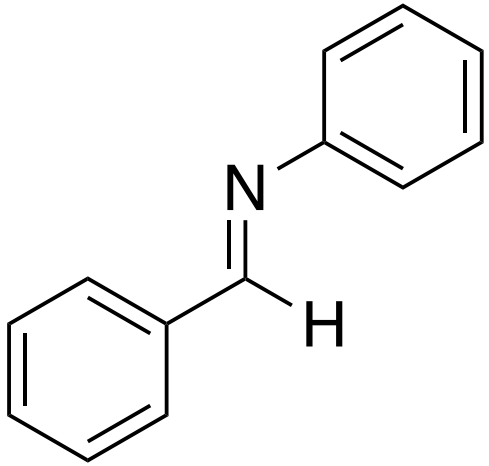
Universidad Nacional Autónoma de México

Química Orgánica III (1506)
Laboratorio
Semestre 2026 - 2

M. en C. Arturo García Zavala



Práctica 7

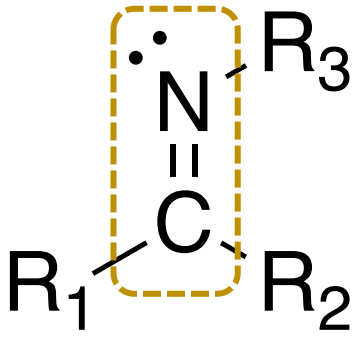
Carbonilos I: Síntesis de iminas

8/04/2026

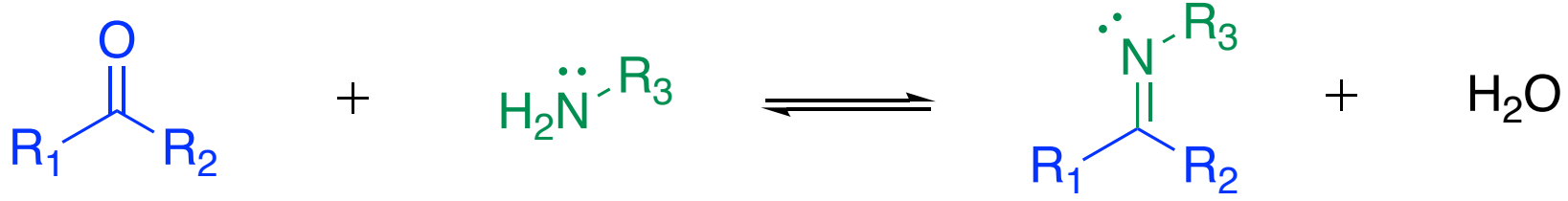
Iminas (también conocidas como bases de Schiff)

Hugo Schiff, dando clase, 24 de abril de 1915.

1864



Grupo imina o azometino



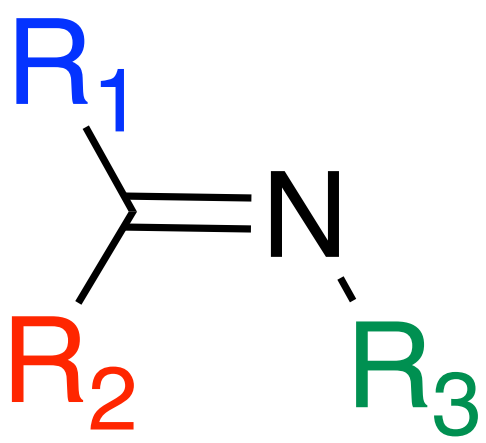
compuesto carbonílico (aldehído o cetona)

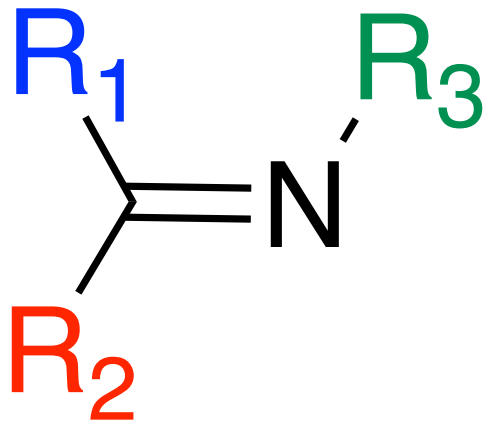
amina primaria

imina (Base de Schiff) aldiminas o cetiminas

¡Si se utiliza una amina secundaria se obtendrá una enamina!

Isomería alrededor del enlace C=N





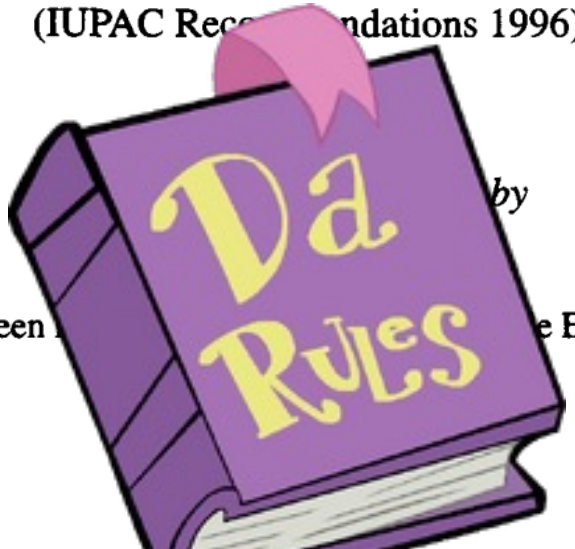
Pure & Appl. Chem., Vol. 68, No. 12, pp. 2193–2222, 1996.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION
COMMISSION ON NOMENCLATURE OF ORGANIC CHEMISTRY (III.1)
COMMISSION ON PHYSICAL ORGANIC CHEMISTRY (III.2)

BASIC TERMINOLOGY OF STEREOCHEMISTRY

(IUPAC Rec ndations 1996)



by

Department of Chemistry, Queen e End Road, London, E1 4NS, UK

E*, *Z

The approved *stereodescriptors* of stereoisomeric alkenes $R^1R^2C{=}CR^3R^4$ ($R^1 \neq R^2$, $R^3 \neq R^4$; neither R^1 nor R^2 need be different from R^3 or R^4), cumulenes $R^1R^2C[{=}C{=}C]_n{=}CR^3R^4$ and related systems *e.g.* $R_1R_2C{=}NOH$, $HON{=}C\{[CH_2]_n\}_2C{=}NOH$. The group of highest *CIP priority* attached to one of the terminal doubly bonded atoms of the alkene, oxime, *etc.* or cumulene (*i.e.* R_1 or R_2) is compared with the group of highest precedence attached to the other (*i.e.* R_3 or R_4). The stereoisomer is designated as *Z* (*zusammen* = together) if the groups lie on the same side of a reference plane passing through the double bond and perpendicular to the plane containing the bonds linking the groups to the double-bonded atoms; the other stereoisomer is designated as *E* (*entgegen* = opposite). The descriptors may be applied to structures with a fractional bond order between one and two; and to double bonds involving elements other than carbon. They are not used to describe ring substitution relationships. See also *cis-trans isomers*.

