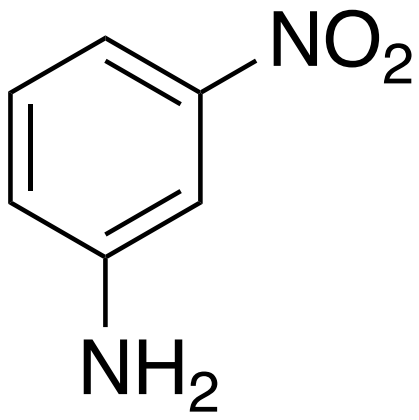
Universidad Nacional Autónoma de México

Química Orgánica III (1506)
Laboratorio
Semestre 2026 - 2

M. en C. Arturo García Zavala

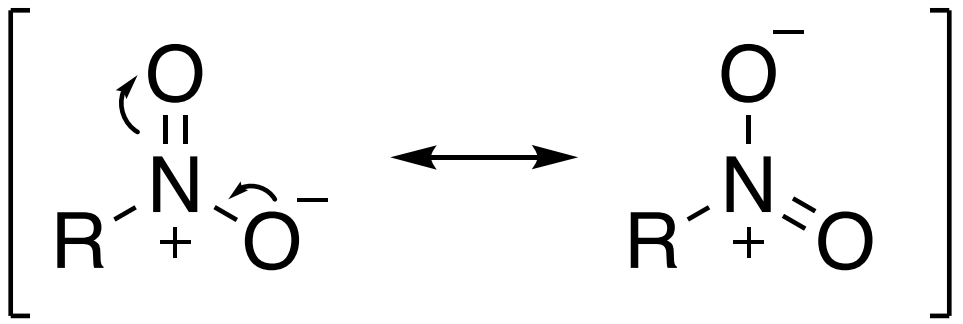


Práctica 2

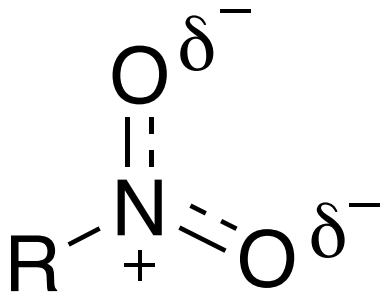
Nitrocompuestos II
Reducción de Zinin

25/02/2026

Grupo nitro (-NO_2)



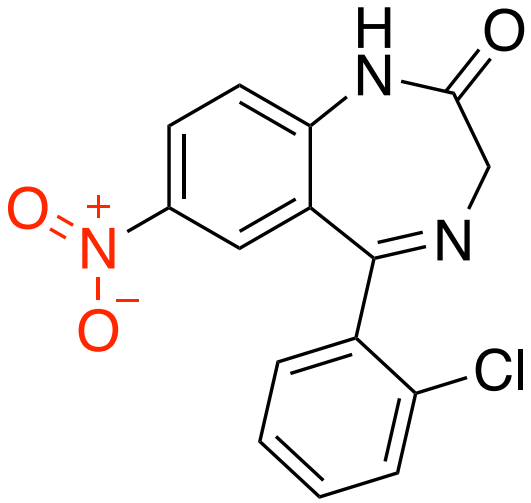
Estructuras resonantes



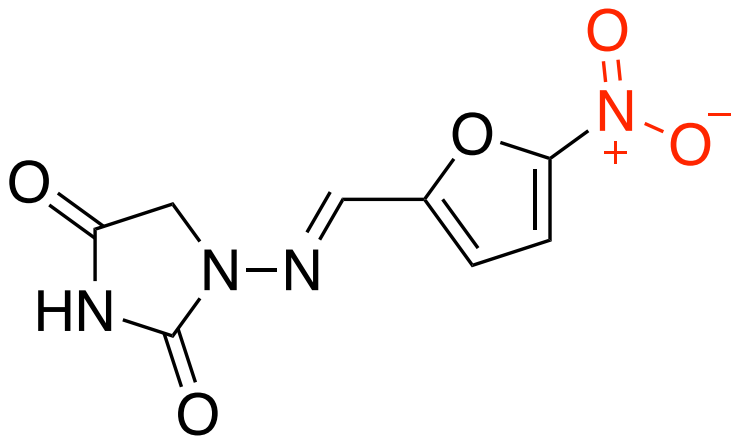
híbrido de resonancia

¡El más electroatractor!

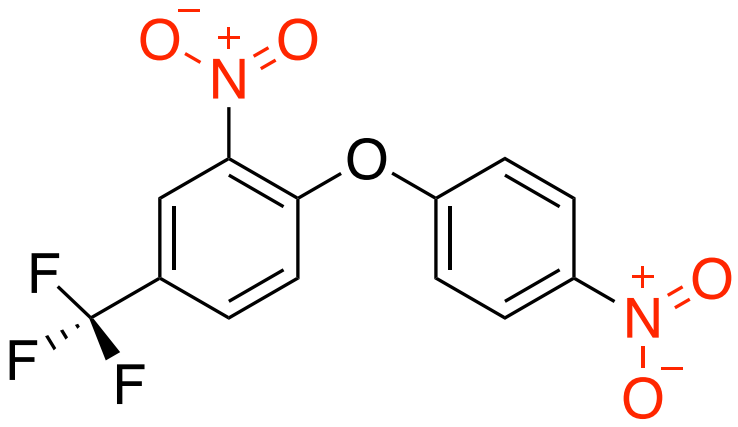
por efecto inductivo (-I) y por efecto resonante (-R)



