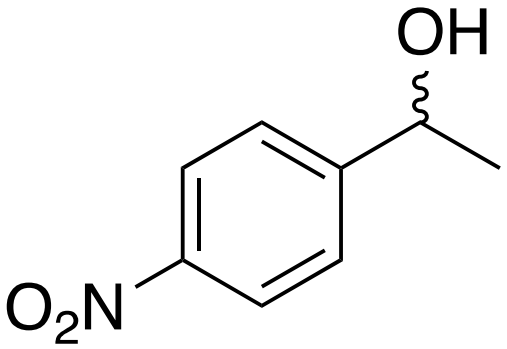
Universidad Nacional Autónoma de México

Química Orgánica III (1506)
Laboratorio
Semestre 2025 - 2

M. en C. Arturo García Zavala



Práctica 1

Nitrocompuestos I

Reducción quimioselectiva de 4-nitroacetofenona

19/2/2025

La mayoría de las moléculas orgánicas contienen múltiples grupos funcionales, los cuales pueden reaccionar de diversas maneras.

La **selectividad** se refiere a **qué grupo funcional** reaccionará, en **qué sitio ocurrirá** la reacción y de **qué manera** se llevará a cabo.

Quimioselectividad

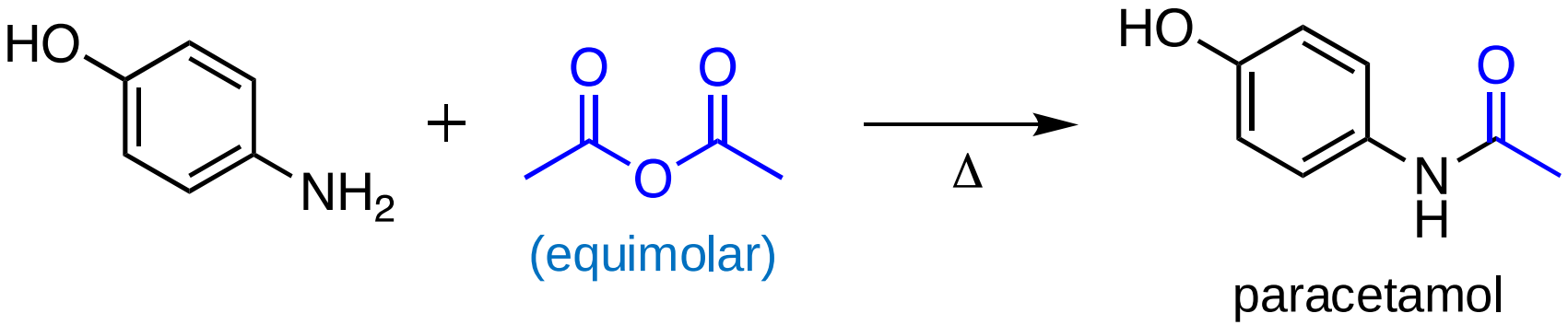
Regioselectividad

Estereoselectividad

Quimioselectividad

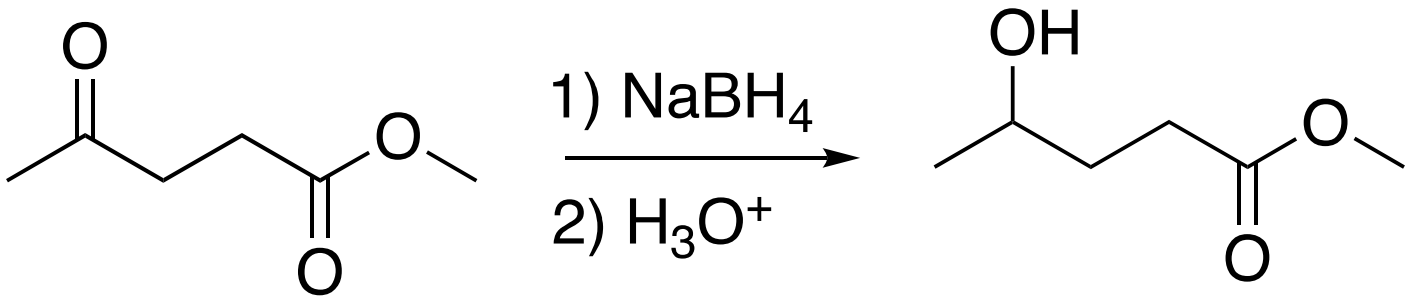
La quimioselectividad es la reacción preferencial de un reactivo químico con uno de dos o más grupos funcionales diferentes.

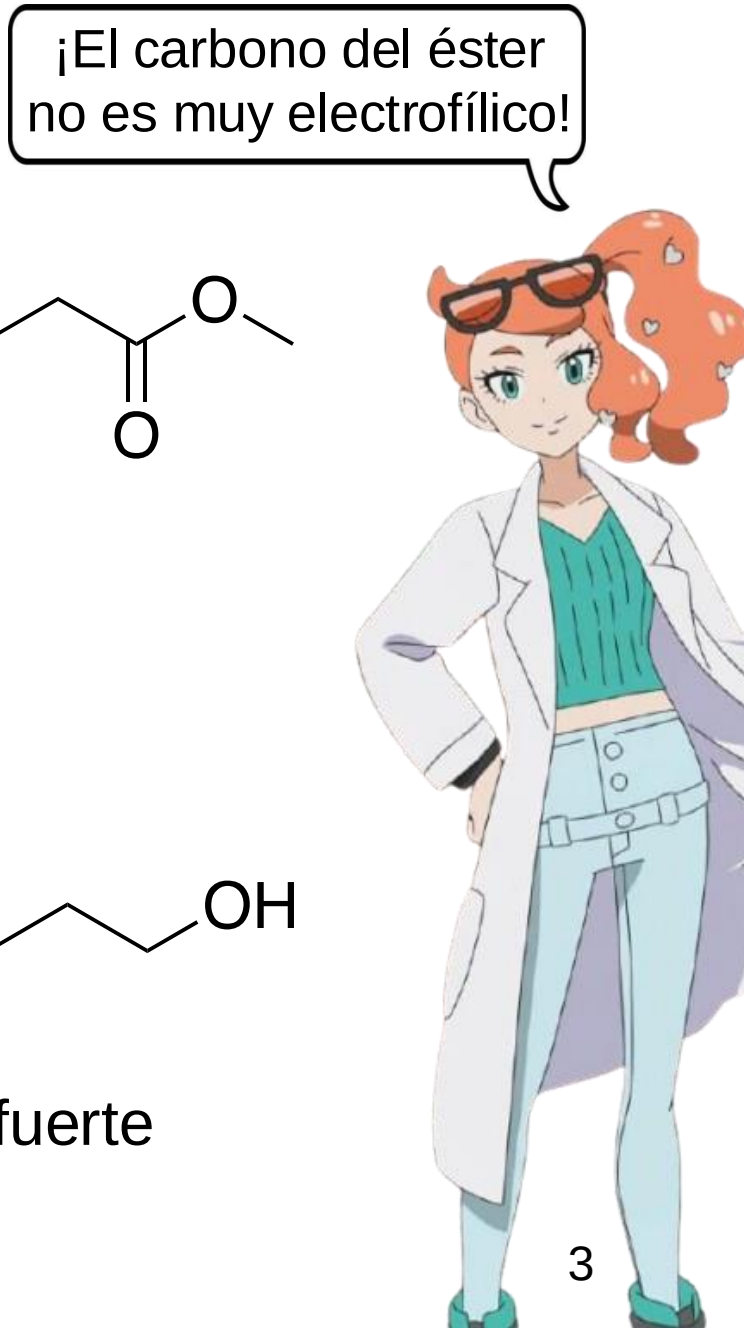
Acetilación quimioselectiva del 4-aminofenol para la obtención de paracetamol.