E*, *Z

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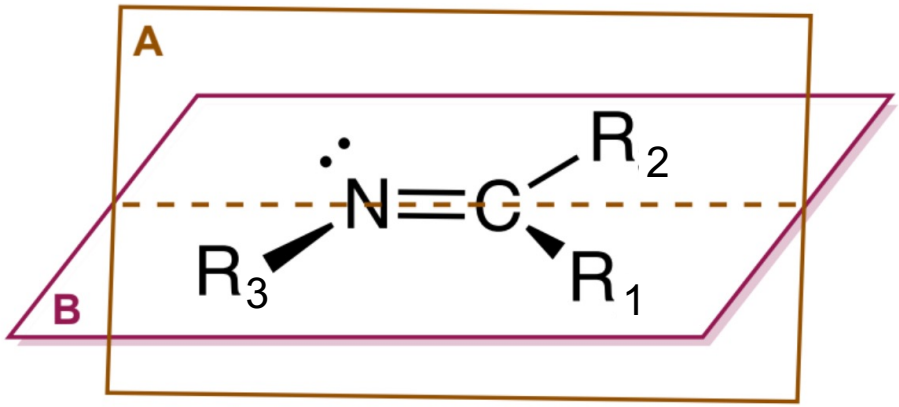
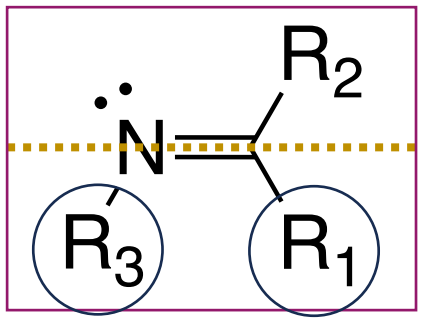
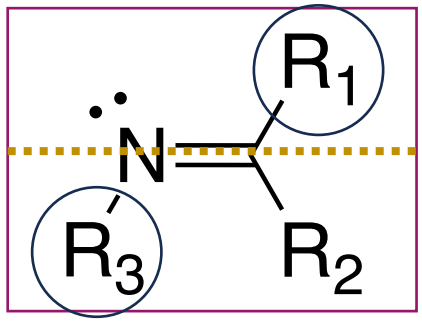


Proridad $R_1 > R_2$



(Z)

zusammen = juntos (mismo lado)



(E)

entgegen = opuestos

Diferente compuesto carbonílico, misma amina

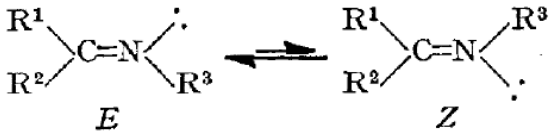


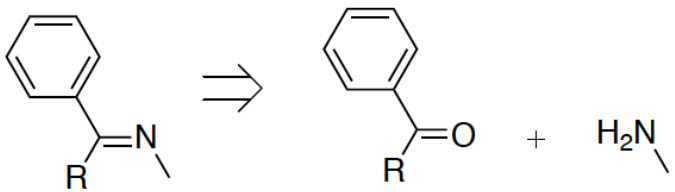
TABLE 1

Equilibrium distribution of *E*–*Z*-imine isomers at ambient temperature

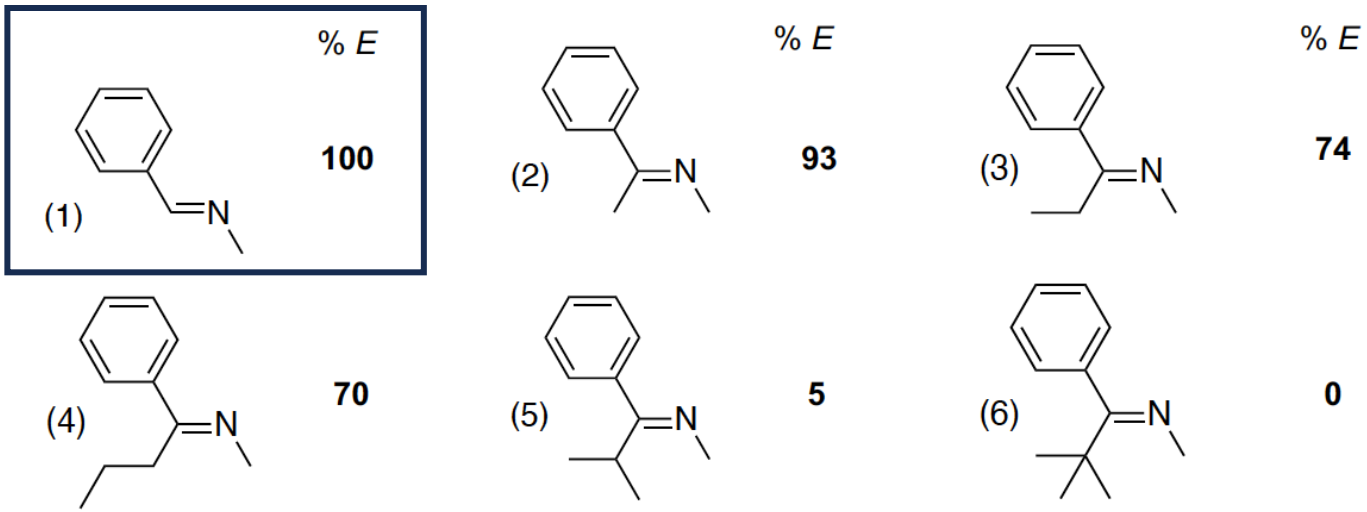
Imine *p*-XC_6H_4·C-R^2=NR^3	X	R^2	R^3	% *E* *
(1)	H	H	Me	100
(2)	H	Me	Me	93
(3)	H	Et	Me	74
(4)	H	Pr	Me	70
(5)	H	Pr^i	Me	5
(6)	H	Bu^t	Me	0
(7)	NO_2	Me	Me	97
(8)	NO_2	Me	Pr^i	95
(9)	NO_2	Me	Bu^t	98

(1-6)

Different carbonyl compound

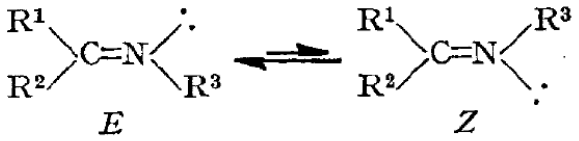


Cuando se usa un aldehído, solo se obtiene el diasteroisómero *E*



Bjørgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B. Equilibrium Distribution of E–Z-Ketimine Isomers. *J. Chem. Soc. Perkin Trans. 2* **1974**, No. 7, 757–762.

Mismo compuesto carbonílico, diferente amina



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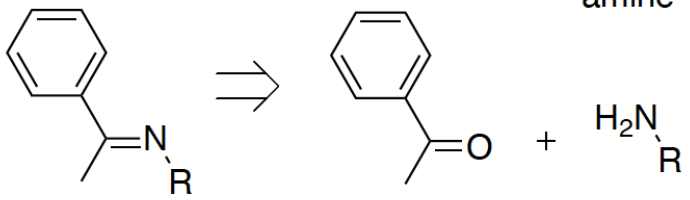
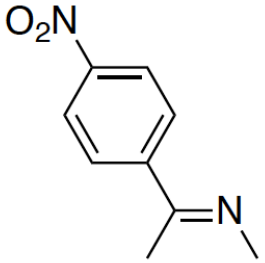
(5)	H	Pr^i	Me	5
(6)	H	Bu^t	Me	0
(7)	NO_2	Me	Me	97
(8)	NO_2	Me	Pr^i	95
(9)	NO_2	Me	Bu^t	98

(7-9)

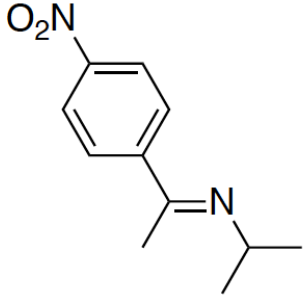
Different primary amine





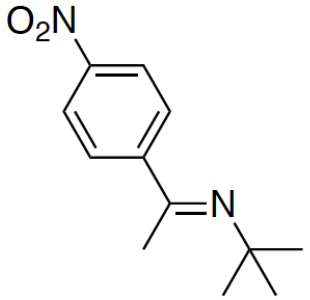
% *E*

97



% *E*

95



% *E*

98

Bjørgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B. Equilibrium Distribution of E–Z-Ketimine Isomers. *J. Chem. Soc. Perkin Trans. 2* **1974**, No. 7, 757–762.

