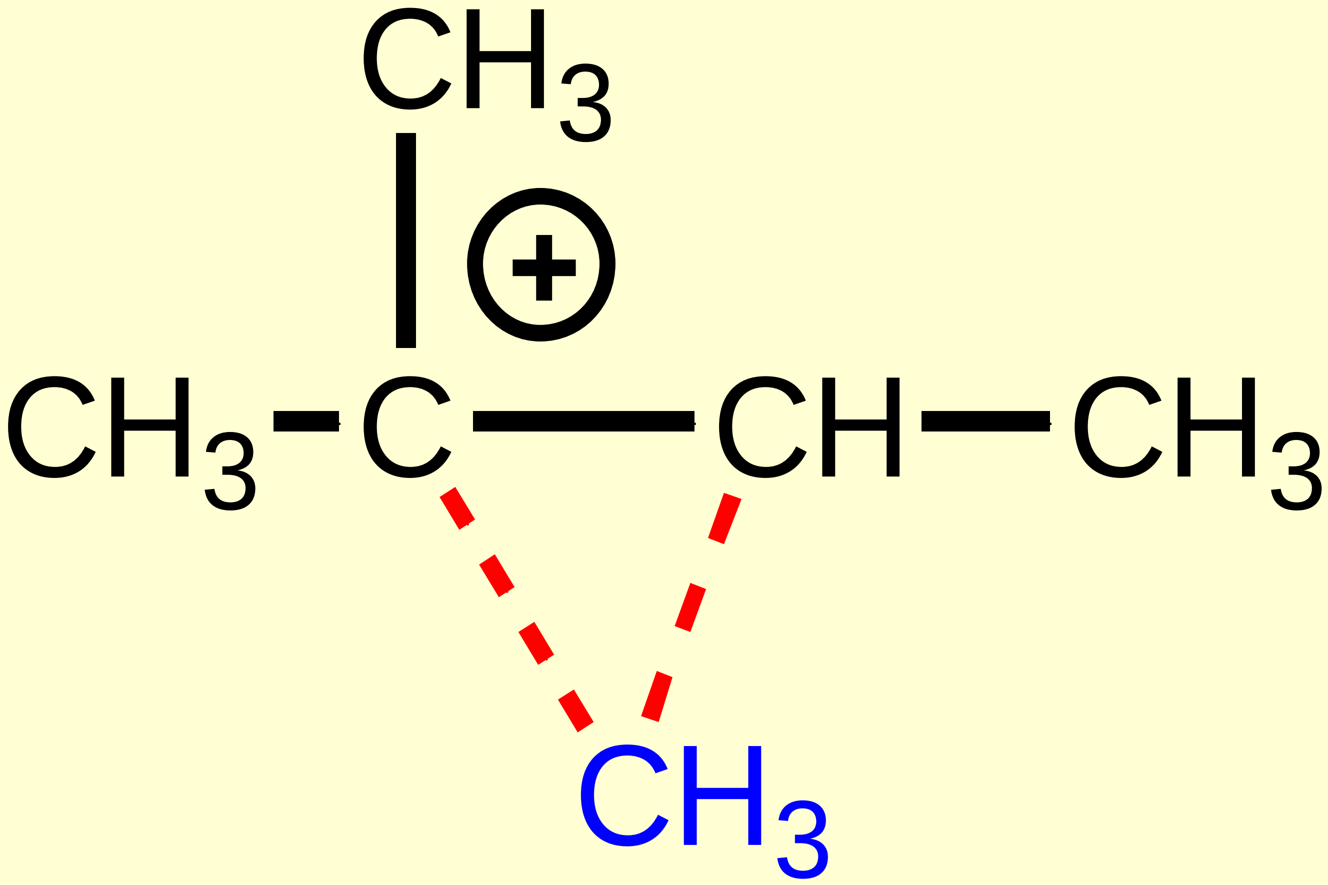
Rearranjo do Carbocátion



Rearranjo do Carbocátion

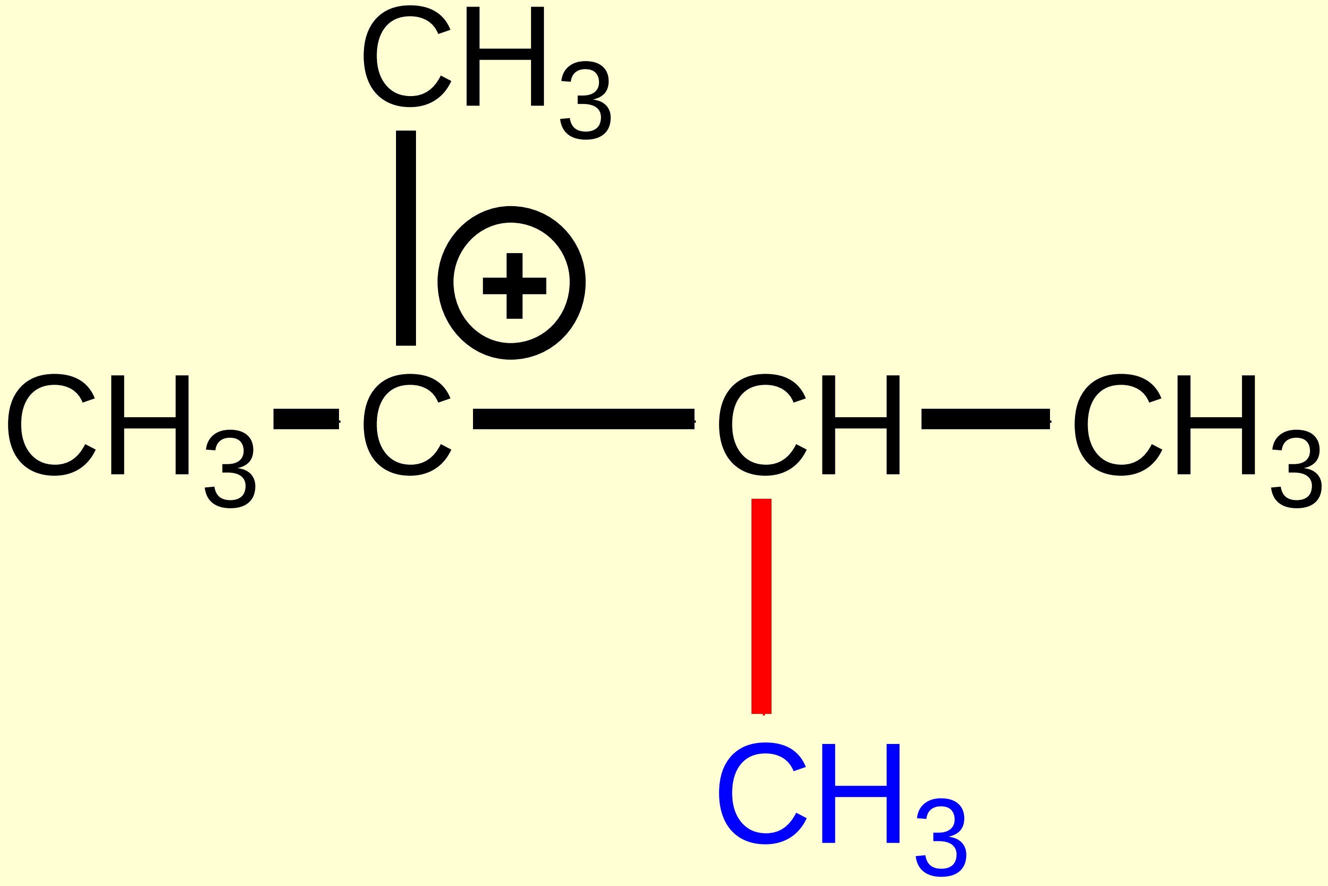


Rearranjo do Carbocátion



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}{}^{\oplus}-CH-CH_3$$

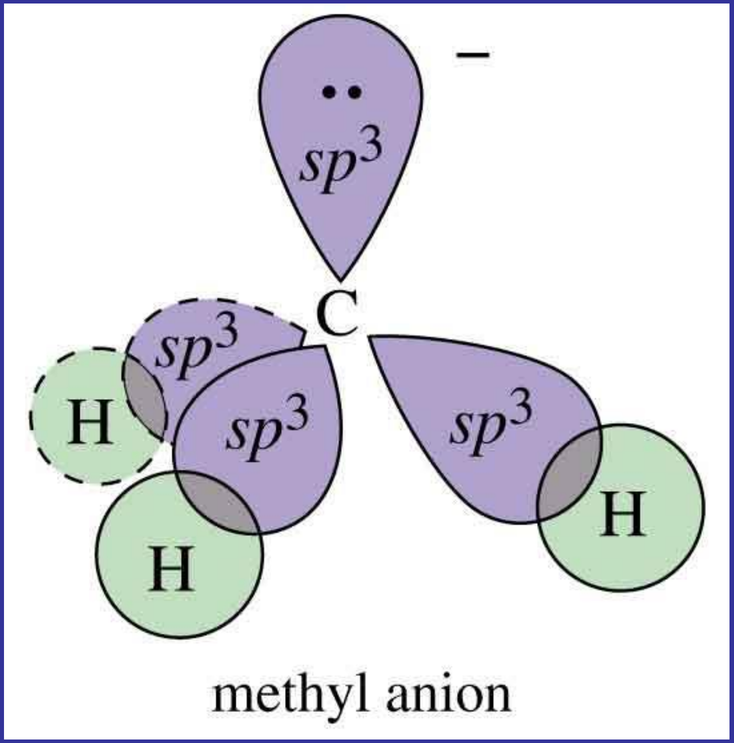
Rearranjo do Carbocátion



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}{}^{\oplus}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Carbânions

