Química Orgánica-III

(1628)

Última versión 2 de abril de 2024

Química de Alimentos

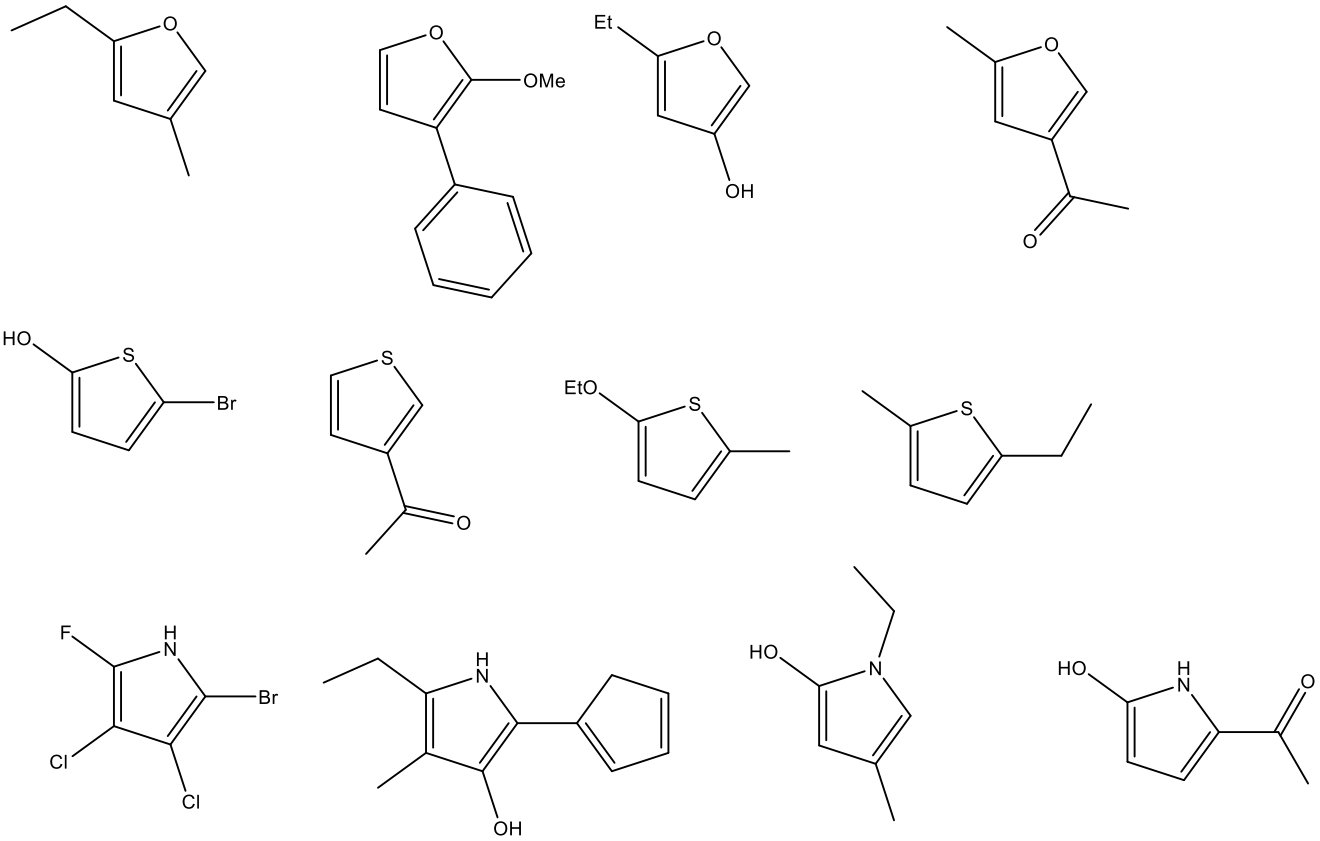
Dr. Miquel Gimeno

Libro de problemas

Capítulo 1

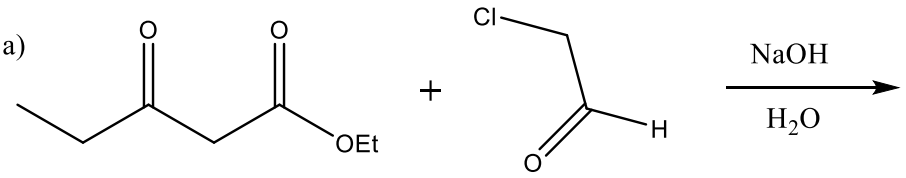
FURANOS TIOFENOS Y PIRROLES

0. Nomenclatura



Pregunta 1. Complete las siguientes transformaciones químicas y escriba el mecanismo que explique la formación del producto

a)



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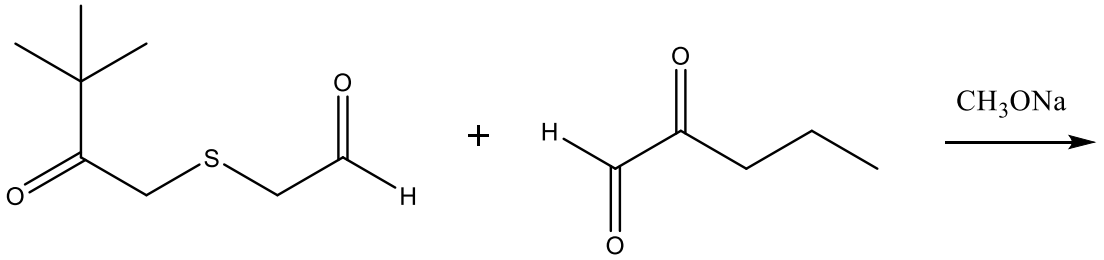

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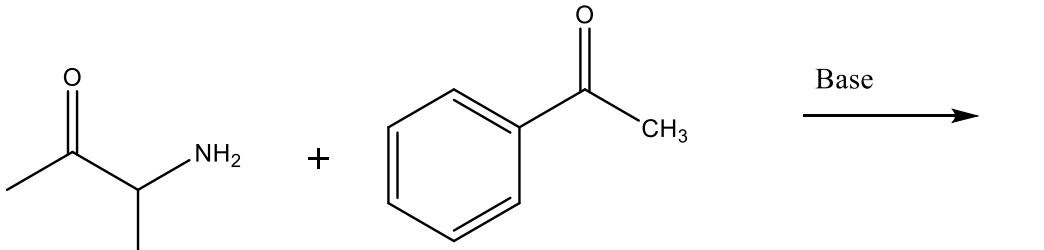

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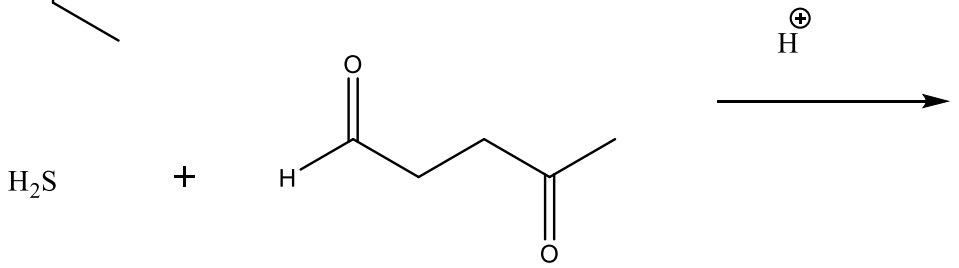

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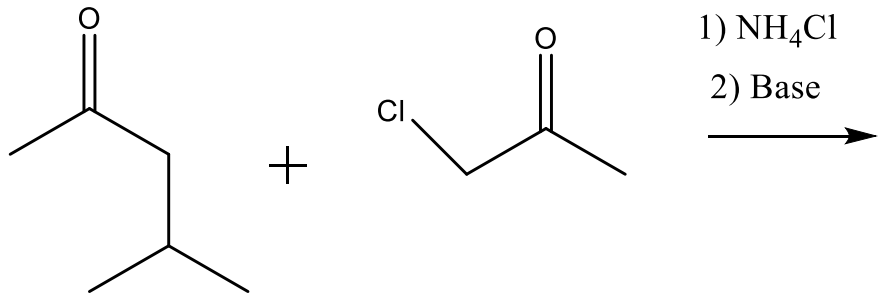
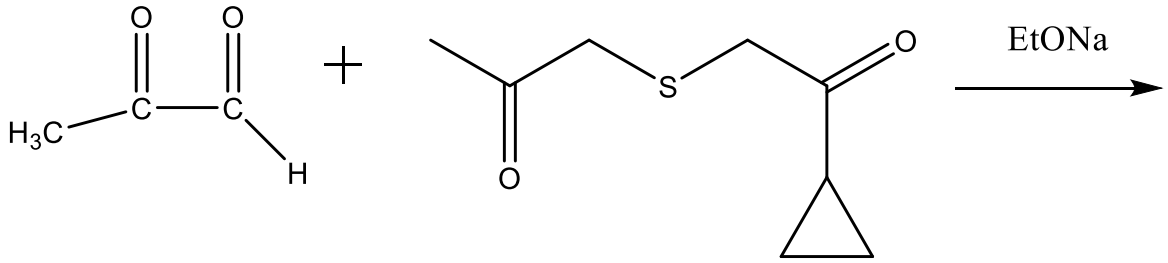
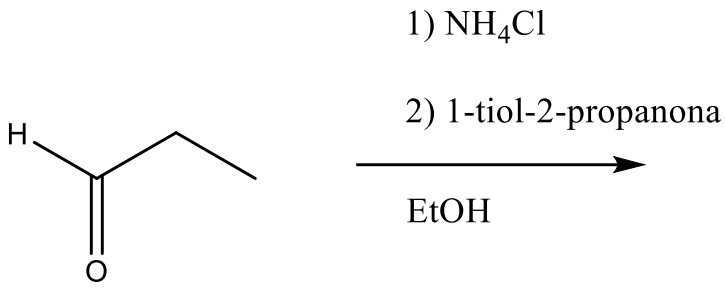

