Química Feijão com Arroz

Substituição Nucleofílica Bimolecular S_N2

Universidade de São Paulo
Instituto de Química

SUBSTITUIÇÃO NUCLEOFÍLICA: CASO GERAL

$$R{-}L + Nu \underset{k_-}{\overset{k}{\rightleftharpoons}} R{-}Nu + L$$

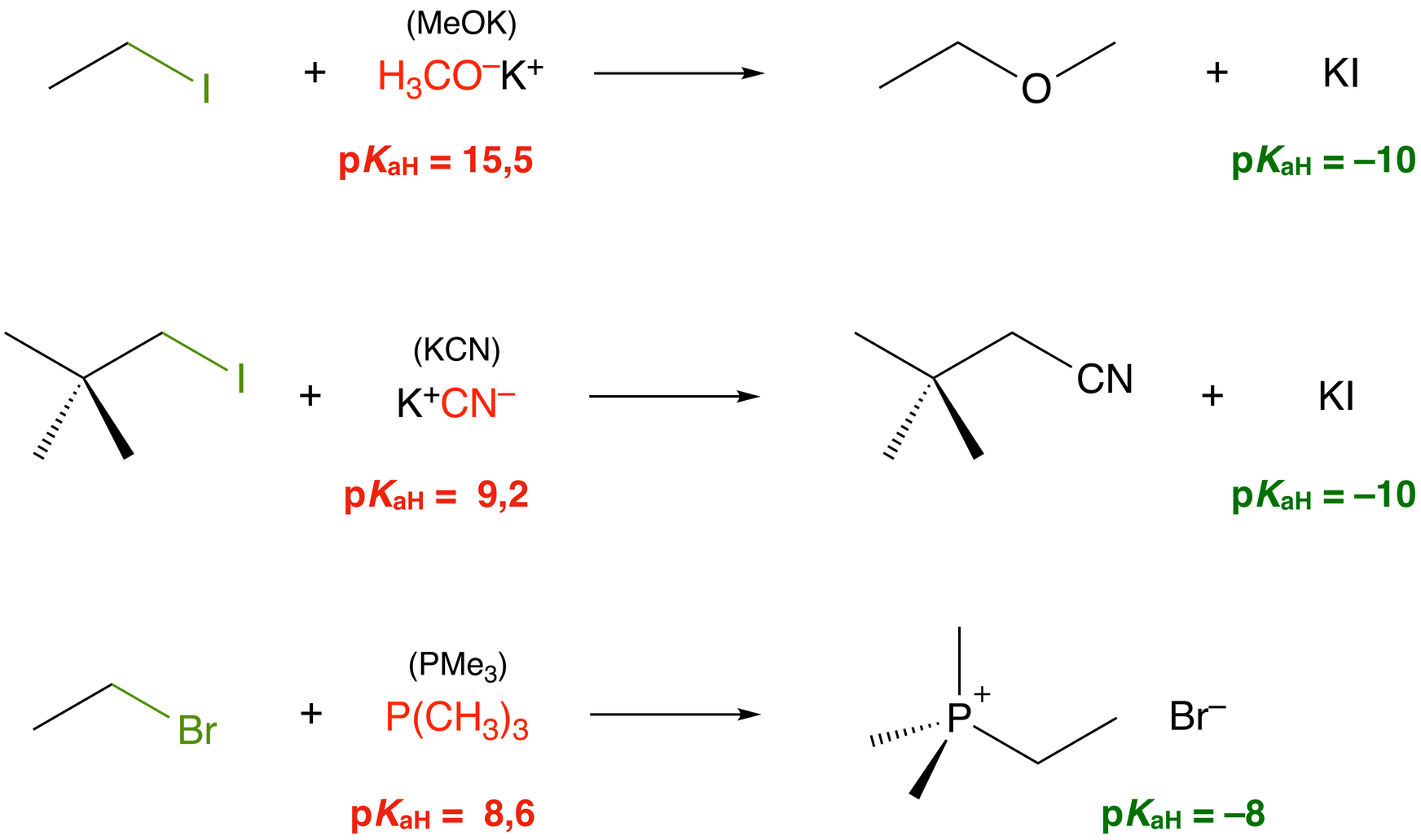
EXEMPLOS:

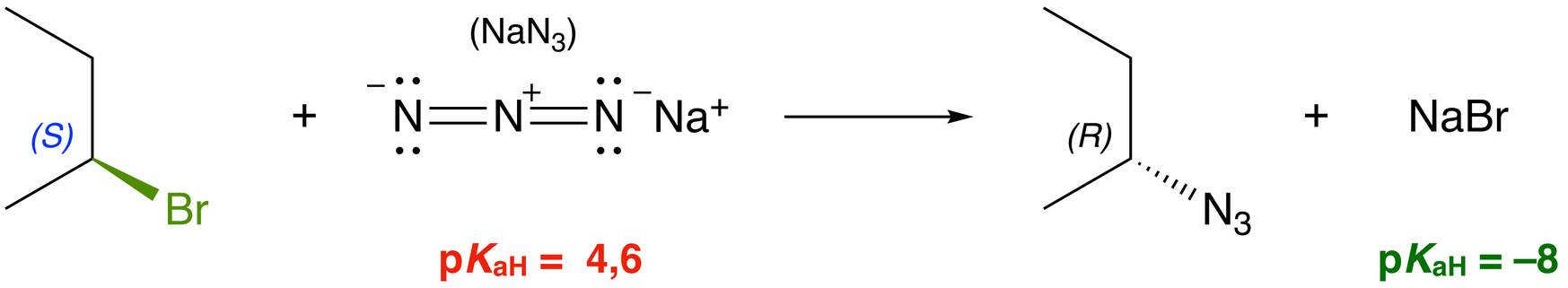
$$H_3C{-}I + HO^- \xrightarrow{\Delta pK_{aH} = -25} H_3C{-}OH + I^-$$

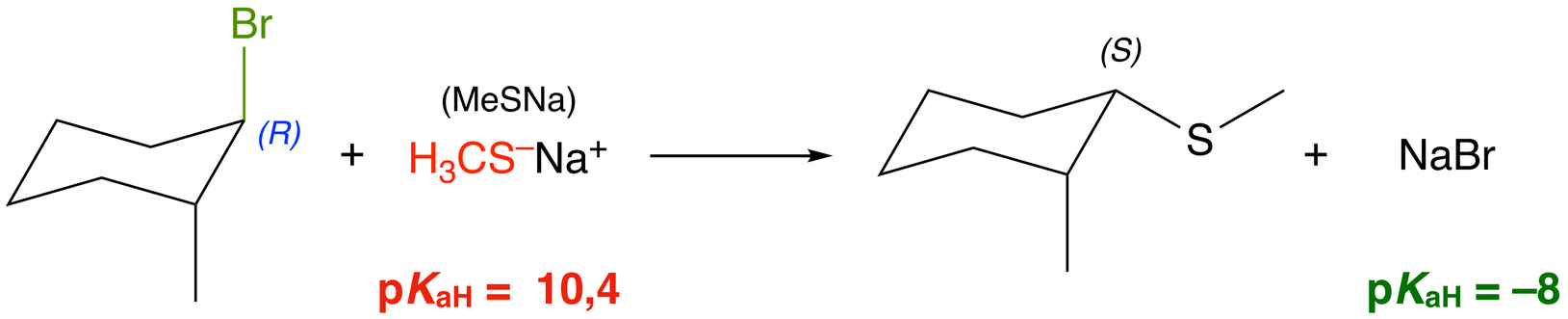
$pK_{aH} = 15{,}7$ $\qquad$ $pK_{aH} = -10$

$$H_3C{-}Br + NH_3 \xrightarrow{\Delta pK_{aH} = -18} H_3C{-}\overset{+}{N}H_3\ Br^-$$

$pK_{aH} = 10$ $\qquad$ $pK_{aH} = -8$

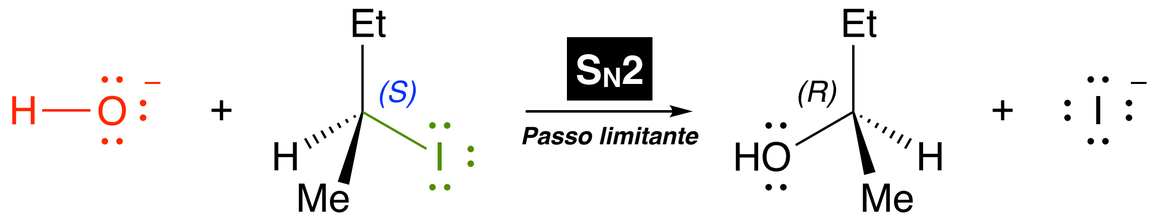

(MeOK)
$H_3CO^-K^+$
pK_{aH} = 15,5
KI
pK_{aH} = –10
(KCN)
K^+CN^-
pK_{aH} = 9,2
CN
KI
pK_{aH} = –10
(PMe$_3$)
$P(CH_3)_3$
pK_{aH} = 8,6
Br^-
pK_{aH} = –8