- Oito elétrons no C: 6 derivados das ligações + um par isolado
- O Carbono tem uma carga negativa.
- Desestabilizado por substituintes alquílicos.
- Metila >1° > 2 ° > 3 °



methyl anion

$$CH_3CH_2CH_2\overset{\delta-}{CH_2}\overset{\delta+}{Li} \xleftarrow{\quad} \; \text{}$$

$$CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Pentano}]{2\ Li} CH_3CH_2CH_2\overset{\delta-}{CH_2}\overset{\delta+}{Li} + LiBr$$

1-Bromobutano — Butil-lítio

$$CH_3Br + 2\ Li \xrightarrow[\text{Pentano}]{} CH_3Li + LiBr$$

Metil-lítio

$$CH_3Li + CuI \xrightarrow[\text{Éter}]{} (CH_3)_2Cu^{\ominus}\ Li^{\oplus} + LiI$$

Metil-lítio

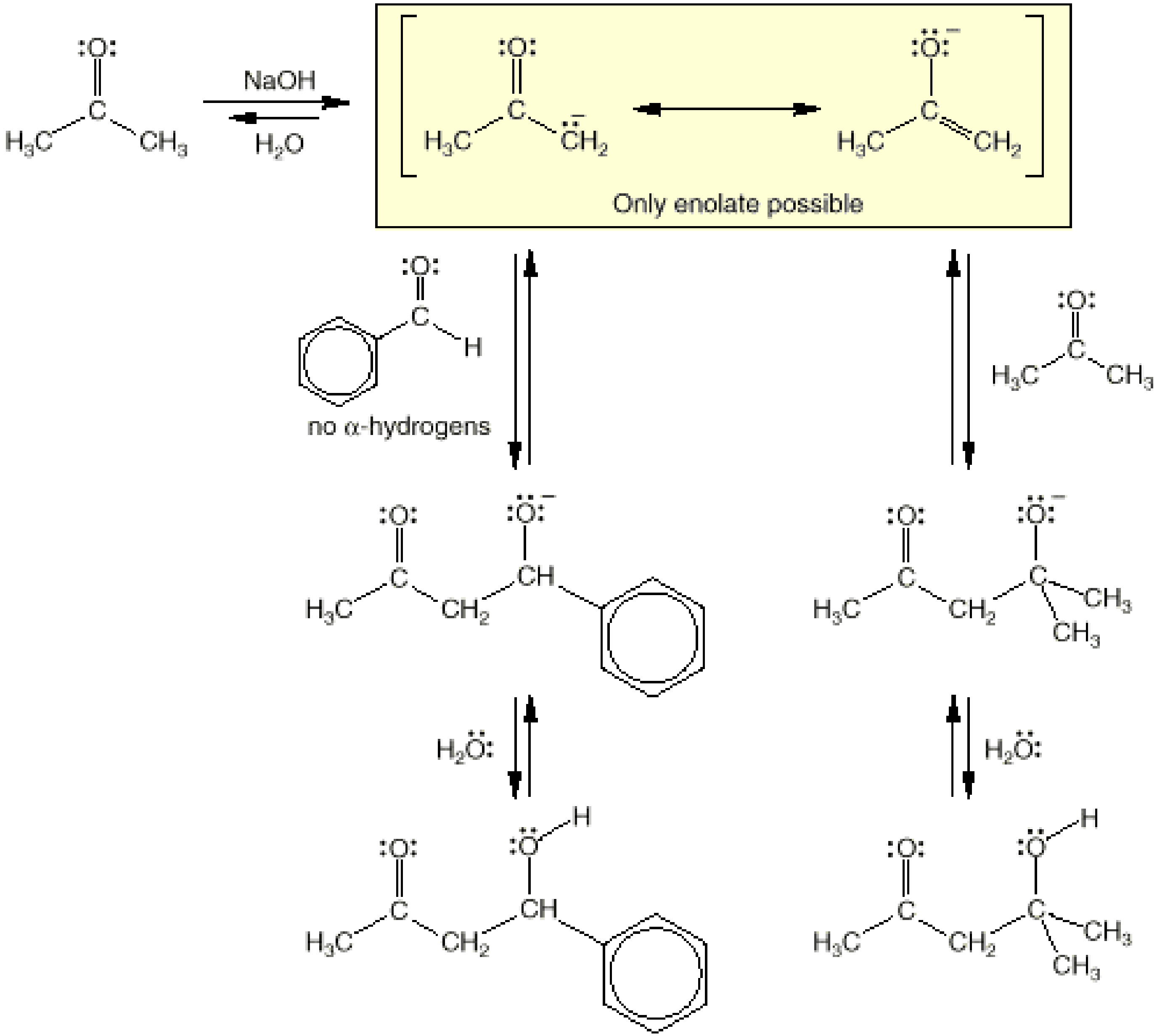
Dimetilcuprato de lítio
(um reagente de Gilman)

$$(CH_3)_2CuLi + CH_3(CH_2)_8CH_2I \xrightarrow[\text{Éter}]{0\ ^{o}C} CH_3CH_2CH_2CH_2Li + LiBr$$

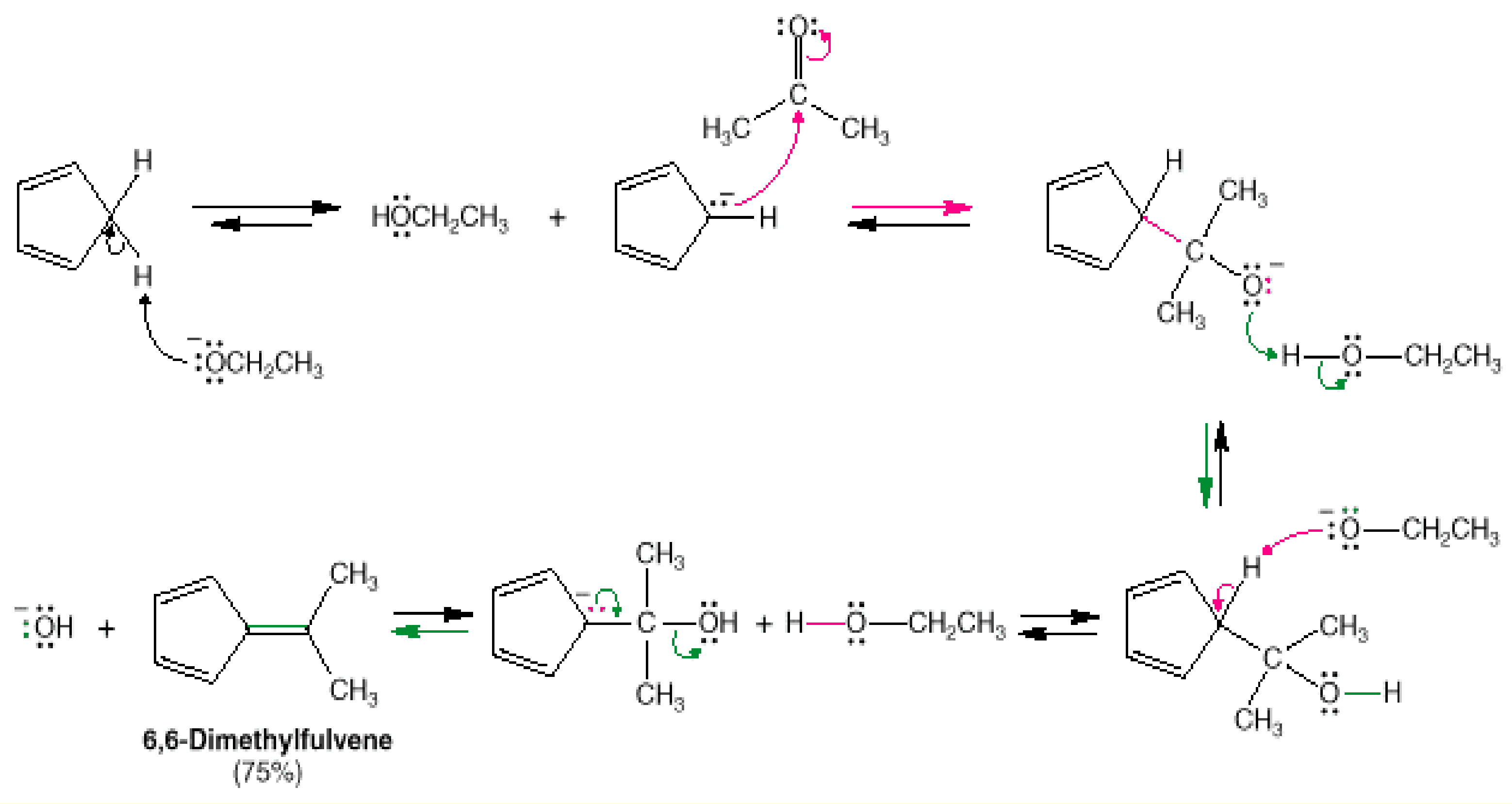
Dimetilcuprato
de lítio

1-Iododecano

Undecano
(90%)