O
Cl
O
1) NH_4Cl
2) Base

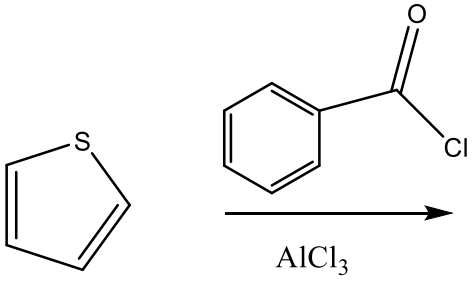
f)

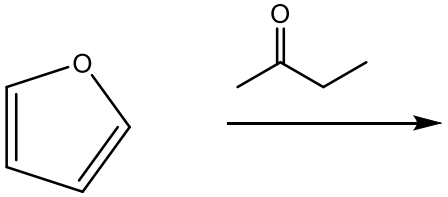

O
O
H_3C
C
C
H
S
O
O
EtONa

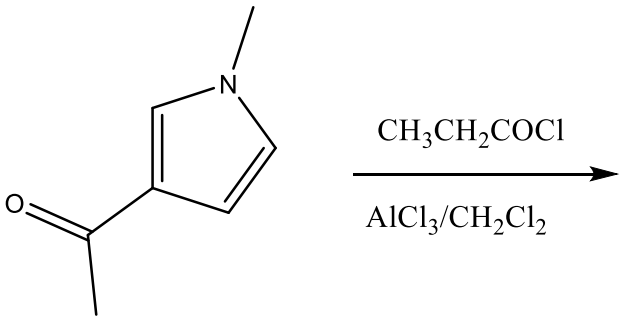
g)

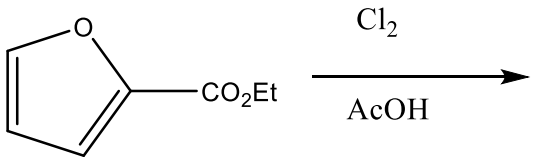

1) NH_4Cl
2) 1-tiol-2-propanona
H
O
EtOH

Pregunta 2. Prediga el producto mayoritario de las siguientes transformaciones químicas

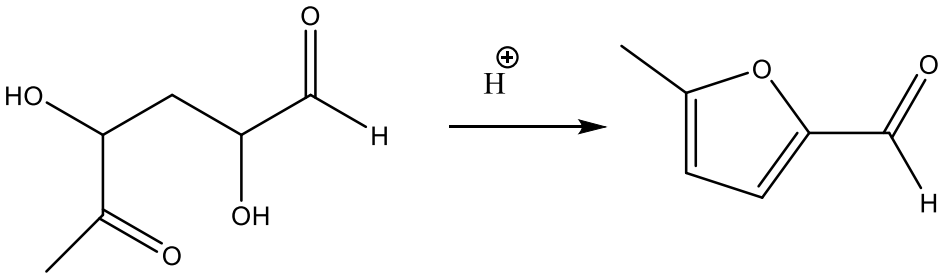


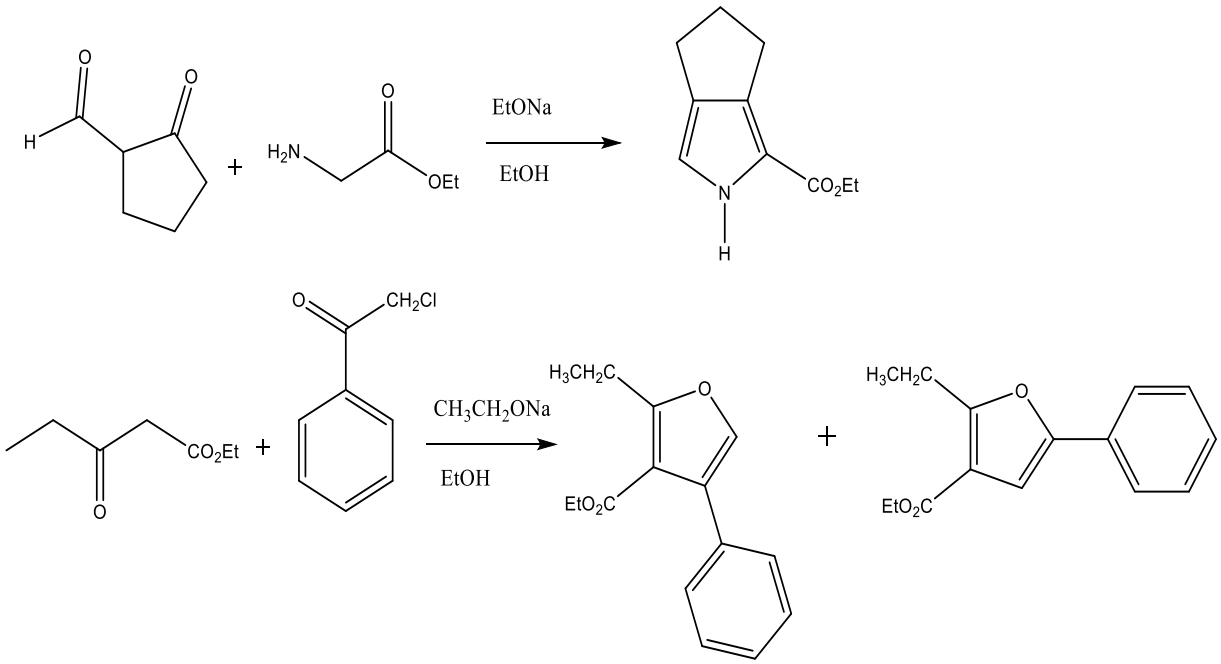




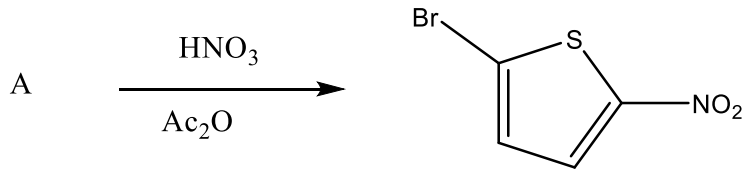


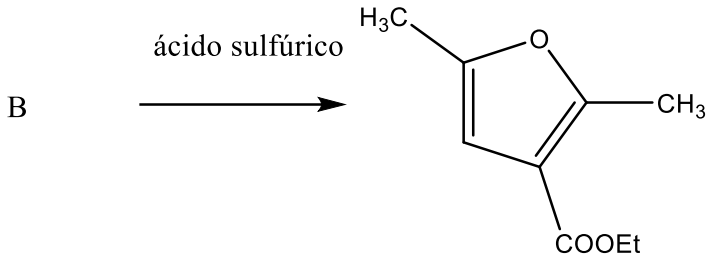
Pregunta 3. Describa el mecanismo para las siguientes transformaciones

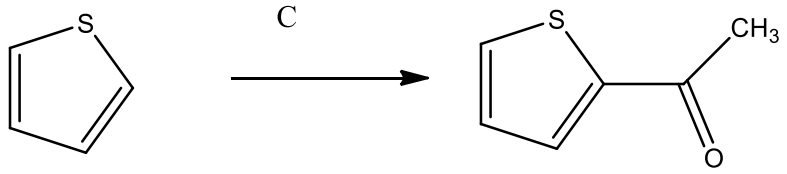


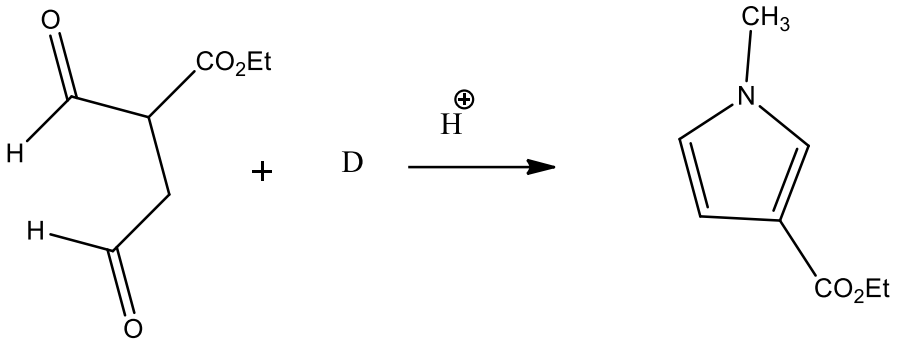


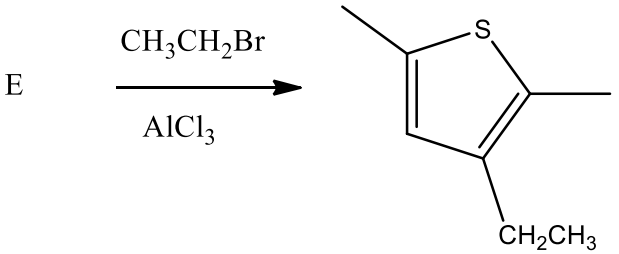
Pregunta 4. Complete las siguientes reacciones químicas indicadas con letras

