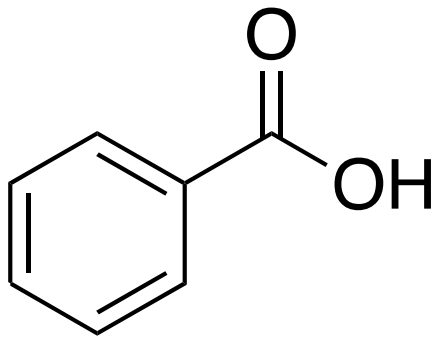
Universidad Nacional Autónoma de México

Química Orgánica IV (1606)
Laboratorio
Semestre 2025 - 2

M. en C. Arturo García Zavala



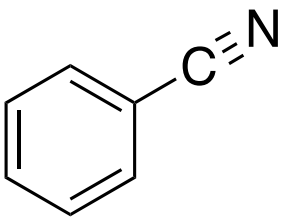
Práctica 2

Ácidos carboxílicos II

Reacción de haloformo

24/2/2025

Síntesis de ácidos carboxílicos

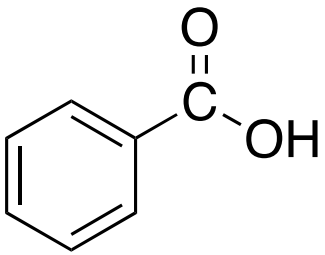


Nitrilos

H_2O, OH^- Δ o

H_2O, H^+ Δ

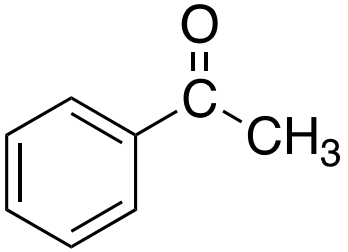
Hidrólisis de nitrilos



NaClO

$NaHSO_3$

Reacción de haloformo

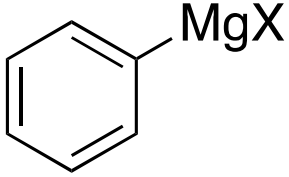


Metil-cetonas

Laboratorio de QO IV

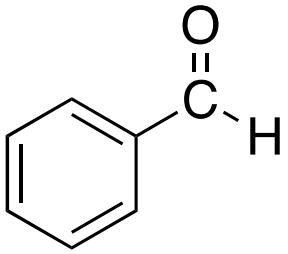
Carboxilación de Grignard

CO_2

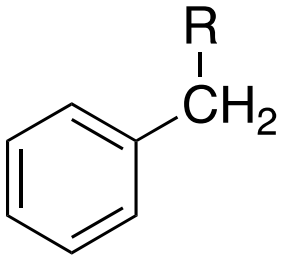


Reactivo de Grignard

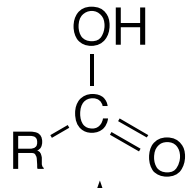
Oxidaciones



Aldehídos

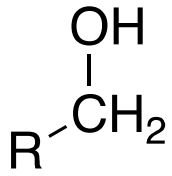


Alquilbencenos



[O]

Alcoholes primarios

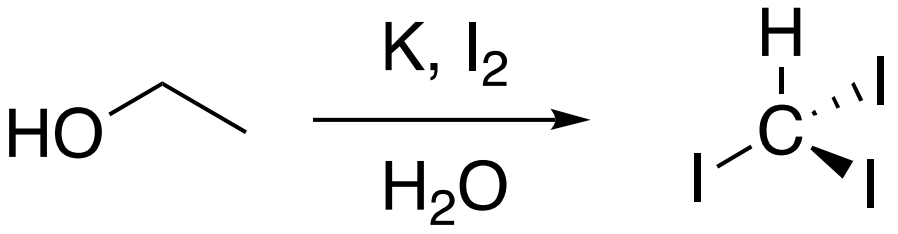


M. en C. Arturo García Zavala

Reacción del haloformo

Georges-Simon Serullas
(1774 - 1832)

