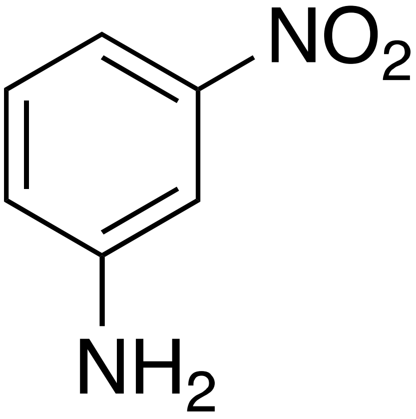
Universidad Nacional Autónoma de México

Química Orgánica III (1506)
Laboratorio
Semestre 2025 - 2

M. en C. Arturo García Zavala



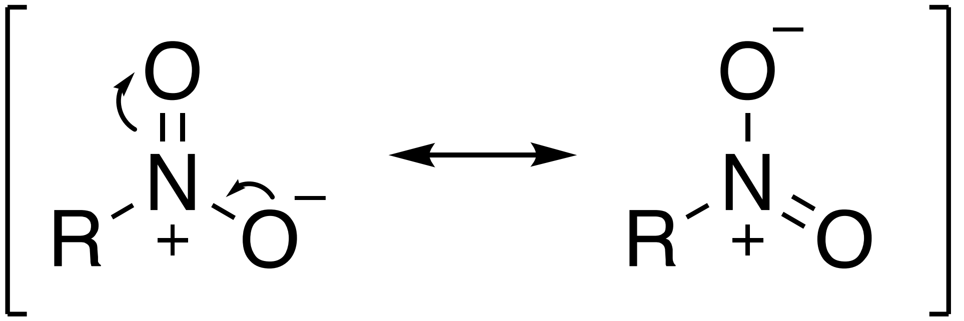
Práctica 2

Nitrocompuestos II

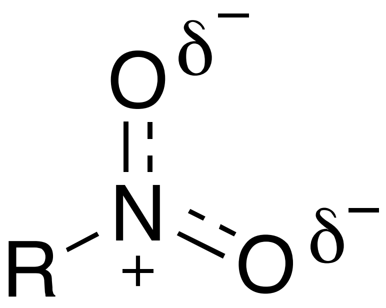
Reducción de Zinin

26/2/2025

Grupo nitro (-NO_2)



Estructuras de resonancia



Híbrido de resonancia

¡Los más electroatractores!

Tanto por efecto inductivo (-I) como por resonante (-R)

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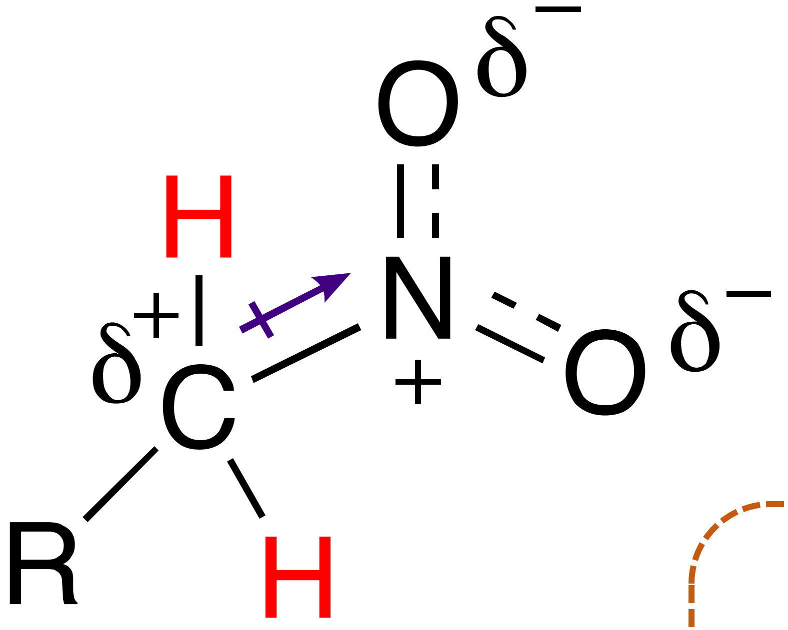
Enlaces carbono-nitrógeno fuertemente polarizados, lo que les confiere acidez a los átomos de hidrógeno.



Hidrógenos ácidos

Utilidad sintética (alifáticos)

-Reacción de Nef

-Reacción de Henry

Utilidad sintética (aromáticos)

-Sustitución electrofílica aromática (SEA): posición *meta*

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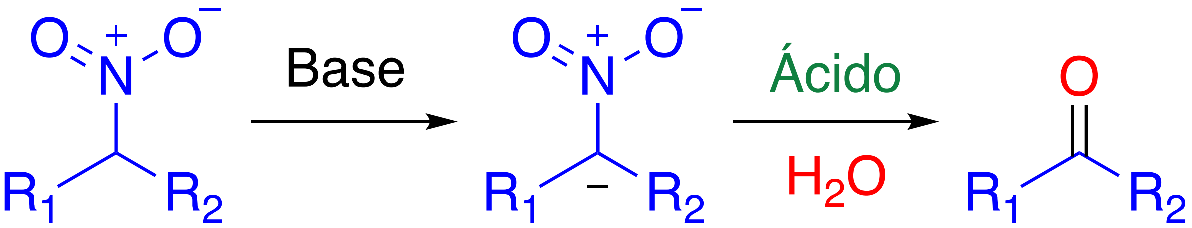
Reactividad: Nitrocompuestos alifáticos

Reacción de Nef

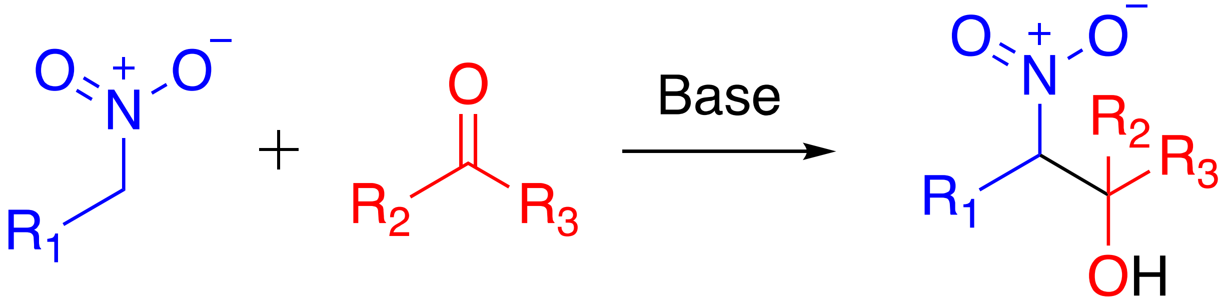


Nitroalcano
(1^{o} o 2^{o})

