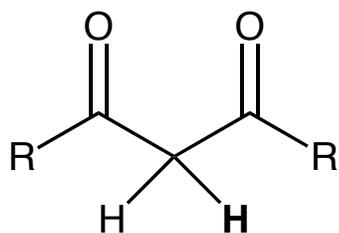
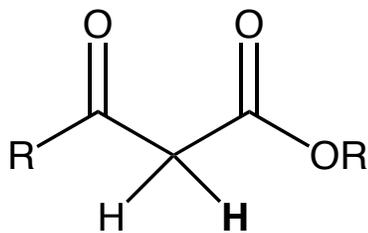


Alkylation de dérivés carbonylés-1,3



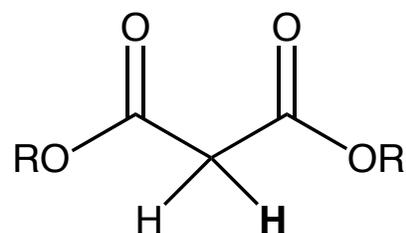
1,3-dicétone

$$pK_a = 9$$



1,3-cétoester

$$pK_a = 11$$

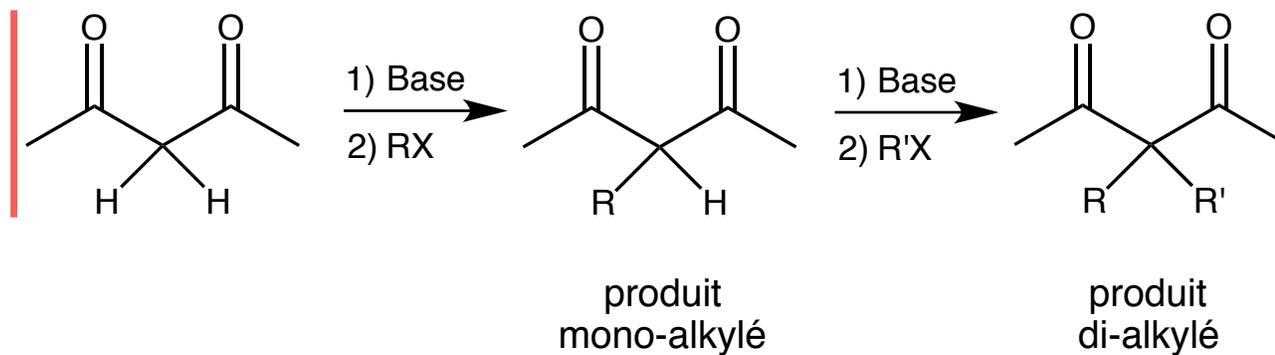


1,3-diester (malonate)

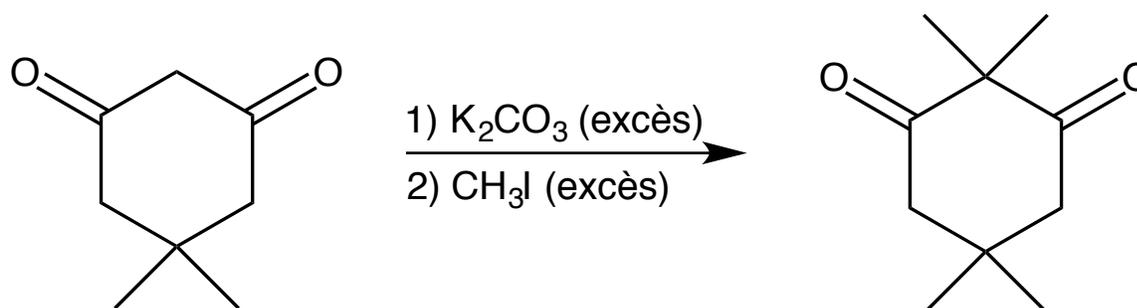
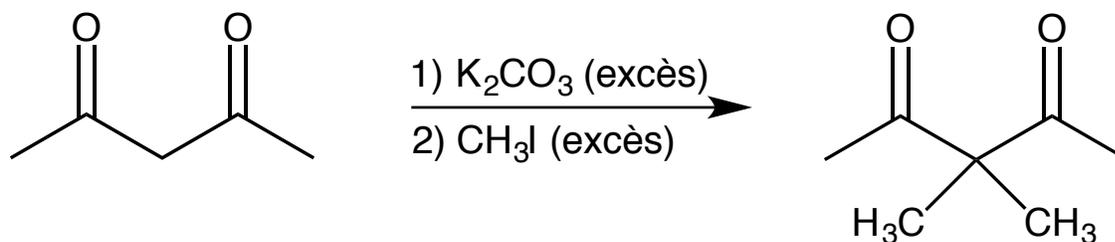
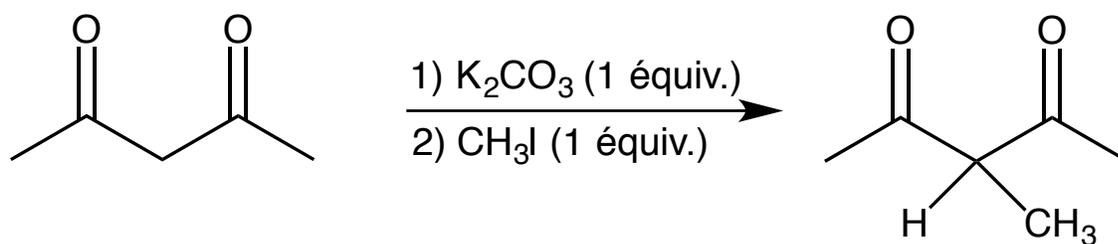
$$pK_a = 13$$

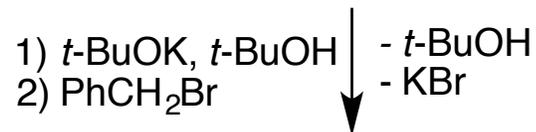
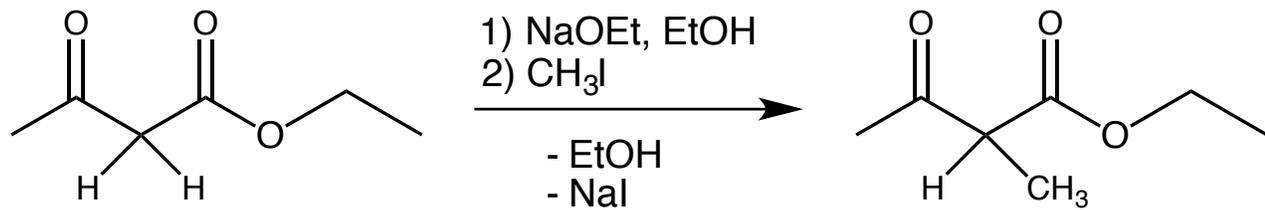
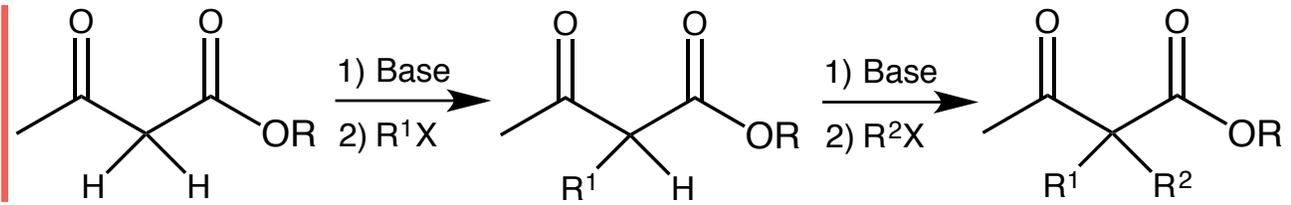
a) Alkylation de 1,3-dicétones

a) Alkylation de 1,3-dicétones (suite)

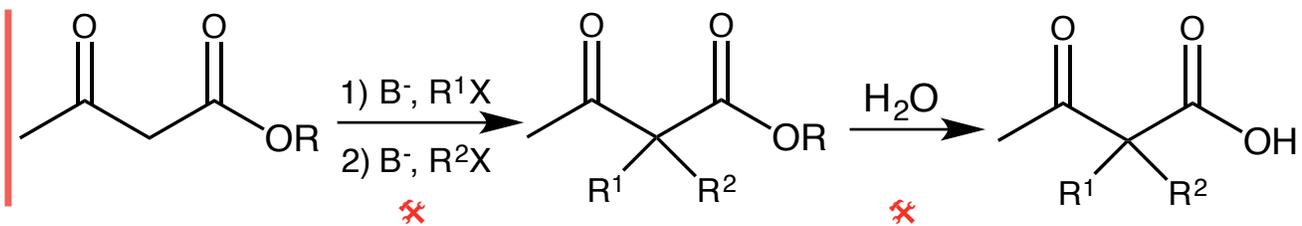


Exemples



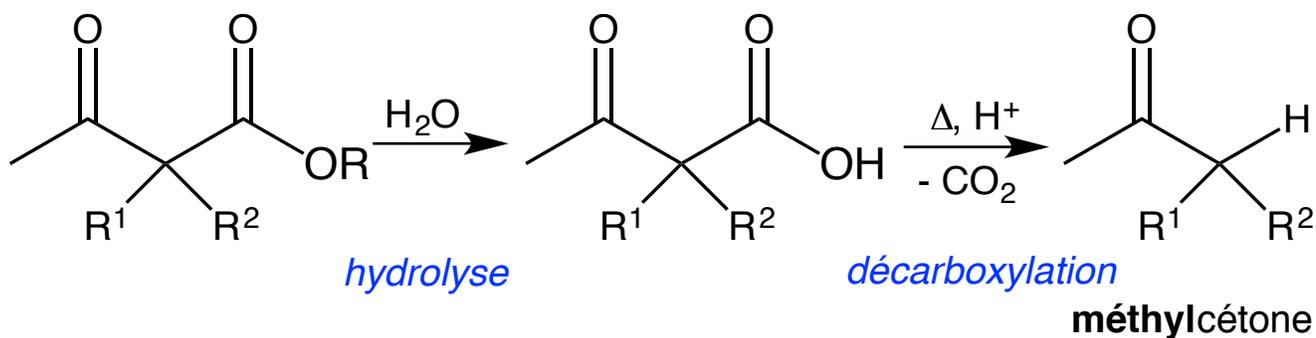
b) Alkylation de β -cétosters

Synthèse acétoacétique (synthèse de méthylcétones)