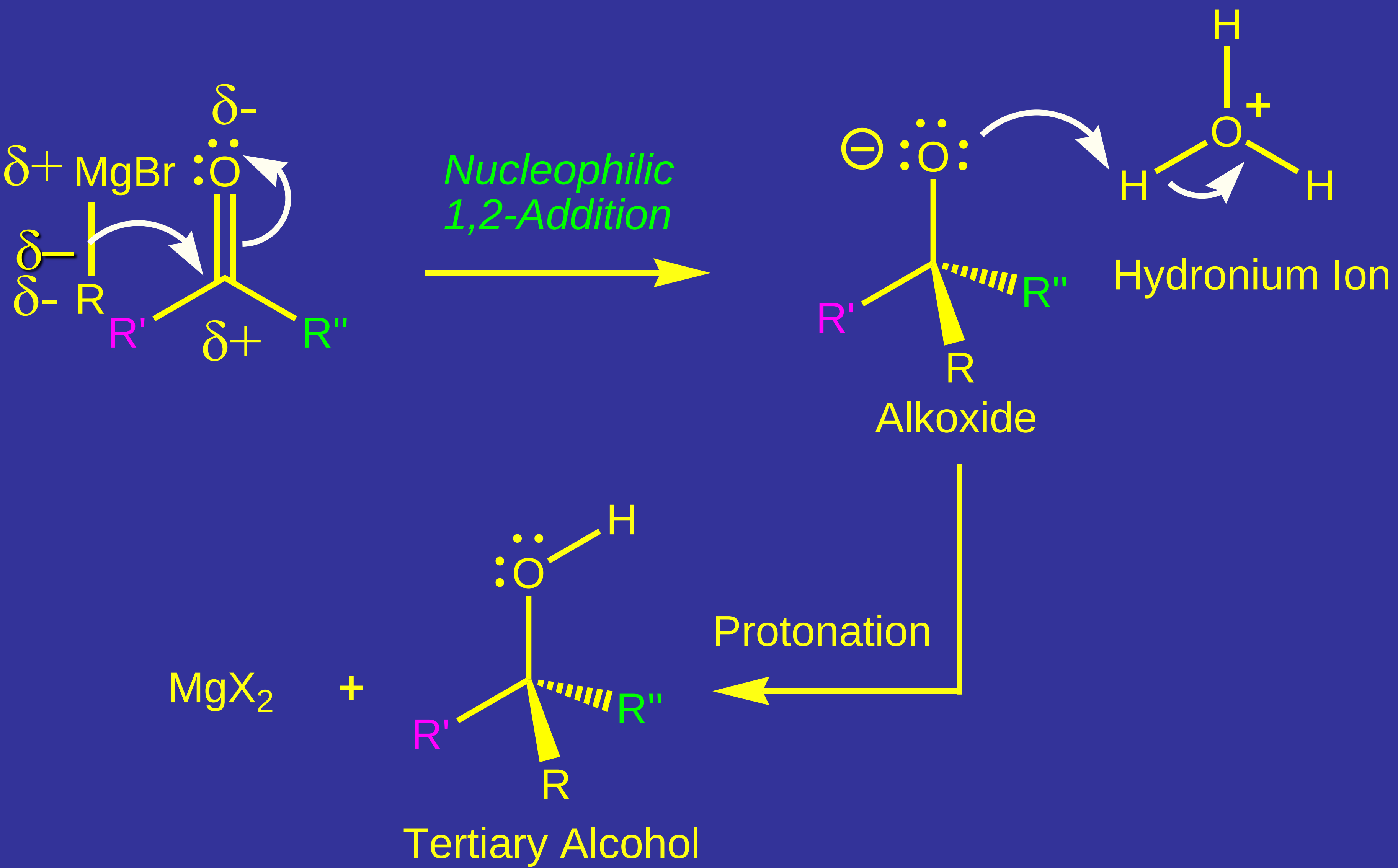

NaOH
H2O
Only enolate possible
no α-hydrogens
H2Ö:
H2Ö:

Reação de Knoevenagel



Reação de condensação formando fulvenos

Reagentes de Grignard reagem com cetonas



Nucleophilic 1,2-Addition

Alkoxide

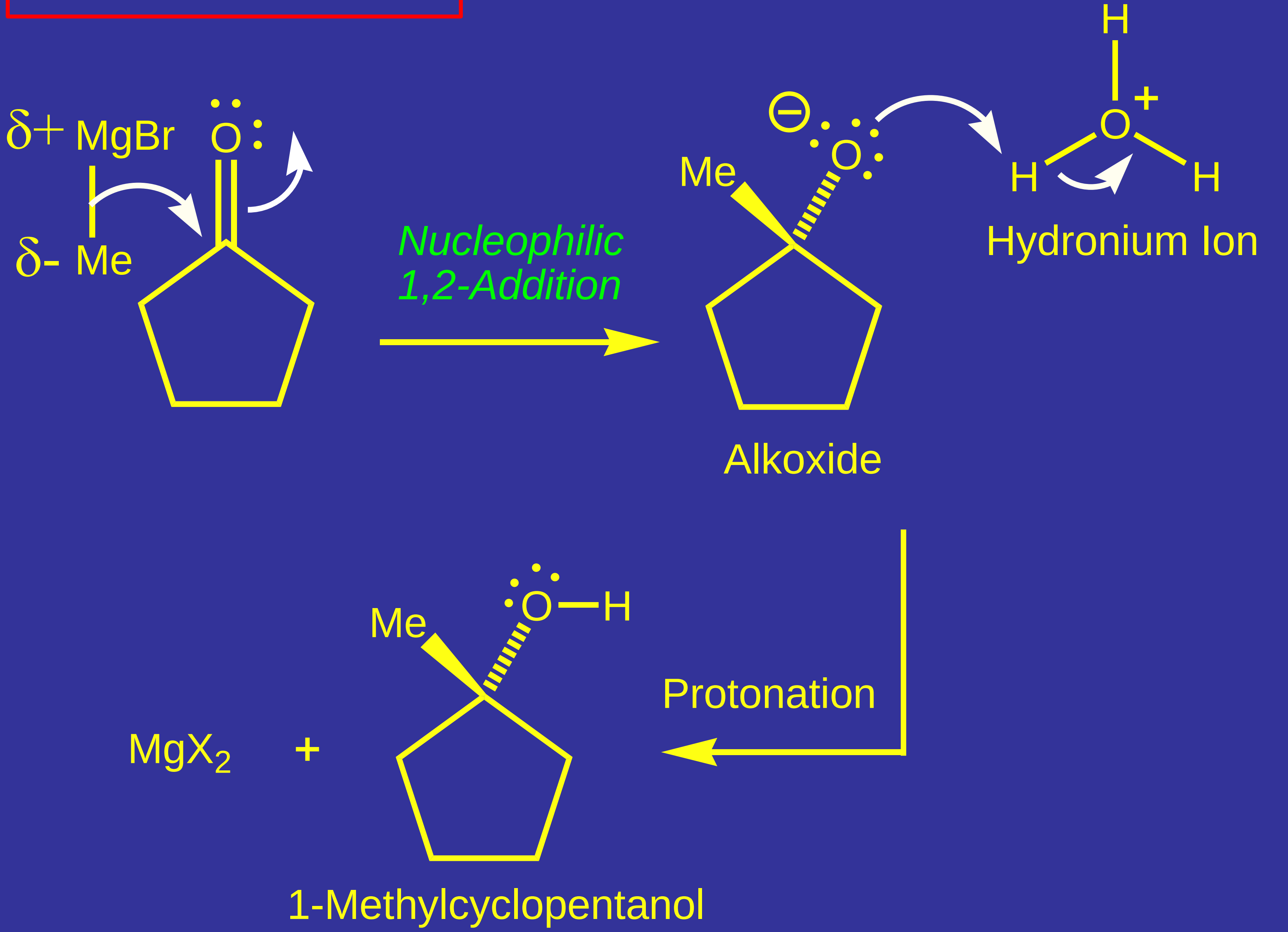
Hydronium Ion

Protonation

MgX_2 +

Tertiary Alcohol

Exemplo



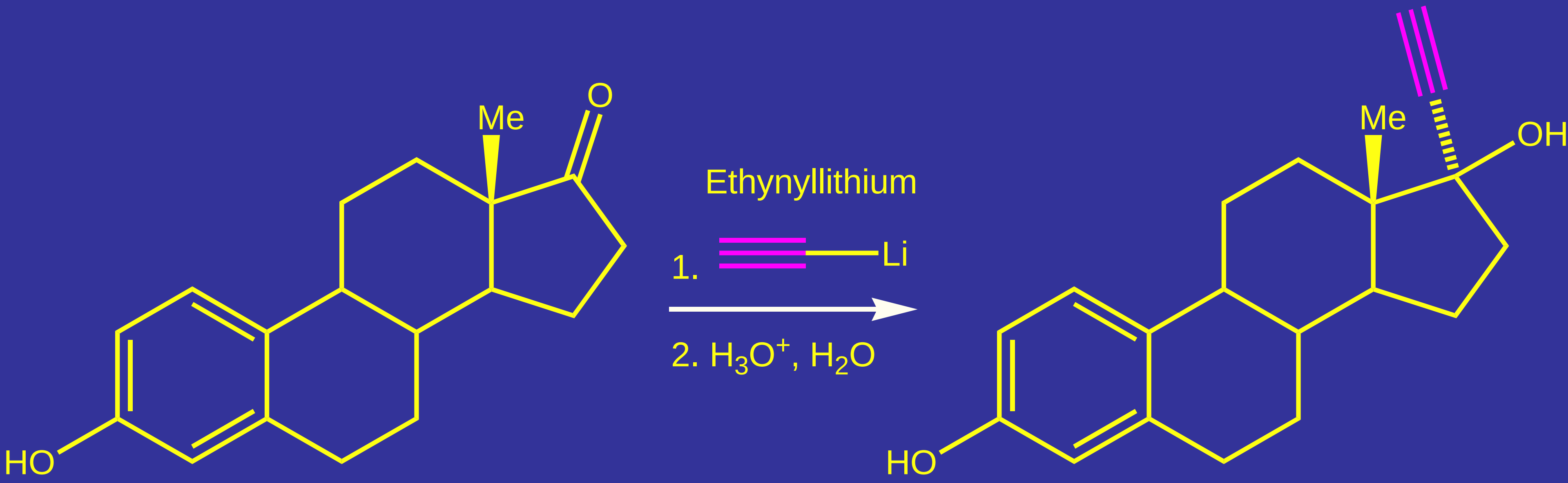
Nucleophilic 1,2-Addition

Alkoxide

Hydronium Ion

Protonation

1-Methylcyclopentanol

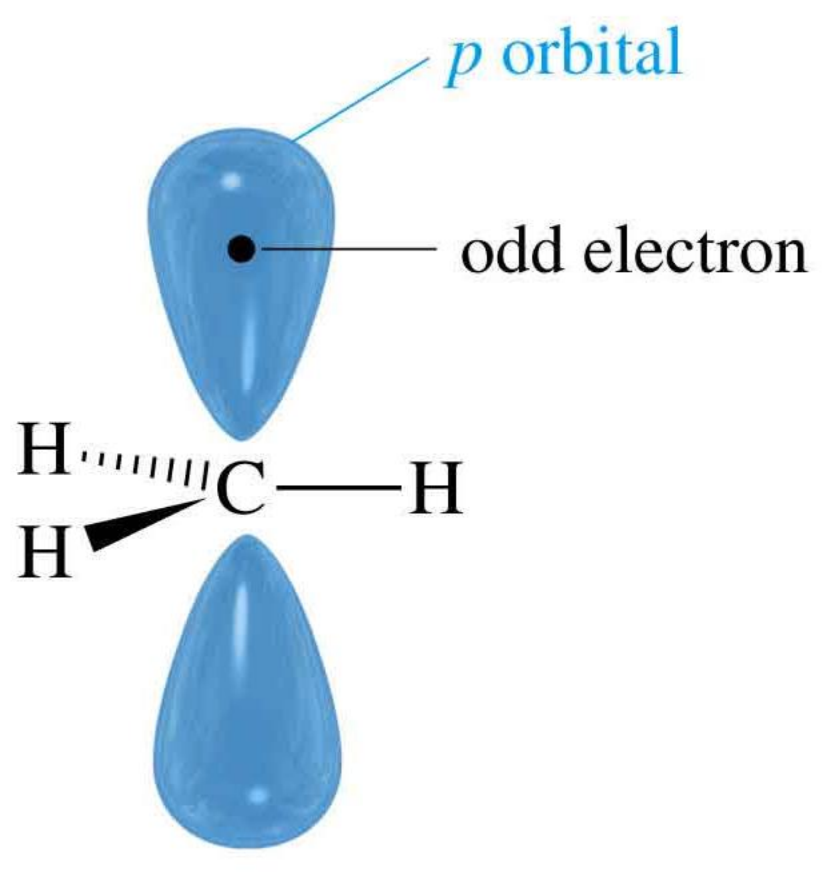


Oestrone
(Female hormone & Ketone)

Ethynyloestradiol
(Contraceptive & Tertiary Alcohol)

Radicais Livres

- Também apresentam deficiência eletrônica
- Estabilizados por substituintes alquílicos
- Ordem de estabilidade: 3° > 2° > 1° > metila



Iniciação

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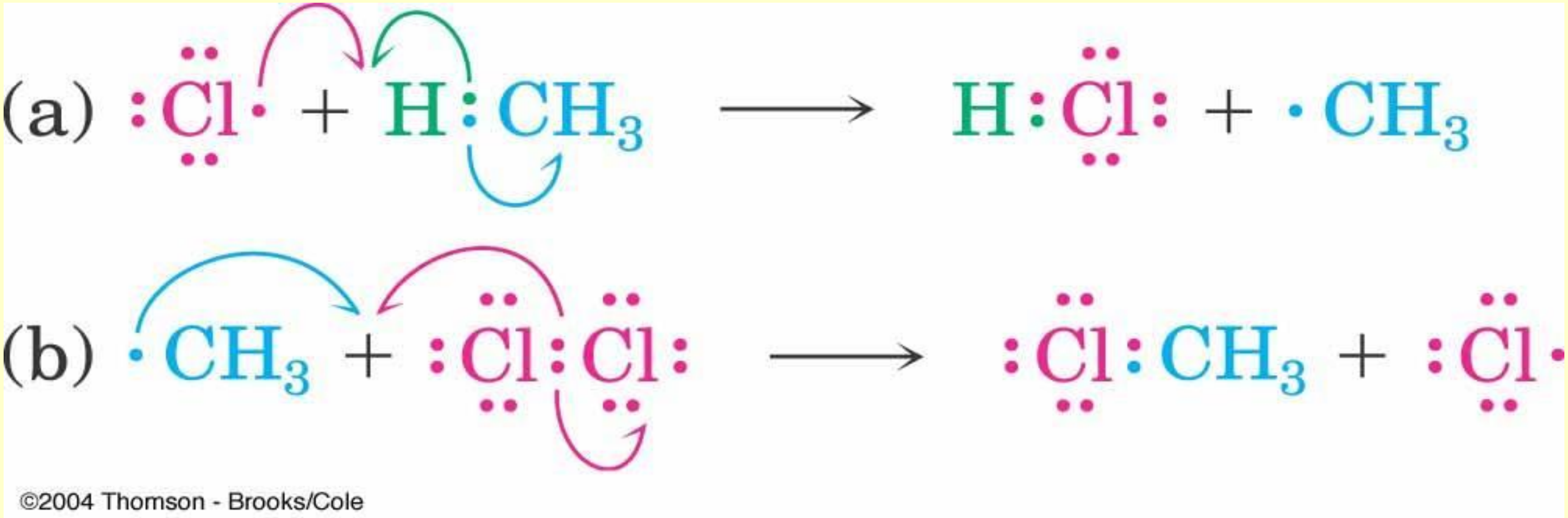
Propagação



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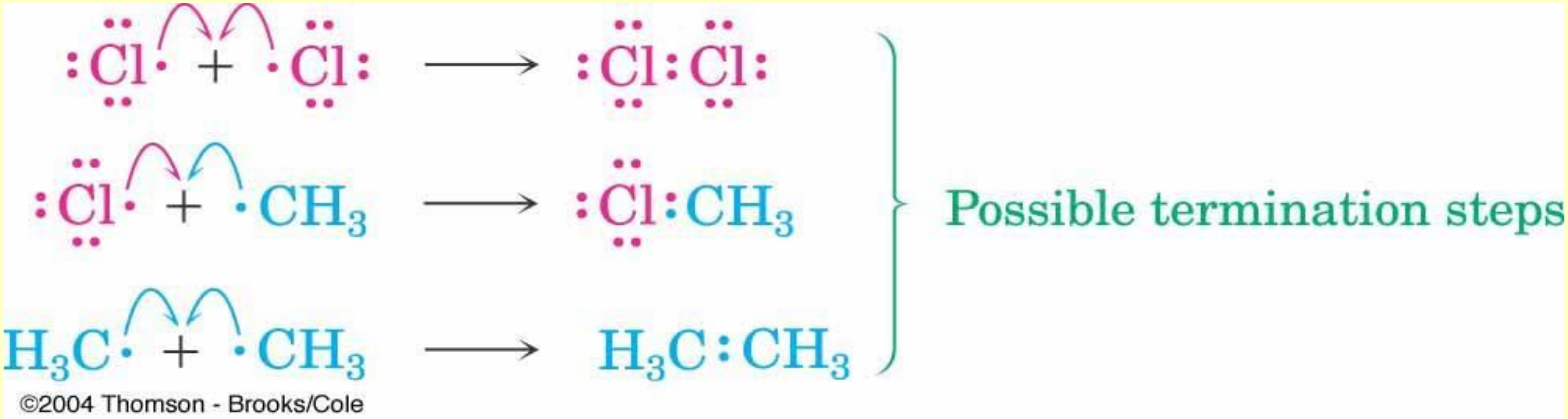
Término



