INTRODUÇÃO A MECANISMOS DE REAÇÃO

NUCLEÓFILOS E ELETRÓLIFOS

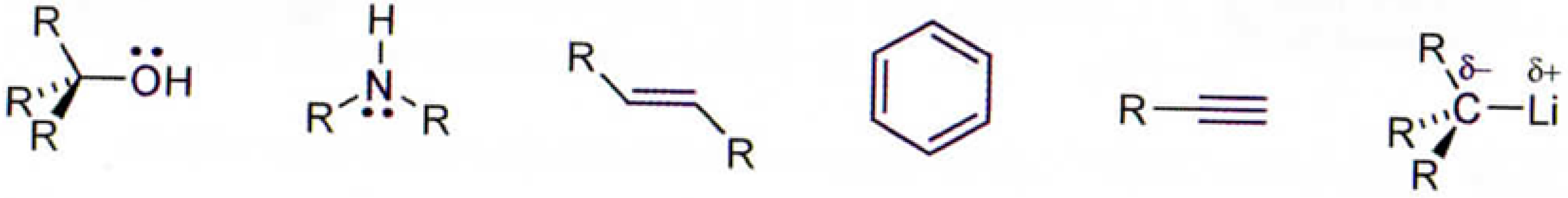
Espécies com carga negativa ou sem carga, que *DOAM UM PAR DE ELÉTRONS* a espécies deficientes de elétrons, com formação de ligação covalente.

Br^- , H_2O , CN^- , HO^- , carbânions etc...

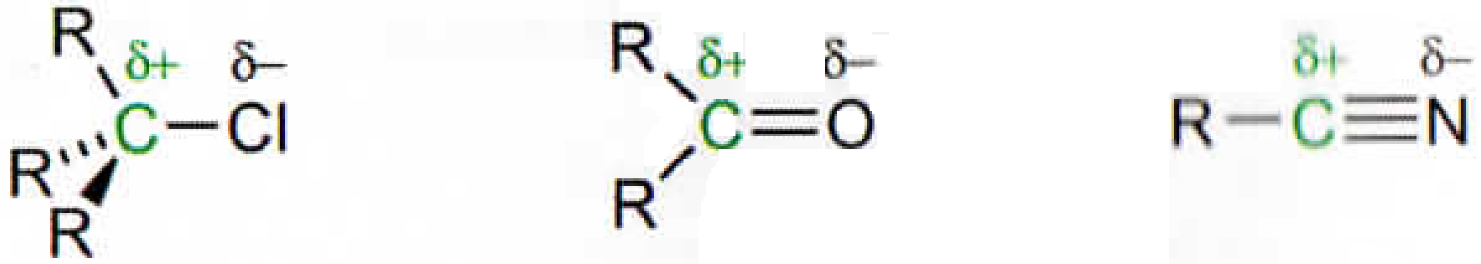
Espécies com carga positiva ou sem carga que *ACEITAM UM PAR DE ELÉTRONS, com formação de ligação covalente.*

NO_2^+ , H^+ , carbocátions , etc....

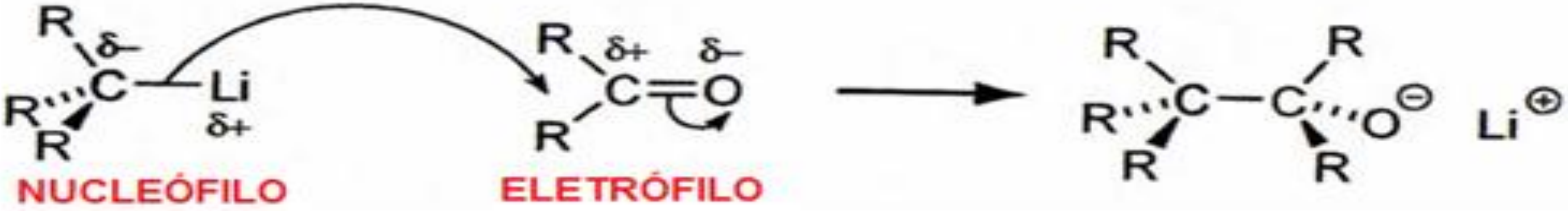
SÍTIOS NUCLEOFÍLICOS EM MOLÉCULAS NEUTRAS



SÍTIOS ELETROFÍLICOS EM MOLÉCULAS NEUTRAS



TRANSFORMAÇÕES QUÍMICAS

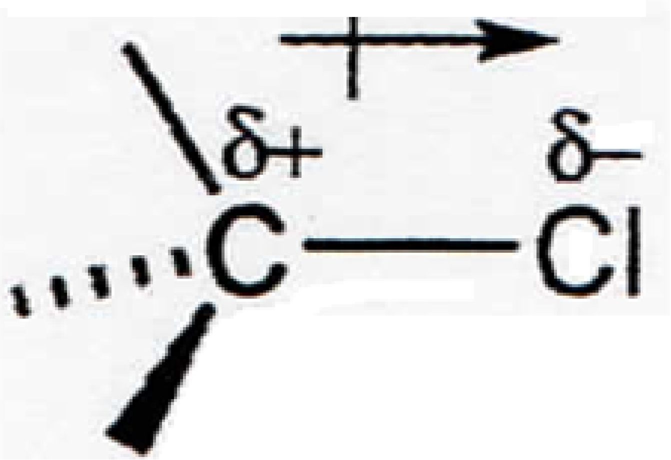


EFEITOS ELETRÔNICOS

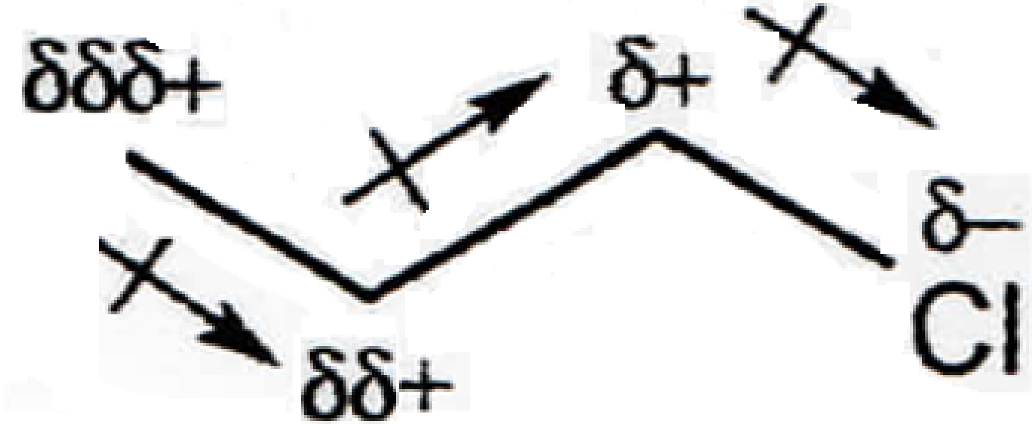
EFEITO INDUTIVO

Resulta da polarização da ligação entre dois átomos de diferente eletronegatividade

EFEITO - I



transmissão ao longo da cadeia



GRUPOS -I

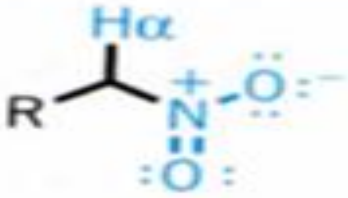
X = F, Cl, Br, OH, OR

CHO, COR, CN, CO_2H, CO_2R

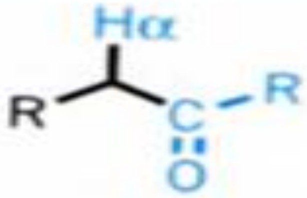
NH_2, NHR, NR_2, NO_2, SO_3H

DUPLA, TRIPLA, FENILA

Magnitude do efeito –I de vários grupos

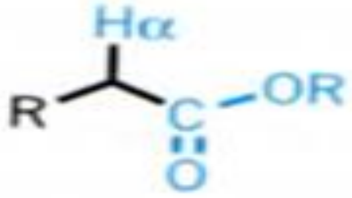


pK$_a$ ~ 10

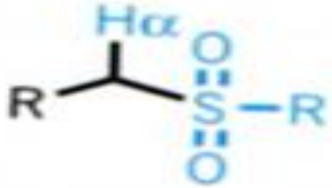


pK$_a$ ~ 20

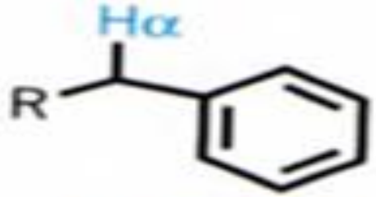
pK$_a$ ~ 25



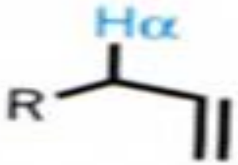
pK$_a$ ~ 25



pK$_a$ ~ 33



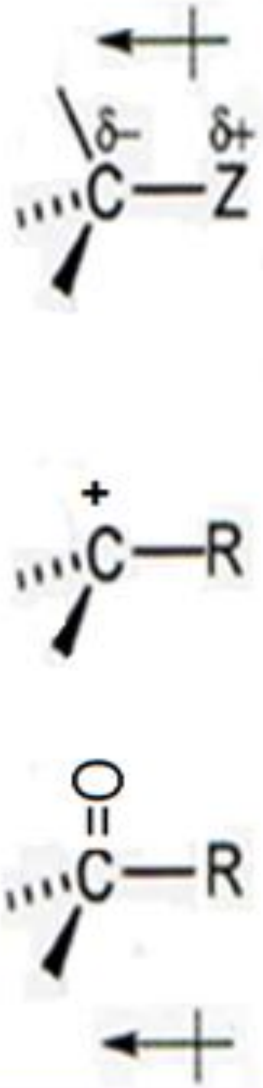
pK$_a$ ~ 41



pK$_a$ ~ 43

pK$_a$ ~ 49

efeito +I



grupos +I

Z = R (alquila), metais (p. ex., Li, Mg)

em organometálicos

eletronegatividade

H	2,2
C	2,5
Li	1,0
Mg	1,3

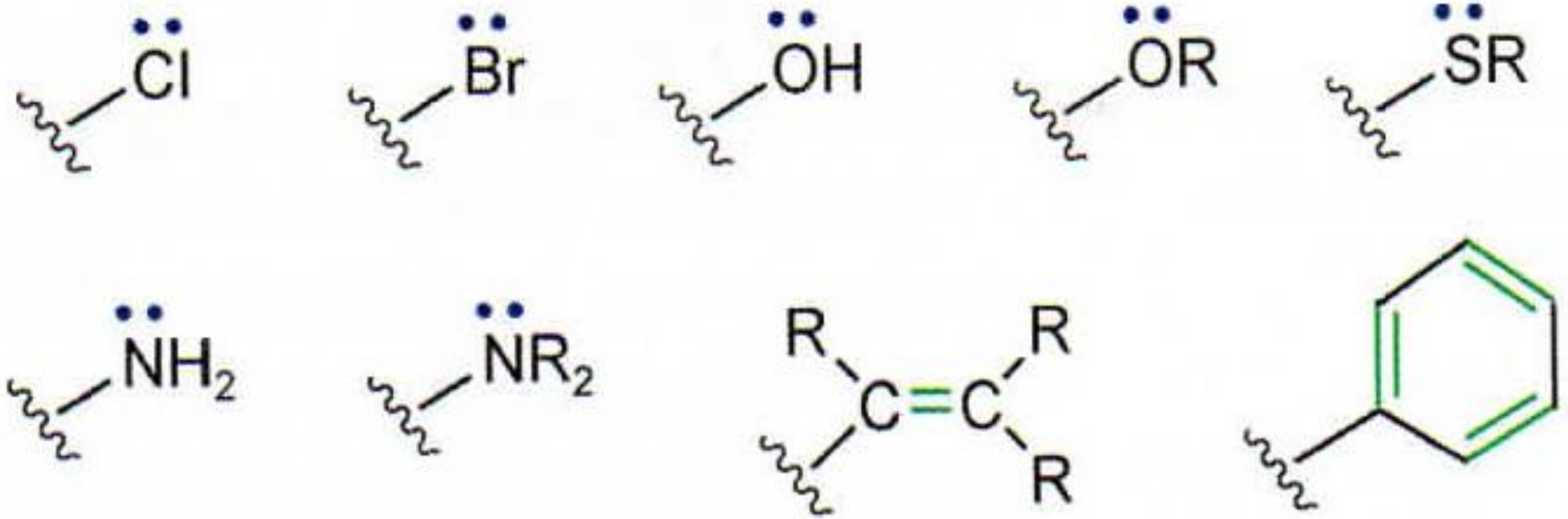
EFEITO MESOMÉRICO

Grupos com efeito +M = doadores de elétrons

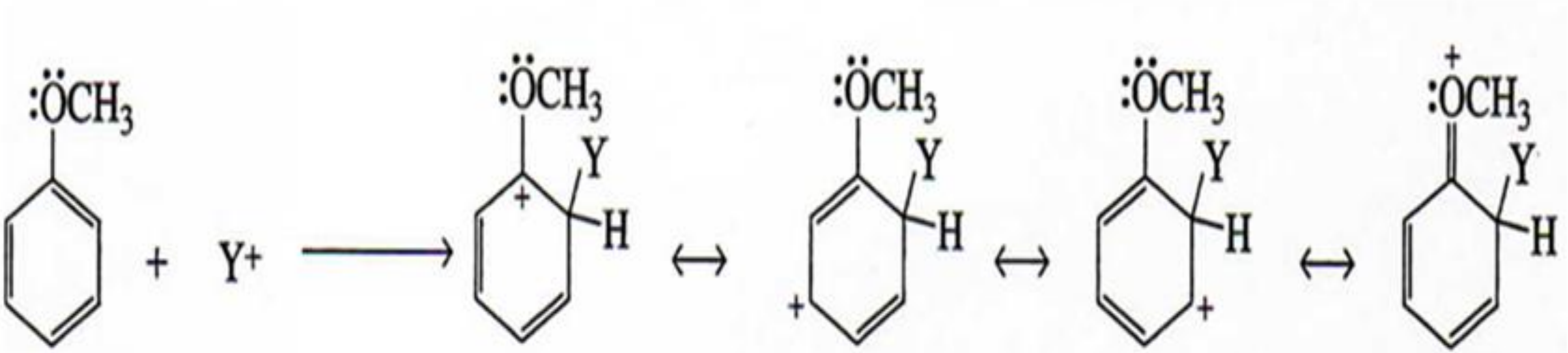
Grupos com efeito -M = receptores de elétrons

Grupos +M

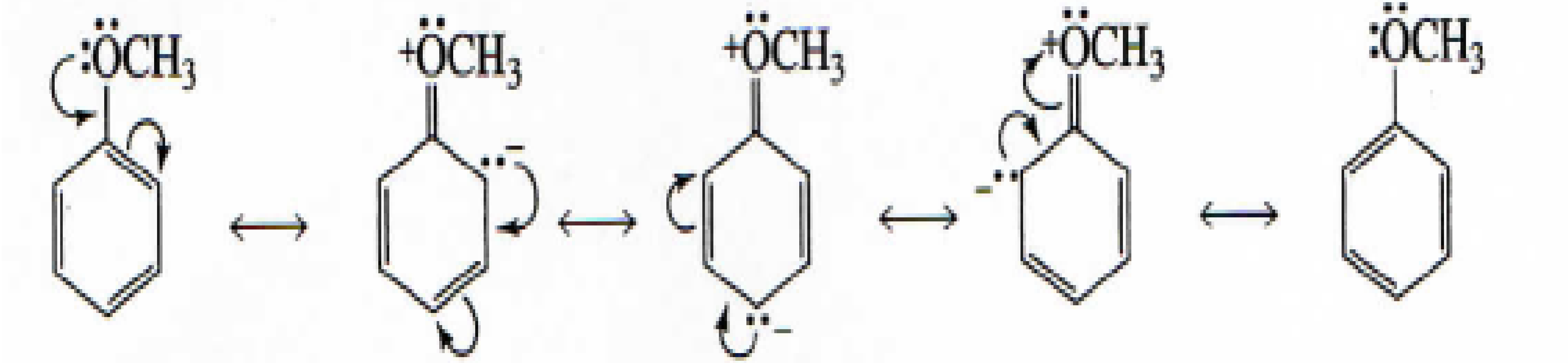
Doadores de elétrons contendo um par isolado ou uma ou mais ligações π



Grupo +M

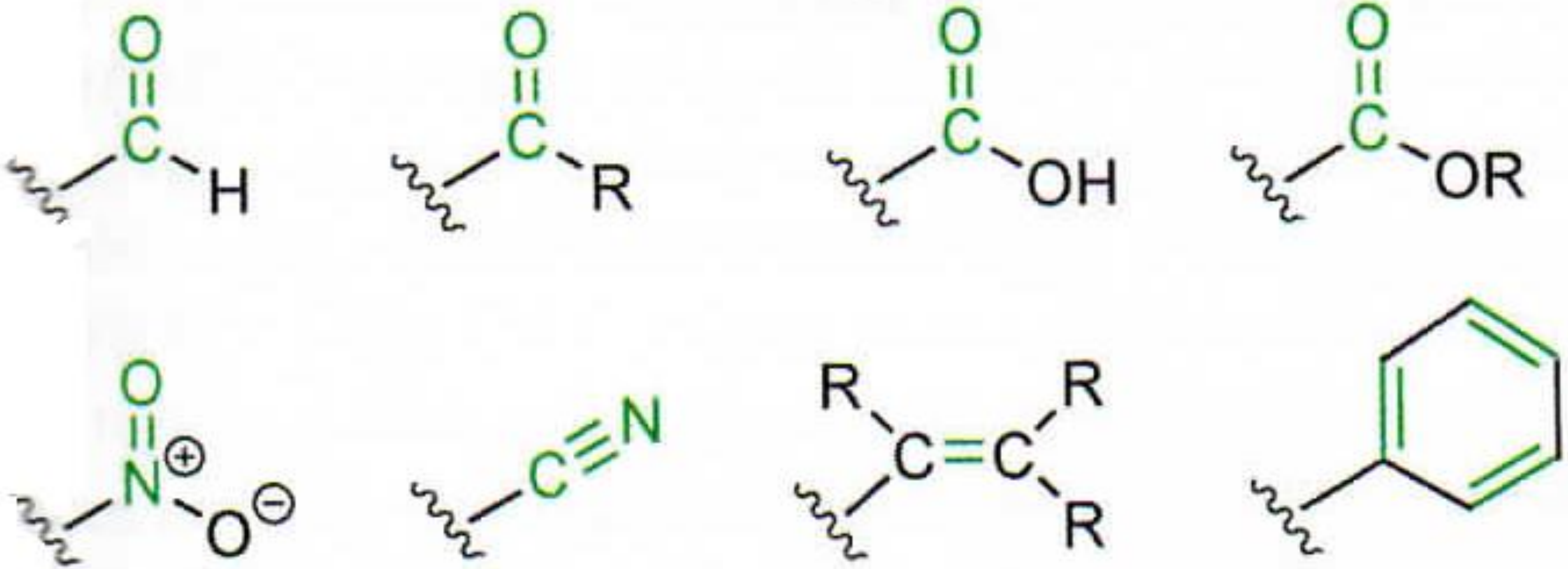


EFEITO +M EM MOLÉCULAS NEUTRAS

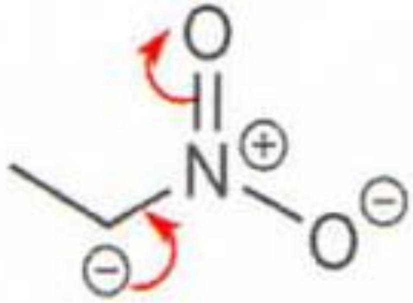


Grupos –M

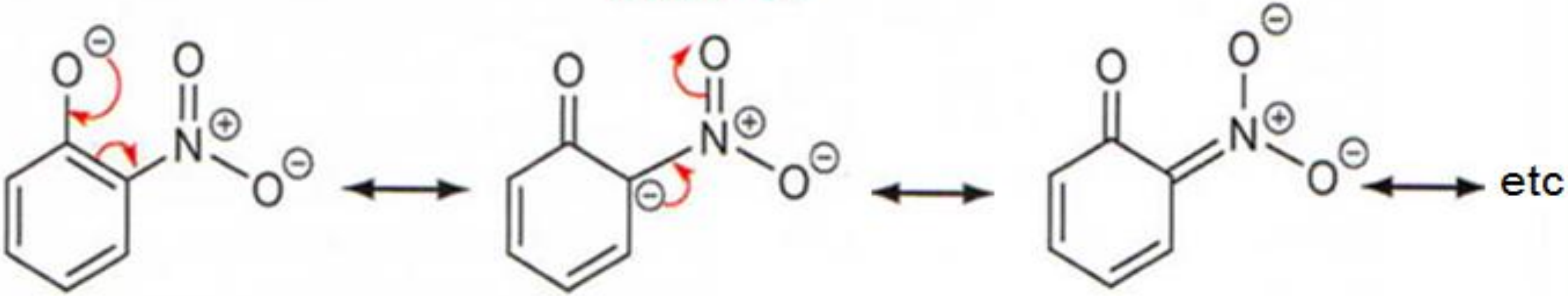
Receptores de elétrons contendo uma ou mais ligações π