Sal de
nitronato

Compuesto
carbonílico

Reacción de Henry



Nitroalcano

Aldehído o
cetona

β-nitro alcohol

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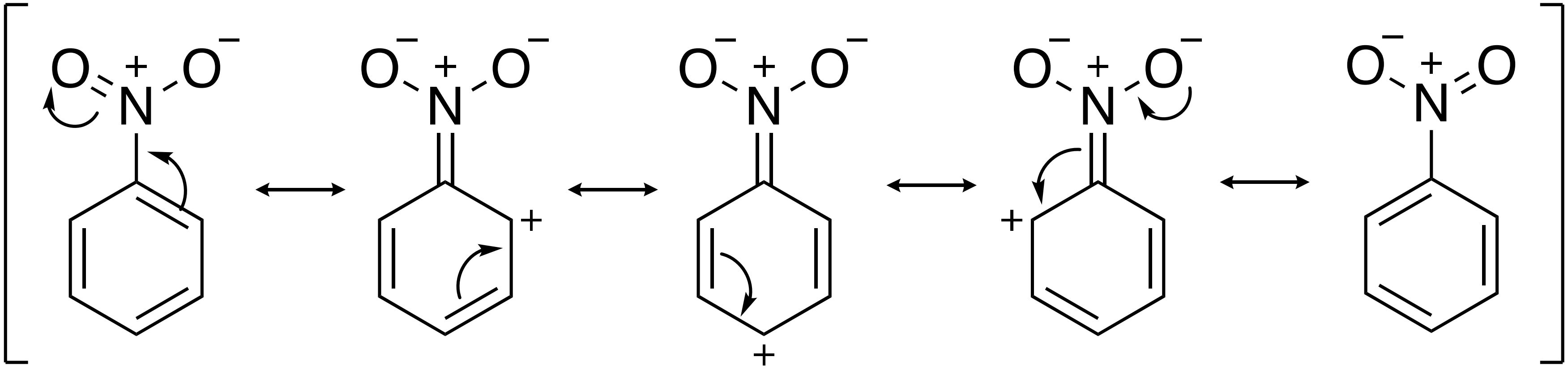
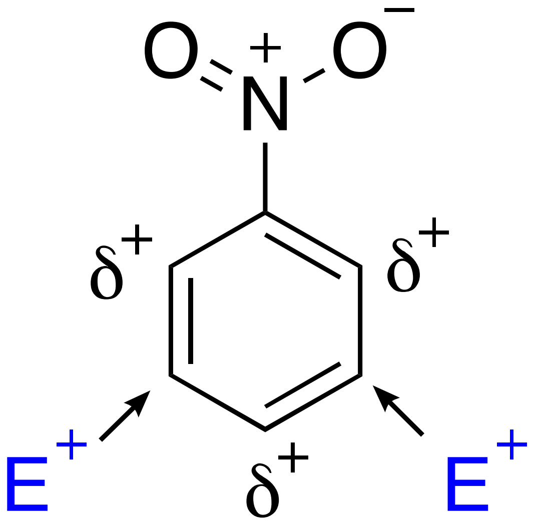
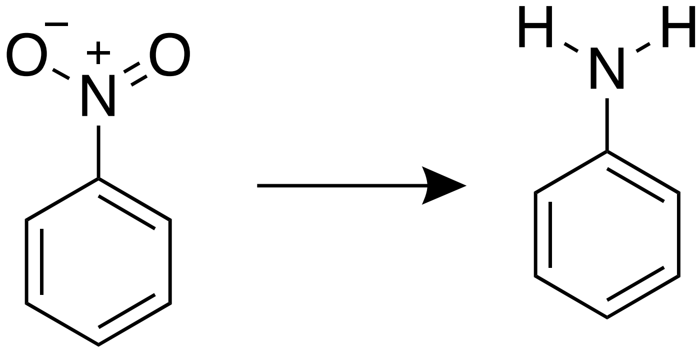
Reactividad: Nitrocompuestos aromáticos





Sustitución electrofílica aromática (SEA): posición *meta*

Reducción de Zinin



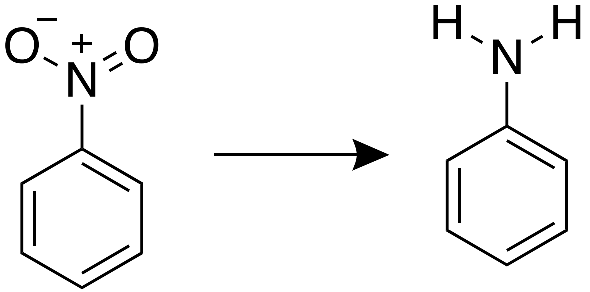
Nitrobenceno

Anilina

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

Nikolái Zinin
(1812 - 1880)