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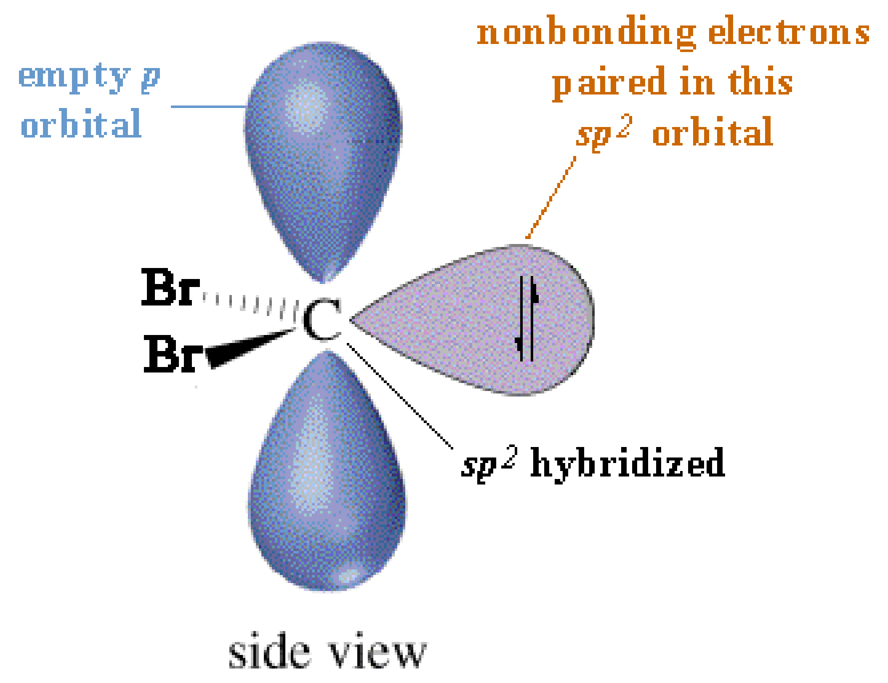
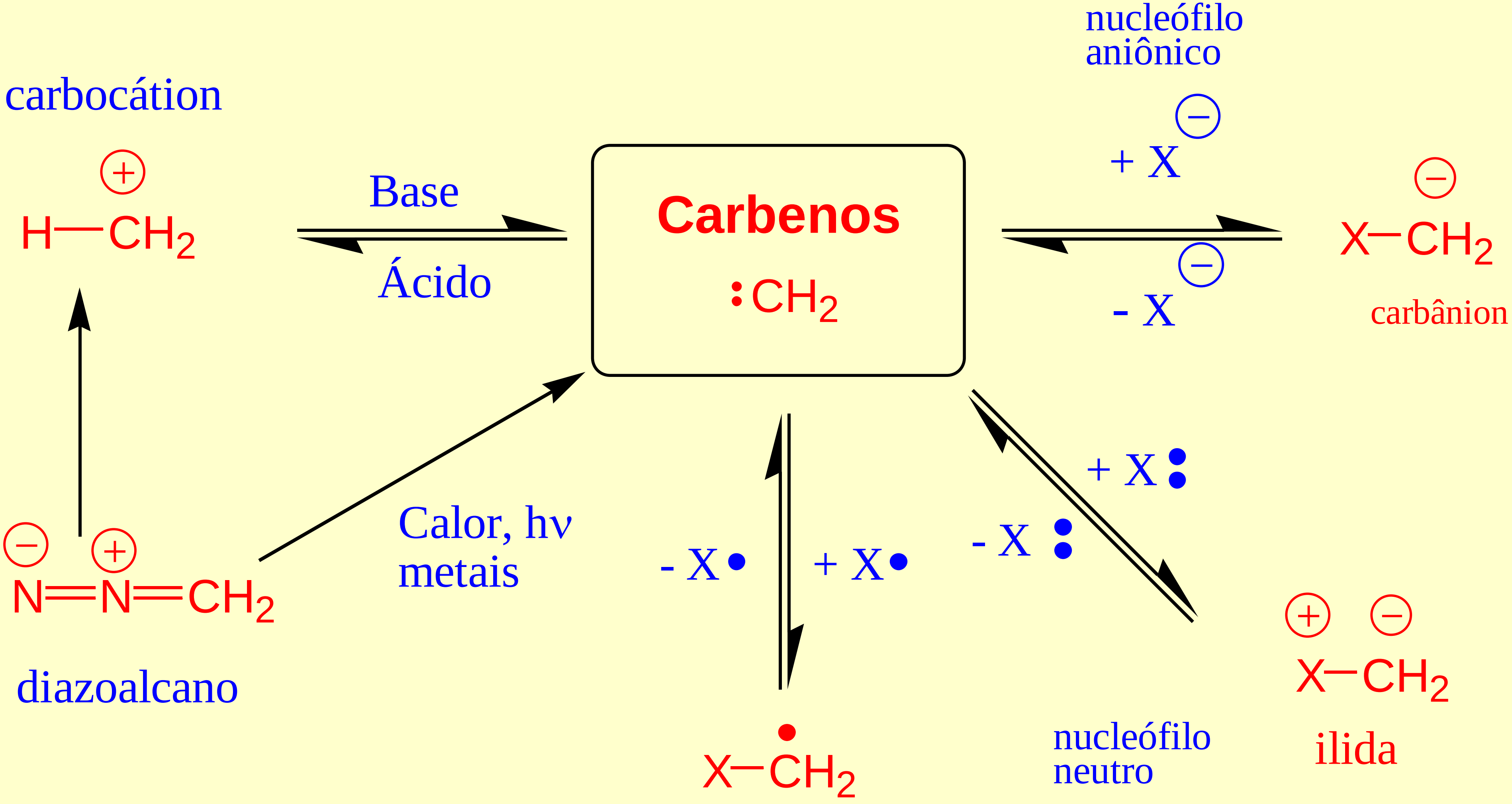
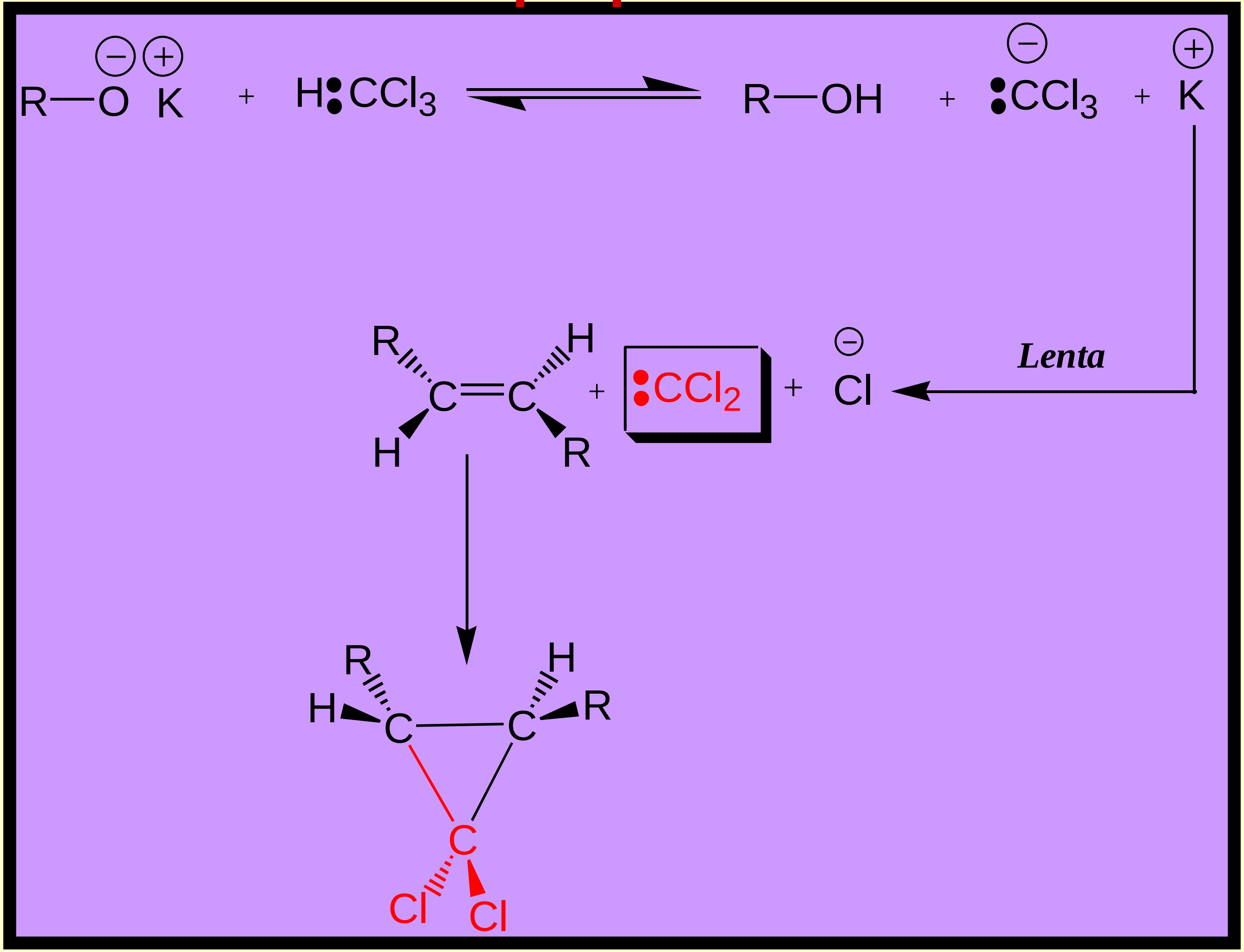
Carbenos