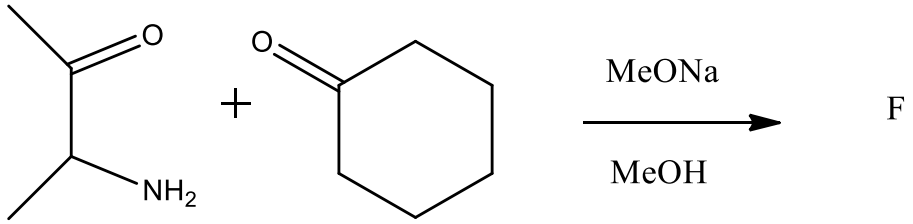


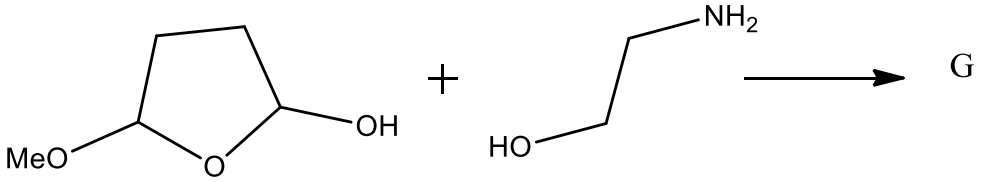



S
C
S
CH3
O

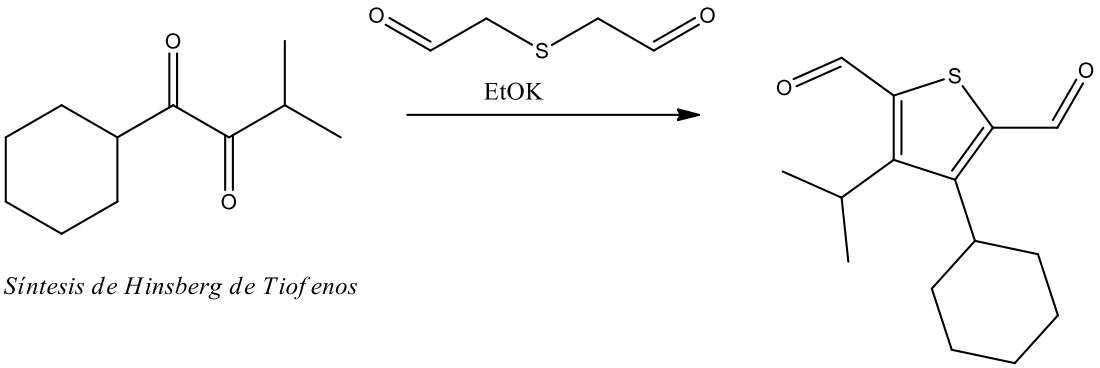

O
CO2Et
H
H
O
+
D
H⊕
CH3
N
CO2Et


E
CH3CH2Br
AlCl3
S
CH2CH3

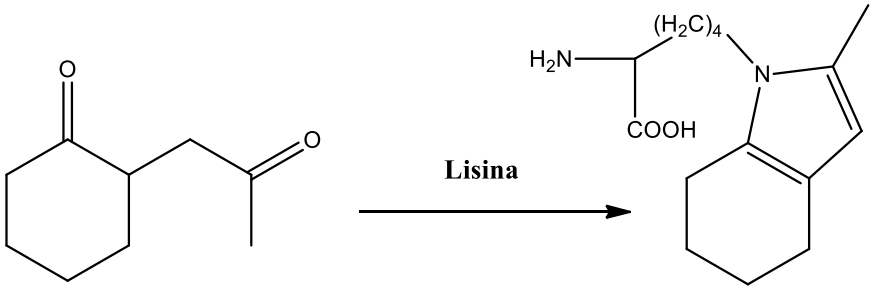

O
NH2
+
O
MeONa
MeOH
F


MeO
O
OH
+
NH2
HO
G

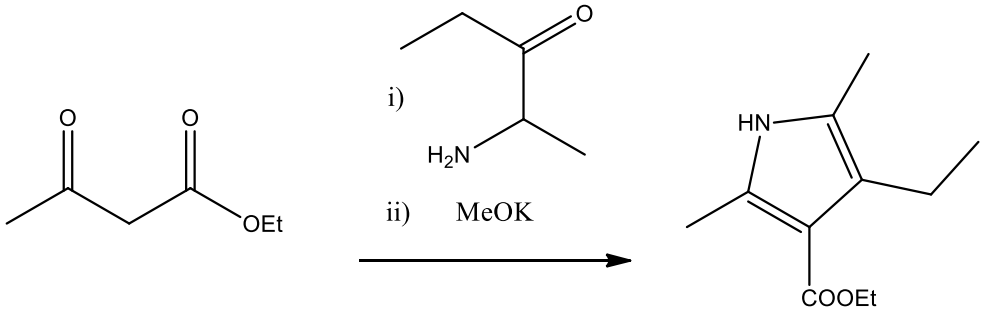
Pregunta 5. Describa el posible mecanismo de reacción de las siguientes transformaciones



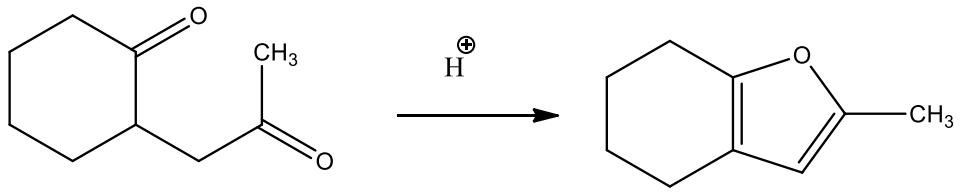
Síntesis de Hinsberg de Tiofenos



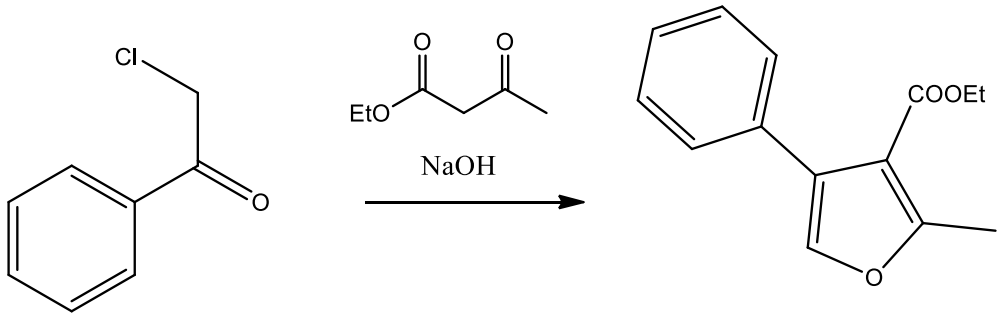
Síntesis de Paal-Knorr de Pirroles



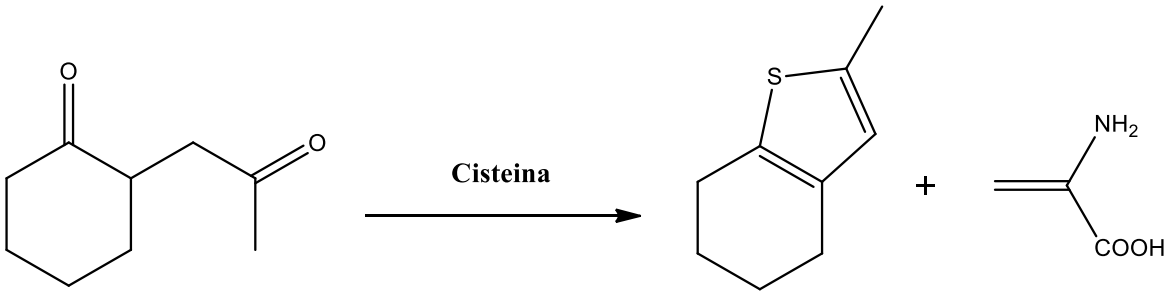
Síntesis de Knorr de Pirroles



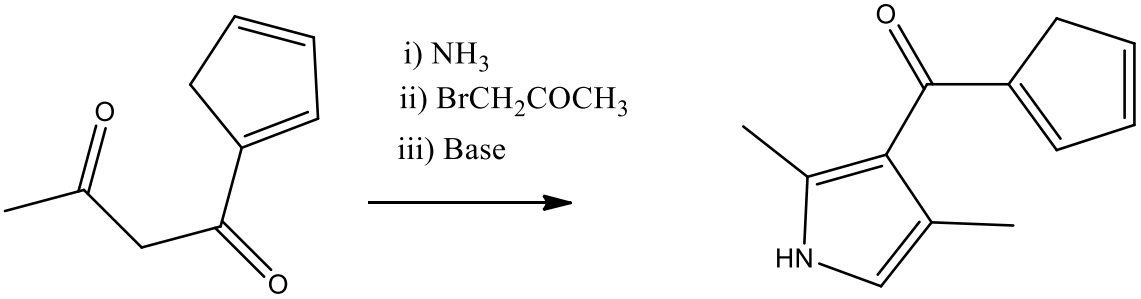
Síntesis de Paal-Knorr de furanos



Síntesis de Feist-Benary de Furanos



Síntesis de Paal-Knorr de Tiofenos

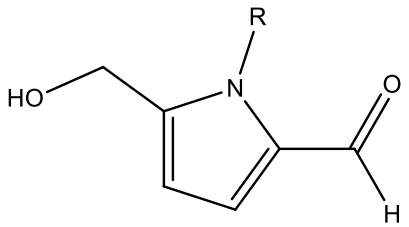


Síntesis de Hantzsch de pirroles

Pregunta 6. Si la pared celular es rica en hexosas se obtiene hidroximetilfurfural (HMF) ¿qué furanoide se obtendrá si es rica en pentosas considerando que el medio es ácido? Describa los posibles mecanismos de obtención desde caramelización o vía Maillard.