1822



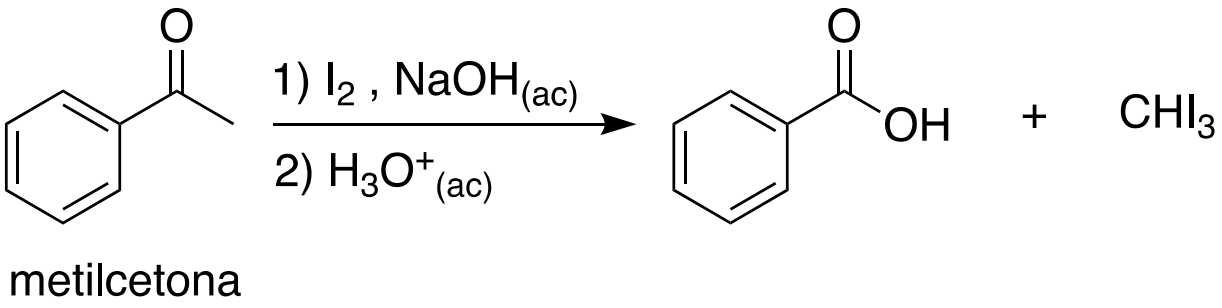
Obtención de yodoformo

G.-S. Serullas, Ann. Chim. Phys. ***1822****, 20, 165–166.*

Reacción del haloformo

Adolf Lieben
(1836 - 1914)