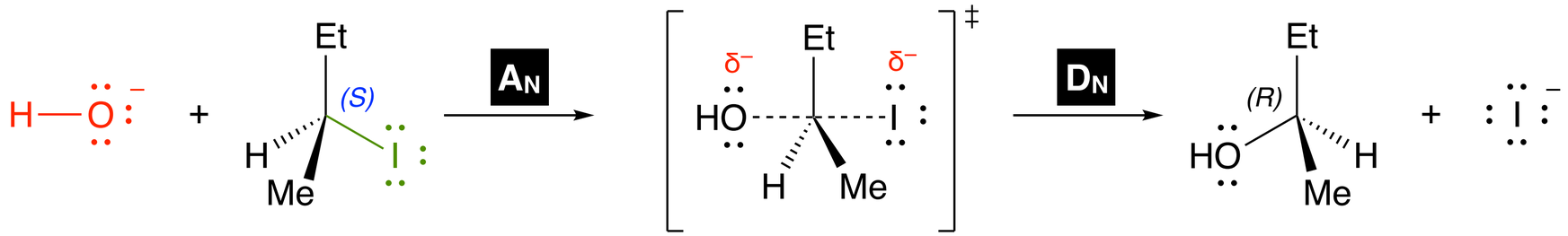

(S)
Br
+
(NaN3)
Na+
(R)
N3
+
NaBr
pKaH = 4,6
pKaH = –8

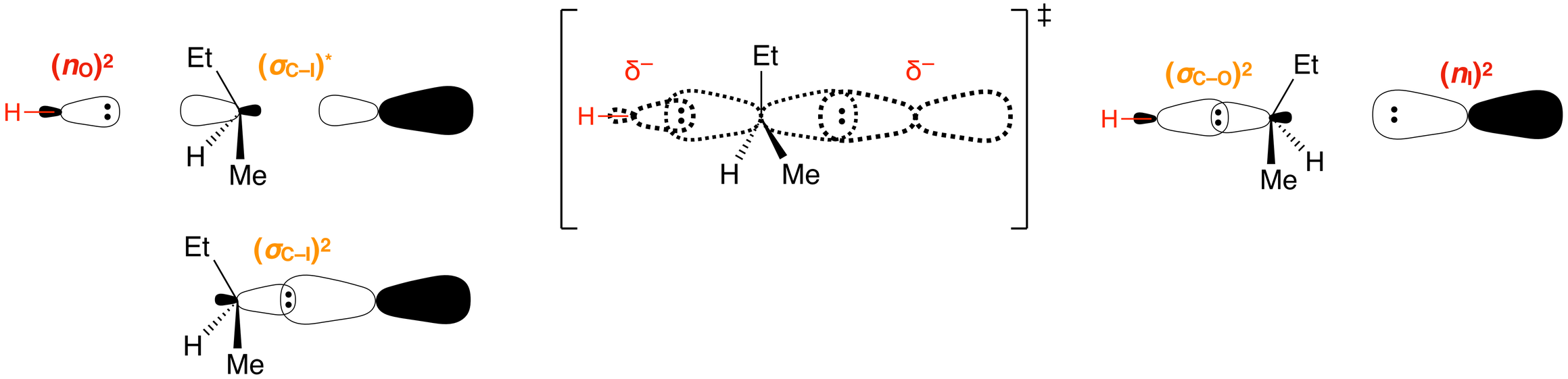

Br
(R)
+
(MeSNa)
H3CS−Na+
(S)
S
+
NaBr
pKaH = 10,4
pKaH = –8

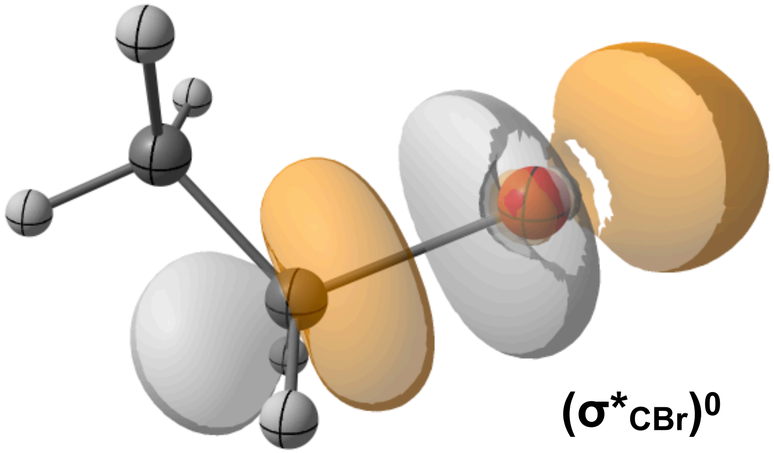
SUBSTITUIÇÃO NUCLEOFÍLICA: ESTEREOESPECÍFICAS

