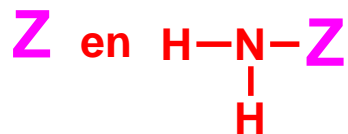
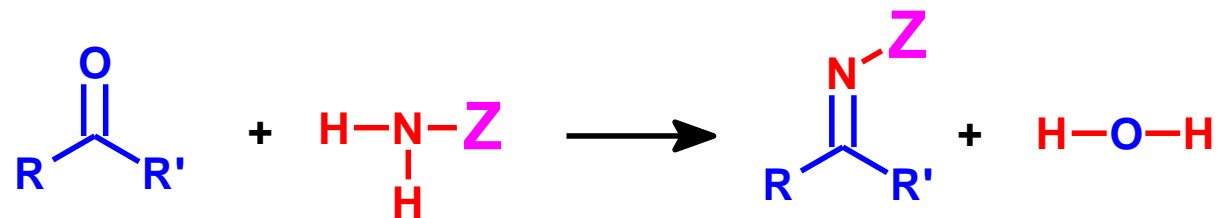


REVISIÓN GRUPO CARBONILO



FORMACIÓN DE IMINAS

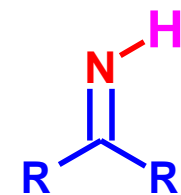




REACTIVO

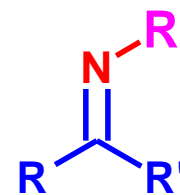
PRODUCTO

—H



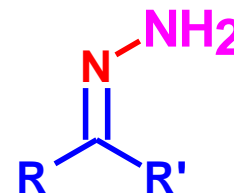
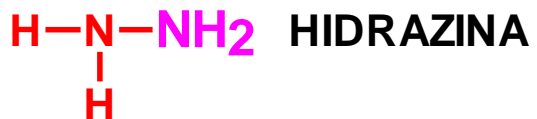
IMINA

—R



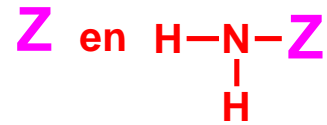
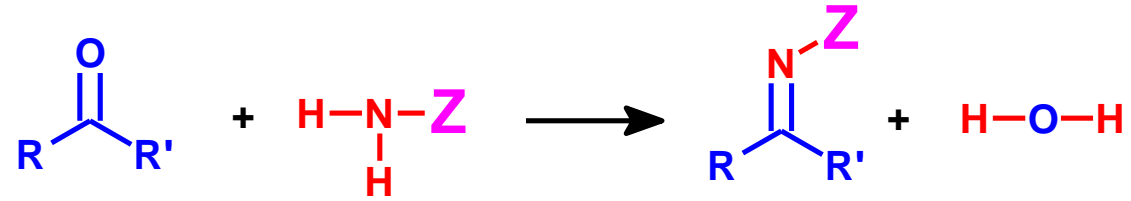
IMINA
BASE DE SCHIFF

—NH₂



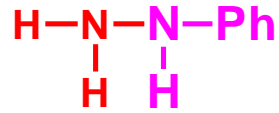
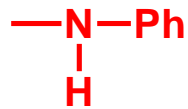
HIDRAZONA



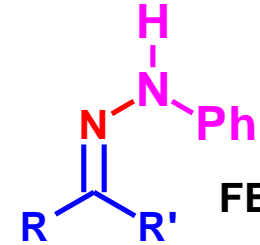


REACTIVO

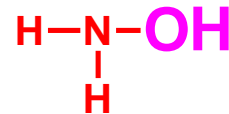
PRODUCTO



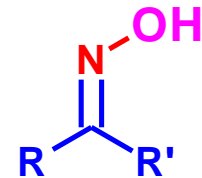
FENILHIDRAZINA



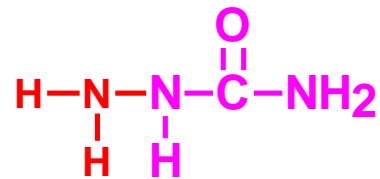
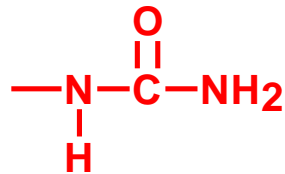
FENILHIDRAZONA



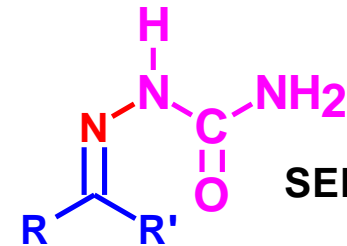
HIDROXILAMINA



OXIMA

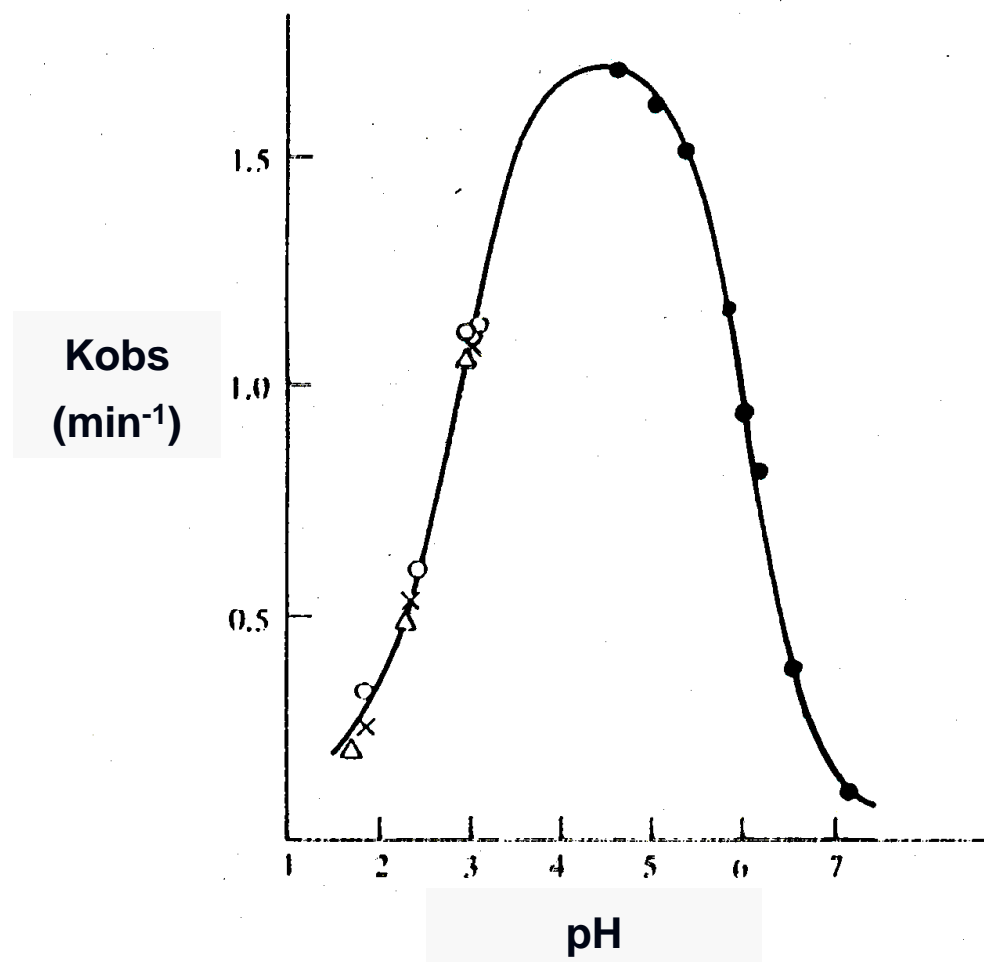
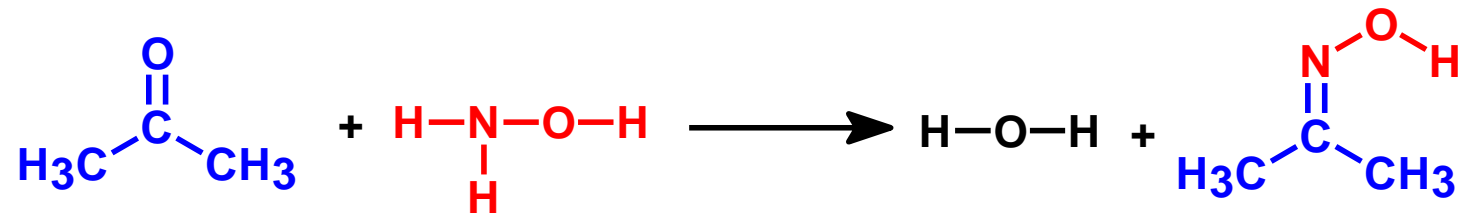


SEMICARBAZIDA



SEMICARBAZONA





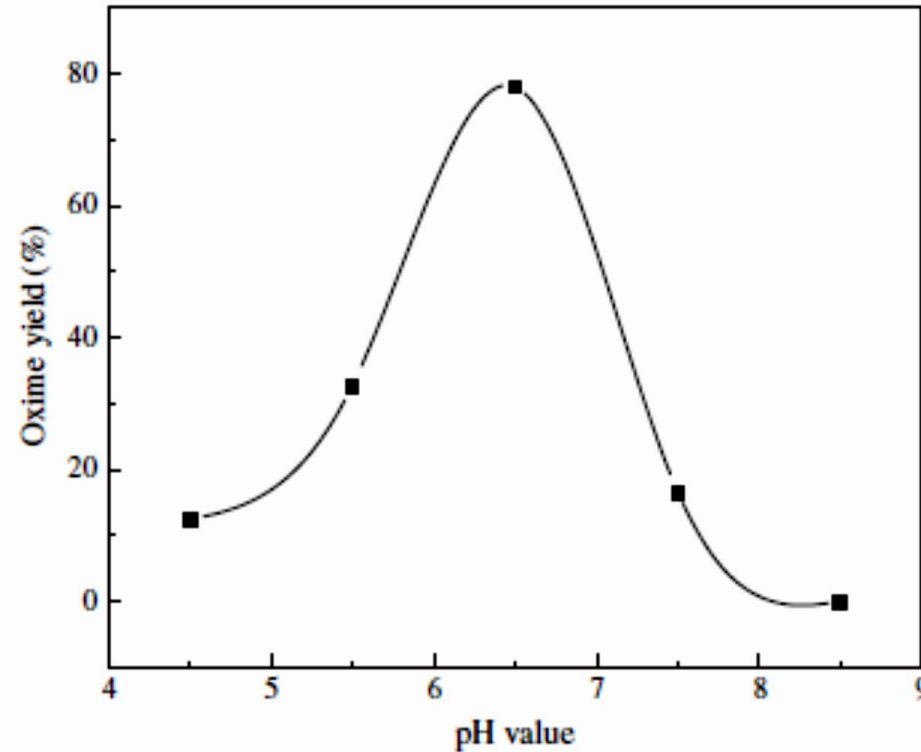
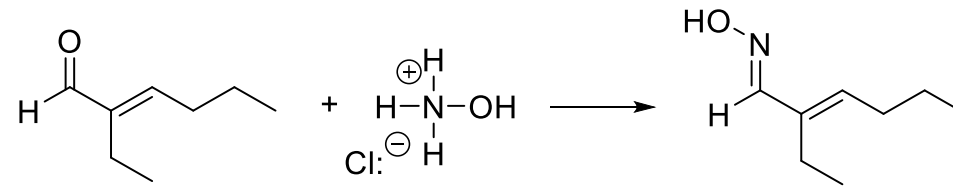
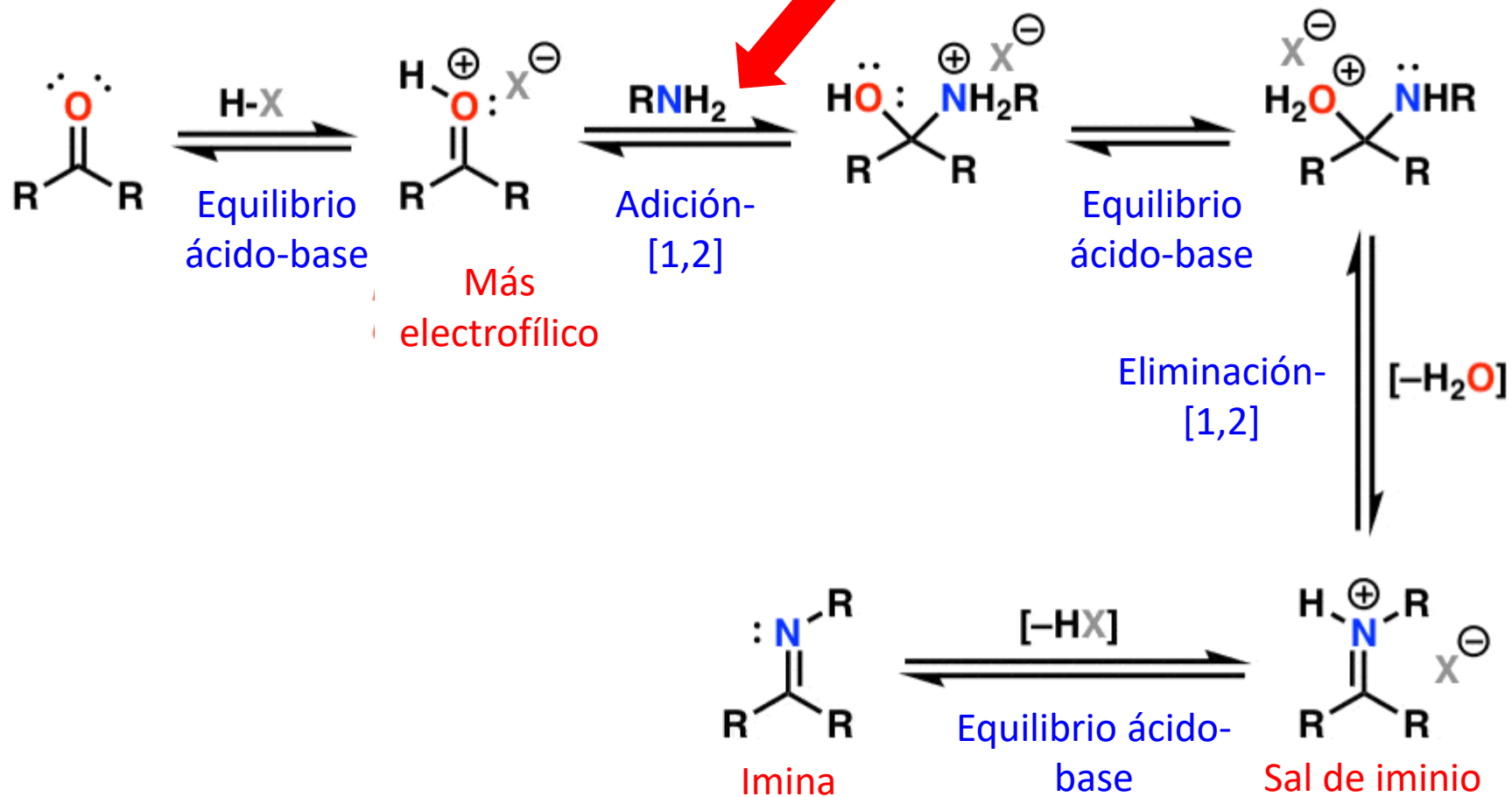


Fig. 5. The effect of pH value on the oximation of 2-ethyl-2-hexenal. Oximation conditions: $\text{NH}_2\text{OH}\cdot\text{HCl}$ /2-ethyl-2-hexenal molar ratio, 1.1; temperature, 45 °C; time, 3 h.