- alkylation(s) avec R^1X , R^2X
- hydrolyse de l'ester
- décarboxylation ($-\text{CO}_2$)

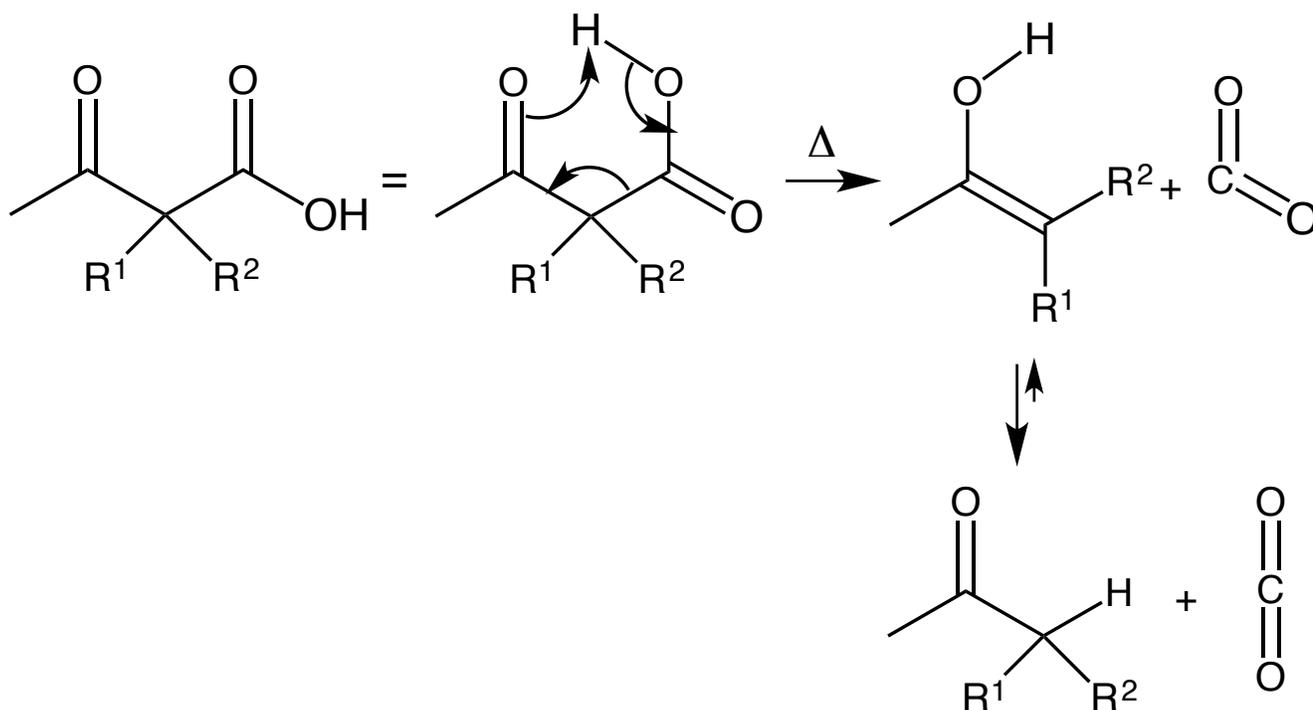
Synthèse acétoacétique (suite)



Hydrolyse « Matière vue à la page Dérivésacides-31

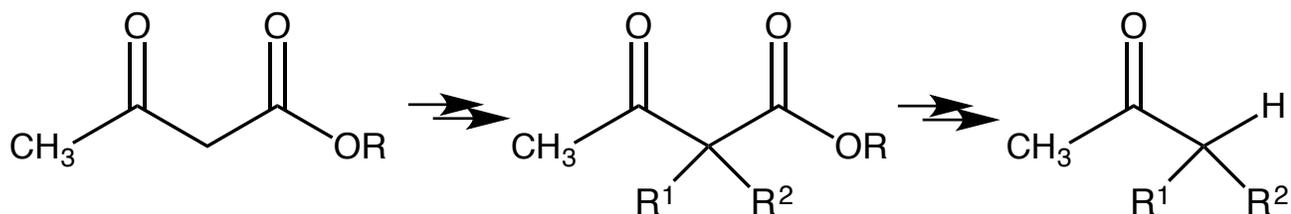
Décarboxylation

= réaction par laquelle un acide carboxylique perd du CO₂

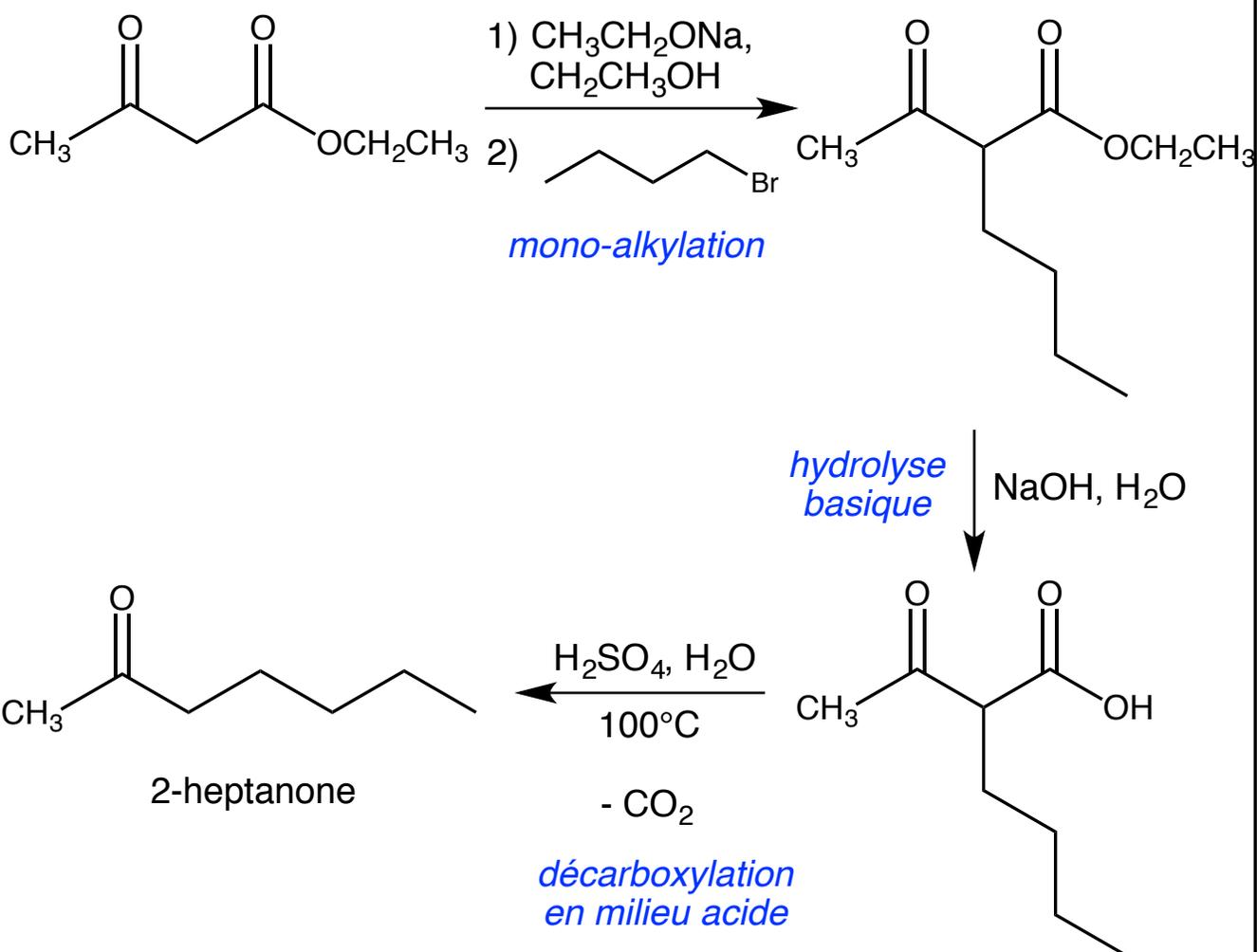


Synthèse acétoacétique (suite)

En résumé :

R¹ ou R² peut être H

Exemple

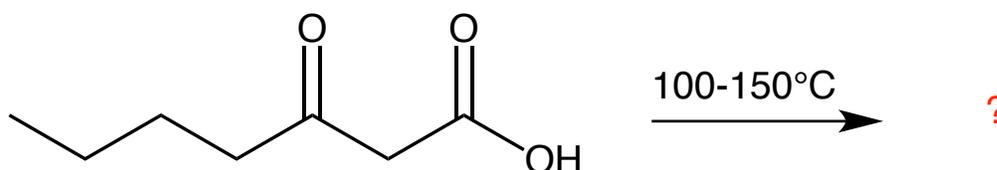


Synthèse acétoacétique (suite)