Clonazepam
(antidepresivo)

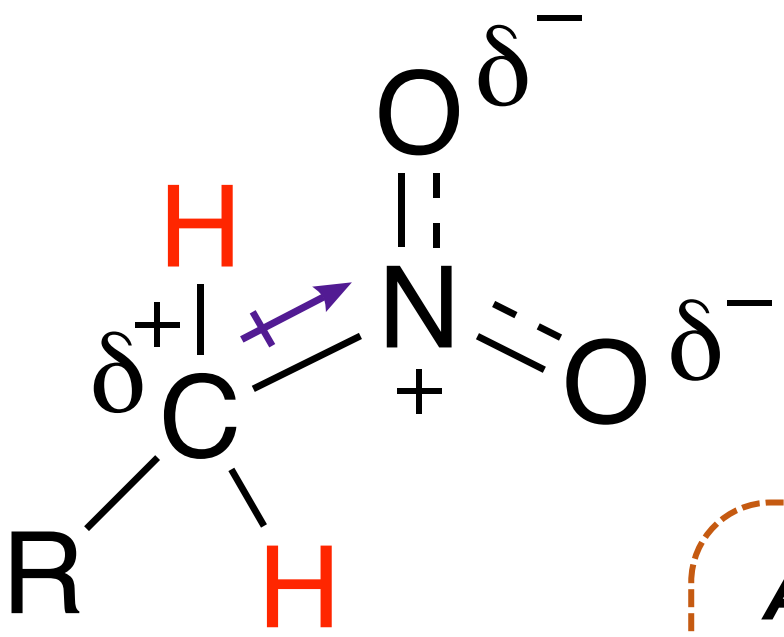


Nitrofurantoína
(antibiótico)



Fluorodifeno
(herbicida)

Enlace carbono–nitrógeno fuertemente polarizado, les confieren acidez a los átomos de hidrógeno.



Hidrógenos ácidos

Aplicaciones sintéticas (alifáticos)

-Reacción de Nef

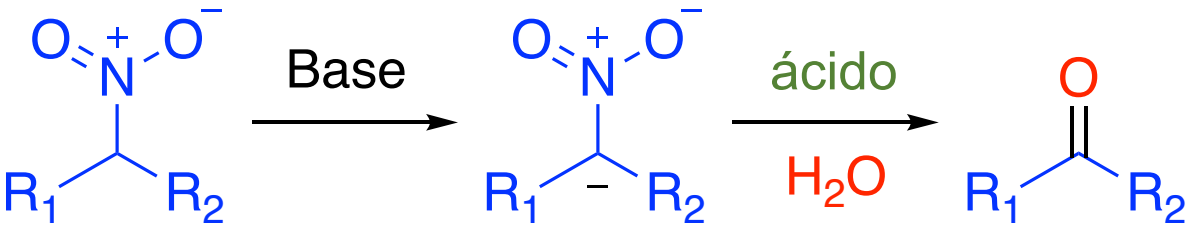
-Reacción de Henry

Aplicaciones sintéticas (aromáticos)

-Sustitución electrofílica aromática (S_EA)