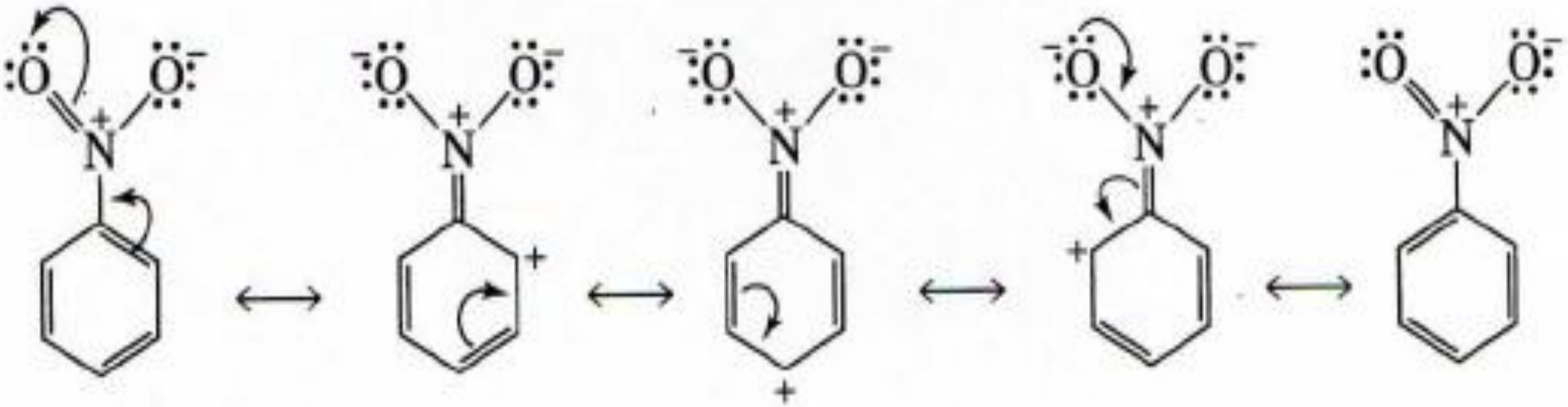
EFEITO -M NA ESTABILIZAÇÃO DE ÂNIONS



Efeito –M

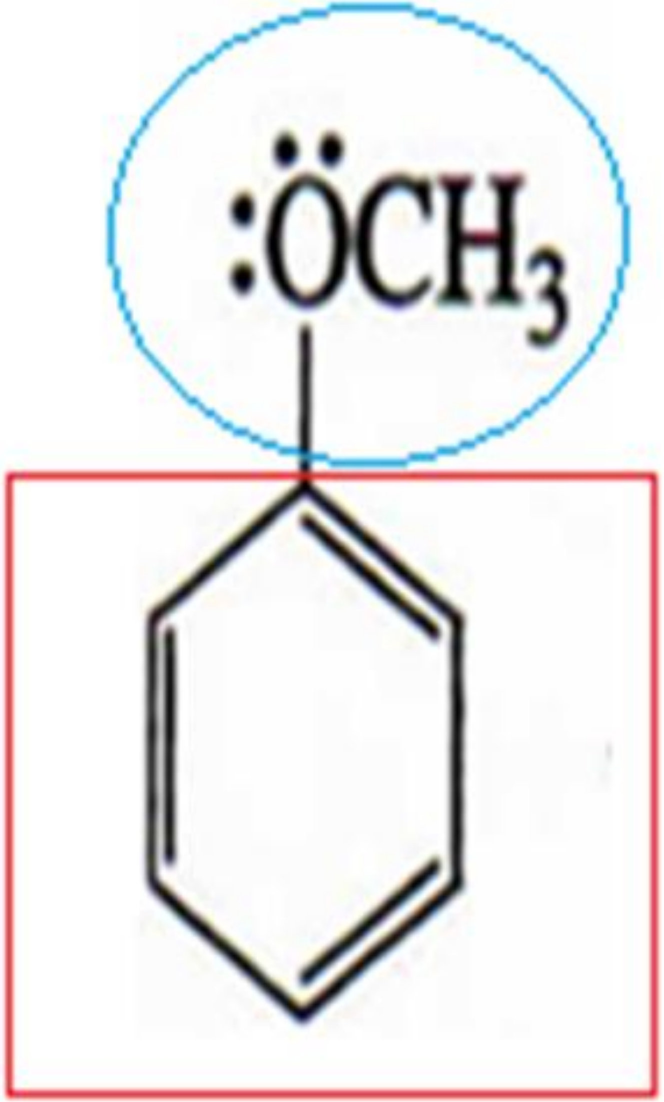


EFEITO -M EM MOLÉCULAS NEUTRAS



Entre o efeito indutivo e o mesomérico, o efeito mesomérico sempre prepondera.

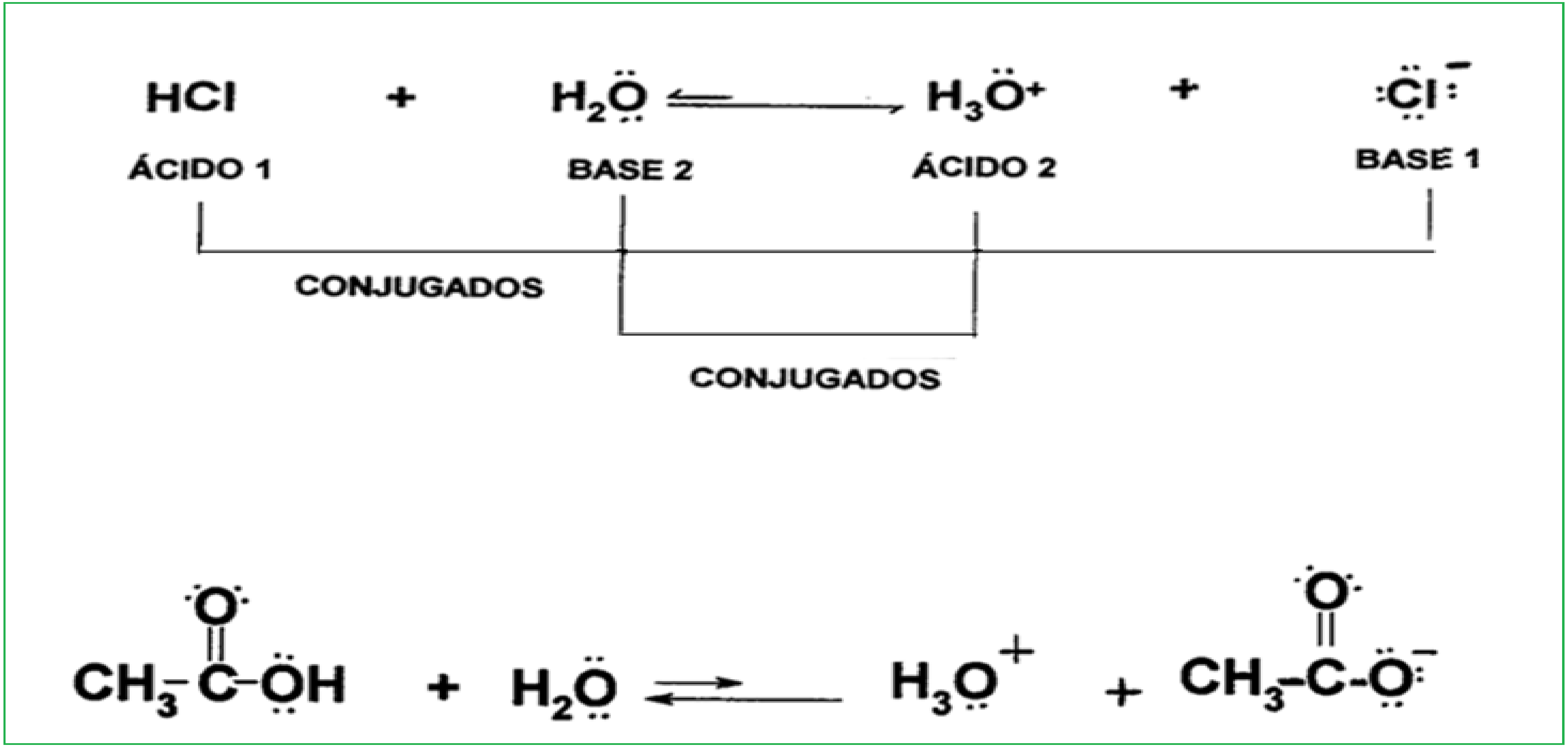
+M, -I



-M, -I

TIPOS DE REAÇÕES

REAÇÕES ÁCIDO-BASE



$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

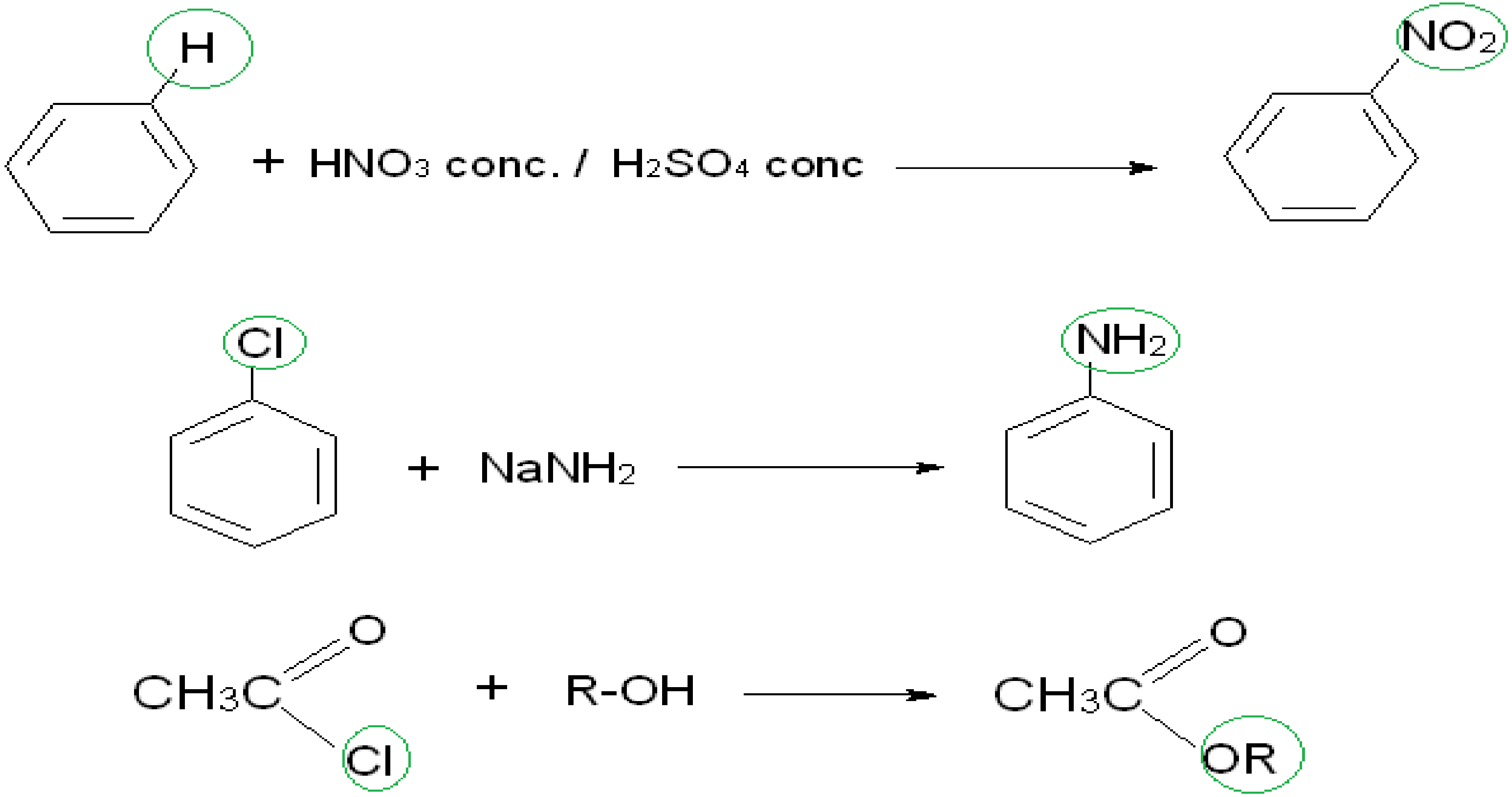
$$CH_3-C(=O)-OH + H_2O \rightleftharpoons H_3O^+ + CH_3-C(=O)-O^-$$

REAÇÕES POLARES

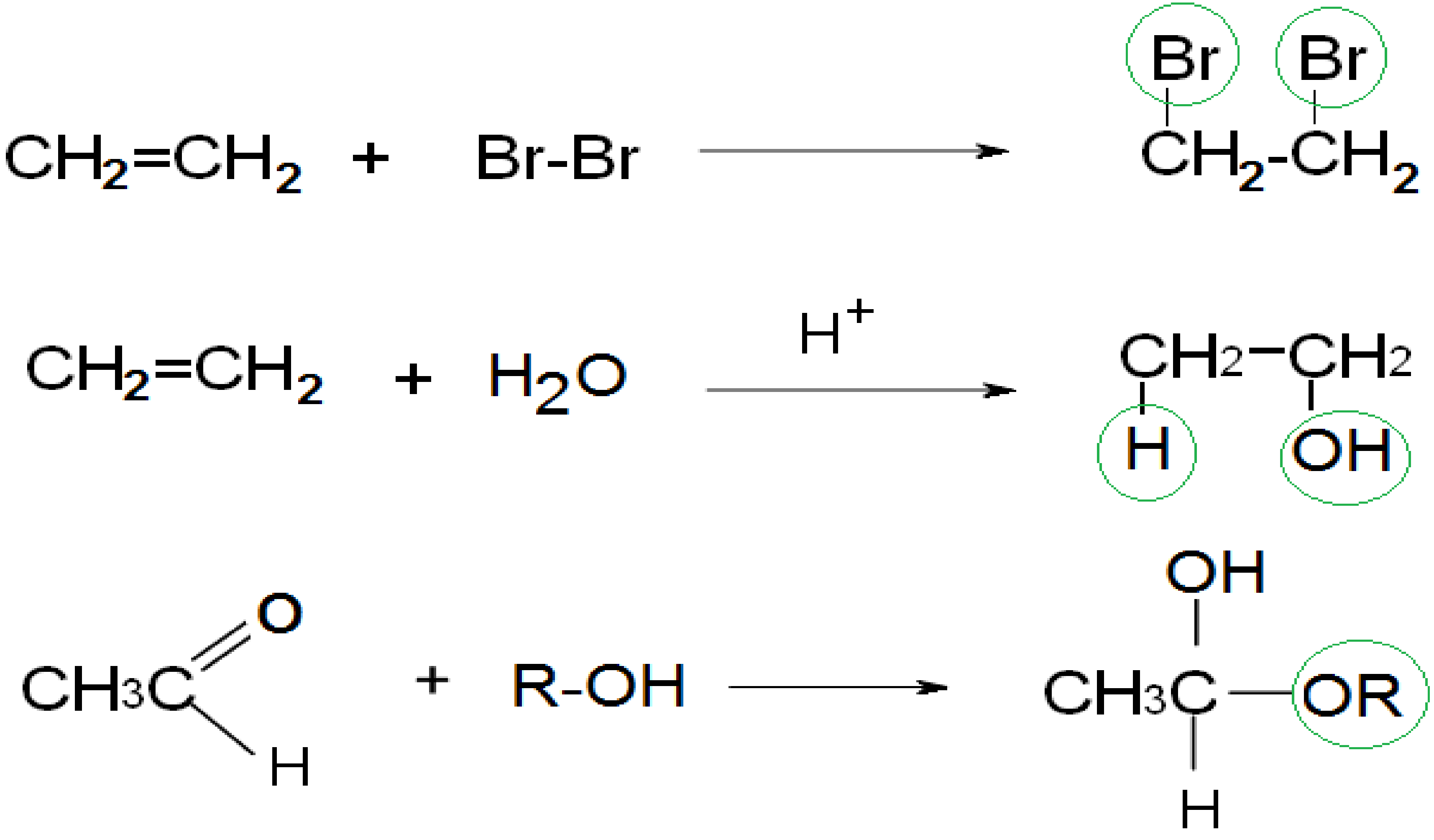
- **SUBSTITUIÇÃO**
- **ADIÇÃO**
- **ELIMINAÇÃO**

SUBSTITUIÇÃO

$$CH_3\text{-}Br + {}^{-}OH \longrightarrow CH_3\text{-}OH + Br^{-}$$



ADIÇÃO

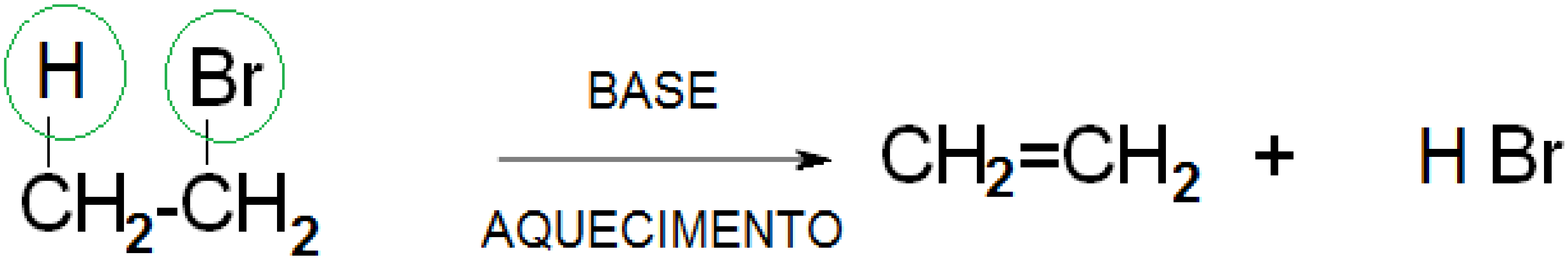


$$CH_2{=}CH_2 + Br{-}Br \longrightarrow \underset{}{\overset{Br}{\overset{|}{C}}H_2}{-}\overset{Br}{\overset{|}{C}}H_2$$

$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} \underset{\underset{H}{|}}{C}H_2{-}\underset{\underset{OH}{|}}{C}H_2$$

$$CH_3CHO + R{-}OH \longrightarrow CH_3\overset{OH}{\overset{|}{\underset{\underset{H}{|}}{C}}}{-}OR$$

ELIMINAÇÃO



$$\overset{H}{\underset{|}{}}\!\!CH_2-\overset{Br}{\underset{|}{}}\!\!CH_2 \xrightarrow[\text{AQUECIMENTO}]{\text{BASE}} CH_2=CH_2 + HBr$$

REAÇÕES RADICALARES

$$Br_2 \xrightarrow{\Delta} 2\,Br\cdot$$

$$Br\cdot + CH_3CH_3 \longrightarrow CH_3\dot{C}H_2 + HBr$$

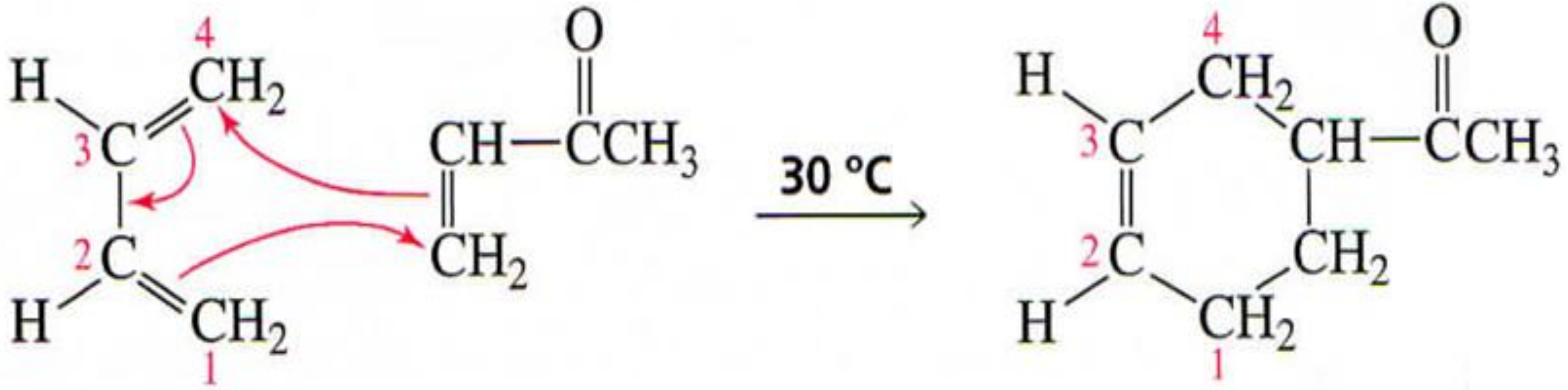
$$CH_3\dot{C}H_2 + Br_2 \longrightarrow \boxed{CH_3CH_2Br} + Br\cdot$$

$$Br\cdot + Br\cdot \longrightarrow Br_2$$

$$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \longrightarrow CH_3CH_2CH_2CH_3$$