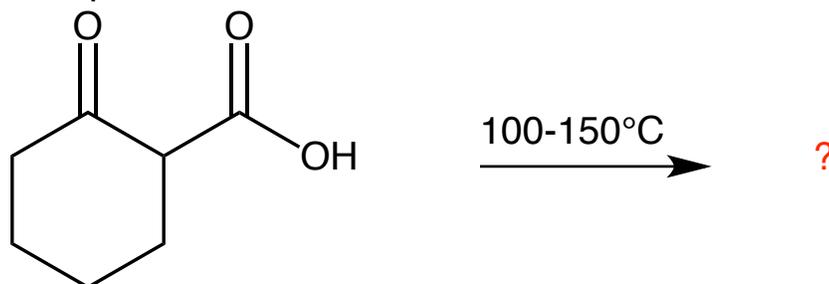


Exercices

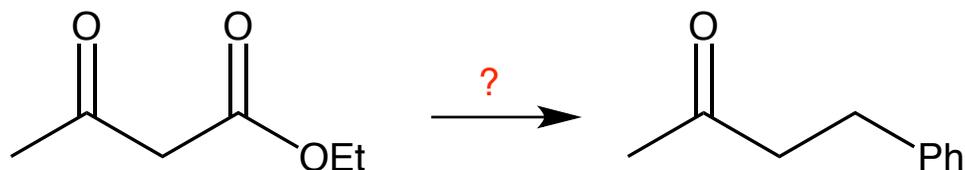
1) Écrivez le produit et le mécanisme de la réaction suivante :



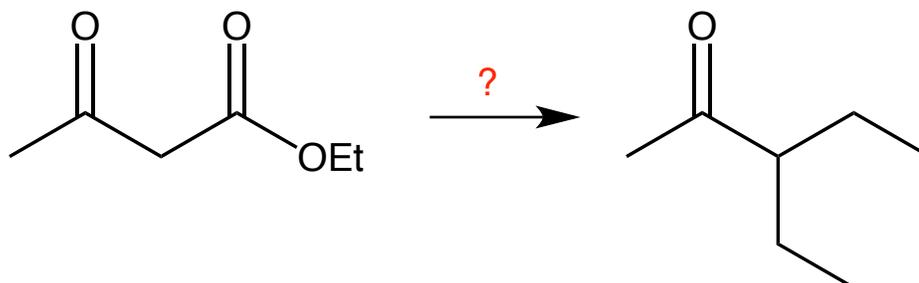
2) Écrivez le produit et le mécanisme de la réaction suivante :



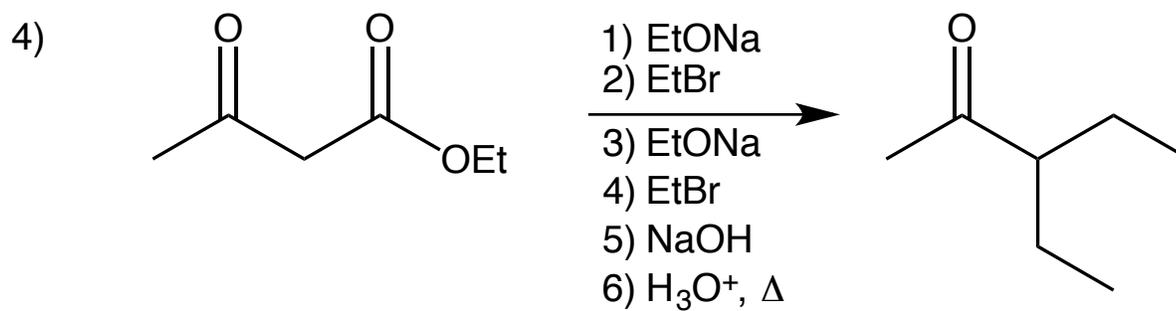
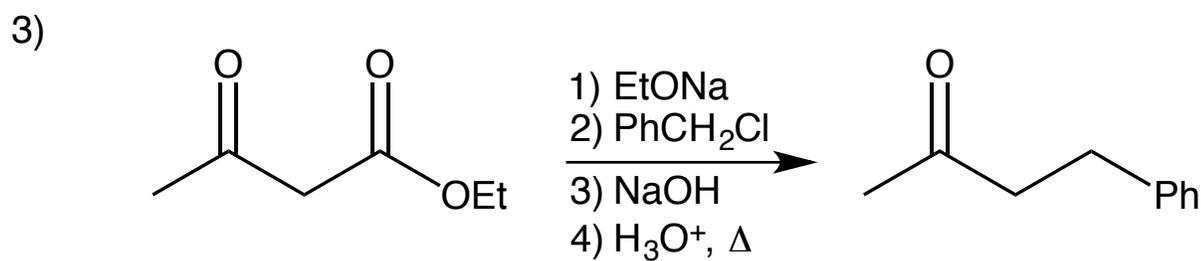
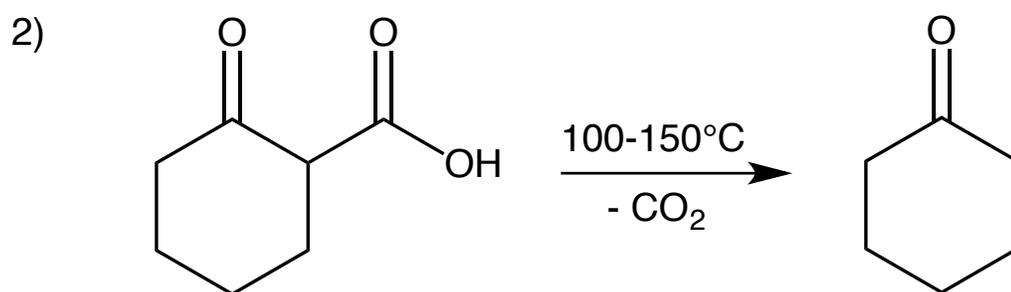
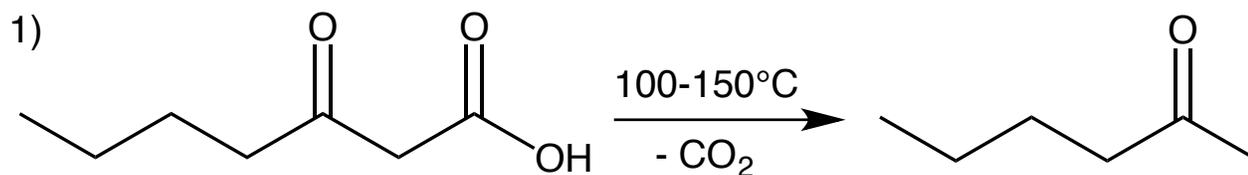
3) Proposez une voie de synthèse pour la 4-phénylbutan-2-one au départ d'acétoacétate d'éthyle :



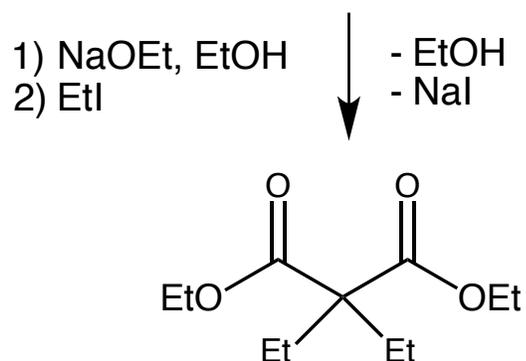
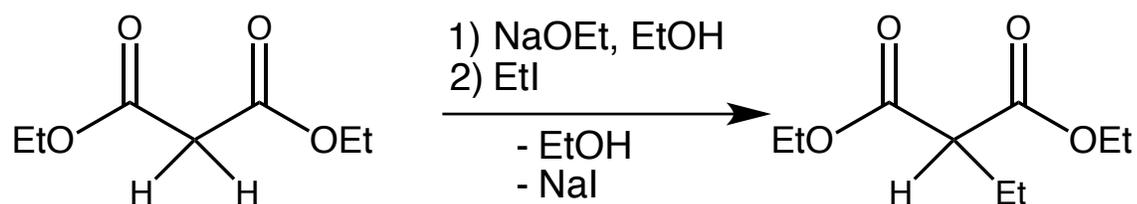
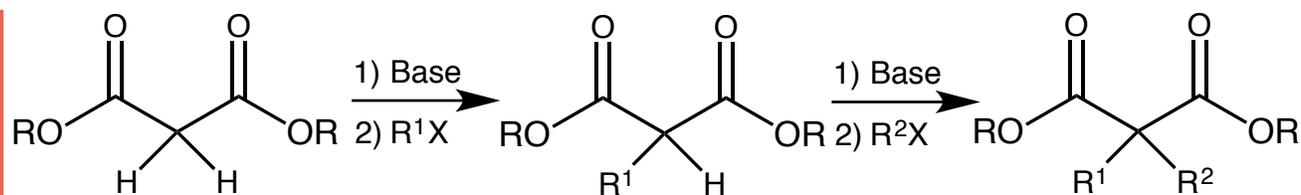
4) Proposez une voie de synthèse pour la 3-éthylpentan-2-one au départ d'acétoacétate d'éthyle :



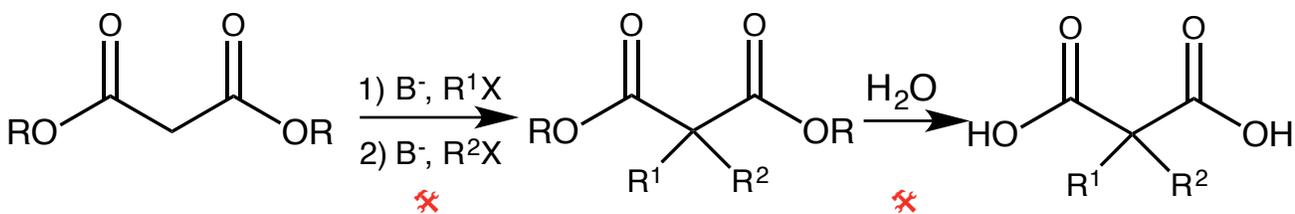
Exercices (solutions)