Comparaciones por pares

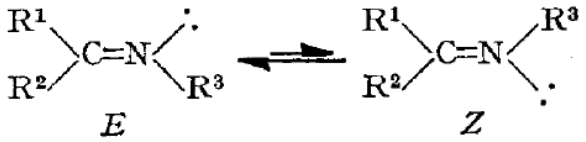
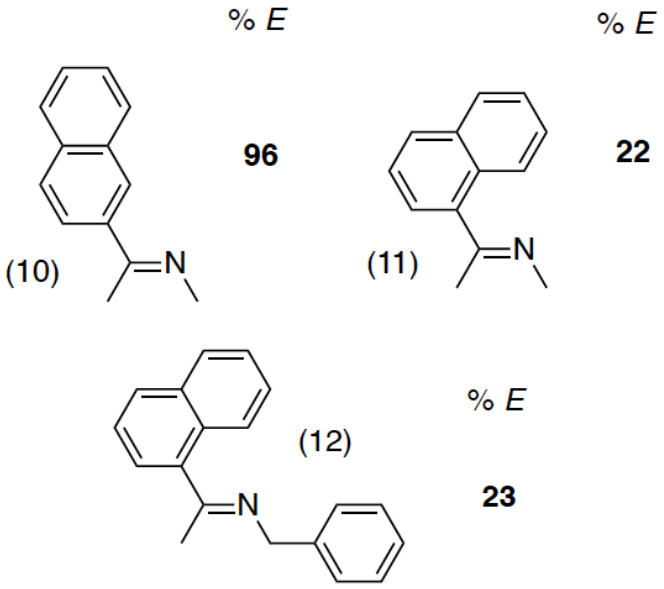
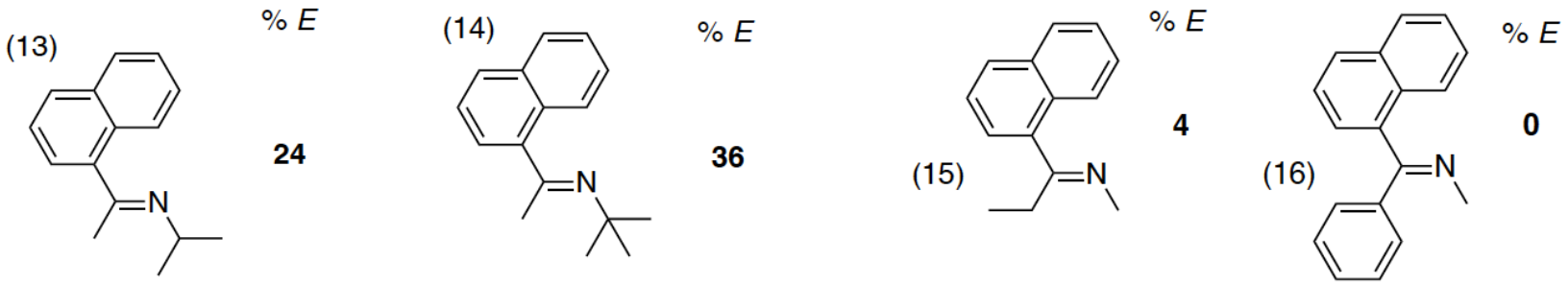


TABLE 2

Equilibrium distribution of *ortho*-substituted *E*–*Z*-imine isomers at ambient temperature

Imine Ar·C(R²)=NR³	Ar	R²	R³	% *E* •
(10)	2-Naphthyl	Me	Me	96
(11)	1-Naphthyl	Me	Me	22
(12)	1-Naphthyl	Me	Bz	23
(13)	1-Naphthyl	Me	Pr^{i}	24
(14)	1-Naphthyl	Me	Bu^{t}	36
(15)	1-Naphthyl	Et	Me	4
(16)	1-Naphthyl	Ph	Me	0



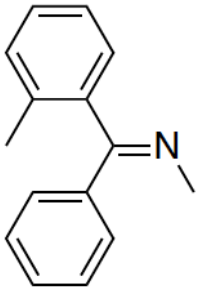


Bjørgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B. Equilibrium Distribution of E–Z-Ketimine Isomers. *J. Chem. Soc. Perkin Trans. 2* **1974**, No. 7, 757–762.

(17)	2-MeC_6H_4	Me	Me	24
(18)	2-MeC_6H_4	Ph	Me	0
(19)	2-$MeOC_6H_4$	Me	Me	42
(20)	2-$NO_2C_6H_4$	Me	Me	43
(21)	Mesityl	Me	Me	5
(22)	9-Anthryl	Me	Me	5

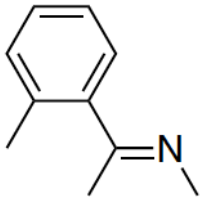
* See footnote to Table 1.