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

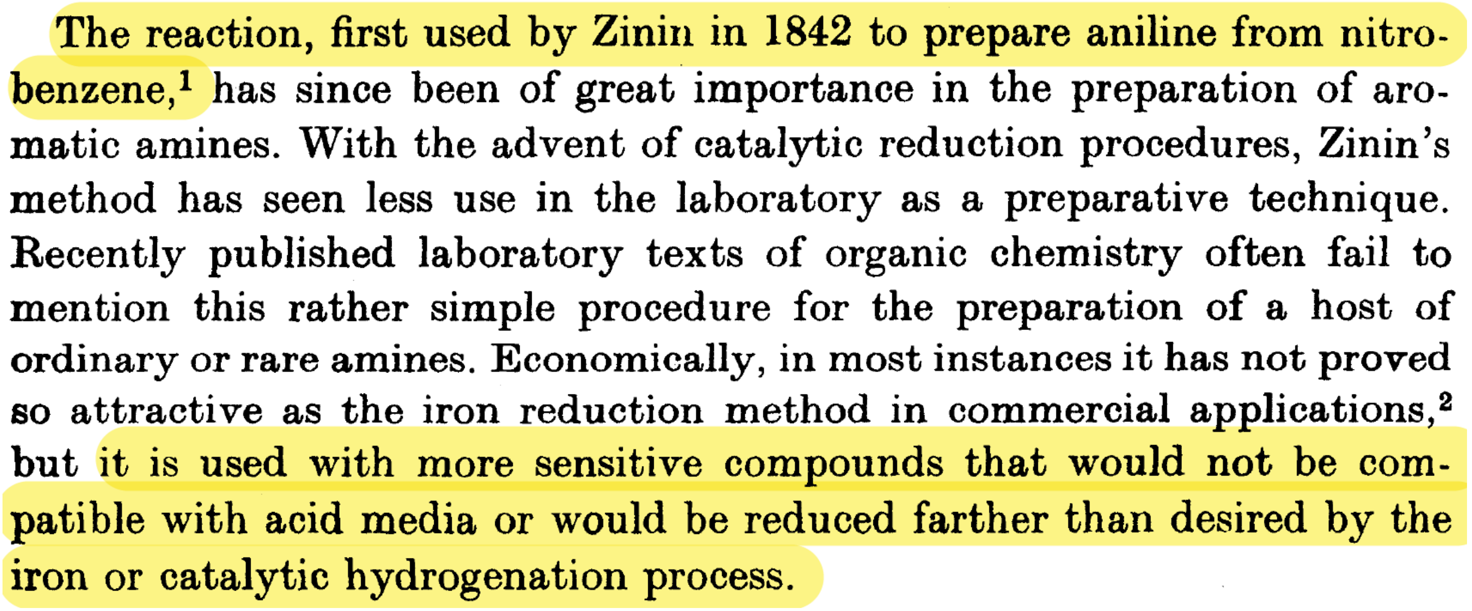


Nitrobenceno

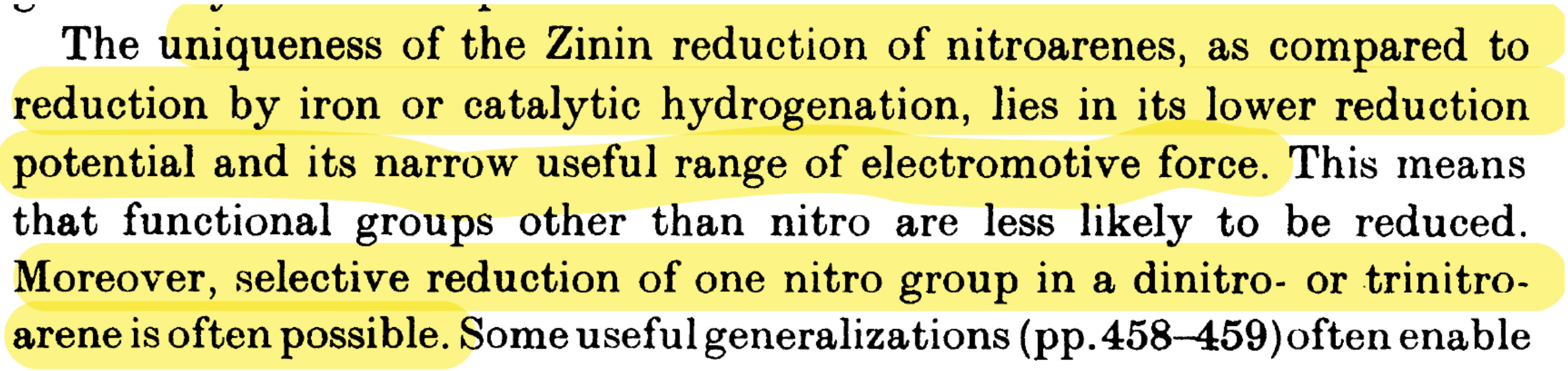
Anilina

Condiciones de Zinin

S^{2-}	sulfuros
SH^{-}	hidrosulfuros
S_n^{2-}	polisulfuros



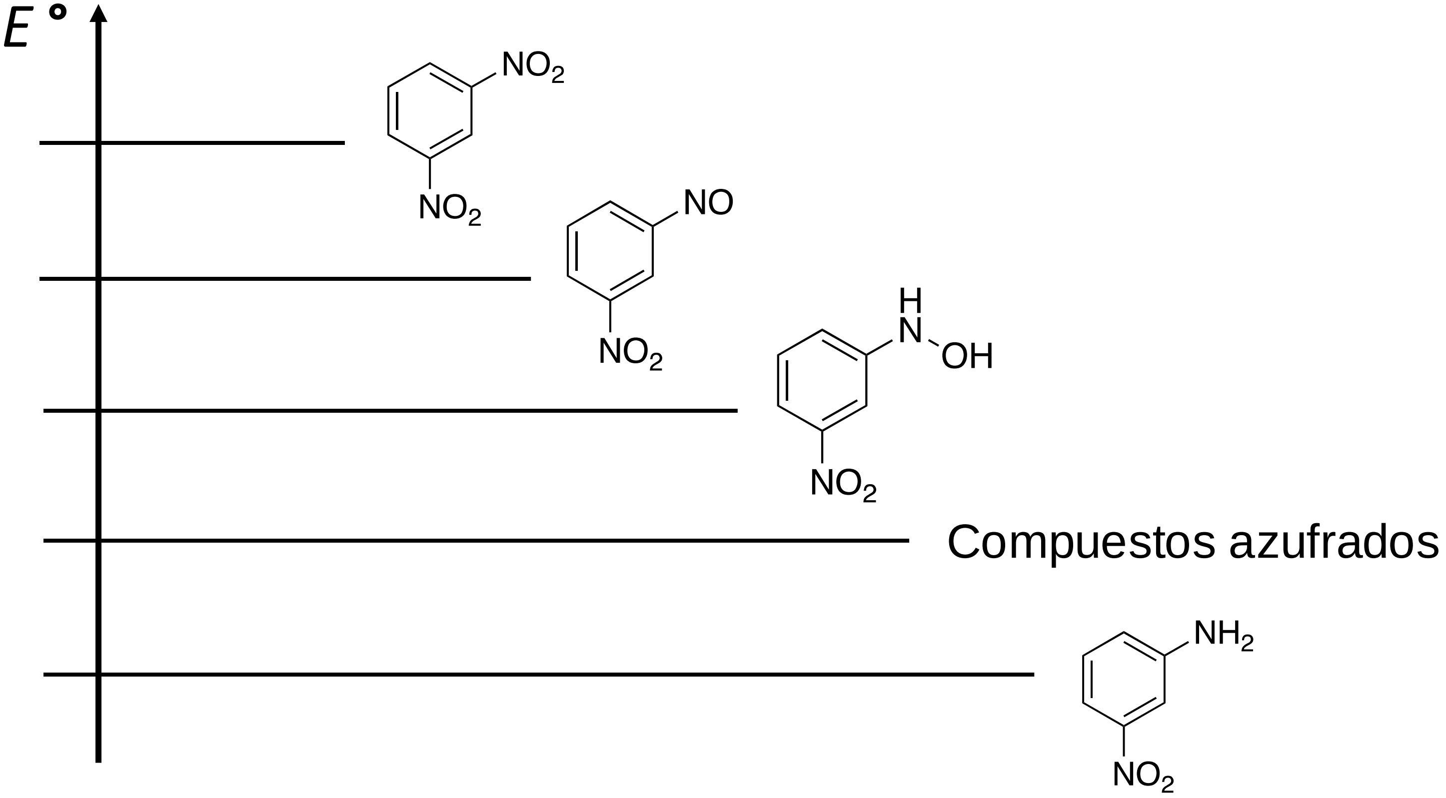
The reaction, first used by Zinin in 1842 to prepare aniline from nitrobenzene,[1] has since been of great importance in the preparation of aromatic amines. With the advent of catalytic reduction procedures, Zinin's method has seen less use in the laboratory as a preparative technique. Recently published 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 trinitroarene is often possible. Some useful generalizations (pp. 458–459) often enable