Haifeng Xu^a, Hong Zhong^{a,b,*}, Shuai Wang^{a,b,*}, Yanan Niu^a, Guangyi Liu^a



MECANISMO PARA LA FORMACIÓN DE IMINAS

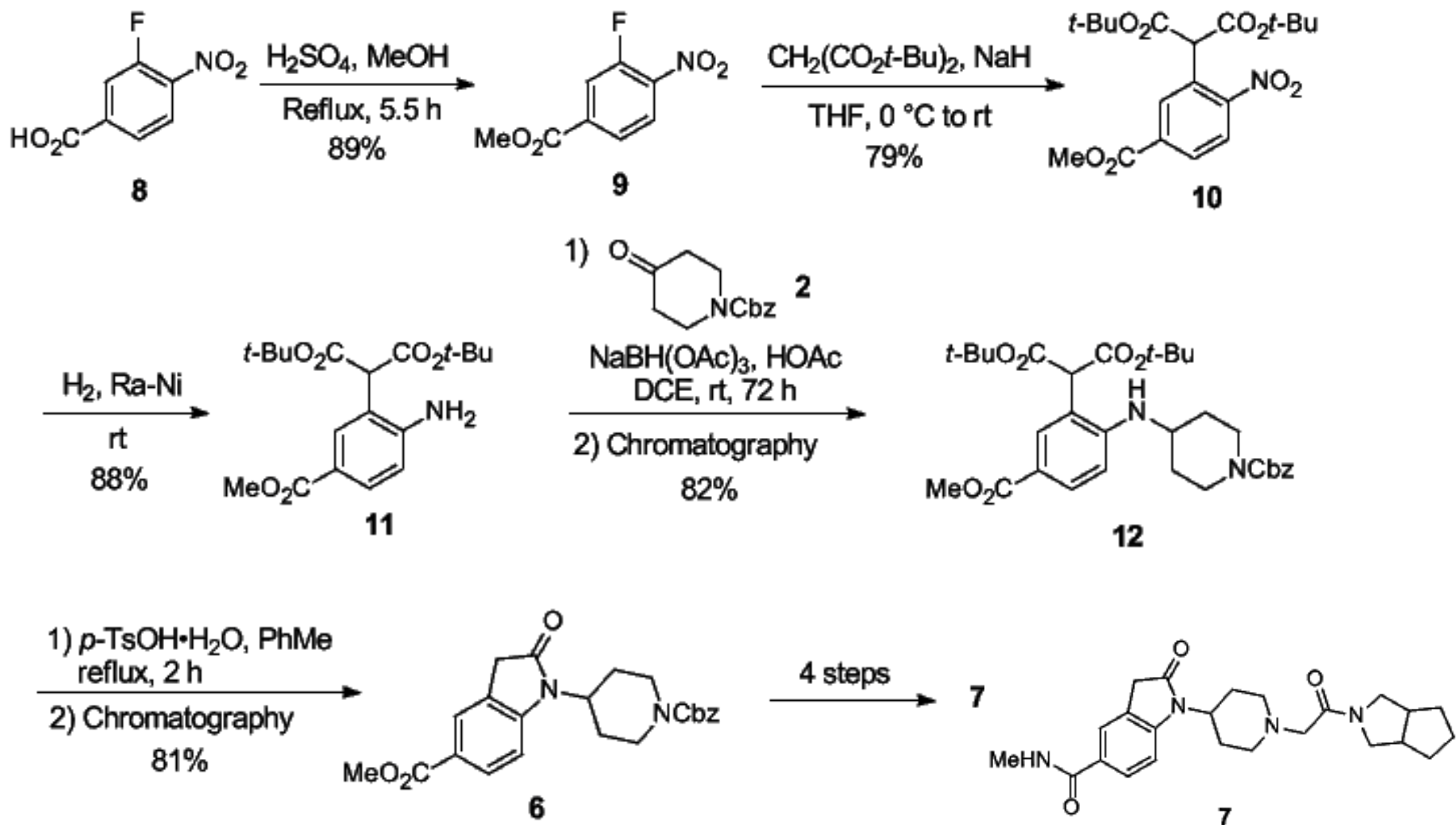


<https://www.masterorganicchemistry.com/2010/05/24/iminines-and-enamines/>



Oxindole Synthesis via Palladium-catalyzed C-H Functionalization

Magano, J.; Jason, E.K.; Shine, R.J.; and Chen, M.H.; *Org. Synth.* **2013**, *90*, 74-86



<http://www.orgsyn.org/content/figures/V90P0074-4.gif>

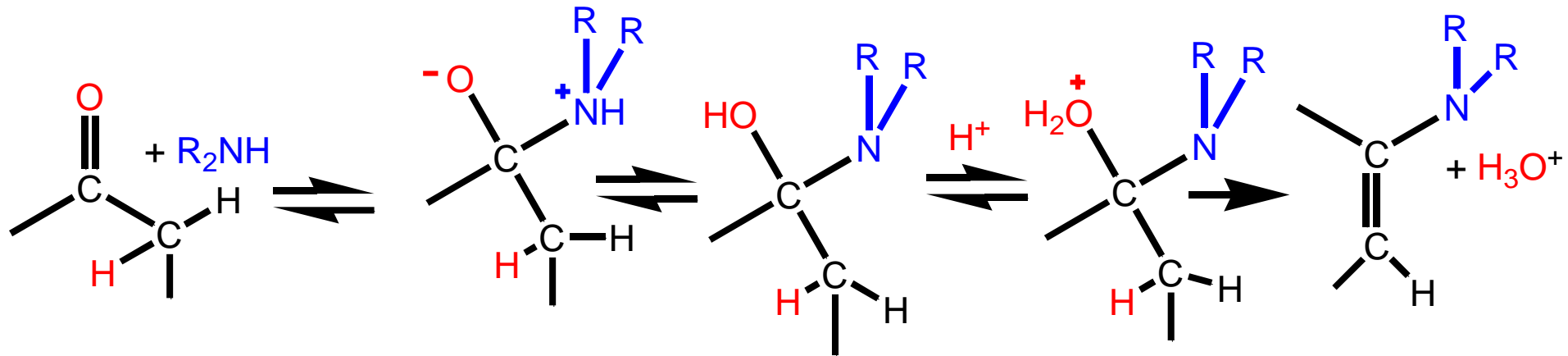


FORMACIÓN DE ENAMINAS



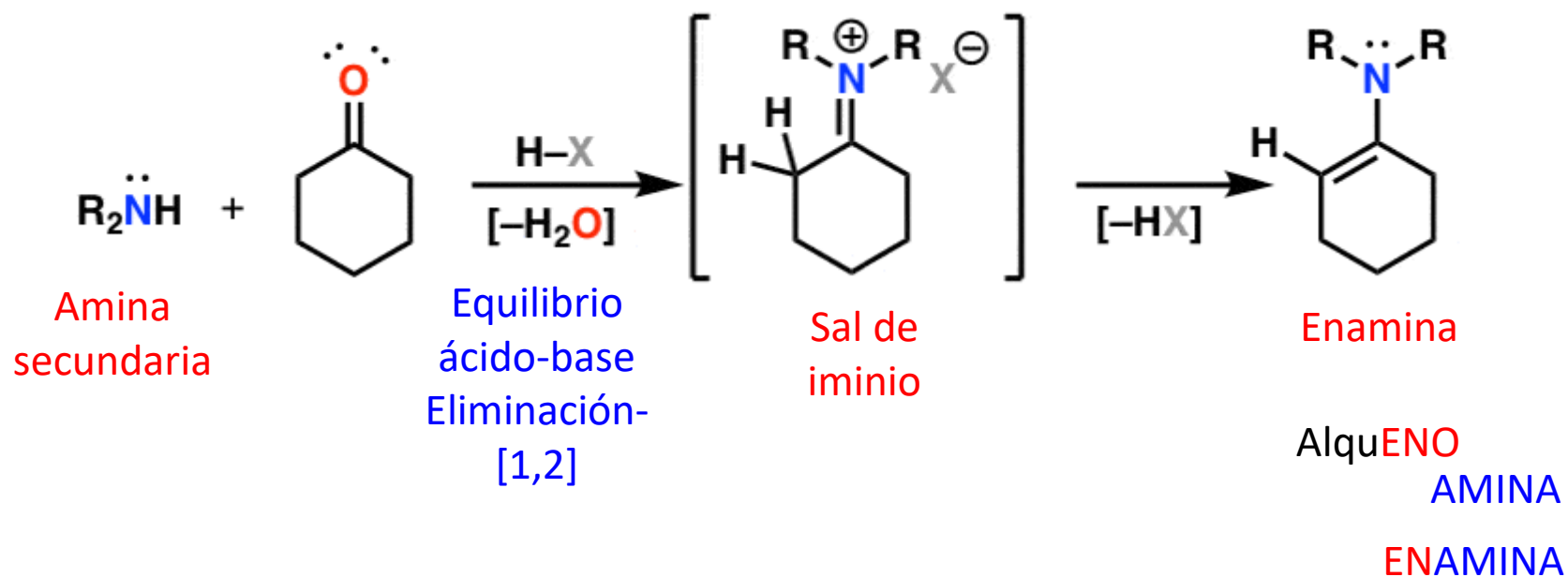
Formación Enaminas

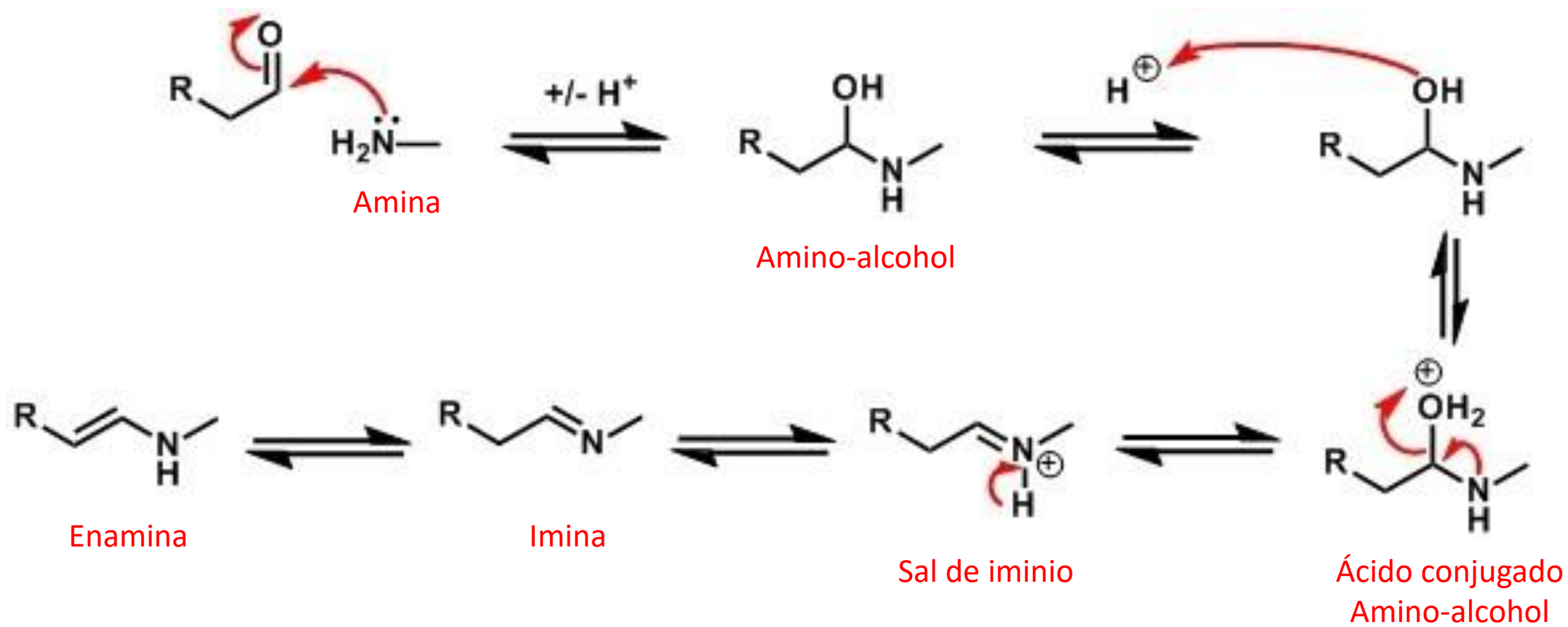
- Después de la adición de R_2NH , el proton se pierde en el átomo de carbono adyacente



Aminas secundarias:

Forman sales de iminio y después forman enaminas





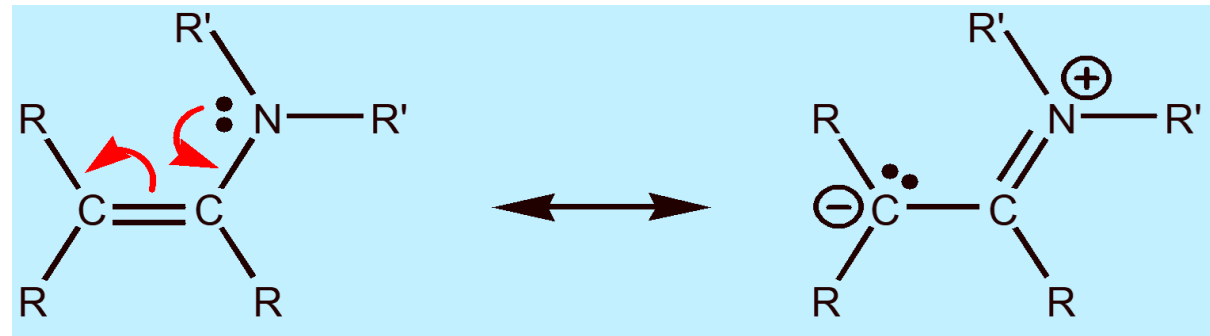
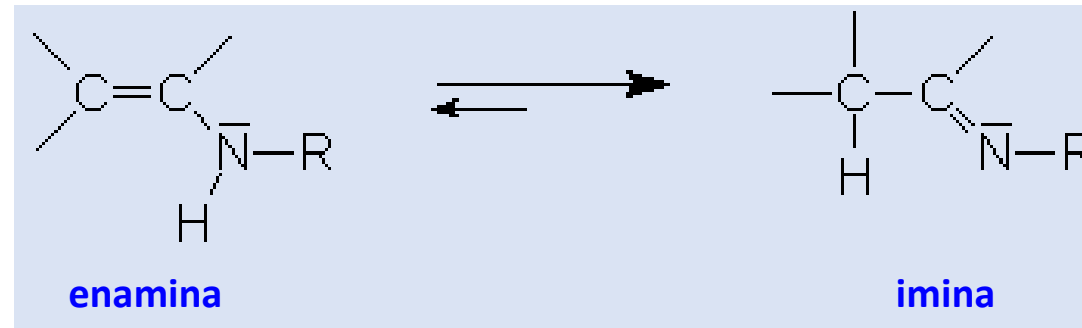


Gilbert Stork

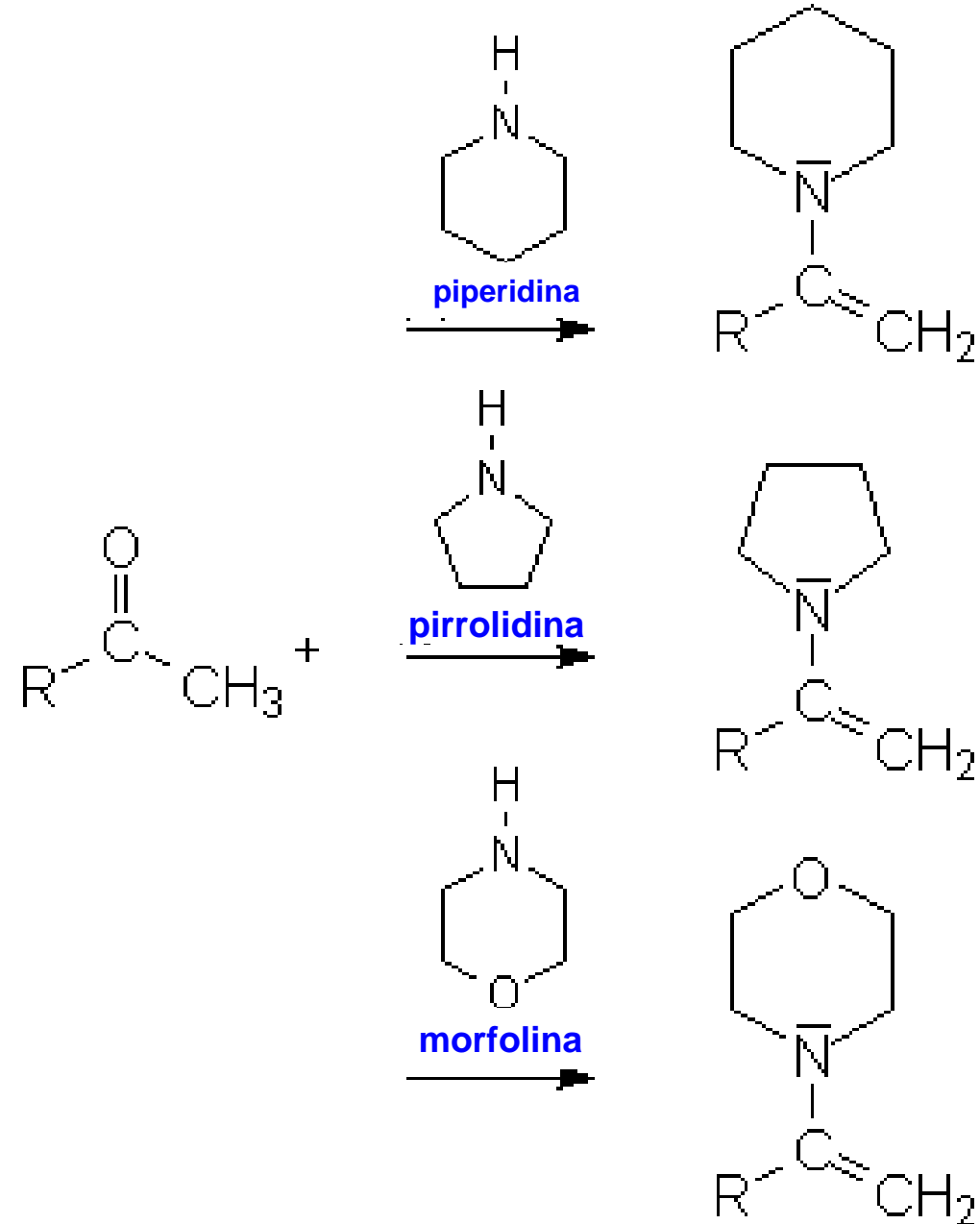
(1921 - 2017)

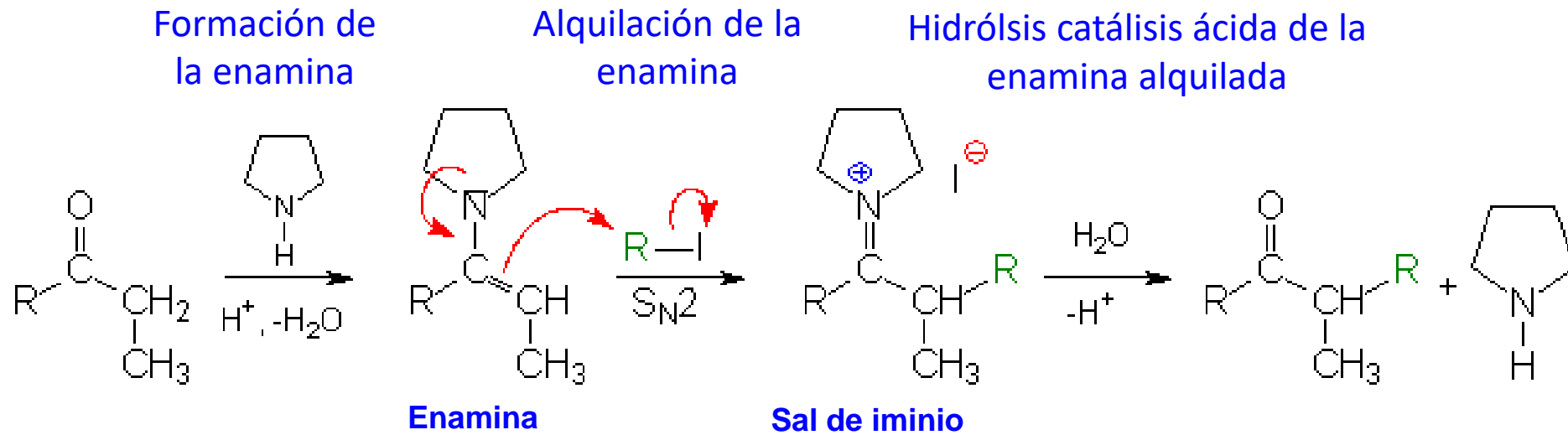
Químico orgánico belga-norteamericano



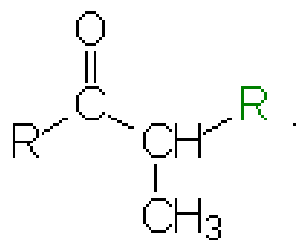


Aminas secundarias más utilizadas



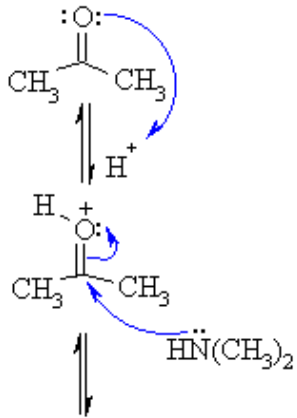


Método para monoalquilar cetonas en posición α

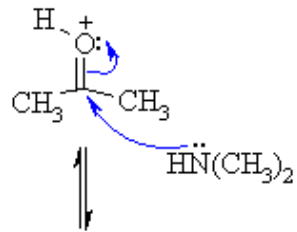


Gilbert Stork and Susan R. Dowd *J. Am. Chem. Soc.*, **1963**, 85(14),2178–80

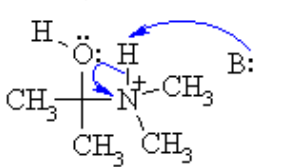




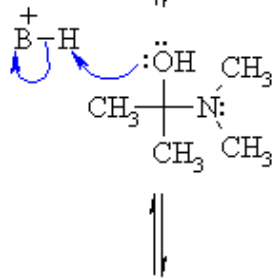
1er. Paso. Activación del grupo carbonilo



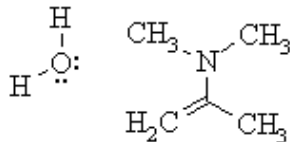
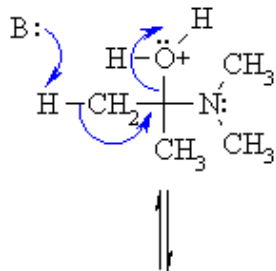
2o. Paso. Adición de la amina 2ª

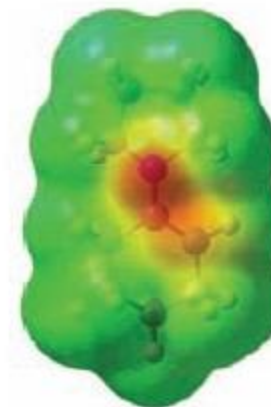
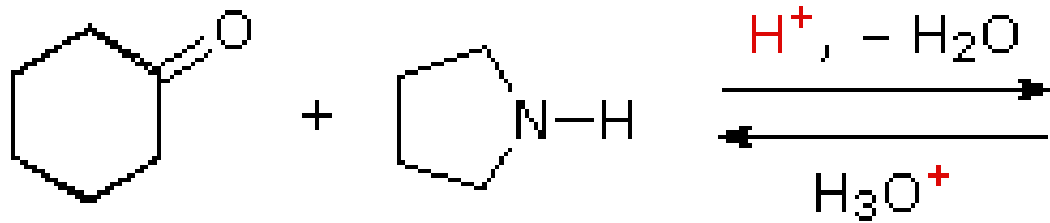
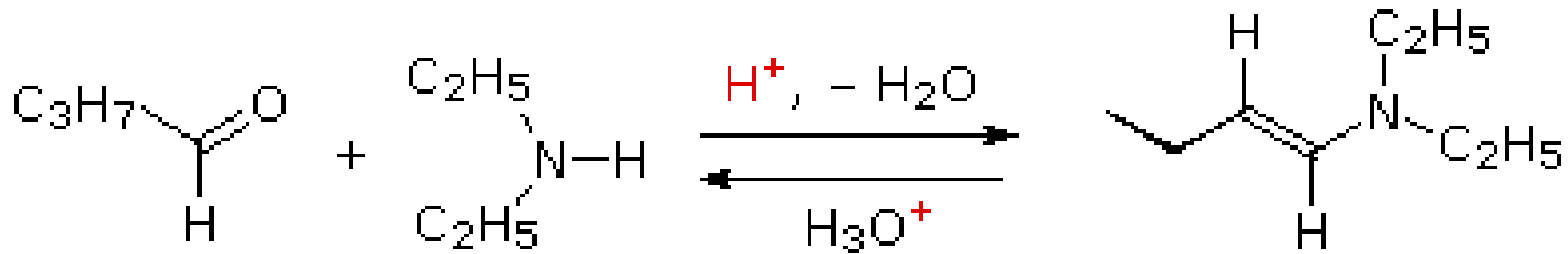