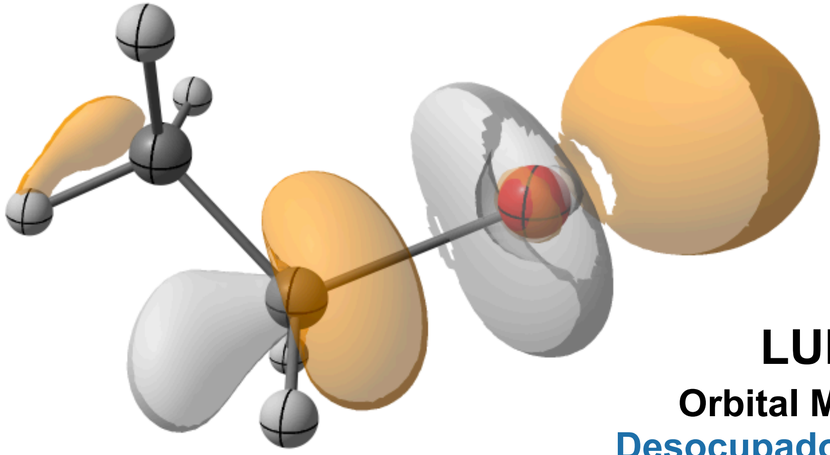
Chemtube3D, https://tinyurl.com/s4grwlu





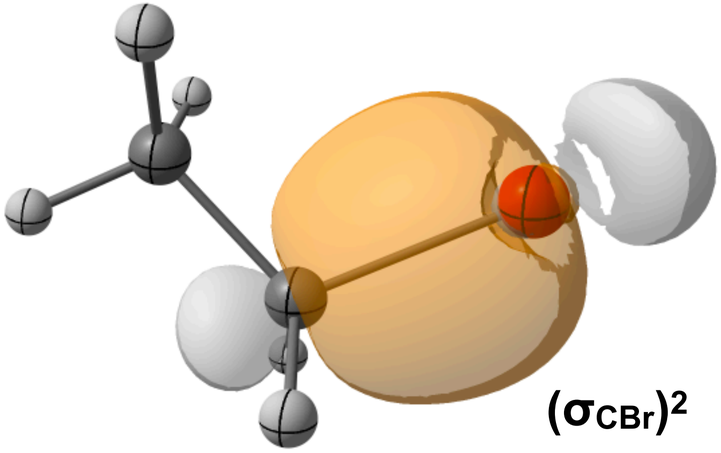


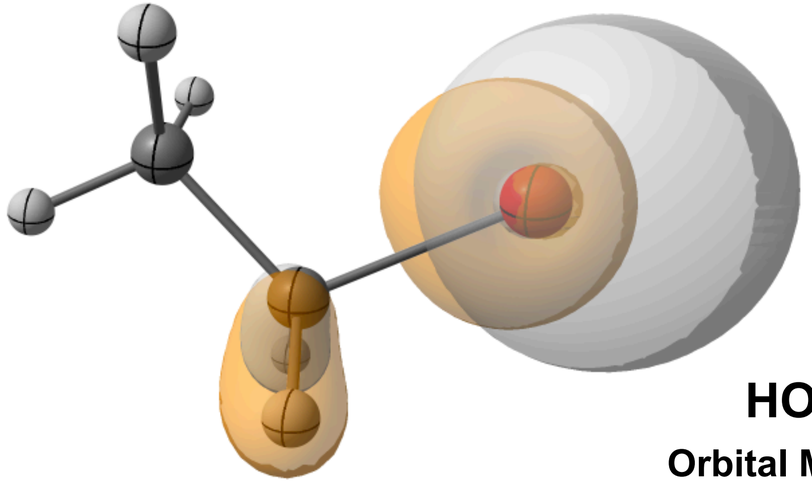