(18) % *E*



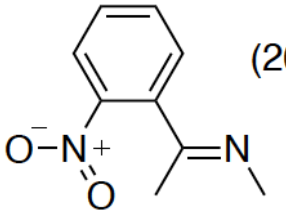
0

(17) % *E*



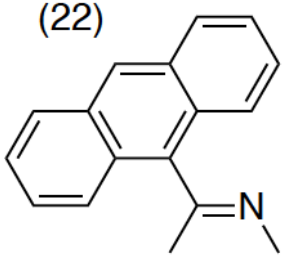
24

(20) % *E*



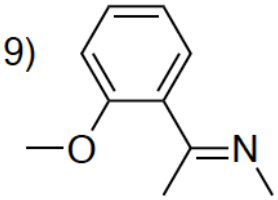
43

(22) % *E*



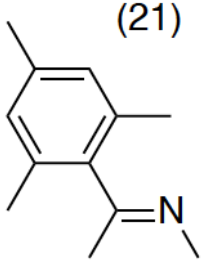
5

(19) % *E*



42

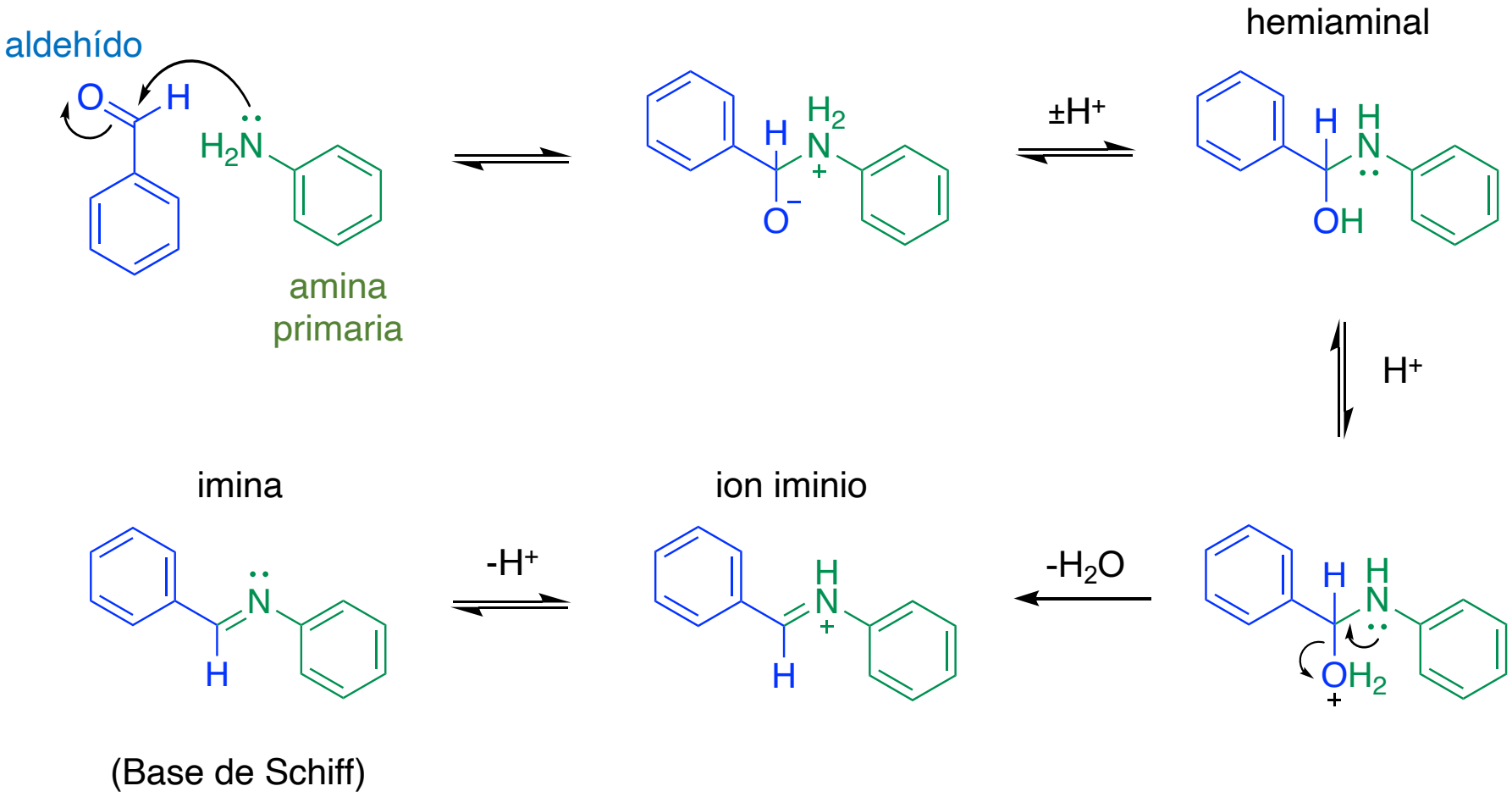
(21) % *E*



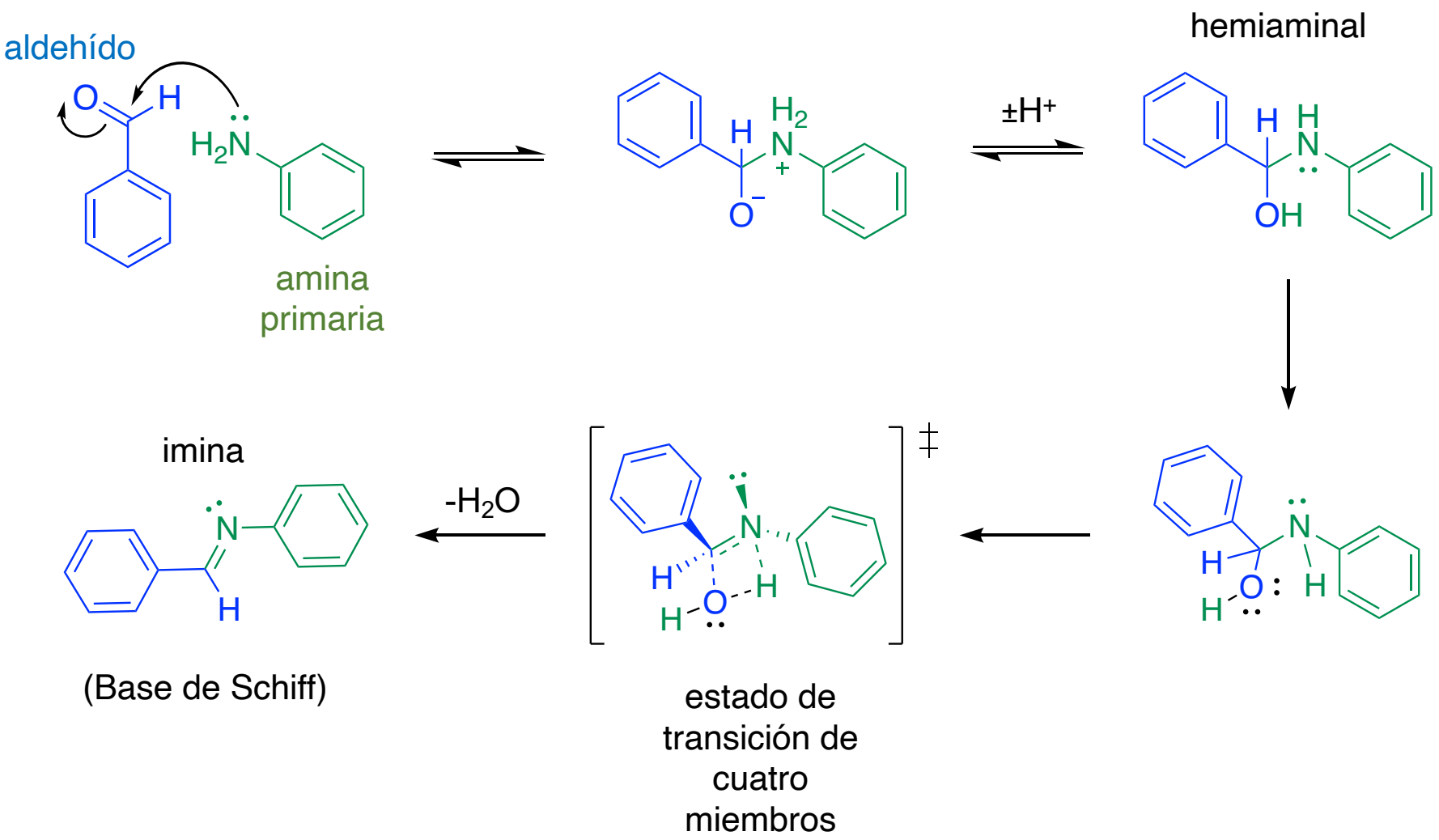
5

Bjørgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B. Equilibrium Distribution of E–Z-Ketimine Isomers. *J. Chem. Soc. Perkin Trans. 2* **1974**, No. 7, 757–762.

Mecanismo


aldehído
amina primaria
hemiaminal
±H+
H+
imina
ion iminio
-H+
-H2O
(Base de Schiff)

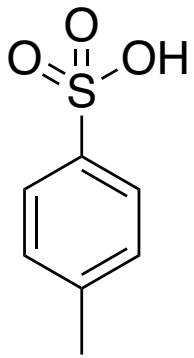
Mecanismo (otro)



¿Cómo mejoro mi síntesis?