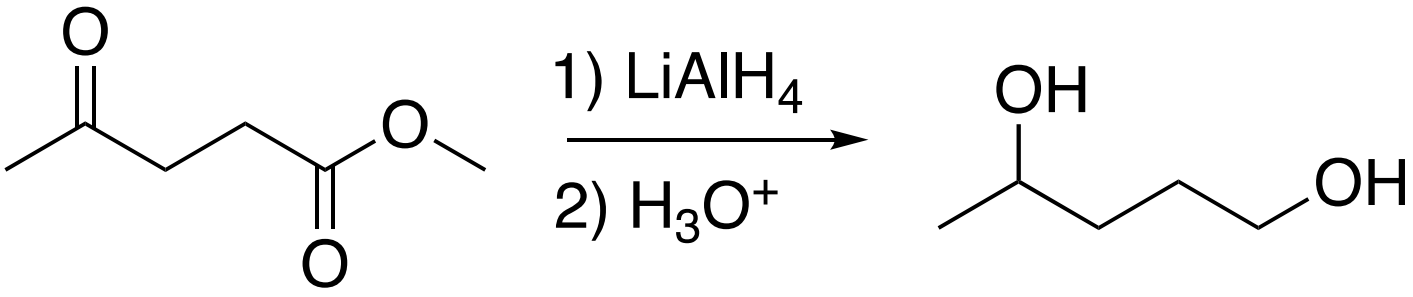
'chemoselectivity (chemoselective)' in *IUPAC Compendium of Chemical Terminology*, 5th ed. International Union of Pure and Applied Chemistry; 2025. Online version 5.0.0, 2025. https://doi.org/10.1351/goldbook.C01051

Reducción quimioselectiva





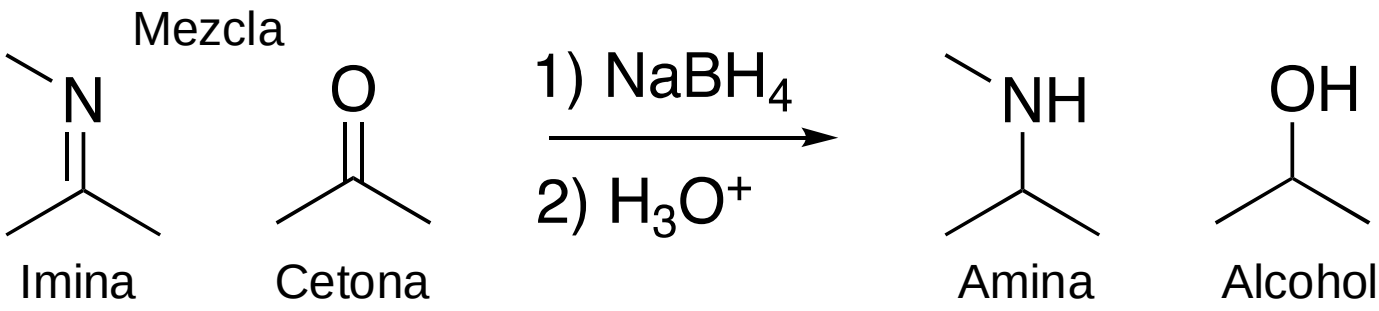
Reducción no quimioselectiva



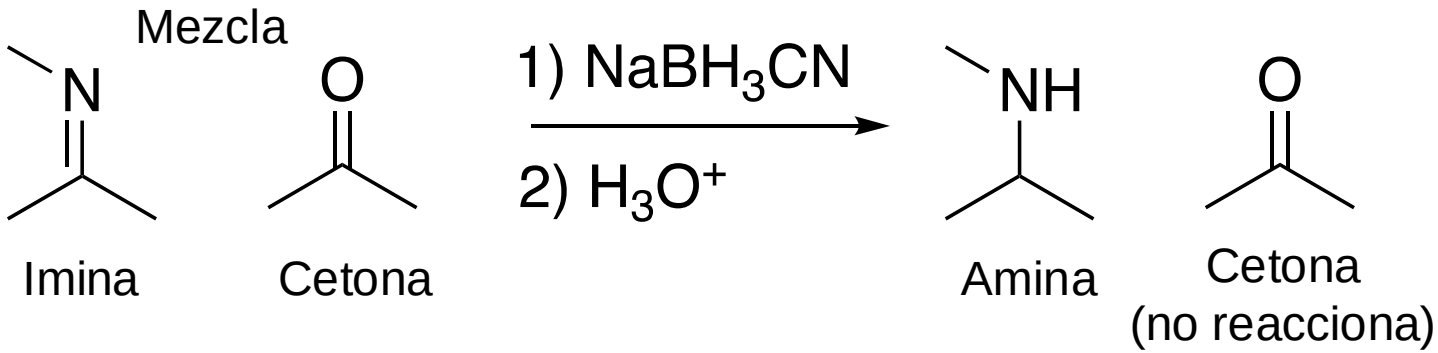
$LiAlH_4$ es un reductor muy fuerte

Cianoborohidruro de sodio como reductor quimioselectivo de iminas

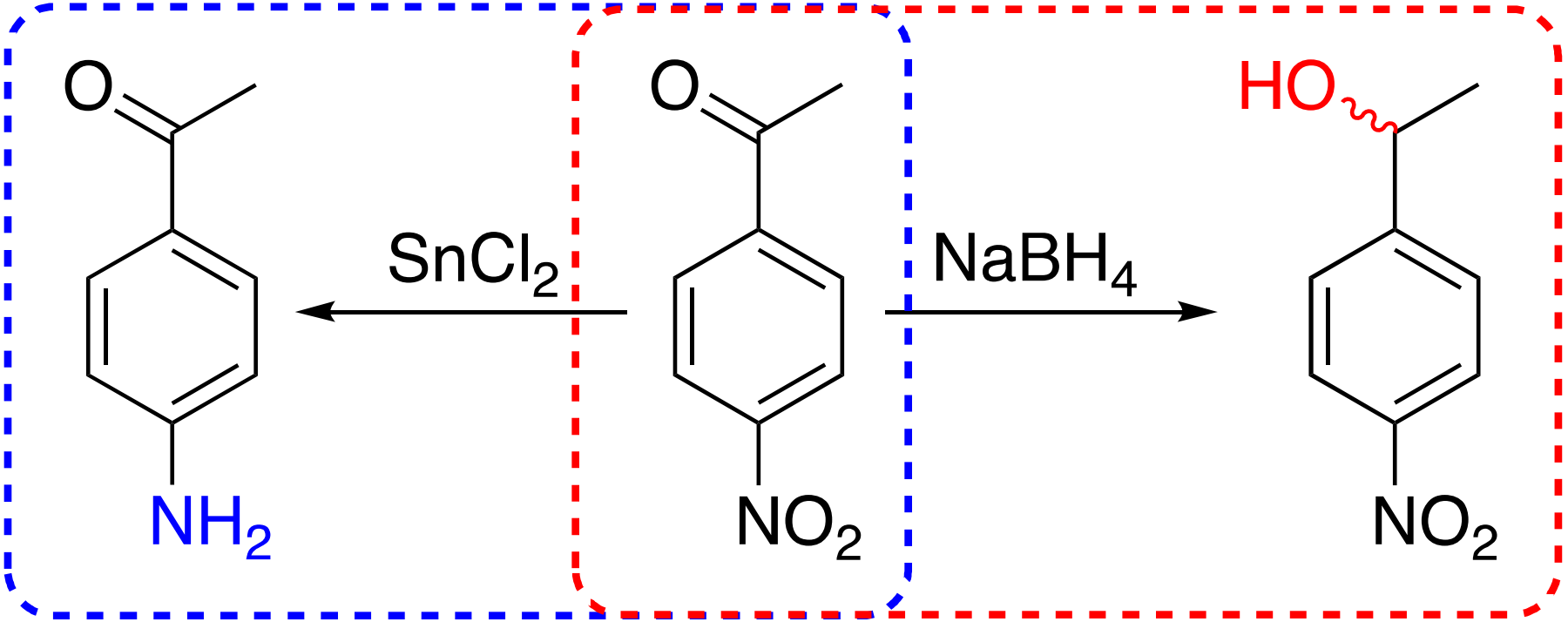
Borohidruro de sodio reduce iminas y cetonas



Cianoborohidruro de sodio solo reduce iminas



Reducción quimioselectiva del grupo carbonilo

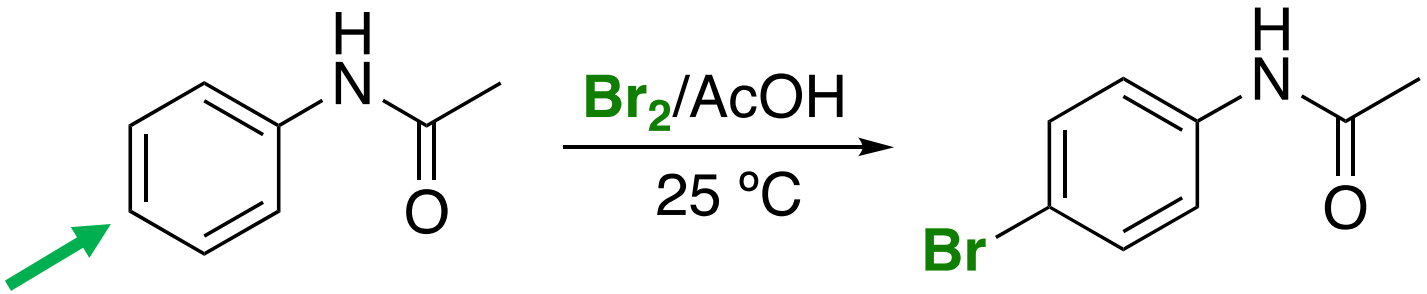


Reducción quimioselectiva del grupo nitro

Regioselectividad

Una reacción regioselectiva es aquella en la que una dirección de formación o ruptura de enlaces ocurre de manera preferente sobre todas las demás posibles.