LUMO

Orbital Molecular Desocupado Mais Baixo





HOMO

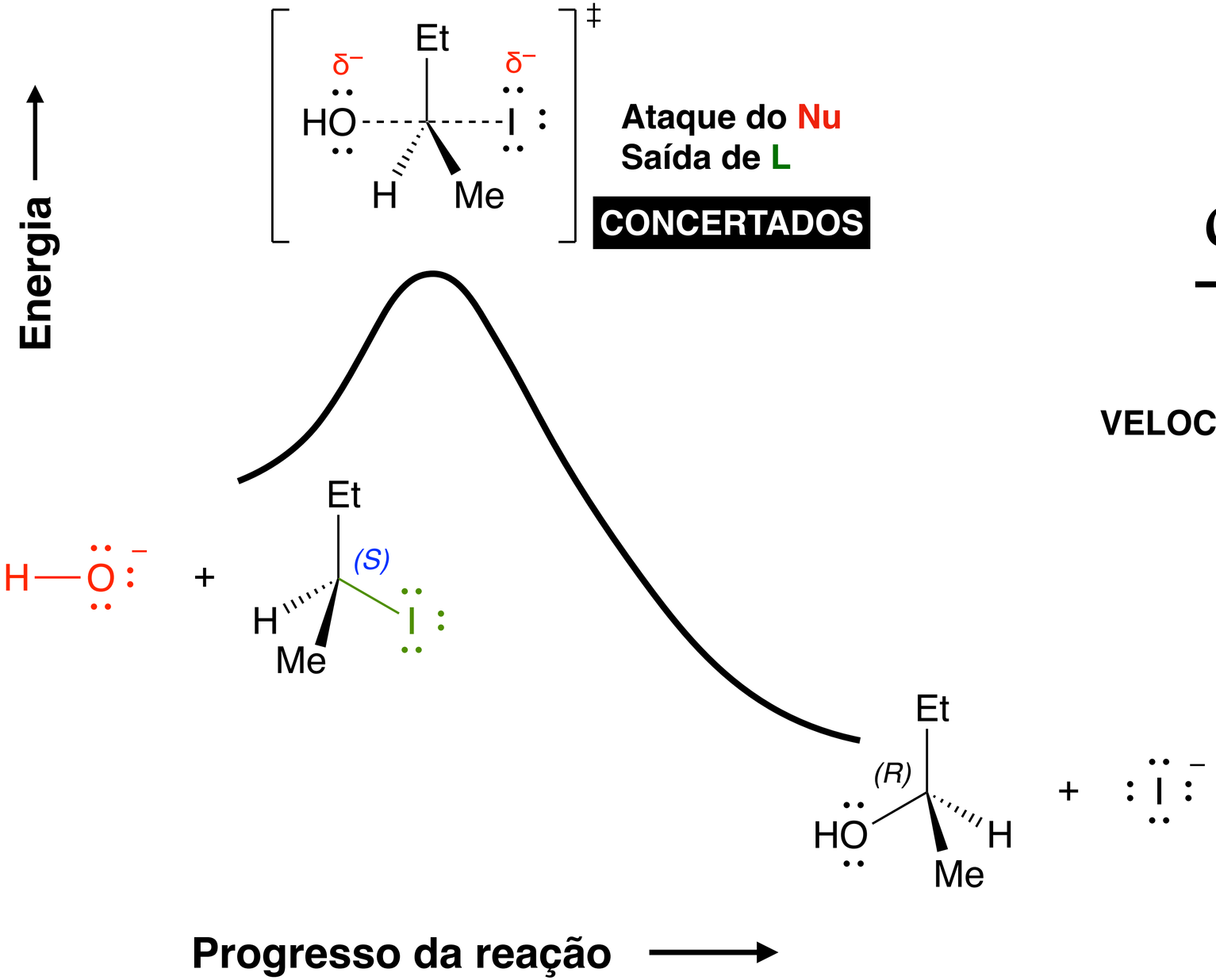
Orbital Molecular Ocupado Mais Alto

Orbitais Naturais de Ligação (NBOs)