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

Potenciales Redox



Compuestos azufrados

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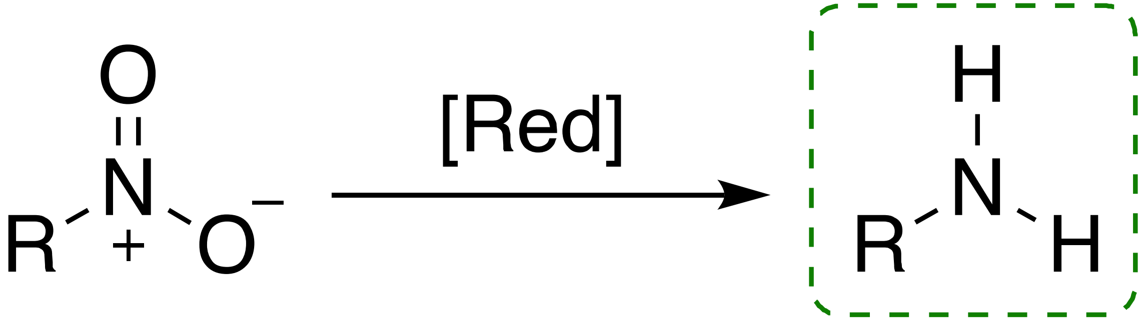
Estados de oxidación

-Cada enlace entre N y otro N no altera el estado de oxidación.
-Cada enlace entre N y H **disminuirá el estado de oxidación en 1**.
-Cada enlace de N a un elemento más electronegativo (como O) **aumentará su estado de oxidación en 1**.
-Cada enlace de N a un elemento menos electronegativo (como C) **disminuirá su estado de oxidación en 1**.