-Catálisis ácida

*p*TsOH, CH_3COOH, H_2SO_4, HCl

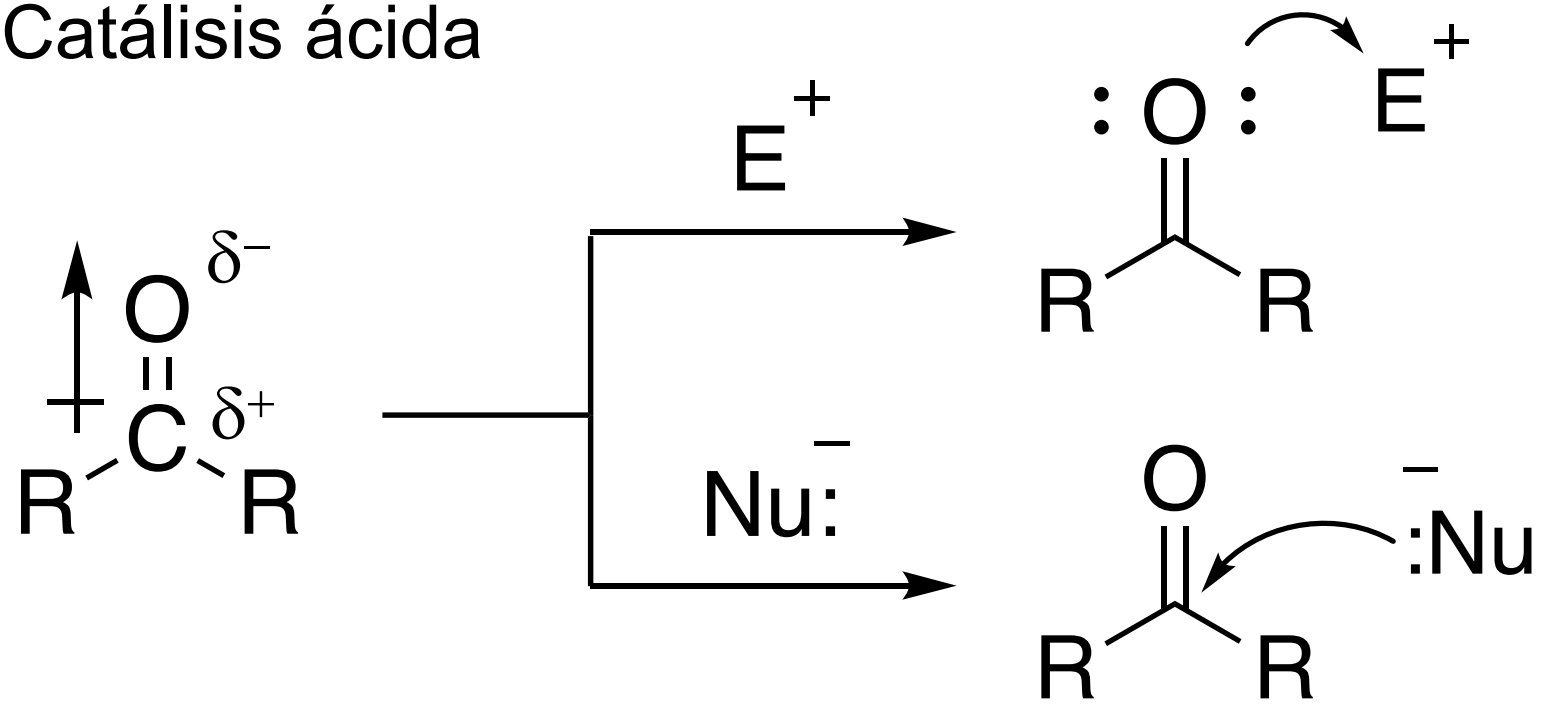


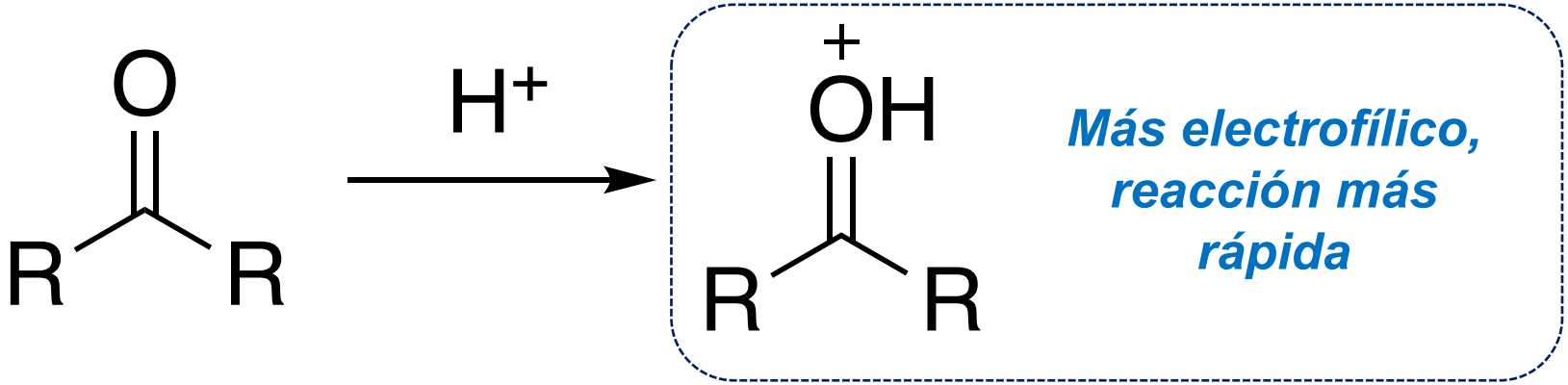
*p*TsOH
Ácido *p*-toluensulfónico

-Evitar aminas no nucleofílicas

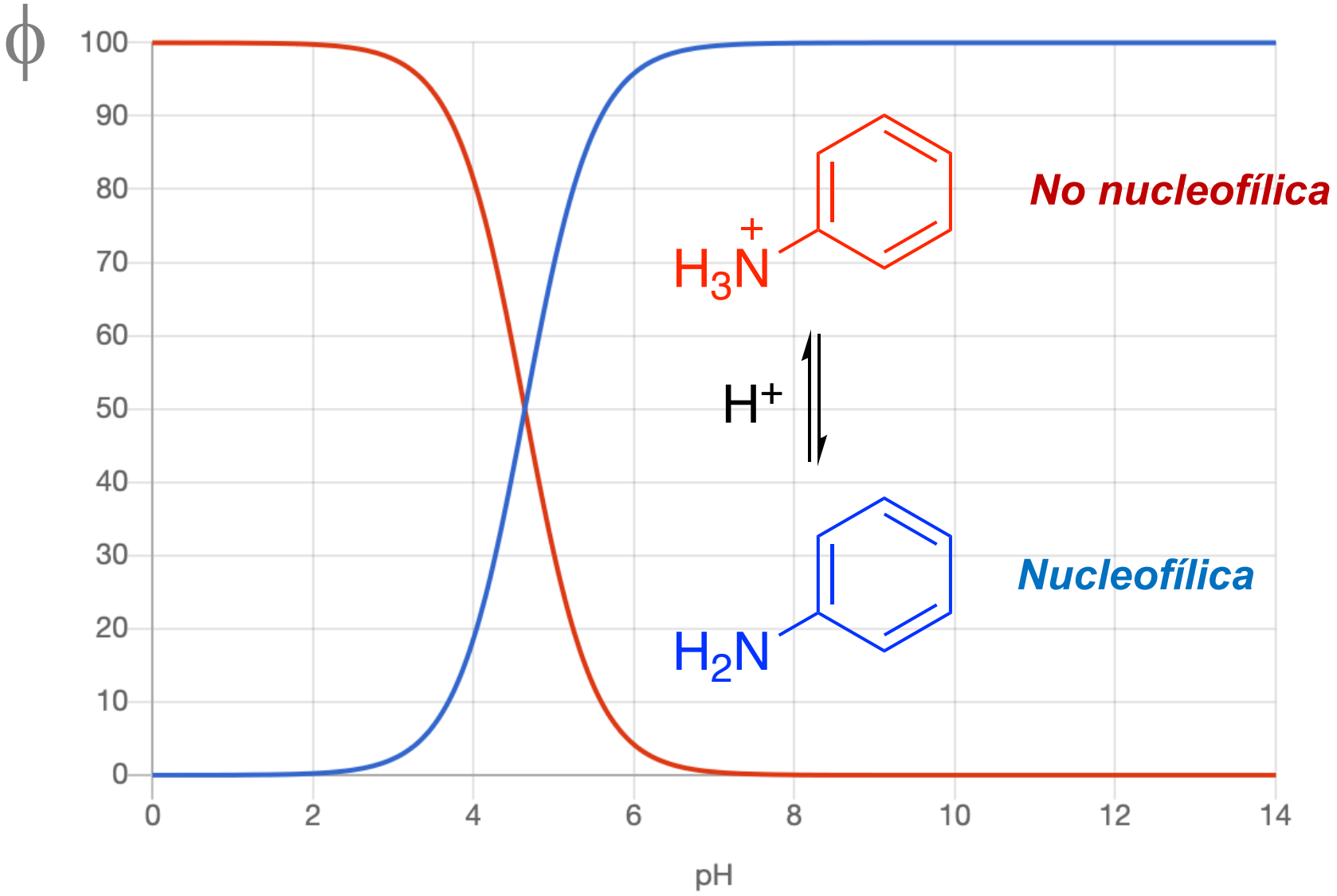
-Principio de Le Chatelier

Catálisis ácida



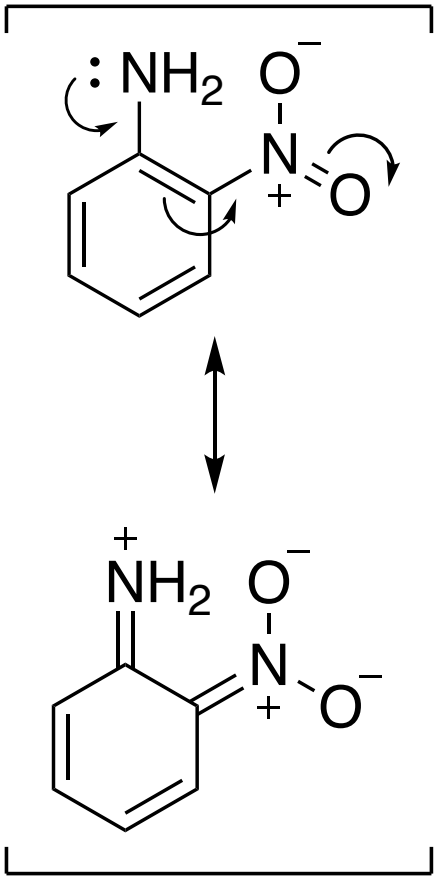


Cátalisis ácida



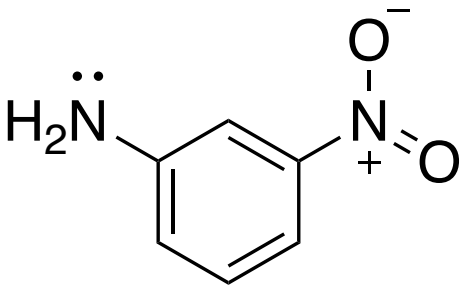