1870's



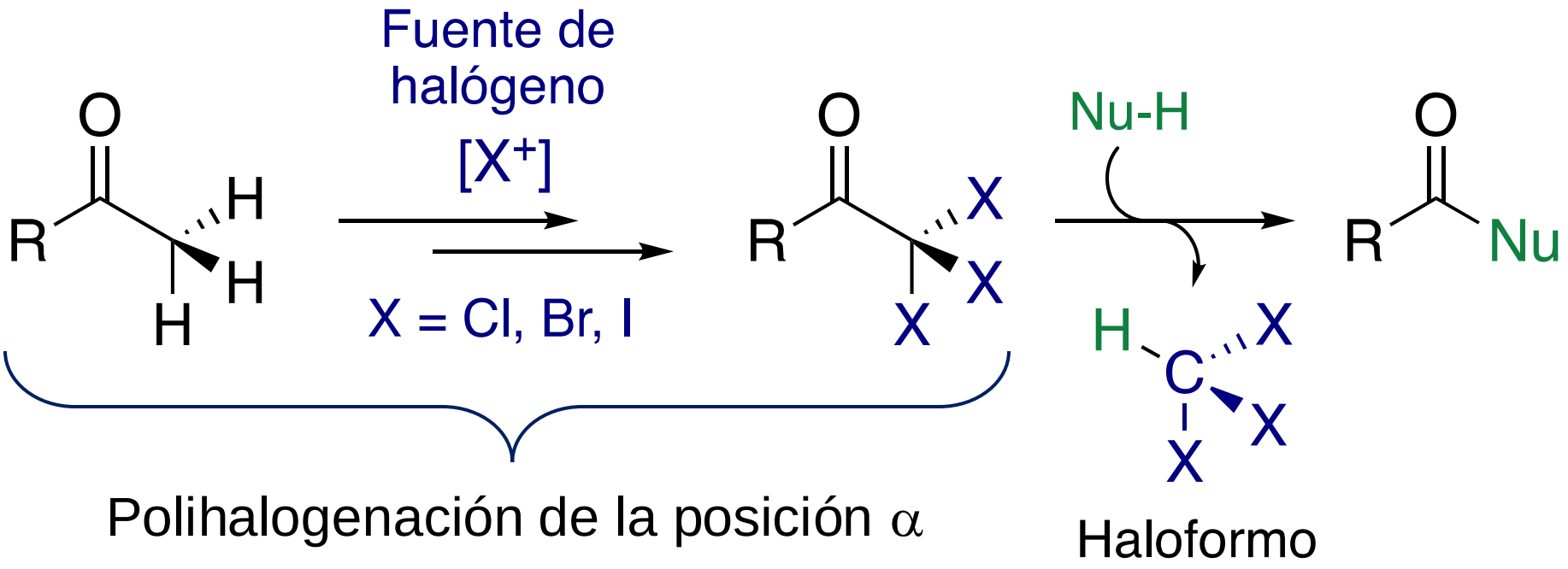
metilcetona

Aplicación en síntesis

G.-S. Annalen der Chemie. Supplementband. ***7****: 218–236.*

Reacción del haloformo

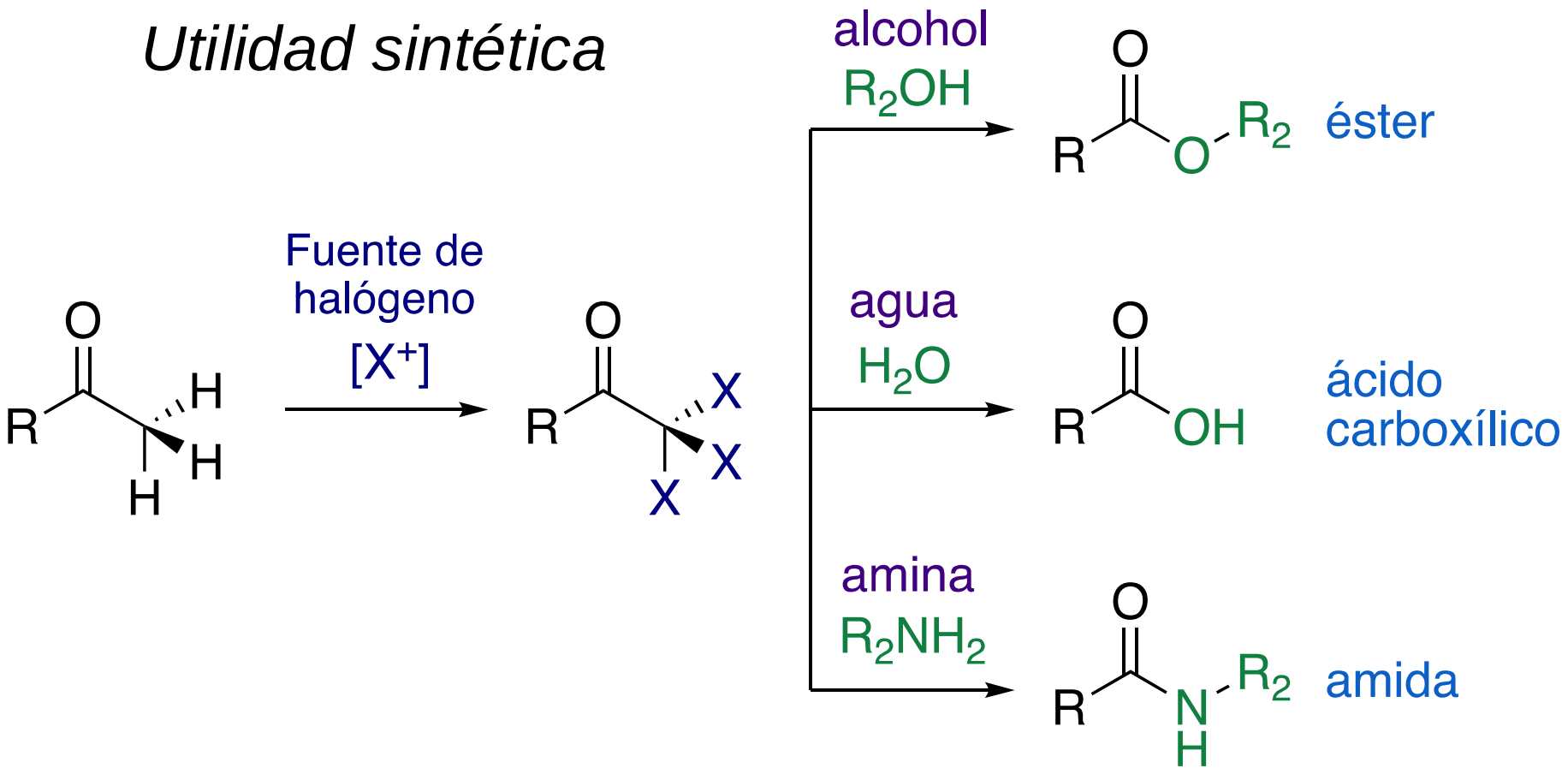
Desmetilación oxidativa de metilcetonas



Chem. – A Eur. J. **2024**, *30* (71), e202403045.

Reacción del haloformo

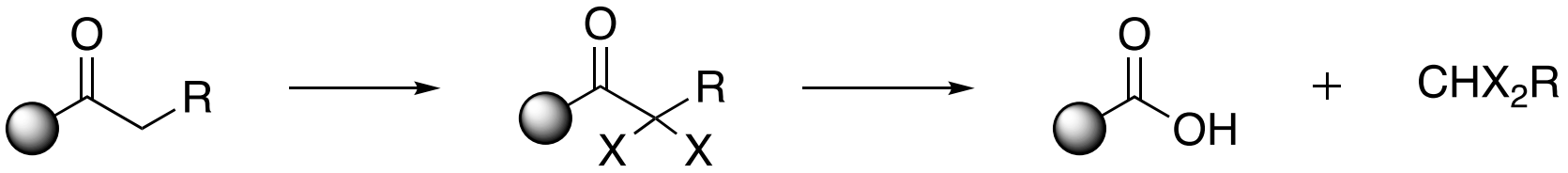
Utilidad sintética



Chem. – A Eur. J. **2024**, *30* (71), e202403045.