(1+)(3) + (1-) + (1+) = 3+

Contribuciones de oxígenos

Contribución de carbono

Carga formal positiva

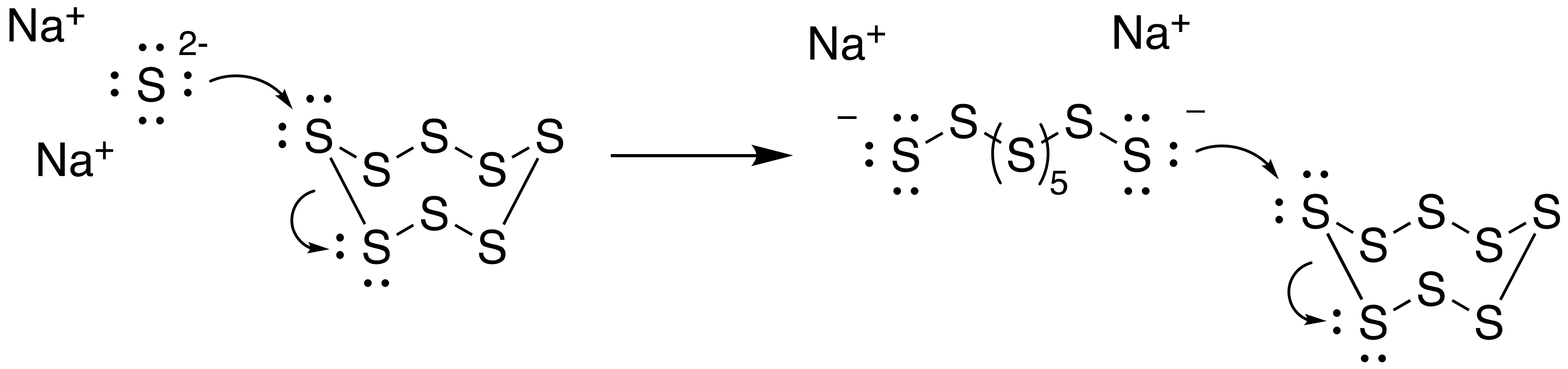
(1-)(2) + (1-) = 3-

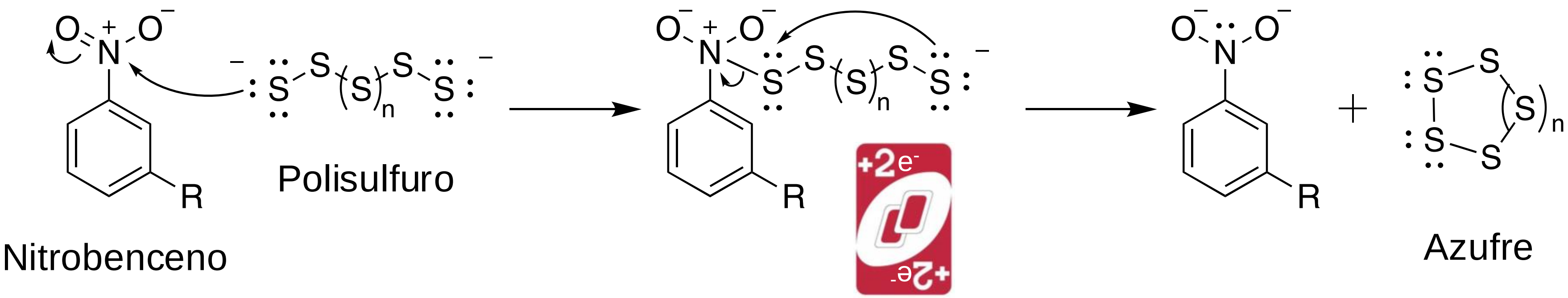
Contribucion de hidrógenos

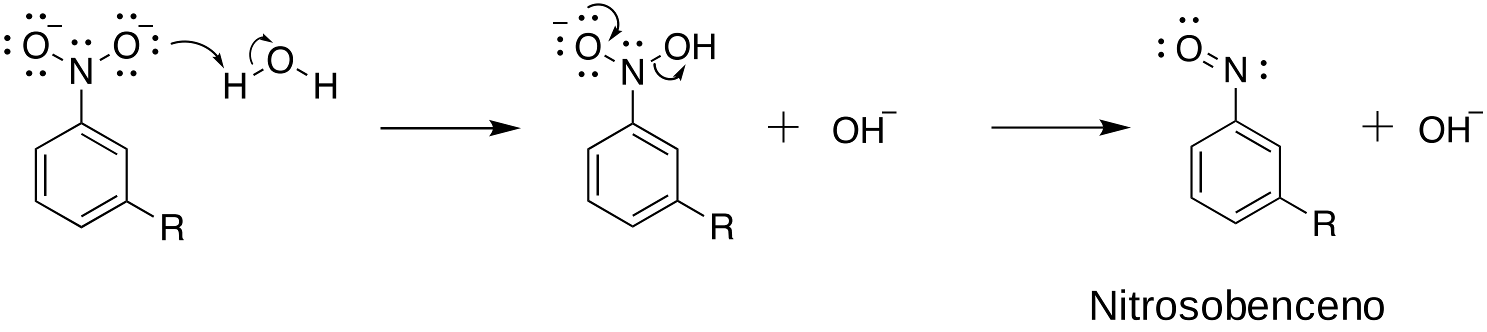
Contribución de carbono

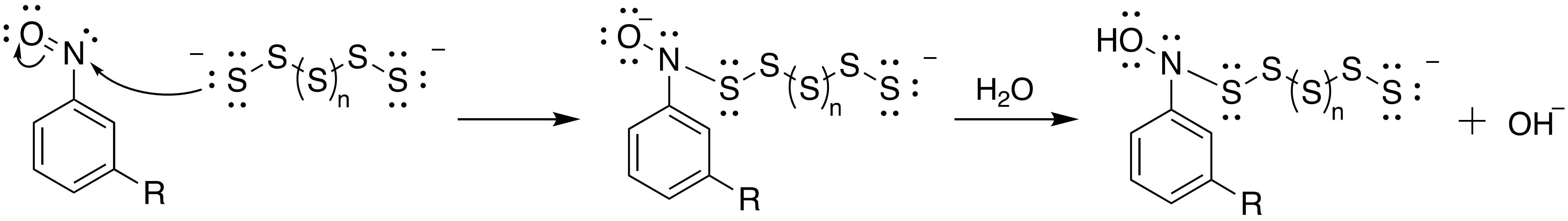
Formación de polisulfuro

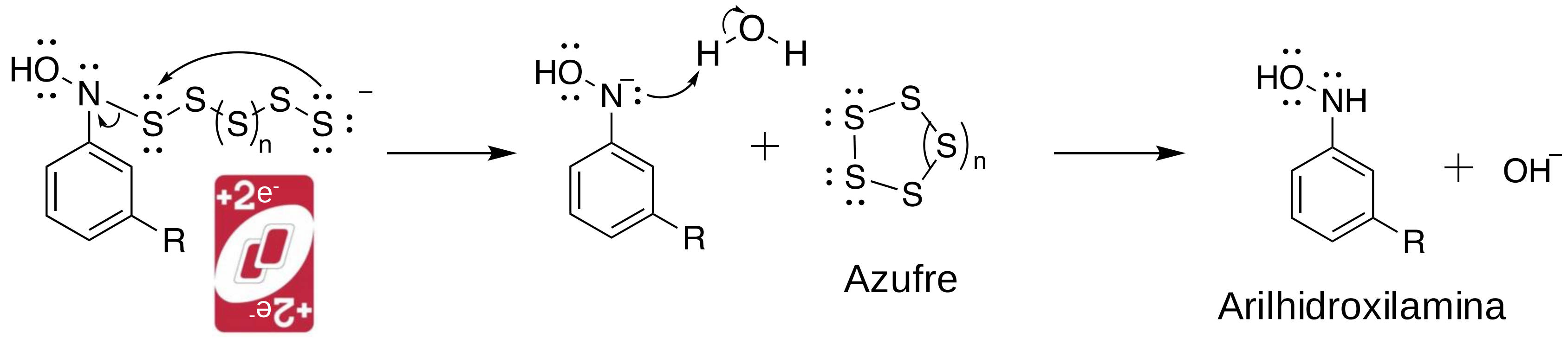
$$Na_2S + S_8^0 \xrightarrow[\Delta]{H_2O} Na_2S_x$$

