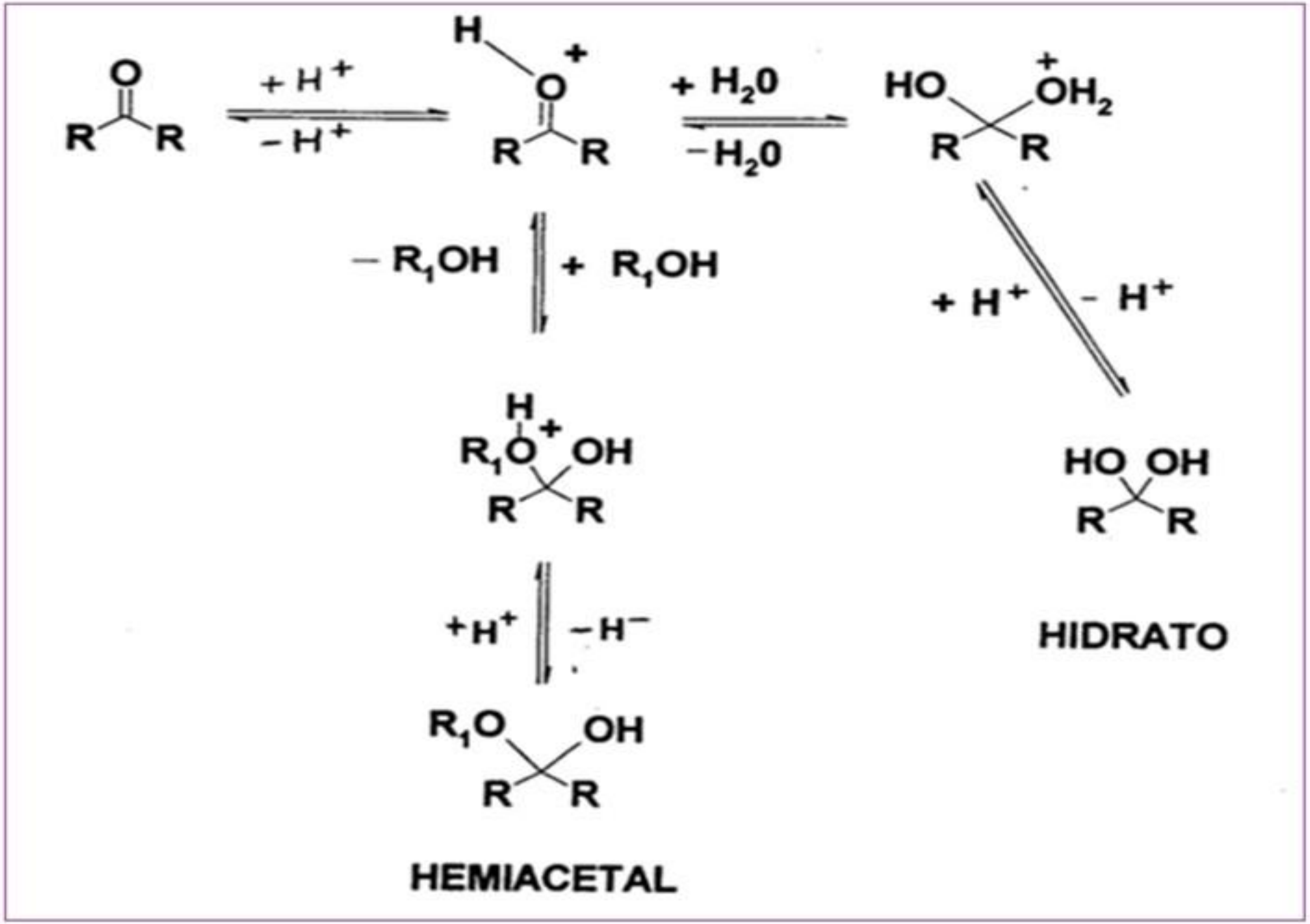
SUBSTITUIÇÃO NUCLEOFÍLICA COM PERDA DO OXIGÊNIO CARBONÍLICO

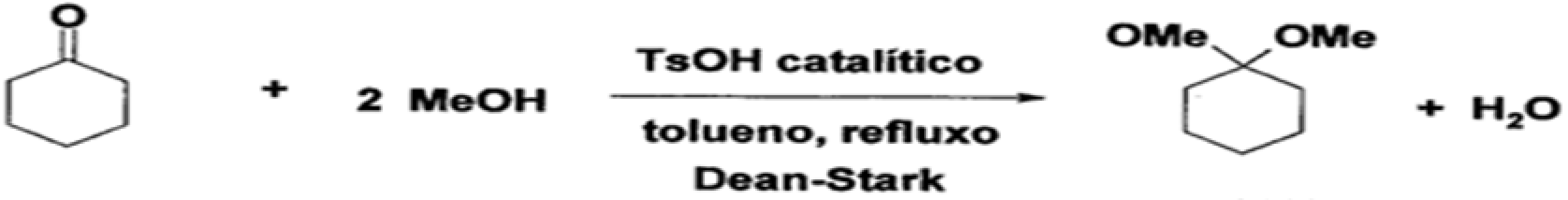
FORMAÇÃO DE HIDRATOS E HEMIACETAIS SOB CATÁLISE ÁCIDA



SUBSTITUIÇÃO NUCLEOFÍLICA EM COMPOSTOS CARBONÍLICOS COM PERDA DO OXIGÊNIO CARBONÍLICO

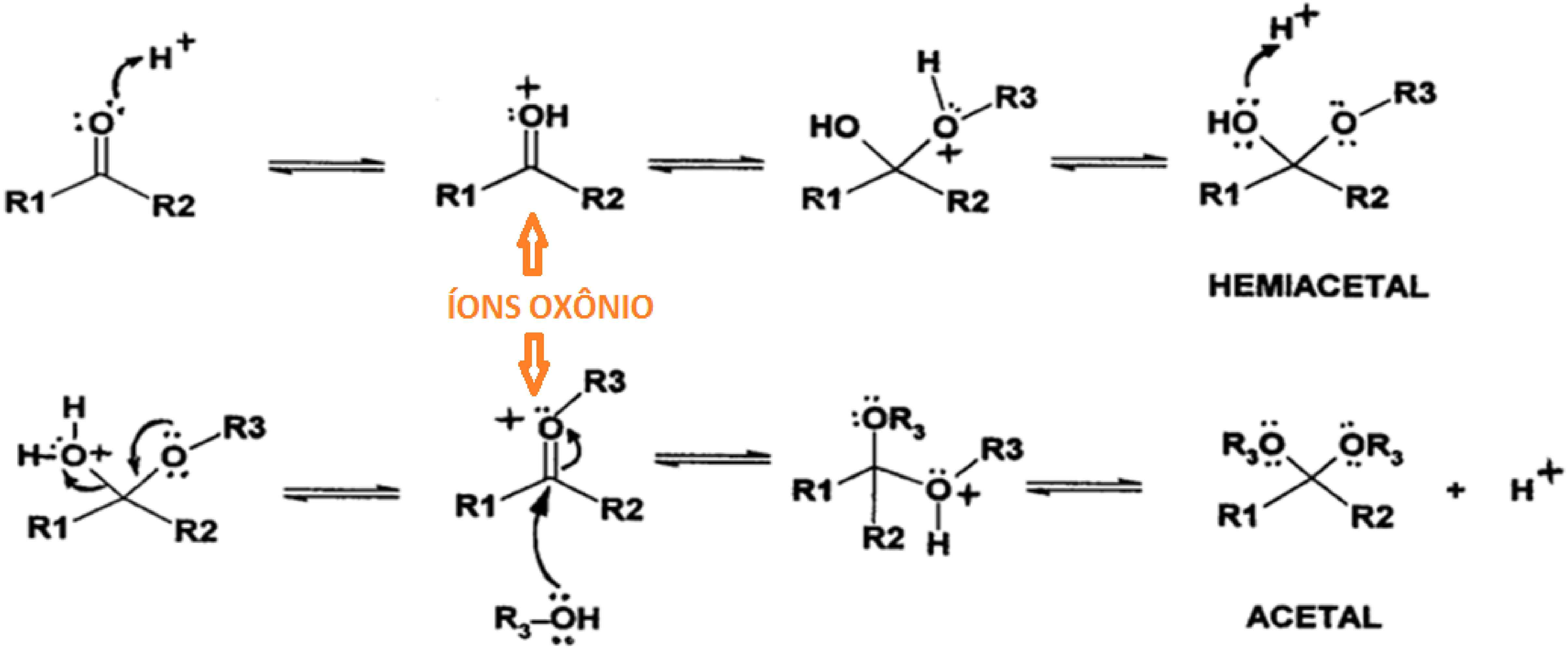
SOB CATÁLISE ÁCIDA → HEMIACETAL → ACETAL