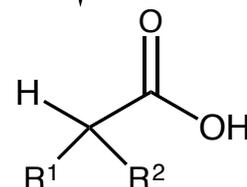
c) Alkylation de diesters-1,3



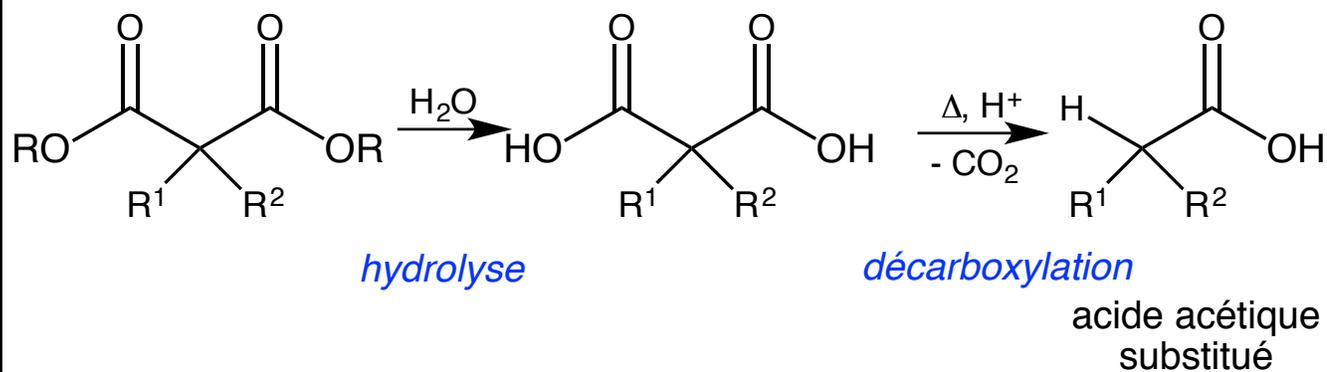
Synthèse malonique (synthèse d'acides acétiques mono-, disubstitués)



- alkylation(s) avec R^1X , R^2X
- hydrolyse du diester
- décarboxylation ($-\text{CO}_2$)

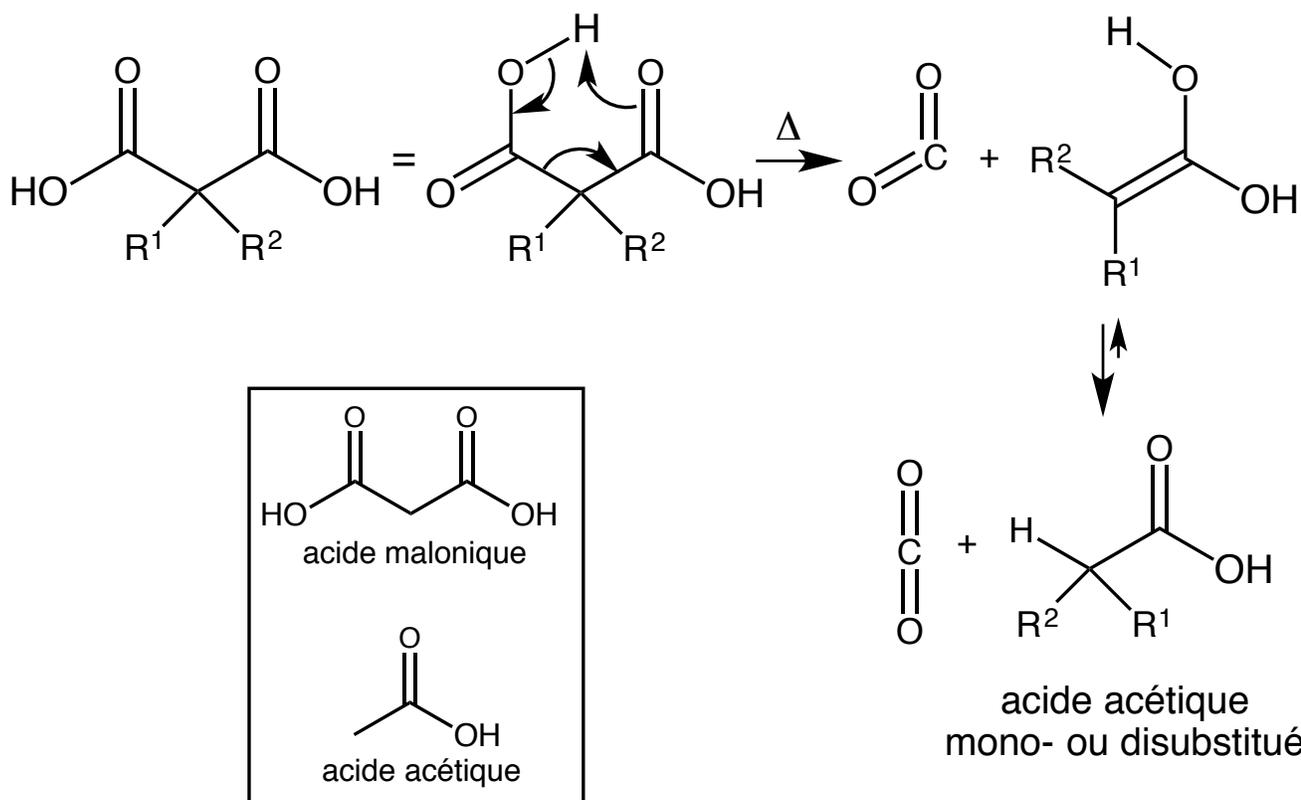


Synthèse malonique (suite)



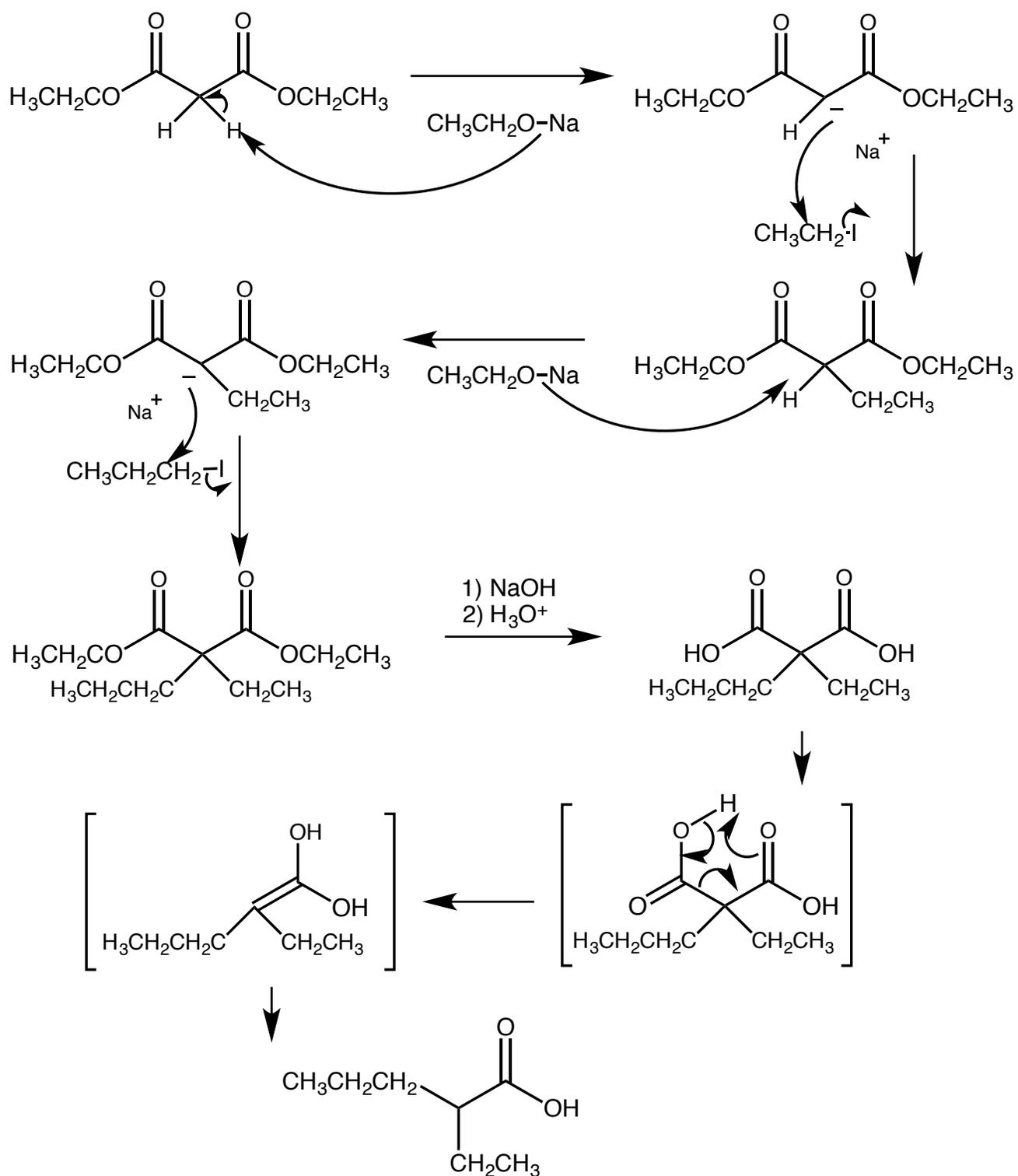
Hydrolyse « Matière vue à la page derivesacides-31