Evitar anilinas no nucleofílicas

o-nitroanilina



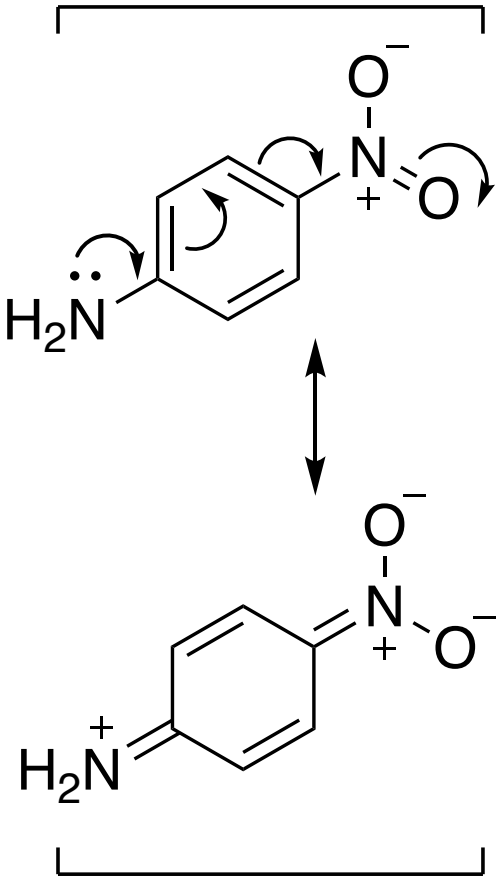
no-nucleofílica

m-nitroanilina



ligeramente nucleofílica

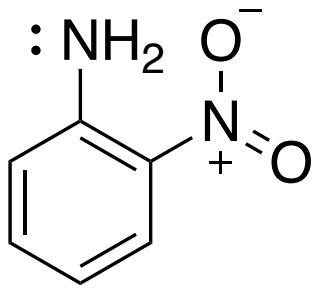
p-nitroanilina

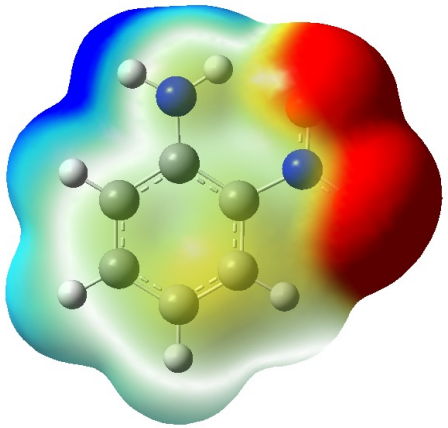


no-nucleofílica

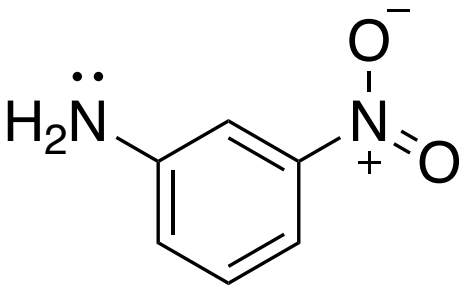
Evitar anilinas no nucleofílicas

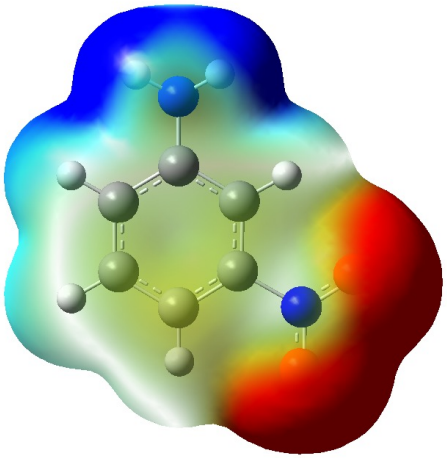
o-nitroanilina