3er. Paso. Equilibrios ácido base
Formación de agua como grupo saliente

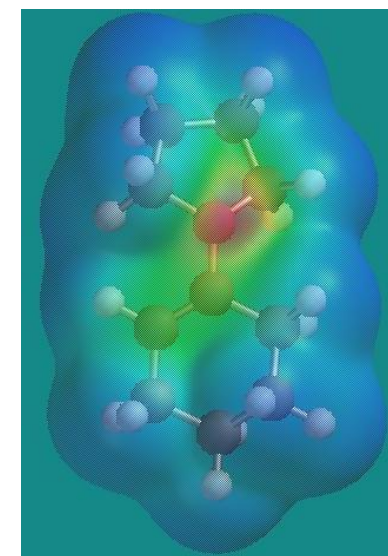
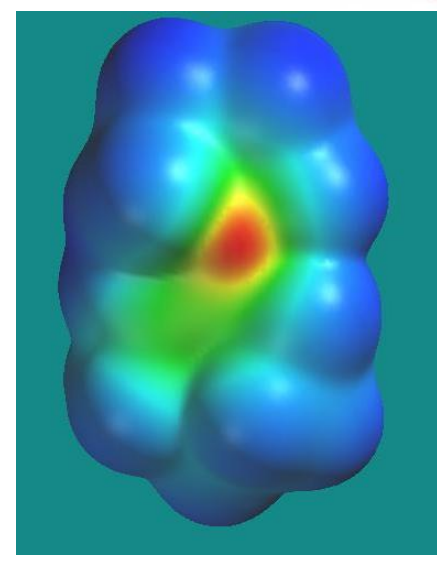
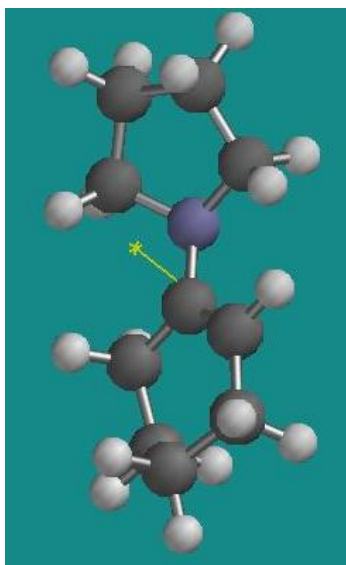


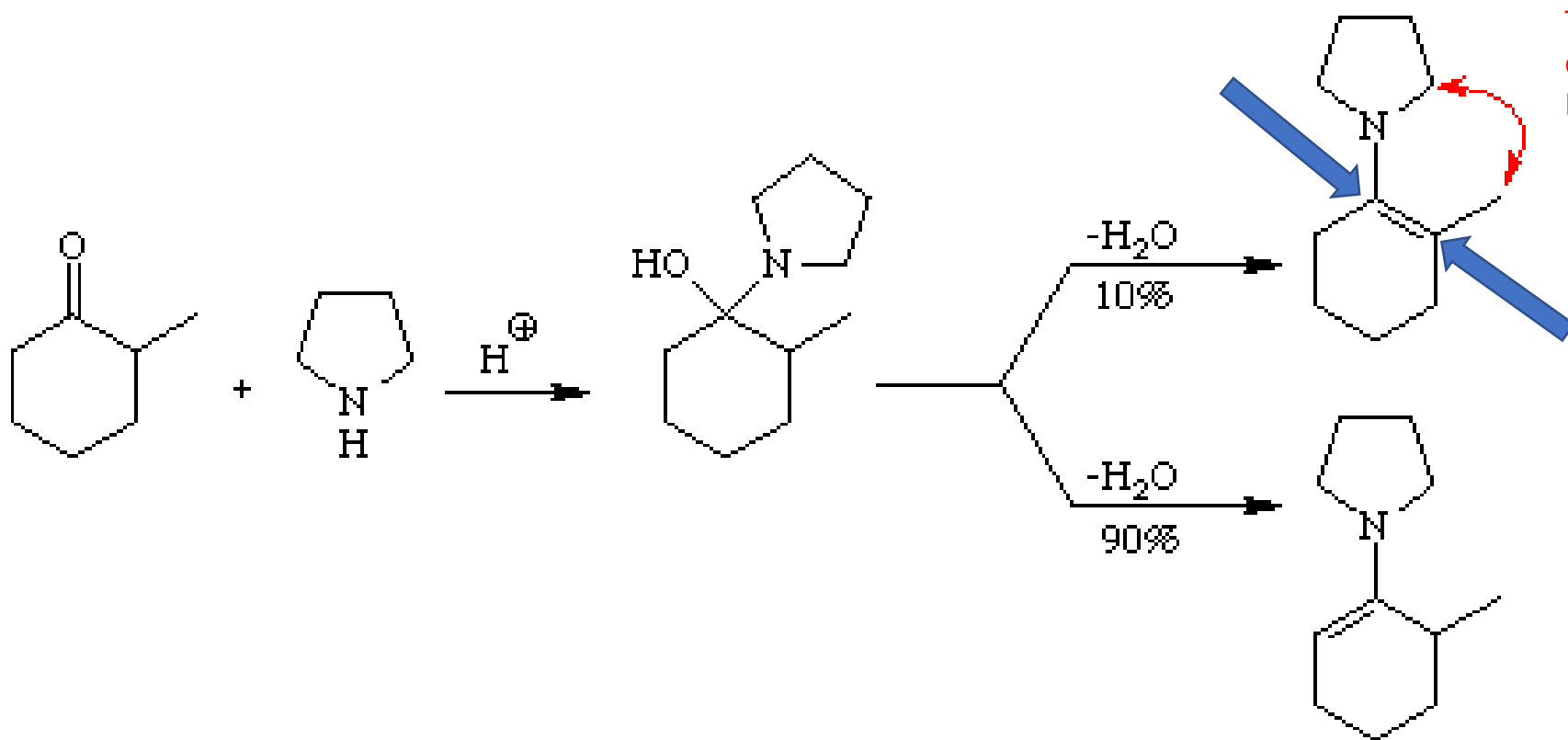
4o. Paso. Eliminación de agua y del protón del carbono β para formar la enamina (pasando por la sal de iminio)





Mapa de potencial
electrostático
Programa Spartan



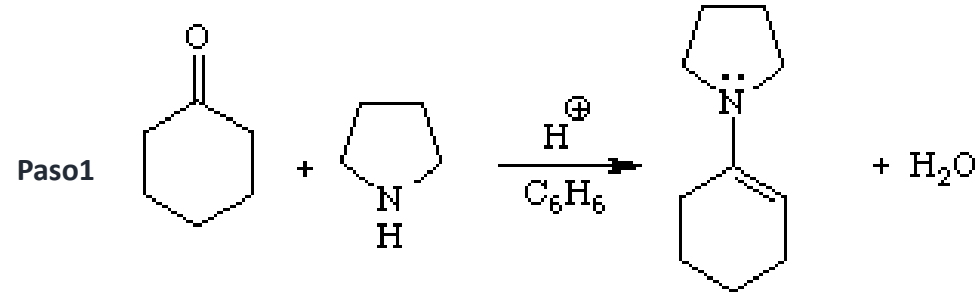


Todos los átomos están en el mismo plano
Impedimento estérico

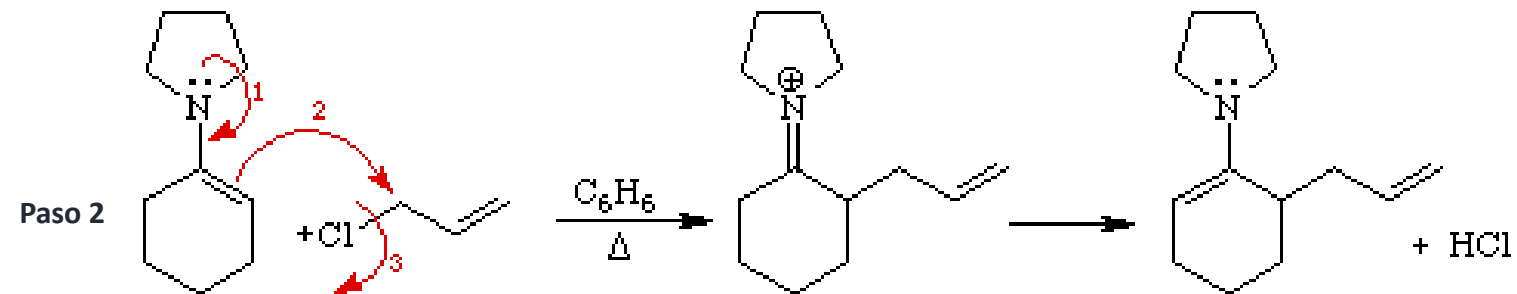
Por impedimento estérico:
siempre se forma la enamina menos impedida



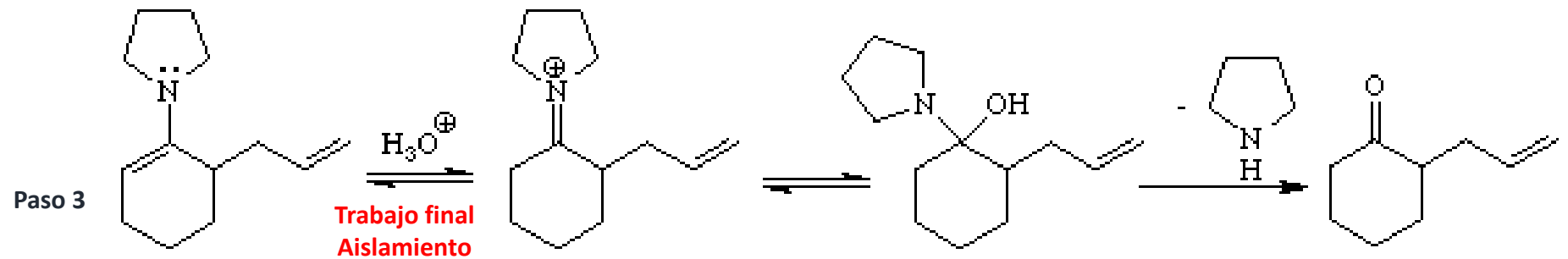
Secuencia sintética a través de la cual se lleva a cabo la monoalquilación de una cetona en posición α