M062x/Def2TZVP Valor de contorno da isosuperfície: 0,06

Orbitais de Fronteira (FOs)

M062x/Def2TZVP Valor de contorno da isosuperfície: 0,06



$S_N2 = A_ND_N$

Pure Appl. Chem., **61**: 23 (1989)

$$\frac{dP}{dt} = k_2[R-L][Nu]$$

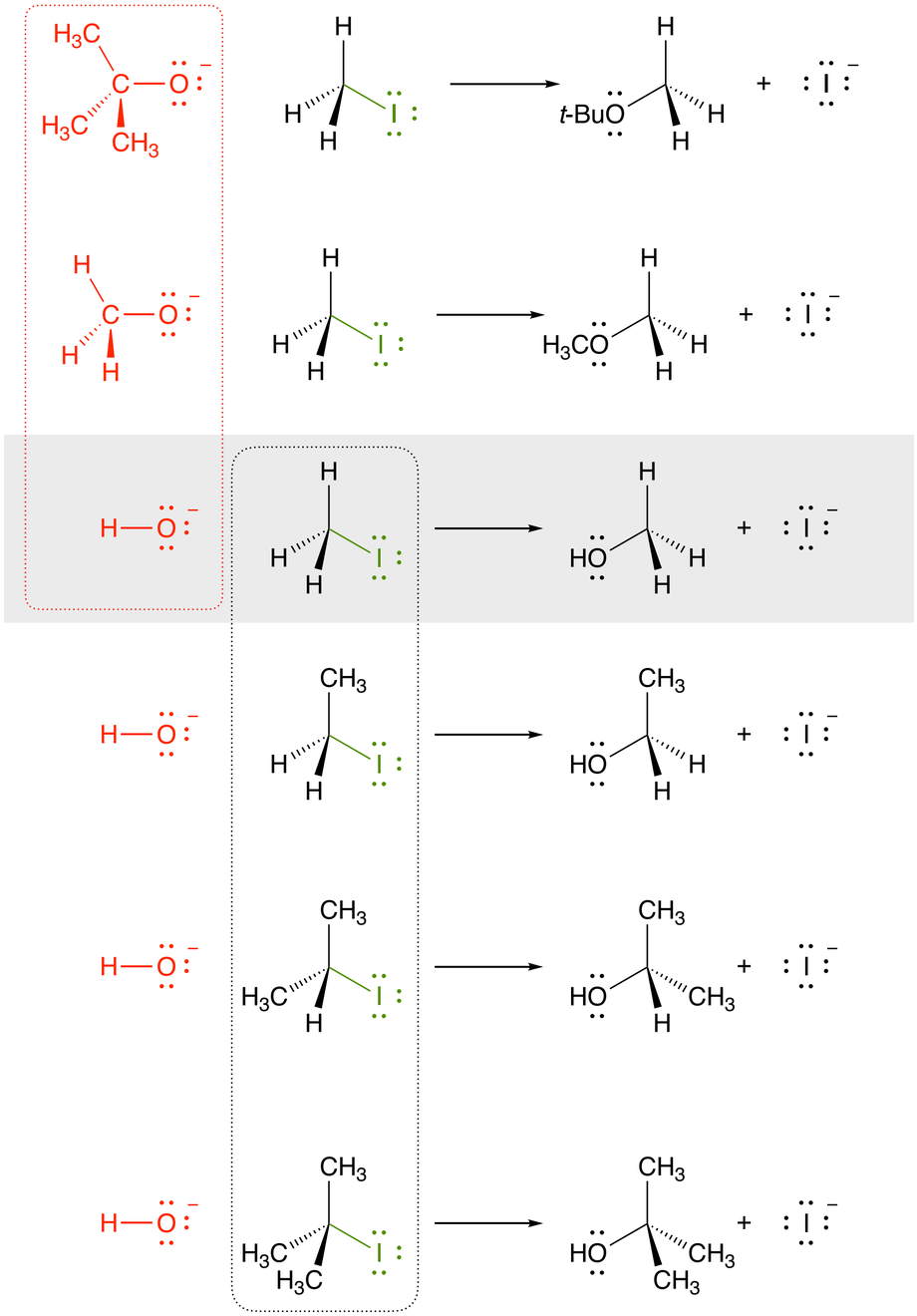
VELOCIDADE DEPENDE DE AMBOS OS REAGENTES