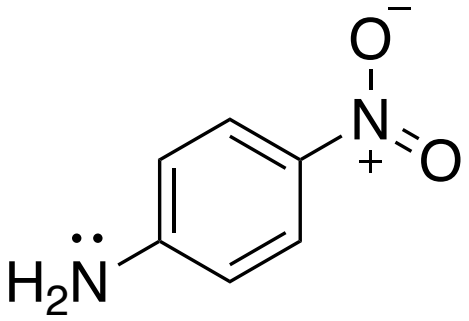


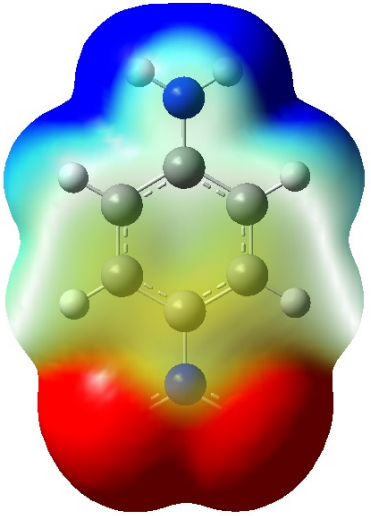
m-nitroanilina





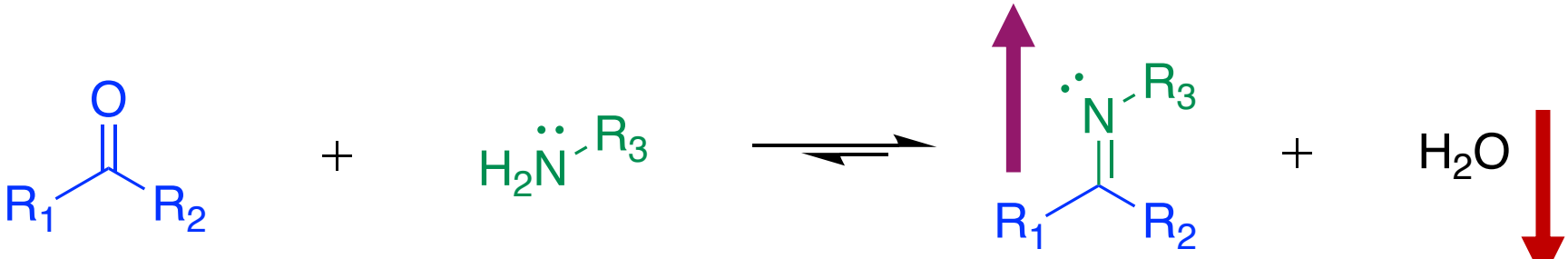
p-nitroanilina





Principio de Le Chatelier

Remoción de agua



compuesto carbonílico (aldehído o cetona)

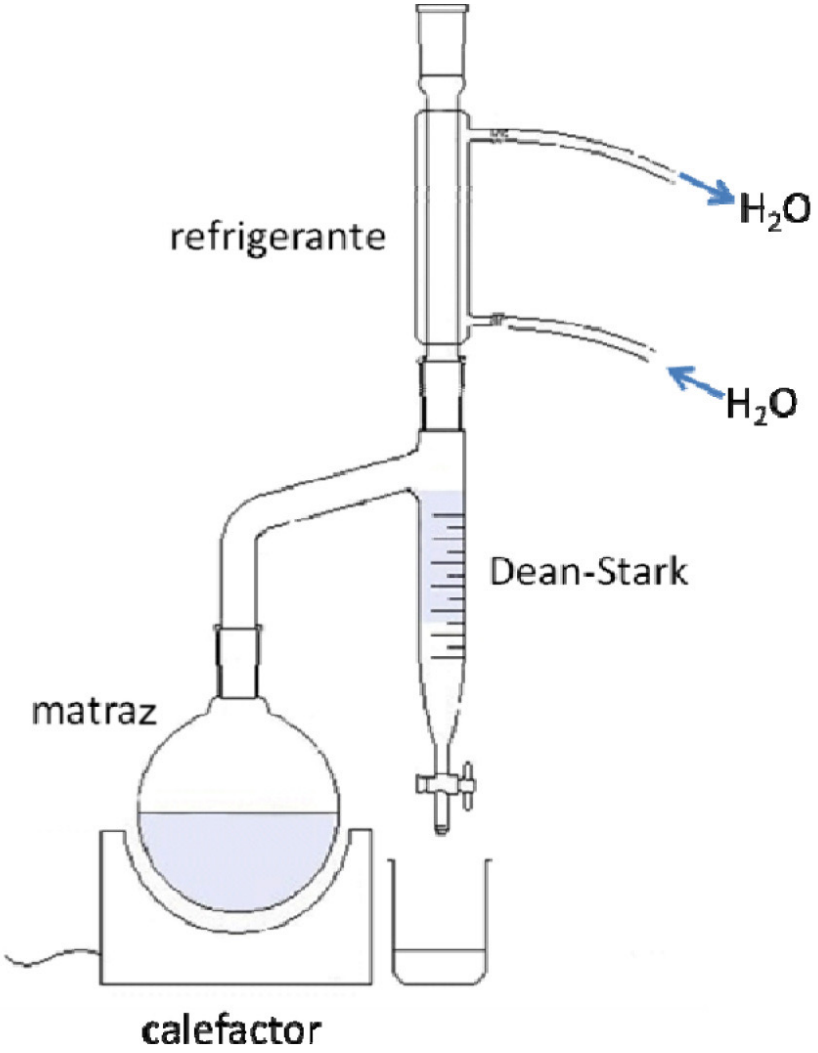
amina primaria

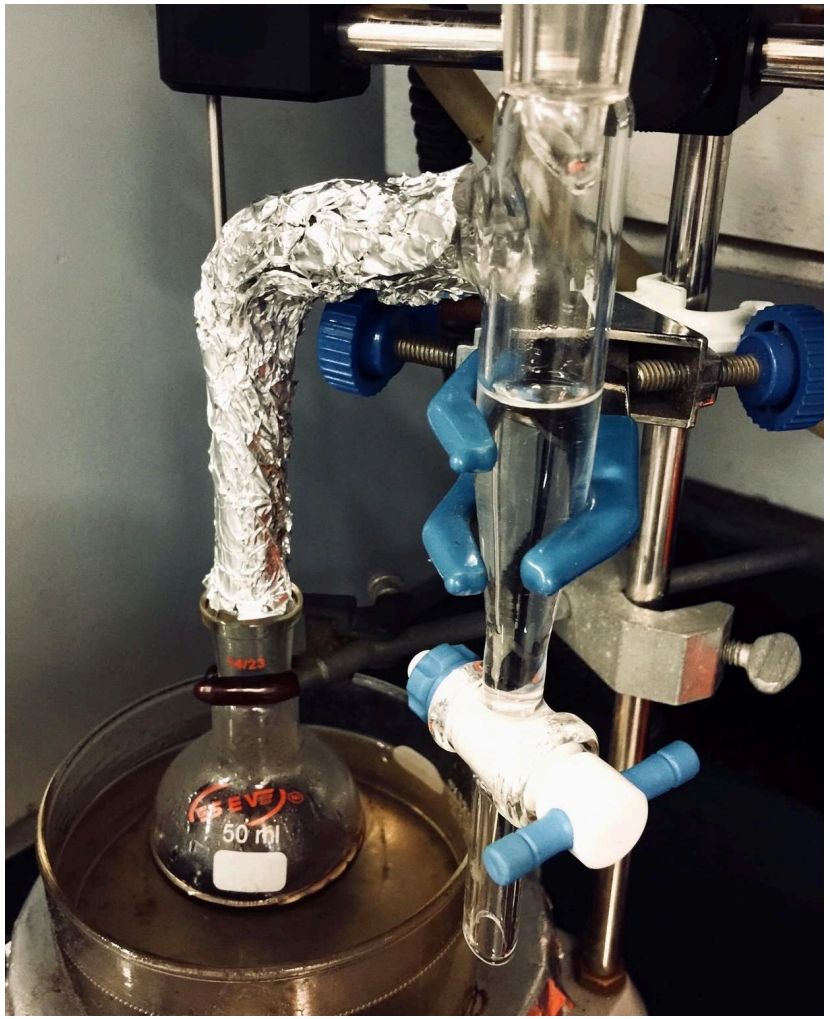
imina (base de Schiff) aldiminas o cetiminas