Formación de la enamina

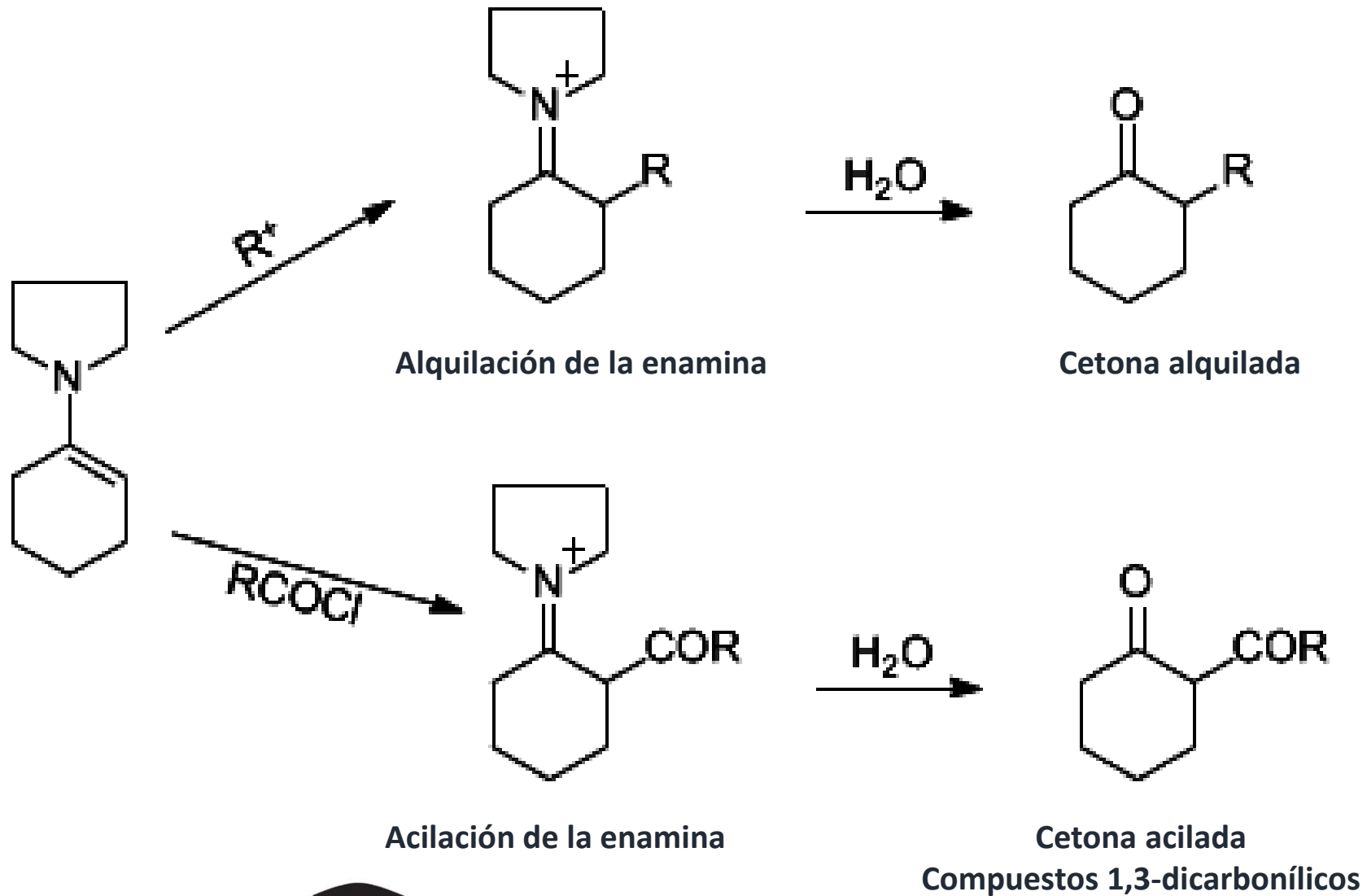


Alquilación de la enamina



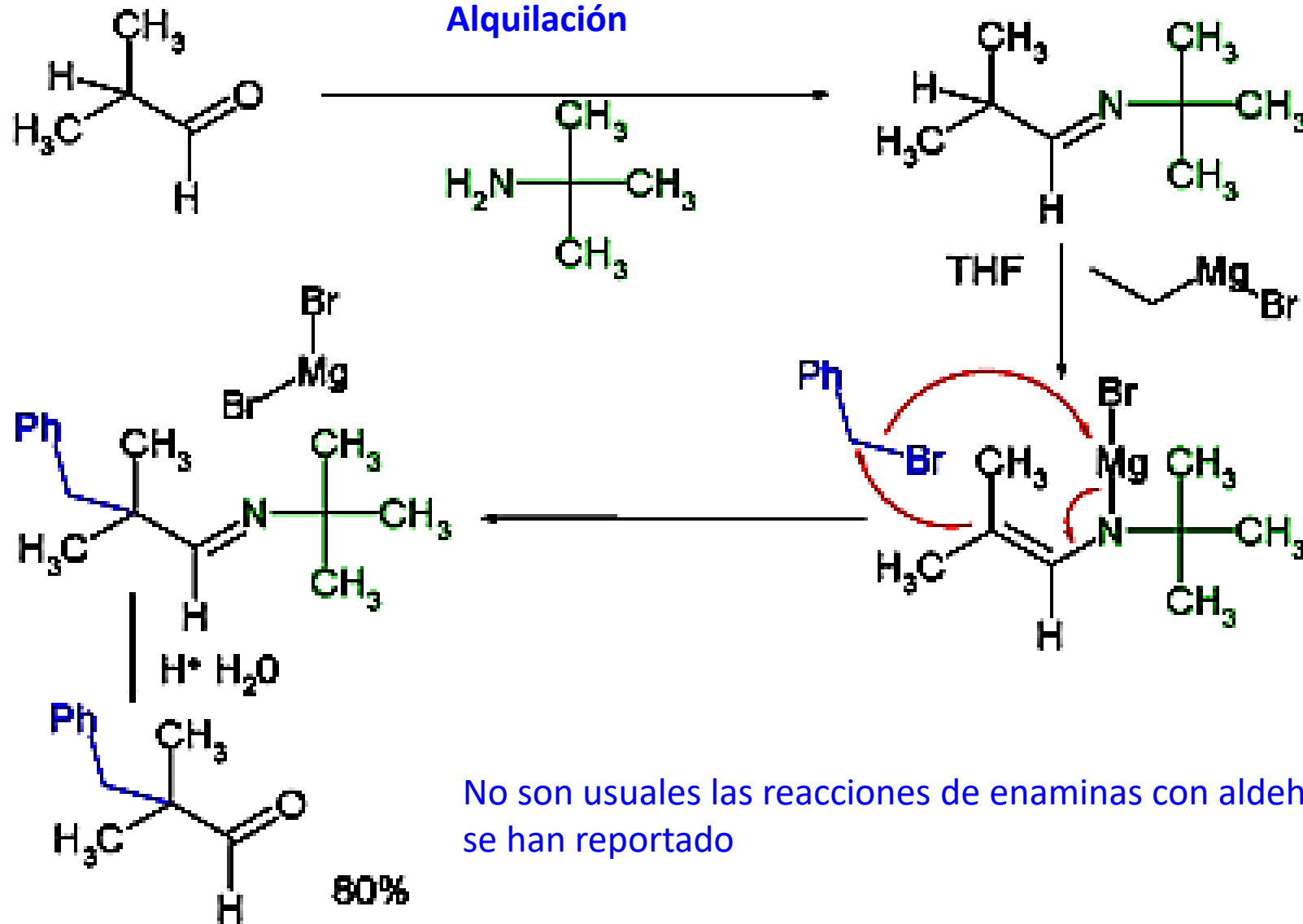
Hidrólisis bajo catálisis ácida de la enamina alquilada





Reacciones de enaminas de aldehídos

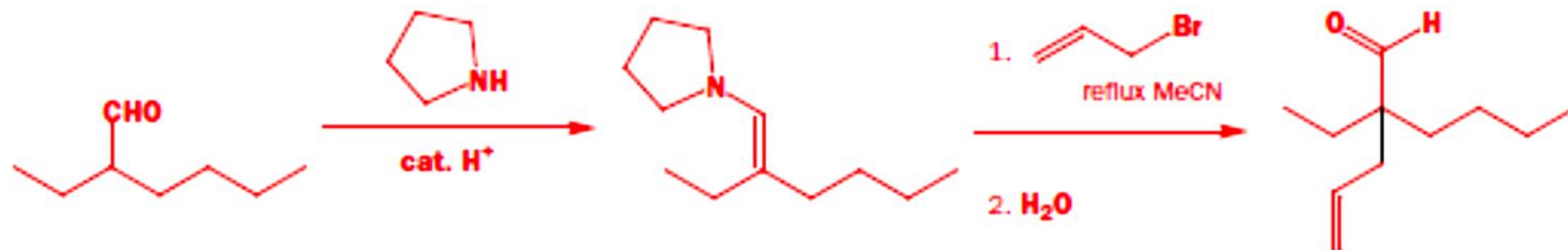
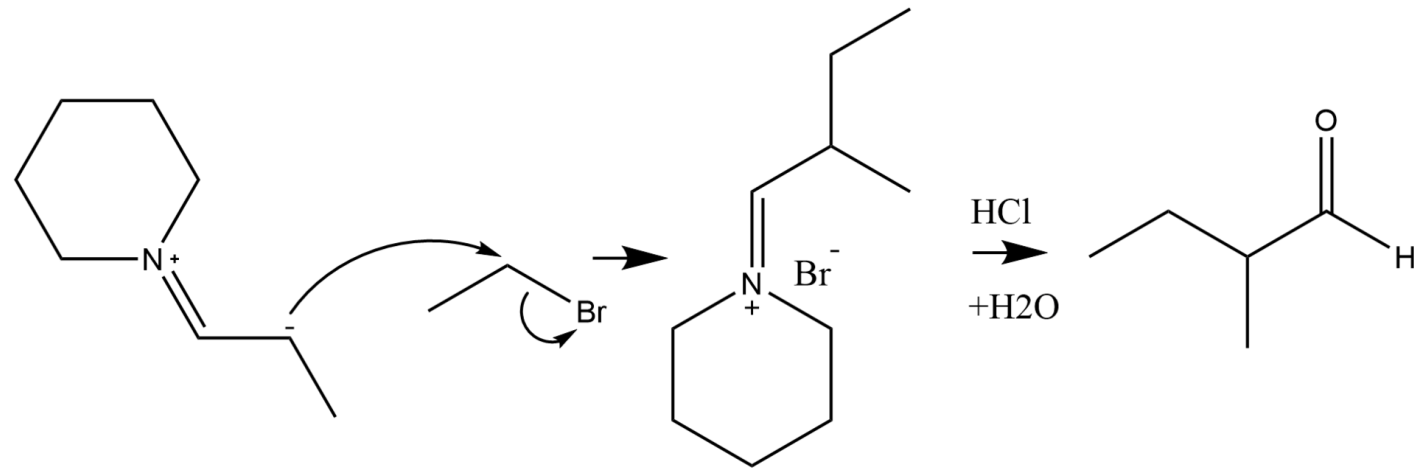
Alquilación



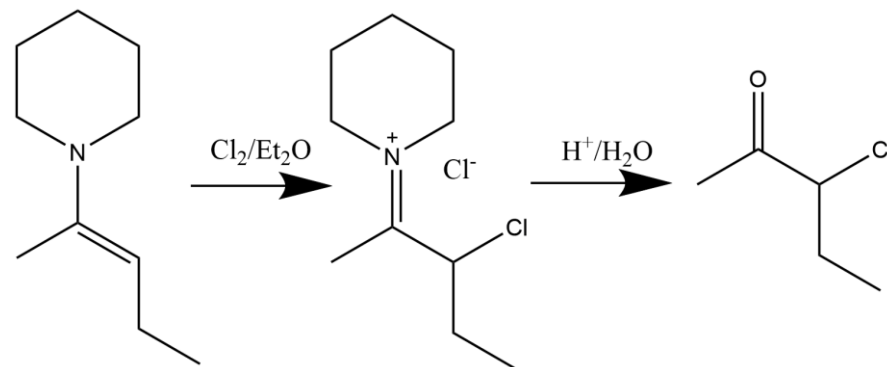
No son usuales las reacciones de enaminas con aldehídos, pero si se han reportado



Reacciones de enaminas de aldehídos: alquilación

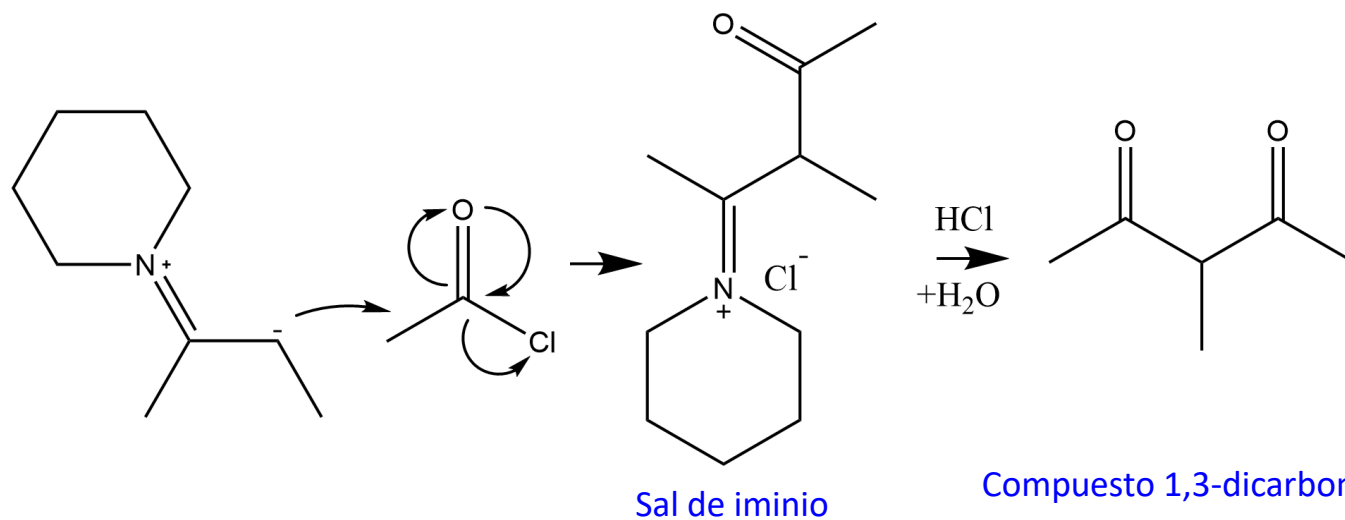


Reacciones de enaminas de cetonas: halogenación



https://en.wikipedia.org/wiki/Enamine#/media/File:Enamine_Halogenation.png

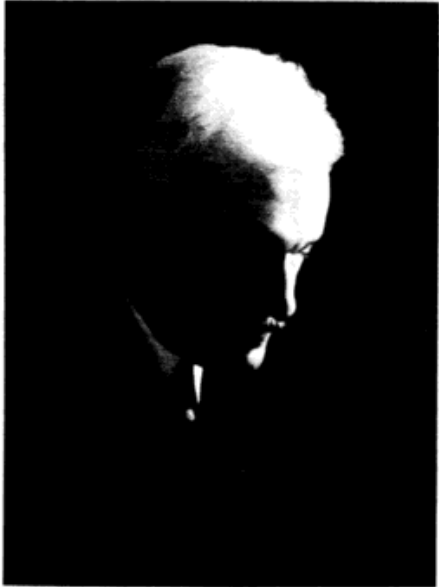
Reacciones de enaminas de cetonas: acilación



https://en.wikipedia.org/wiki/Enamine#/media/File:Enamine_Acylation_to_form_a_Dicarbonyl_Species.png



Reacciones de enaminas de cetonas: adición de Michael

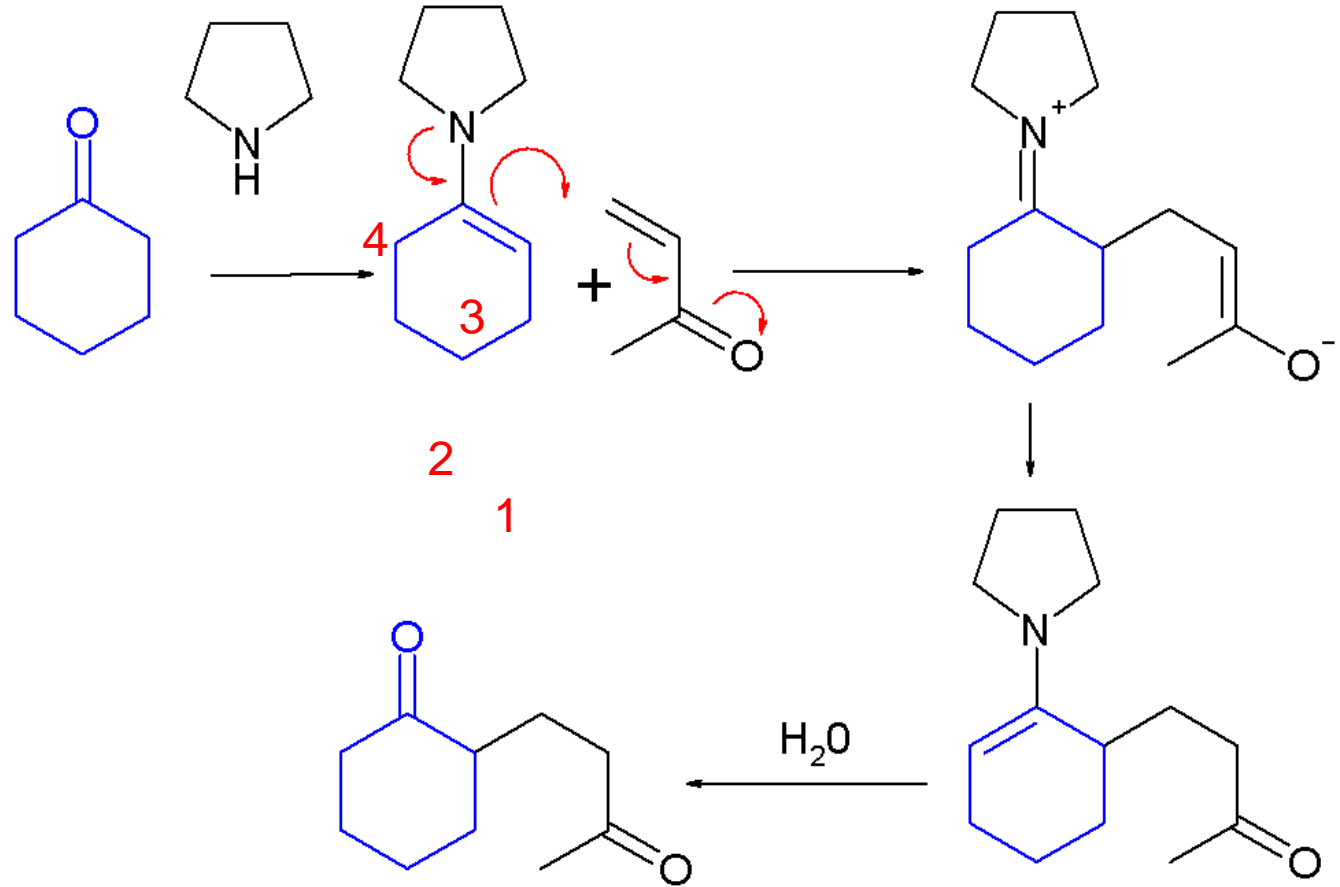


Arthur Michael

Arthur Michael
(1853 – 1942)