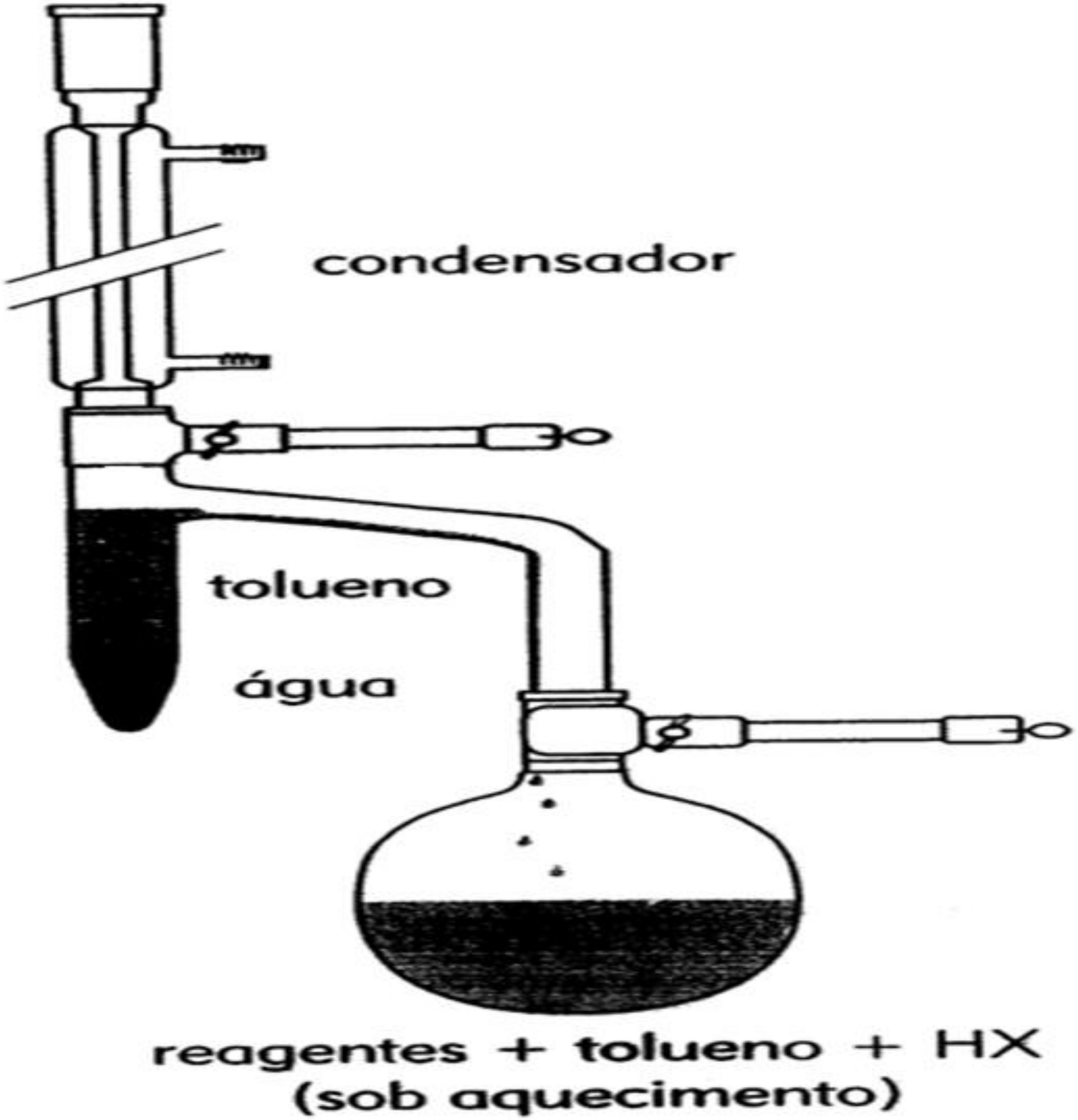
76 %



80%

MECANISMO DE FORMAÇÃO DE ACETAIS

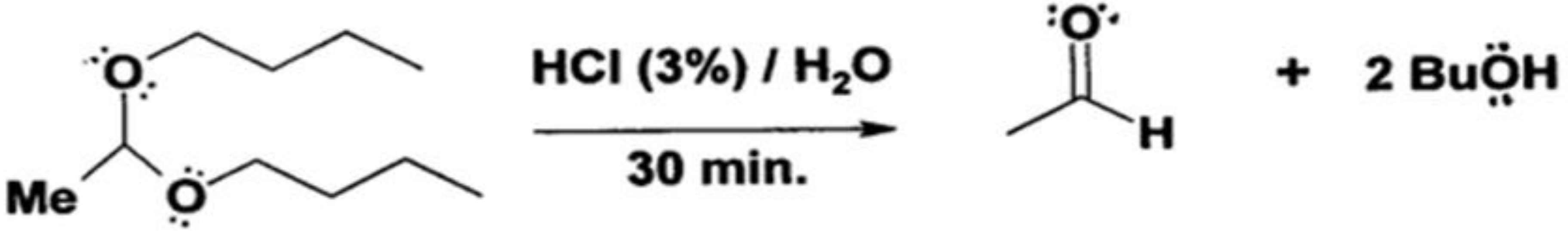




▲ Representação esquemática do sistema Dean-Stark.

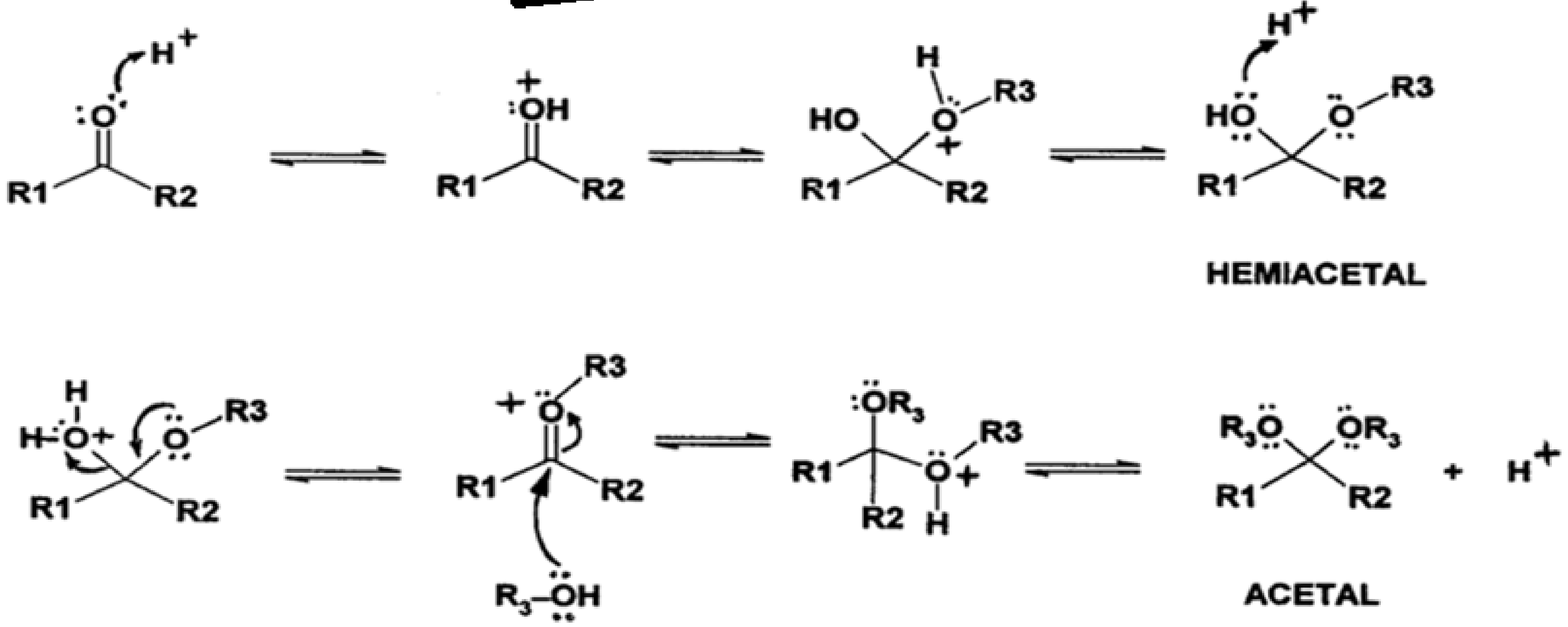
HIDRÓLISE DE ACETAIS

ACETAIS TRATADOS COM ÁCIDO AQUOSO, REGENERAM O ALDEÍDO OU A CETONA



A hidrólise de acetais é a reação reversa de sua formação !