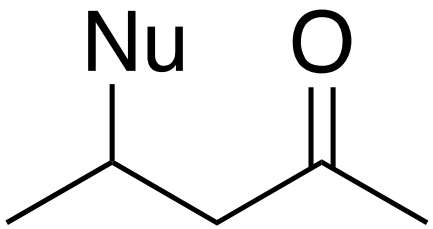
Bromación regioselectiva de benzamida.



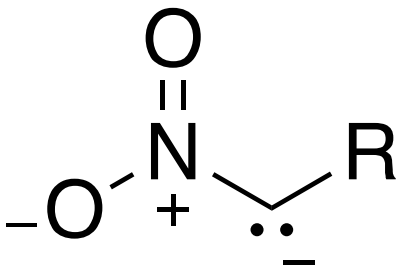
'regioselectivity (regioselective)' in *IUPAC Compendium of Chemical Terminology*, 5th ed. International Union of Pure and Applied Chemistry; 2025. Online version 5.0.0, 2025. https://doi.org/10.1351/goldbook.R05243

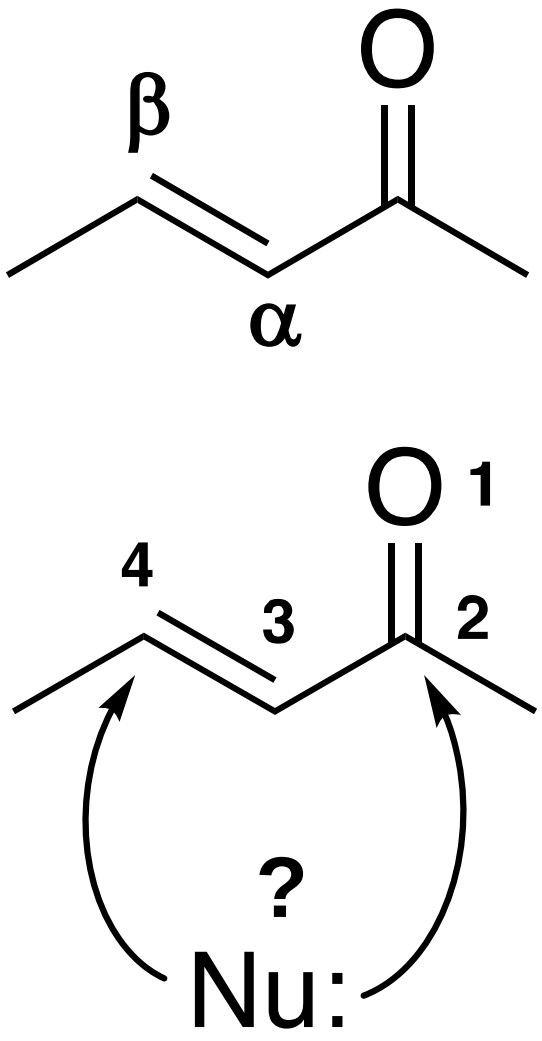
Adiciones a compuestos carbonílicos α,β-insaturados (aceptores de Michael).

Adición conjugada (Adición 1,4)

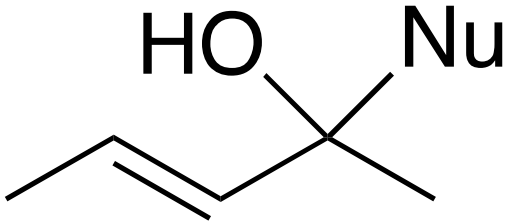


Nucleófilos blandos

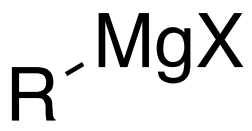




Adición directa (Adición 1,2)



Nucleófilos duros



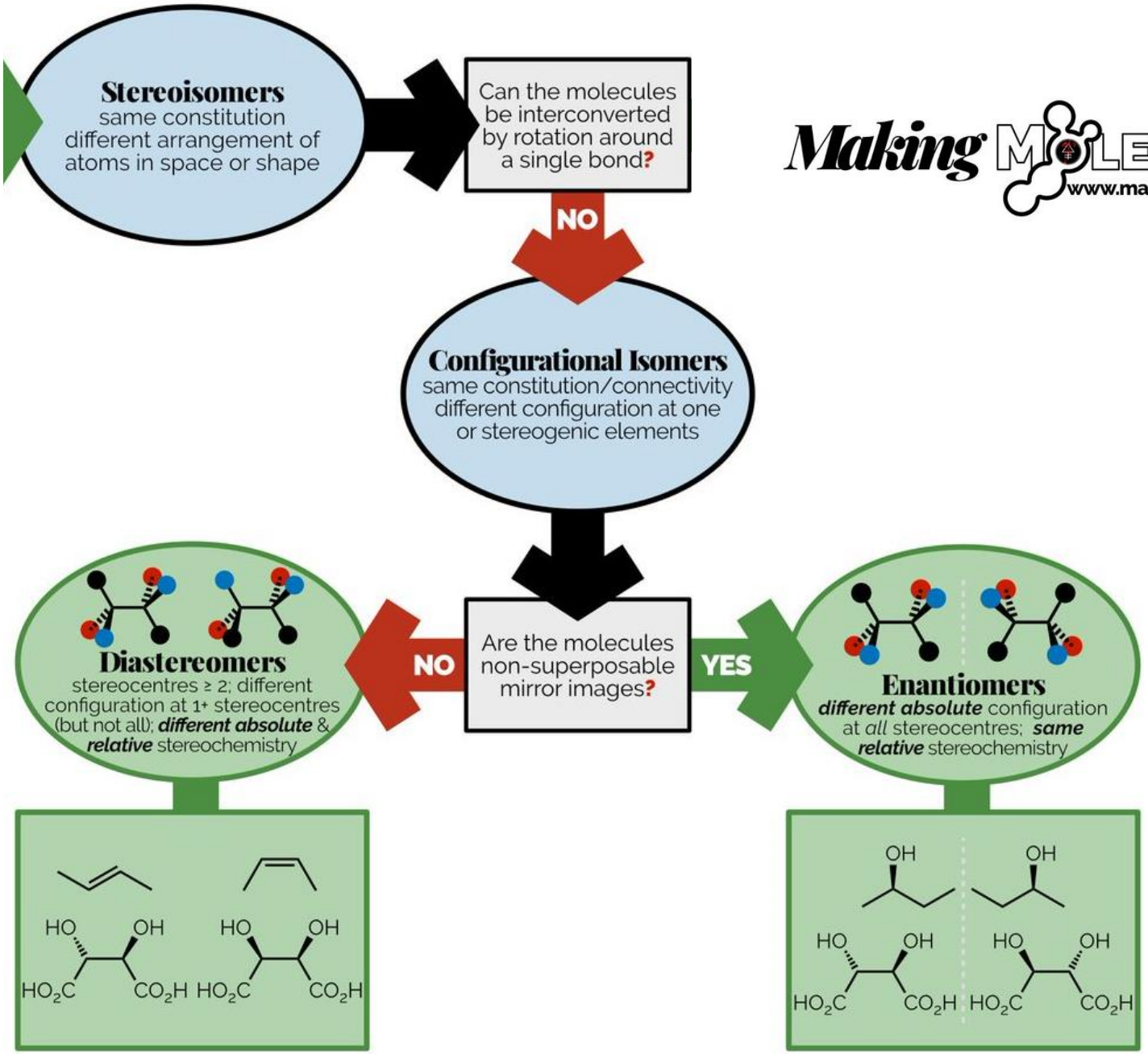
Estereoselectividad

La formación preferencial de un estereoisómero sobre otro en una reacción química.