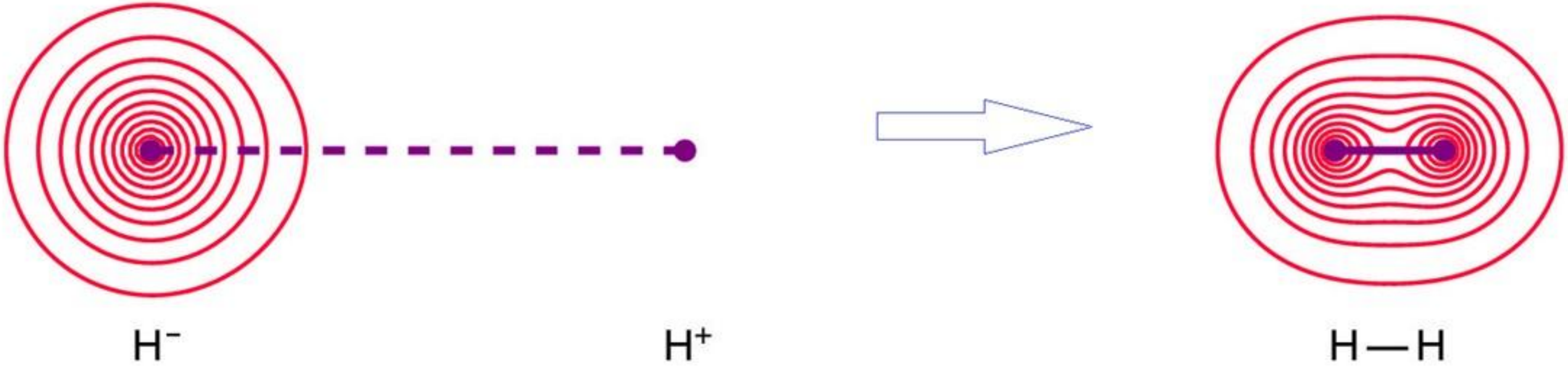
$$CH_3\dot{C}H_2 + Br\cdot \longrightarrow CH_3CH_2Br$$

REAÇÕES PERICÍCLICAS



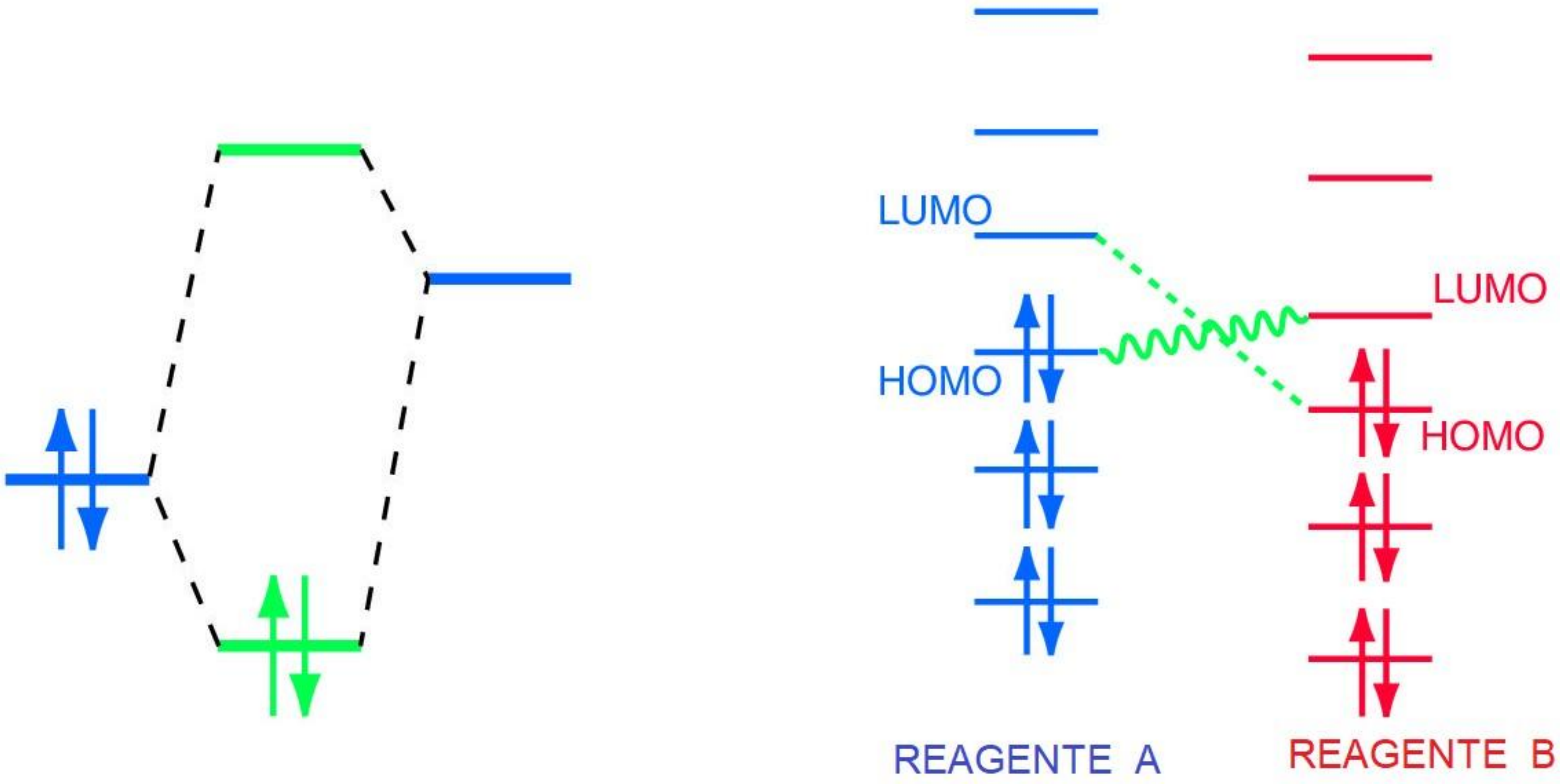
REAÇÕES QUÍMICAS E ORBITAIS MOLECULARES

A REAÇÃO MAIS SIMPLES

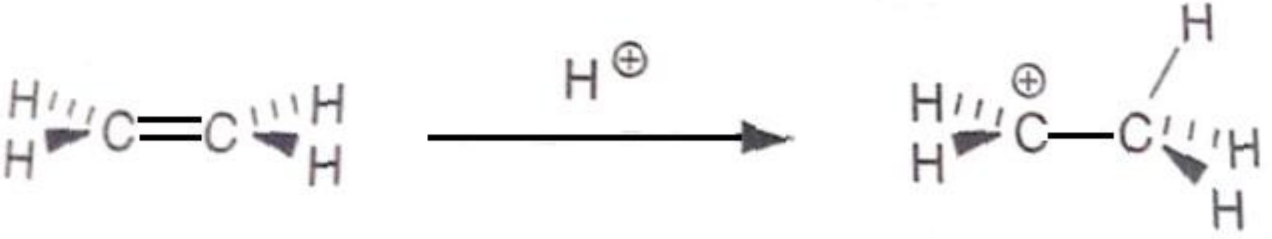


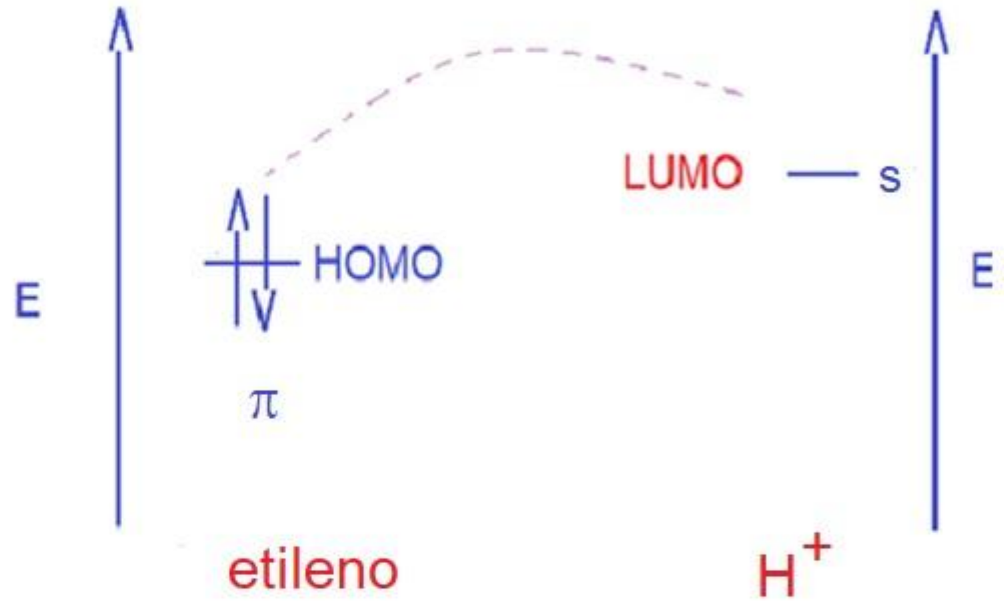
COMO OS ELÉTRONS SE REDISTRIBUEM

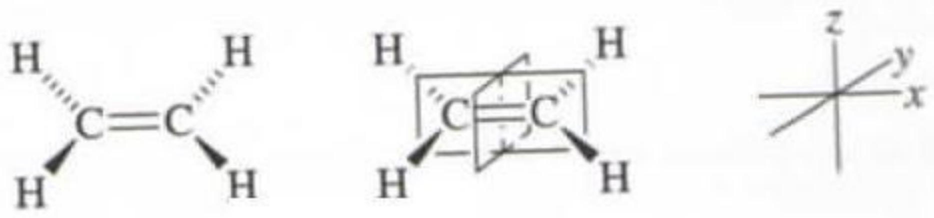
INTERAÇÕES ENTRE HOMO E LUMO



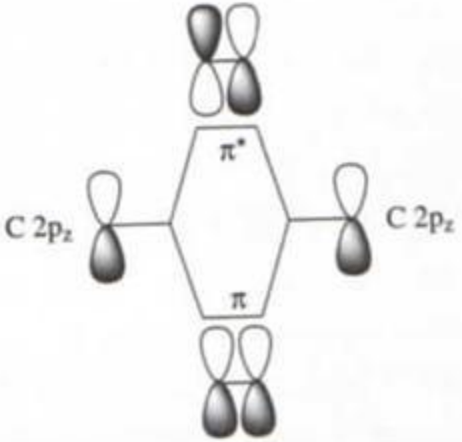
outro exemplo:

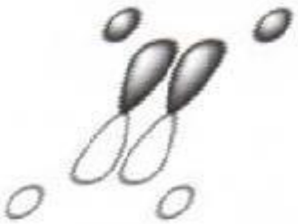






ETILENO




A


B


C


D

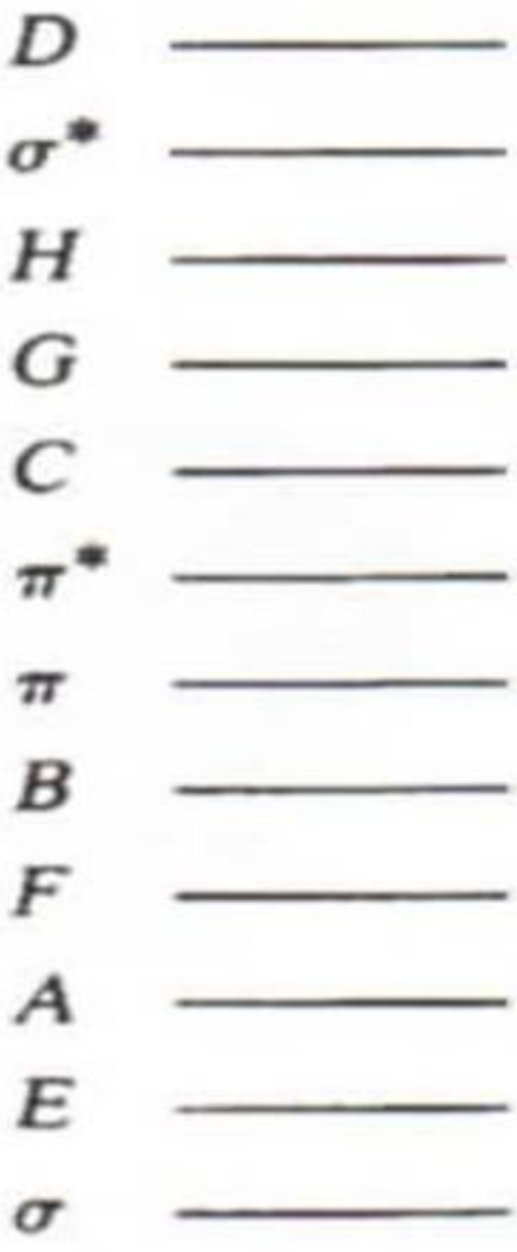

E


F


G


H

ORDEM CRESCENTE DE ENERGIA

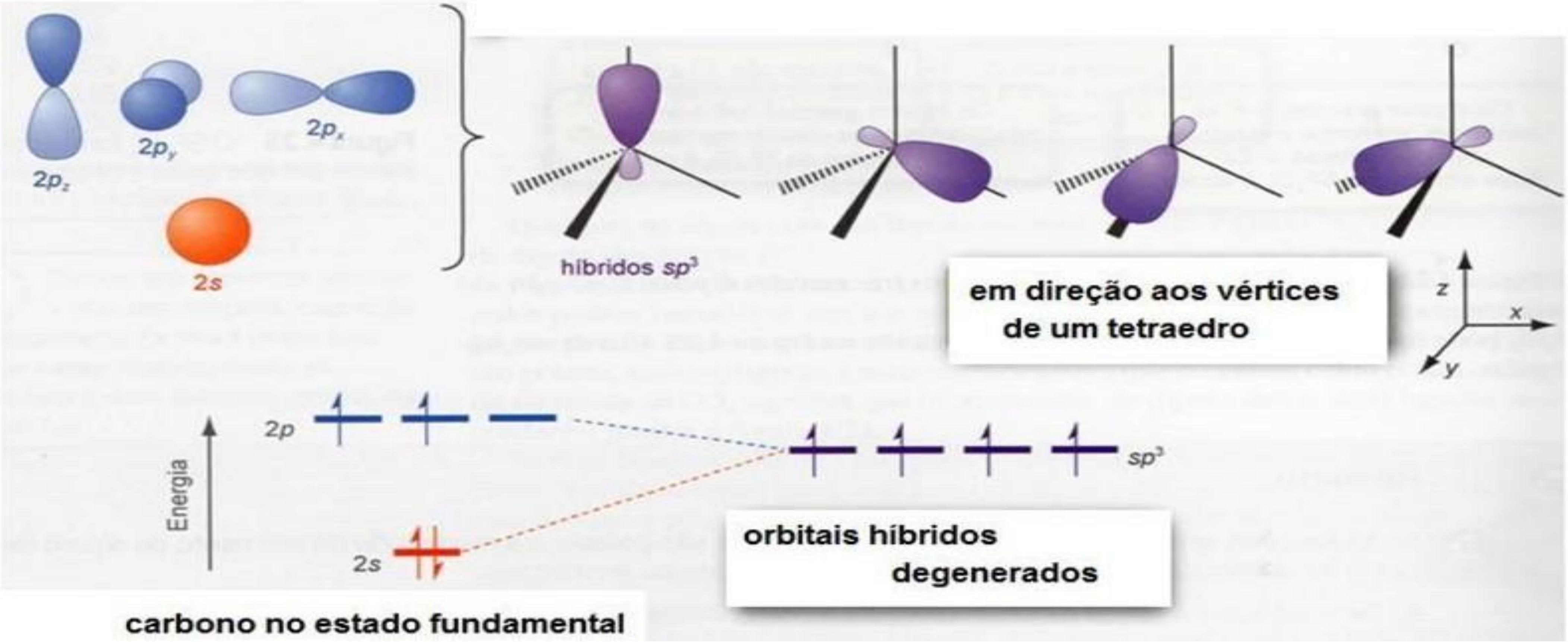


orbitais moleculares do etileno

PORÉM, PARA CONSTRUIR OS DIAGRAMAS DE ORBITAIS MOLECULARES,

UTILIZAREMOS ORBITAIS ATÔMICOS HÍBRIDOS

HIBRIDIZAÇÃO sp^3

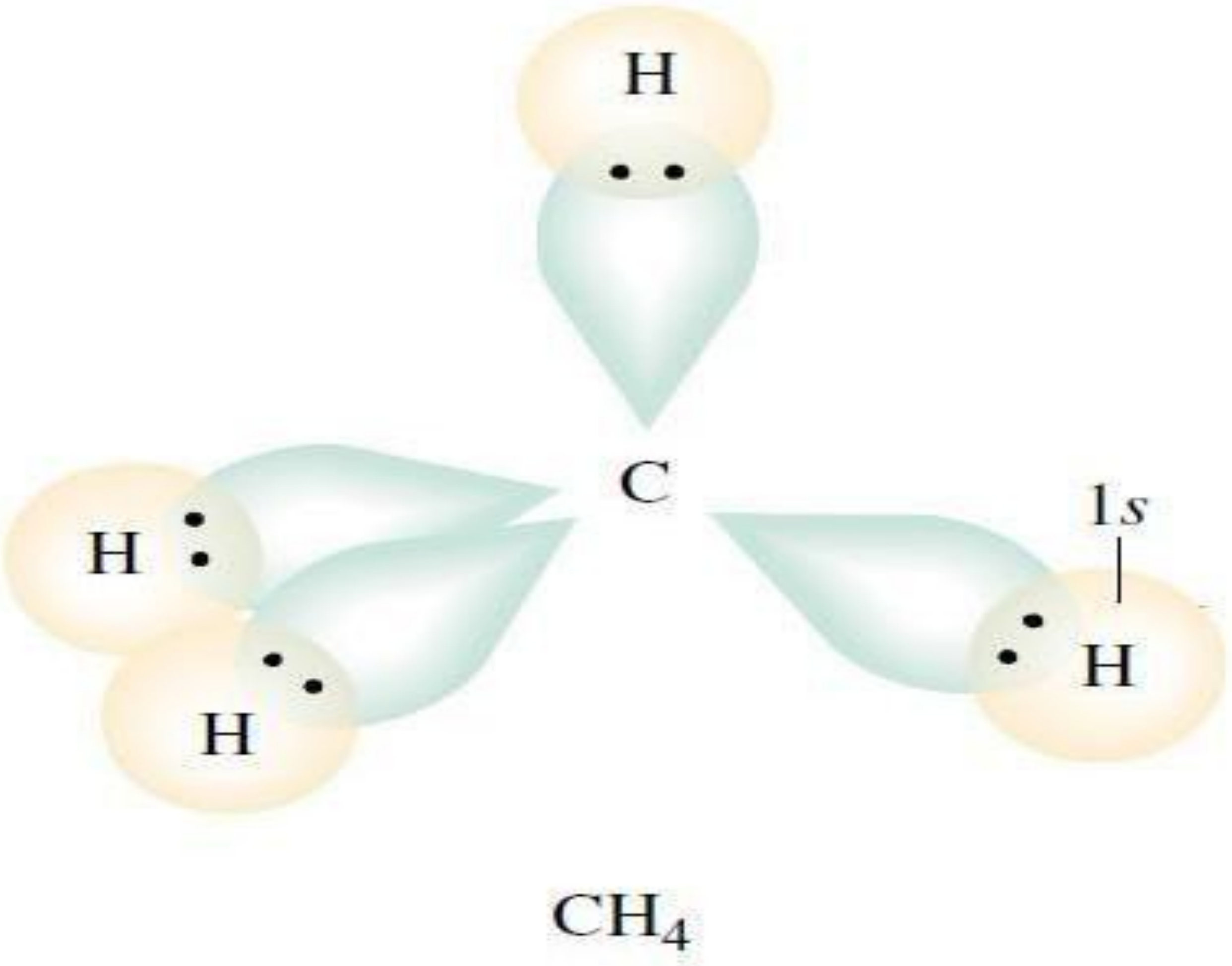


em direção aos vértices
de um tetraedro

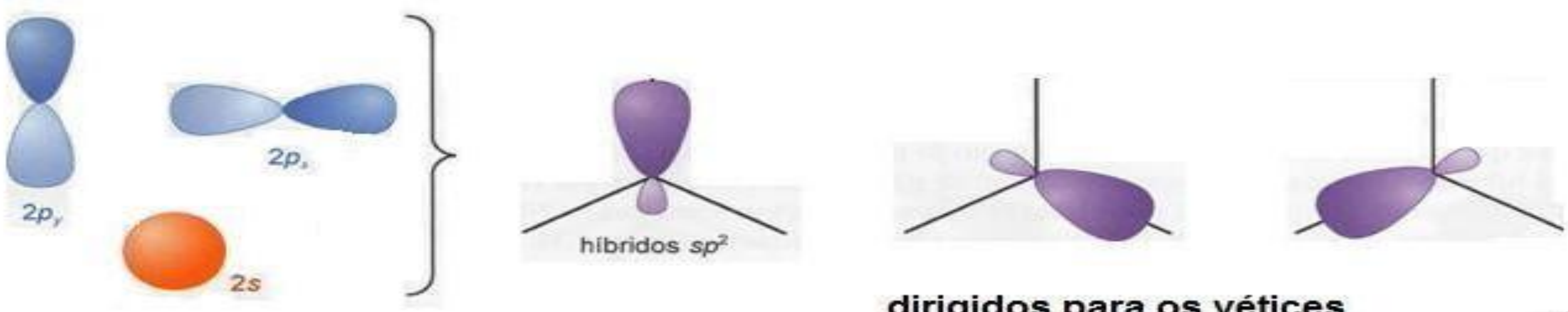
orbitais híbridos
degenerados

carbono no estado fundamental

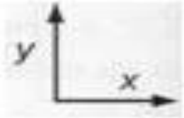
PARA A METANO MOLÉCULA DE CH_4

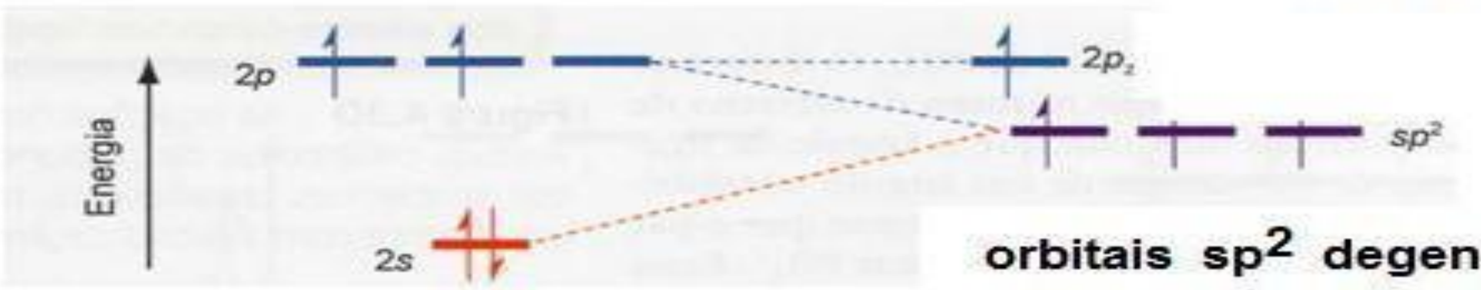


HIBRIDIZAÇÃO sp^2



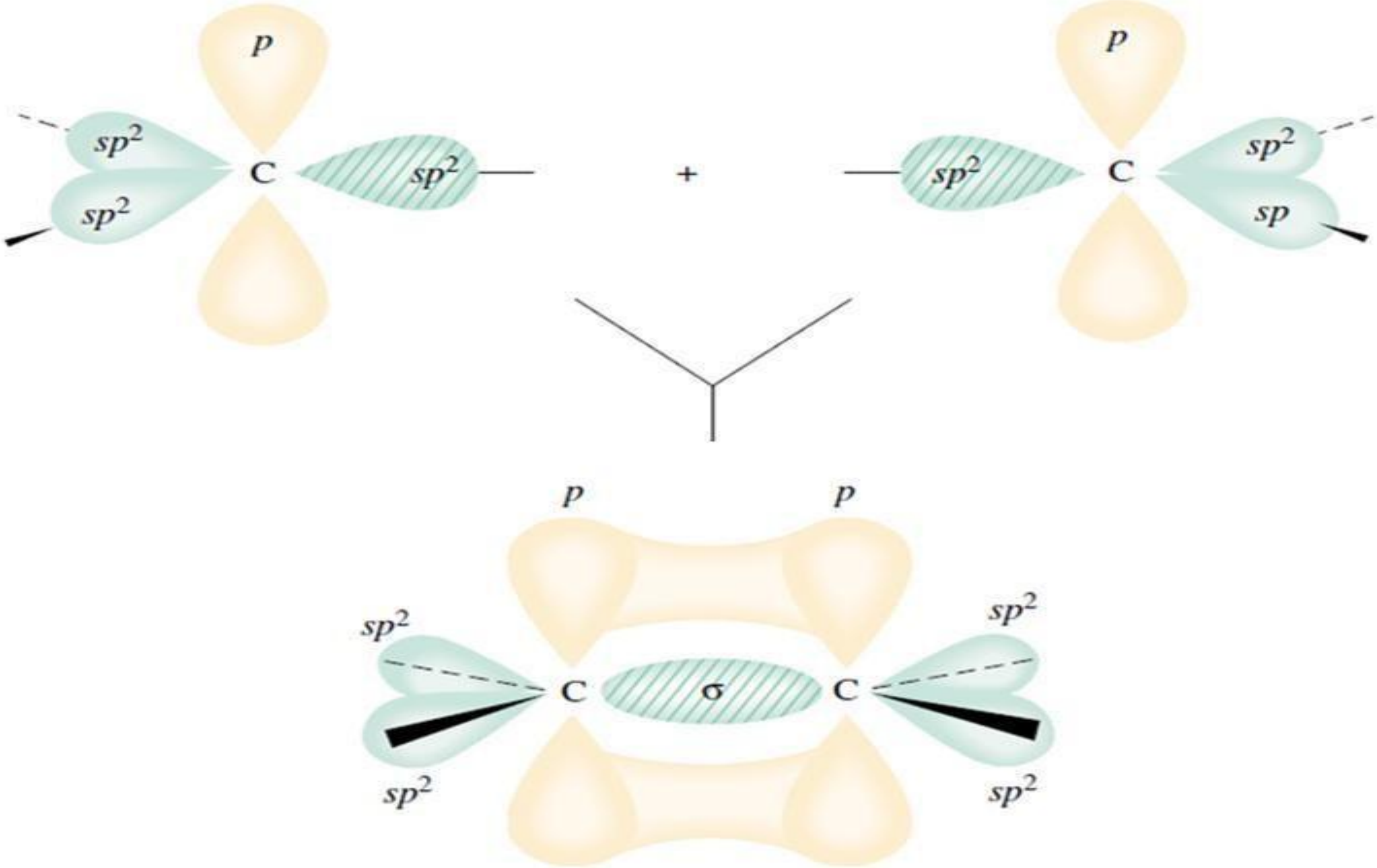
dirigidos para os vétices
de um triângulo