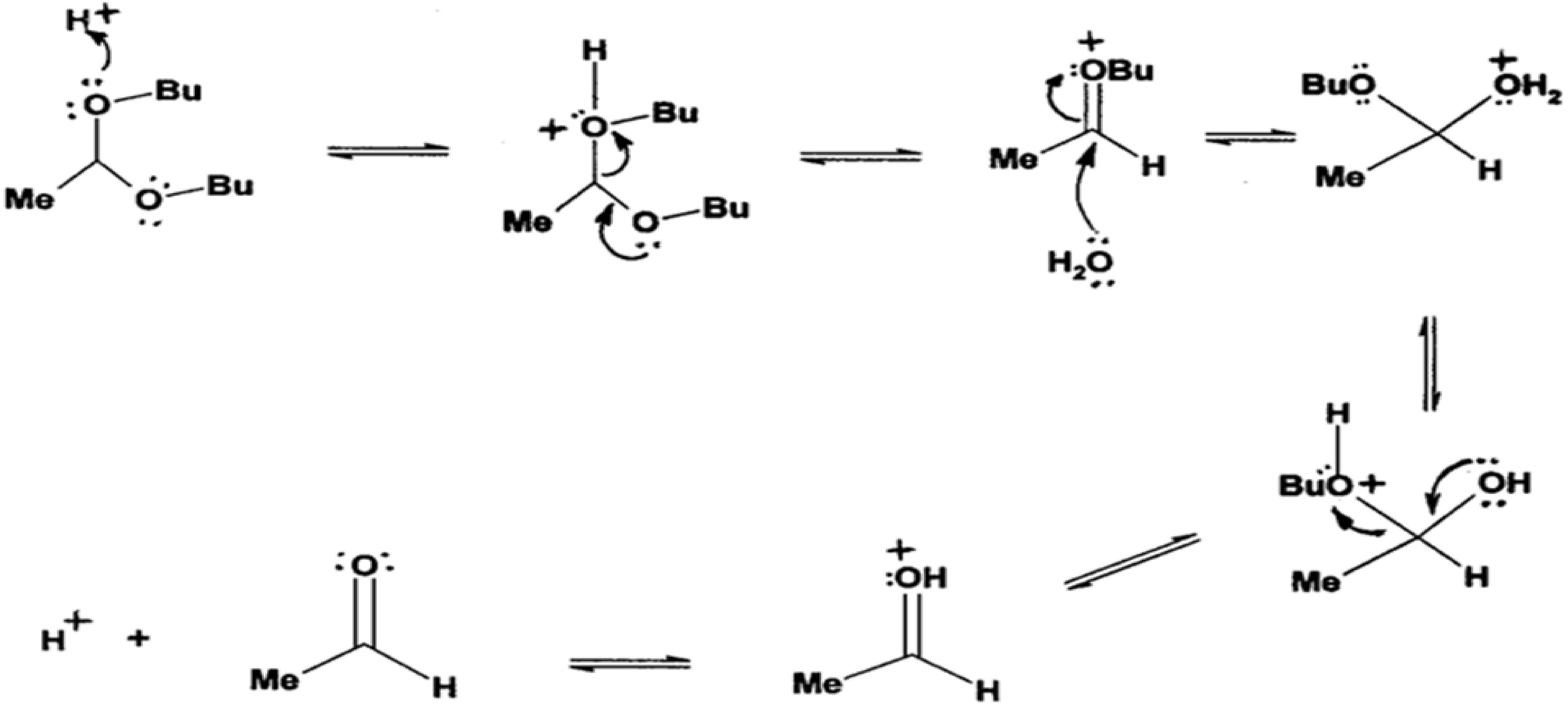
FORMAÇÃO DE ACETAIS



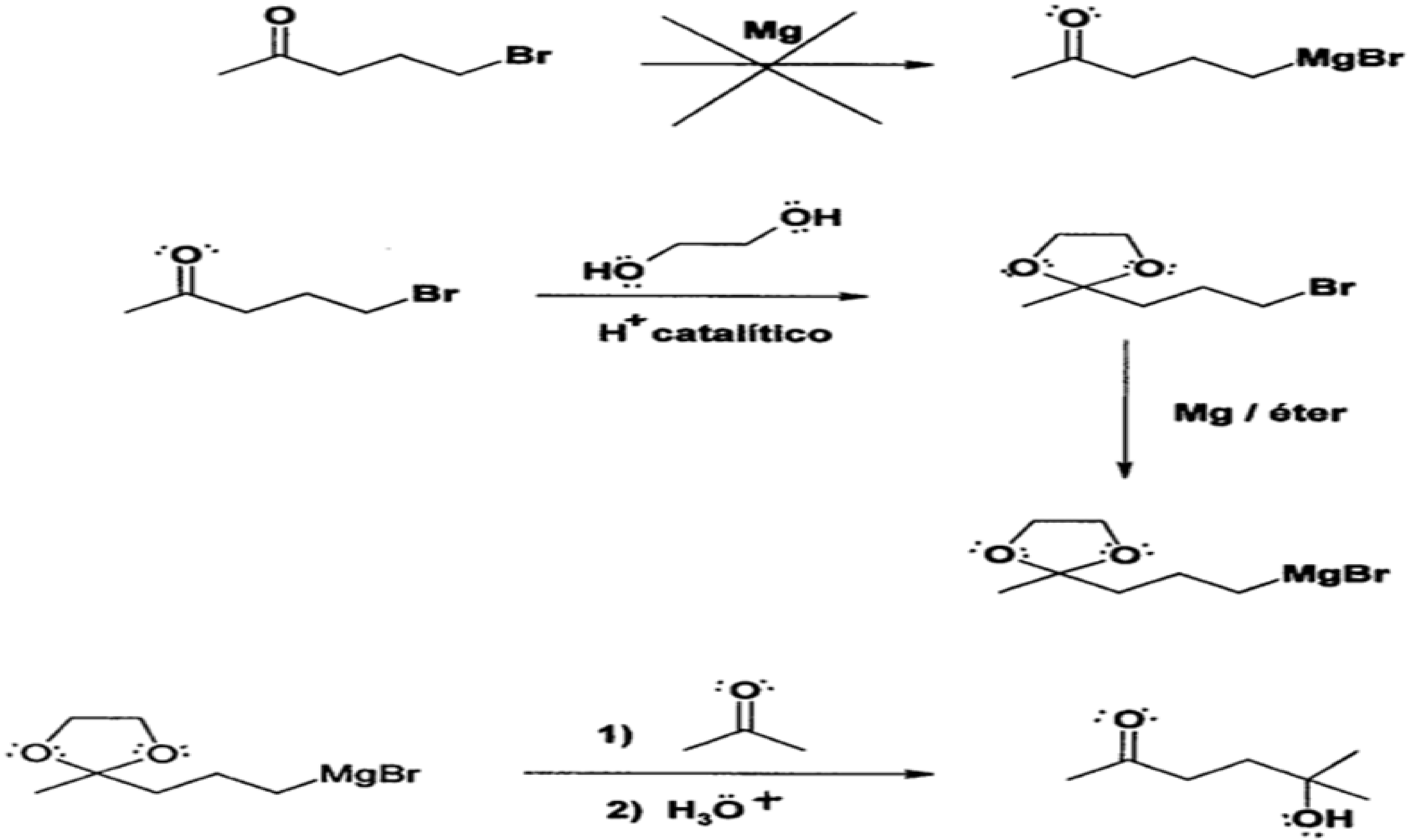
HIDRÓLISE

MECANISMO DE HIDRÓLISE DE ACETAIS

MECANISMO DE HIDRÓLISE DE ACETAIS



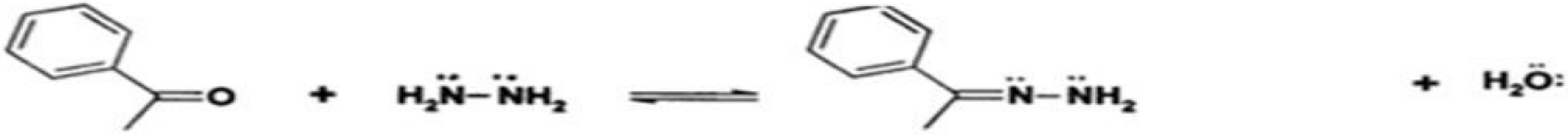
ACETAIS COMO GRUPO DE PROTEÇÃO



REAÇÃO DE ALDEÍDOS E CETONAS COM AMINAS
FORMAÇÃO DE IMINAS E ENAMINAS

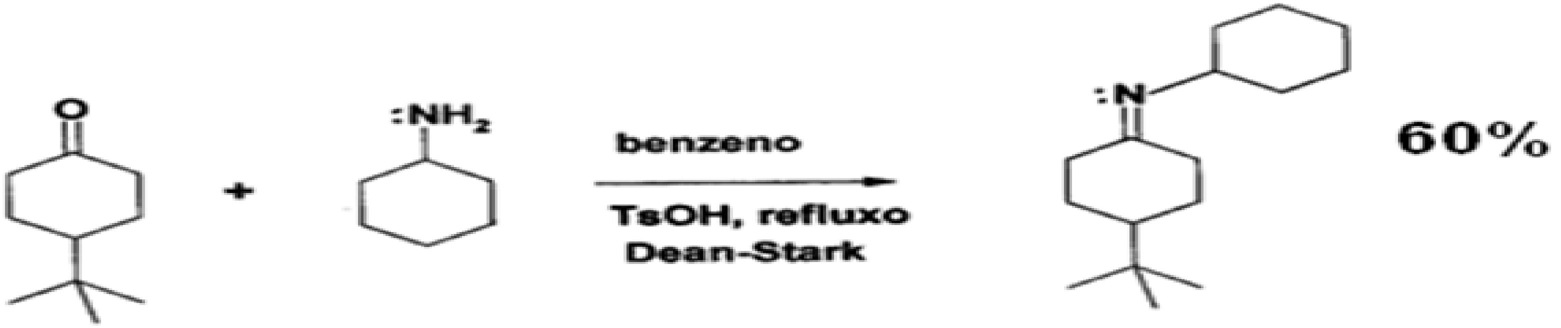
UMA IMINA

UMA OXIMA

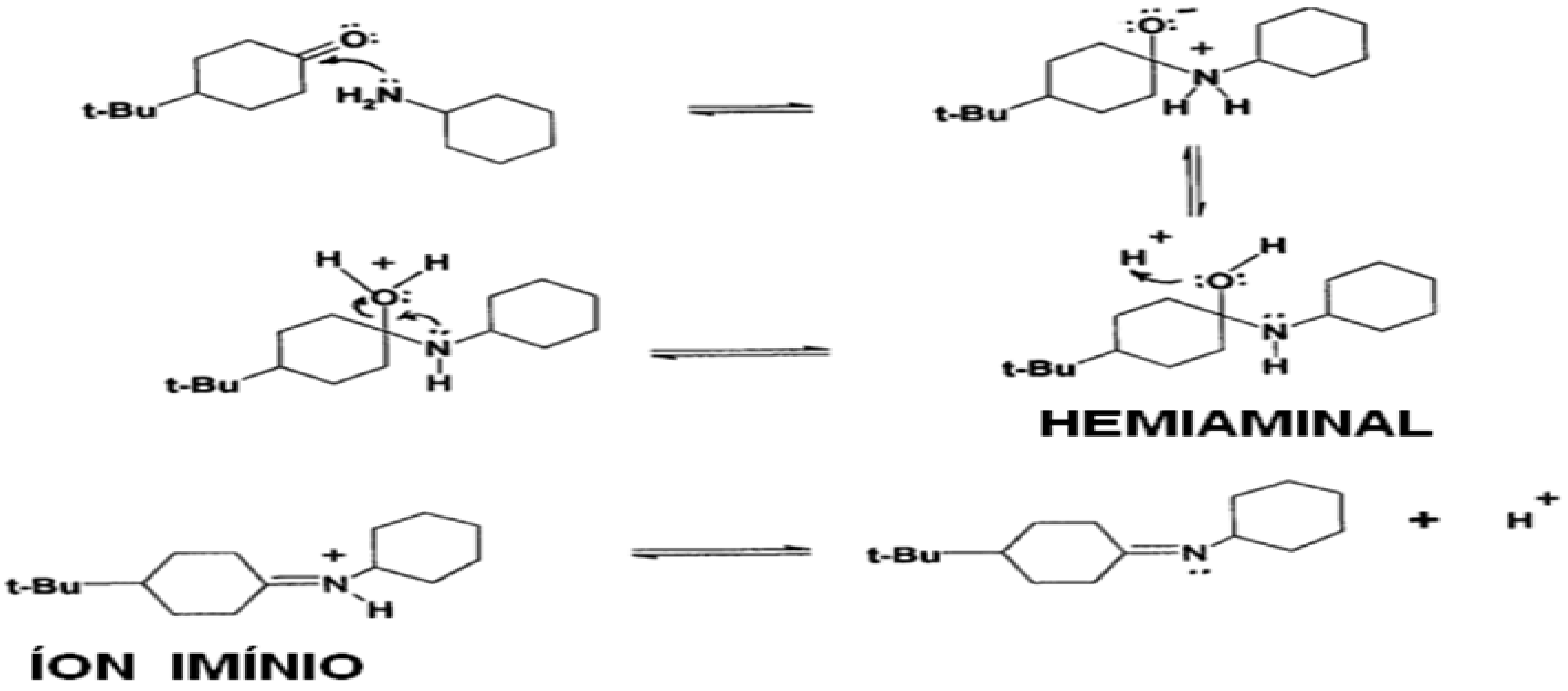


UMA HIDRAZONA

UMA SEMICARBAZONA


:NH₂
benzeno
TsOH, refluxo
Dean-Stark
:N
60%