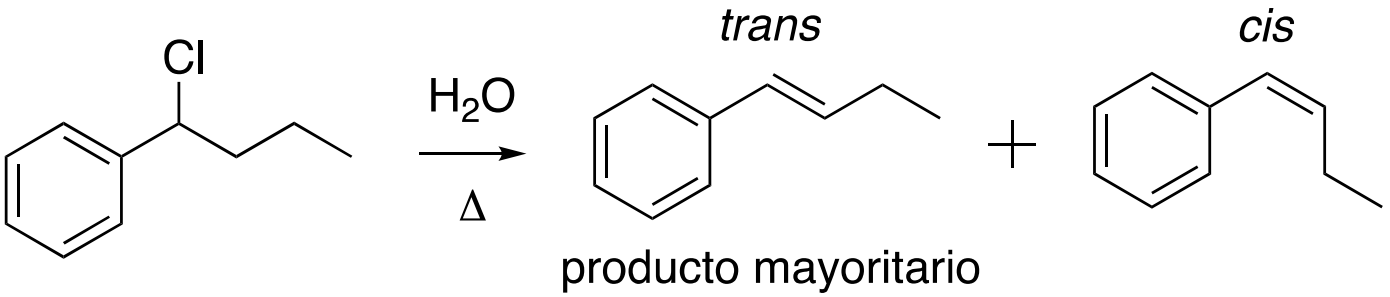
Cuando los estereoisómeros son enantiómeros, este fenómeno se denomina enantioselectividad.

Cuando son diastereoisómeros, se denomina diastereoselectividad.

'stereoselectivity' in *IUPAC Compendium of Chemical Terminology*, 5th ed. International Union of Pure and Applied Chemistry; 2025. Online version 5.0.0, 2025. https://doi.org/10.1351/goldbook.S05991

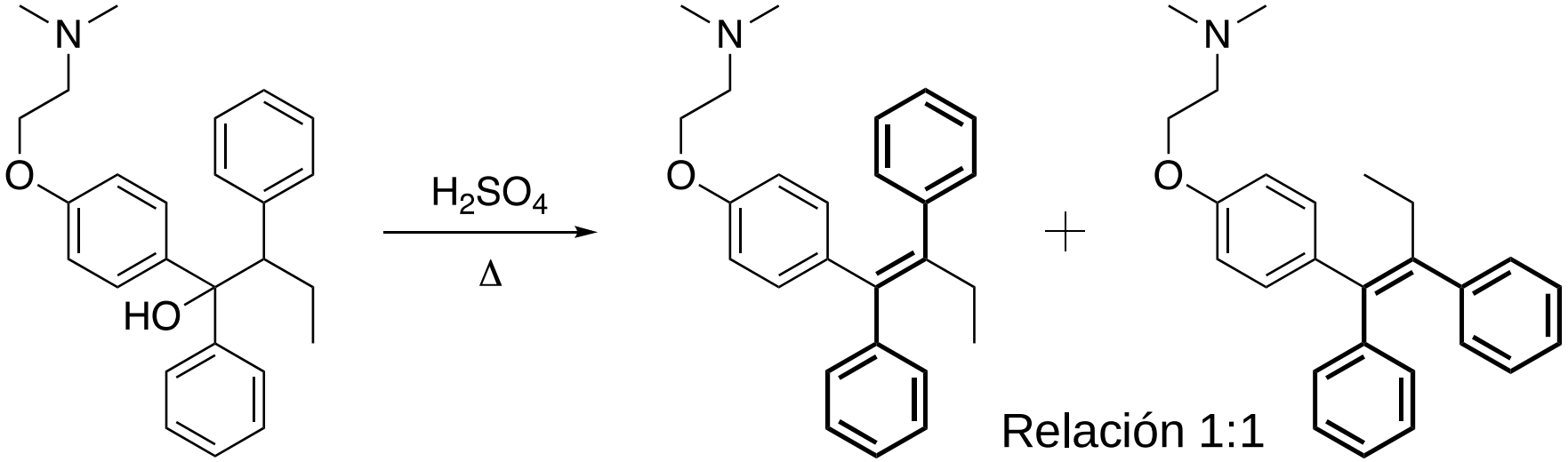

Stereoisomers
same constitution
different arrangement of
atoms in space or shape
Can the molecules
be interconverted
by rotation around
a single bond?
NO
Configurational Isomers
same constitution/connectivity
different configuration at one
or stereogenic elements
Are the molecules
non-superposable
mirror images?
NO
YES
Diastereomers
stereocentres ≥ 2; different
configuration at 1+ stereocentres
(but not all); different absolute &
relative stereochemistry
Enantiomers
different absolute configuration
at all stereocentres; same
relative stereochemistry
HO
OH
HO
OH
HO2C
CO2H
HO2C
CO2H
OH
OH
HO
OH
HO
OH
HO2C
CO2H
HO2C
CO2H

Las eliminaciones de primer orden (E1) son estereoselectivas



producto mayoritario

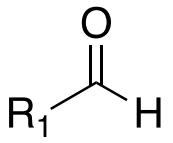
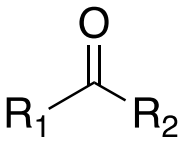
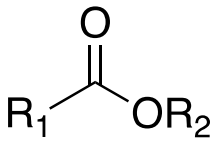
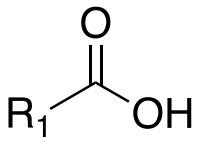
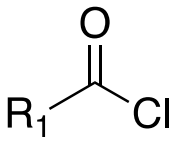
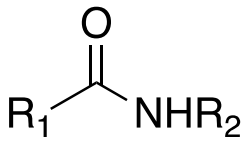
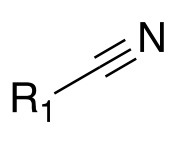
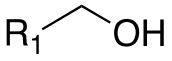
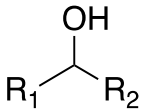
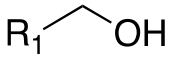
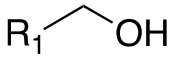
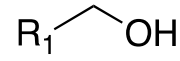
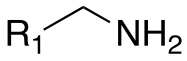
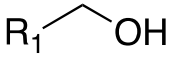
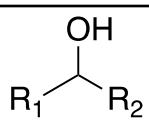
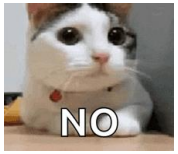
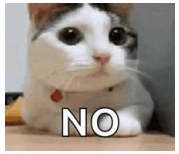
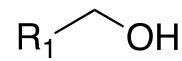
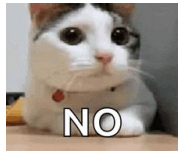
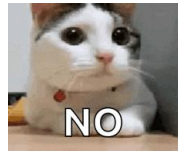
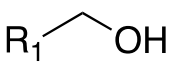
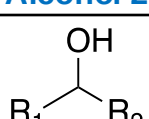
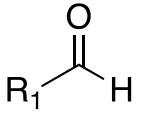
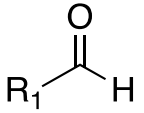
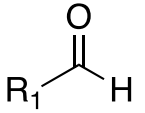
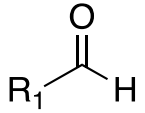
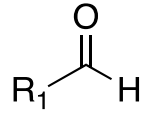
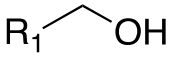
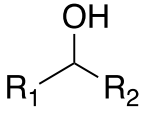
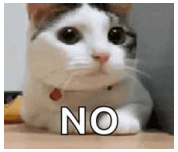
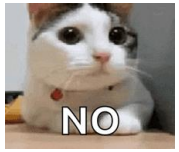
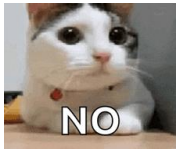
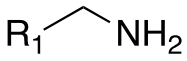
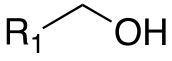
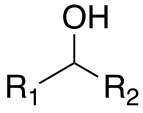
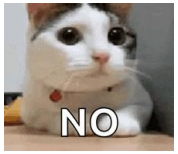
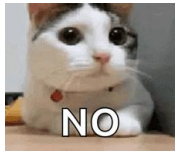
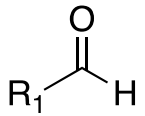
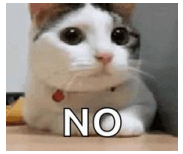
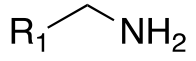
Deshidratación no estereoselectiva