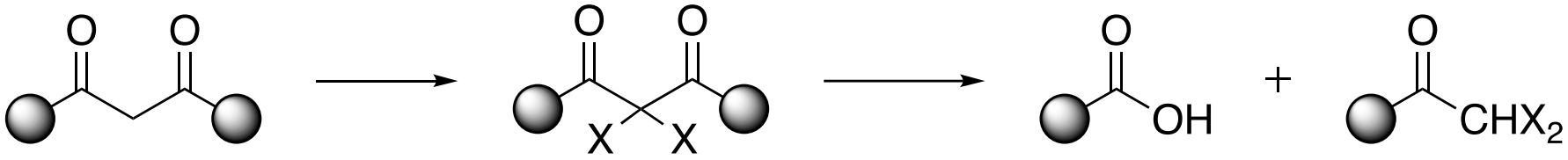
Utilidad sintética

alquilcetonas



R = H, Alquilo

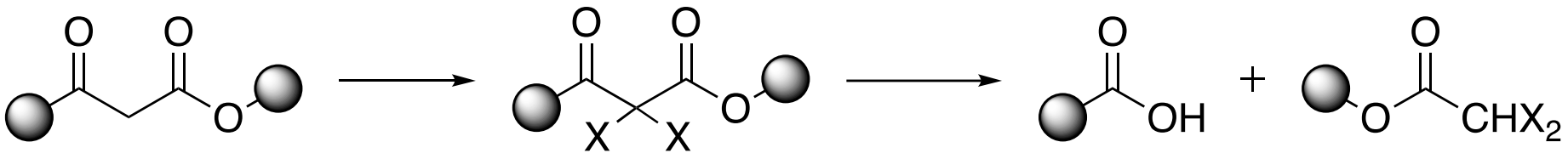
1,3-dicetonas



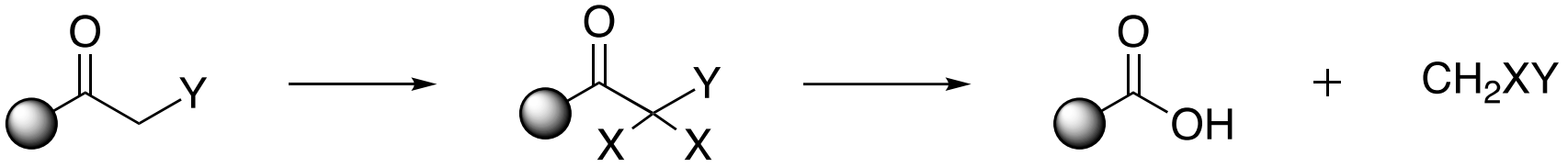
Chem. – A Eur. J. **2024**, *30* (71), e202403045.