Químico orgánico norteamericano

ADICIÓN DE MICHAEL: ADICIÓN-1,4



https://en.wikipedia.org/wiki/Stork_enamine_alkylation#/media/File:Stork_enamine_reaction.png



Costa, A. B. (April 1971). "Arthur Michael (1853-1942). The meeting of thermodynamics and organic chemistry". *Journal of Chemical Education*. **48** (4): 243–346. Bibcode:1971JChEd..48..243C. doi:10.1021/ed048p243

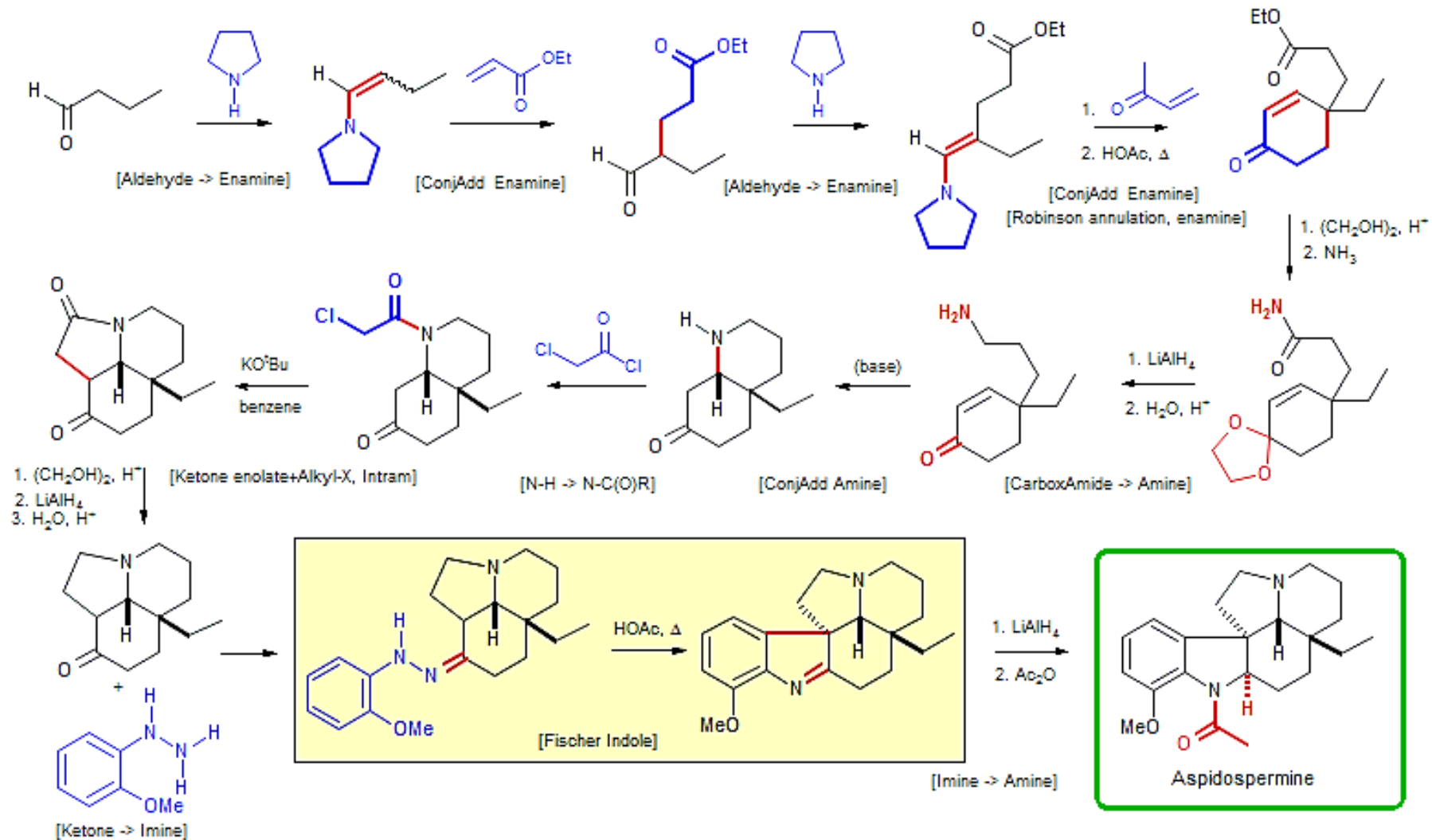
<https://www.nap.edu/read/569/chapter/13>



Aspidospermine

63-05

Stork, G.; Dolfini, J. E. *J. Am. Chem. Soc.* 1963, 85, 2872-2873.



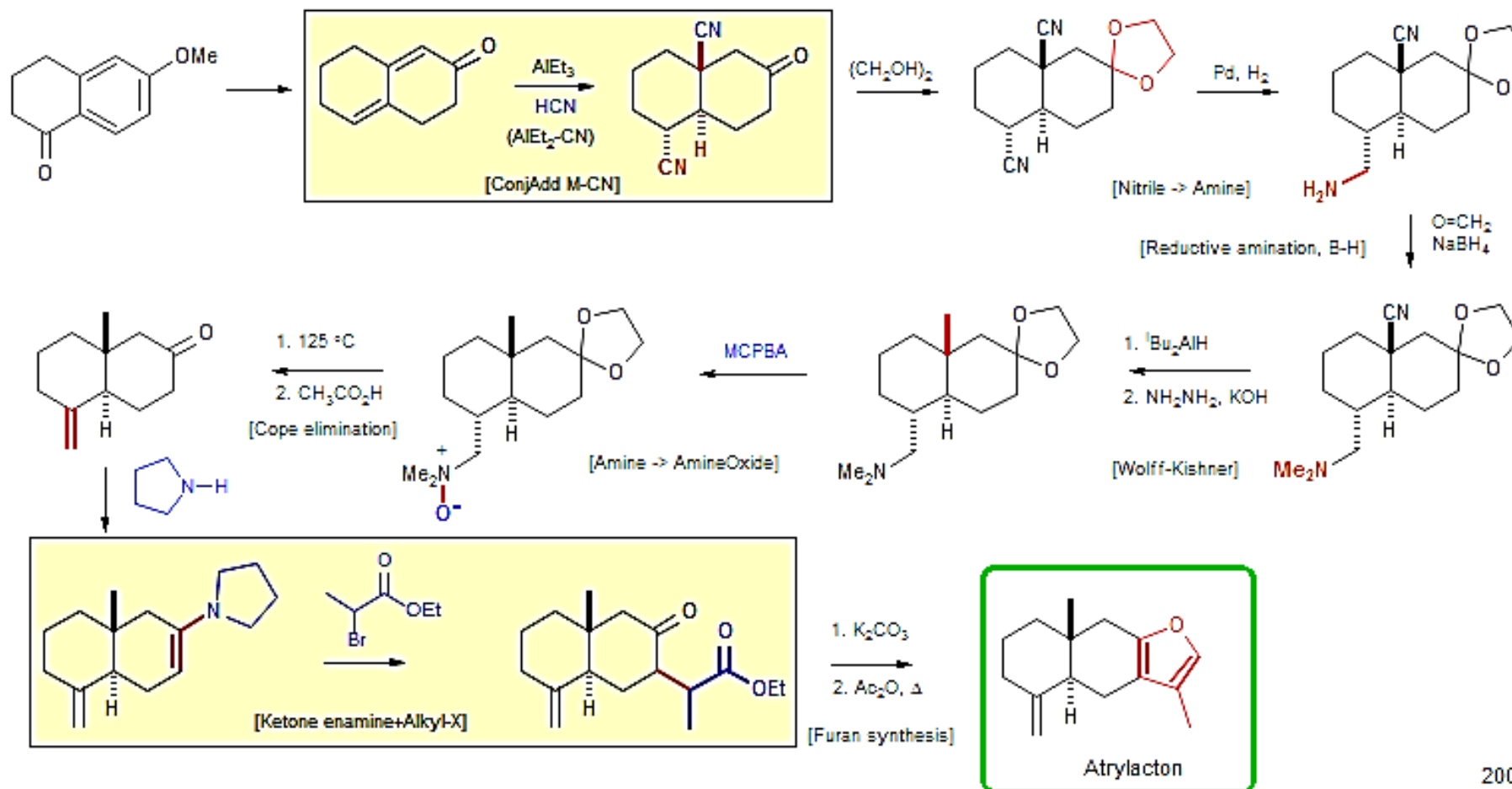
2012-07-24



Atrylacton

Minato, H.; Nagasaki, T. *Chem. Comm.* 1965, 377.

65-01



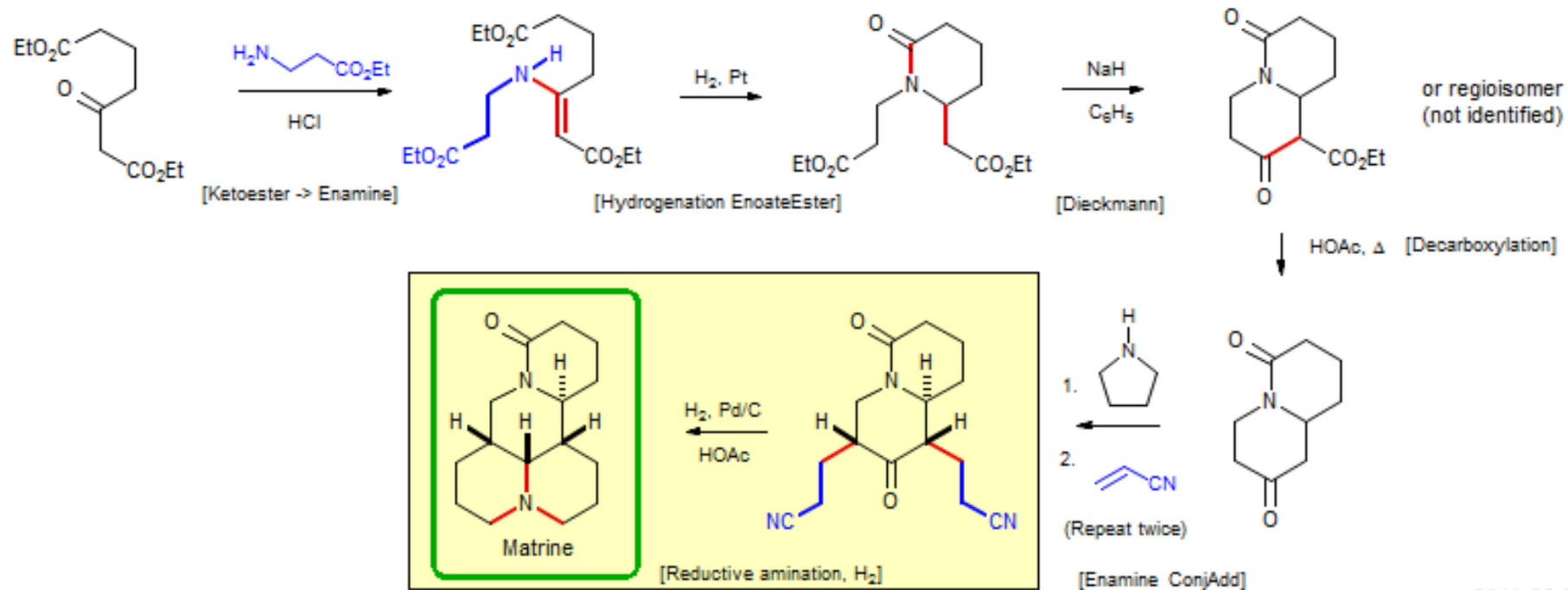
2008-05-17



Matrine

65-02

Mandell, L.; Gresham, J. T.; Freeman, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 8234–8236.