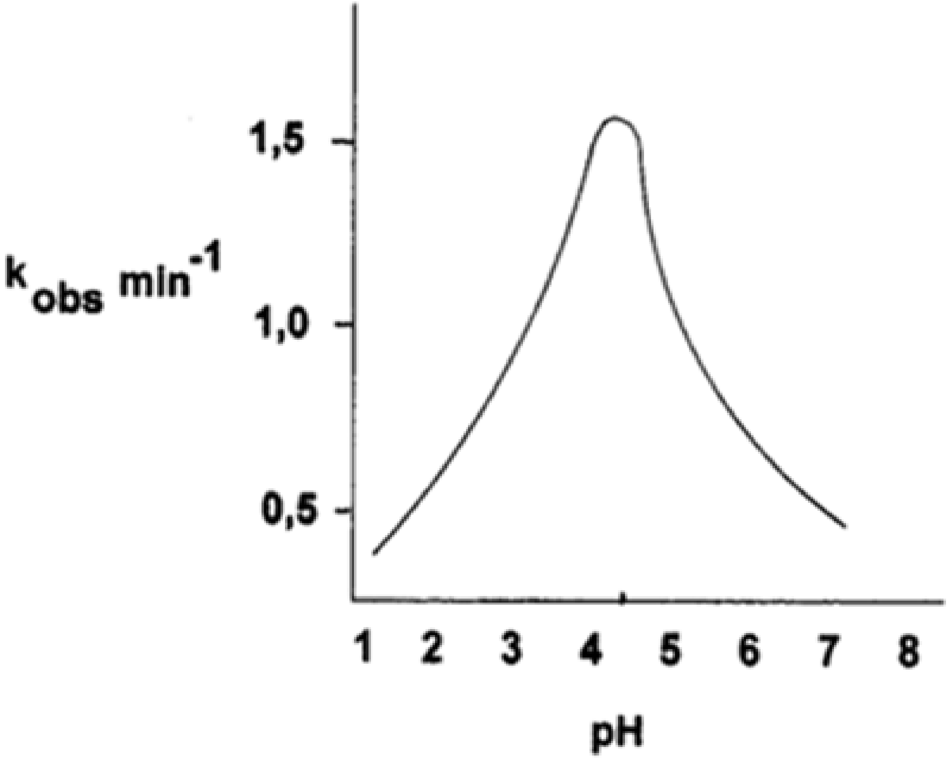
MECANISMO

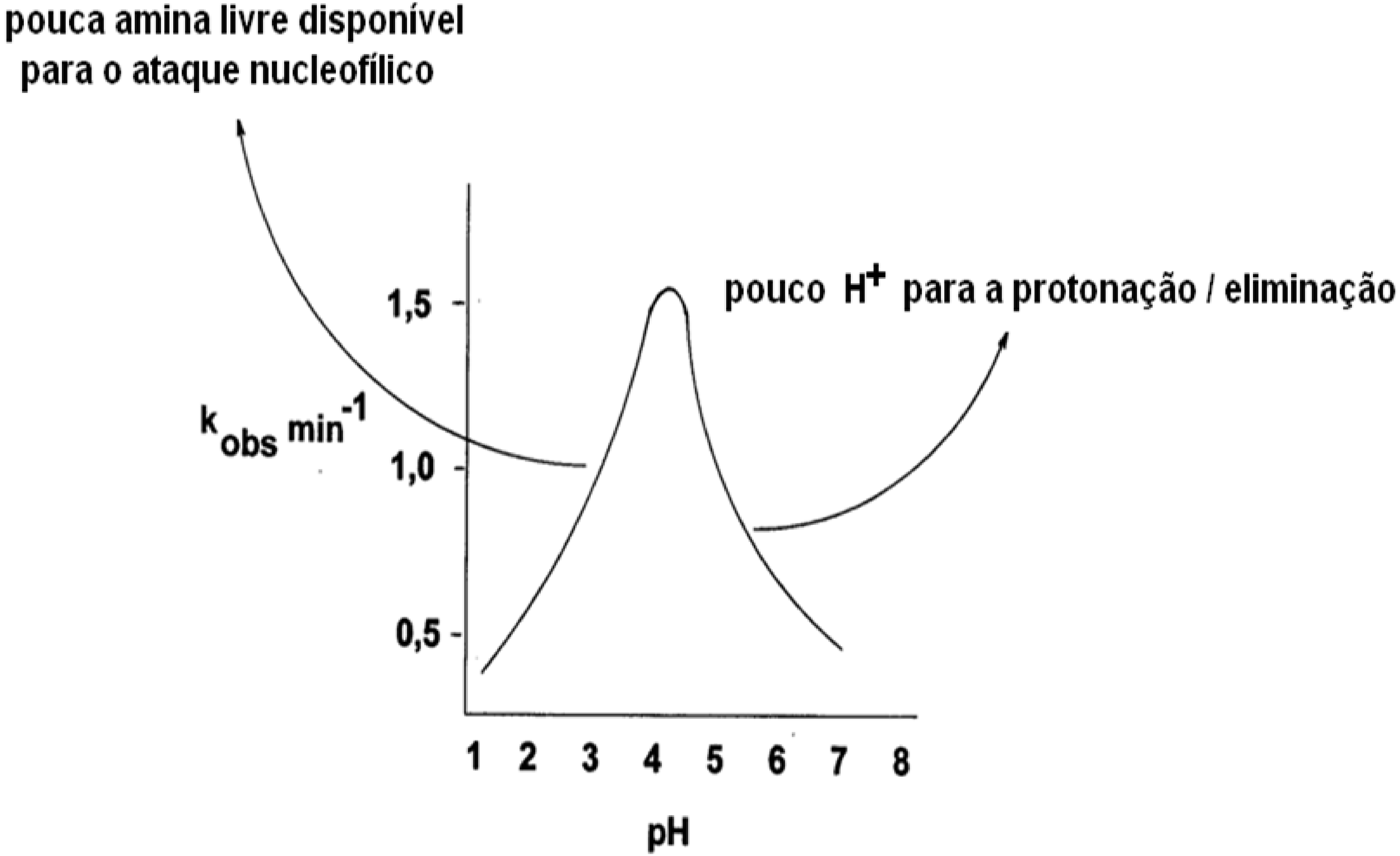

t-Bu
H₂N
t-Bu
H H
H⁺
H
t-Bu
H + H
t-Bu
H
HEMIAMINAL
t-Bu
H
ÍON IMÍNIO
t-Bu
N
+ H⁺

A FORMAÇÃO DE IMINAS E SEUS DERIVADOS É FORTEMENTE DEPENDENTE DO pH DO MEIO REACIONAL

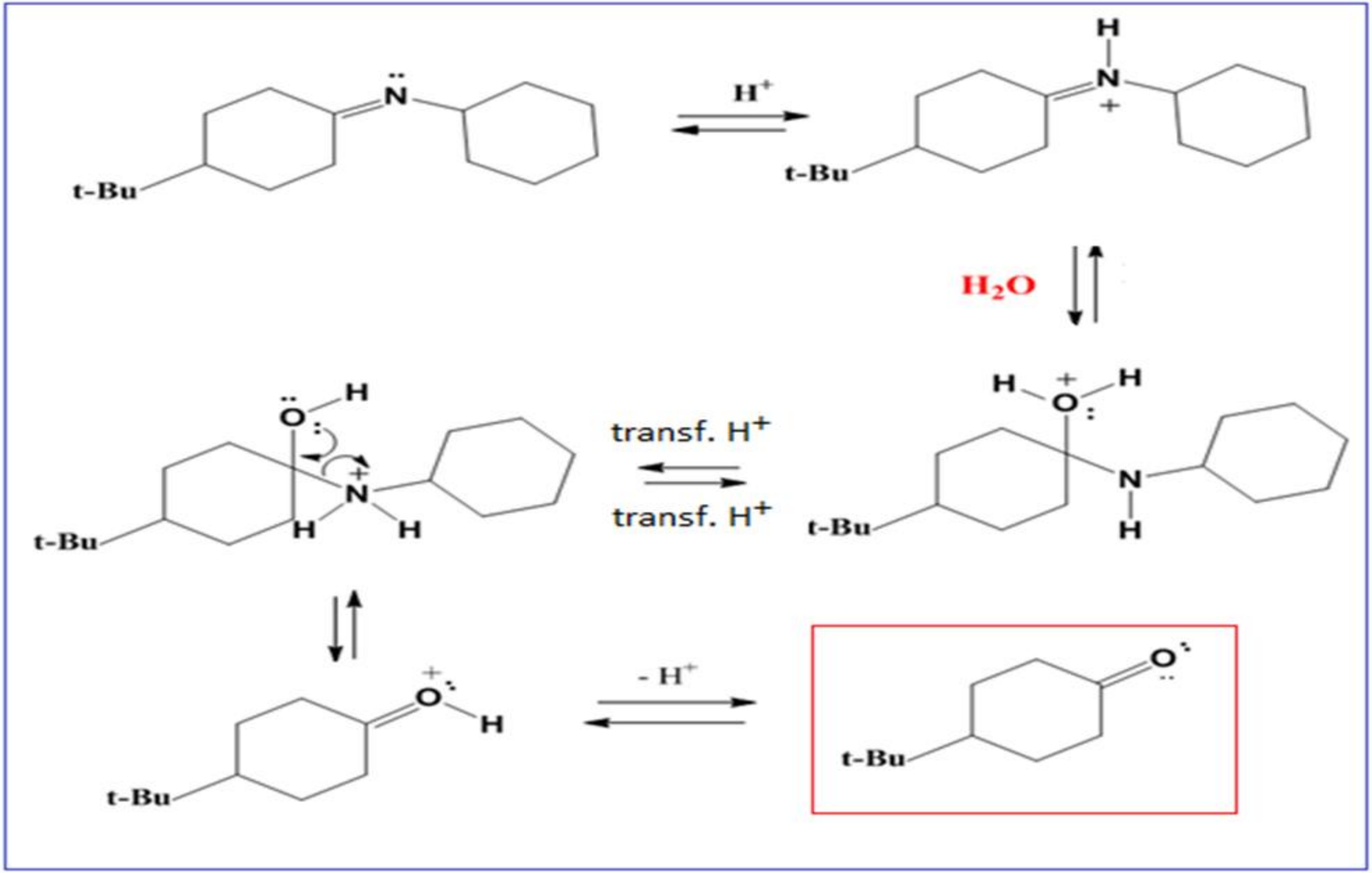
HIDROXILAMINA

pK_{aH} = 6,0



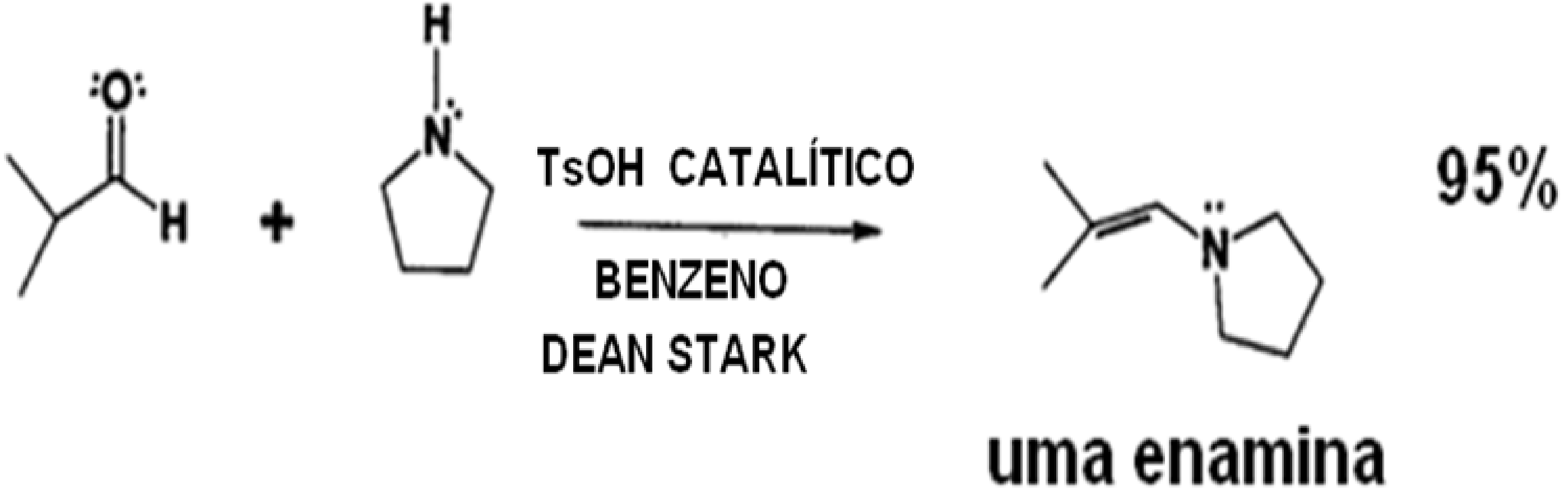

pouca amina livre disponível
para o ataque nucleofílico
pouco H^+ para a protonação / eliminação
k_{obs} min^{-1}
1,5
1,0
0,5
1
2
3
4
5
6
7
8
pH