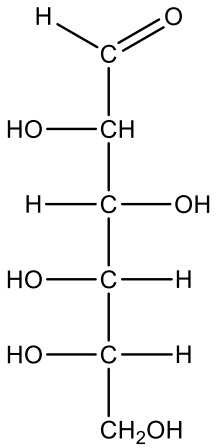
Pregunta 7, Describa el mecanismo de degradación de Strecker partiendo de serina y del producto de la retroaldólisis de 1,2-dicarbonilo 3 deoxisona.

Pregunta 8. Una de las reacciones más importantes en la química de los alimentos es el conjunto de reacciones de Maillard, que explica como se oscurecen los alimentos al ser calentados. Una de ellas es la tranformación o reacción de Amadori. Propoga un mecanismo que explique la formación de un 5-hidroximetil-2-carboxaldehídopirrol (1) sustituido en N desde glucosa.

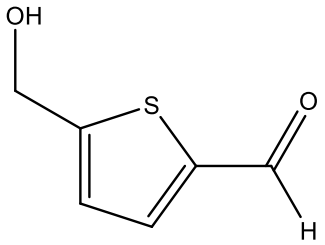


(1)

Pregunta 9. El reordenamiento de Amadori puede producir tiofenos sustituidos con ayuda de los compuestos sulfurados producidos en la degradación de cisteina o metionina. Proponga un mecanismo desde la aldosa (2) al tiofeno (3).

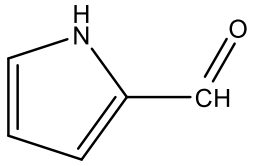


(2)



(3)

Pregunta 10. Los pirroles son compuestos nitrogenados que se supone derivan de la prolina y de la hidroxiprolina mediante la degradación de Strecker. Sin embargo, también se pueden formar por la ruta de Maillard debido a la reacción entre las proteínas y los azúcares. Entre los más conocidos está el 2-formilpirrol (4). Describa el mecanismo que da lugar a este compuesto.

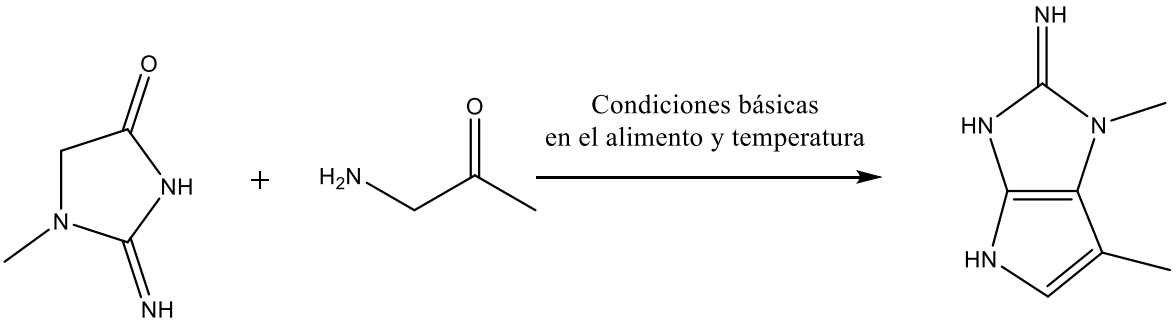


(4)

Pregunta 11. Describa el mecanismo al heterociclo aromático de 5 miembros que se podría obtener al calentar alimentos si el alfa-aminoacetaldehído, el cual es un subproducto de la degradación de Strecker desde glioxal, reacciona vía aldólica con el ion enolato del piruvaldehído (metilglioxal) seguido de los pasos de ciclación /deshidratación.

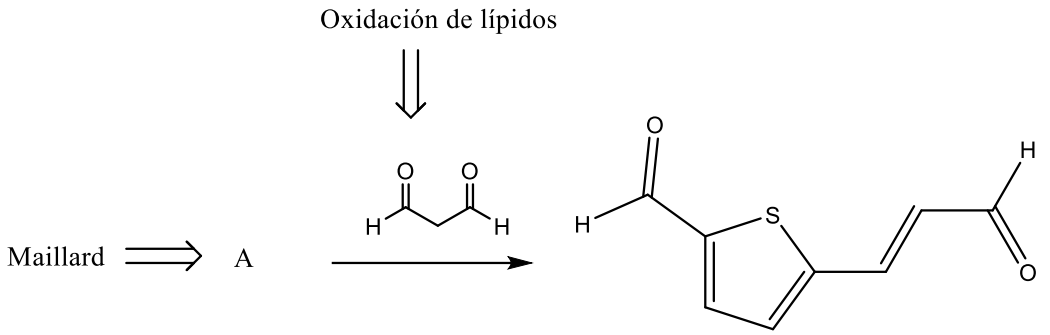
Pregunta 12. Describa el mecanismo si los productos principales de la degradación de Strecker desde piruvaldehído y cisteína (aminoacetona y tiolacetaldehído) reaccionan entre si para dar lugar a un pirrol sustituido. Describa el mecanismo que daría lugar a un tiofeno sustituido.

Pregunta 13. Al calentar alimentos se pueden producir compuestos de glicosilación avanzada complejos de anillos fusionados ricos en nitrógeno. Estos pueden llegar a ser mutágenos. Describa el mecanismo de la siguiente transformación entre la creatinina, que es un producto derivado de la creatina, la cual se encuentra en carnes rojas y mariscos, y el subproducto de la degradación de Strecker de piruvaldehído

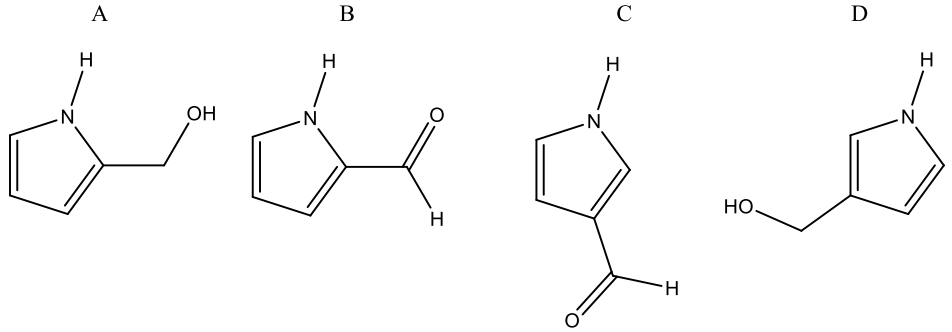


Pregunta 14. Escribe en el recuadro el nombre de la molécula A

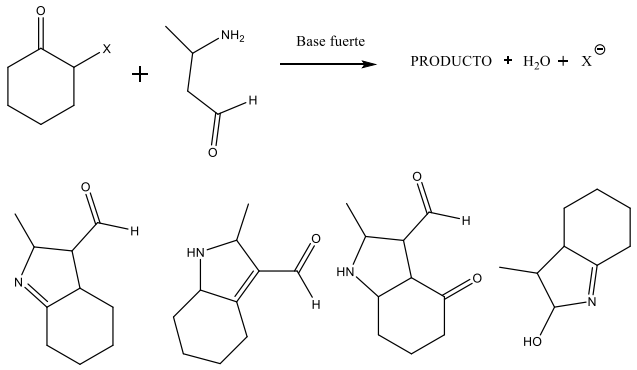
A:



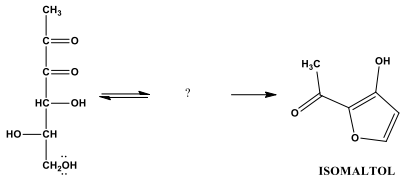
Pregunta 15. Indica el pirrol que se podría obtener al calentar alimentos si el aminoacetaldehído, el cual es un subproducto de la degradación de Strecker desde glioxal, reacciona vía aldólica con el ion enolato del piruvaldehído (metilglioxal) seguido de los pasos de ciclación y deshidratación.

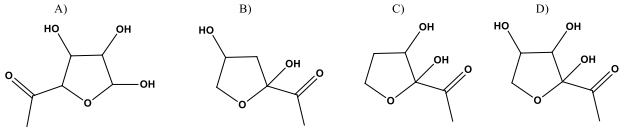


Pregunta 16. ¿Cuál es el producto más probable de la siguiente ruta sintética de tres pasos? considerando que el primer paso es un ataque nucleófilo de la amina al carbonilo de la 2-bromomociclohexanona, y el último, una deshidratación

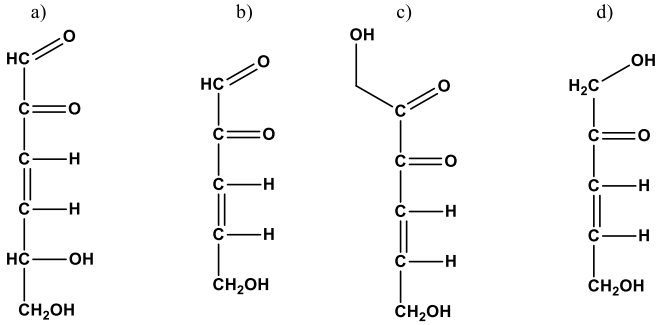


Pregunta 17. Indica cual será la estructura molecular del intermedio de esta reacción para dar lugar al isomaltol





Pregunta 18 ¿Qué sacárido o intermedio de la reacción de Maillard daría directamente el Furfural por ciclación interna?