Relación 1:1

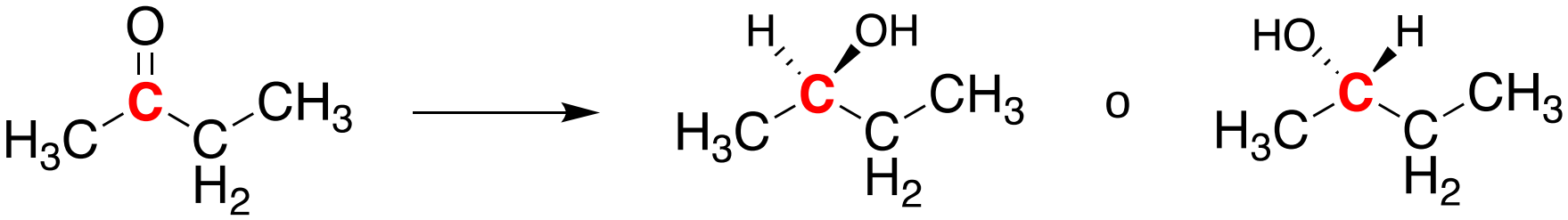
tamoxifeno

Otros agentes reductores

Agentes reductores	Sustratos: Aldehído	Cetona	Éster	Ácido	Cloruro de ácido	Amida	Nitrilo
							
$LiAlH_4$	 Alcohol 1º	 Alcohol 2º	 Alcohol 1º	 Alcohol 1º	 Alcohol 1º	 Amina 2º	 Amina 1º
$NaBH_4$	 Alcohol 1º	 Alcohol 2º			 Alcohol 1º		
DIBAL-H	 Alcohol 1º	 Alcohol 2º	 Aldehído	 Aldehído	 Aldehído	 Aldehído	 Aldehído
H_2, Ni Raney	 Alcohol 1º	 Alcohol 2º				 Amina 2º	 Amina 1º
H_2, Pd/C	 Alcohol 1º	 Alcohol 2º			 Aldehído		 Amina 1º

Proquiralidad

Molécula o entidad aquiral que contiene un sistema trigonal y que puede volverse quiral al adicionarse un nuevo átomo o grupo aquiral.

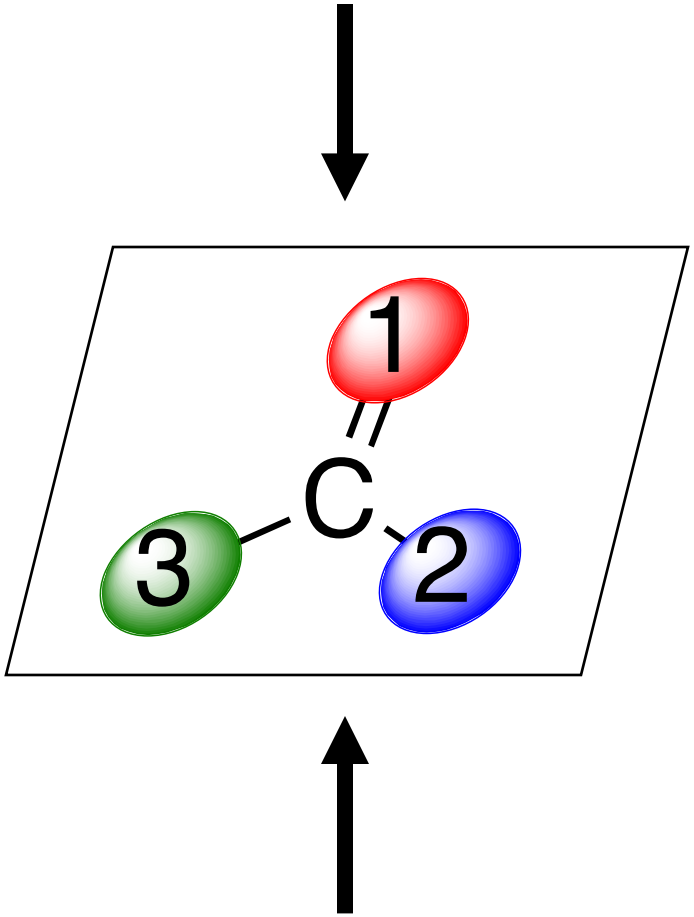


butan-2-ona
proquiral

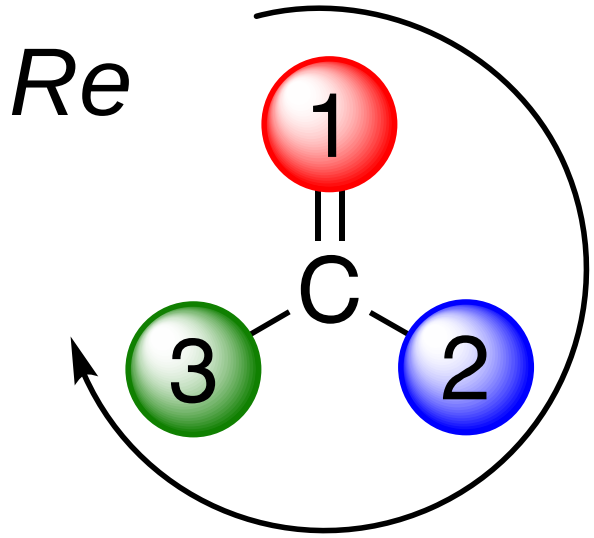
(*R*)-butan-2-ol
quiral

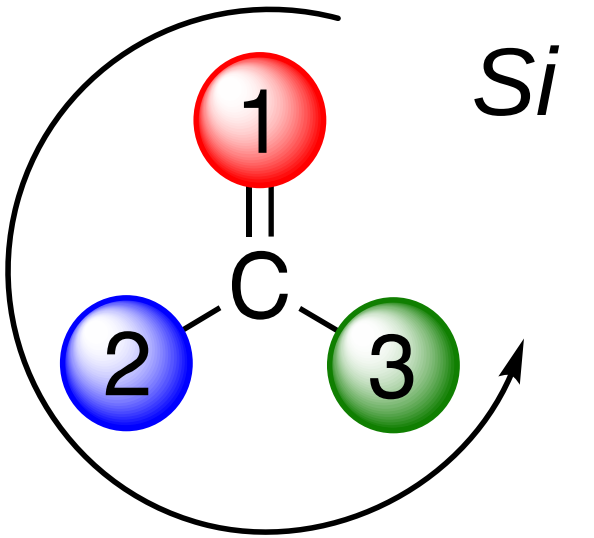
(*S*)-butan-2-ol
quiral

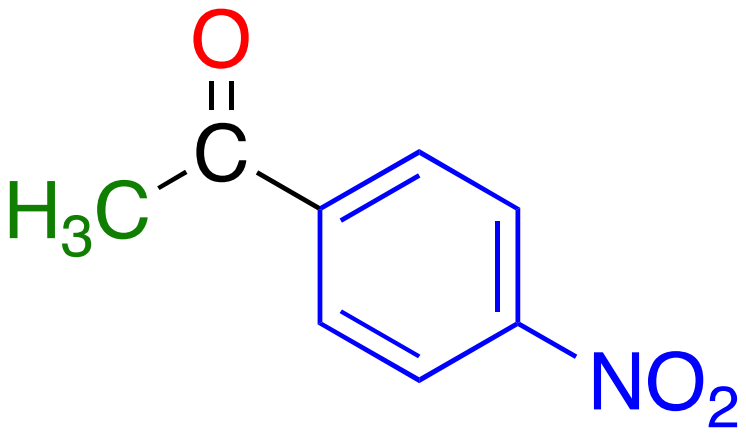
'prochirality' in *IUPAC Compendium of Chemical Terminology*, 5th ed. International Union of Pure and Applied Chemistry; 2025. Online version 5.0.0, 2025. https://doi.org/10.1351/goldbook.P04859