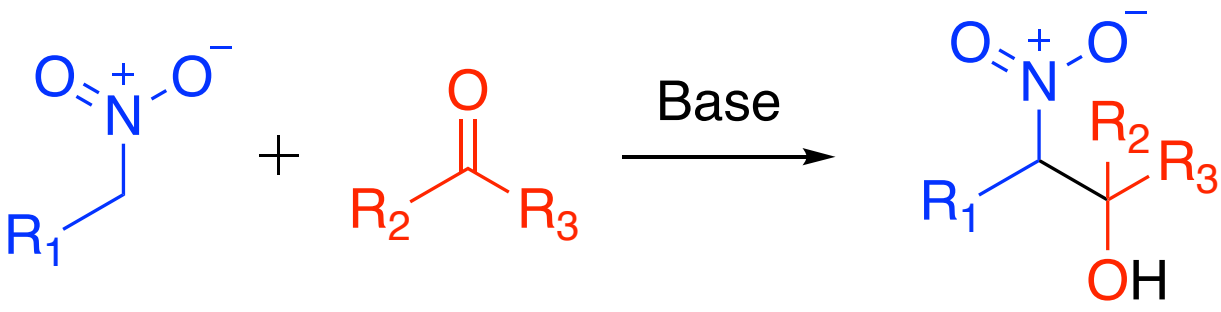
Reactividad: Nitrocompuestos alifáticos

Reacción de Nef



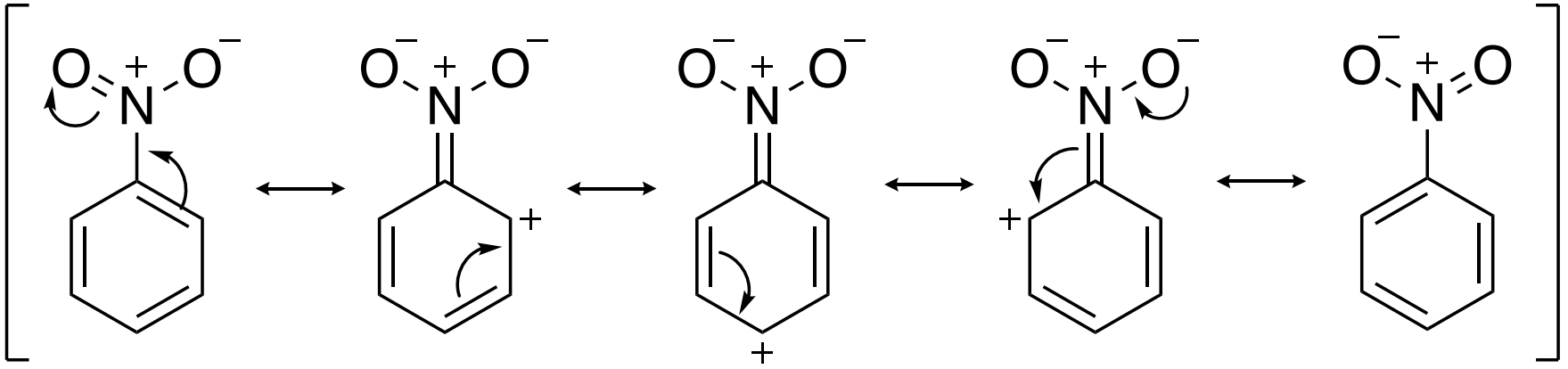
nitroalcano (1º o 2º) | sal de nitronato | compuesto carbonílico

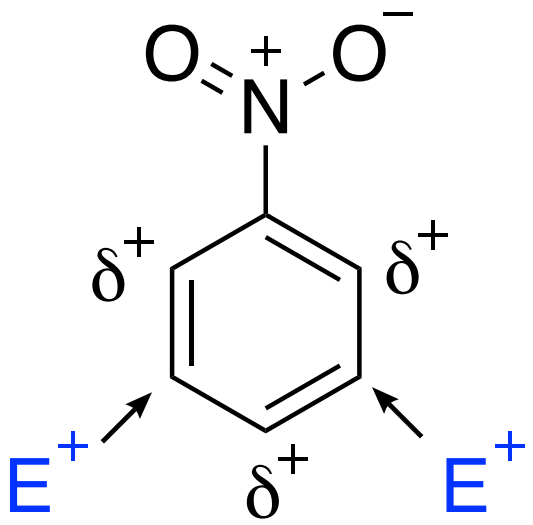
Reacción de Henry



nitroalcano | aldehído o cetona | β-nitro alcohol

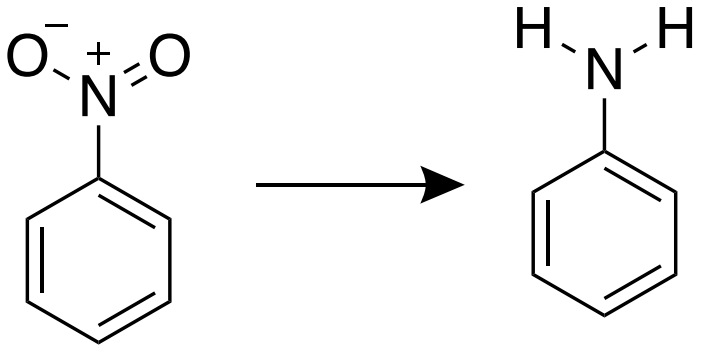
Reactividad: Nitrocompuestos aromáticos





Sustitución electrofílica aromática (S_EA): posición *meta*

Reducción de Zinin

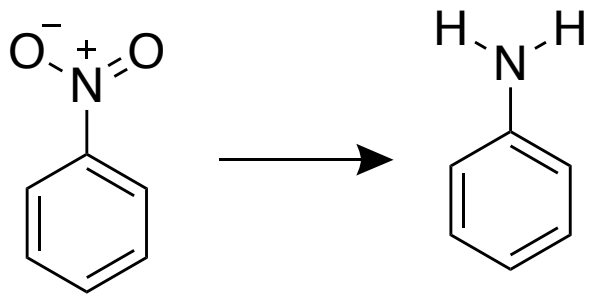


Nitrobenceno Anilina

N. Zinin, *J. Prakt. Chem.*, [1] **27**, 149 (1842).

Nikolái Zinin
(1812 - 1880)