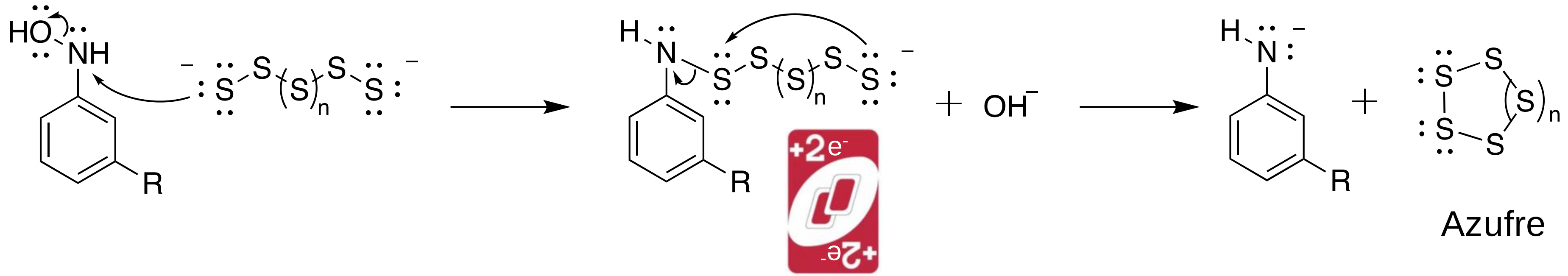


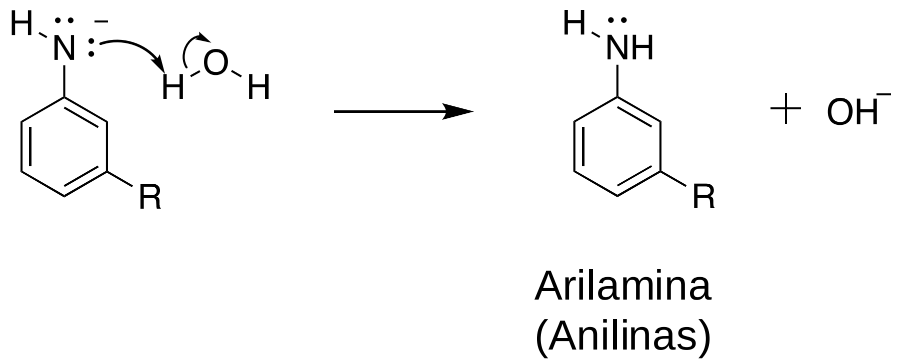

Nitrobenceno
Polisulfuro
+2e-
Azufre

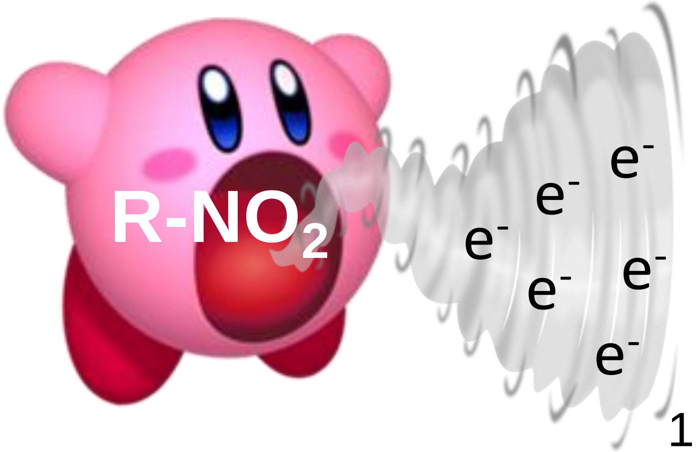

OH
Nitrosobenceno


H2O
HO
OH


+2e-
Azufre
Arilhidroxilamina
+ OH⁻


+2e-
+ OH⁻
Azufre

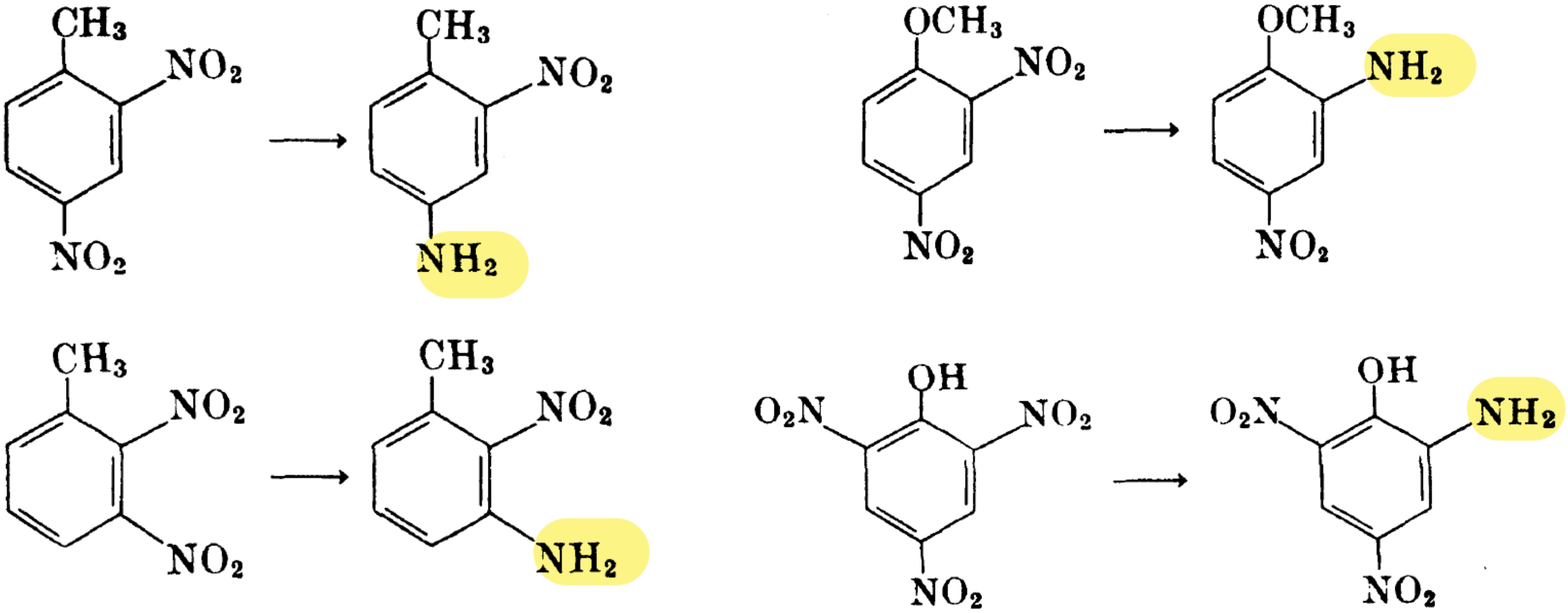

+ OH⁻
Arilamina
(Anilinas)


R-NO2
e-
e-
e-
e-
e-
e-
e-

Alcance y limitaciones

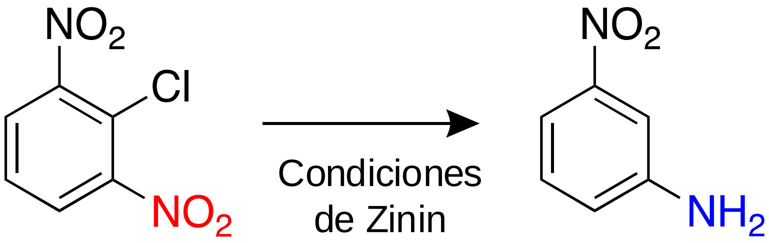
THE ZININ REDUCTION OF NITROARENES

H. K. PORTER

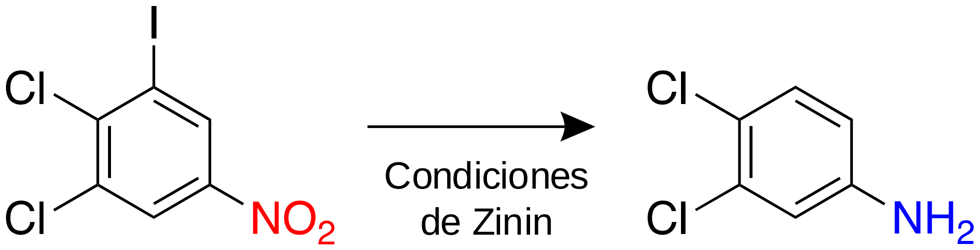


Reacciones secundarias

Deshalogenación



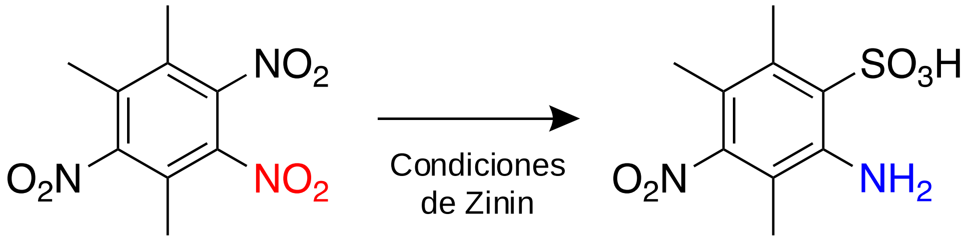
[16] G. Koerner and A. Contardi, *Atti Acad. Lincei*, [5] **22**, 835 (1914); F. Beilstein, *Handbuch der Organischen Chemie*, Vol. XI–XII, 4th Ed., First Supplement, Julius Springer, Berlin (1933), p. 301.



[17] W. Borsche and D. Rantscheff, *Ann.*, **379**, 160 (1911).

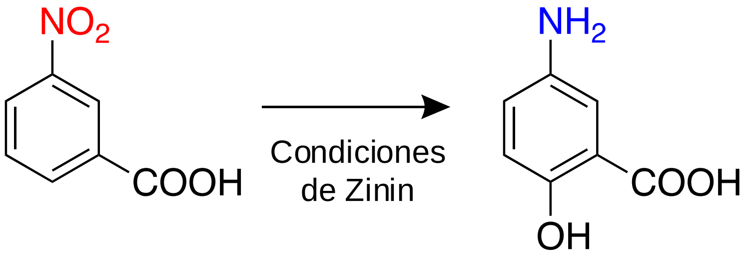
Reacciones secundarias

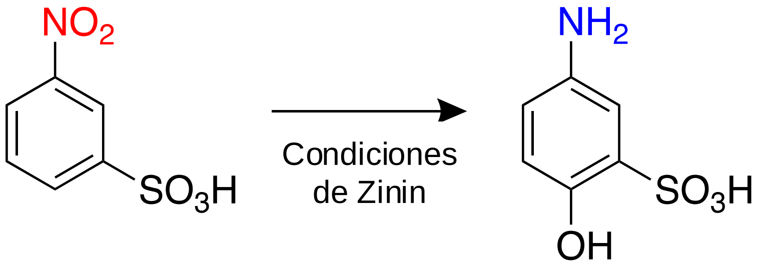
Formación del ácido sulfónico



[18] J. J. Blanksma, *Rec. Trav. Chim. Pays-Bas*, **34**, 17 (1915).

Hidroxilación



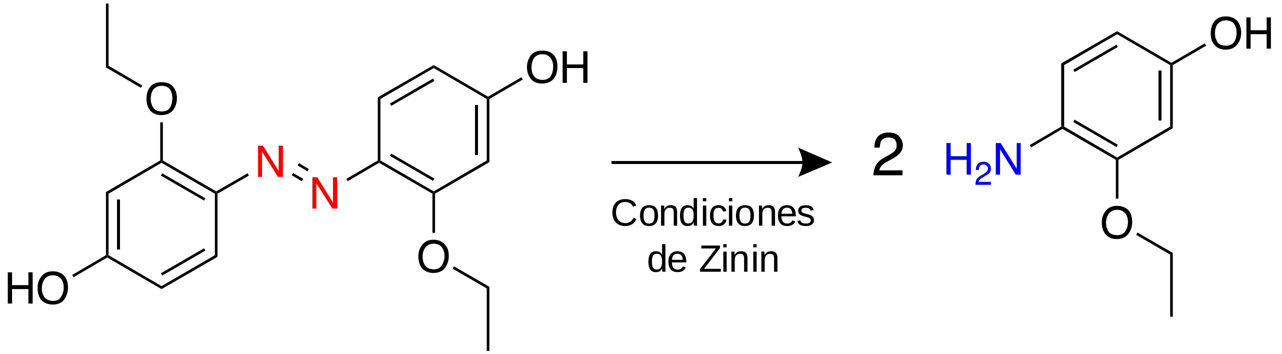


[5] H. Goldschmidt and H. Larsen, *Z. Phys. Chem.* (Leipzig), **71**, 437 (1910).

[22] H. Goldschmidt and H. Larsen, *Z. Phys. Chem.* (Leipzig), **71**, 440 (1910).

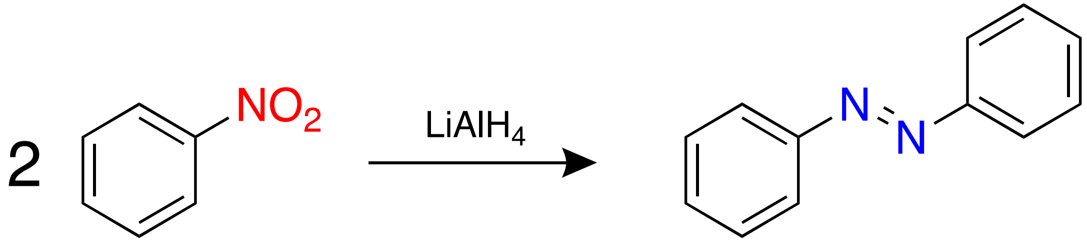
Reacciones secundarias

Ruptura de grupos azo



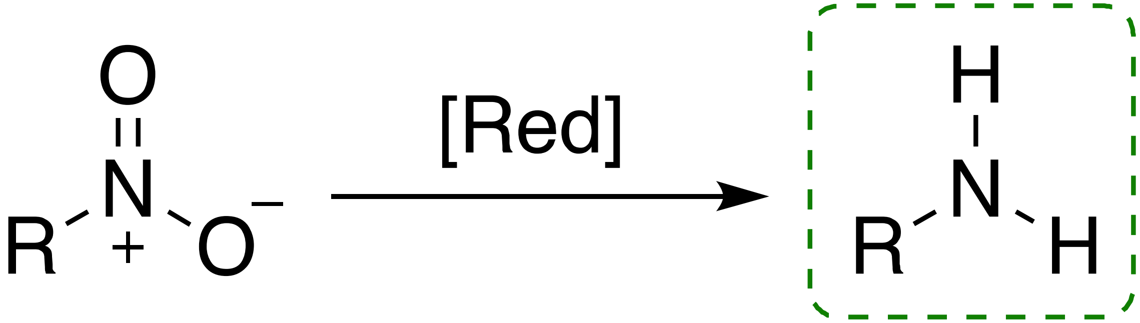
[37] M. Heidelberger and W. A. Jacobs, *J. Amer. Chem. Soc.*, **41**, 1467 (1919).