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

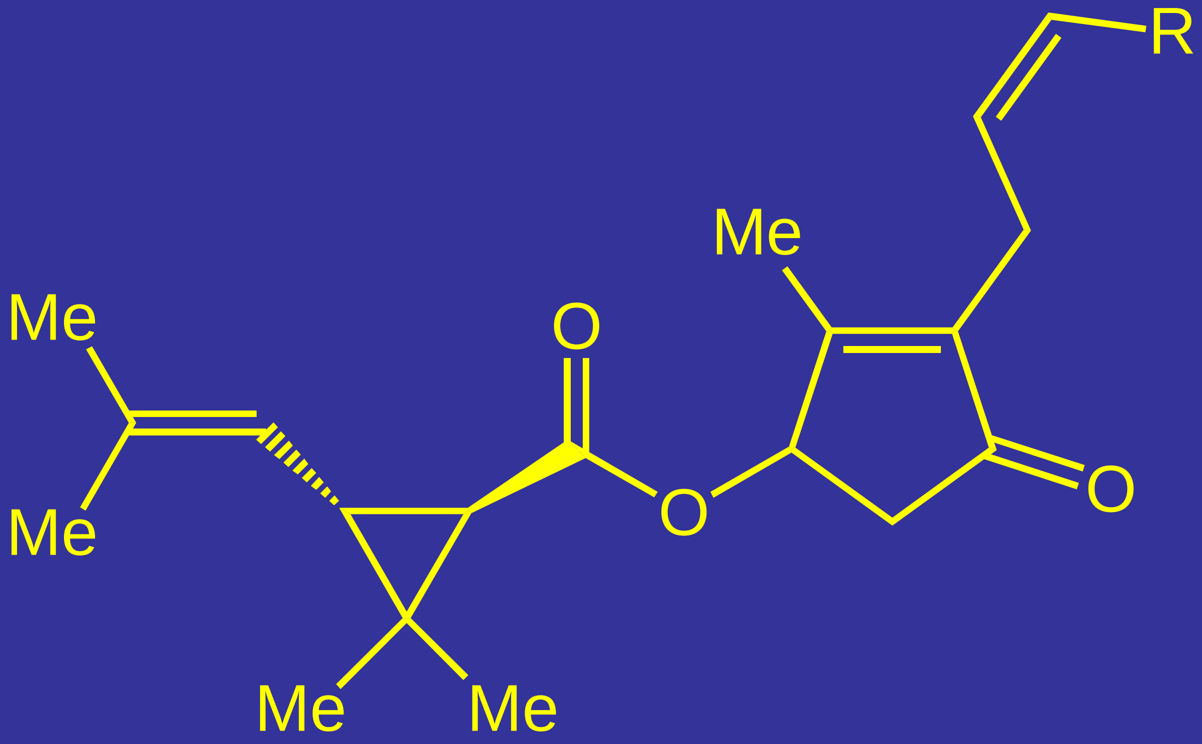



carbocátion
$H-\overset{+}{C}H_2$
Base
Ácido
Carbenos
$:CH_2$
nucleófilo aniônico
$+ X^-$
$- X^-$
$X-\overset{-}{C}H_2$
carbânion
$\overset{-}{N}=\overset{+}{N}=CH_2$
diazoalcano
Calor, hν
metais
$- X\bullet$
$+ X\bullet$
$X-\dot{C}H_2$
$+ X:$
$- X:$
nucleófilo neutro
$\overset{+}{X}-\overset{-}{C}H_2$
ilida

Di-halocarbenos: Formação de derivados ciclo-propânicos

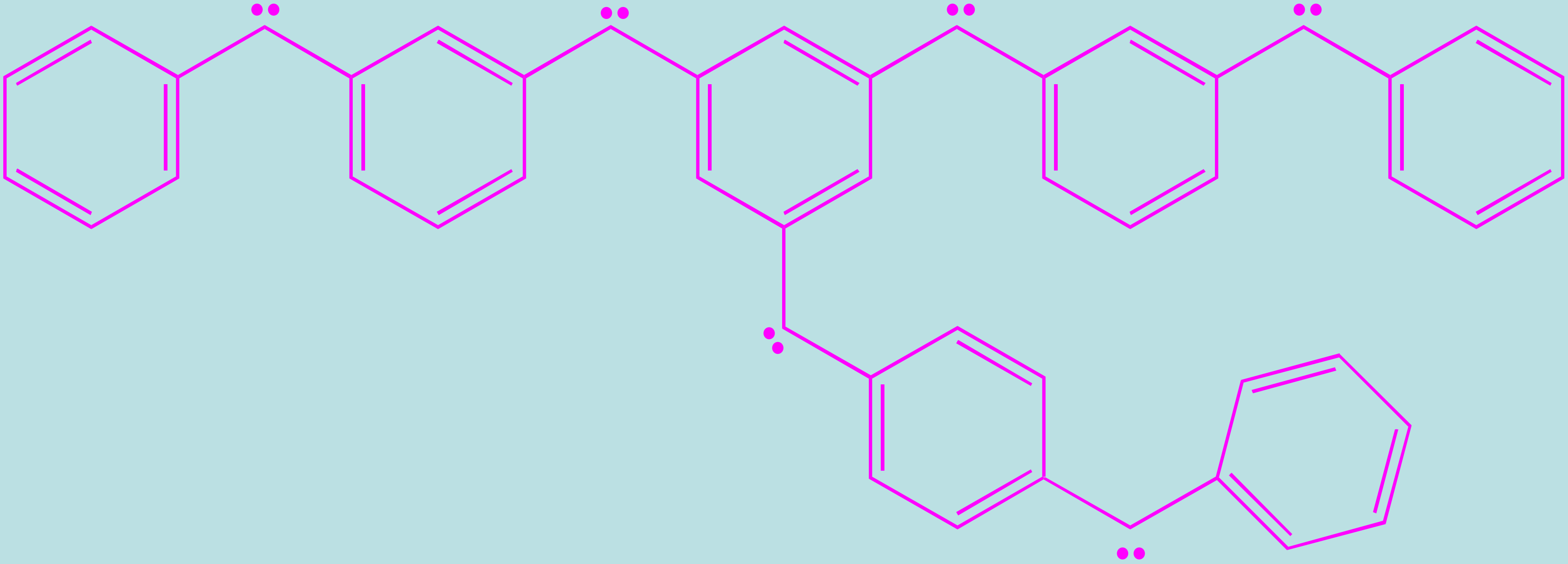


Por que os ciclopropanos são importantes?

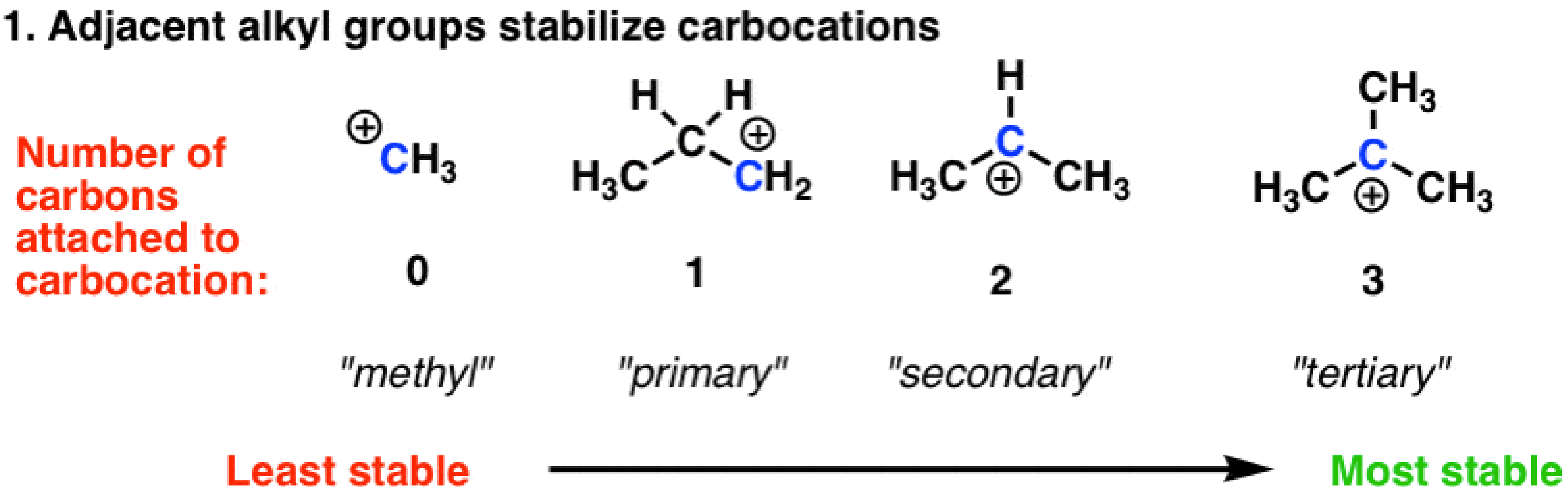


Pyrethrin

(Natural Insecticide in RAID^{TM})

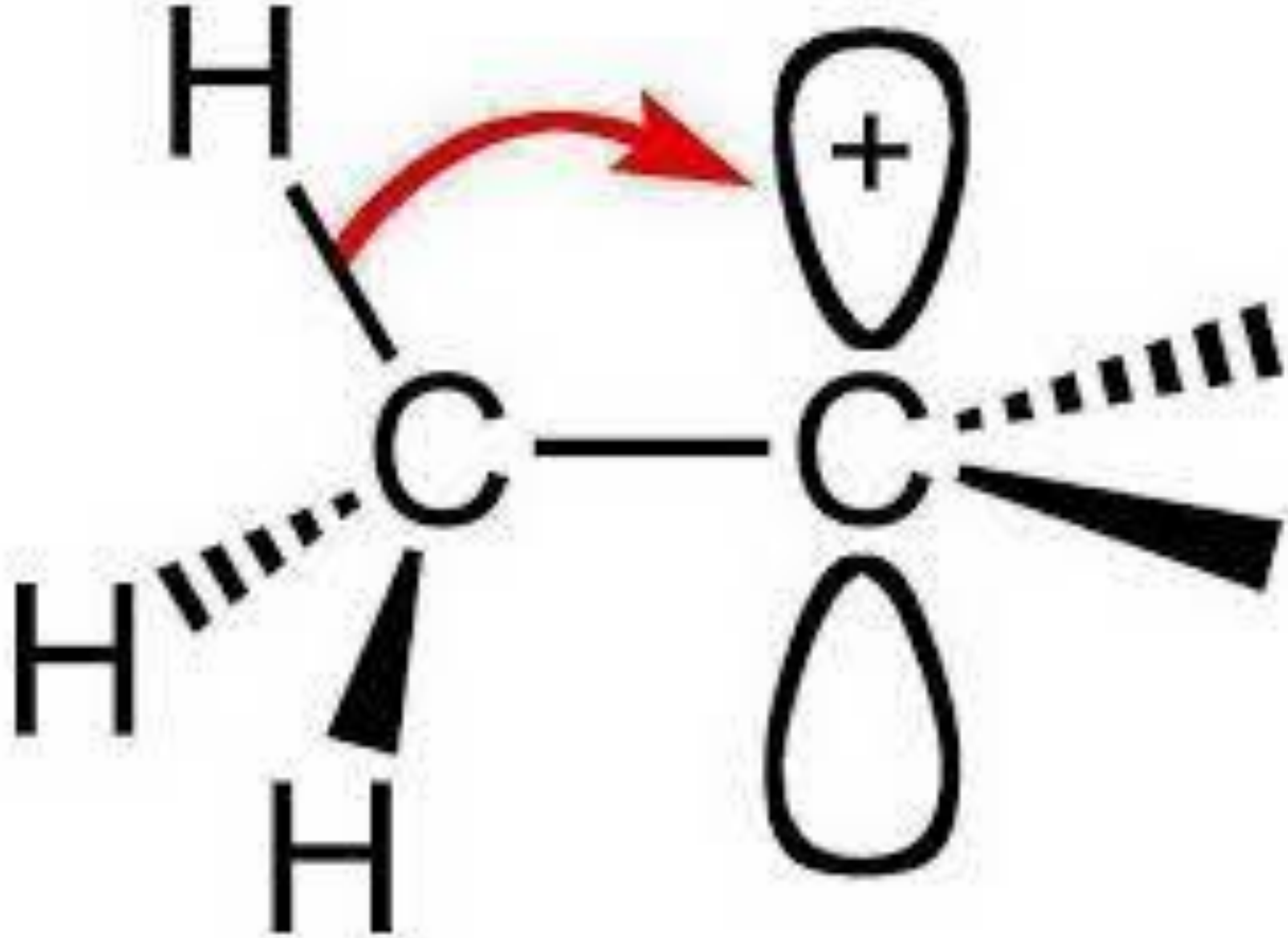


Hexacarbeno



Hiperconjugação; formação de alcenos; rearranjo de carbocátions; compreensão de reações S_N1 e E1