N. Zinin, *J. Prakt. Chem.*, [1] **27**, 149 (1842).



Nitrobencene Aniline

Condiciones de Zinin

S^{2-} sulfuros

SH^{-} hidrosulfuros

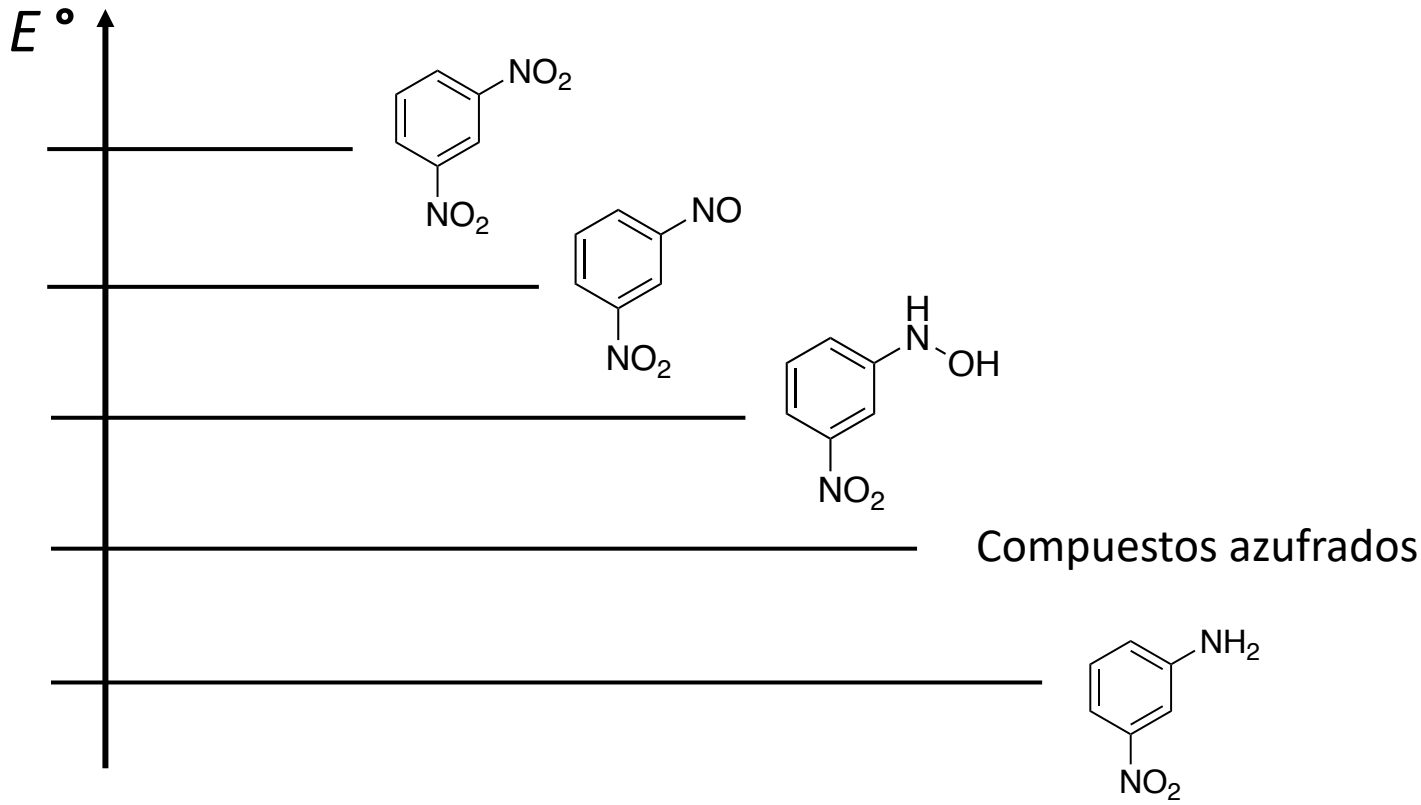
S_n^{2-} polisulfuros

The reaction, first used by Zinin in 1842 to prepare aniline from nitrobenzene,[1] has since been of great importance in the preparation of aromatic amines. With the advent of catalytic reduction procedures, Zinin's method has seen less use in the laboratory as a preparative technique. Recently published laboratory texts of organic chemistry often fail to mention this rather simple procedure for the preparation of a host of ordinary or rare amines. Economically, in most instances it has not proved so attractive as the iron reduction method in commercial applications,[2] but it is used with more sensitive compounds that would not be compatible with acid media or would be reduced farther than desired by the iron or catalytic hydrogenation process.

The uniqueness of the Zinin reduction of nitroarenes, as compared to reduction by iron or catalytic hydrogenation, lies in its lower reduction potential and its narrow useful range of electromotive force. This means that functional groups other than nitro are less likely to be reduced. Moreover, selective reduction of one nitro group in a dinitro- or trinitro-arene is often possible. Some useful generalizations (pp. 458–459) often enable

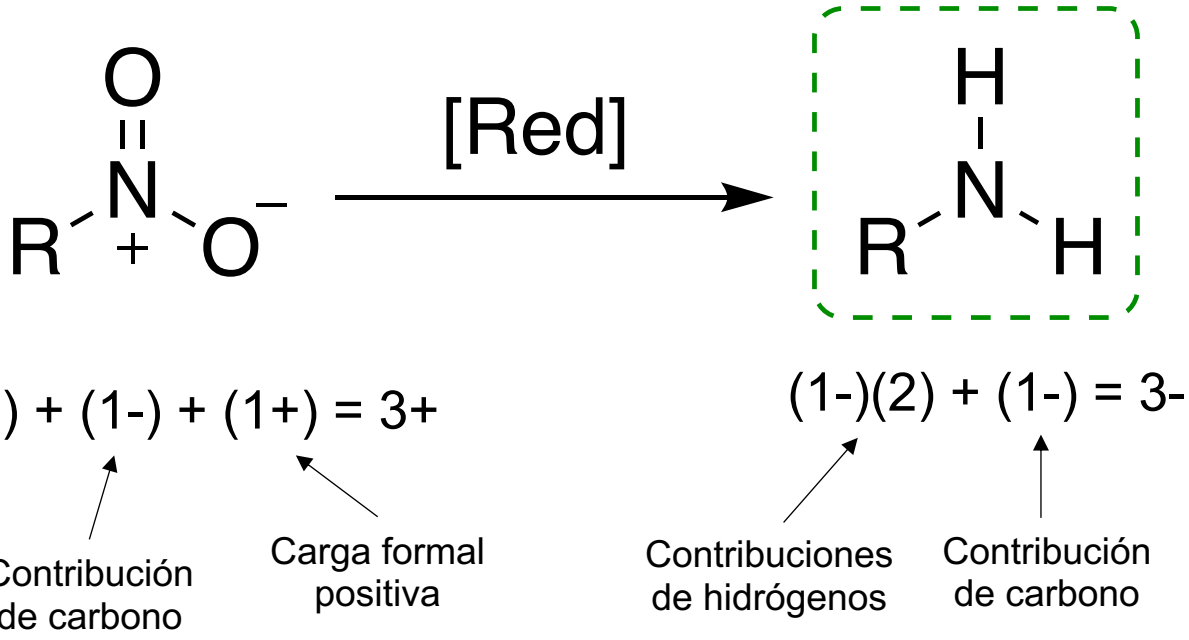
N. Zinin, *J. Prakt. Chem.*, [1] **27**, 149 (1842).