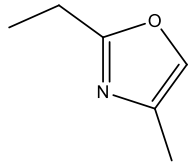


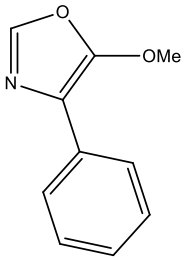
Libro de problemas

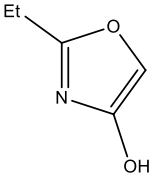
Capítulo 2

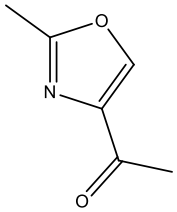
IMIDAZOLES, TIAZOLES Y OXAZOLES

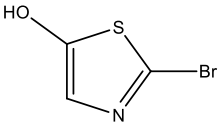
0. Nomenclatura

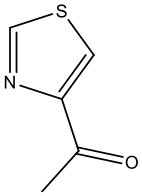


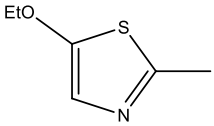


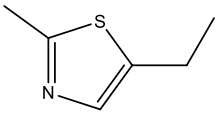


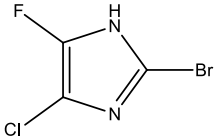


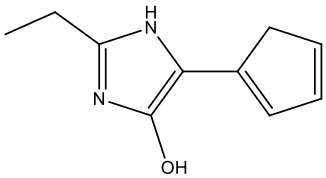


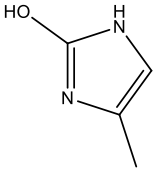


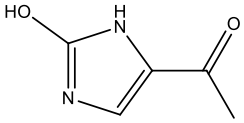






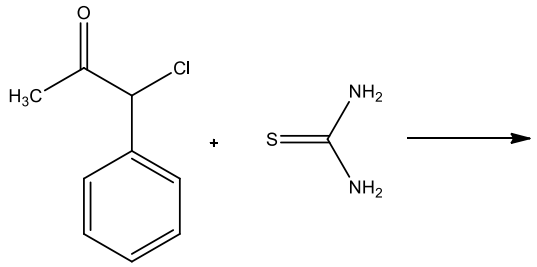






Pregunta 1 Complete las siguientes reacciones y explique el mecanismo

a)



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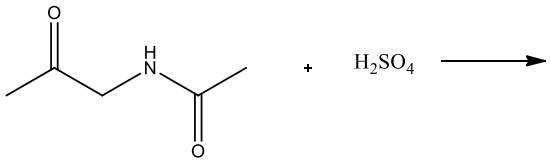

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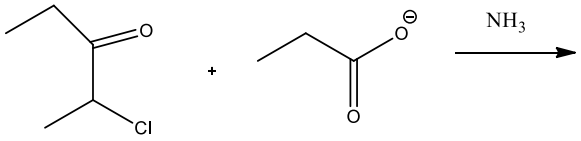

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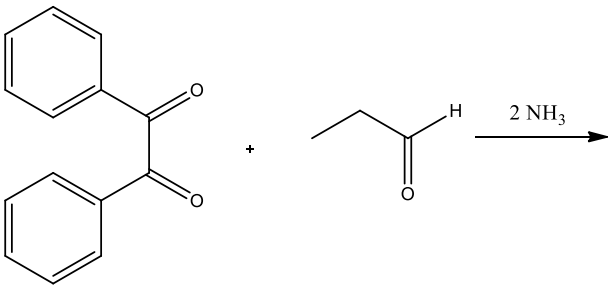

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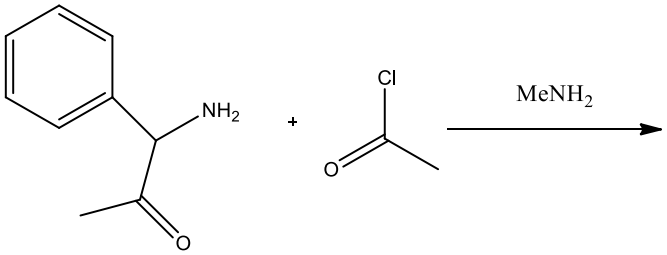

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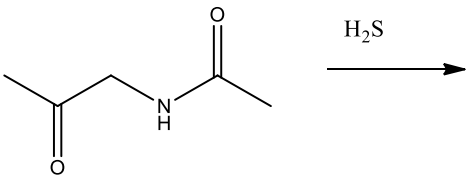
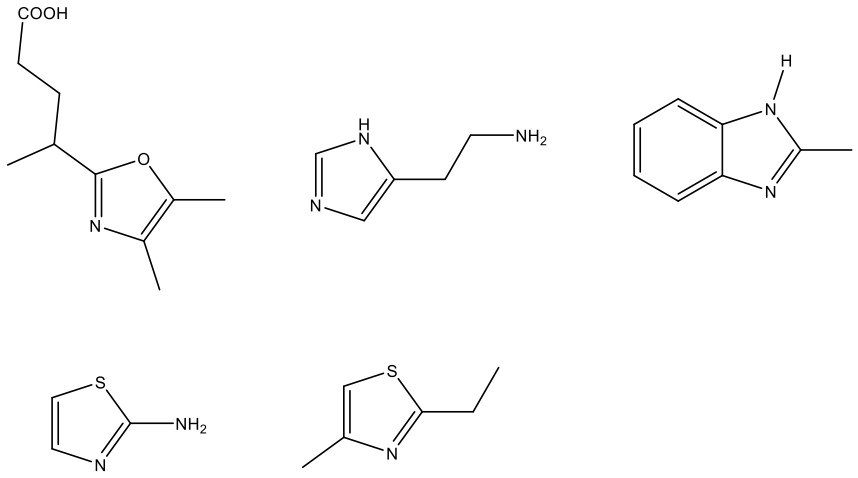
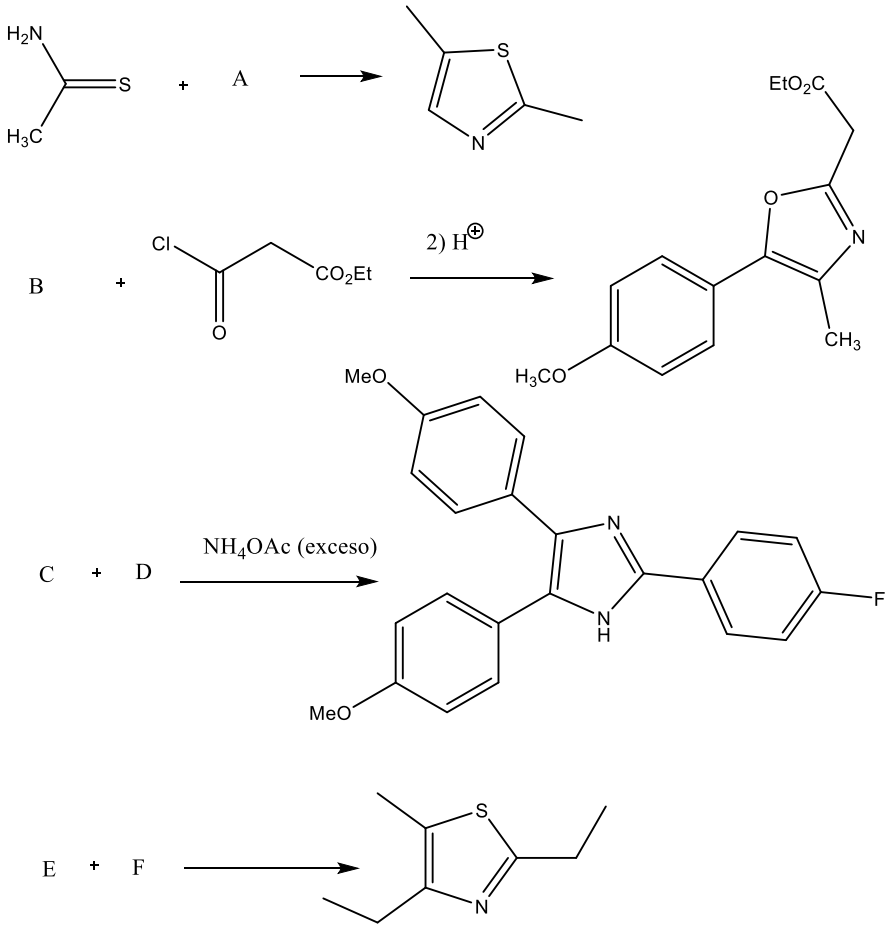


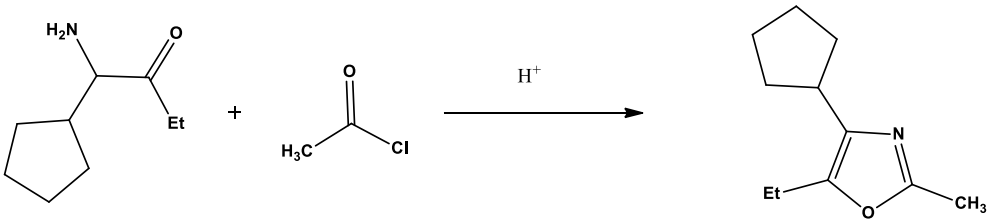
2. Diseñe una ruta sintética para los siguientes compuestos:



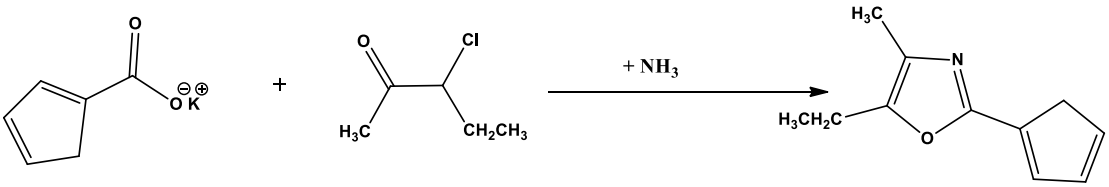
3. Complete las siguientes reacciones y escriba mecanismo para cada una de ellas



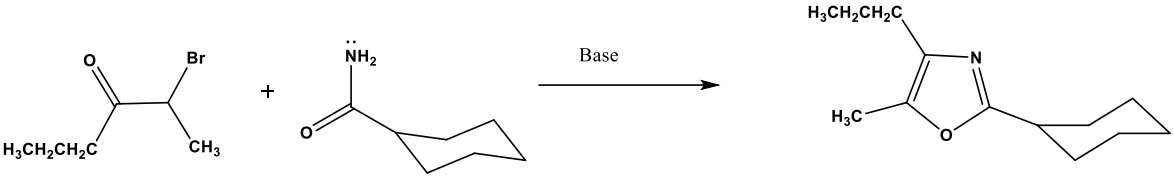
4. Desbribe los mecanismos de las siguientes transformaciones



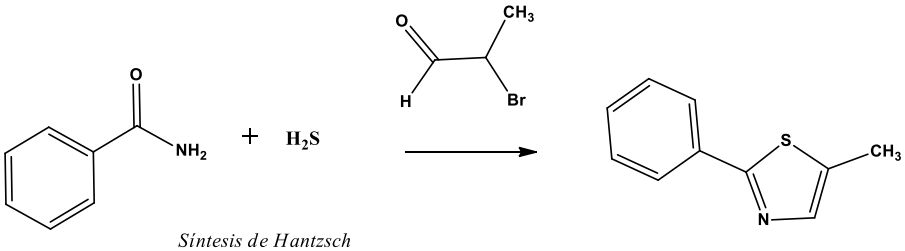
Robinson Gabriel de oxazoles



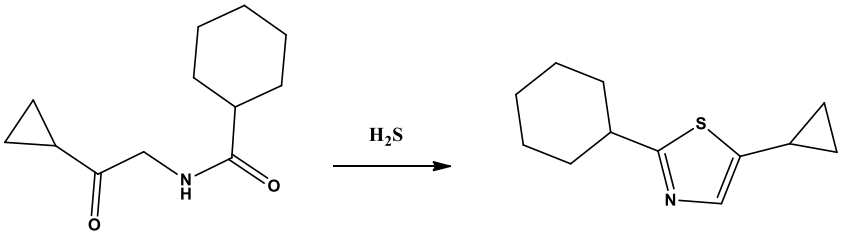
Alcóxidos con α-halocarbonilos en presencia de amonico



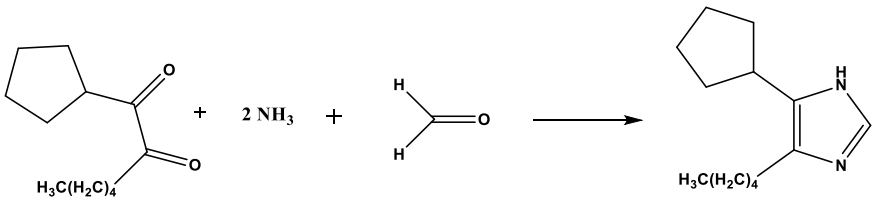
Blümlein-Lewy



Síntesis de Hantzsch



Síntesis de Gabriel



1,2-dicarbonilos (α-dicarbonilos) en presencia de un aldehído y amoniaco en exceso

Libro de problemas

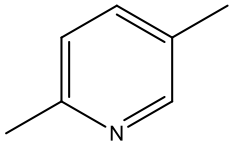
Capítulo 3

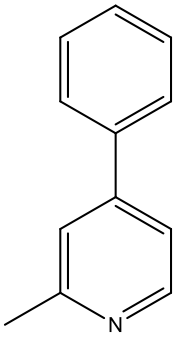
Piridinas

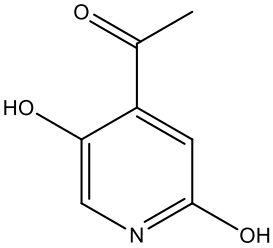
y

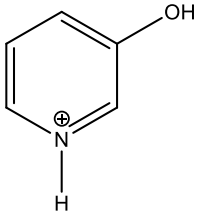
Pirazinas

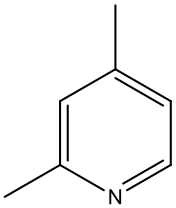
0. Nomenclatura

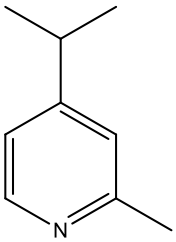


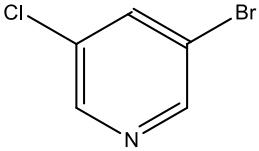


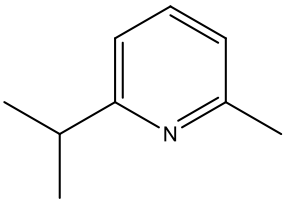


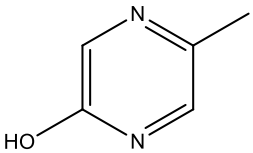


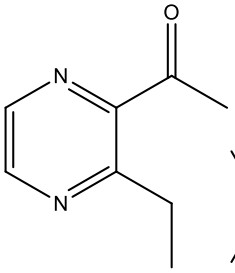


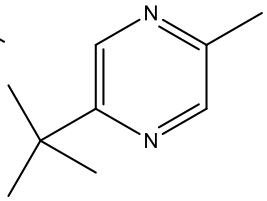


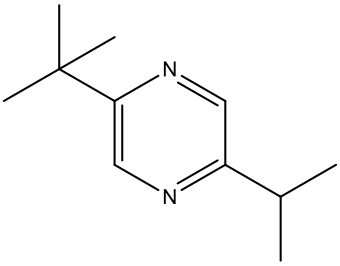






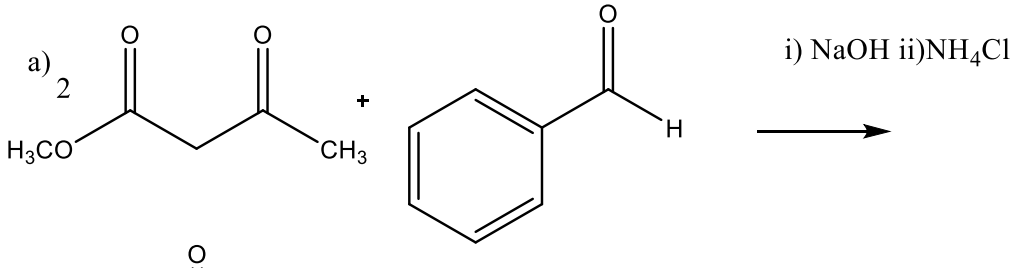






1. (piridinas) Complete las siguientes transformaciones indicando el mecanismo. ALGUNAS TRANSFORMACIONES INCLUYEN UN PASO FINAL DE OXIDACIÓN

a)



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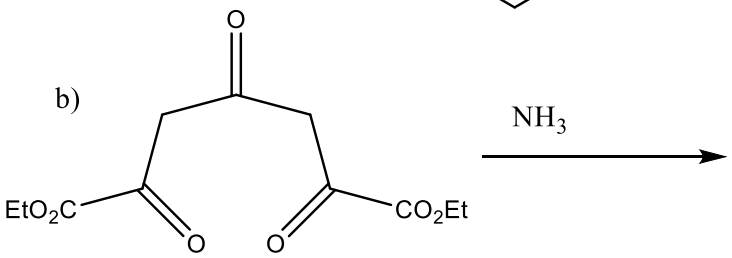
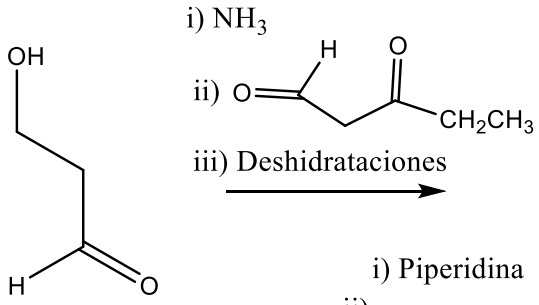
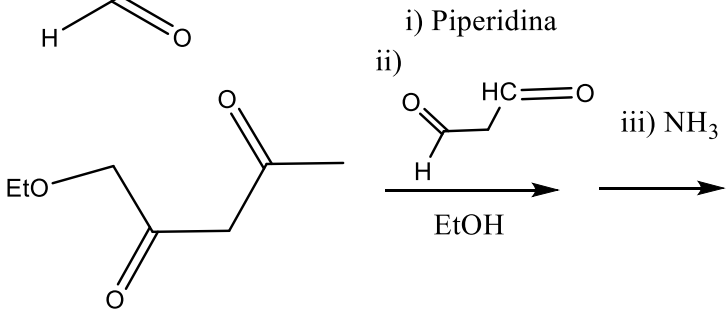


c)



d)