Décarboxylation



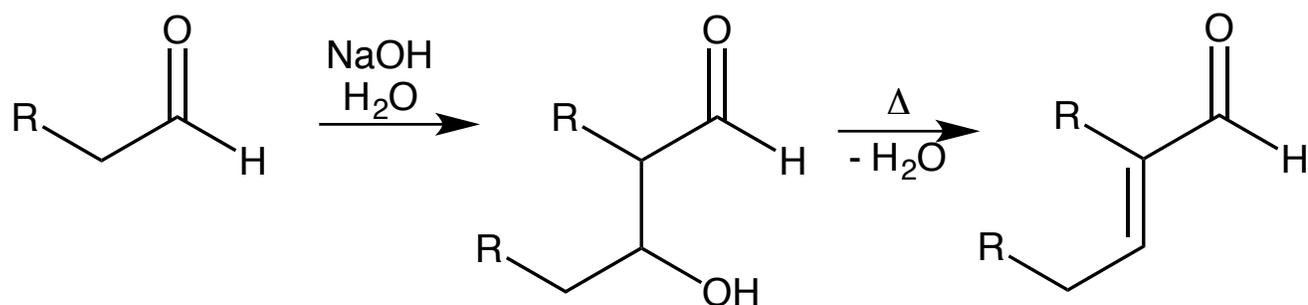
Synthèse malonique (suite)

Exemple

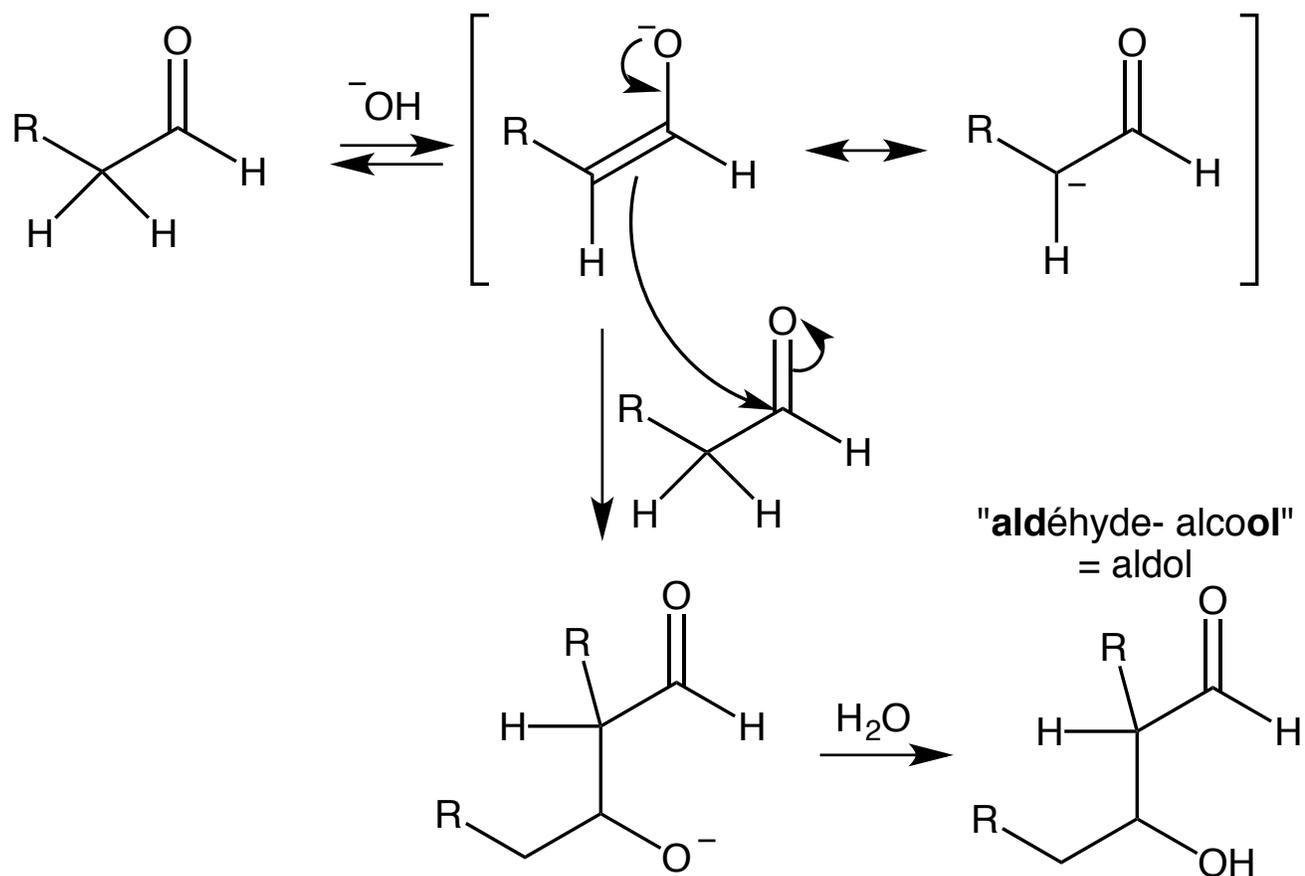


Réactions des énols et des énolates (suite)

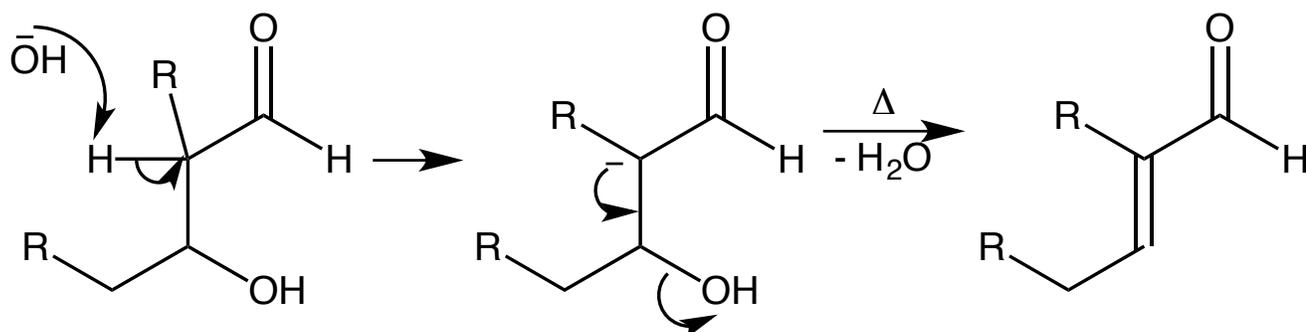
4) Réactions des énolates avec des dérivés carbonylés



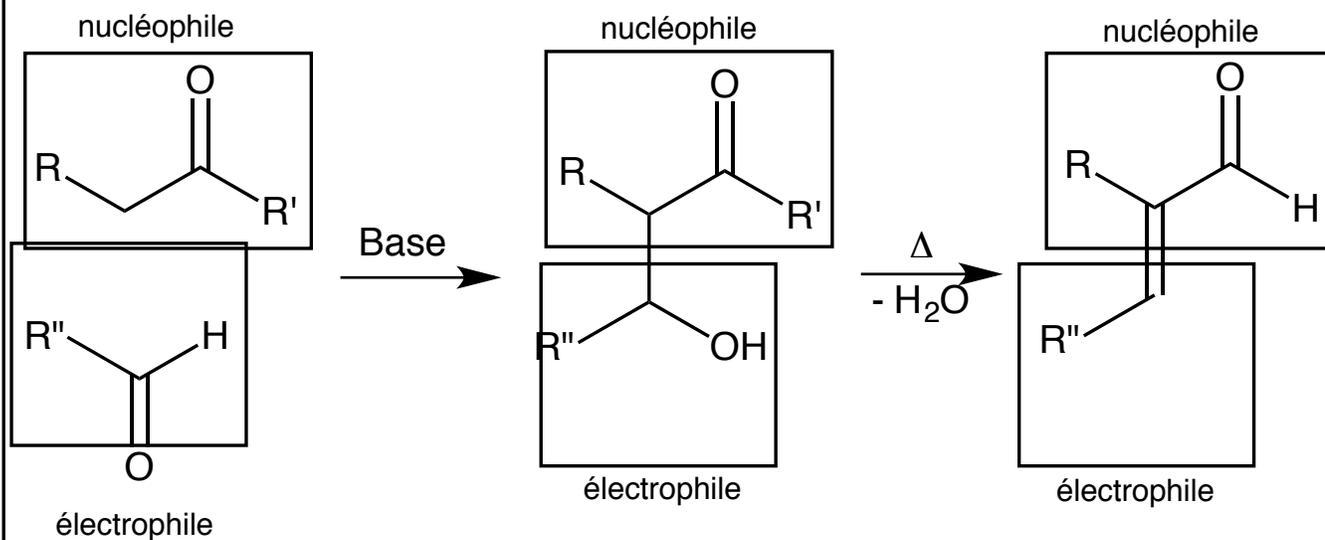
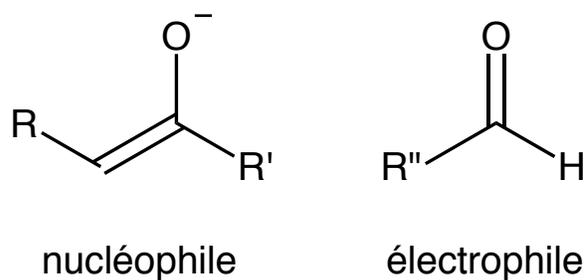
Condensation aldolique