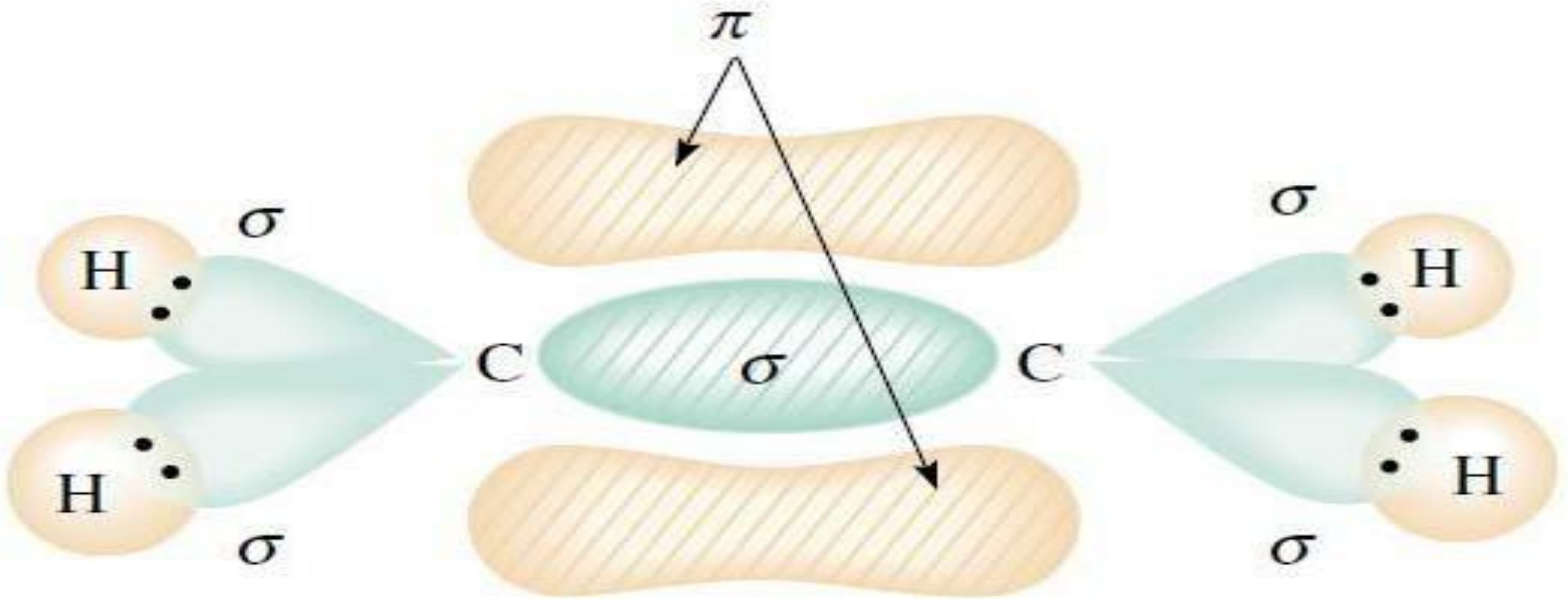


orbitais sp^2 degenerados

carbono no estado fundamental

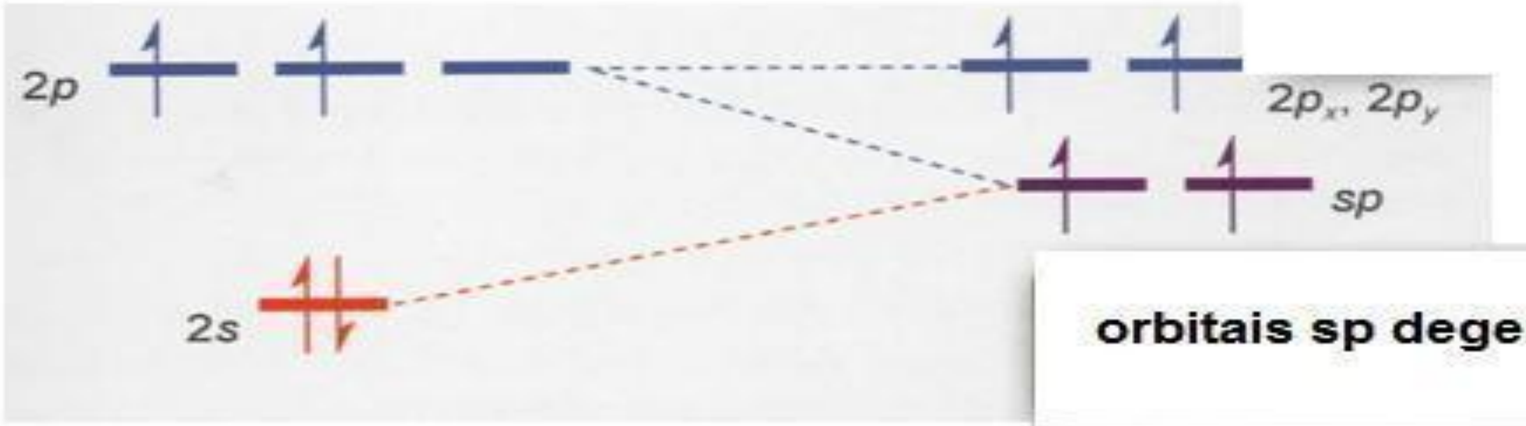

p
sp²
sp²
C
sp²
+
sp²
C
p
sp²
sp
p
p
sp²
C
σ
C
sp²
sp²
sp²

PARA A MOLÉCULA DE ETILENO H_2CCH_2



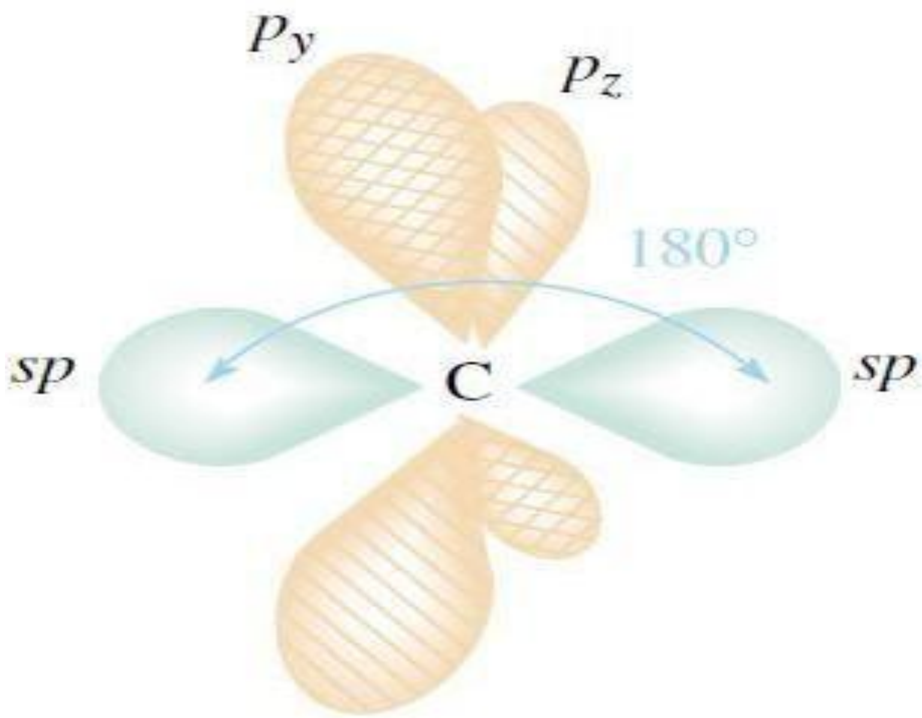
HIBRIDIZAÇÃO sp

orbitais híbridos direcionados a 180°



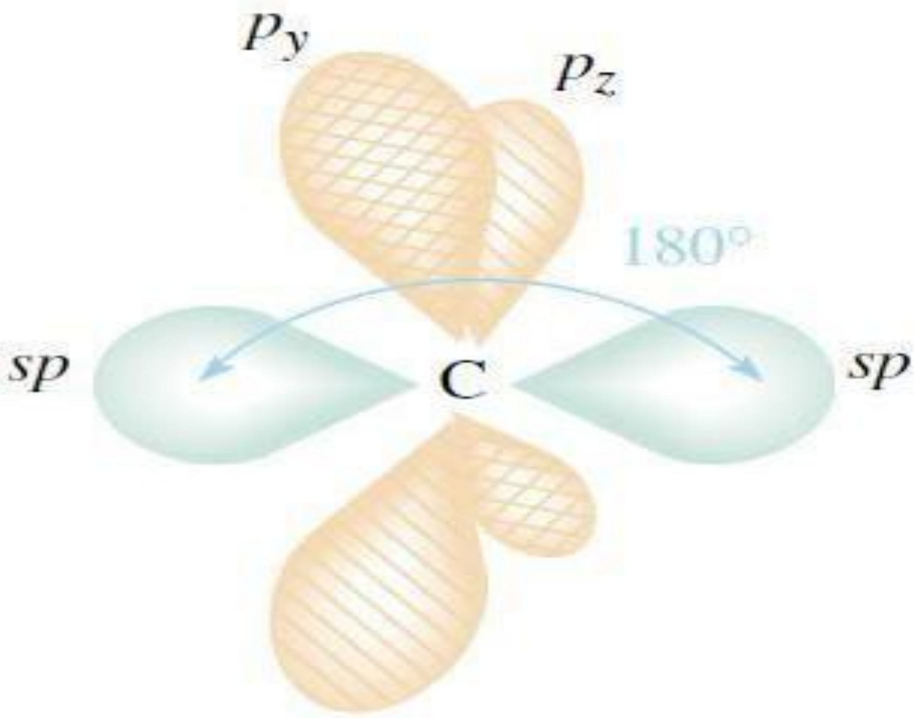
orbitais sp degenerados

átomo de carbono no estado fundamental



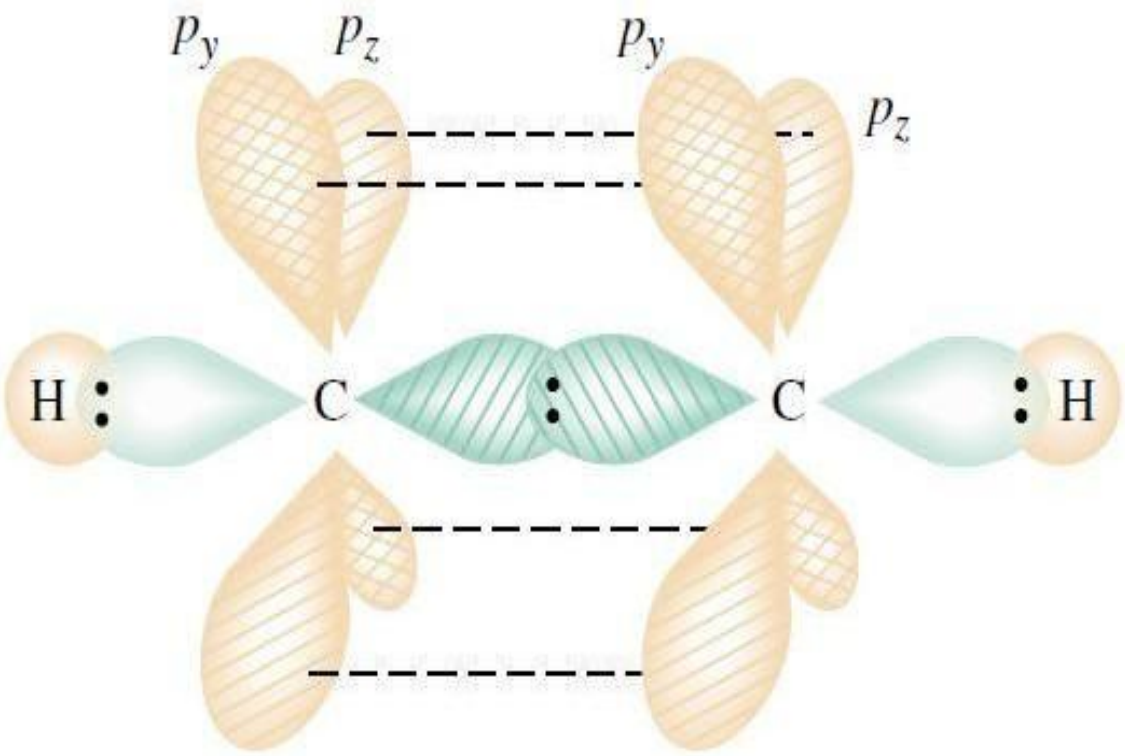
p_y
p_z
180°
sp
C
sp

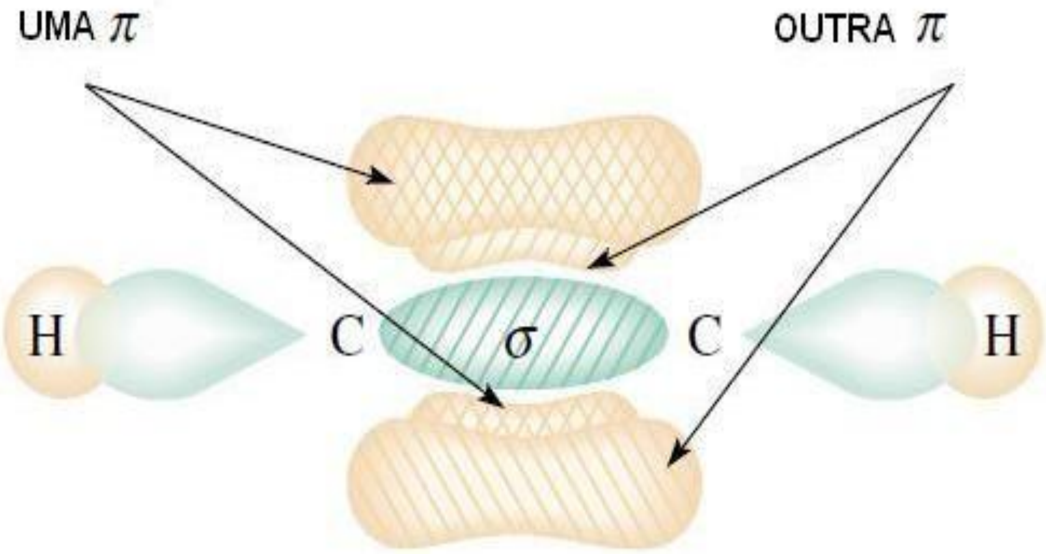
+

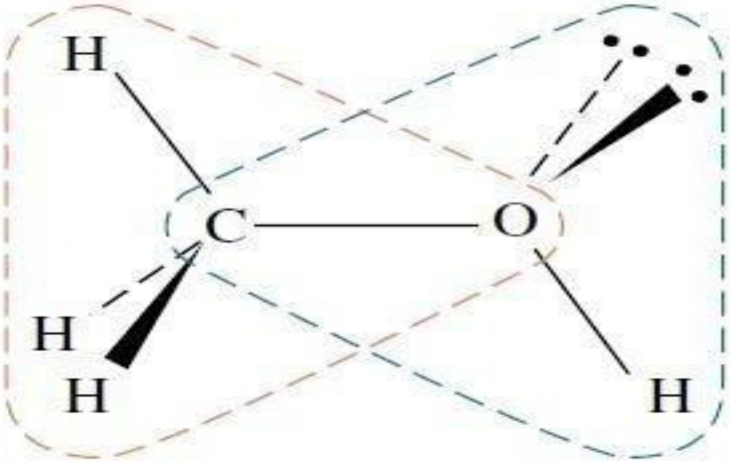


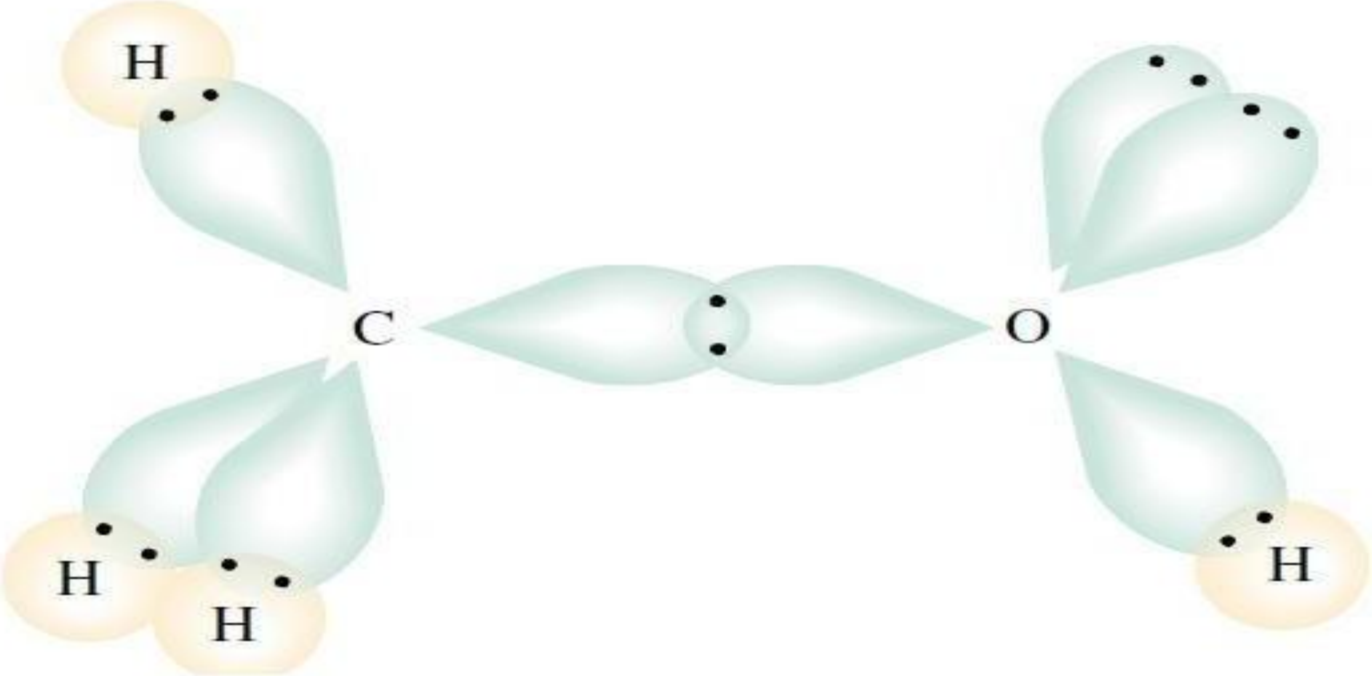
p_y
p_z
180°
sp
C
sp

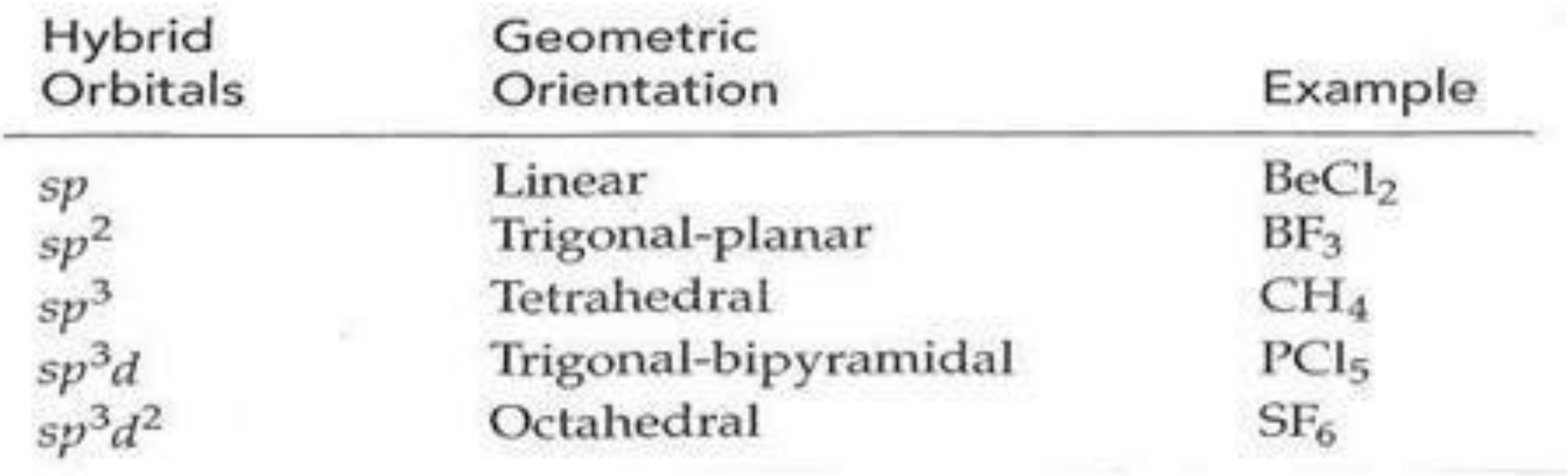
PARA A MOLÉCULA DE ACETILENO HCCH





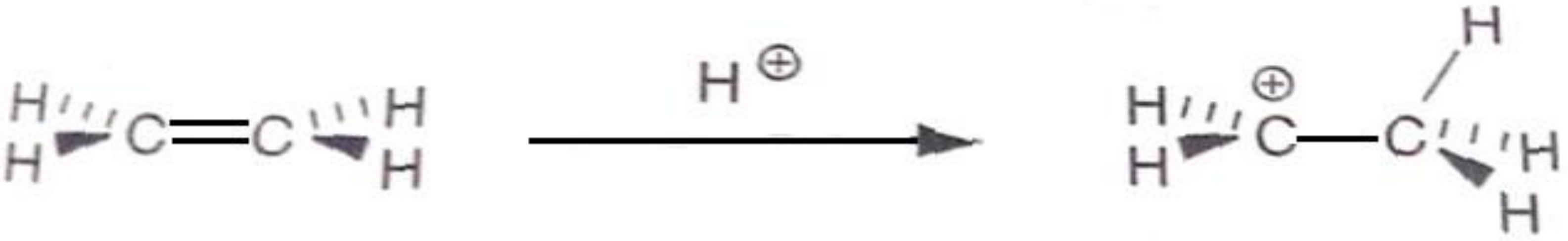

H
C
O
H
H
H

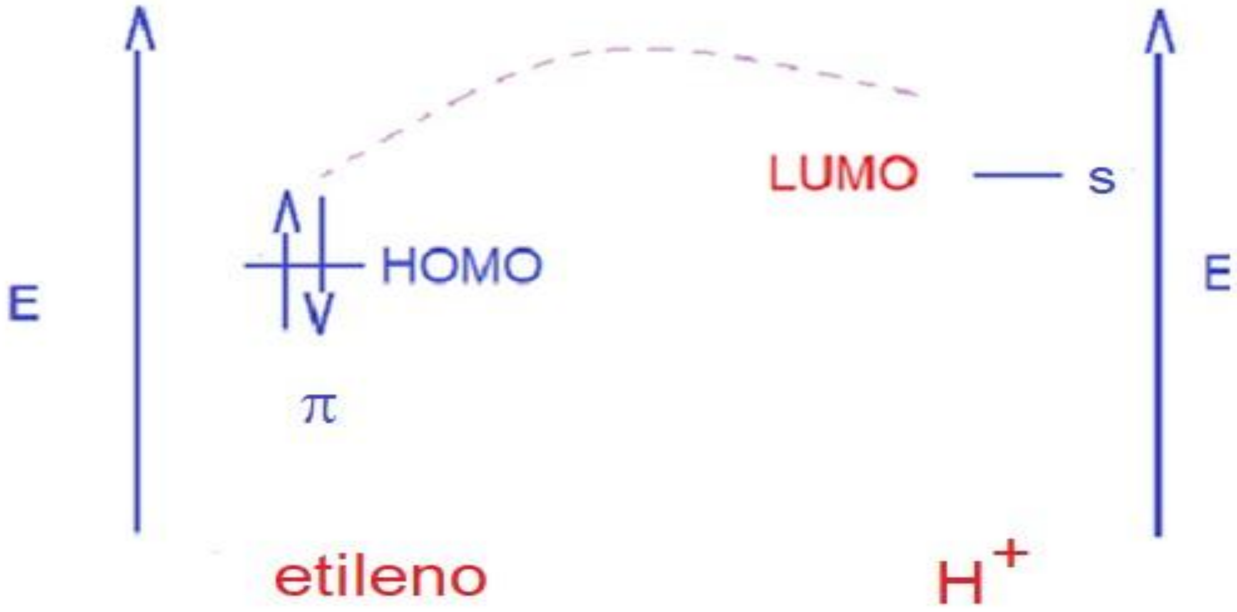

H
C
O
H
H
H



Hybrid Orbitals	Geometric Orientation	Example
sp	Linear	$BeCl_2$
sp^2	Trigonal-planar	BF_3
sp^3	Tetrahedral	CH_4
sp^3d	Trigonal-bipyramidal	PCl_5
sp^3d^2	Octahedral	SF_6

outro exemplo:




E

HOMO

π

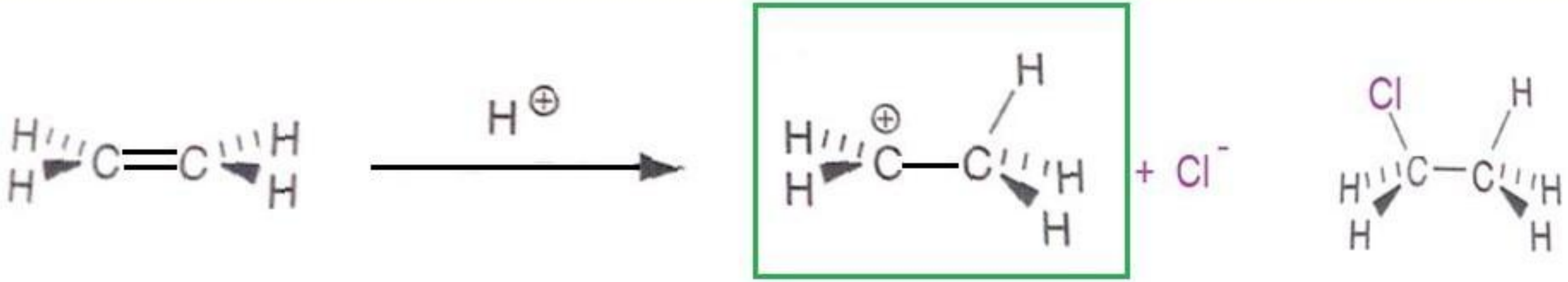
etileno

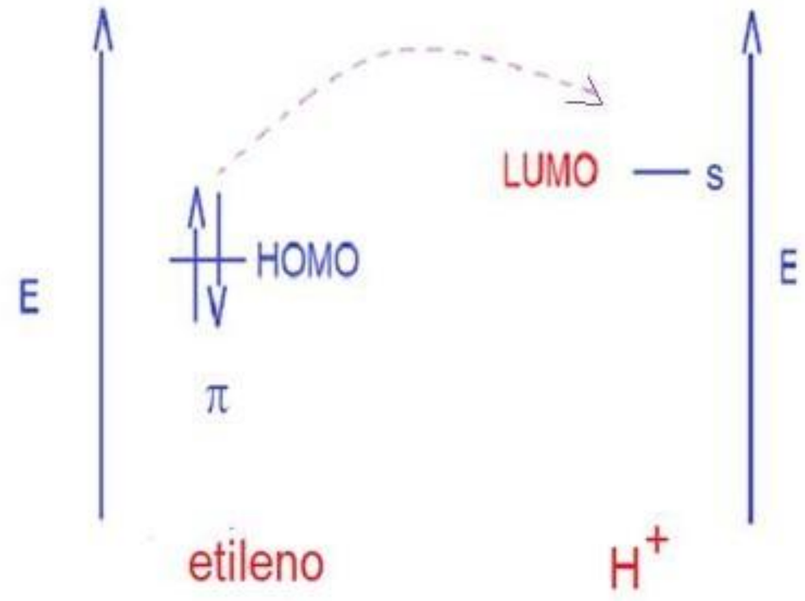
LUMO

s

E

H^+

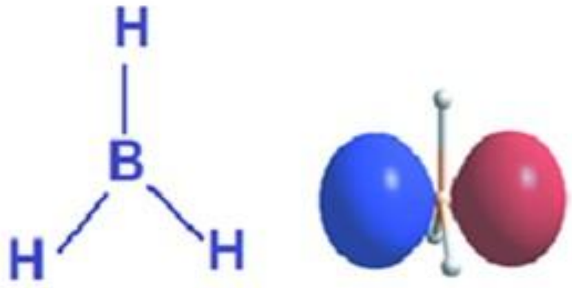

H⊕
+ Cl⁻
Cl

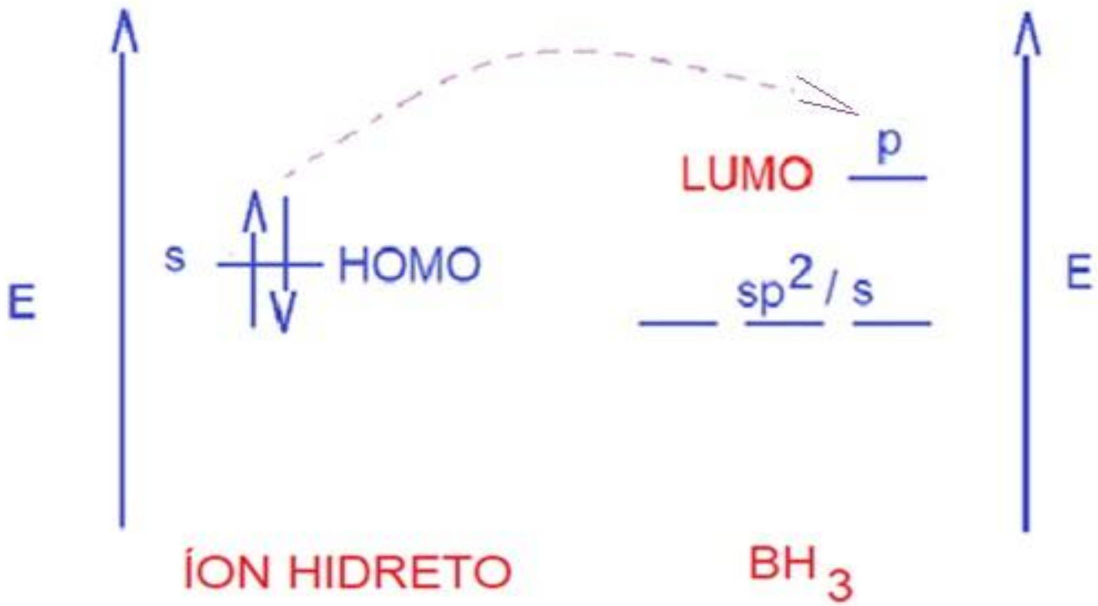

E
HOMO
π
etileno
LUMO
s
E
H+

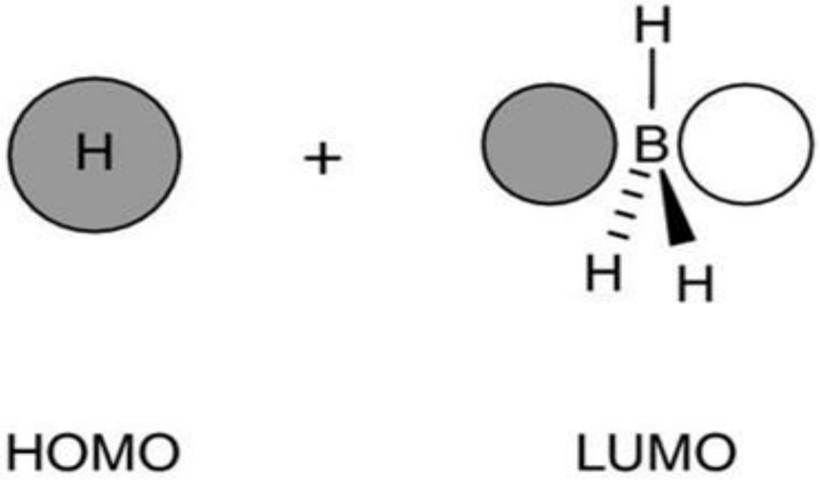

grande separação
final
H+

QUANDO O LUMO É UM "orbital vazio s ou p"