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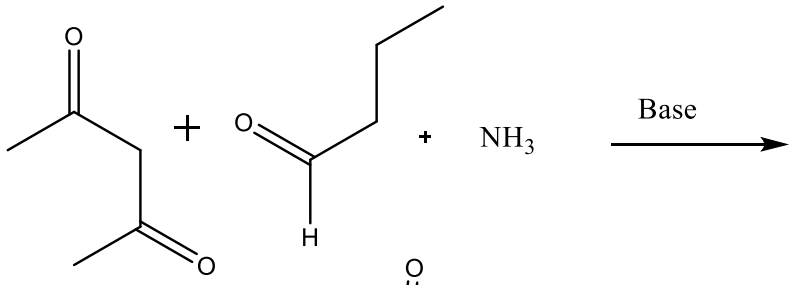

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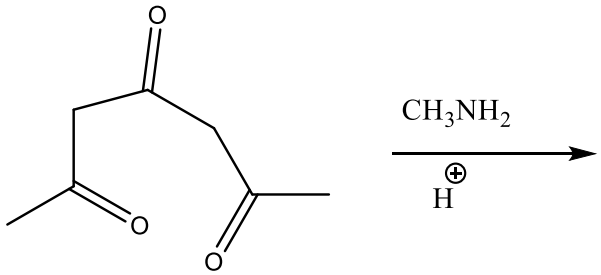

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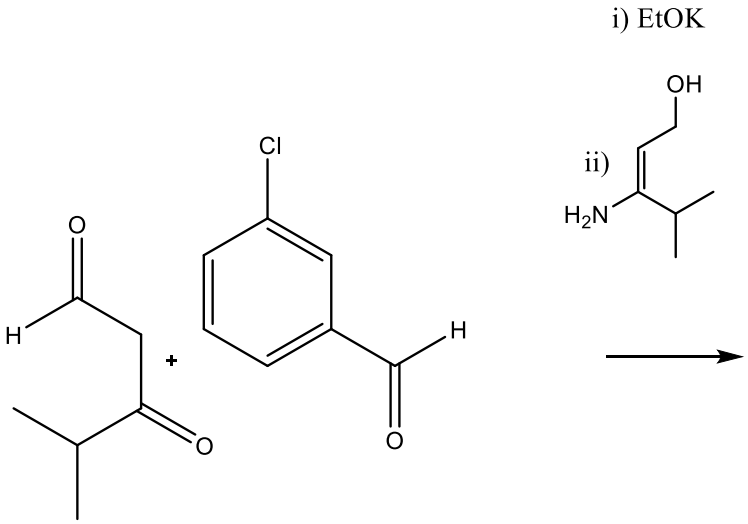

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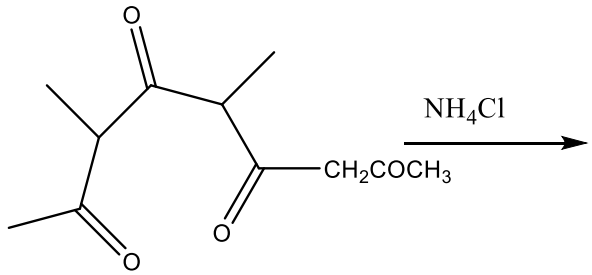
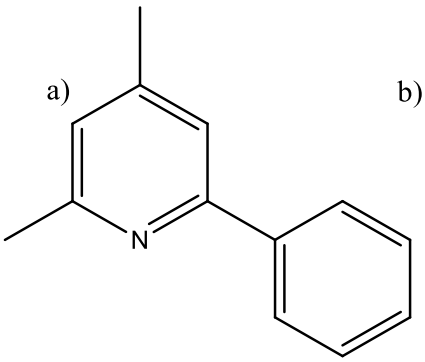
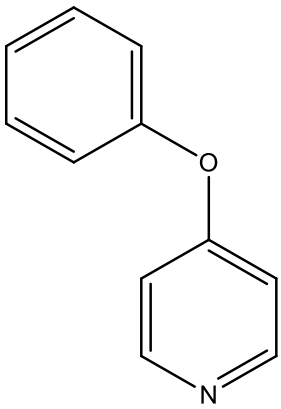


2. Sugiere materias primas y/o reactivos necesarios para una posible síntesis de a) y b)

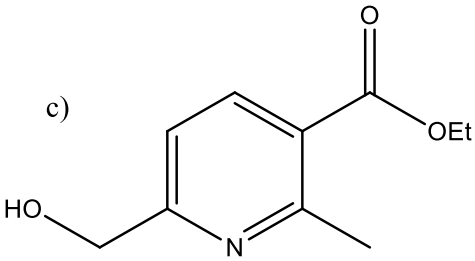
a)



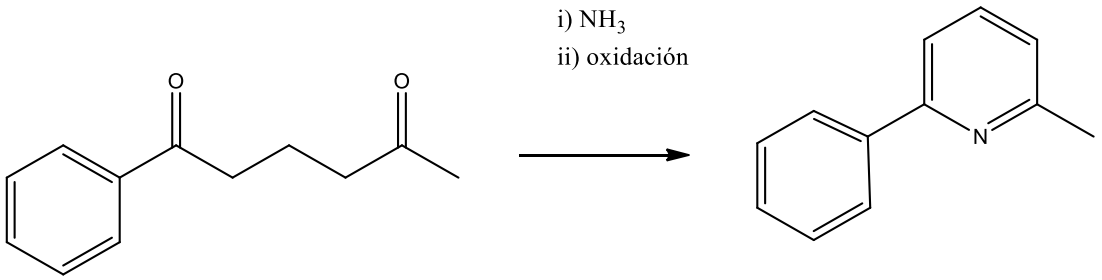
b)



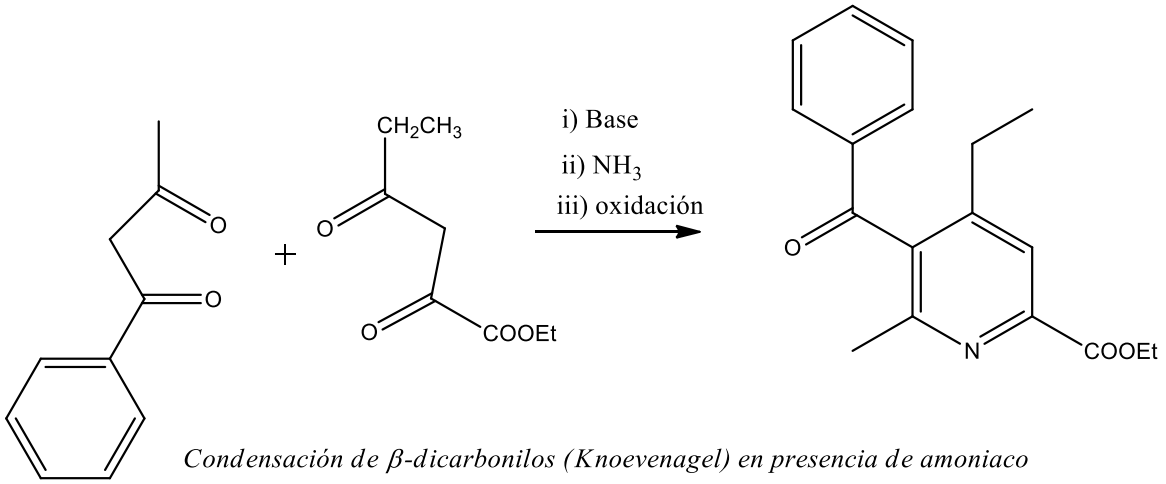
c)



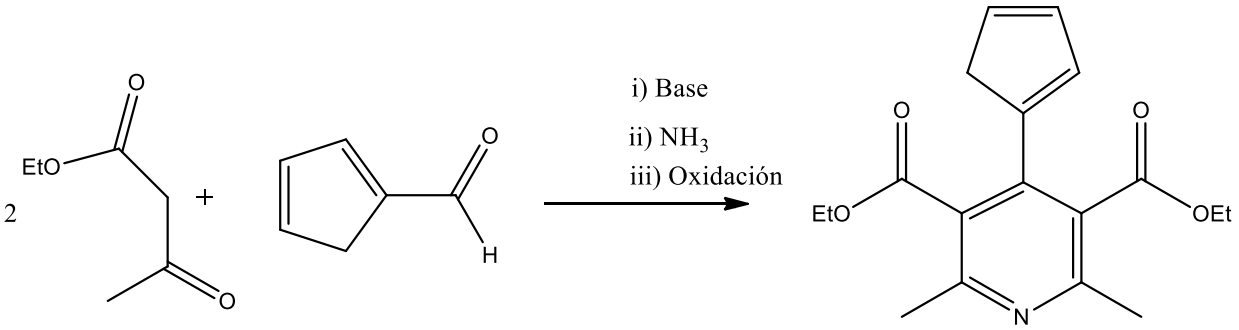
3. Describe los mecanismos de las siguientes reacciones