Utilidad sintética

β-cetoésteres



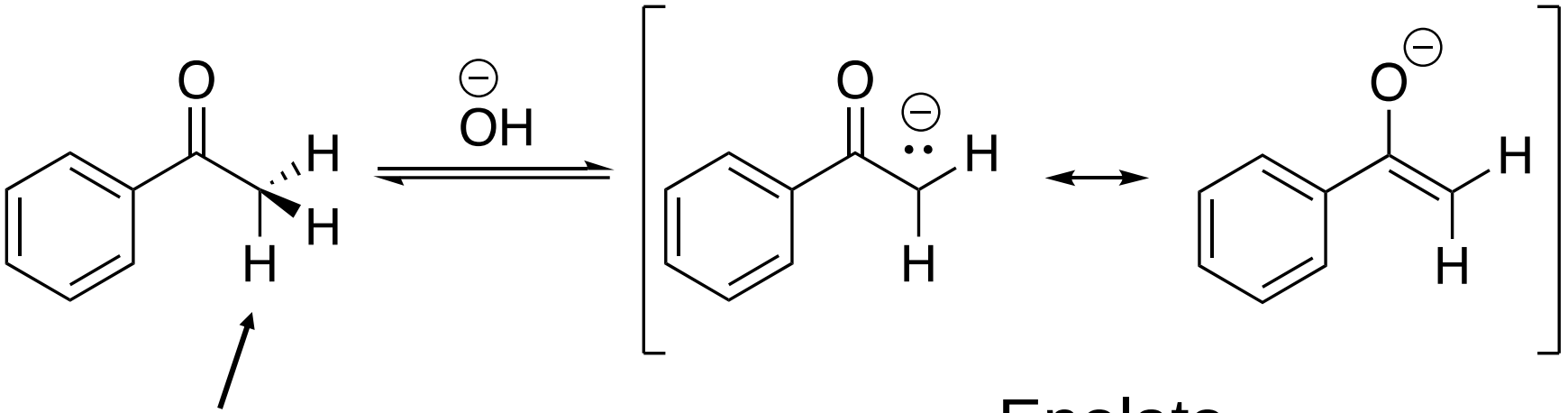
α-nitro/arilcetonas



Y = NO_2, Arilo

Chem. – A Eur. J. **2024**, *30* (71), e202403045.

Desprotonación del carbono alfa (α)

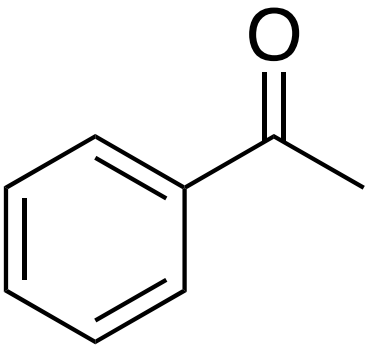


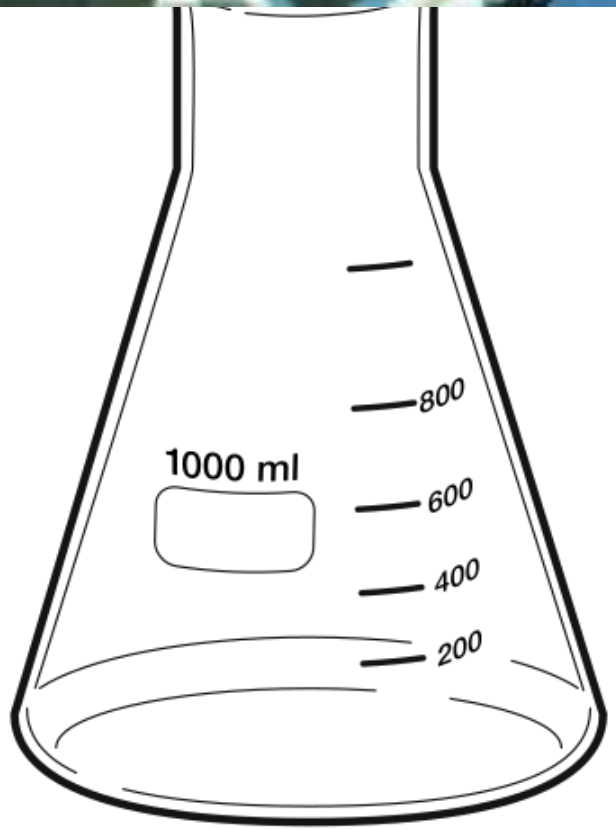
pK_a = 15.8

Enolato

Estabilizado por resonancia

¿De dónde viene el hidróxido?