Potenciales redox



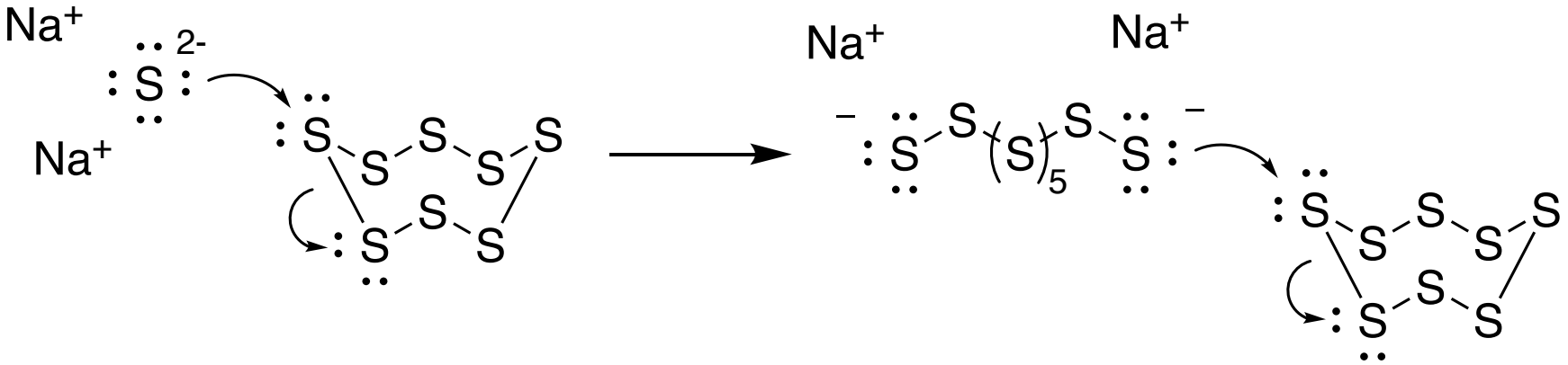
Estados de oxidación

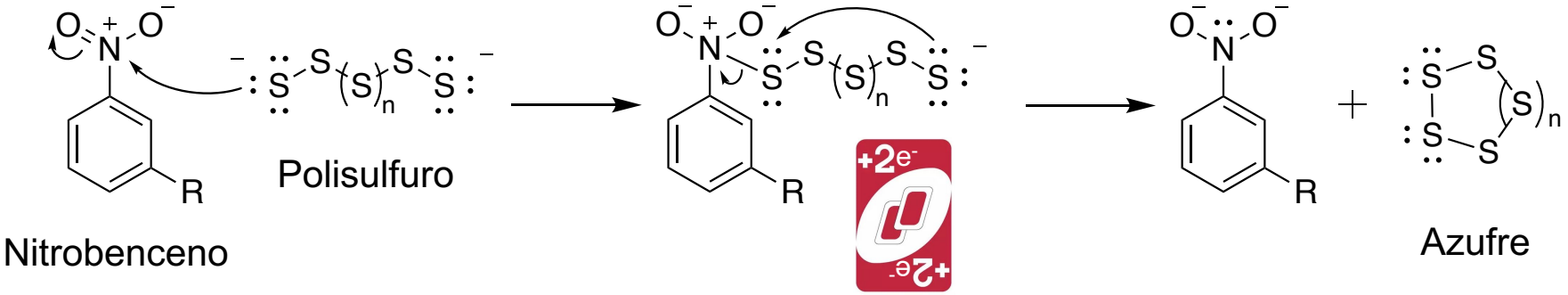
- Cada enlace entre N y otro N no modifica el estado de oxidación.
- Cada enlace entre N y H disminuye el estado de oxidación en 1.
- Cada enlace desde N hacia un elemento más electronegativo (como O) aumenta su estado de oxidación en 1.
- Cada enlace desde N hacia un elemento menos electronegativo (como C) disminuye su estado de oxidación en 1.