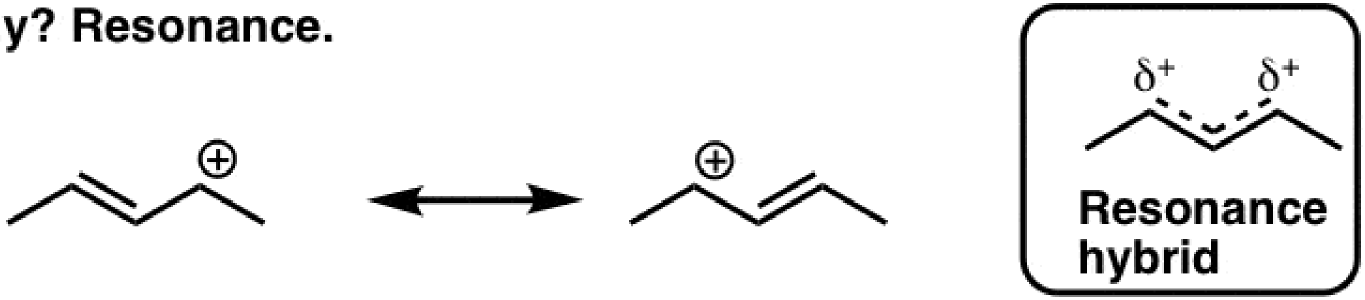
https://www.masterorganicchemistry.com/2011/03/11/3-factors-that-stabilize-carbocations/


H
+
C
C
H
H

Ligações π entre carbonos, adjacentes ao carbocátion, o estabilizam

Ressonância

Why? Resonance.

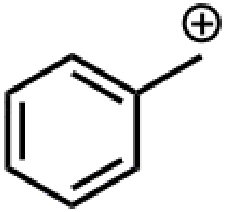


Resonance allows for the positive charge to be distributed over multiple carbons, diminishing the magnitude of the positive charge borne by each individual atom

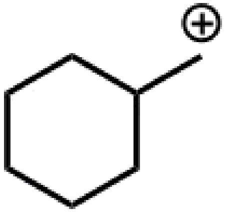
Examples:

is more stable than

is more stable than



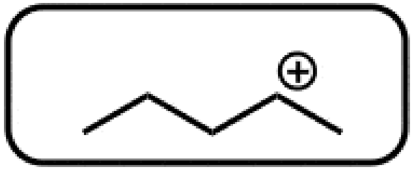
is more stable than



is more stable than

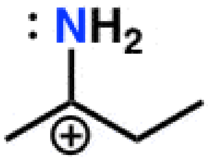
(note how the effect is additive)

A carbocation not stabilized by resonance:

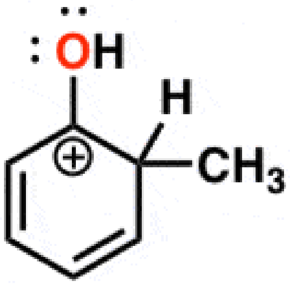


No adjacent pi bonds or lone pairs

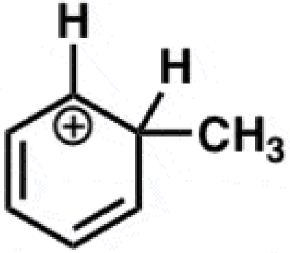
3. Carbocations Are Stabilized By Adjacent Atoms Bearing Lone Pairs

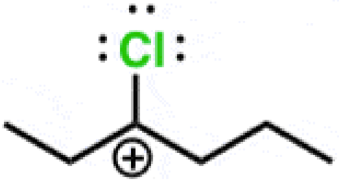


is more stable than

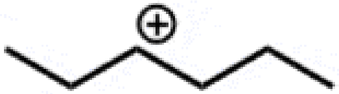


is more stable than





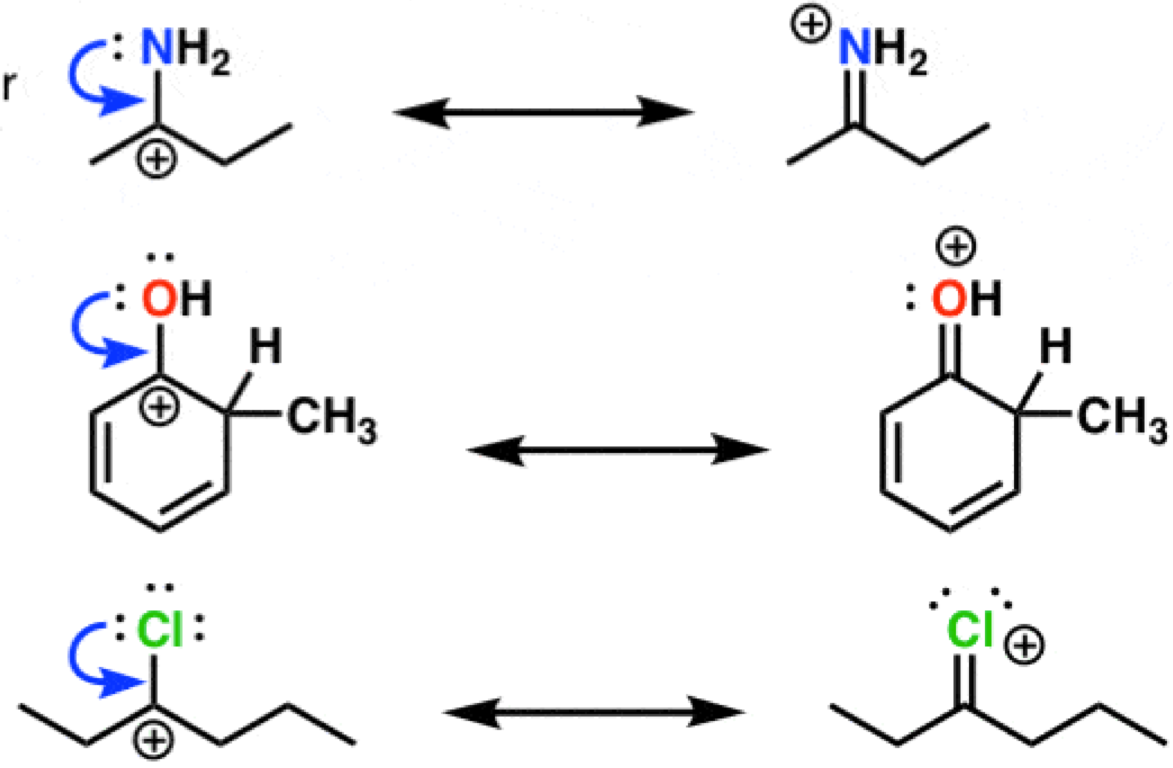
is more stable than



(yes - halides too!)

Why? Resonance (again)

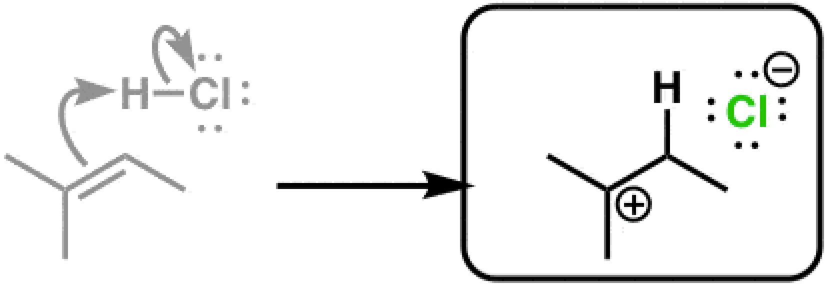
Donation of a lone pair by the atom allows for formation of a new π bond, which is a stabilizing influence



Even though Cl is fairly electronegative the lone pair can still form a π bond!

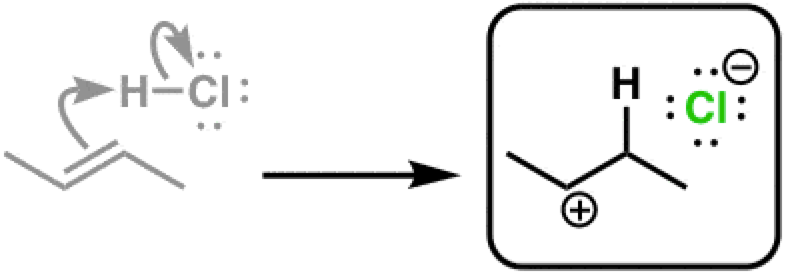
Formation of a Carbocation Is often the rate-limiting step In a reaction mechanism. So by understanding how carbocations are stabilized, you can understand the effect of substituents on reaction rates.