Irónicamente..



Robert F. Nystrom, and Weldon G. Brown. *J. Am. Chem. Soc.*, **1948**, 70 (11), 3738-3740.

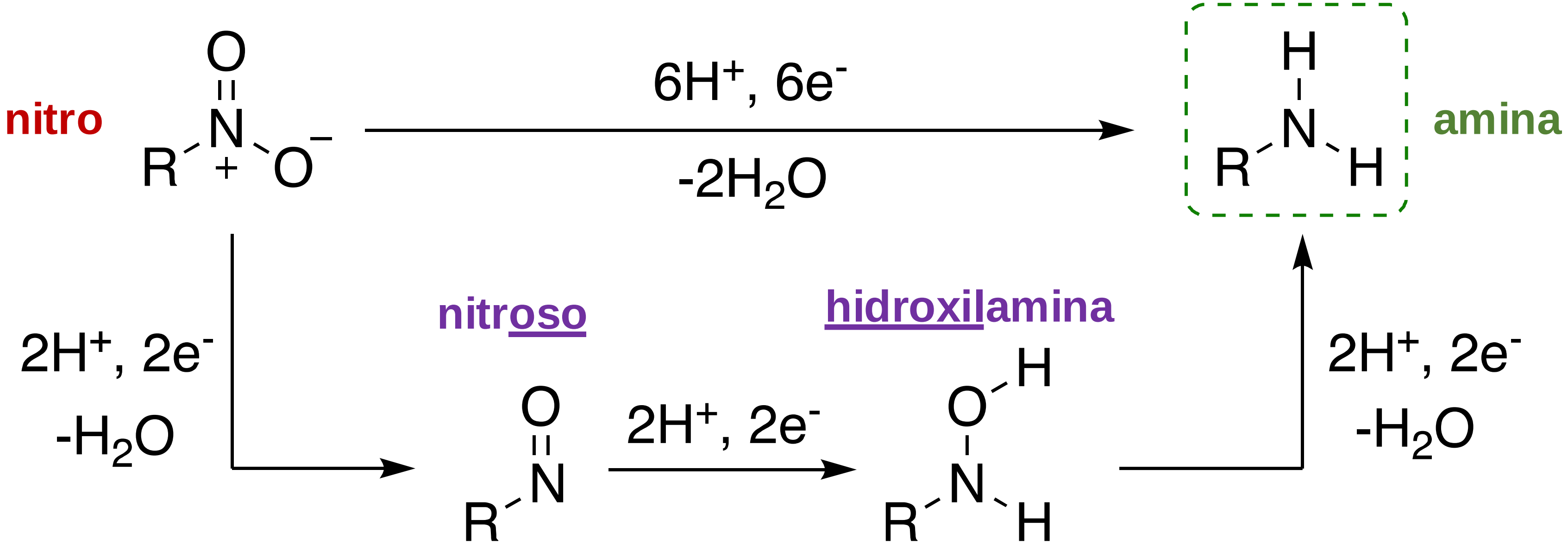
Otros agentes reductores:



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

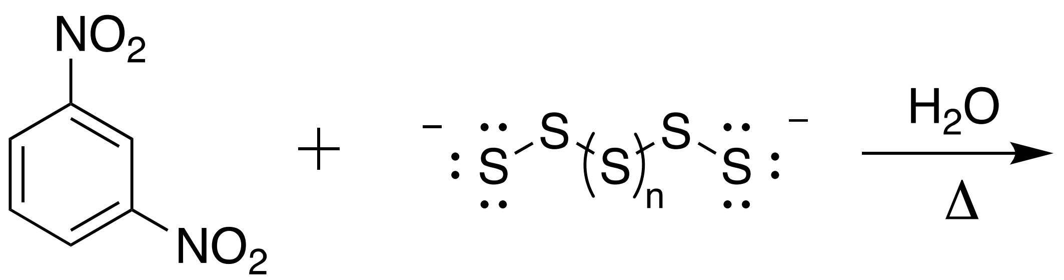
- Pd / H_2
- $Na_2S_2O_4$ / H_2O
- SmI_2

Proceso general de reducción de un grupo nitro

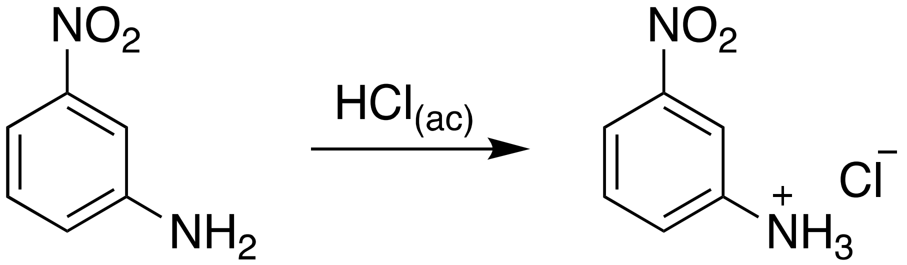


$$Na_2S + S_8^{0} \xrightarrow[\Delta]{H_2O} Na_2S_x$$

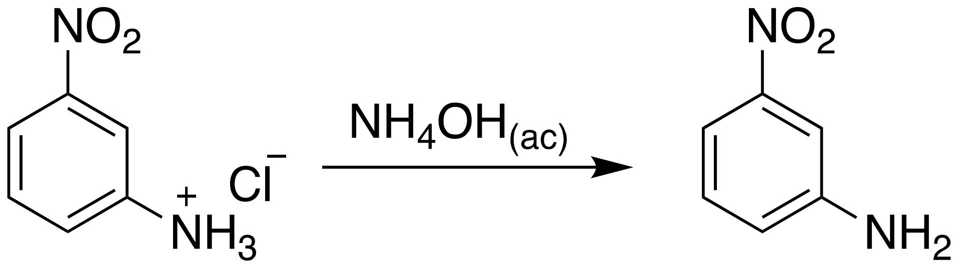
Paso 1: Formación del polisulfuro



Paso 2: Reducción



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



Paso 4: Desprotonación de la sal de amonio (precipitar la amina)