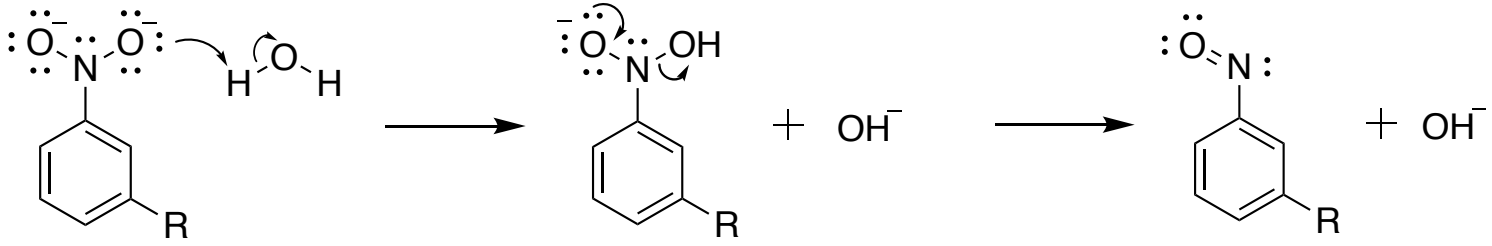


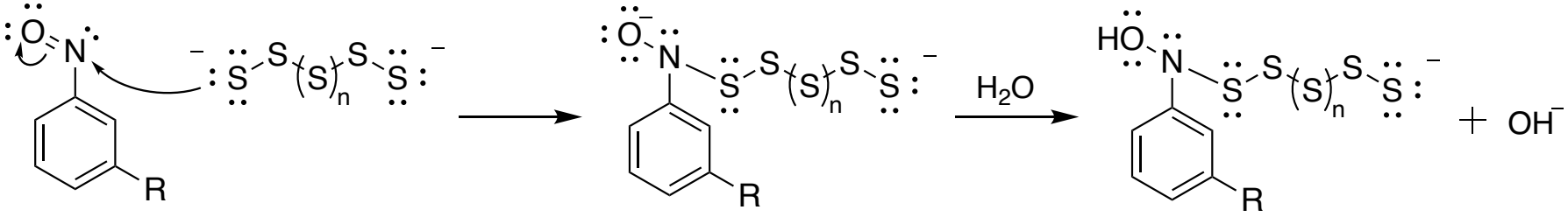
Formación de polisulfuro

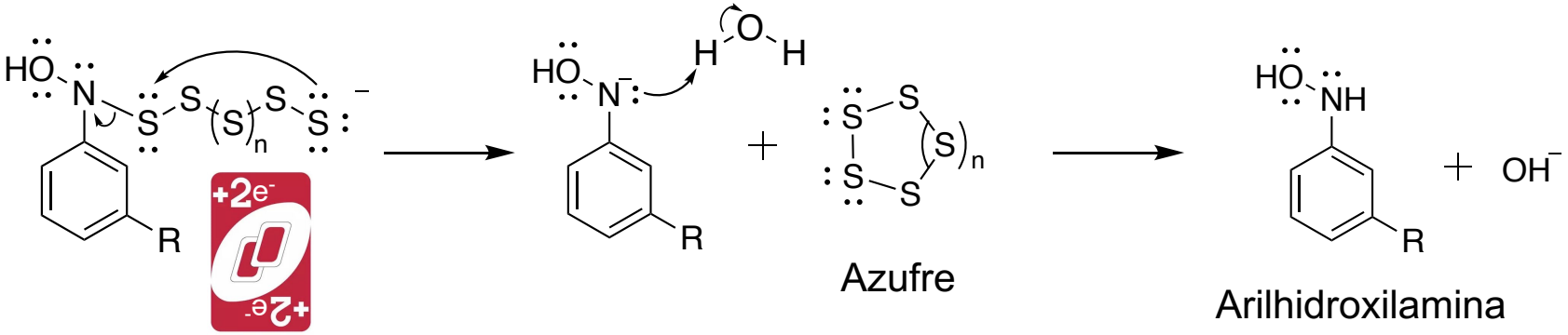
$$Na_2S + S_8^0 \xrightarrow[\Delta]{H_2O} Na_2S_x$$