OS DERIVADOS NITROGENADOS SÃO HIDROLISADOS EM MEIO ÁCIDO AQUOSO, REGENERANDO O COMPOSTO CARBONÍLICO

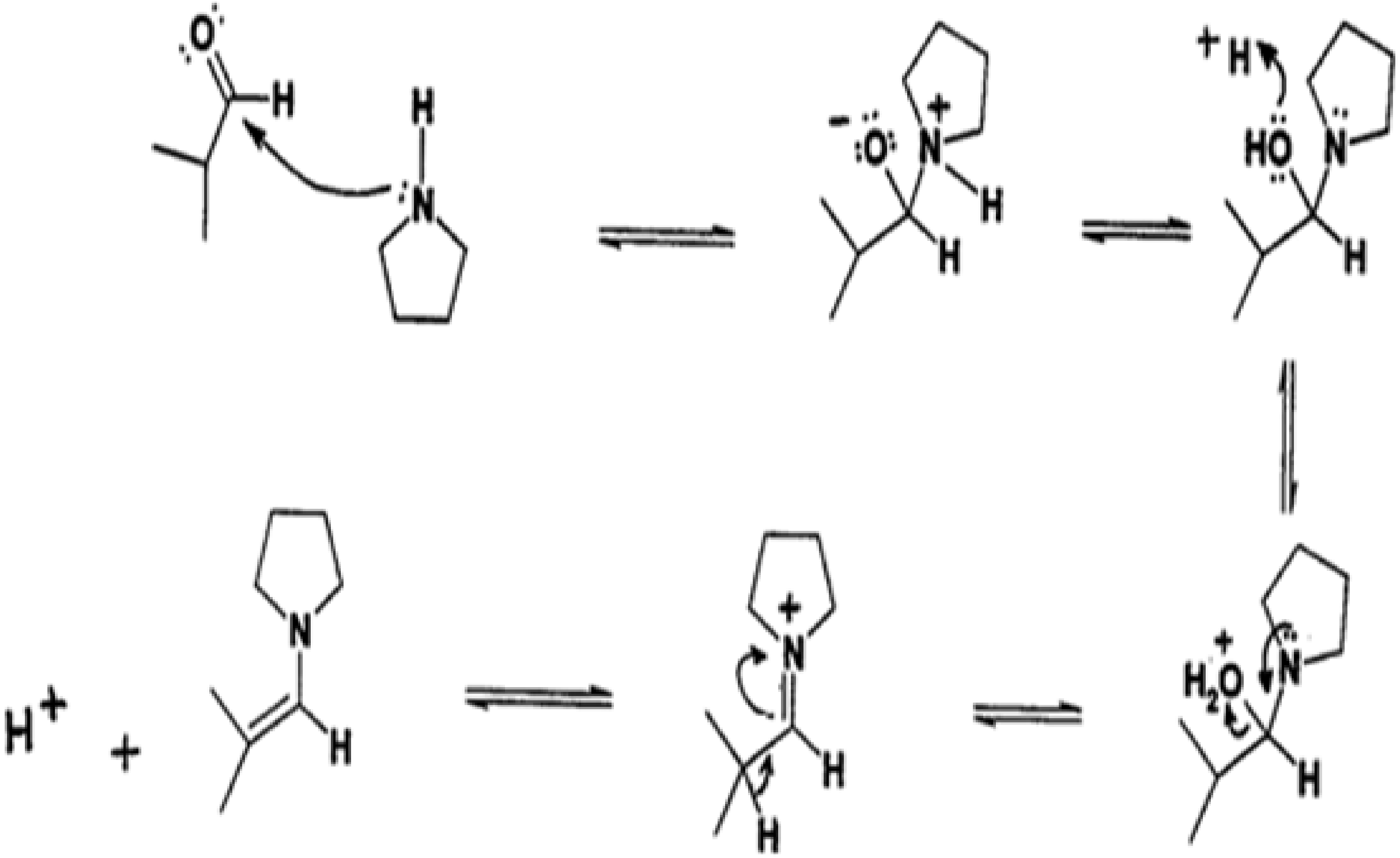


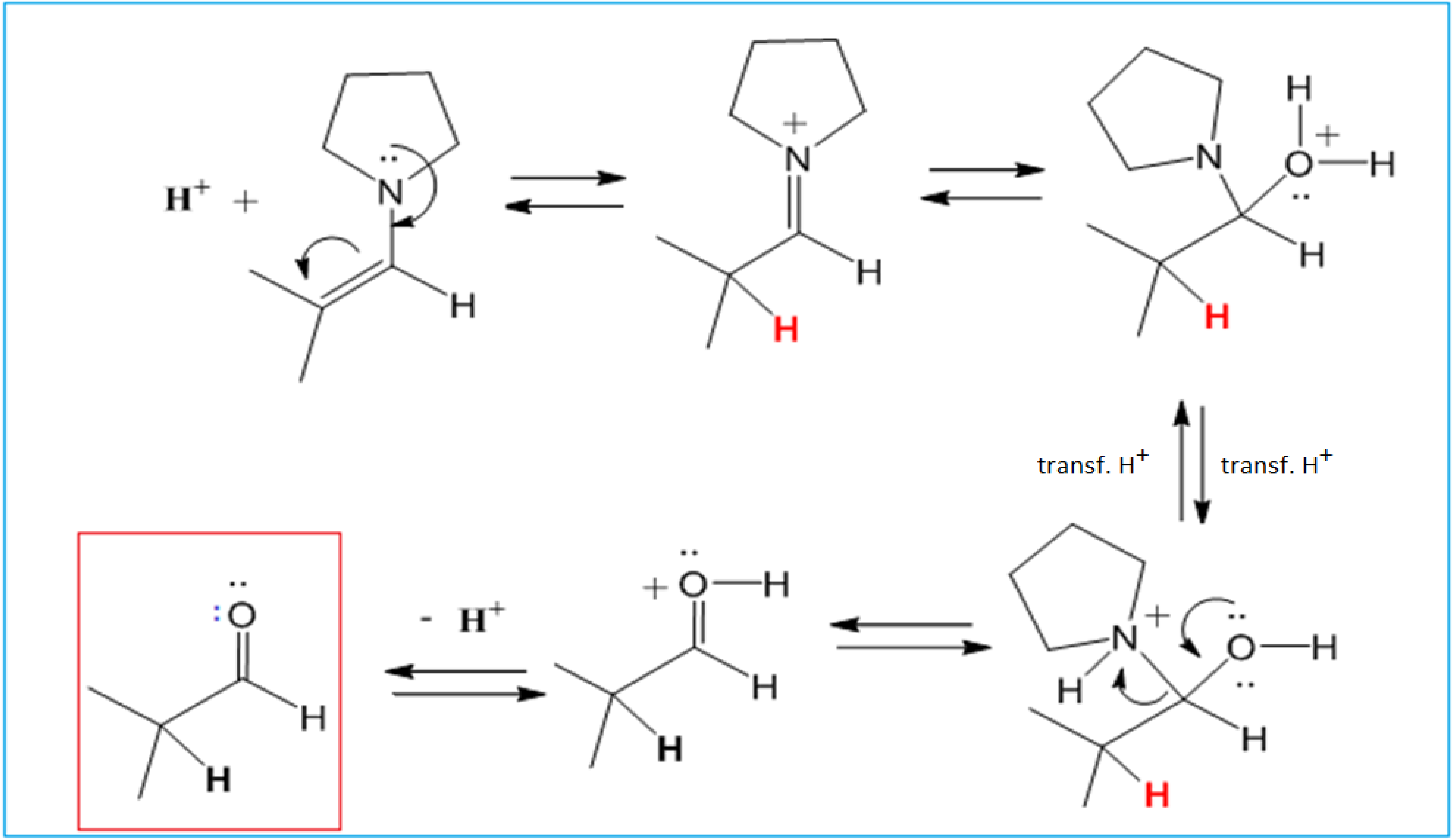
t-Bu
H^+
H_2O
transf. H^+
transf. H^+
$- H^+$