aldolisation

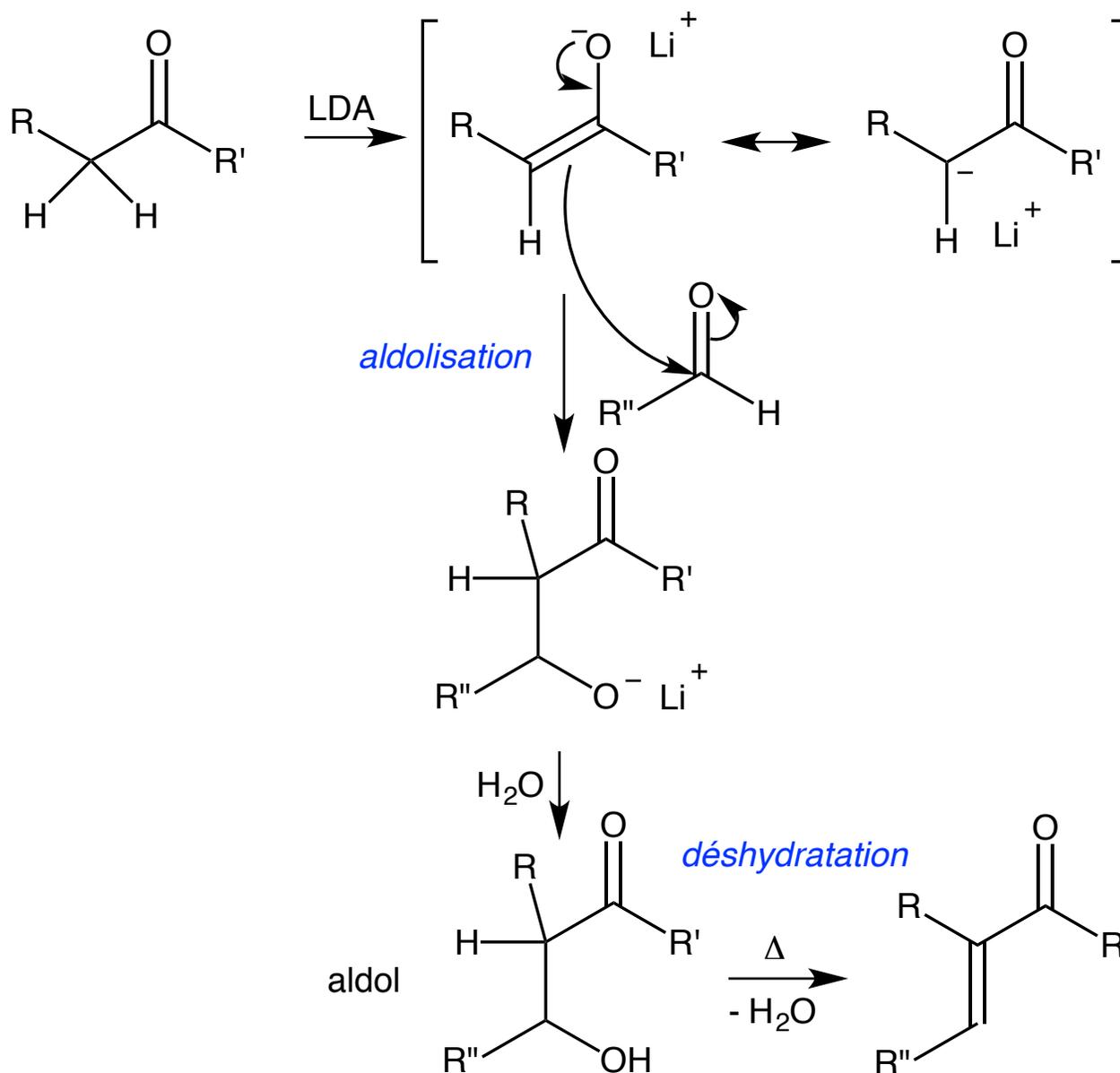
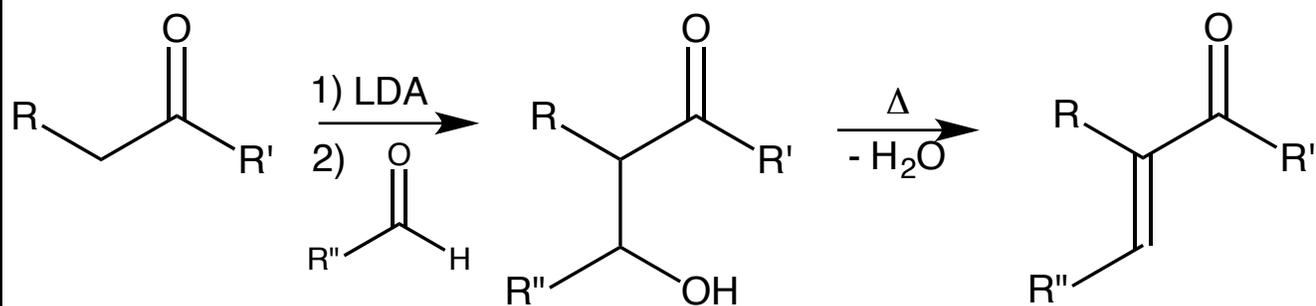
4) Réactions des énolates avec des dérivés carbonylés (suite)

déshydratation

Réaction d'un nucléophile (énolate) avec un électrophile (un composé carbonylé)



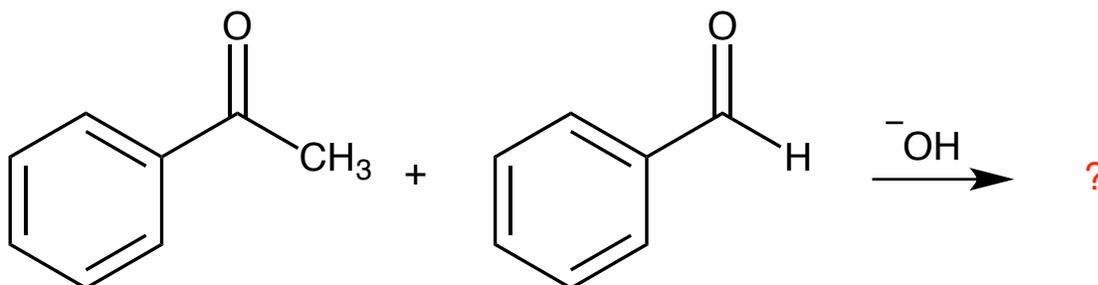
4) Réactions des énolates avec des dérivés carbonyles (suite)



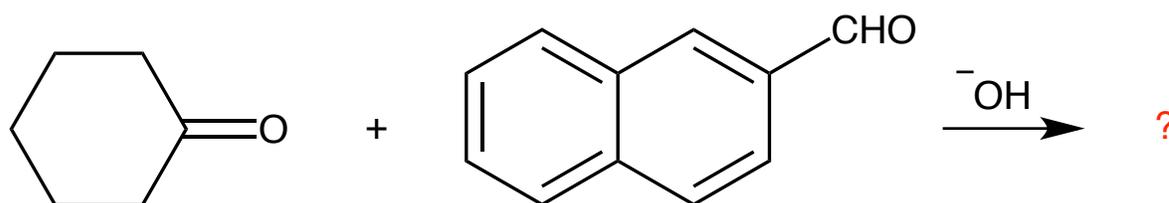
Exercices

Complétez les réactions suivantes :

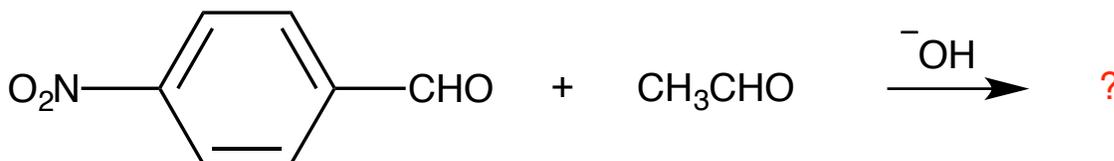
1)



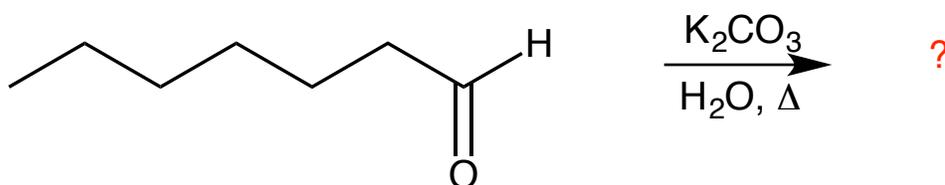
2)



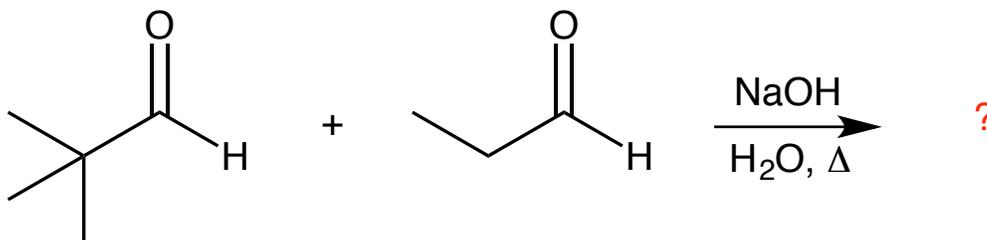
3)