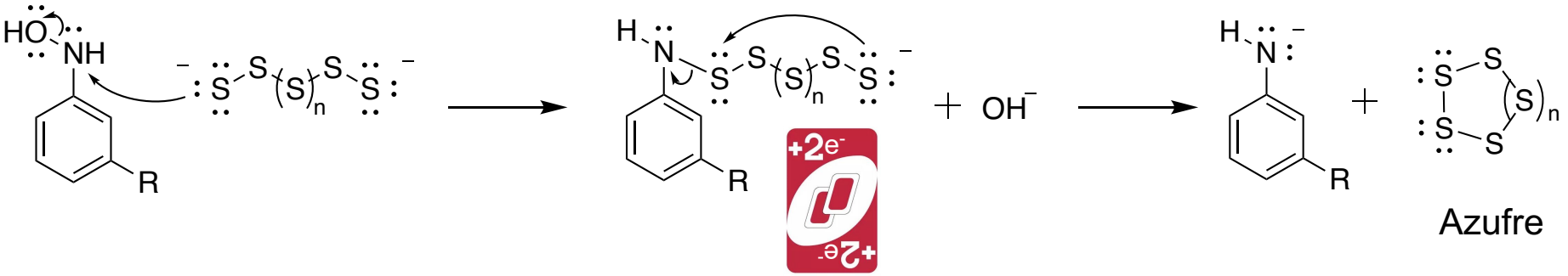


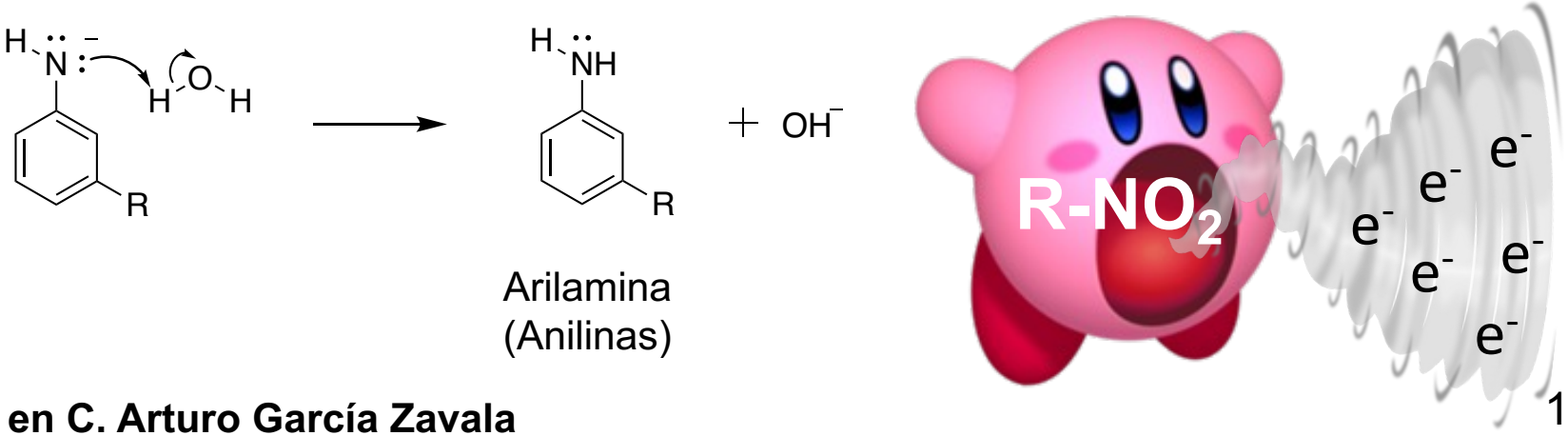

Polisulfuro
+2e⁻
+2e⁻
Nitrobenceno
Azufre


OH⁻
OH⁻
Nitrosobenceno

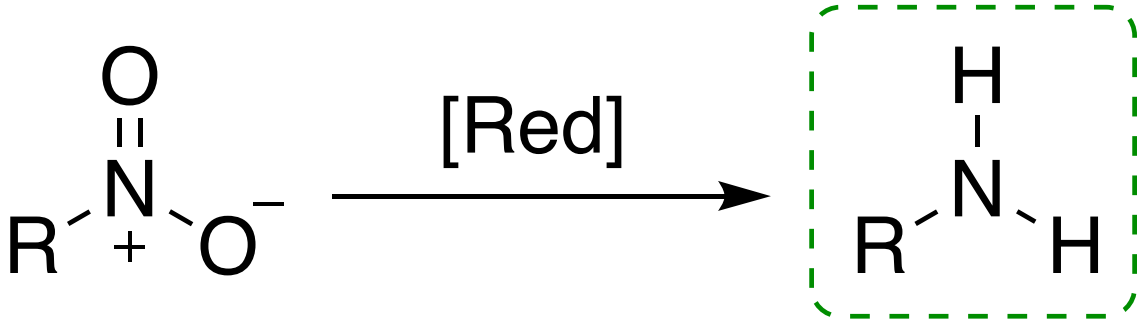

H₂O
OH⁻


+2e⁻
+2e⁻
Azufre
Arilhidroxilamina
+ OH⁻


+2e⁻
+2e⁻
+ OH⁻
Azufre


+ OH⁻
Arilamina
(Anilinas)
R-NO2
e-
e-
e-
e-
e-
e-

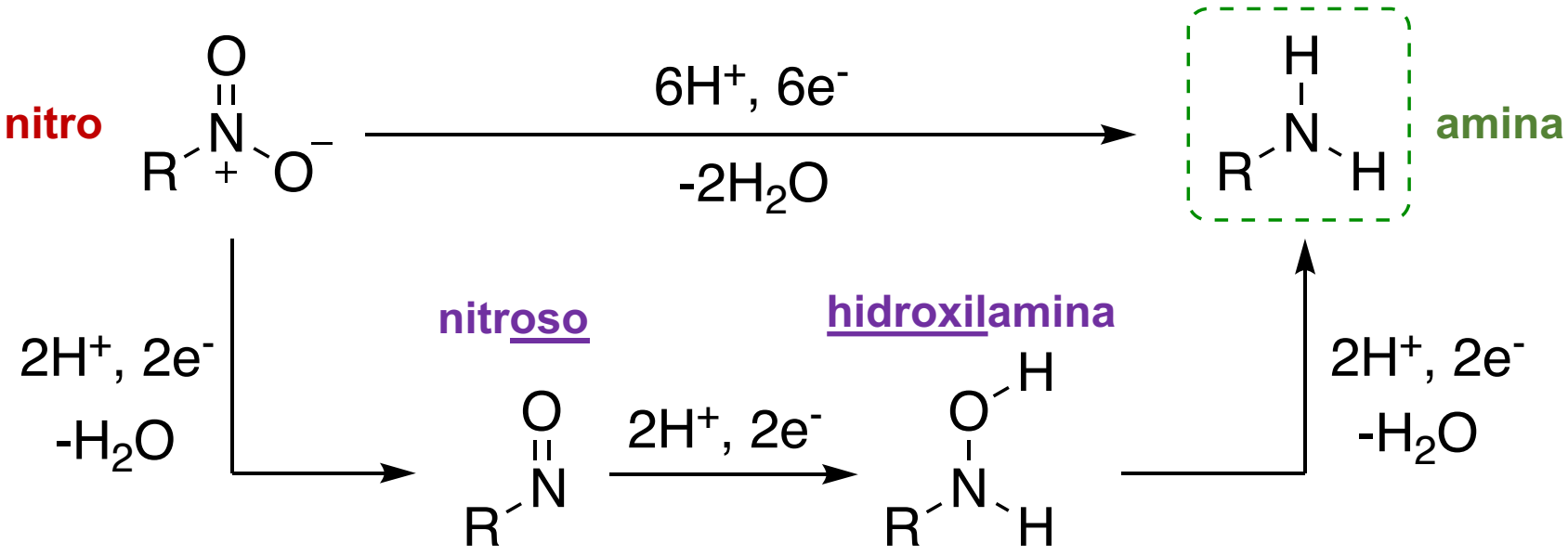
Otros agentes reductores:

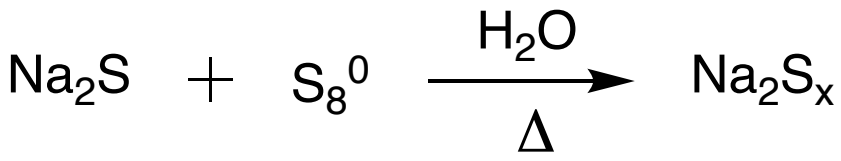


-Zn^0 / $HCl_{(ac)}$
-Sn^0 / $HCl_{(ac)}$
-$SnCl_2$ / $HCl_{(ac)}$

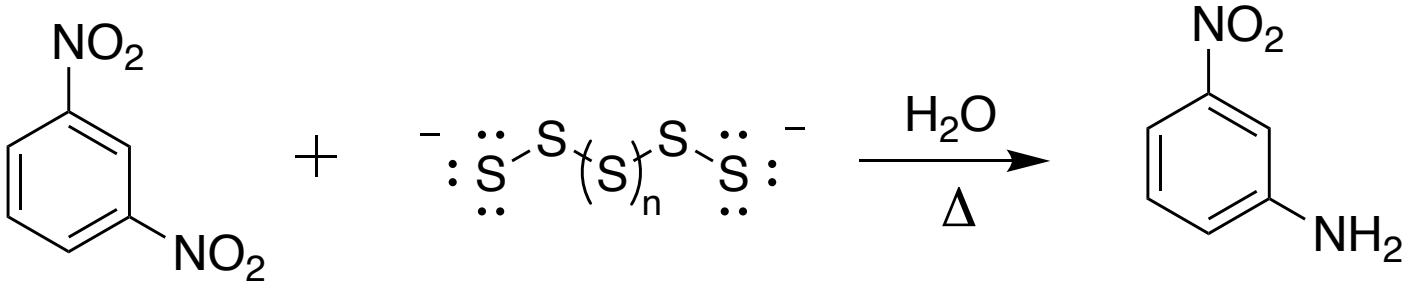
-Pd / H_2
-$Na_2S_2O_4$ / H_2O
-SmI_2

Proceso general de reducción de un grupo nitro

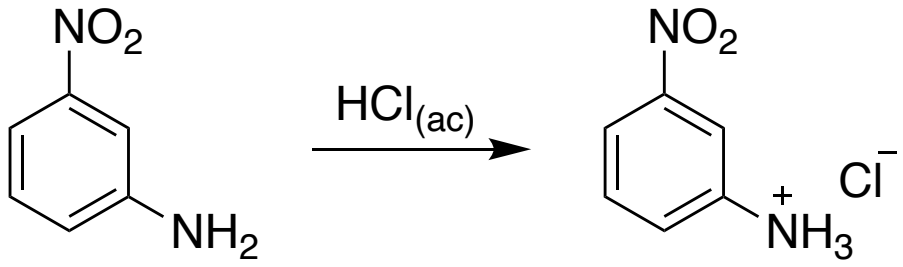




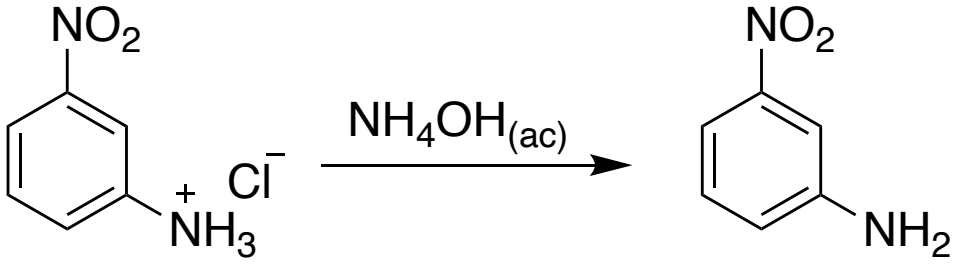
Paso 1: Formación de polisulfuro



Paso 2: Reducción



Paso 3: Protonación de la anilina (solubilizándola formando su sal)



Paso 4: Desprotonación de su sal de amonio (para precipiar la amina)