AMINAS SECUNDÁRIAS REAGEM COM CARBONÍLICOS FORMANDO ENAMINAS



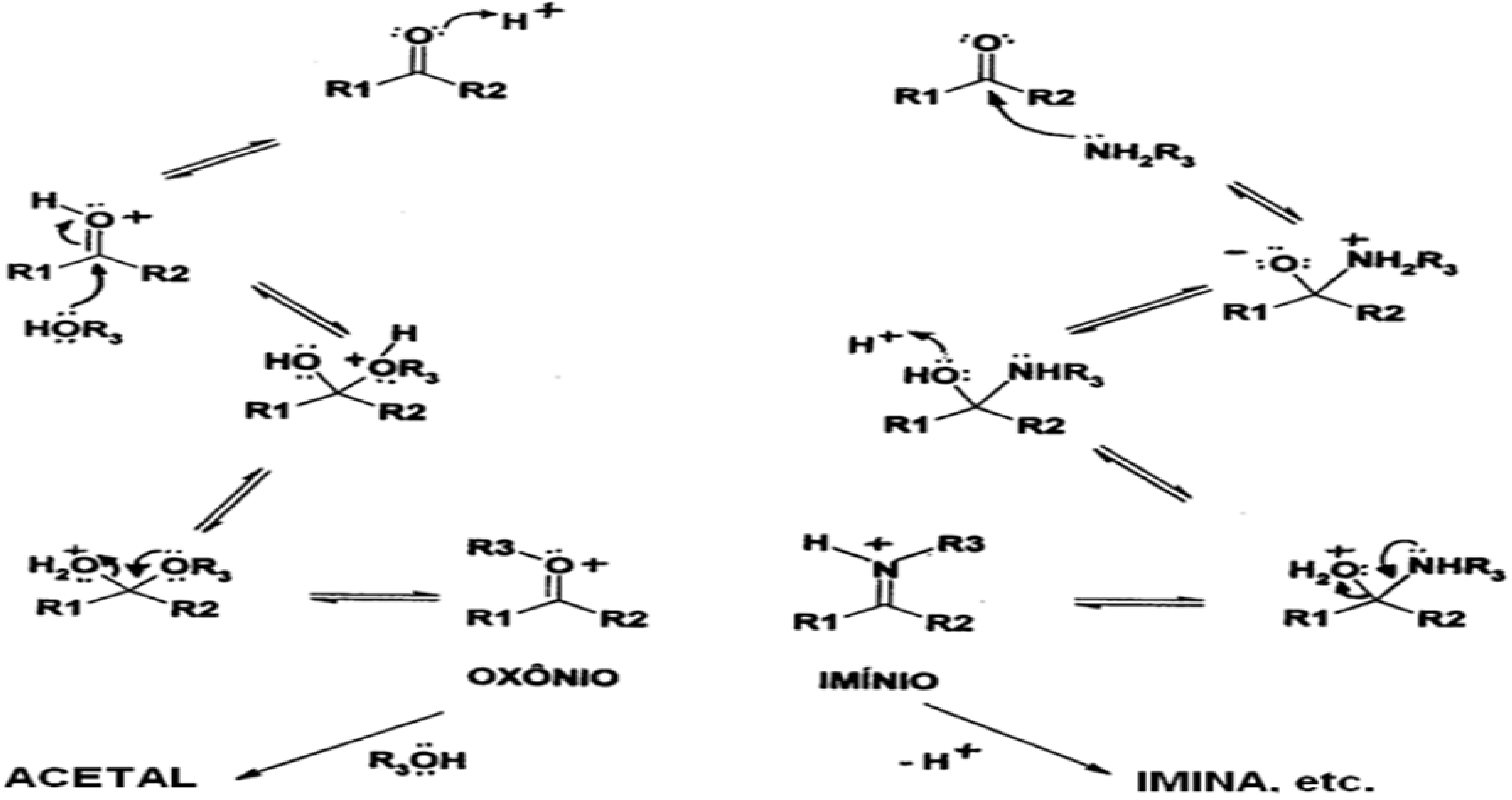
MECANISMO



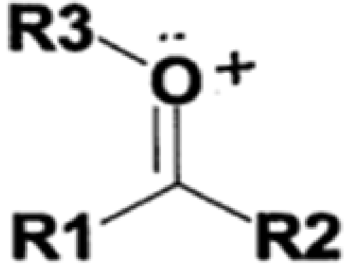


H+ +
N
H
N
H
H
N
O
H
H
H
H
transf. H+
transf. H+
N
H
O
H
H
H
+ O
H
H
H
- H+
O
H
H

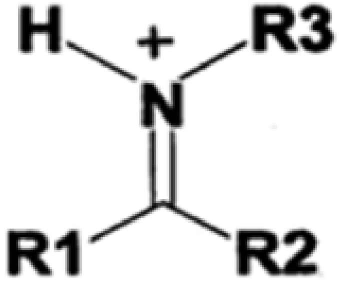
COMPARAÇÃO DOS MECANISMOS DE FORMAÇÃO DE ACETAIS E DERIVADOS NITROGENADOS



oxônio



um eletrófilo

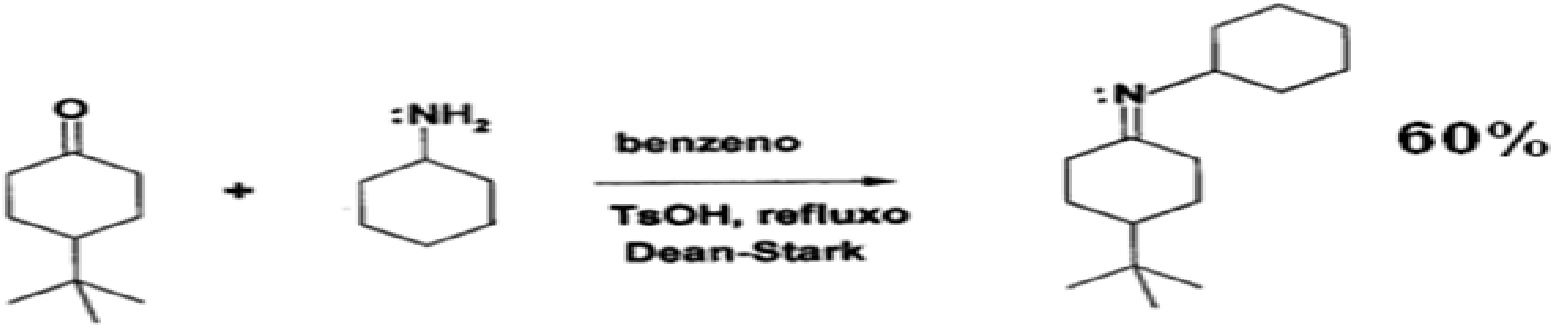


IMÍNIO

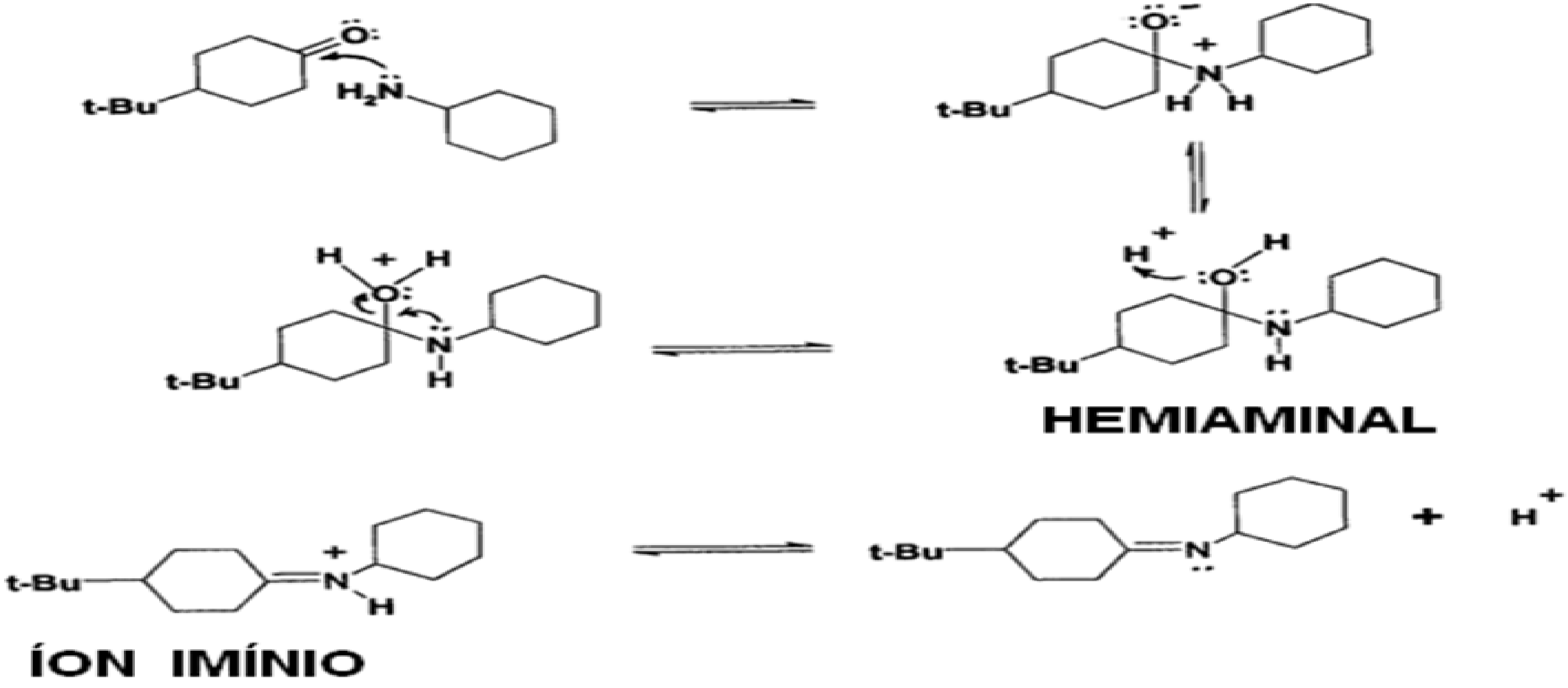
um ácido, mas também
um eletrófilo

íons imínio também reagem com nucleófilos

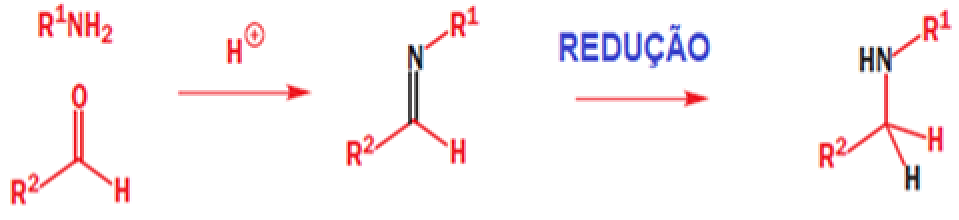
AINDA IMINAS E ÍONS IMÍNIO : ALGUNS DETALHES IMPORTANTES


:NH₂
benzeno
TsOH, refluxo
Dean-Stark
:N
60%

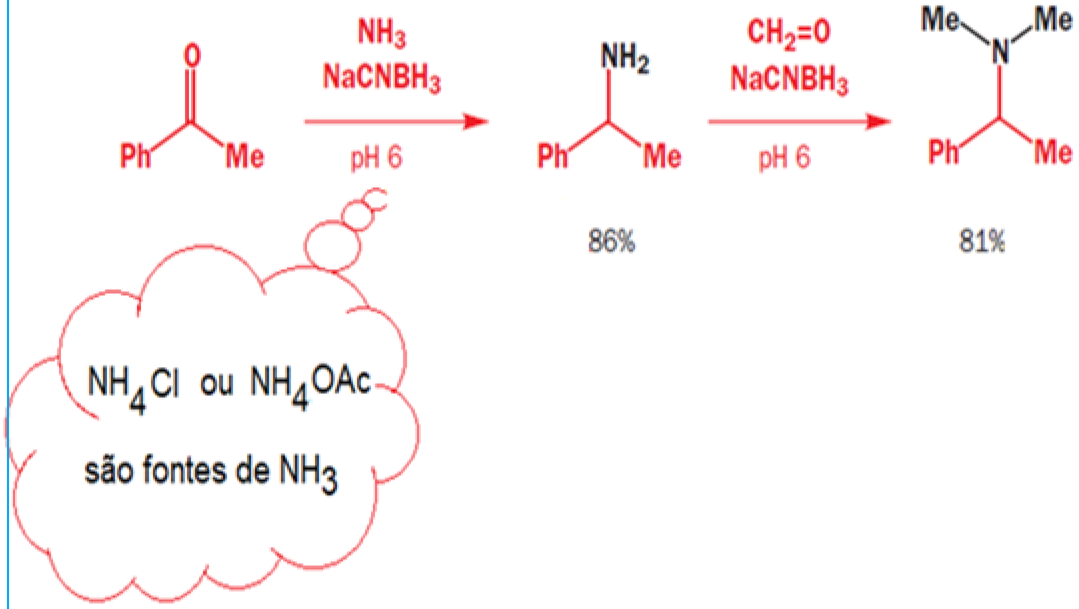
MECANISMO


t-Bu
H₂N
HEMIAMINAL
ÍON IMÍNIO
H⁺

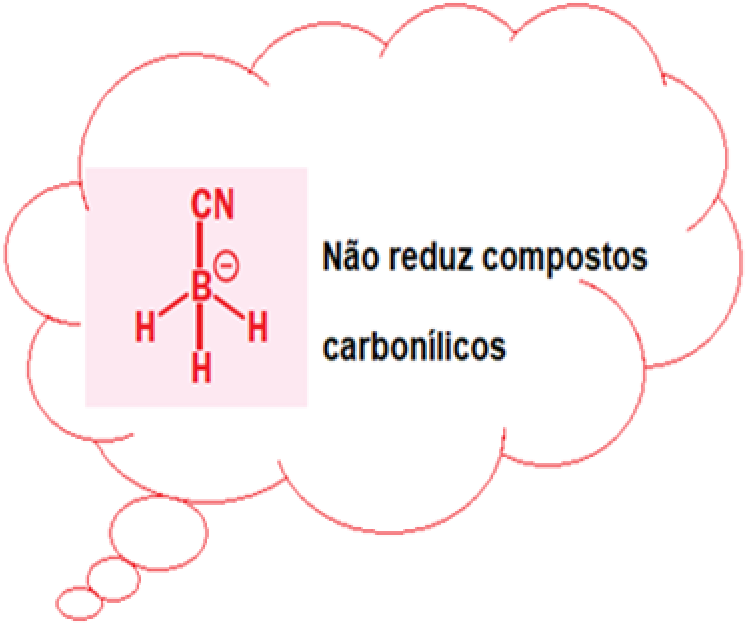
3. A AMINAÇÃO REDUTIVA: DE UM COMPOSTO CARBONÍLICO A UMA AMINA SECUNDÁRIA