-Métodos químicos: Na_2SO_4, $MgSO_4$

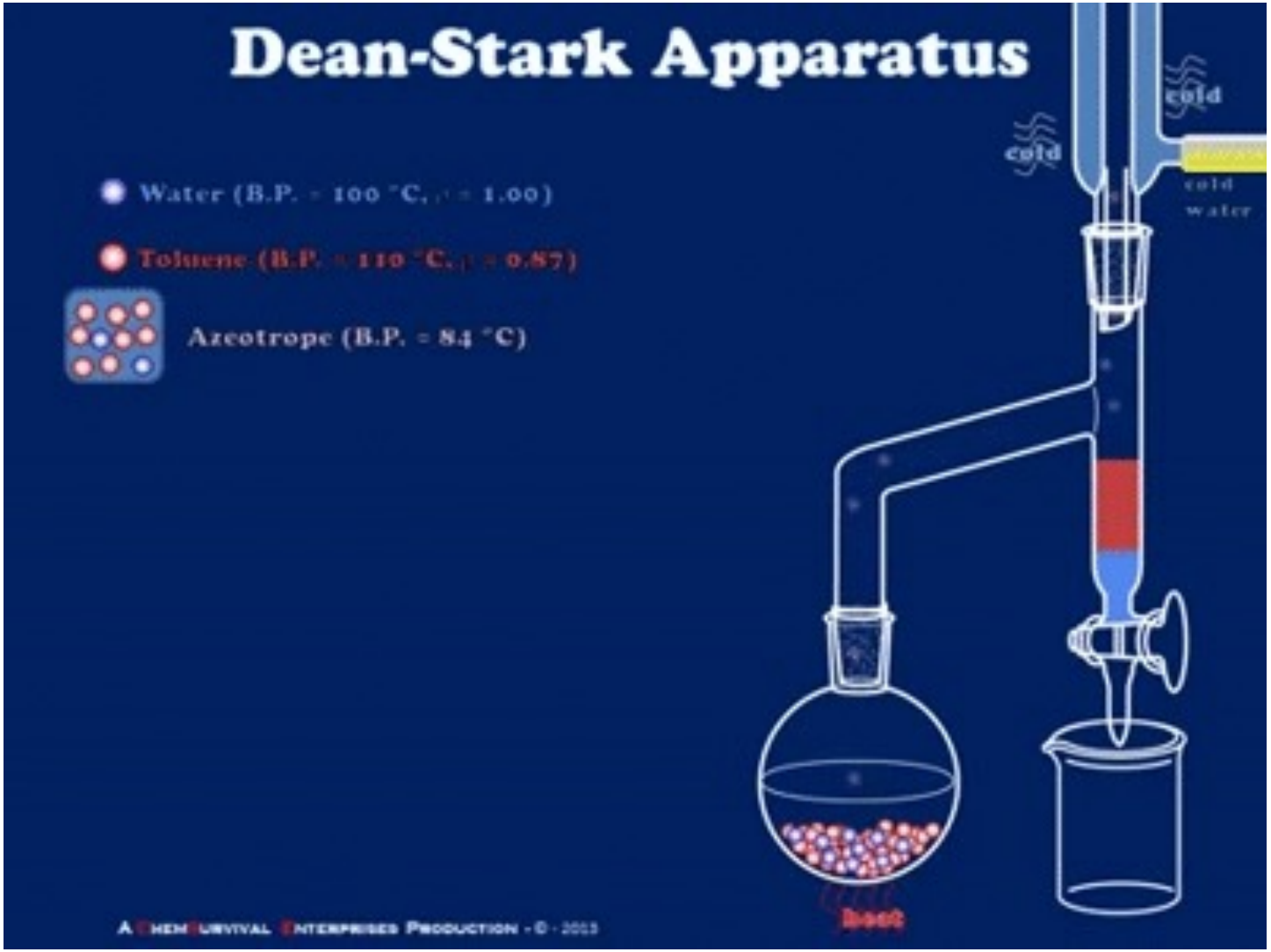
-Métodos físicos: Trampa de Dean-Stark

Trampa de Dean-Stark

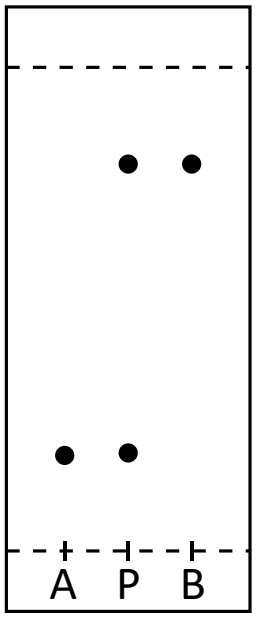




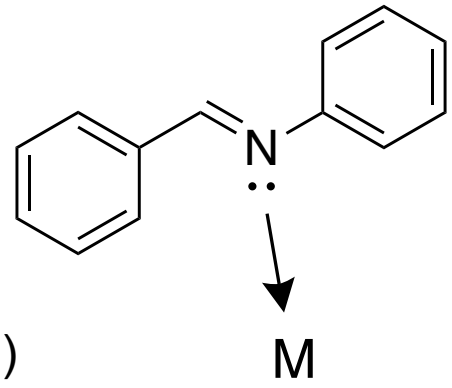
Trampa de Dean-Stark

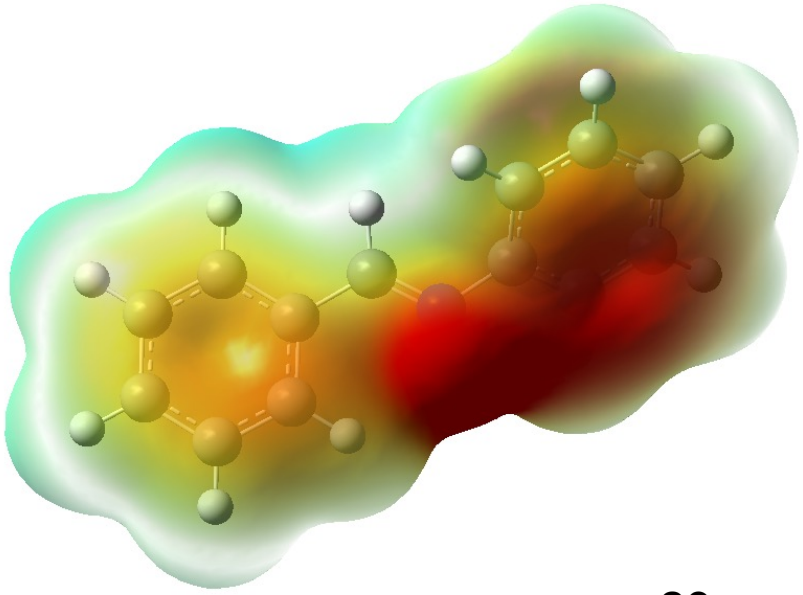


Descomposición bajo condiciones ácidas



- Las iminas son inestables en la sílice y tienden a descomponerse en cromatografía en columna y capa fina.
- La sílice promueve su hidrólisis de regreso al compuesto carbonílico y la amina correspondiente.
- Por esta razón, se prefiere purificarlas por recristalizacíón y/o filtración al vació.





A: Anilina

P: Producto (imina)

B: Aldehído