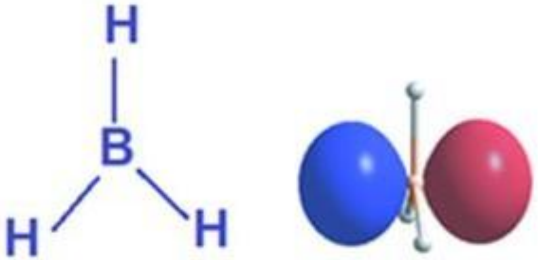
$BH_3 + H^- \longrightarrow BH_4^-$

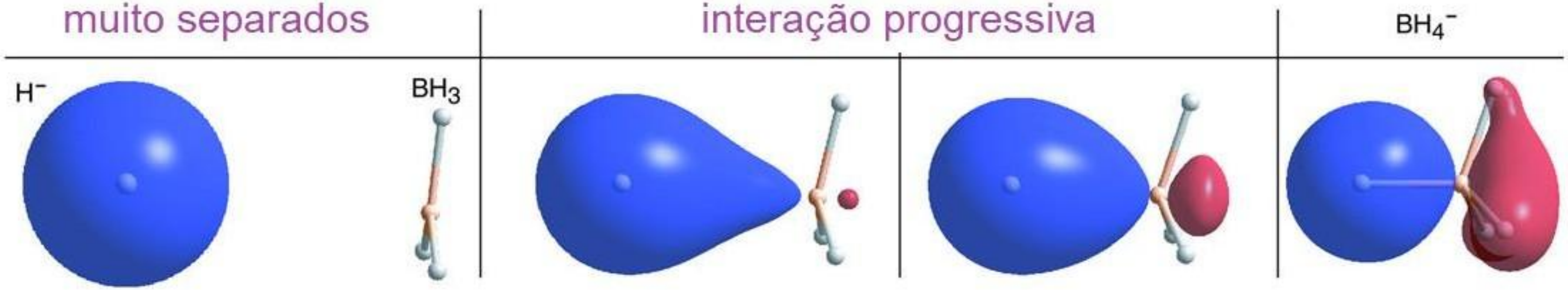






A MUDANÇA NA DISTRIBUIÇÃO DA DENSIDADE ELETRÔNICA



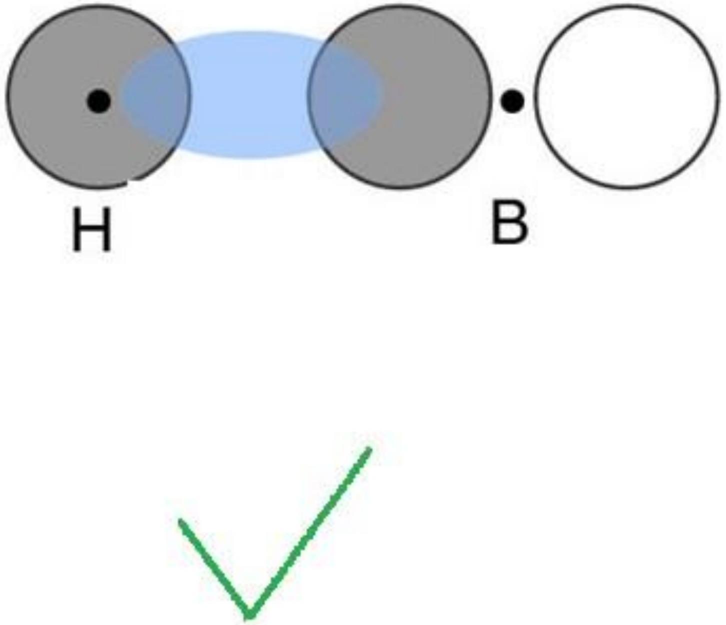


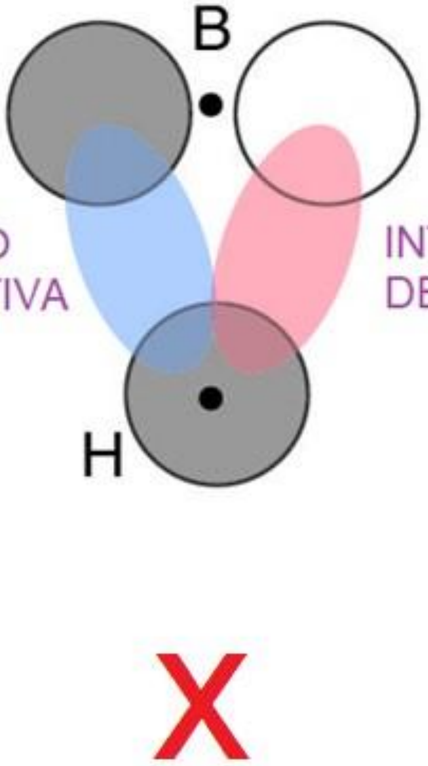
muito separados

interação progressiva

BH_4^-

O ÂNGULO DE ATAQUE





INTERAÇÃO
CONSTRUTIVA

INTERAÇÃO
DESTRUTIVA

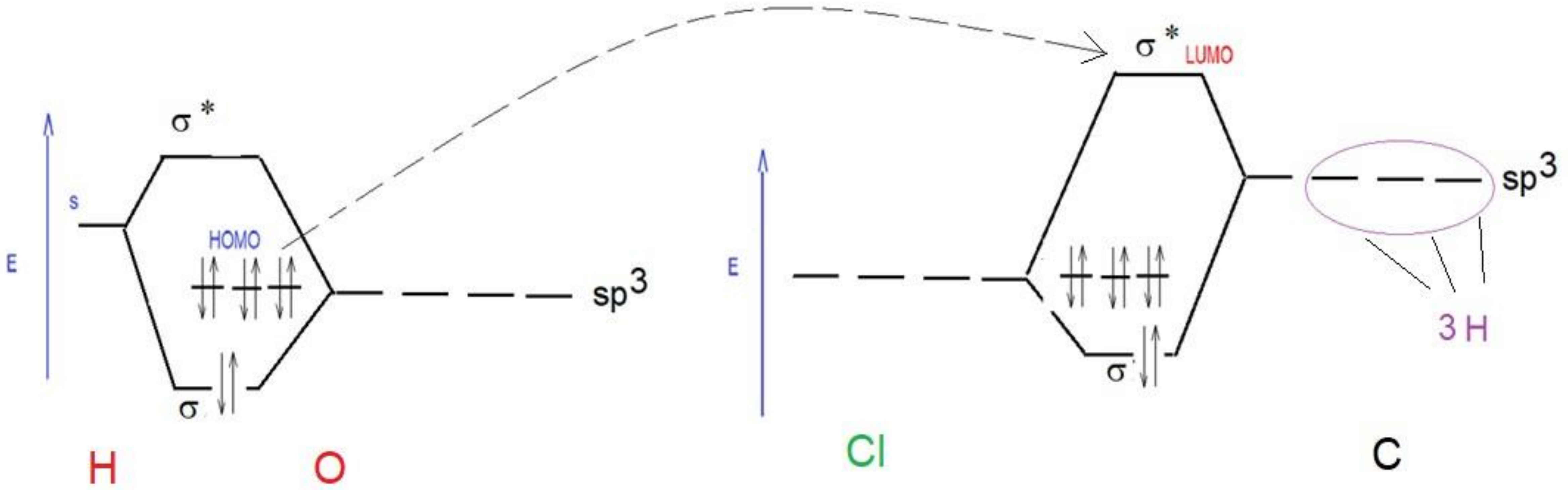
$$BH_3 + H^- \longrightarrow BH_4^-$$

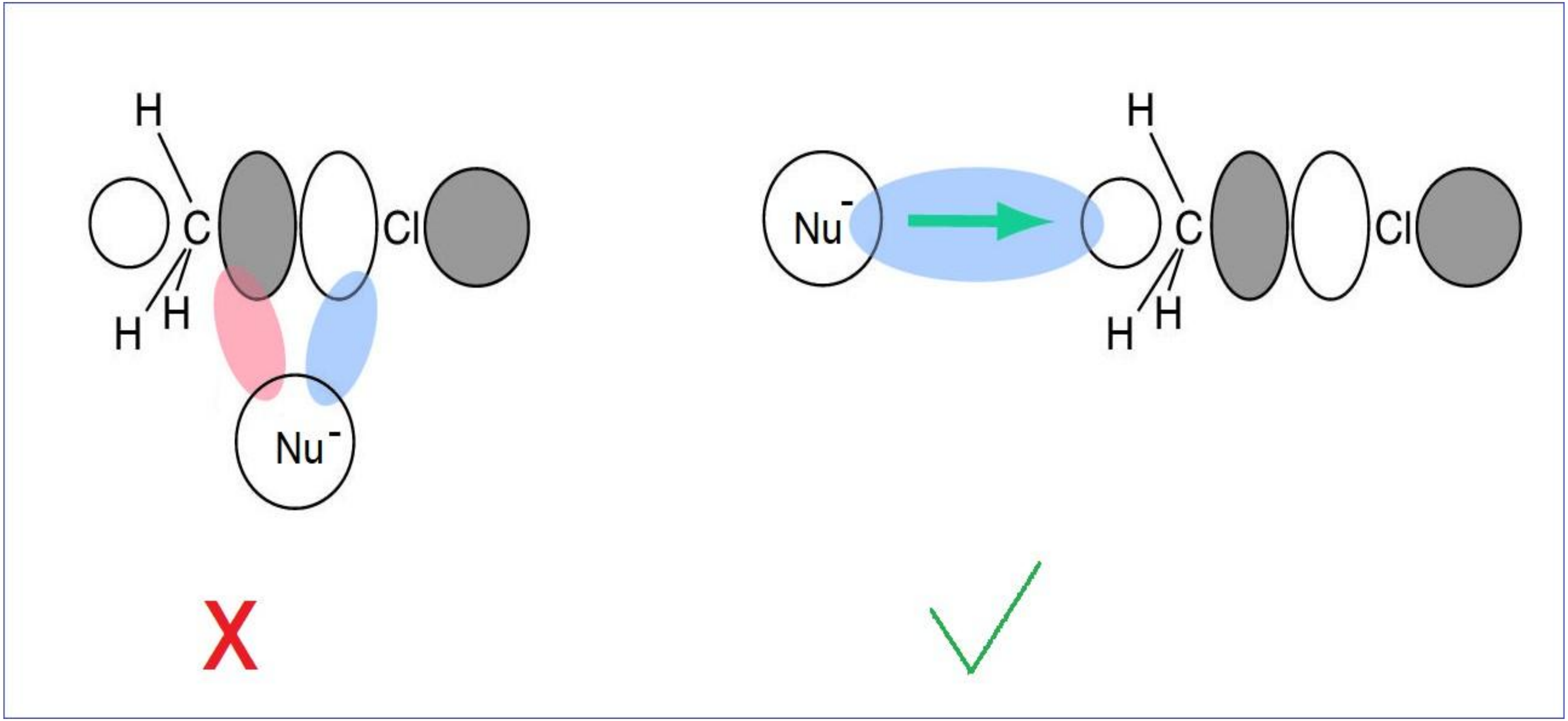
ÁCIDO DE LEWIS

BASE DE LEWIS

QUANDO O LUMO É UM ORBITAL σ^*

$$\underset{\text{Nu}^-}{\underset{\downarrow}{:\underset{..}{\ddot{O}}H^-}} + \underset{\text{Ele}}{\underset{\downarrow}{CH_3\text{-}\underset{..}{\ddot{Cl}}:}} \longrightarrow CH_3\text{-}OH + :\underset{..}{\ddot{Cl}}:^-$$