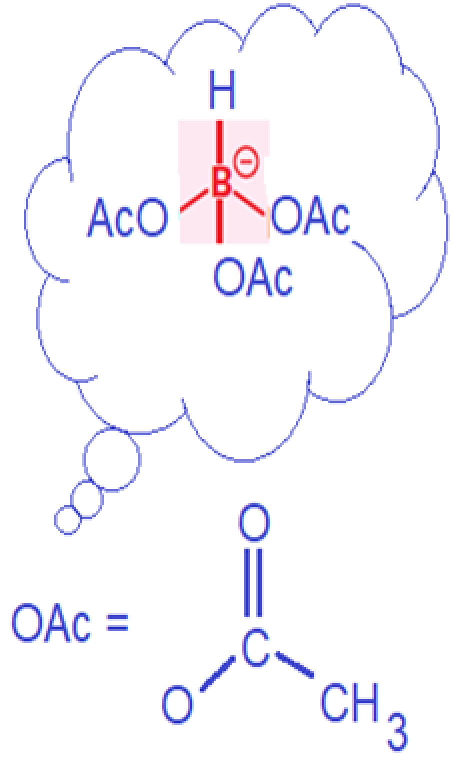
Exemplo:

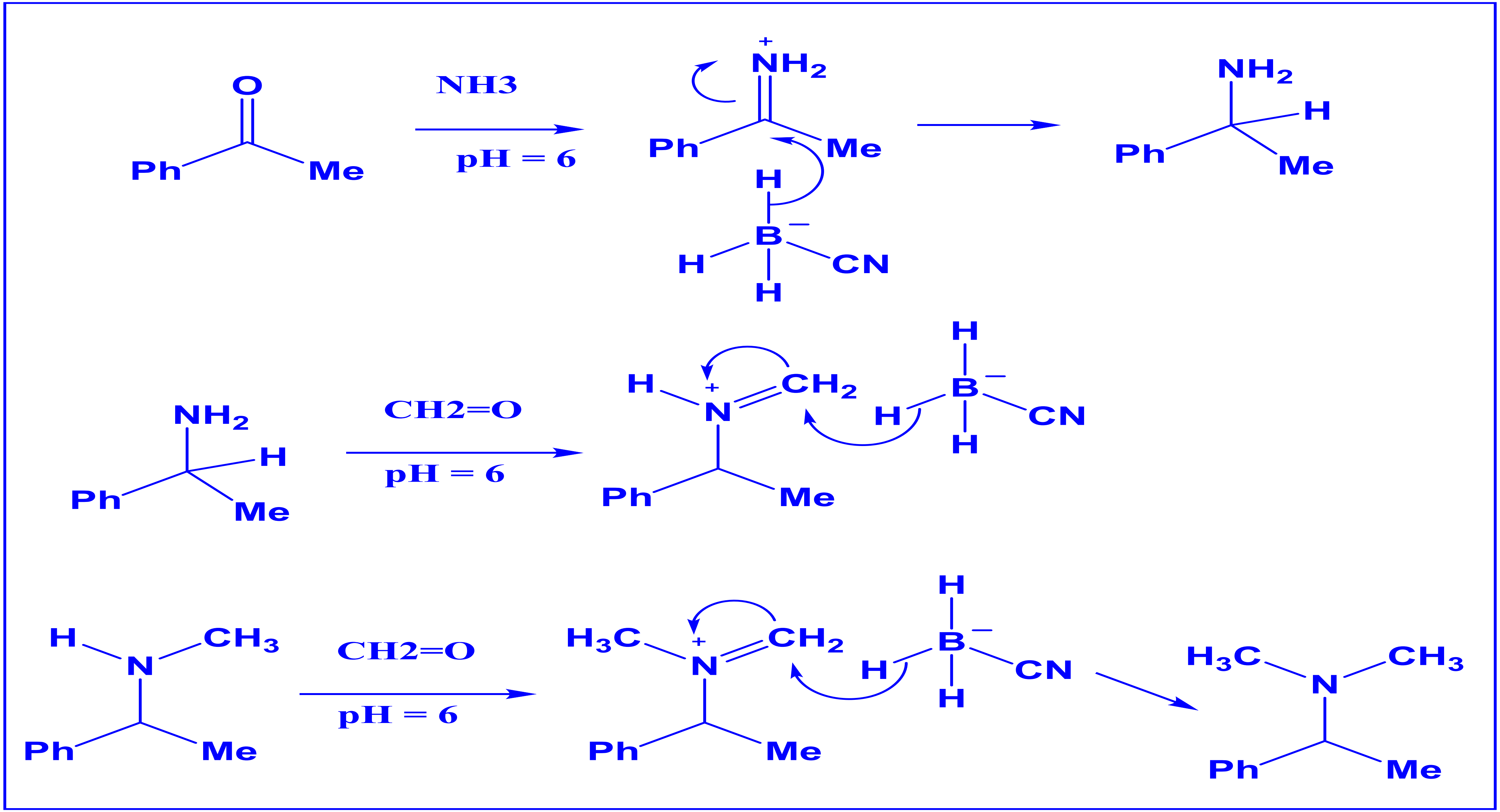


NH_4Cl ou NH_4OAc são fontes de NH_3



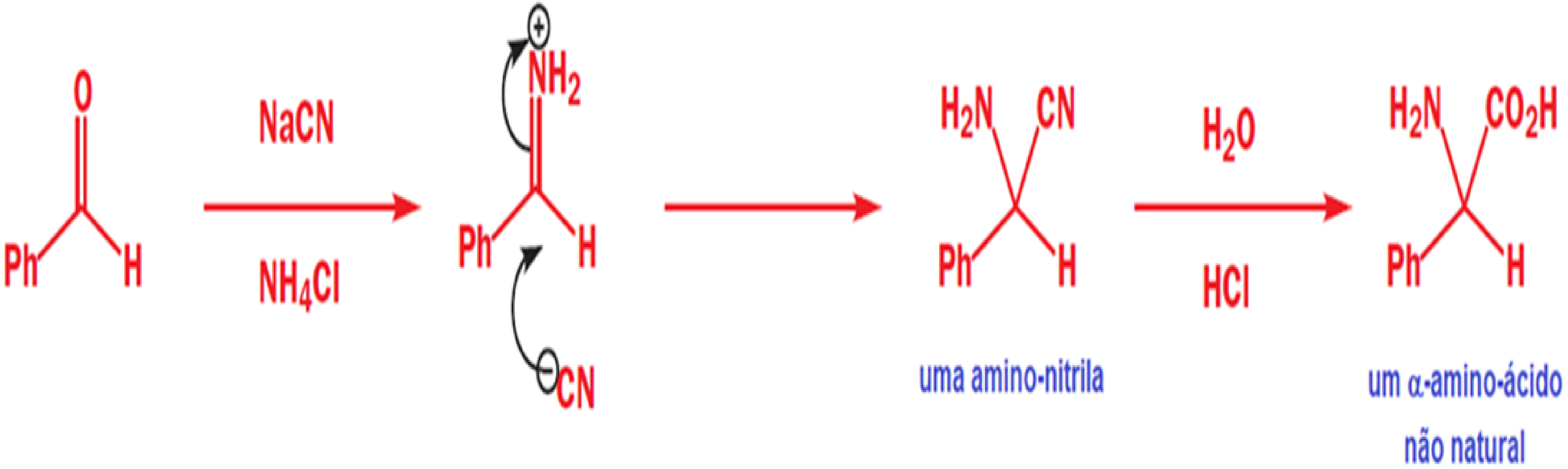
Não reduz compostos carbonílicos



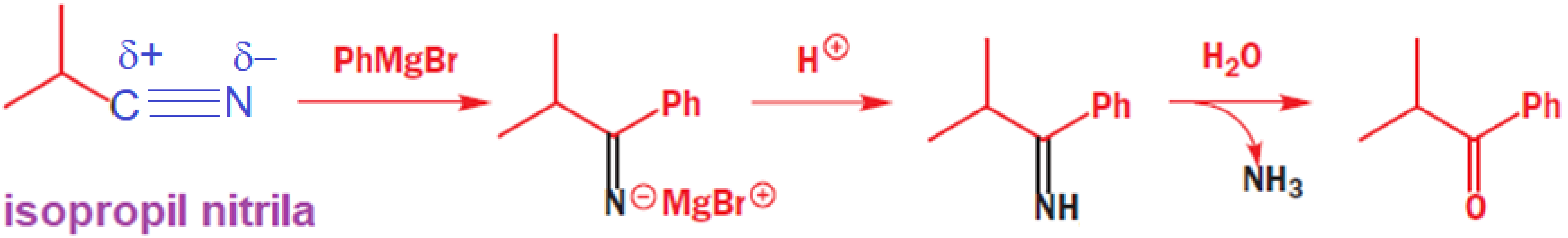


O
Ph
Me
NH3
pH = 6
+
NH2
Ph
Me
H
B
−
H
CN
H
NH2
H
Ph
Me
NH2
H
Ph
Me
CH2=O
pH = 6
H
+
N
CH2
Ph
Me
H
B
−
H
CN
H
H
N
CH3
Ph
Me
CH2=O
pH = 6
H3C
+
N
CH2
Ph
Me
H
B
−
H
CN
H
H3C
N
CH3
Ph
Me