Desde 1,5-dicarbonilos y amoniaco



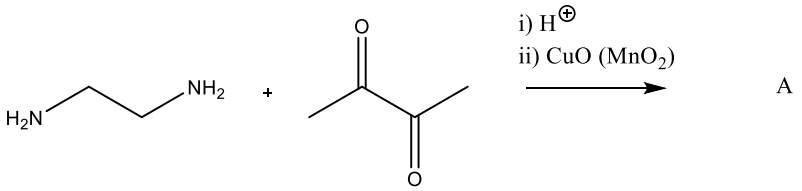
Condensación de β-dicarbonilos (Knoevenagel) en presencia de amoniaco



Síntesis de Hantzsch

4. (pirazinas) Sugiere la estuctura de productos o reactivos y describe mecanismos

a)



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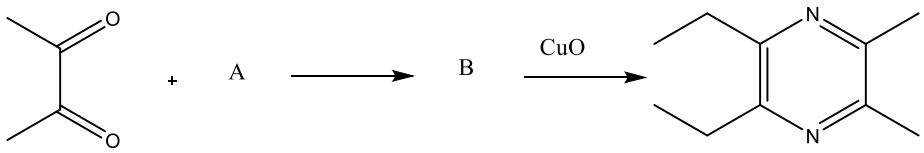
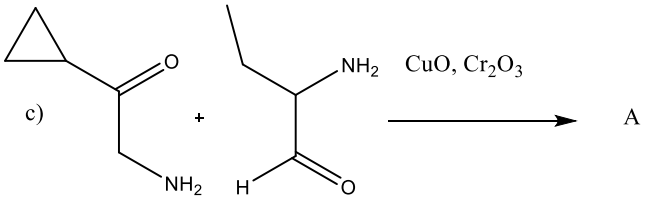
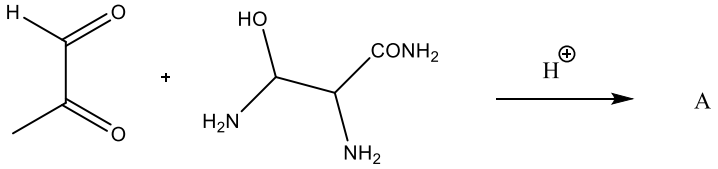


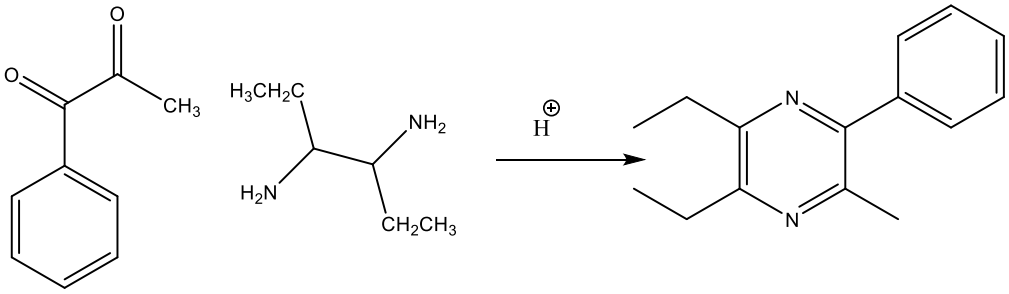
c)

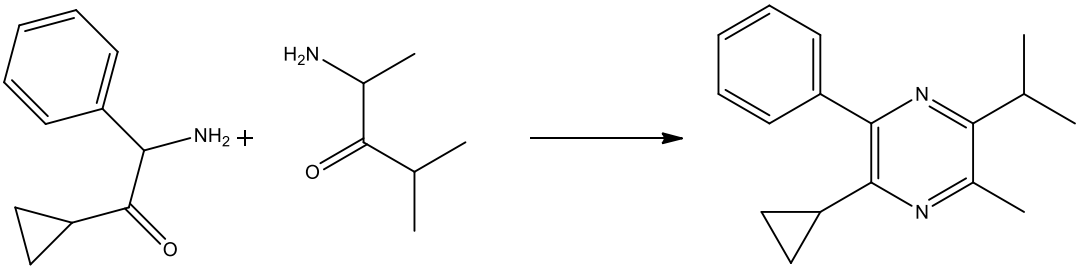


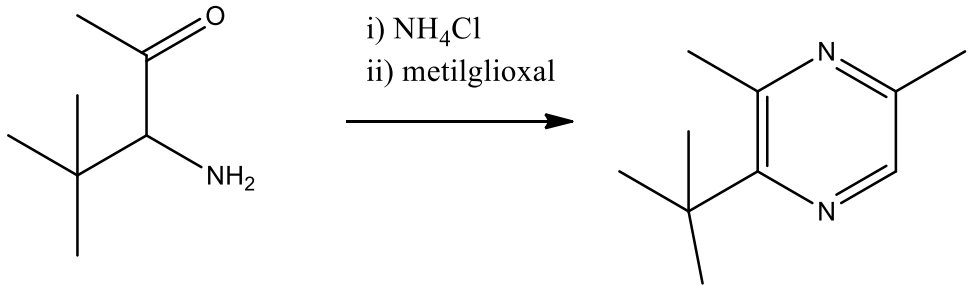
d)

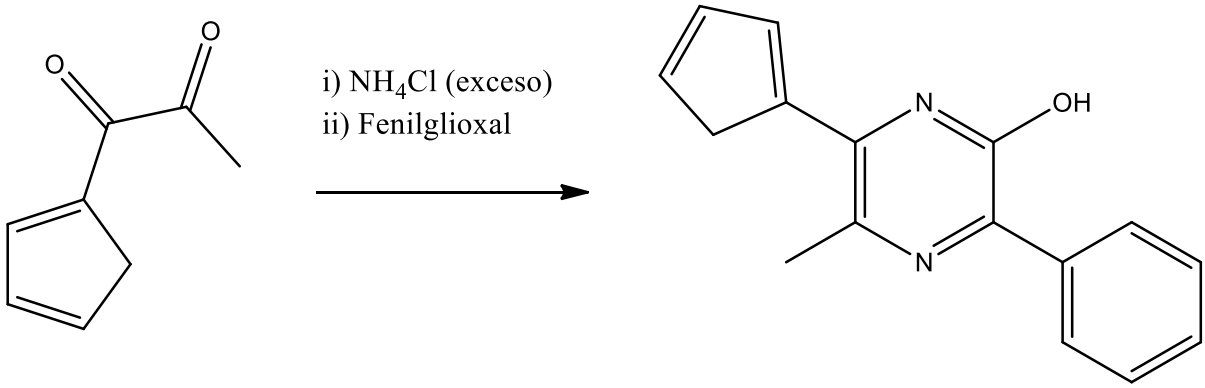


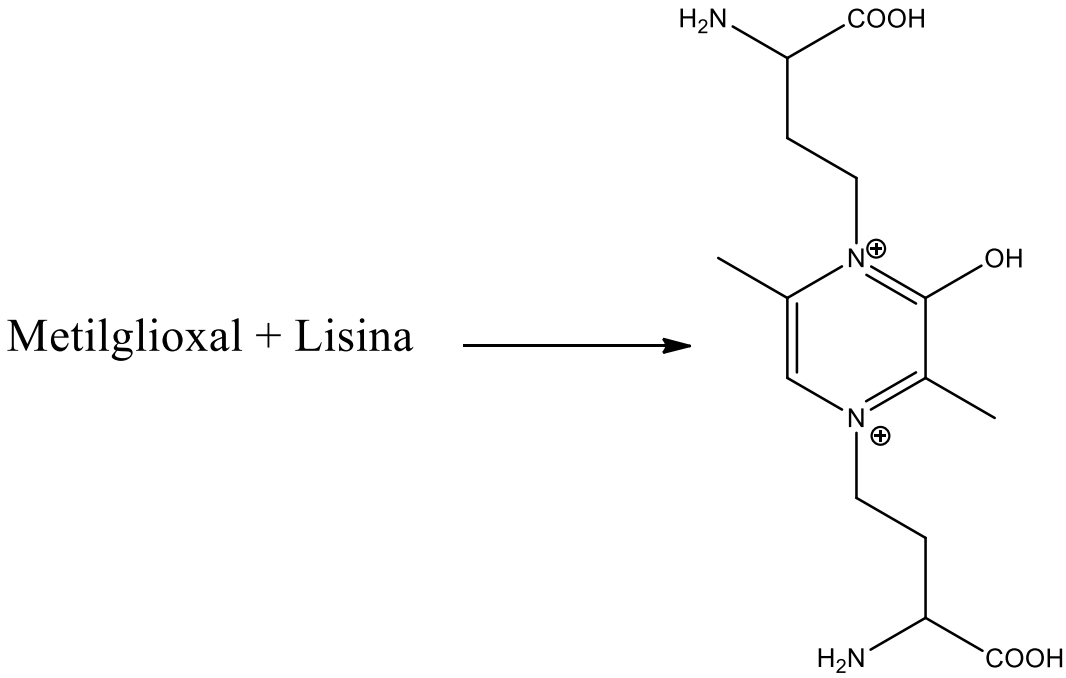
5. Proponga los mecanismos de las siguientes reacciones
(puede ser necesario un paso de oxidación final)






O
NH2
i) NH4Cl
ii) metilglioxal
N
N


O
O
i) NH4Cl (exceso)
ii) Fenilglioxal
N
OH
N


Metilglioxal + Lisina
H2N
COOH
N
OH
N
H2N
COOH