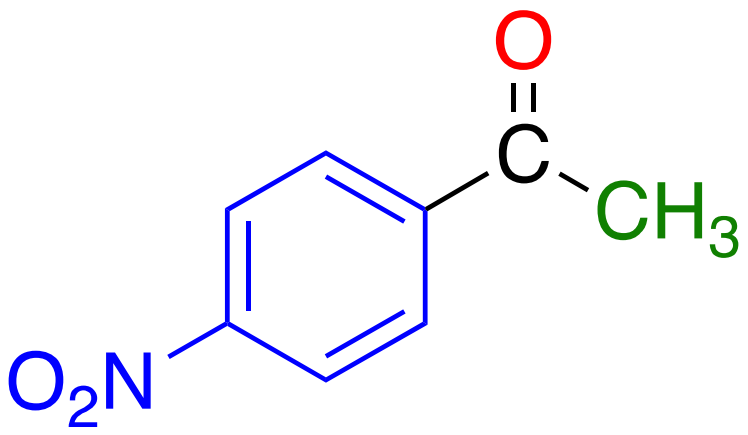


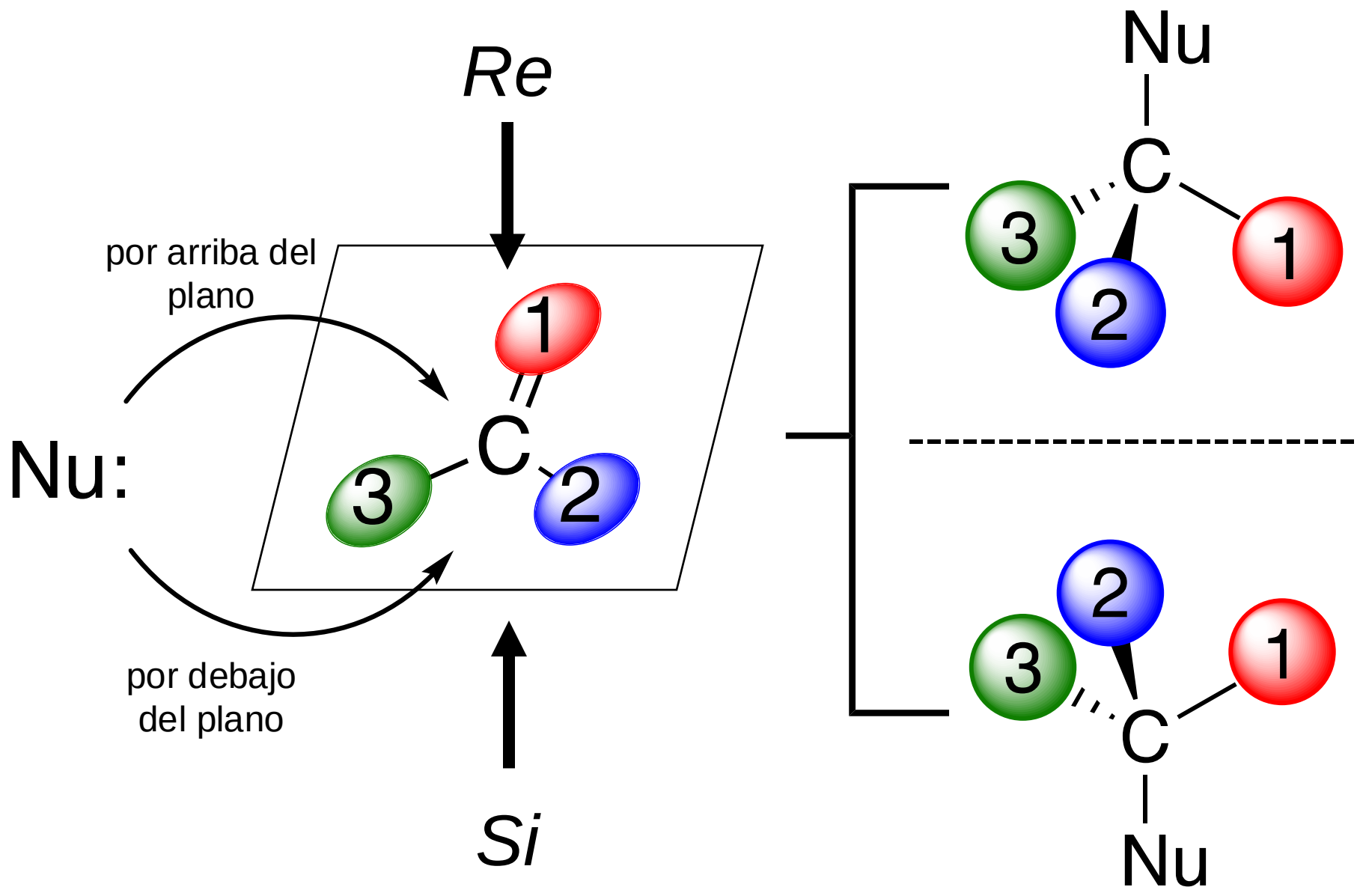
Para nombrar las caras se siguen las mismas reglas de prioridad de Cahn-Ingold-Prelog que se usan para designar enantiómeros *R* o *S*.


Re
1
C
3
2

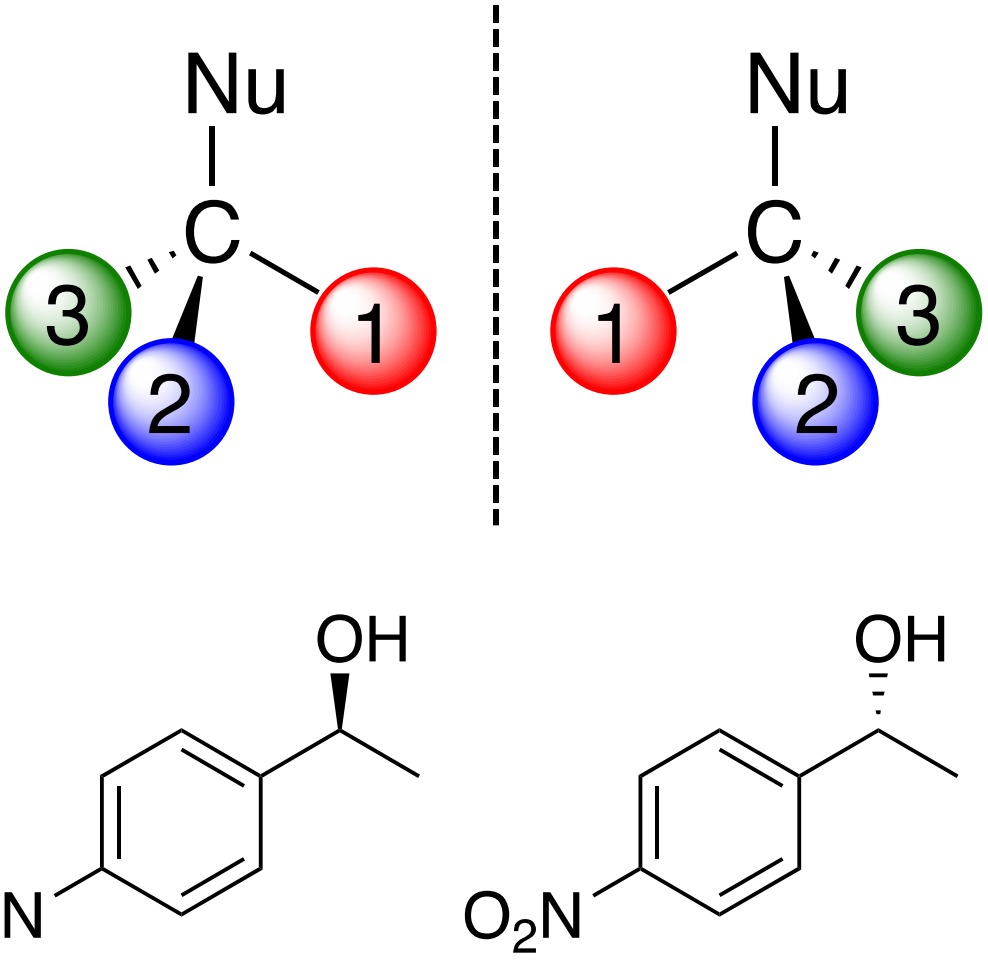

Si
1
C
2
3


O
C
H3C
NO2

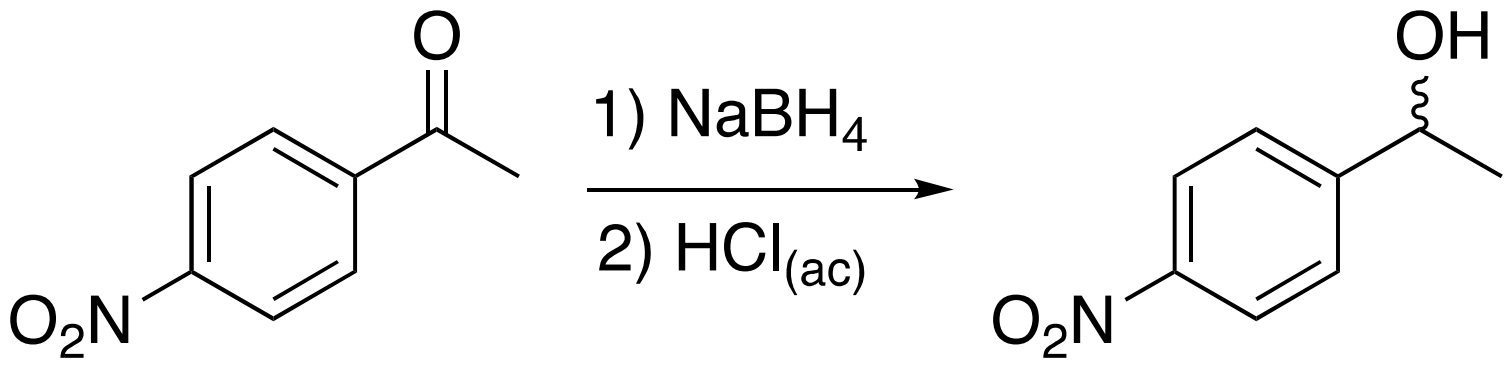

O
C
CH3
O2N


Re
por arriba del plano
Nu:
1
C
3
2
por debajo del plano
Si
Nu
C
3
2
1
2
3
1
C
Nu