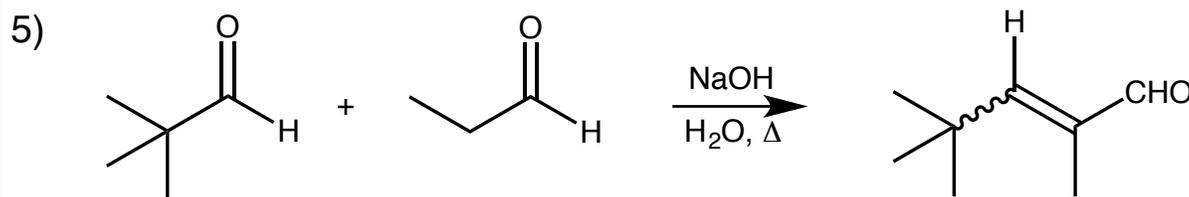
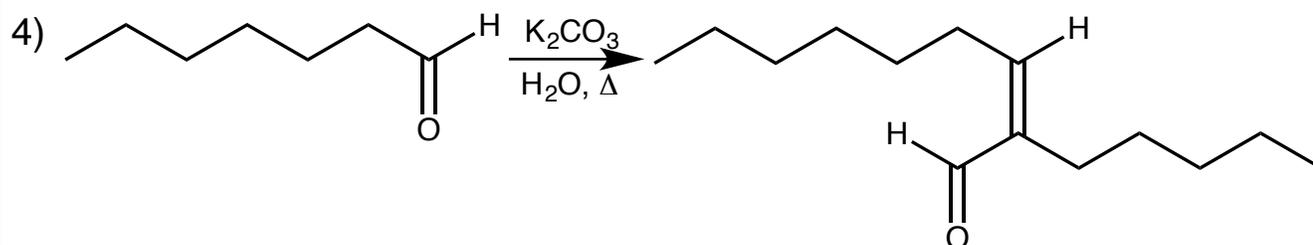
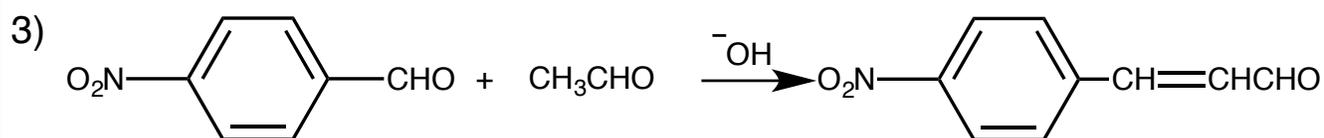
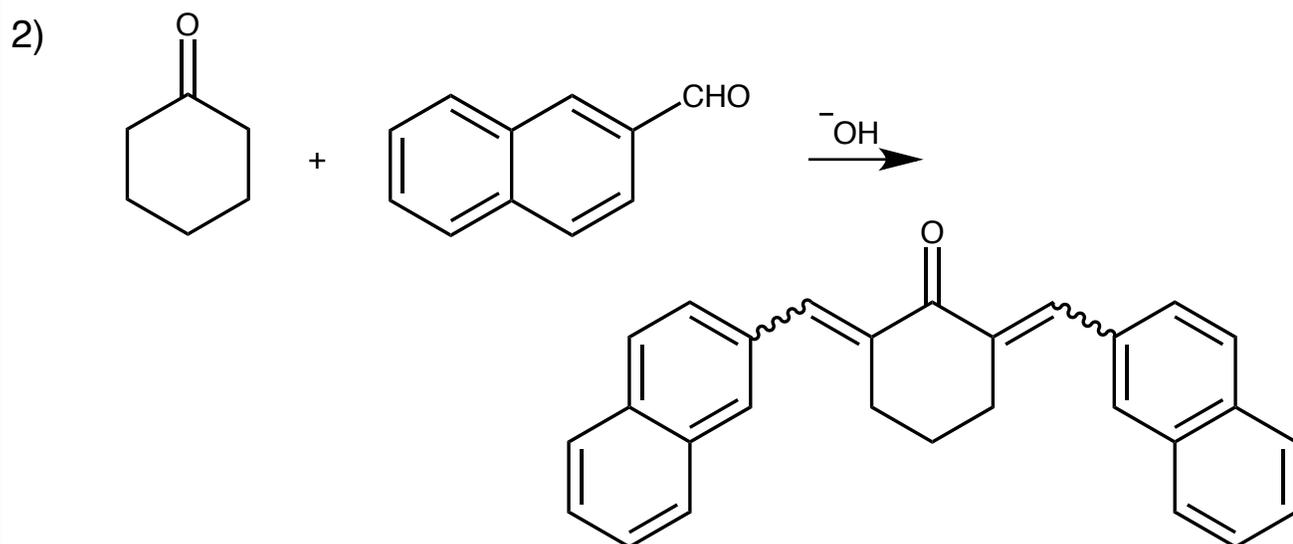
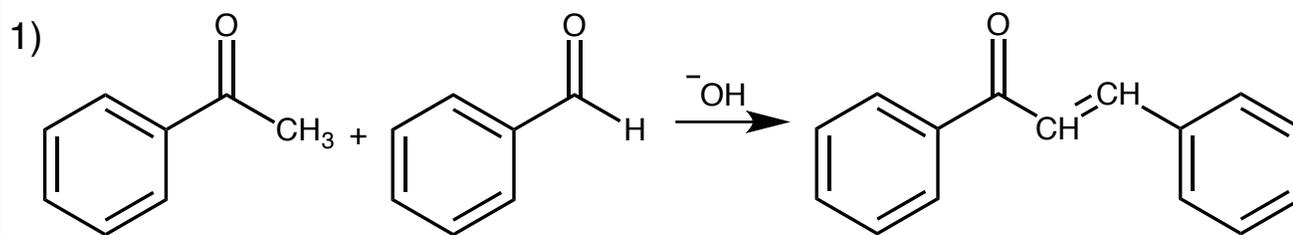
4)



5)

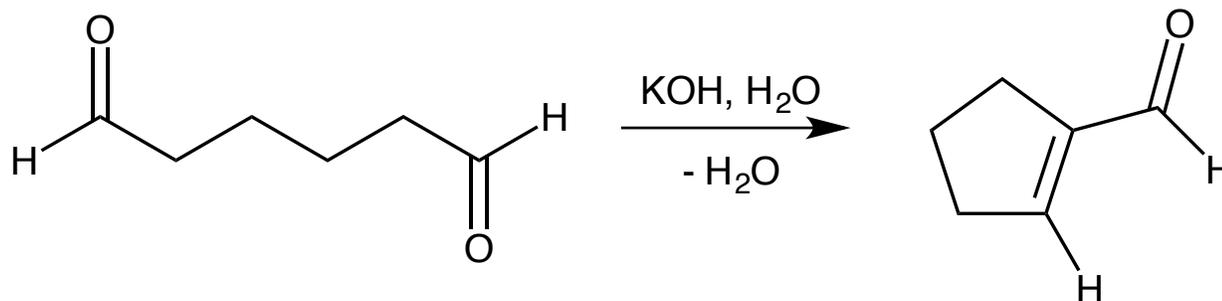


Solutions



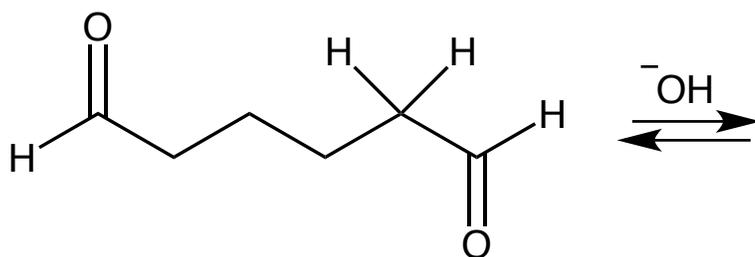
4) Réactions des énolates avec des dérivés carbonylés (suite)

Condensation aldolique intramoléculaire

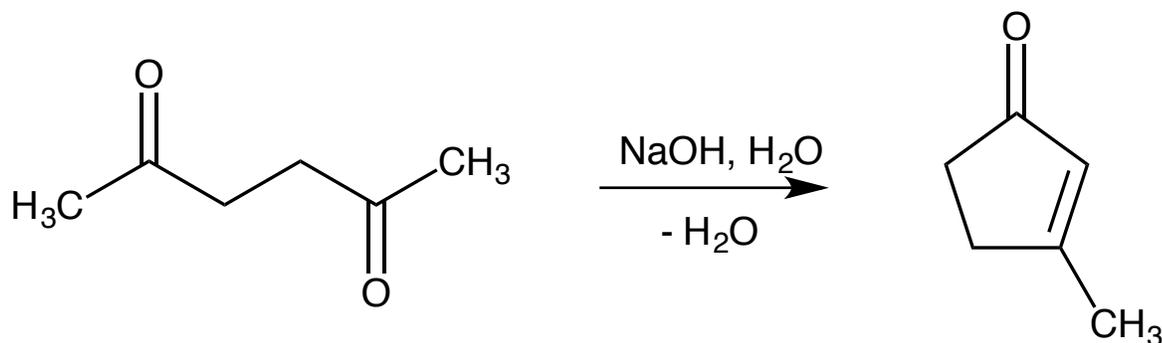


La réaction **intramoléculaire** est favorisée par rapport à une réaction **intermoléculaire**.

Mécanisme

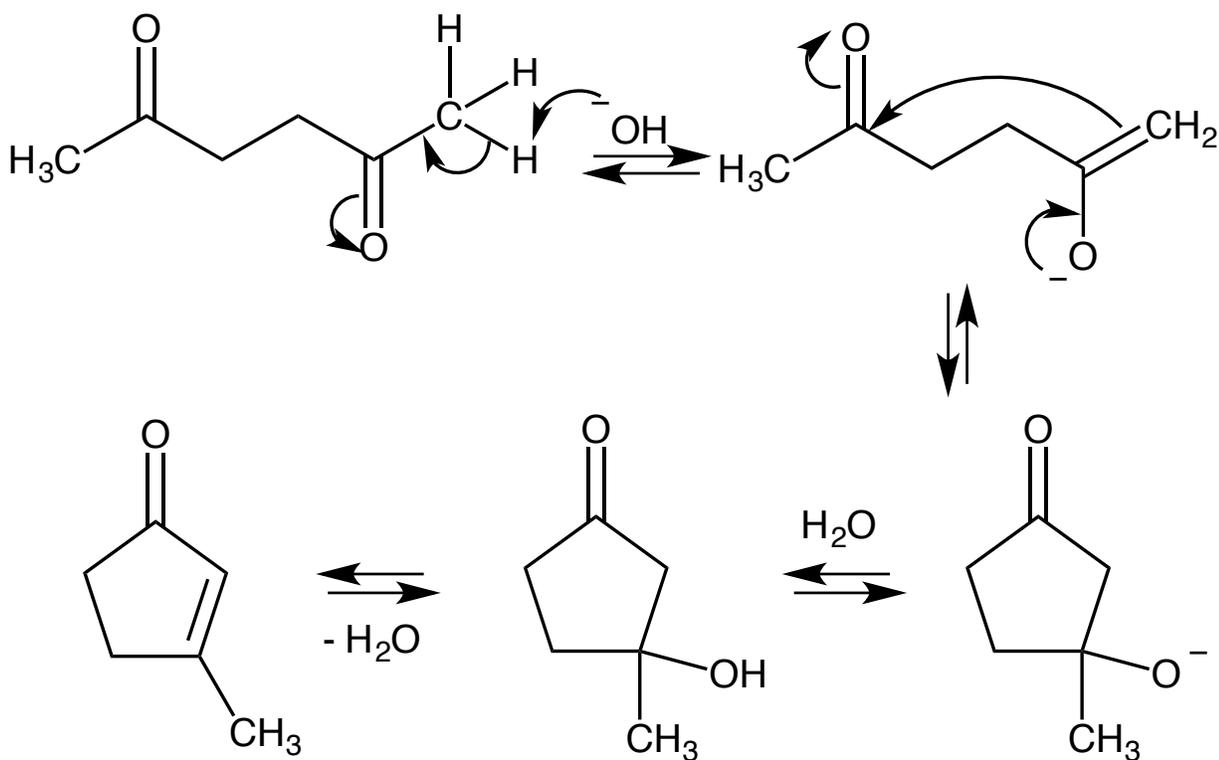


Condensation aldolique intramoléculaire (suite)



Habituellement, c'est le cycle le moins tendu qui se forme, soit souvent des cycles à 5 ou à 6 atomes..