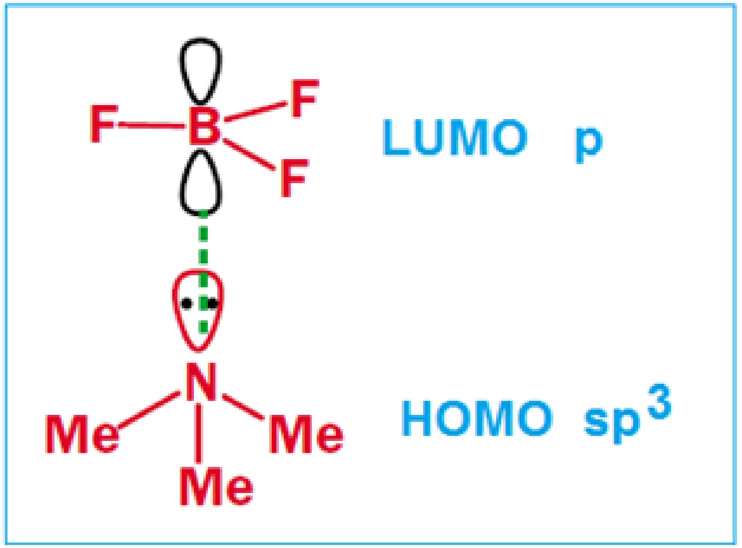


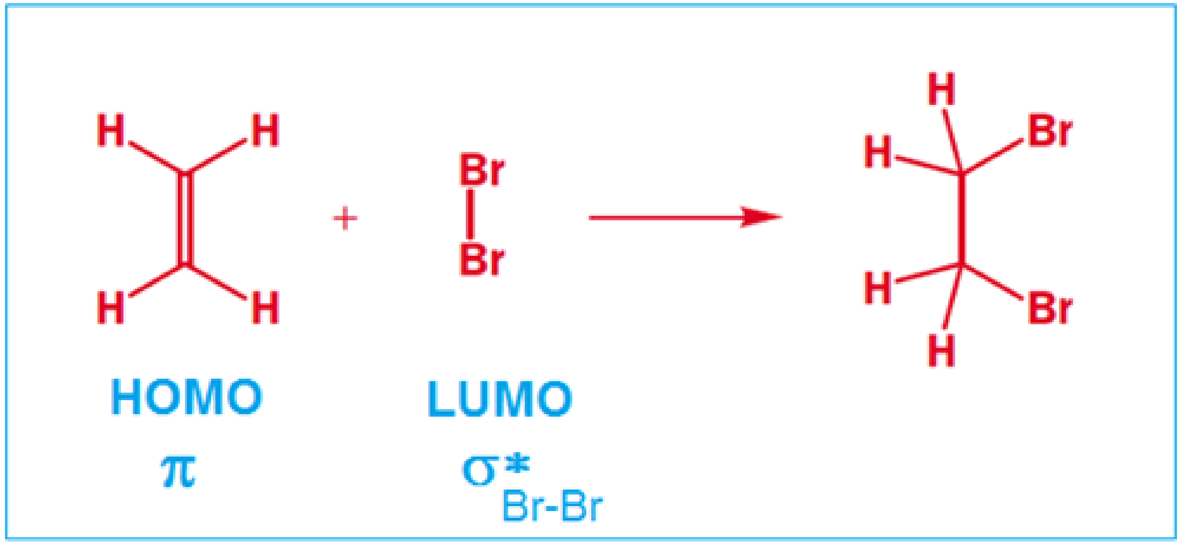

H
C
H
H
Cl
Nu⁻
X
Nu⁻
H
C
H
H
Cl
✓

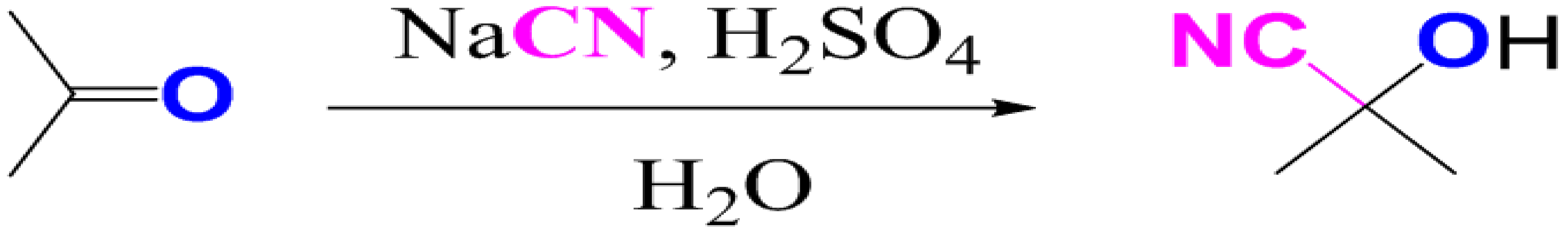
INTERAÇÃO HOMO - LUMO

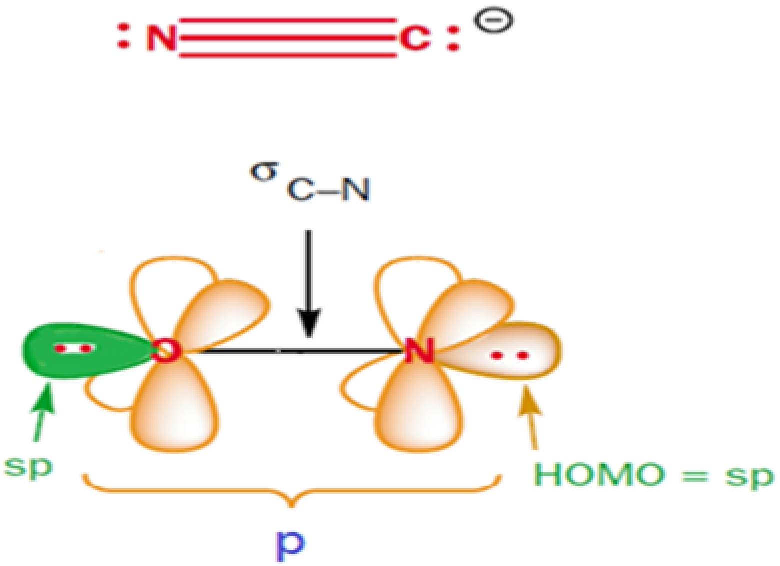
NUCLEÓFILO : rico em elétrons

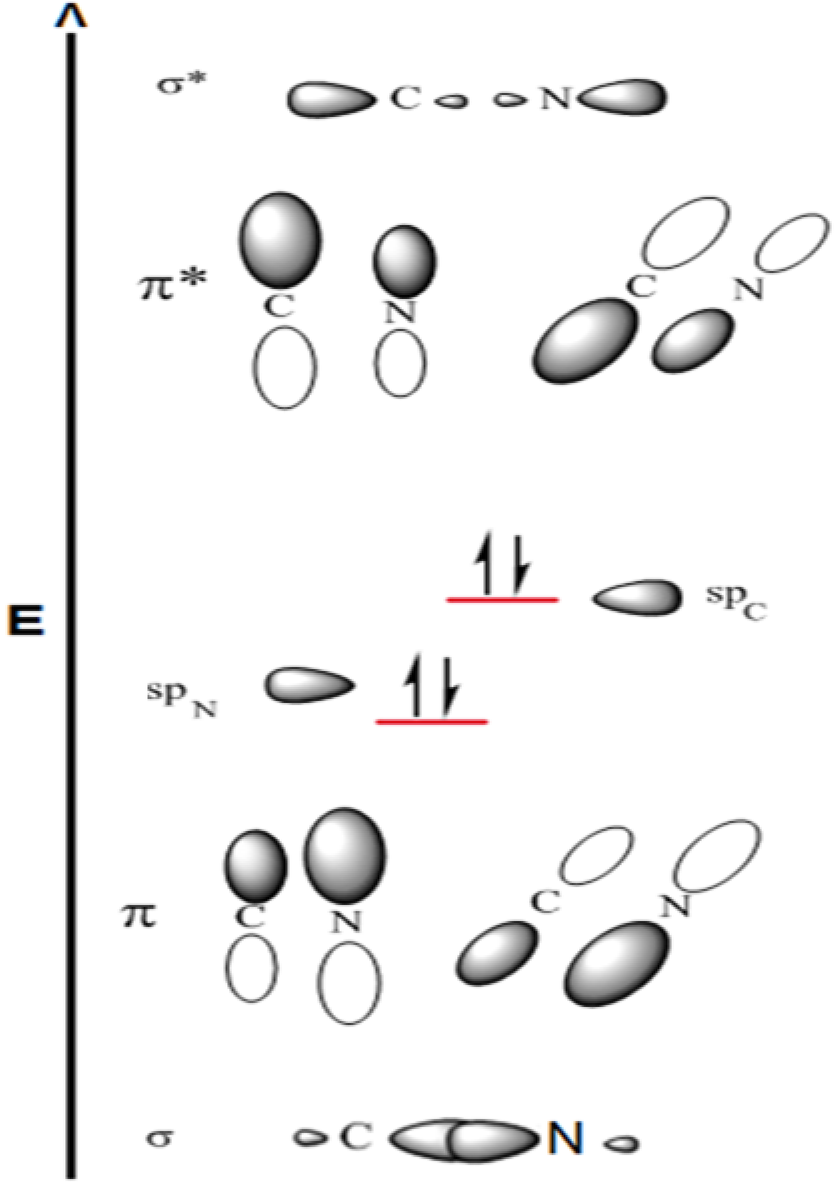
ELETRÓFILO : deficiente em elétrons

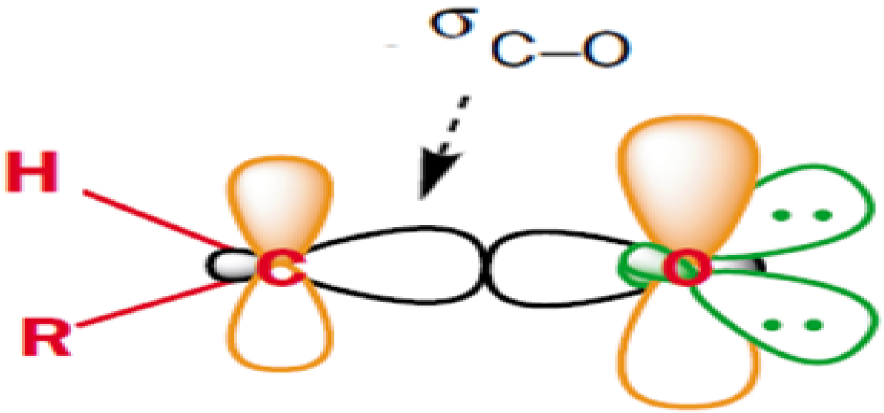


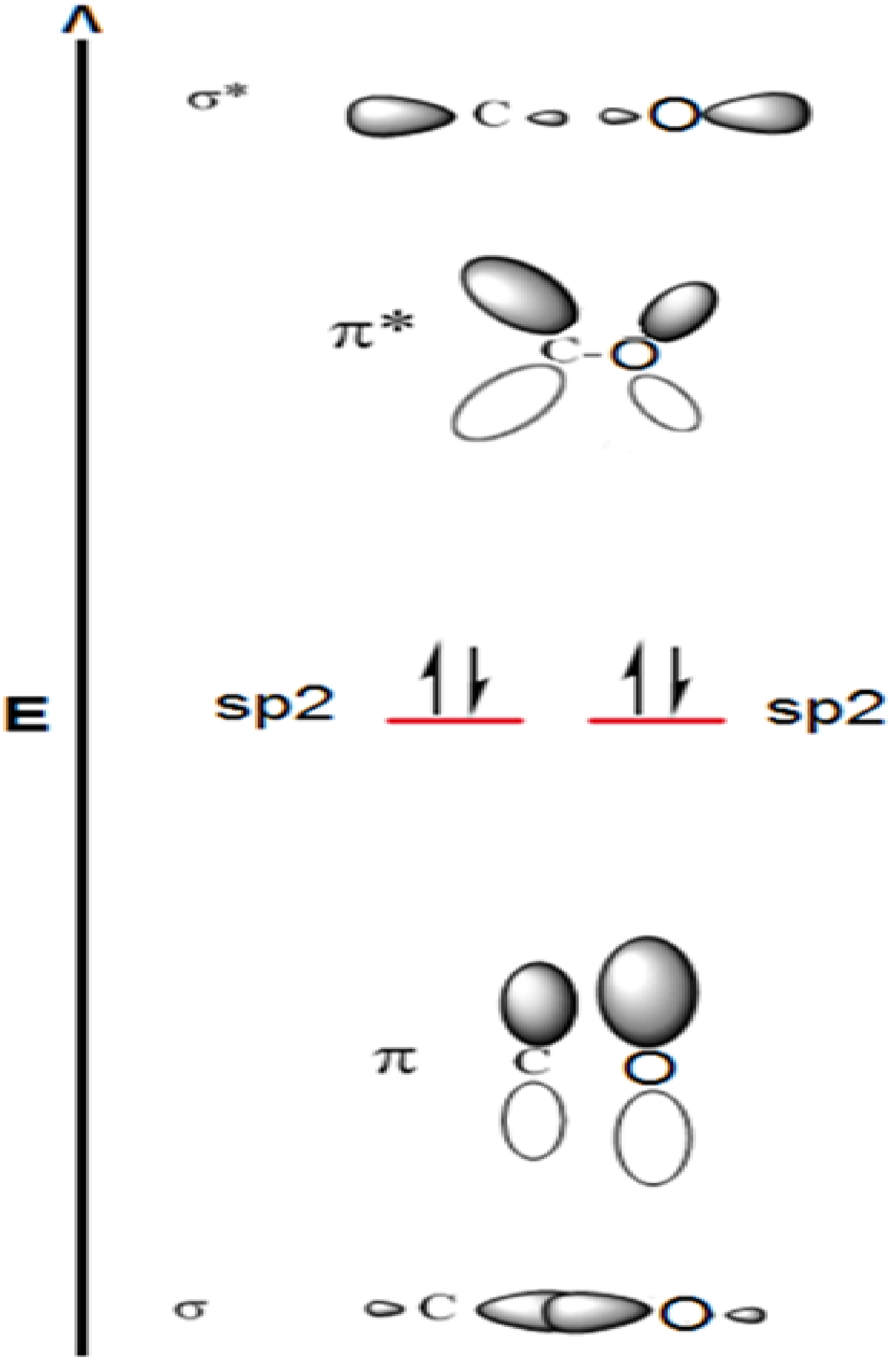


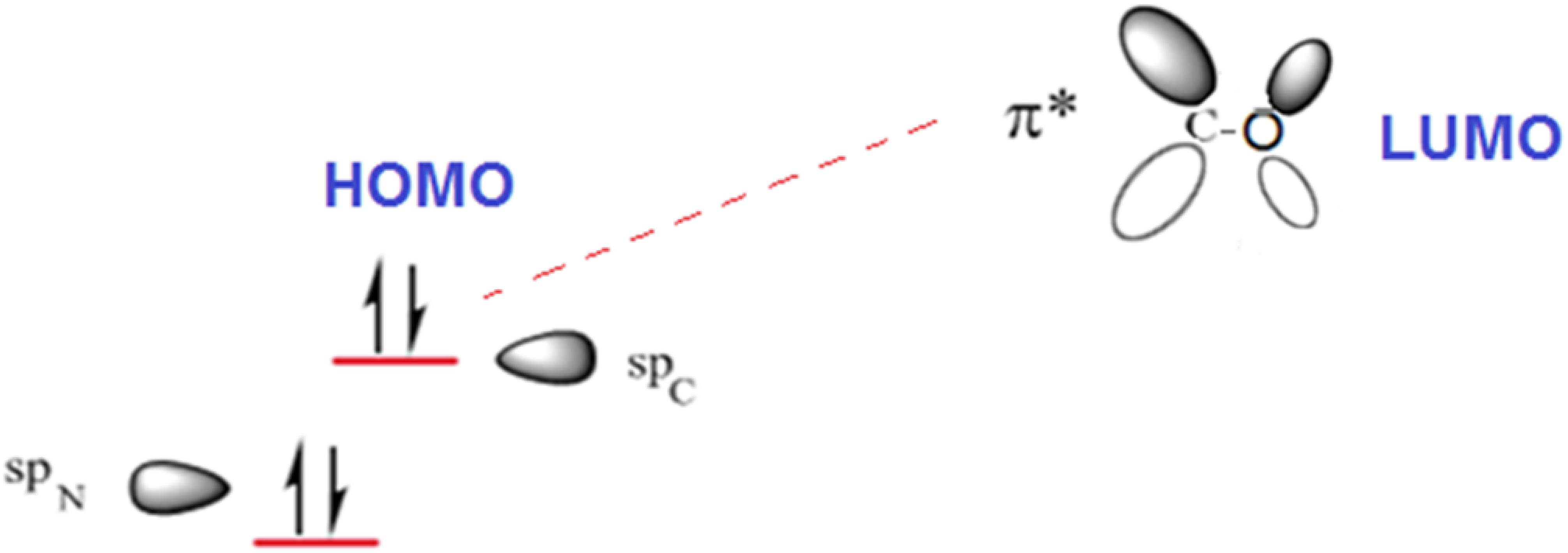

O
NaCN, H_2SO_4
H_2O
NC
OH

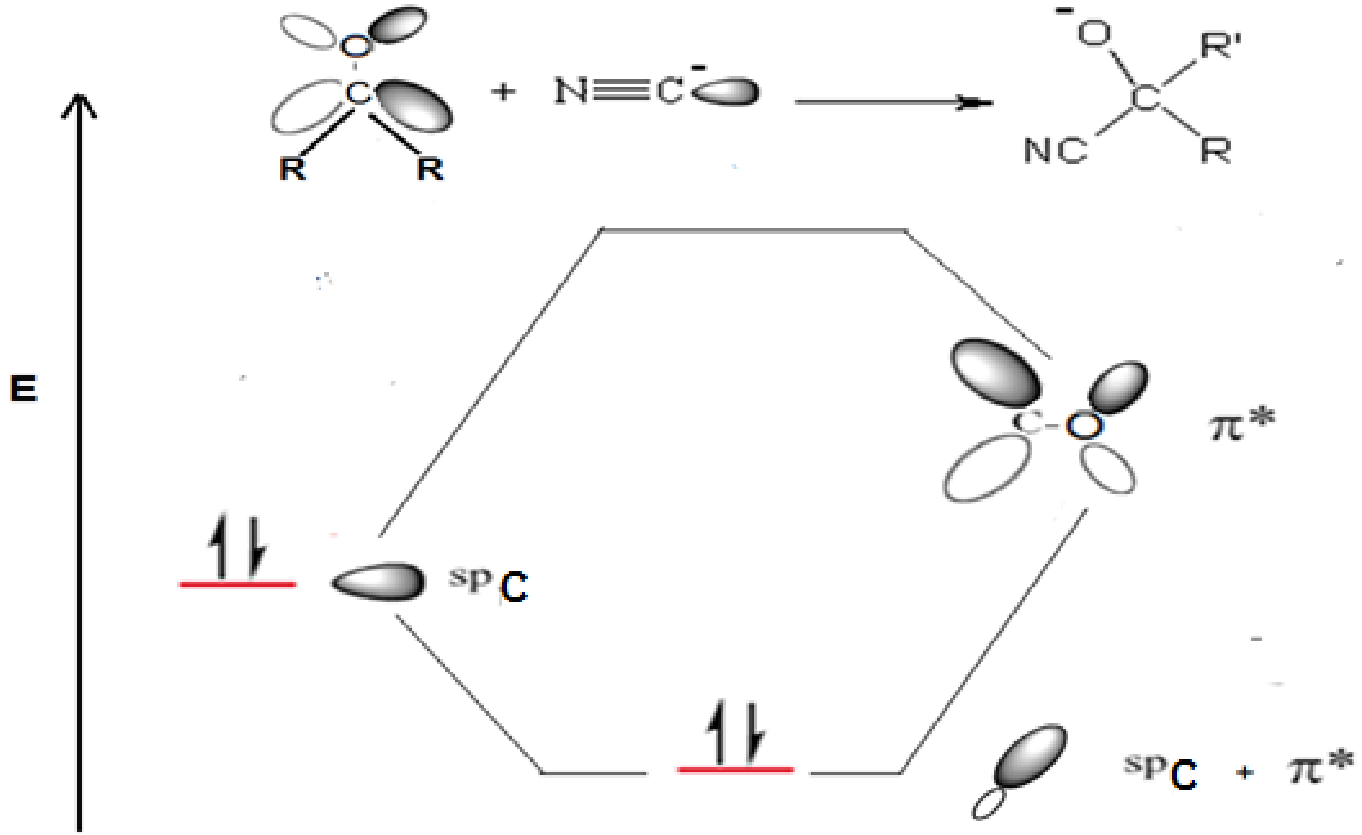

:N≡C:⊖
$\sigma_{C–N}$
O
N
sp
HOMO = sp
p


E
σ*
C
N
π*
C
N
C
N
sp_C
sp_N
π
C
N
C
N
σ
C
N

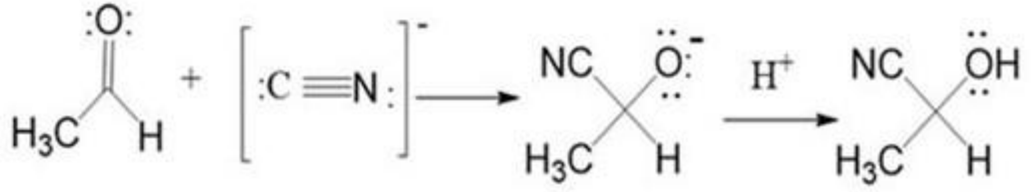

σ_{C-O}
H
R
C
O

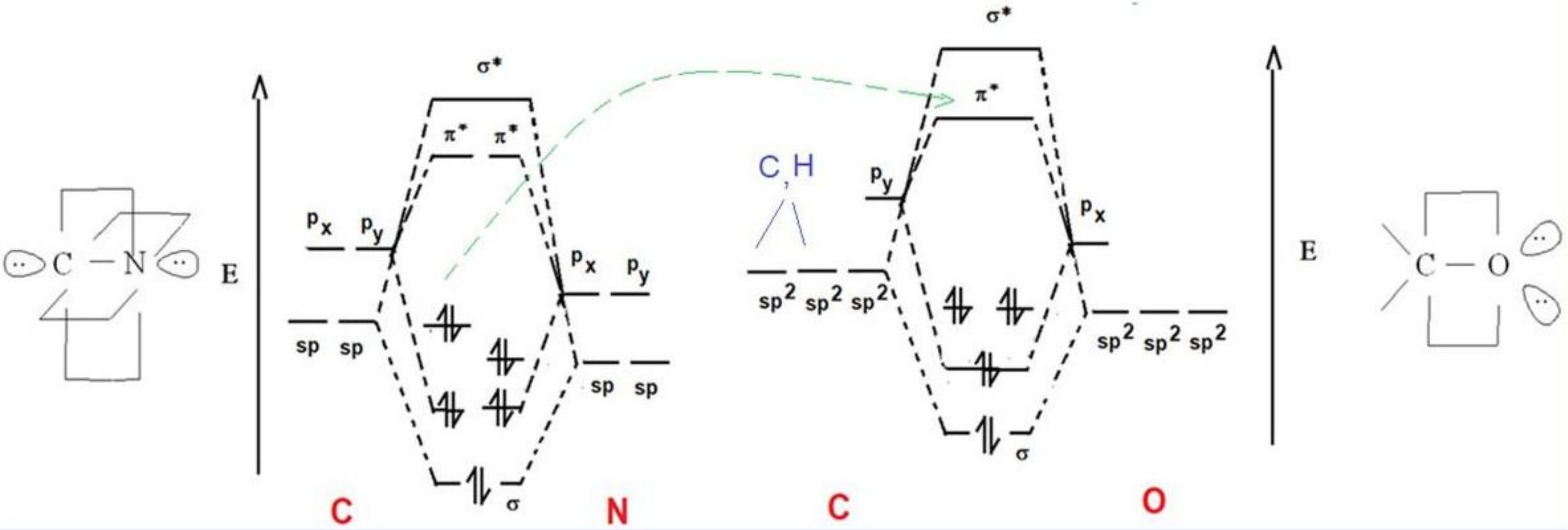

E
σ*
C
O
π*
C-O
sp2
sp2
π
C
O
σ
C
O

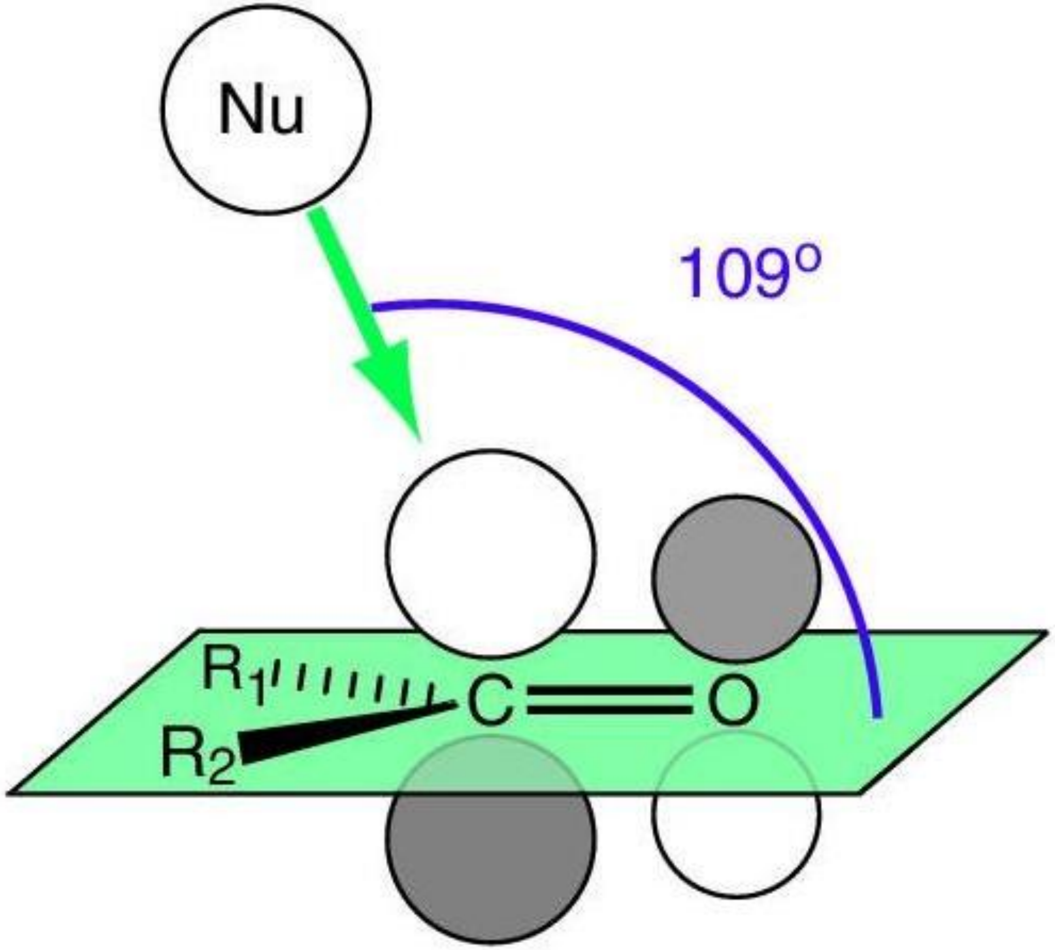

π*
C–O
LUMO
HOMO
sp_C
sp_N


O
C
R
R
+
N≡C⁻
⁻O
R'
C
NC
R
E
C-O
π*
spC
spC + π*

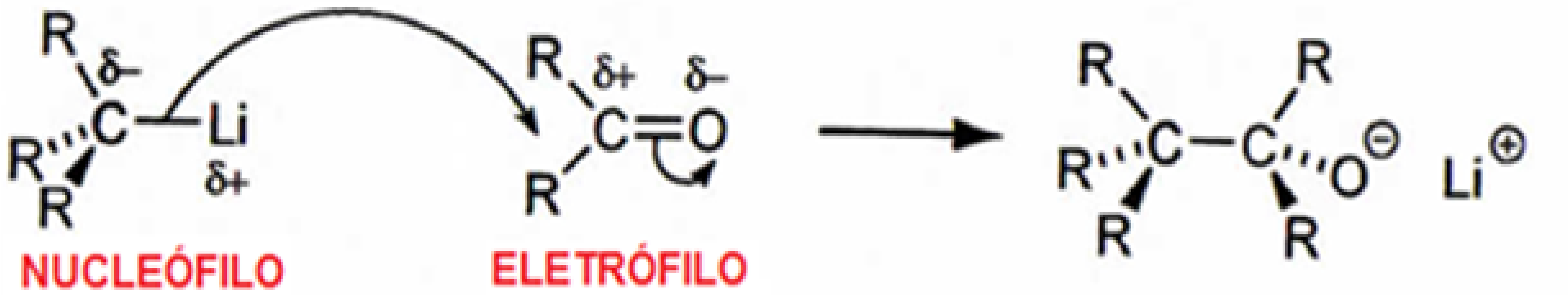
QUANDO O LUMO É UM ORBITAL ANTI-LIGANTE π^*



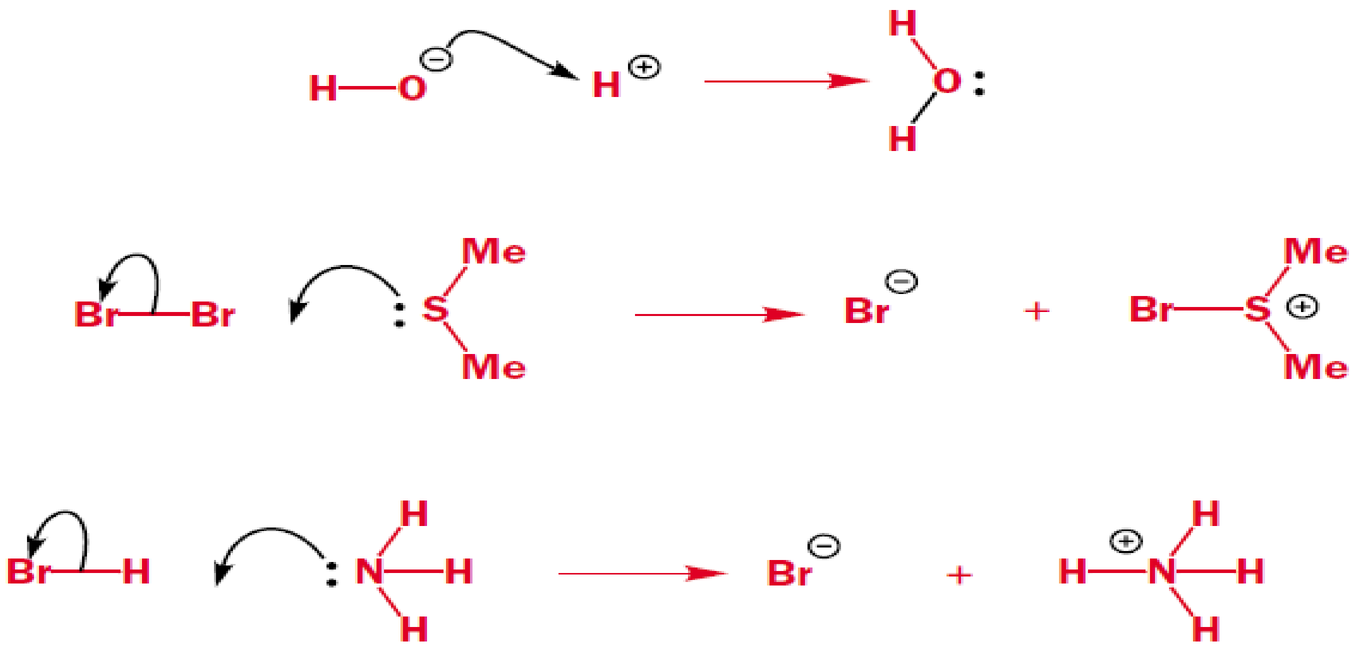



Nu
109°
R1
R2
C
O

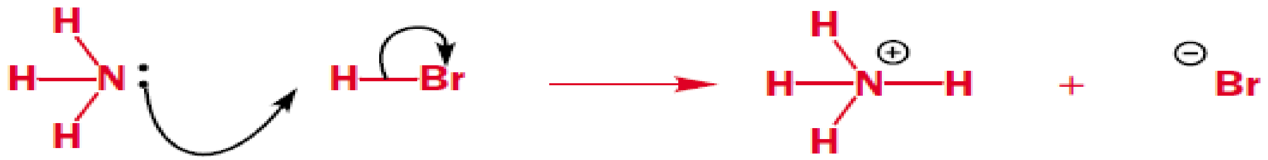
as setas curvas representam o deslocamento de um par de elétrons, quer seja do nucleófilo para o eletrófilo, quer seja de um par de elétrons para um dos átomos de um grupo funcional.