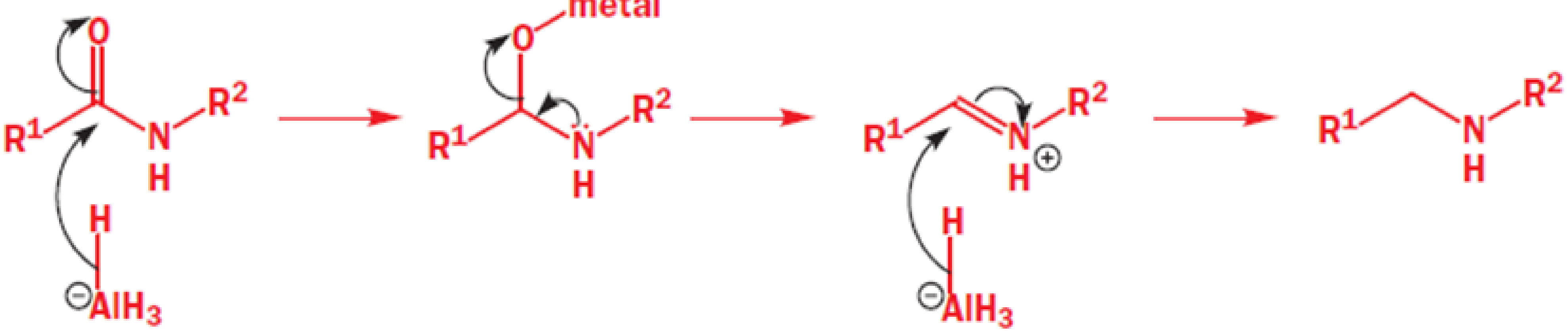
4. A SÍNTESE DE STRECKER



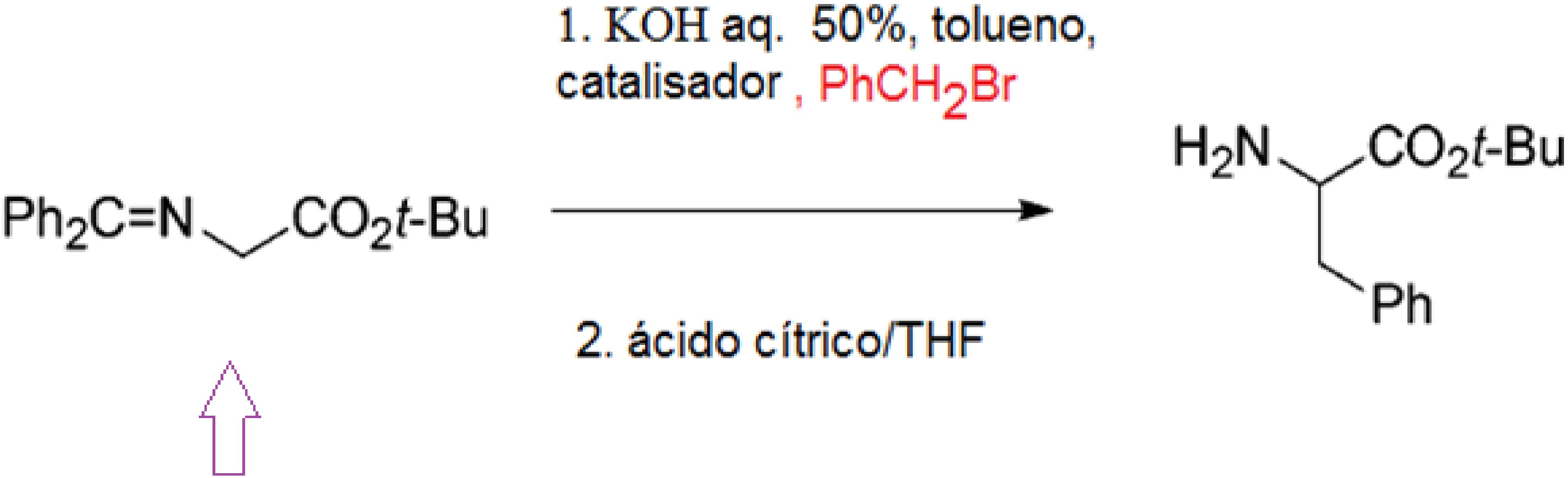
1. IMINAS SÃO INTEMEDIÁRIOS NA REAÇÃO DE NITRILAS COM ORGANOMETÁLICOS



2. ÍONS IMÍNIO SÃO INTERMEDIÁRIOS NA REDUÇÃO DE AMIDAS A AMINAS

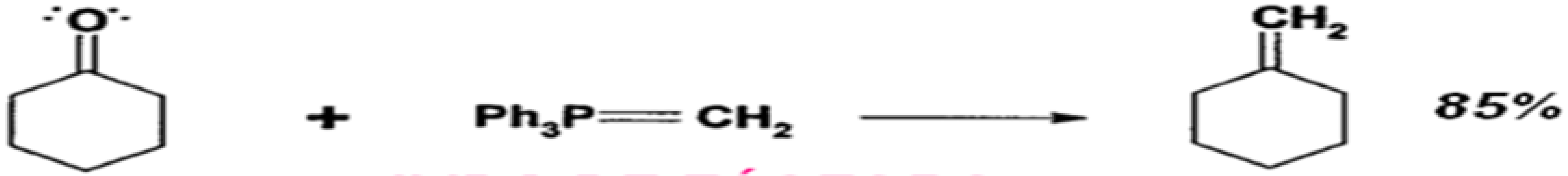


5. UMA MODERNA SÍNTESE DE α-AMINOÁCIDOS



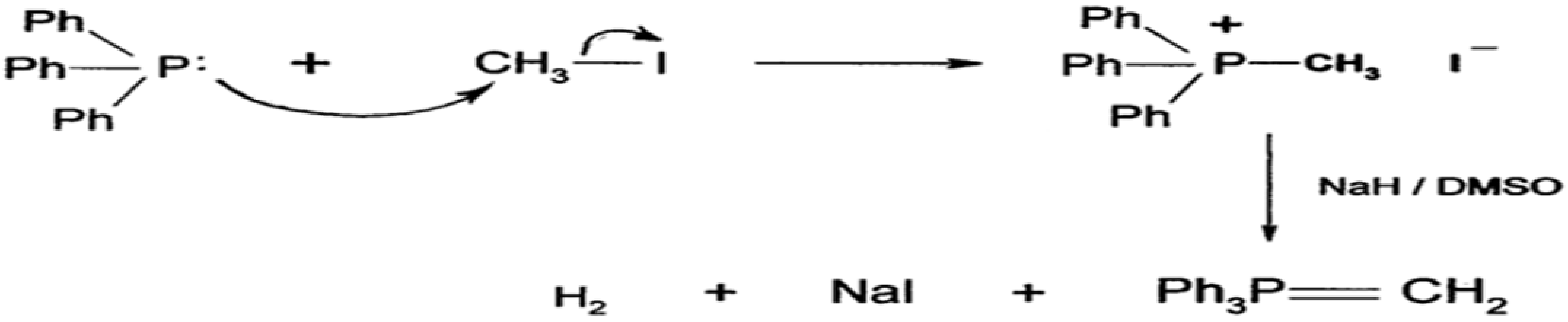
COMERCIAL

A REAÇÃO DE WITTIG

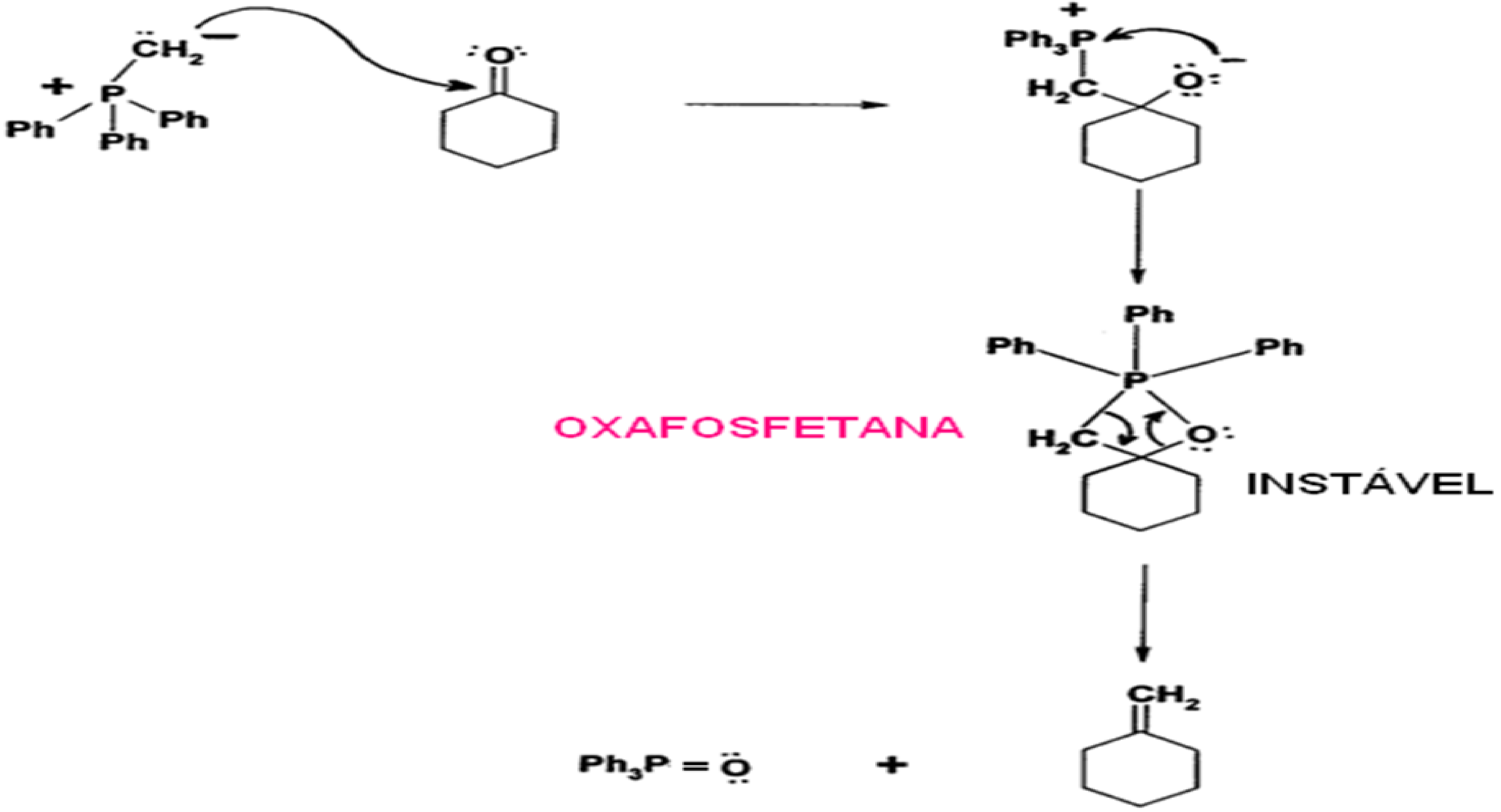


ILIDA DE FÓSFORO

$$\left[\; Ph_3\overset{+}{P}-\overset{-}{\ddot{C}}H_2 \longleftrightarrow Ph_3P=CH_2 \;\right]$$



MECANISMO



OXAFOSFETANA

INSTÁVEL

VANTAGENS DA REAÇÃO DE WITTIG

REGIOSSELETIVA *ESTEREOSSELETIVA*