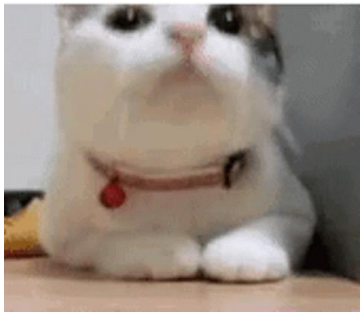
Generación de enantiómeros



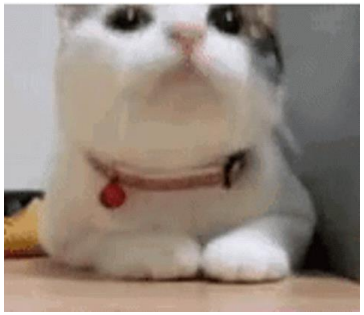
Considere la siguiente reacción:



¿Es quimioselectiva?

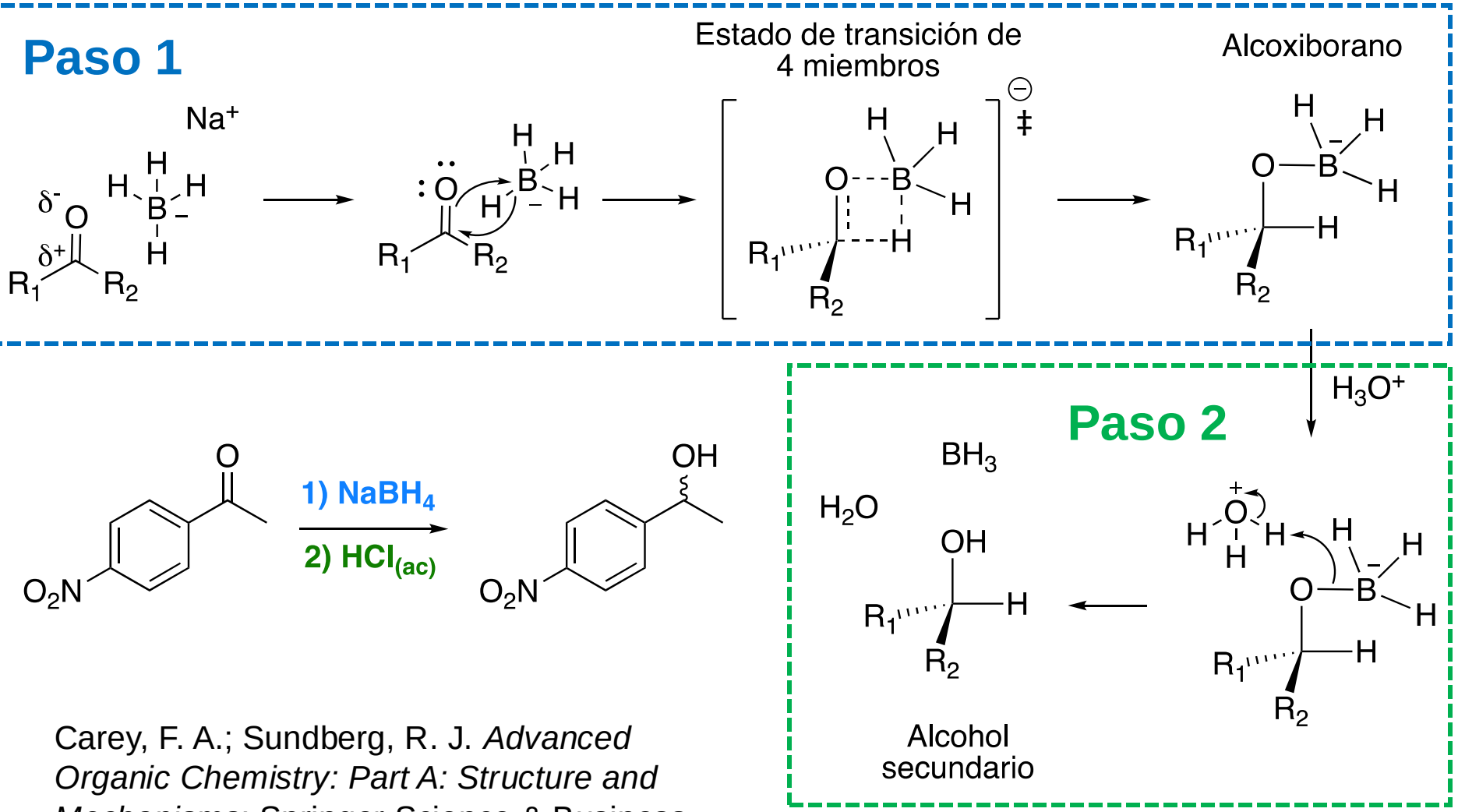


¿Es regioselectiva?

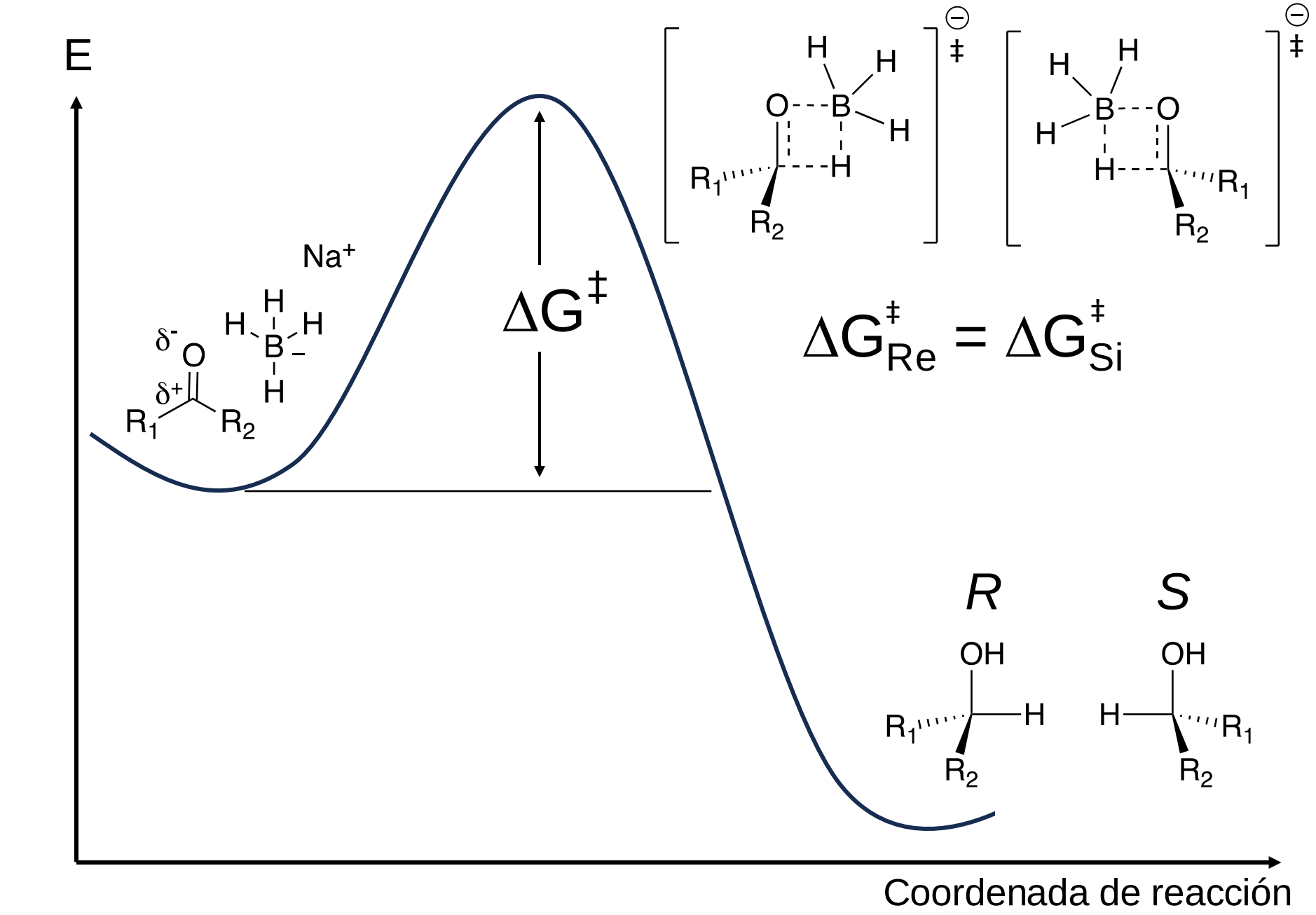


¿Es estereoselectiva?