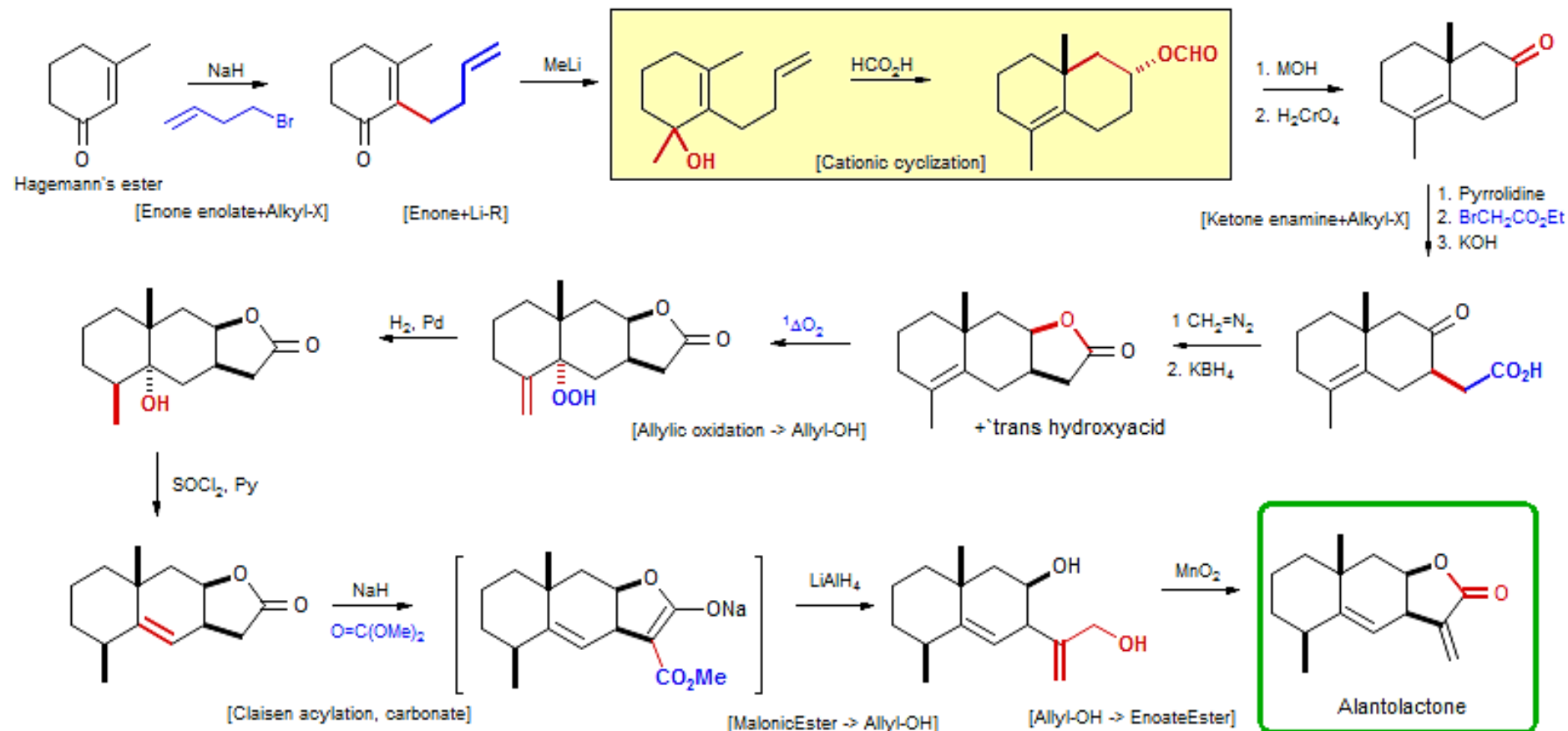
2011-05-29

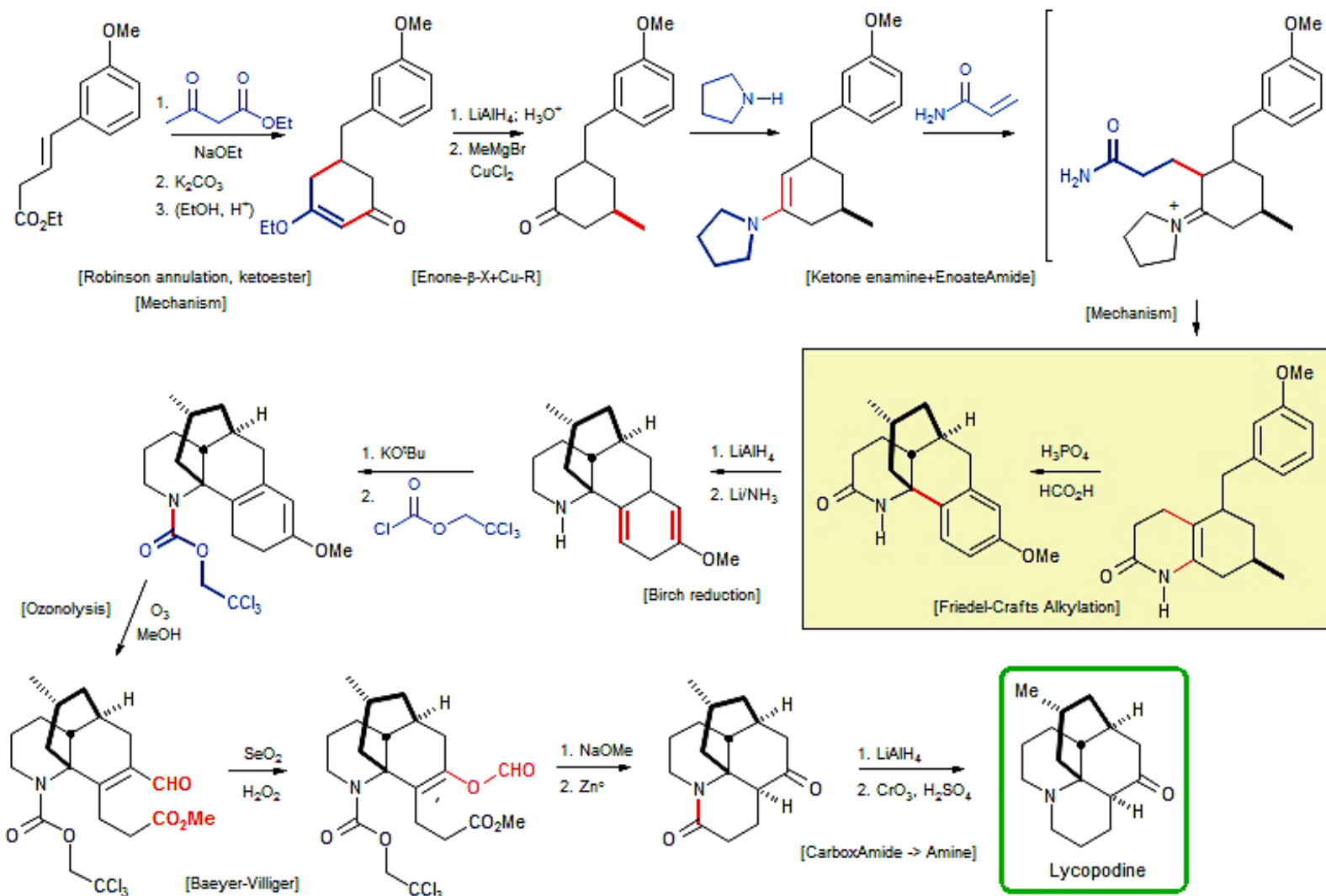


Alantolactone

65-04

Marshall, J. A.; Cohen, N. J. *Am. Chem. Soc.* **1965**, *87*, 2773-2774.



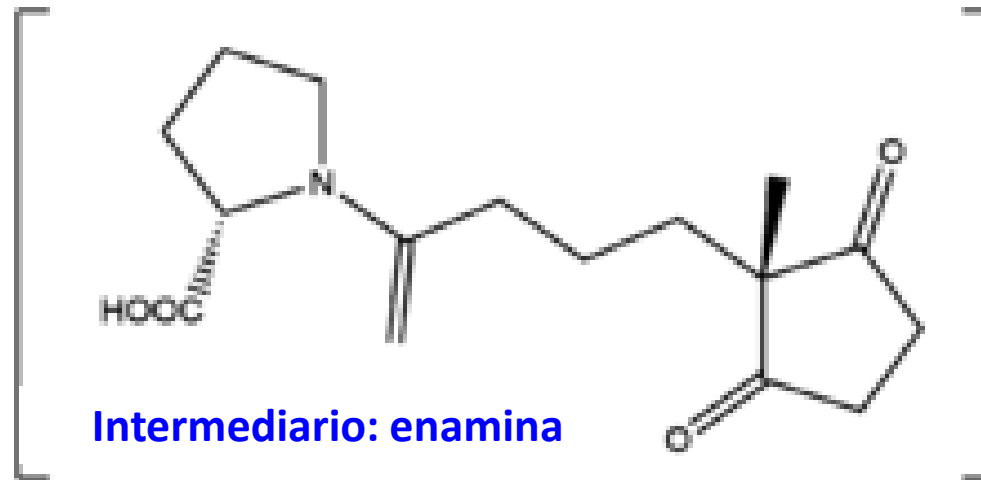
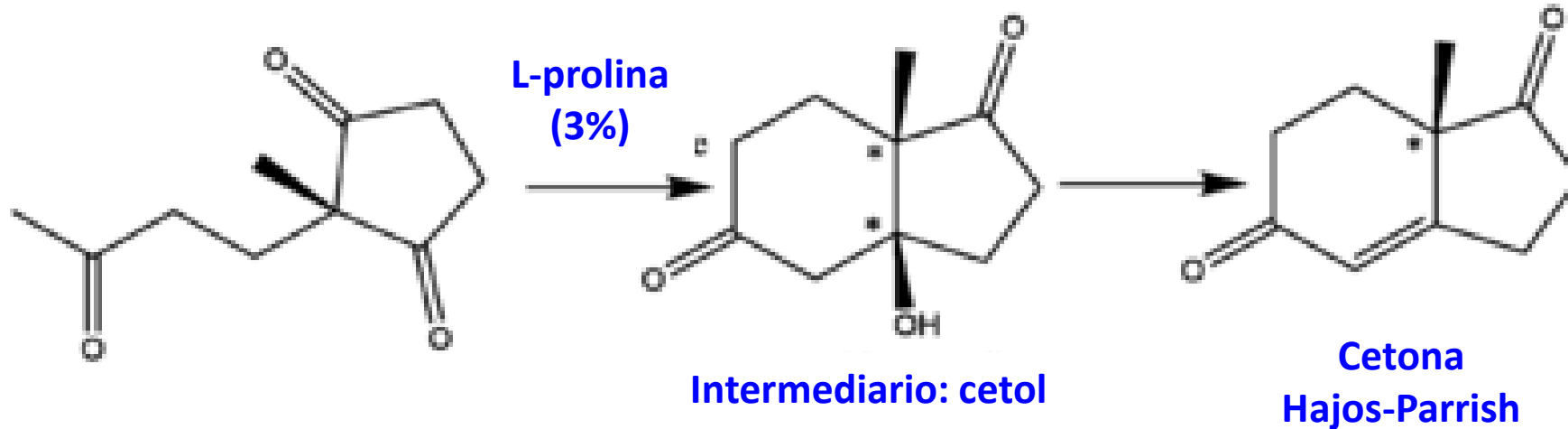
Stork, G.; Kretschmer, R. A.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 1647-1648.From Nicolaou *Angew. Chem. Int. Ed.* **2000**, *39*, 44-122

2007-08-20



Reacciones de enaminas de cetonas

Reacción Hajos–Parrish–Eder–Sauer–Wiechert



Wang, Zerong (2009). *Comprehensive organic name reactions and reagents*. Hoboken, N.J.: John Wiley.





Carl Ludwig Paal
(1860 – 1935)
Químico austriaco
Universidad de Leipzig

Paal, C. (1884), "Ueber die Derivate des Acetophenonacetessigesters und des Acetylacetessigesters", Berichte der deutschen chemischen Gesellschaft, 17 (2): 2756–2767, doi:10.1002/cber.188401702228



Ludwig Knorr
(1859 -1921)
Químico alemán

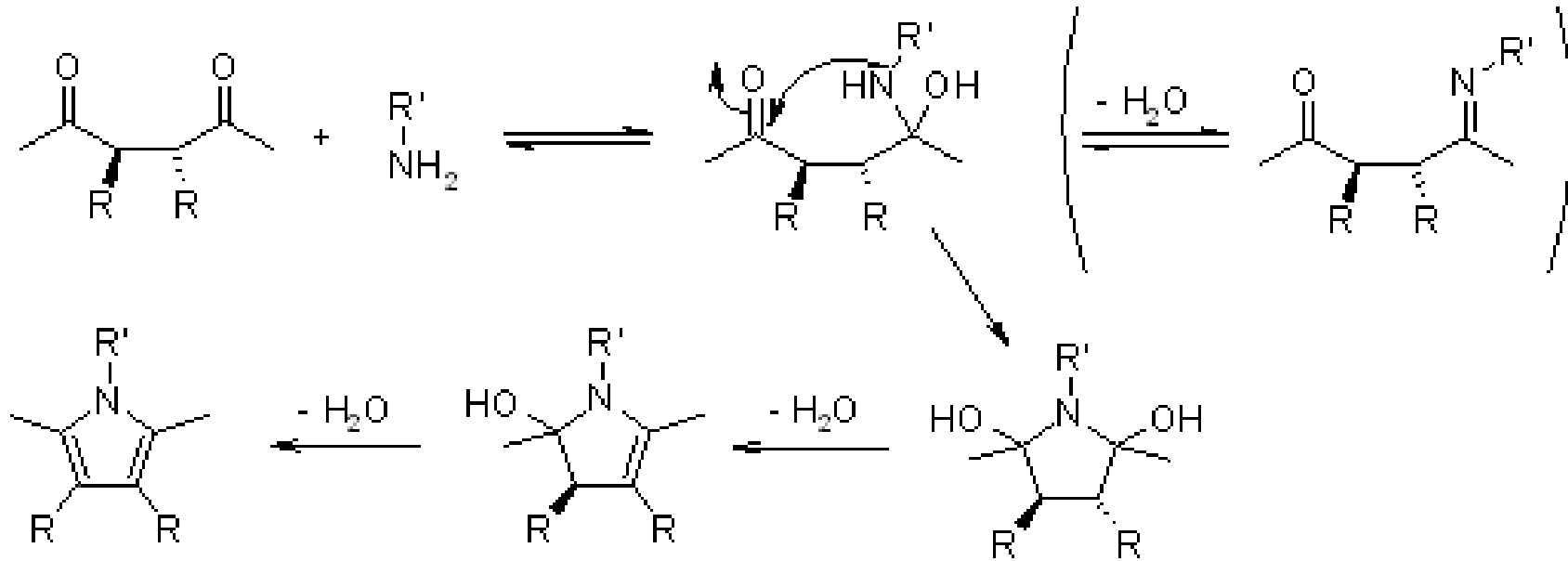
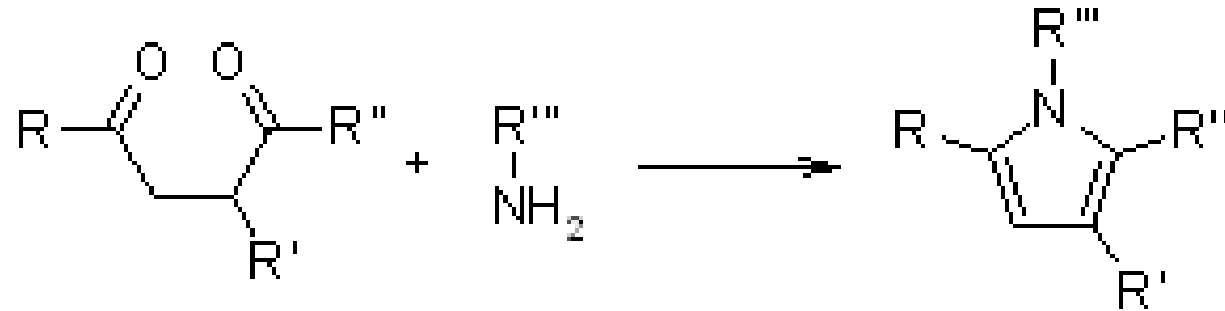
Tumba en el panteón
"Alter Südfriedhof" en
Múnich / Alemania