REPRESENTANDO MECANISMOS DE REAÇÃO USANDO SETAS CURVAS

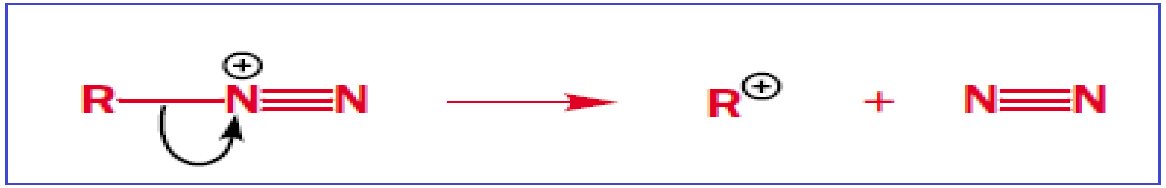


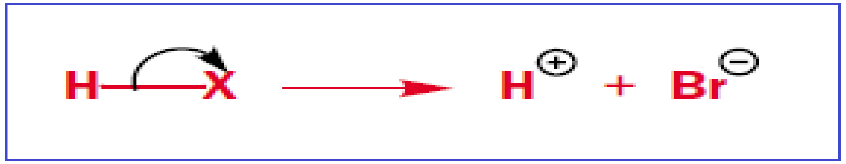
OU

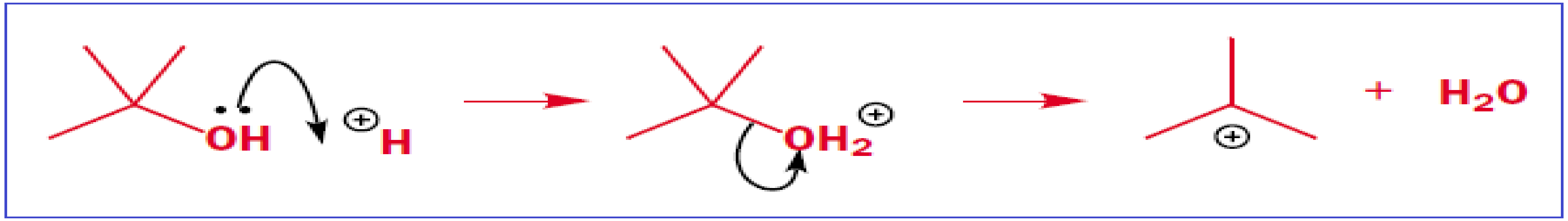


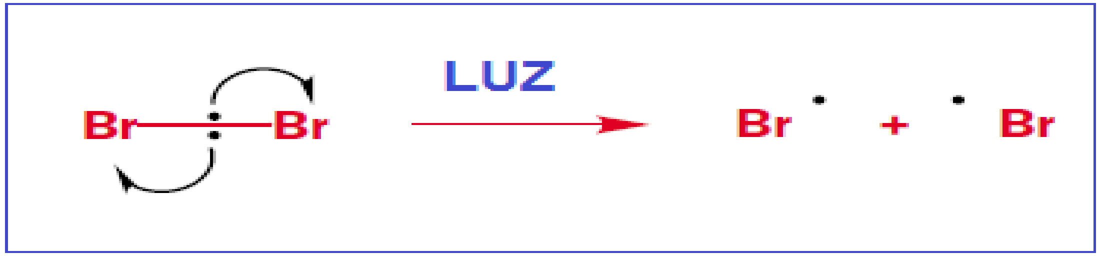
A SETA VAI SEMPRE DO NUCLEÓFILO PARA O ELETRÓFILO !!!!

REPRESENTANDO DECOMPOSIÇÕES E IONIZAÇÕES

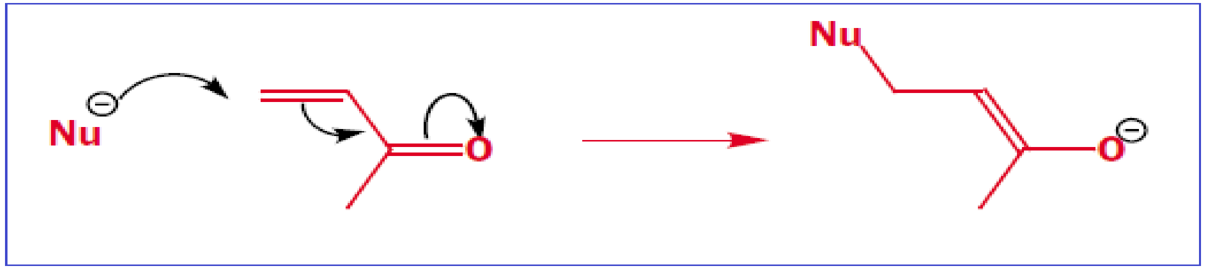


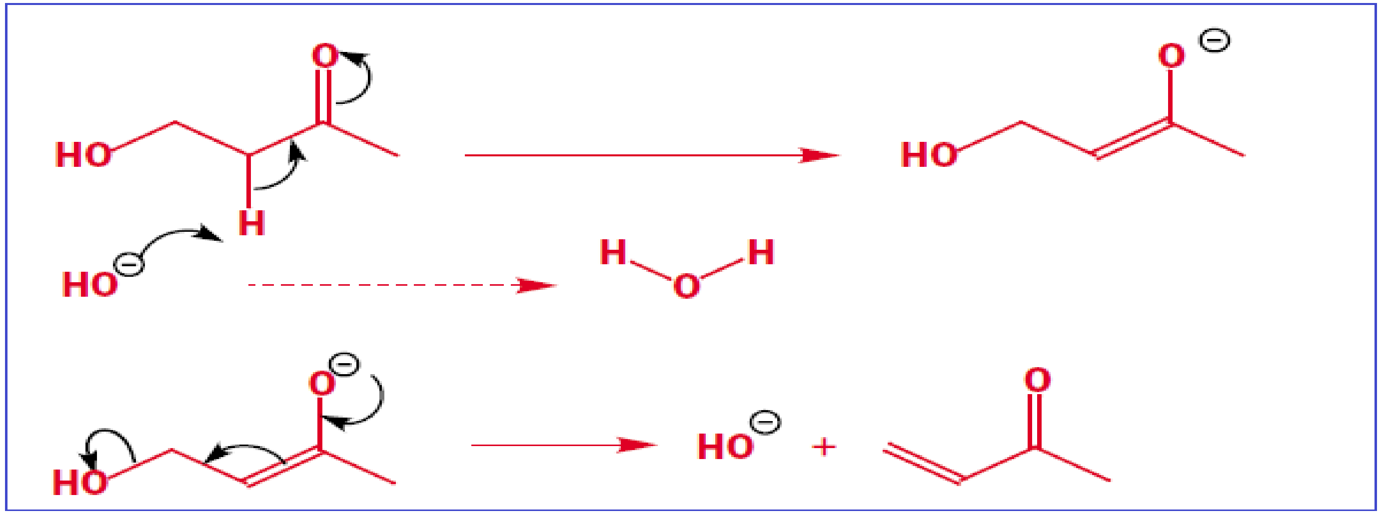


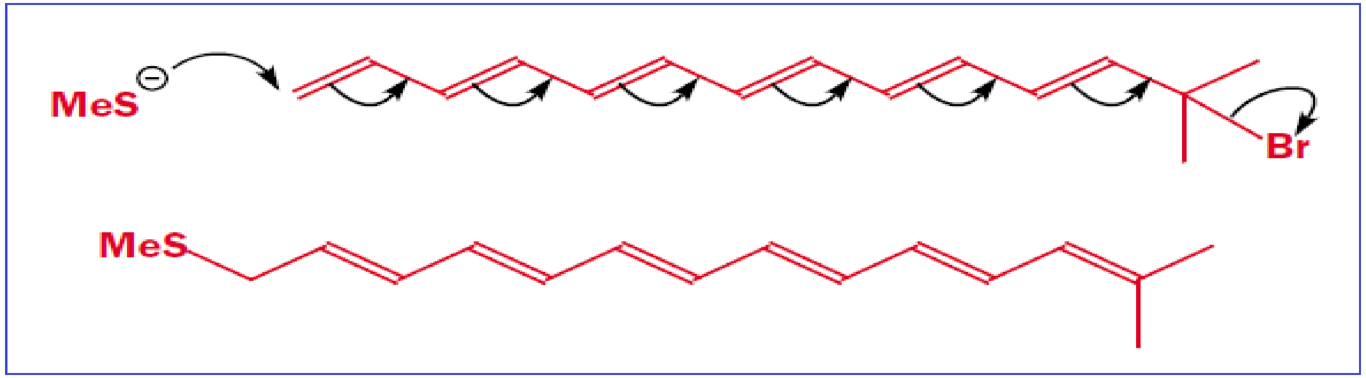




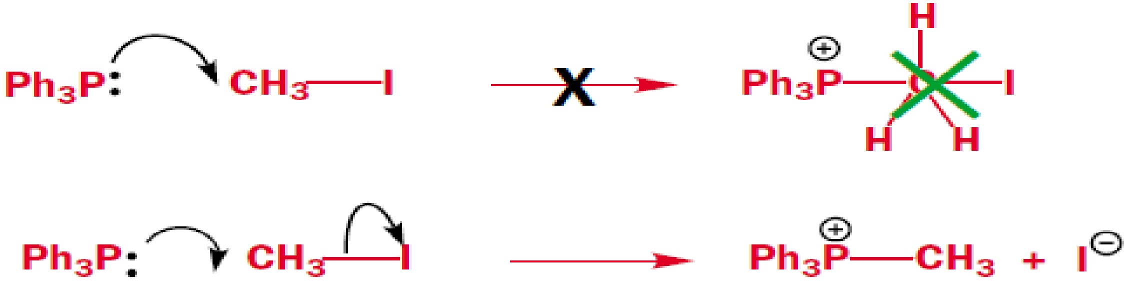
MOVIMENTAÇÕES DE ELÉTRONS DENTRO DA MESMA MOLÉCULA





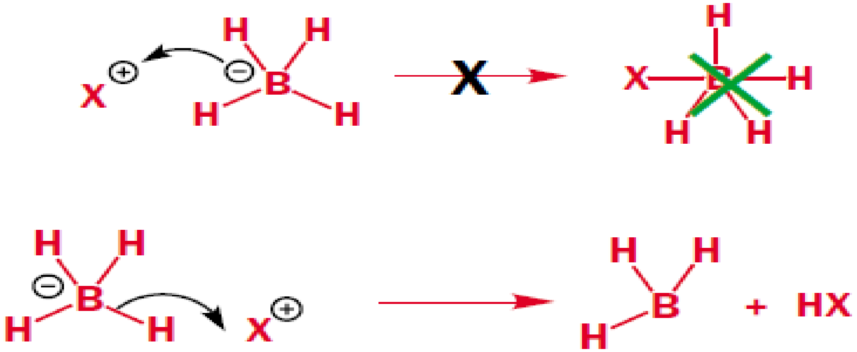


O QUE É ERRADO FAZER E O CORRETO

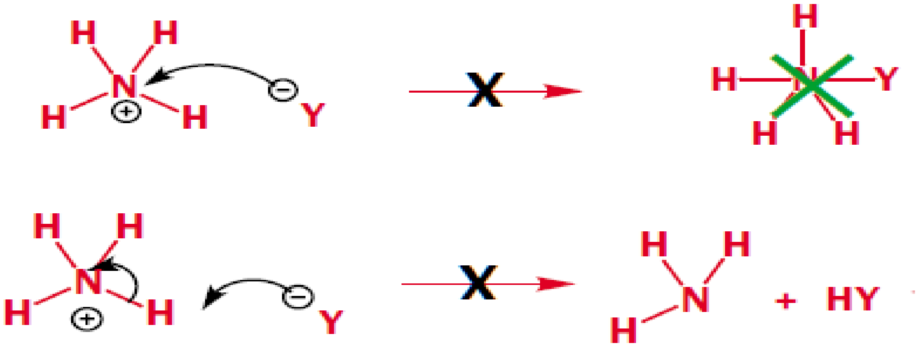


CARBONO PENTAVALENTE?!!!!!

CORRETO !

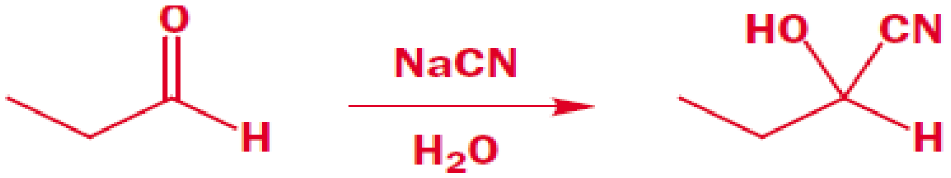


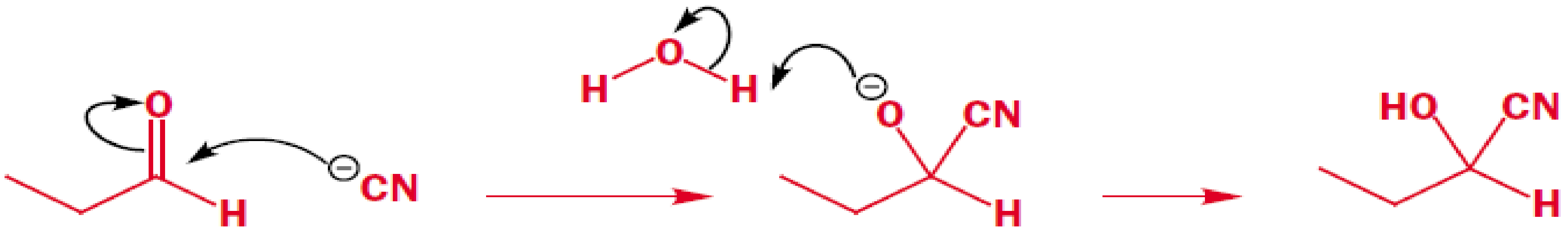
CORRETO !



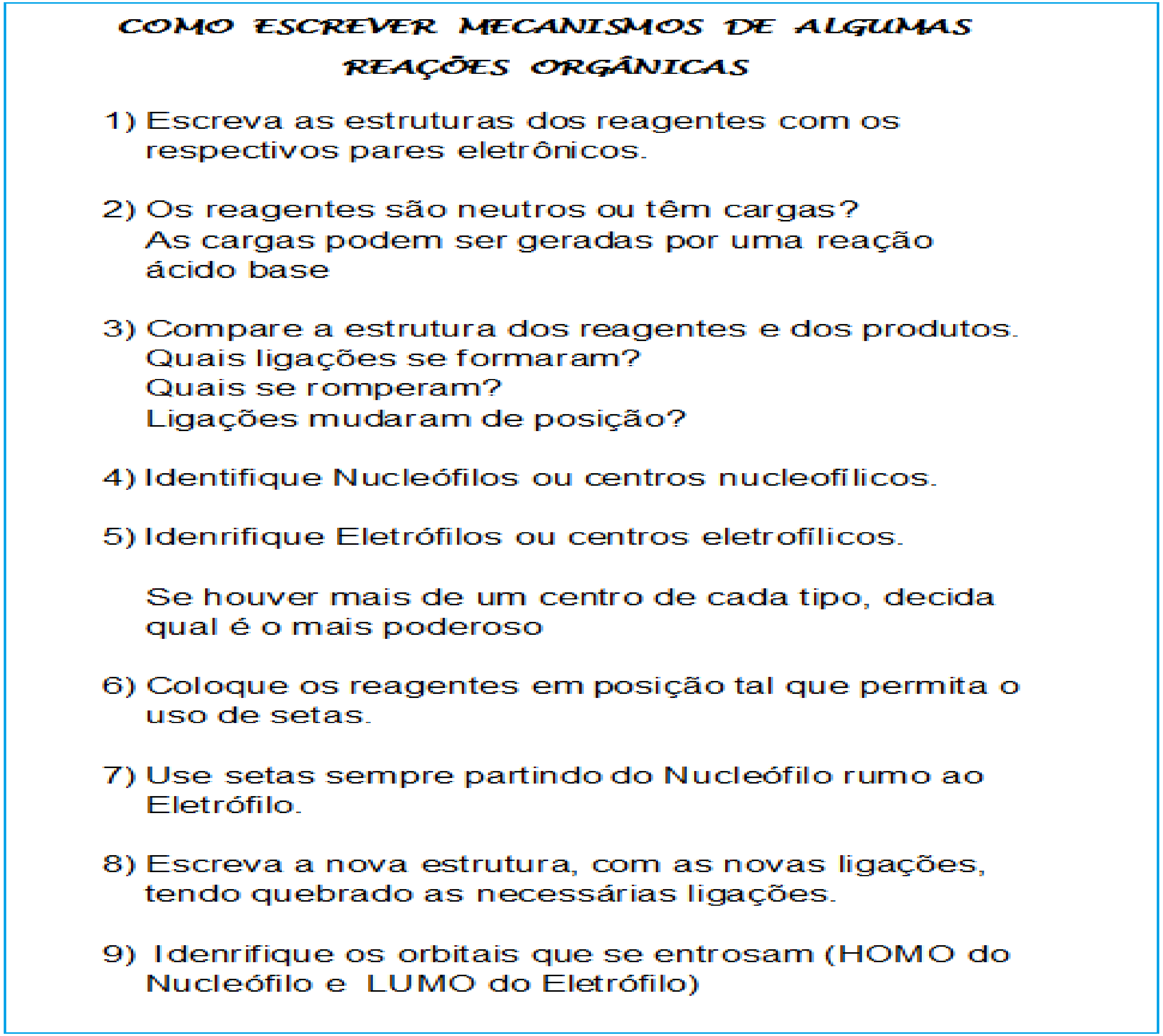
CORRETO !

PASSOS DE UM MECANISMO DE REAÇÃO





PRIMEIRO PASSO SEGUNDO PASSO PRODUTO



COMO ESCREVER MECANISMOS DE ALGUMAS REAÇÕES ORGÂNICAS

1) Escreva as estruturas dos reagentes com os respectivos pares eletrônicos.

2) Os reagentes são neutros ou têm cargas?
As cargas podem ser geradas por uma reação ácido base

3) Compare a estrutura dos reagentes e dos produtos.
Quais ligações se formaram?
Quais se romperam?
Ligações mudaram de posição?

4) Identifique Nucleófilos ou centros nucleofílicos.

5) Idenrifique Eletrófilos ou centros eletrofílicos.

Se houver mais de um centro de cada tipo, decida qual é o mais poderoso

6) Coloque os reagentes em posição tal que permita o uso de setas.

7) Use setas sempre partindo do Nucleófilo rumo ao Eletrófilo.

8) Escreva a nova estrutura, com as novas ligações, tendo quebrado as necessárias ligações.

9) Idenrifique os orbitais que se entrosam (HOMO do Nucleófilo e LUMO do Eletrófilo)