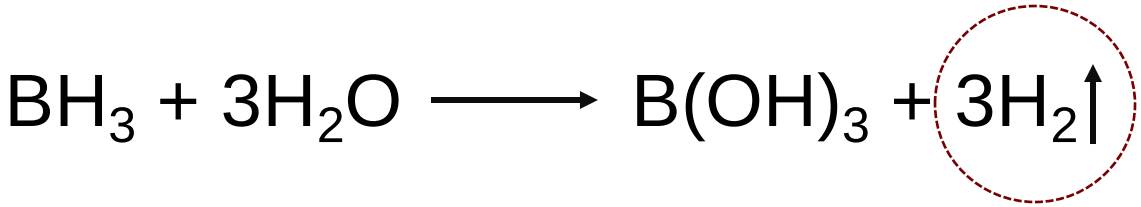
Mecanismo



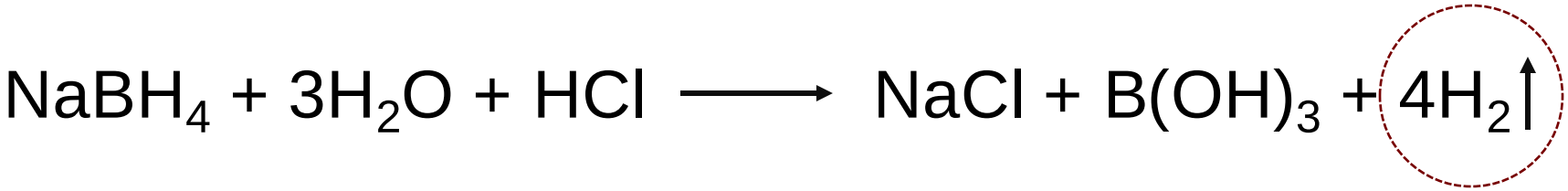
Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; Springer Science & Business Media, **2007**.


E
Na+
δ-
O
δ+
H
B
R1
R2
ΔG‡
ΔG‡Re = ΔG‡Si
R
S
OH
Coordenada de reacción

Hidrólisis del borano generado



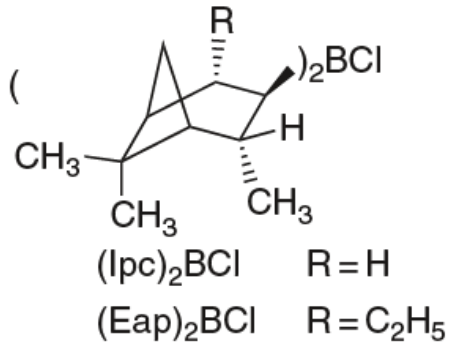
Hidrólisis del borohidruro de sodio remanente



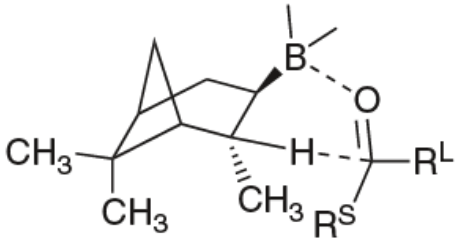
Netskina, O. V; Filippov, T. N.; Komova, O. V; Simagina, V. I. Hydrogen Generation by Both Acidic and Catalytic Hydrolysis of Sodium Borohydride. **2018**, *5* (1), 41–48.

¿Es posible realizar reducciones enantioselectivas?

Sí, con un agente reductor quiral.



In most cases, the enantioselectivity can be predicted by a model that places the smaller carbonyl substituent toward the isopinocampheyl methyl group.[149]

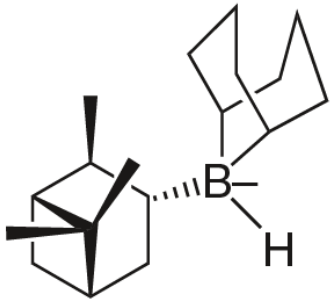


Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; Springer Science & Business Media, **2007**.

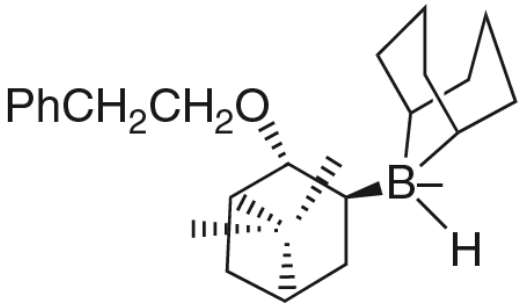
Table 2.6. Enantioselective Reduction of Ketones

Reagent	Ketone	% e.e.	Configuration
Alpine-Borane©[a]	3-Methyl-2-butanone	62	*S*
NB-Enantride©[b]	2-Octanone	79	*S*
Eapine-Hydride[c]	2-Octanone	78	*S*
$(Ipc)_2BCl$[d]	2-Acetylnaphthalene	94	*S*
(Ipc)(*t*-Bu)BCl[e]	Acetophenone	96	*R*
$(Ipc)_2BCl$[f]	2,2-Dimethylcyclohexanone	91	*S*
$(Eap)_2BCl$[g]	3-Methyl-2-butanone	95	*R*

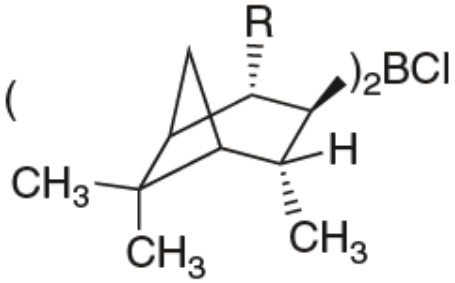
NOTE: © Trademark of Sigma Aldrich Corporation.



Alpine-Hydride*



NB-Enantride*



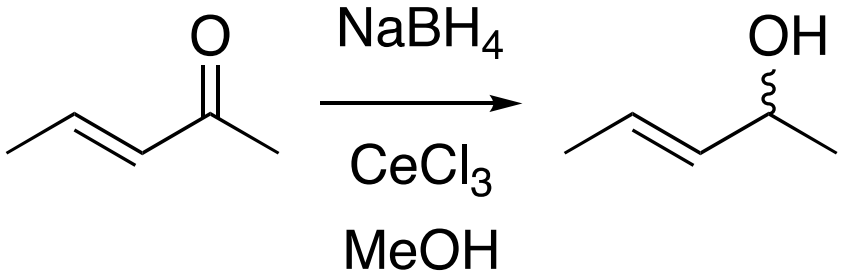
$(Ipc)_2BCl$ R = H

$(Eap)_2BCl$ $R = C_2H_5$

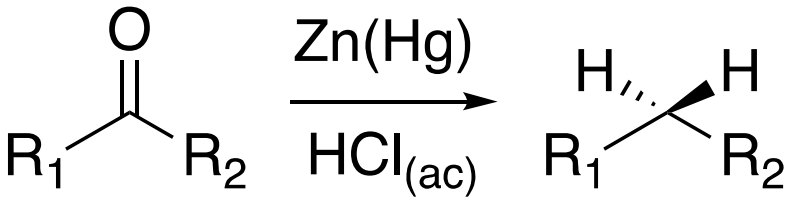
Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; Springer Science & Business Media, **2007**.

Otras reducciones

Reducción de Luche



Reducción de Clemmensen



Reducción de Wolff-Kishner