REAÇÃO BIMOLECULAR

$$R \rightarrow S$$
$$S \rightarrow R$$

INVERSÃO DE CONFIGURAÇÃO

ESTEREOESPECÍFICA


t-BuO
H3CO
HO
CH3
H3C

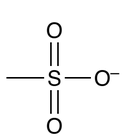
pK_{aH} mais baixo = base mais fraca

pK_{aH} mais baixo

Melhor grupo de saída (L)

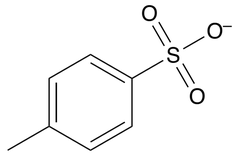
Bons L	pK_{aH}
TfO^-	–13
I^-	–10
Br^-	–8
Cl^-	–7
HSO_4^-	–3
TsO^-	–3
MsO^-	–2
H_3O^+	–1,7
$CH_3SO_3^-$	–1,2

Ruins L	pK_{aH}
F^-	3,2
$CH_3CO_2^-$	4,7
NC^-	9,2
CH_3S^-	10
CH_3O^-	15,5
HO^-	15,7
H_2N^-	35
H^-	38
H_3C^-	50



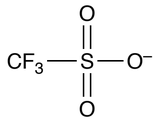
Mesilato (MsO^-)

pK_{aH} = –2



Tosilato (TsO^-)

pK_{aH} = –3



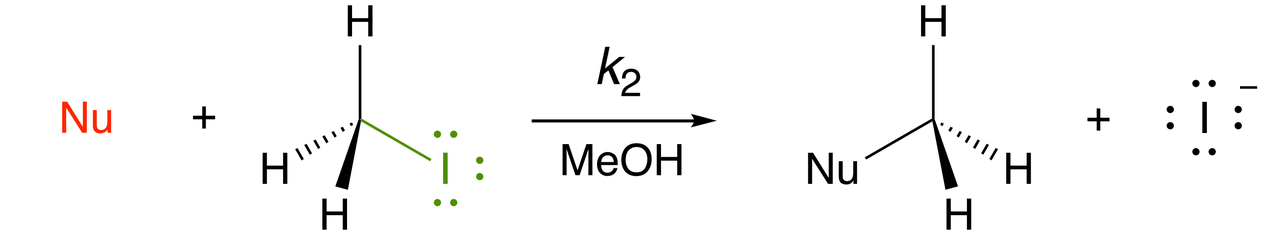
Triflato (TfO^-)

pK_{aH} = –13

Maior polarizabilidade (macio/duro)

Menos solvatado

Melhor nucleófilo



Nucleofilicidade

Solventes próticos

$F^- < Cl^- < Br^- < I^-$

Solventes apróticos

pK_{aH} aumenta

Nu	pK_{aH} [a]	*N* Mayr, [b]	v_{rel}	
H_3COH	–2,0	7,5 (MeOH)	$1,0 \times \mathbf{10^0}$	**Pior**
NO_3^-	–1,3		$3,2 \times 10^1$	
F^-	3,2	7,7 (H_2O)	$5,0 \times 10^2$	
AcO^-	4,7		$2,0 \times 10^4$	
Cl^-	–7,0	10,1 (H_2O)	$2,3 \times 10^4$	
Et_2S	–6,7		$2,2 \times 10^5$	
NH_3	9,2	9,5 (H_2O)	$3,2 \times 10^5$	
Me_2S	–7,0		$3,5 \times 10^5$	
N_3^-	4,6	15 - 16	$6,0 \times 10^5$	
Br^-	–8	11,7 (H_2O)	$6,2 \times 10^5$	
CH_3O^-	15,5	15,8 (MeOH)	$1,9 \times 10^6$	
Me_2Se	<< 0		$2,1 \times 10^6$	
CN^-	9,2		$5,0 \times 10^6$	
I^-	–10		$2,6 \times 10^7$	
HS^-	7,0	> 20	$1,0 \times \mathbf{10^8}$	**Melhor**

[a] Laurence e Gal, Lewis Basicity and Affinity Scales: Data and Measurement (2010) Wiley: DOI:10.1002/9780470681909
[b] https://www.cup.lmu.de/oc/mayr/reaktionsdatenbank/

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DEZ MINUTOS ORGÂNICOS

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