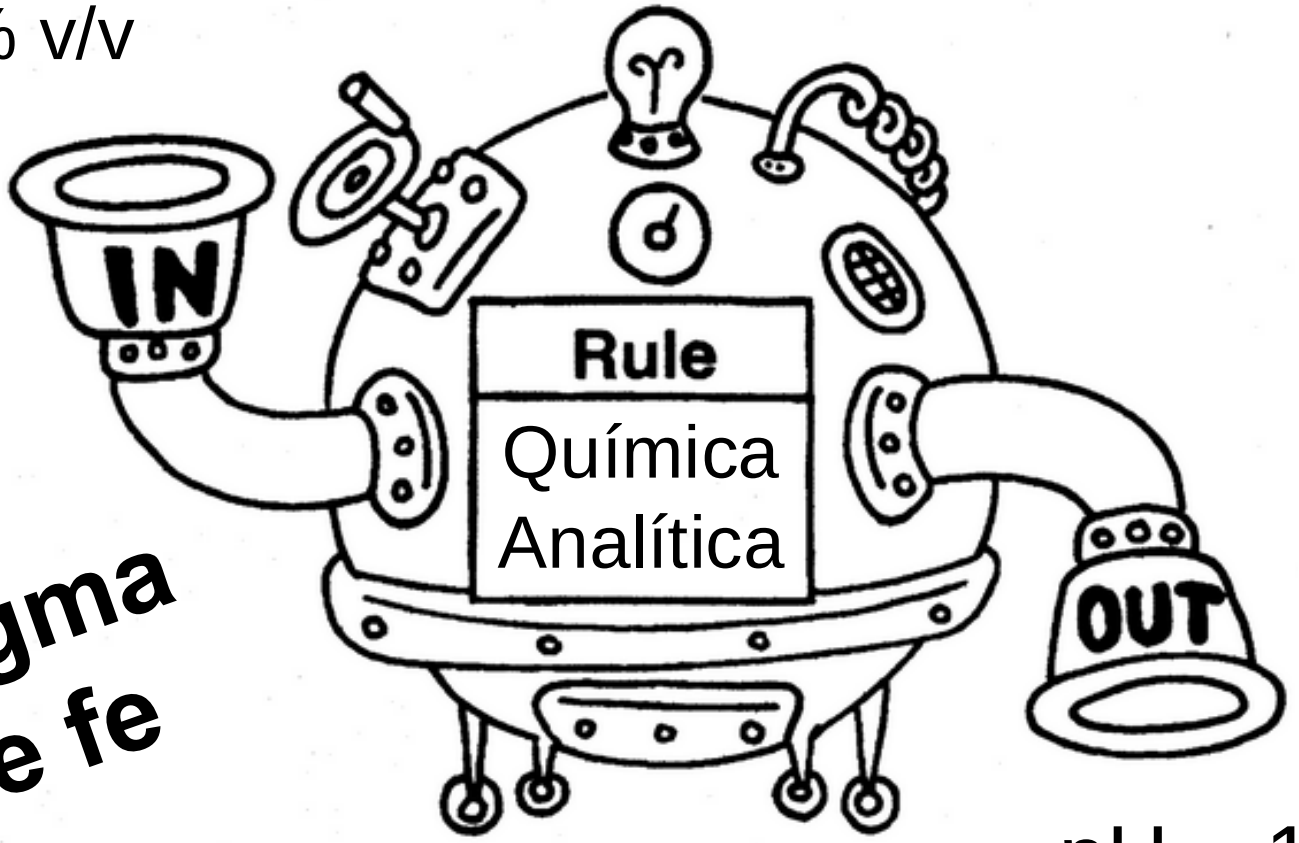
NaClO

H_2O

$ClO^- + H_2O \leftrightharpoons OH^- + HClO$

$pK_a = 7.54$

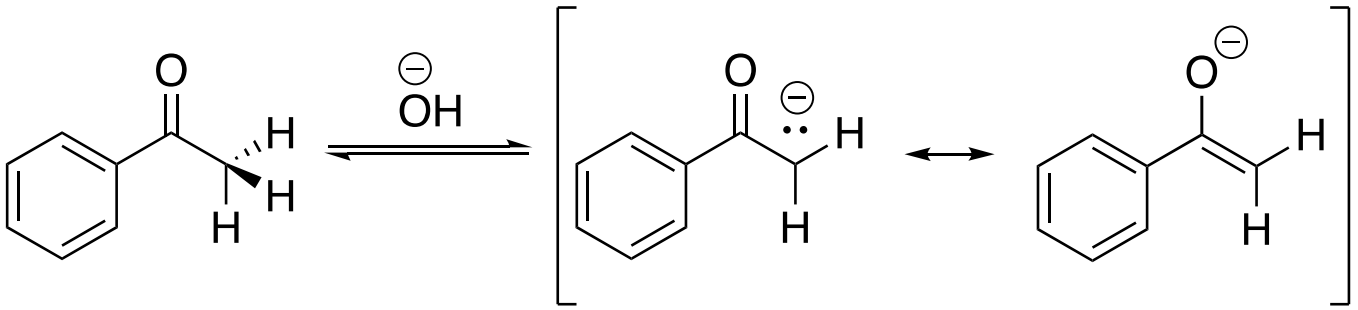
13 % v/v



Dogma de fe

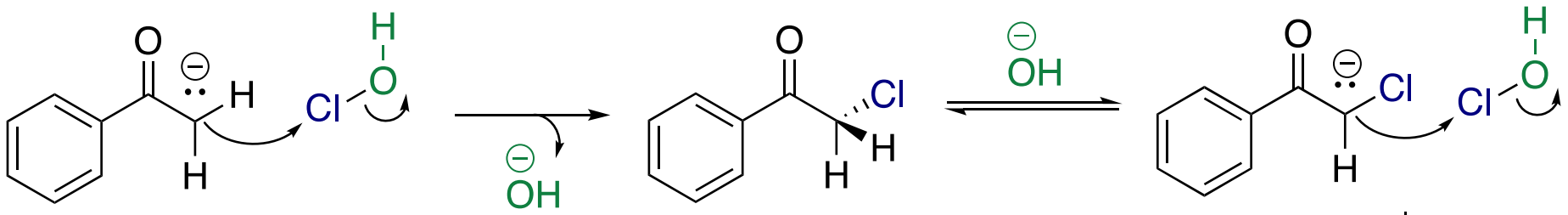
pH = 11

Mecanismo

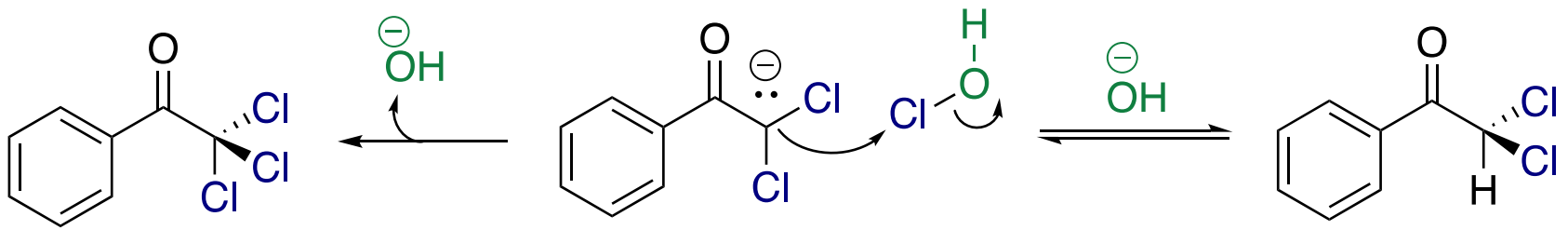


Formación de enolato: paso lento.