Mécanisme



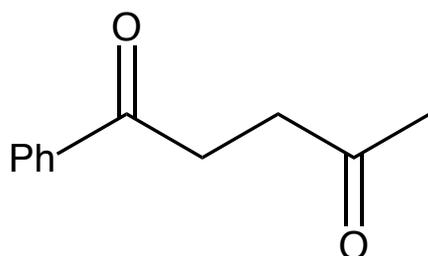
Le cycle à 3 carbones trop tendu ne se formera pas.

Condensation aldolique intramoléculaire Suite)

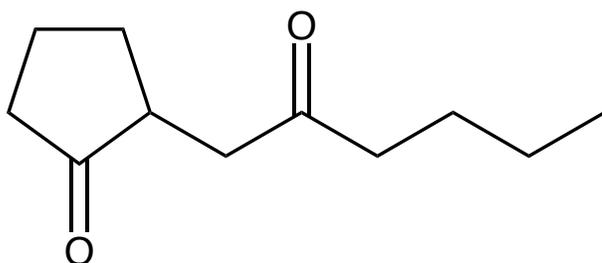
Exercices

Prédire l'issue des condensations aldoliques intramoléculaires des composés suivants.

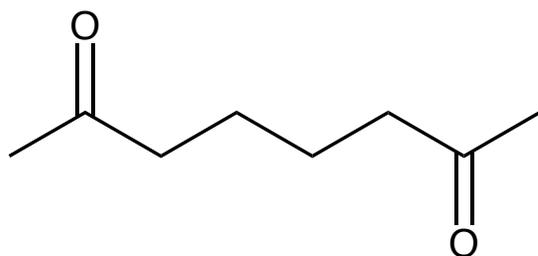
1)



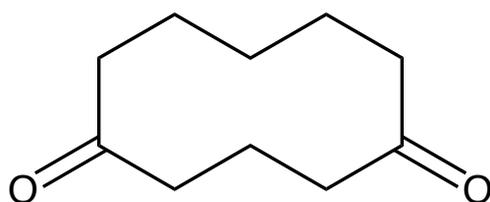
2)



3)

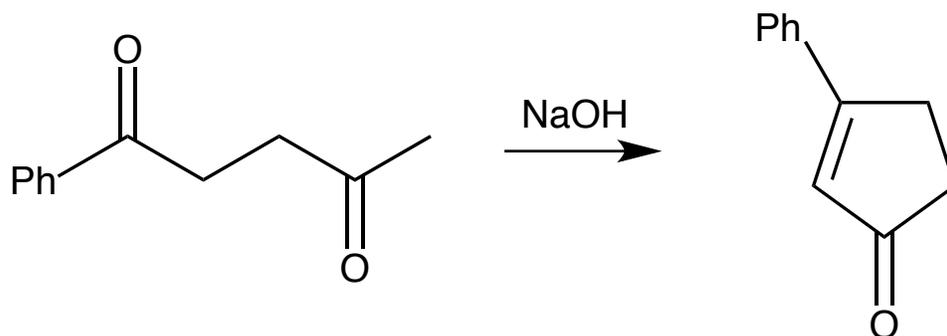


4)



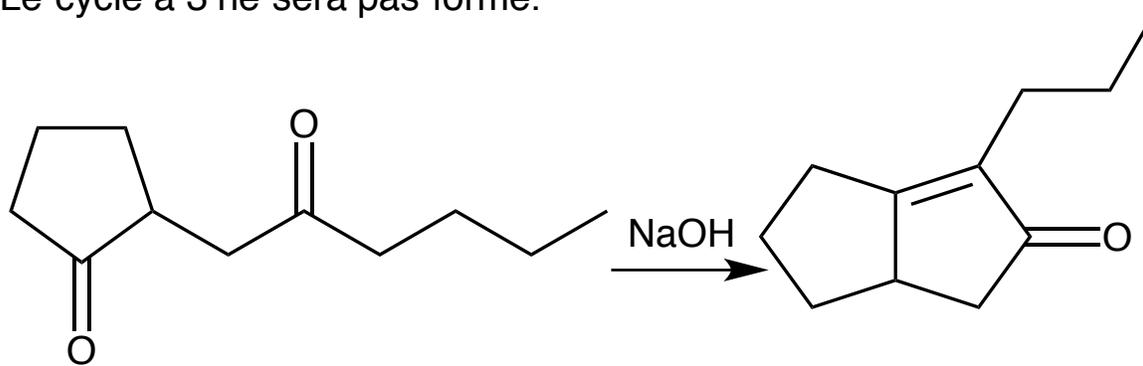
Solutions

1)



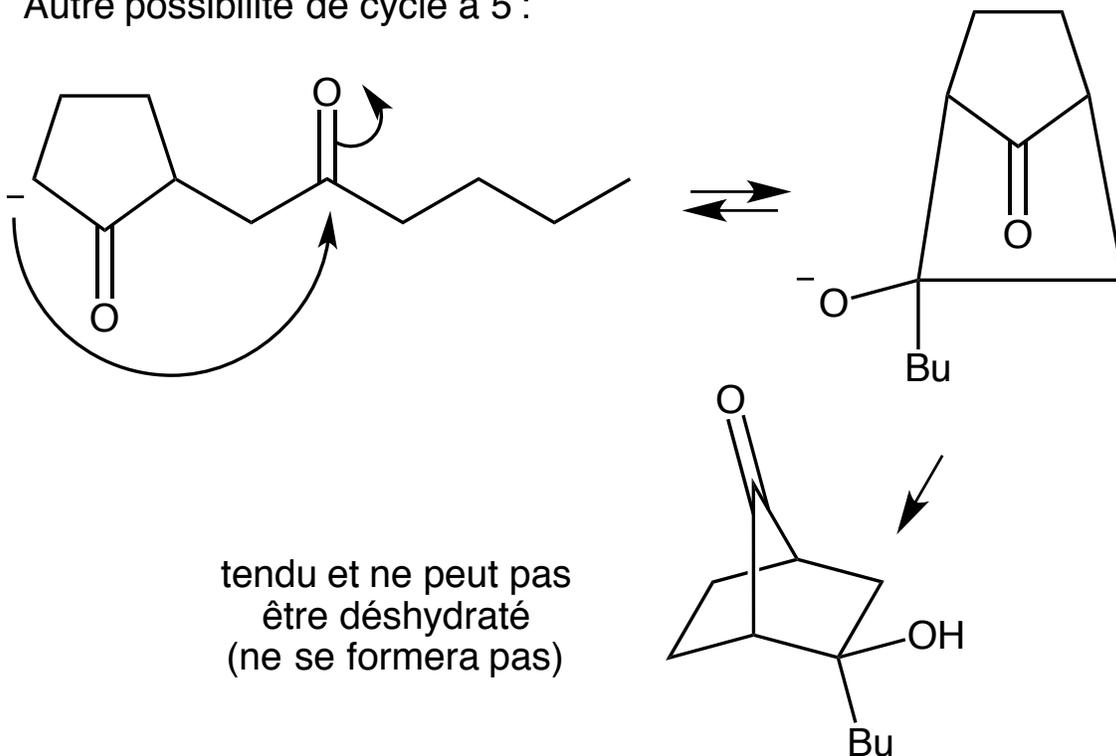
Le cycle à 3 ne sera pas formé.

2)

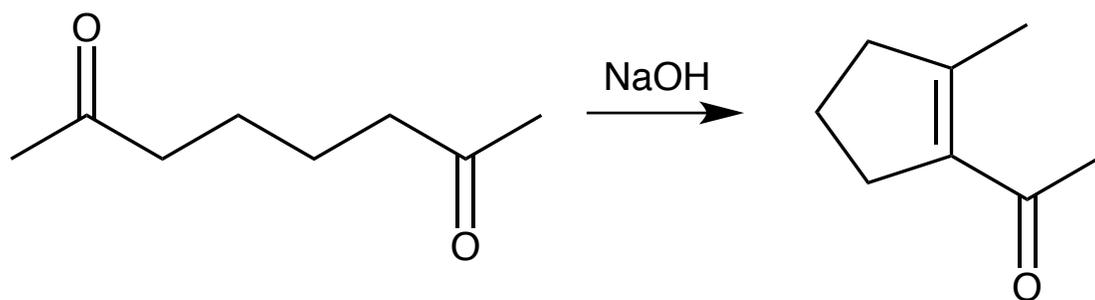


Les cycles à 3 ne seront pas formés.

Autre possibilité de cycle à 5 :



3)



4)