Aplicando o conceito: qual dos carbocátions representado a seguir seria o mais mais estável?



A

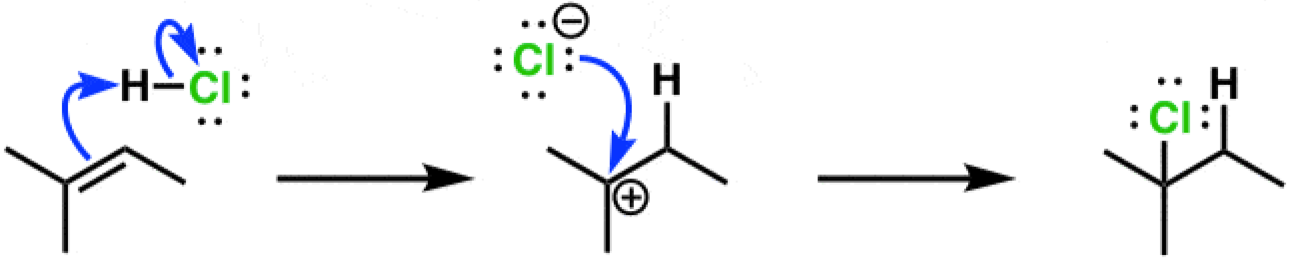
vs.



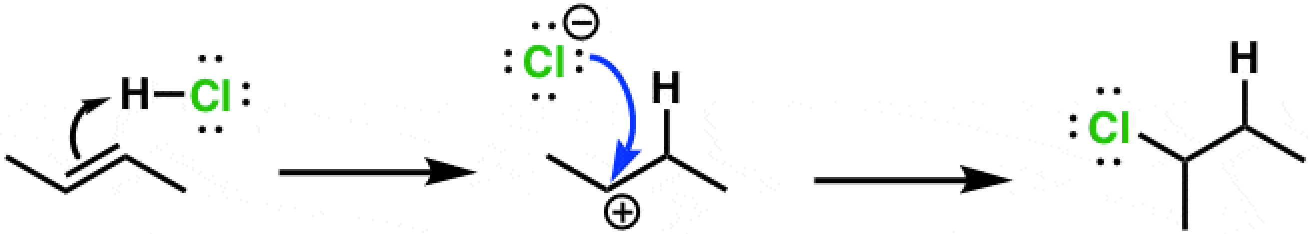
B

For A and B, if you assume carbocation formation is the rate limiting step, which reaction will be faster?

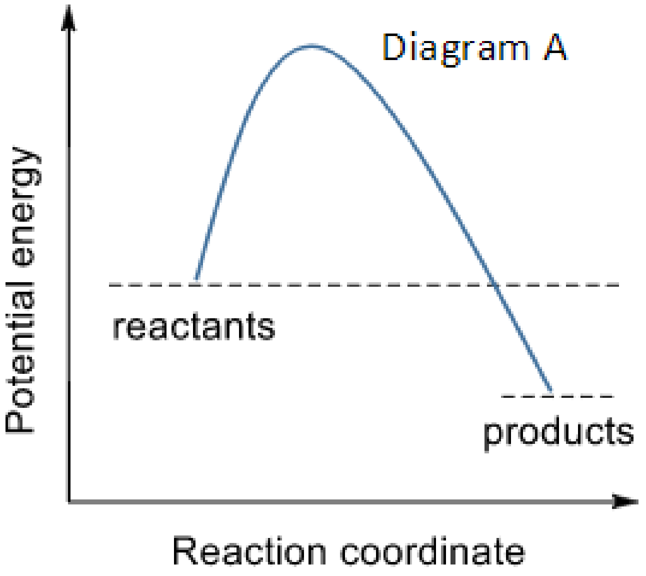
Reaction A

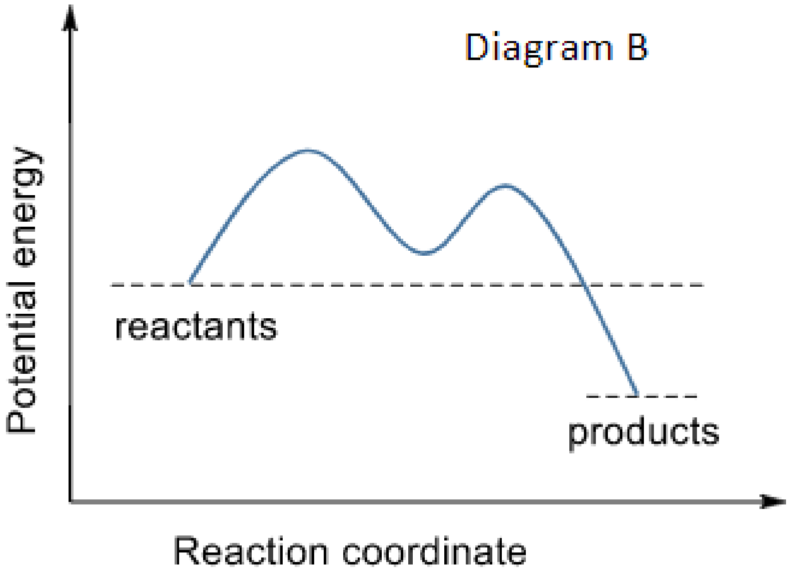


Reaction B



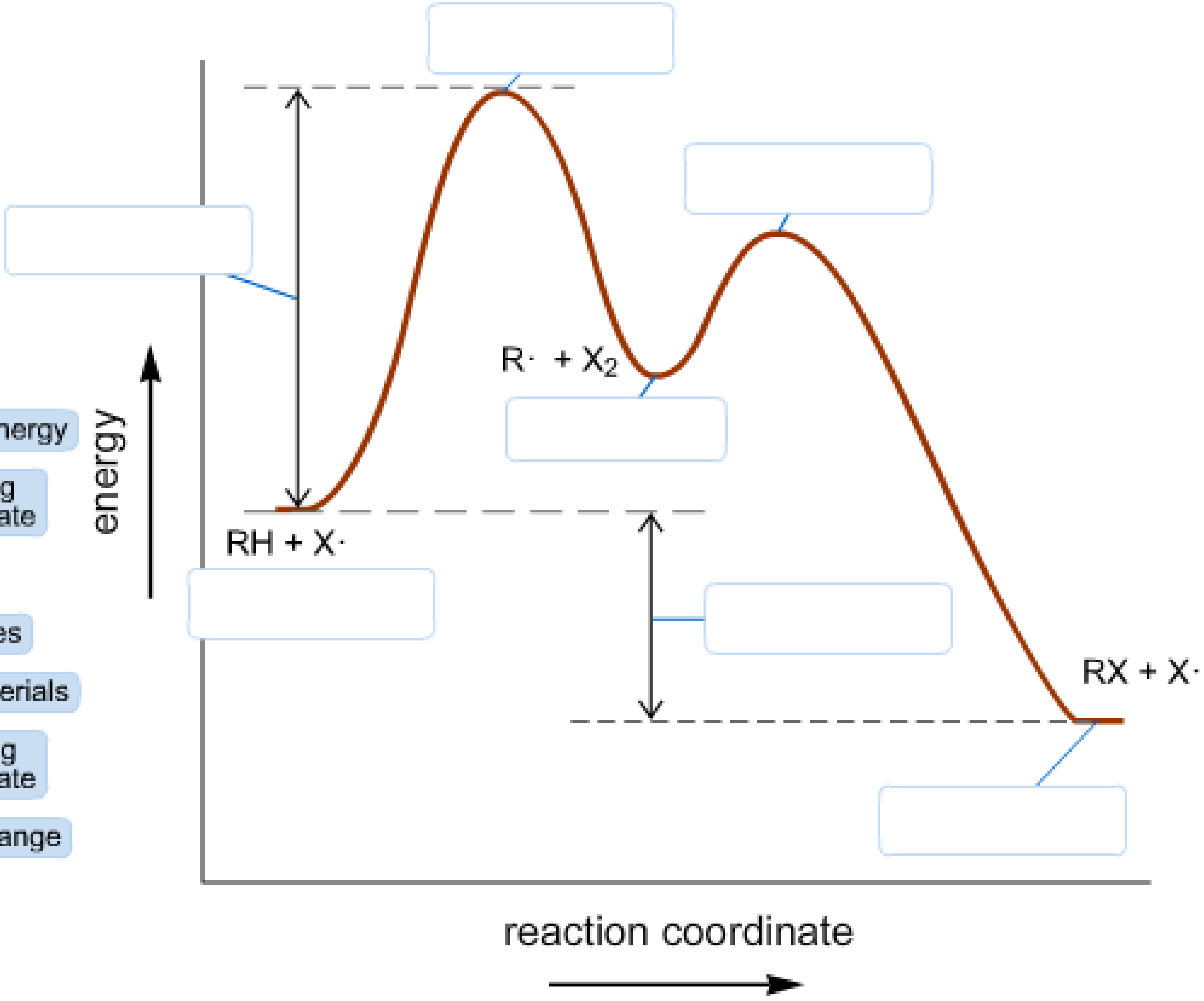
Qual dos gráficos representa uma reação onde ocorre formação de intermediários?





https://www.youtube.com/watch?v=_1jKWnzCNps

Label the energy diagram for a two-step reaction.



- activation energy
- non-limiting transition state
- products
- intermediates
- starting materials
- rate-limiting transition state
- enthalpy change