Limitante de rapidez



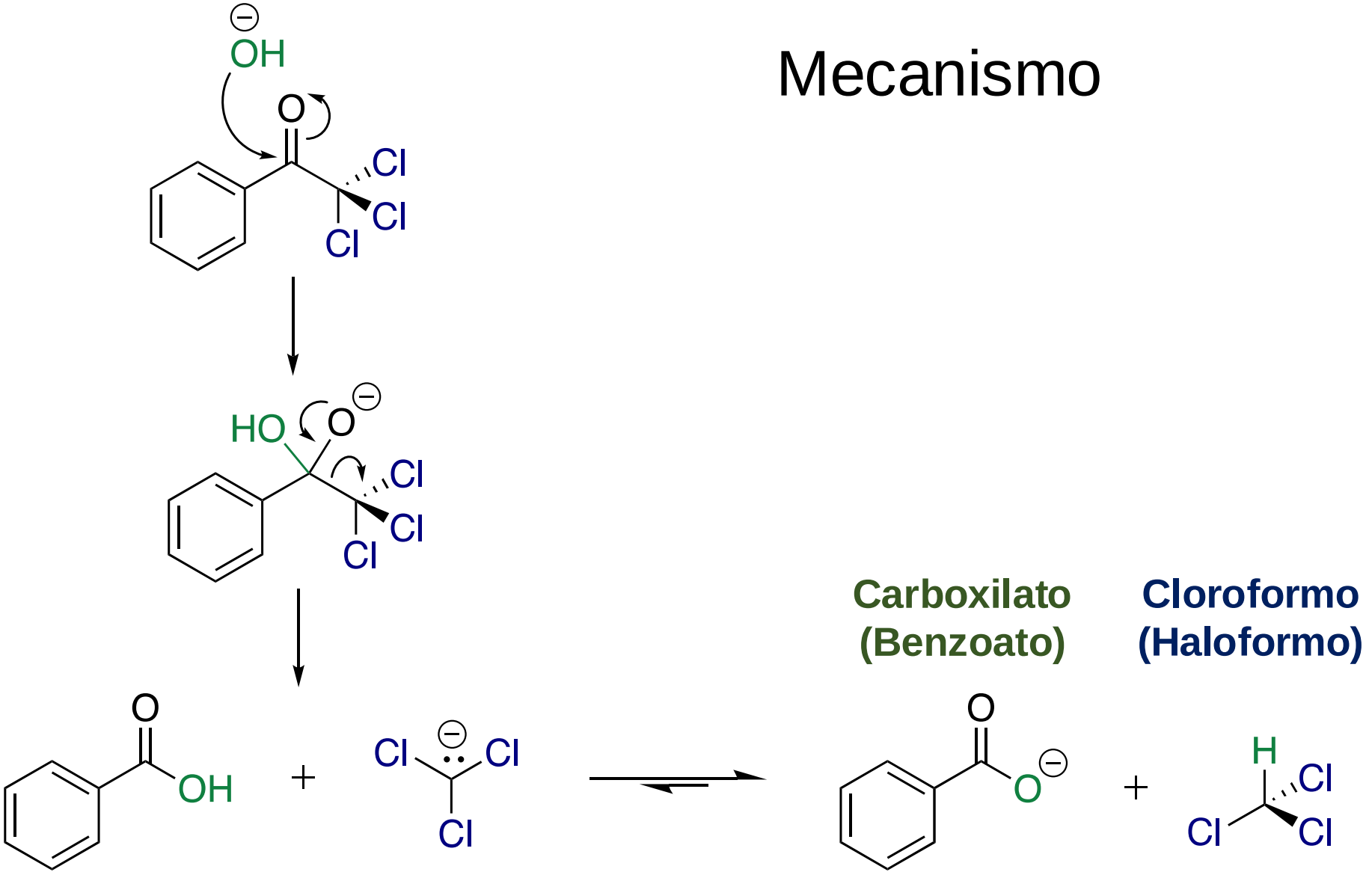
α–clorocetona



α,α,α–triclorocetona

α,α–diclorocetona

Mecanismo



Carbanión estabilizado por efecto inductivo (-I)

-Neutralización del hipoclorito remanente

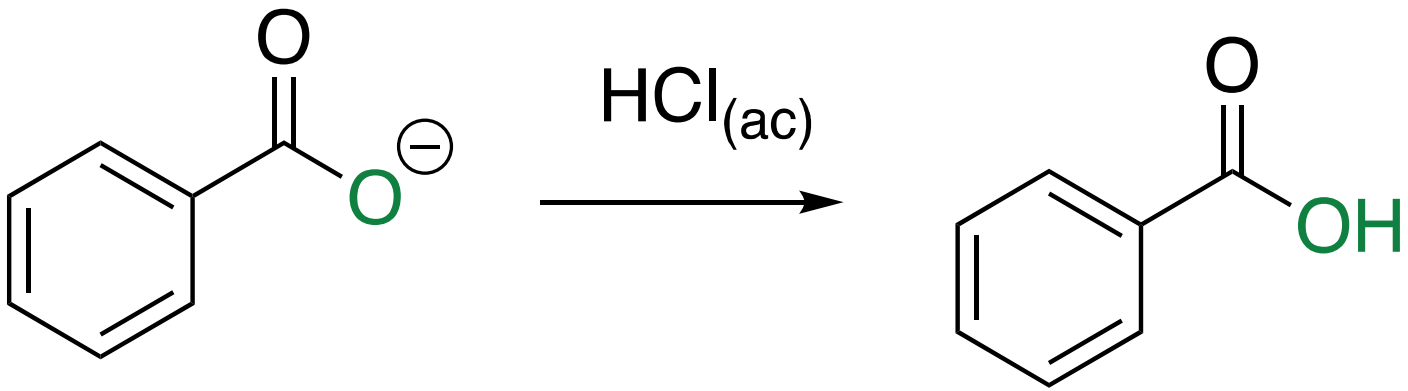
$$ClO^- + HSO_3^- \rightarrow HSO_4^- + Cl^-$$

-Prueba con disolución ácida de KI

Reacción positiva (ClO^- remanente)

$$ClO^- + 2I^- + 2H^+ \rightarrow Cl^- + \mathbf{I_2} + H_2O$$

Color marrón



Carboxilato (Benzoato)

Ácido benzoico