Knorr, L. (1884), "Synthese von Furfuranderivaten aus dem Diacetbernsteinsäureester", Berichte der deutschen chemischen Gesellschaft, 17 (2): 2863–2870, doi:10.1002/cber.188401702254

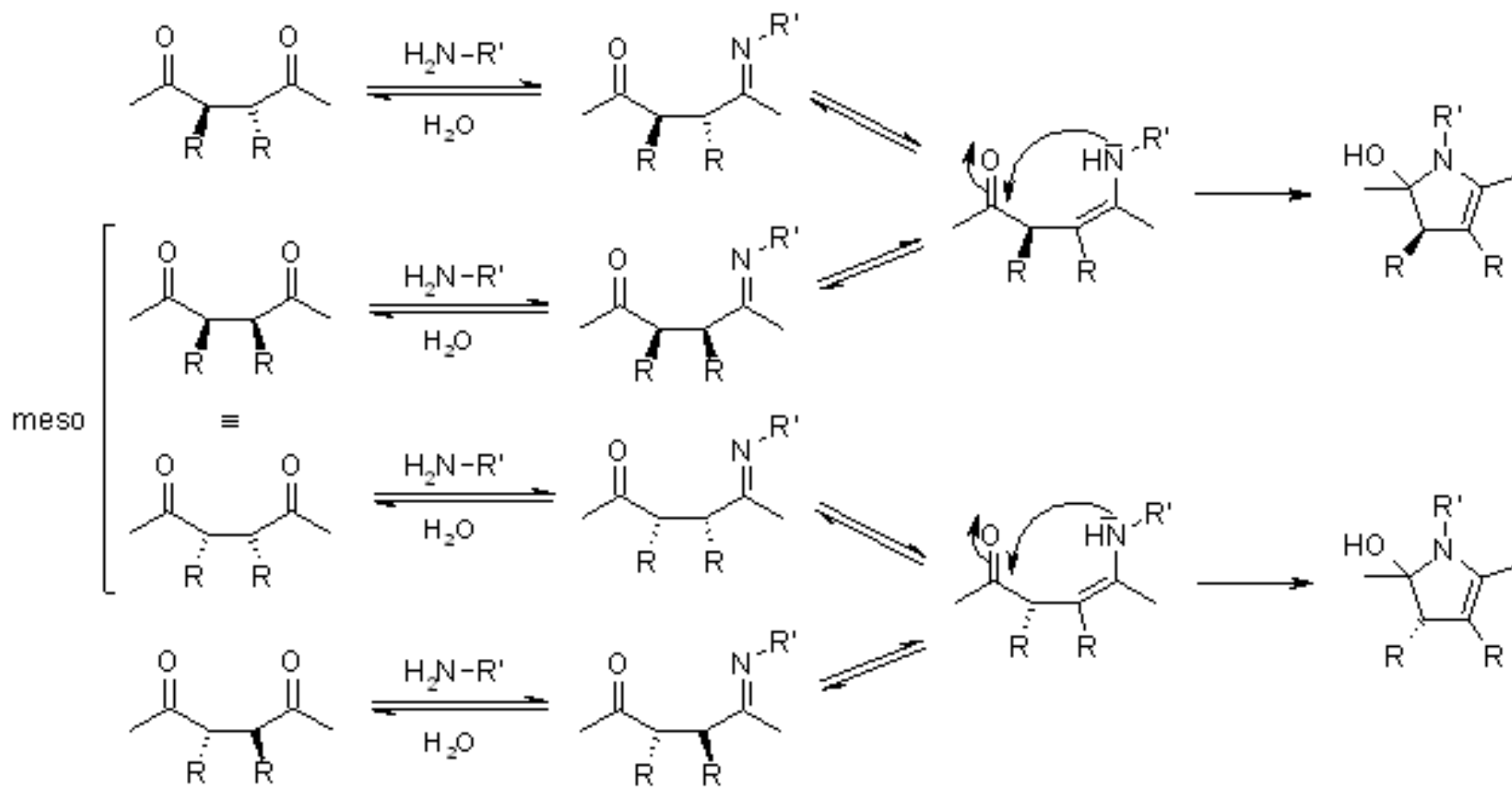
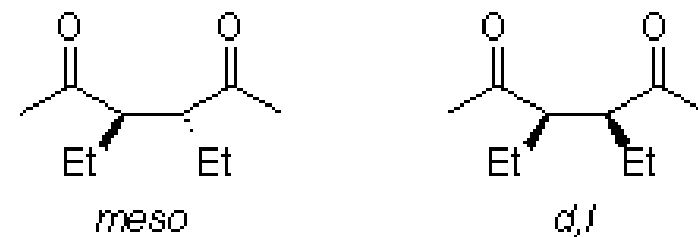


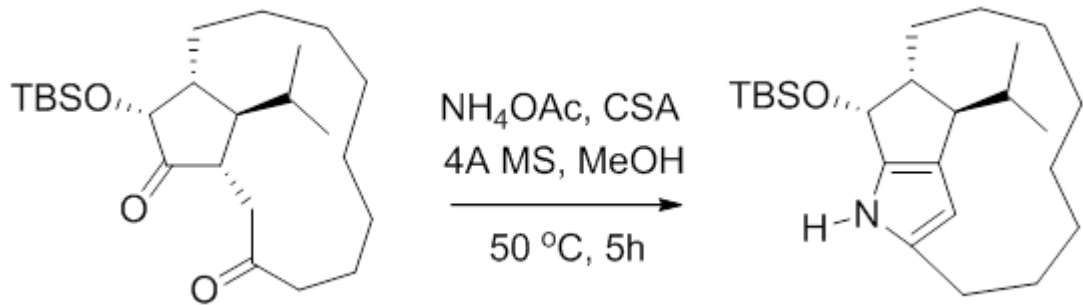
En esta reacción

¿Qué funcionalidad hay en los reactivos y en el producto?

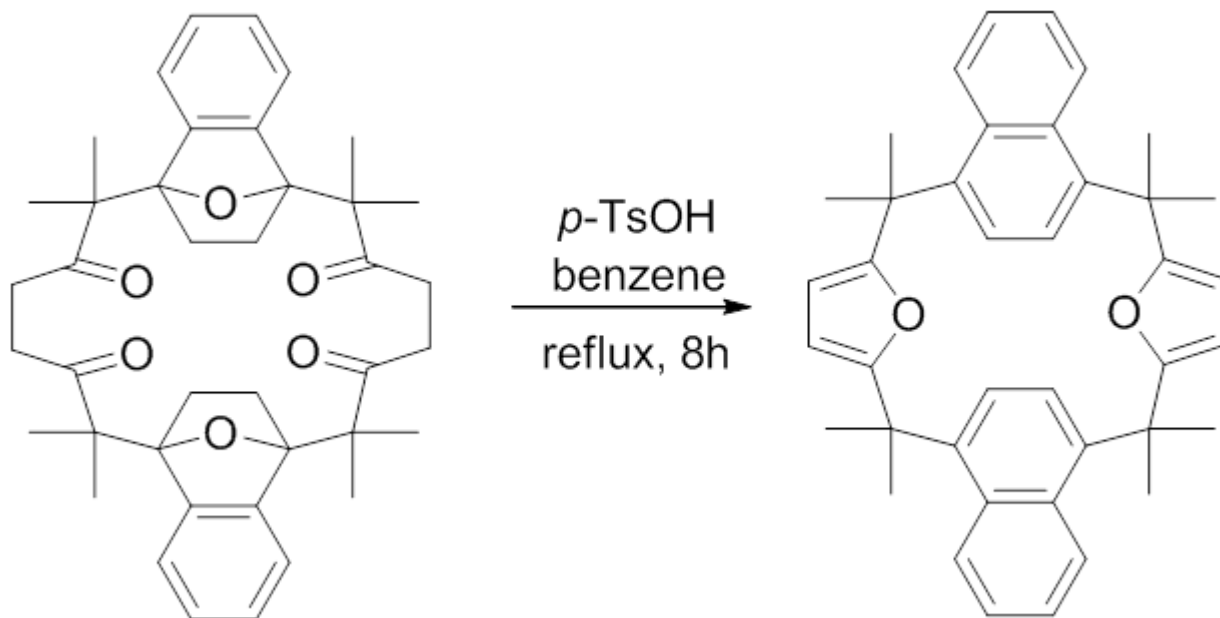


Venkataraman Amarnath has shown (J. Org. Chem., **1991**, 56, 6924) that *meso*- and *dl*-3,4-diethyl-2,5-hexanediones cyclize at unequal rates, and that the stereochemical configuration of the unchanged dione is preserved during the reaction. Any mechanism such as the following one that involves the formation of an enamine before the rate-determining step - the cyclization - must be ruled out.





Trost, B. M.; Doherty, G. A. (2000), "An Asymmetric Synthesis of the Tricyclic Core and a Formal Total Synthesis of Roseophilin via an Enyne Metathesis", *Journal of the American Chemical Society*, **122** (16): 3801–3810, doi:10.1021/ja9941781



Hart, H.; Takehira, Y. (1982), "Adducts derived from furan macrocycles and benzyne", *The Journal of Organic Chemistry*, **47** (22): 4370–4372, doi:10.1021/jo00143a049



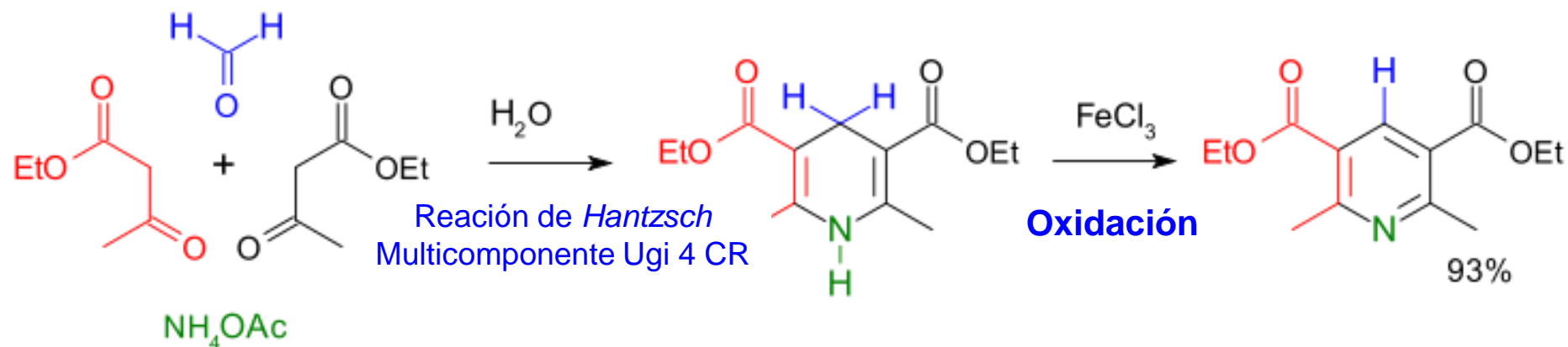
SÍNTESIS DE HANTZSCH PARA 1,4-DIHIDROPIRIDINAS



Arthur Rudolf Hantzsch
(1857 –1935)
Químico alemán

En esta reacción

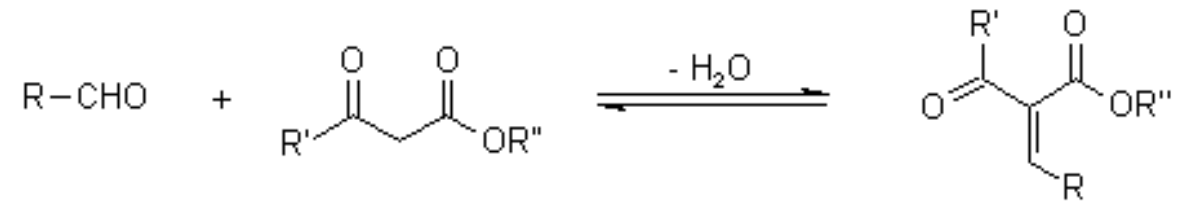
¿Qué funcionalidad hay en los reactivos y en el producto?



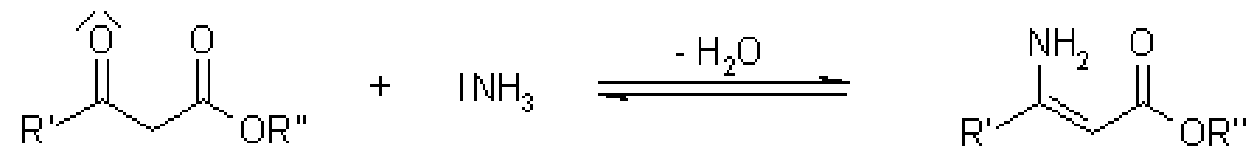
Mecanismo de la síntesis de Hantzsch para obtener 1,4-Dihidropiridinas

Dos intermediarios clave:

1) Producto de la Condensación de Knoevenagel, formación de un compuesto carbonílico α,β -insaturado:



2) Una enamina éster:



3) Adición de Michael, ciclización y deshidratación:

