

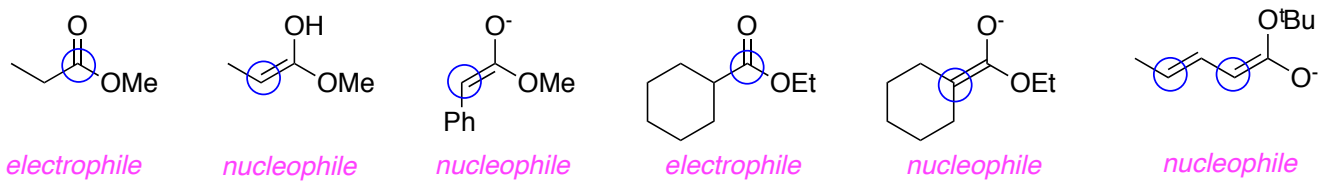
Reactions Of Ester Enolates With Esters

from chapter(s) _____ in the recommended text

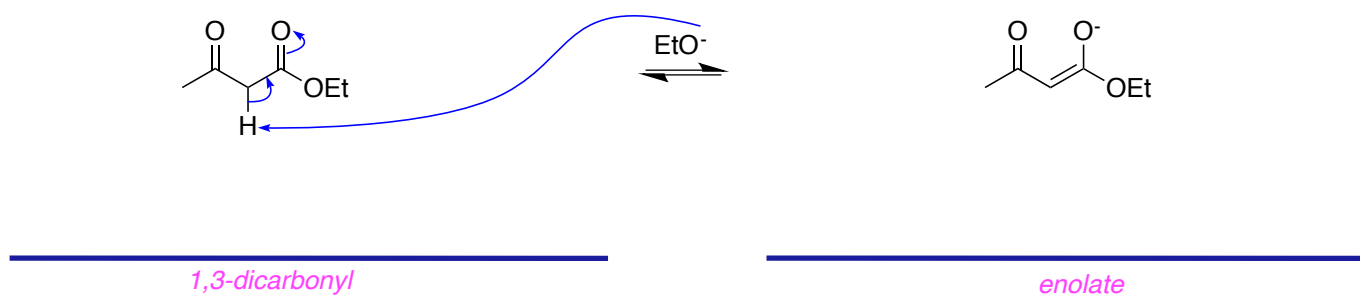
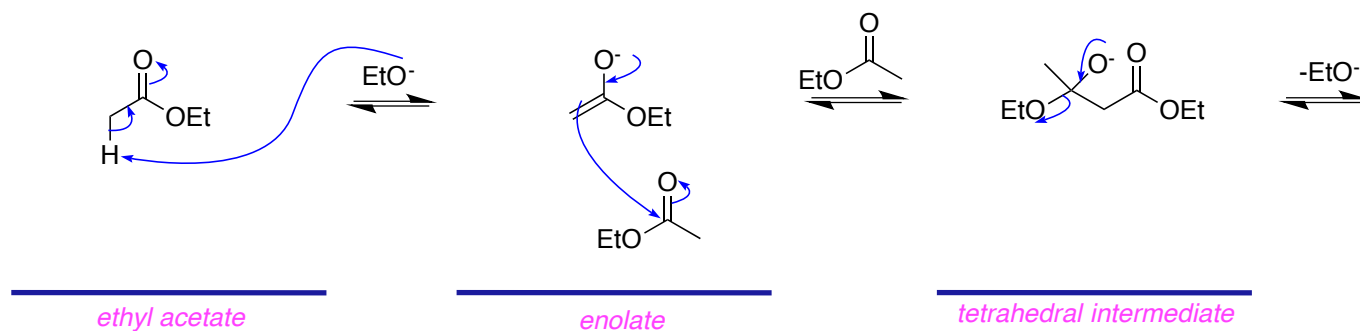
A. Introduction

B. Enolates With Ester Electrophiles (Claisen Condensations)

Homocoupling Of Esters



enolates with esters.

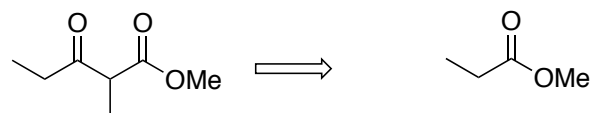
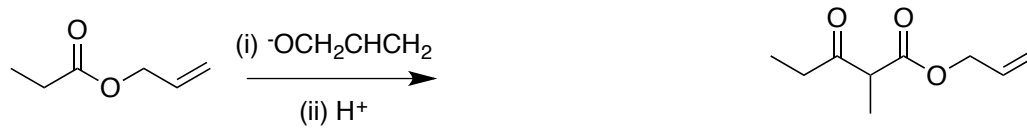


*more
stiochiometric.*

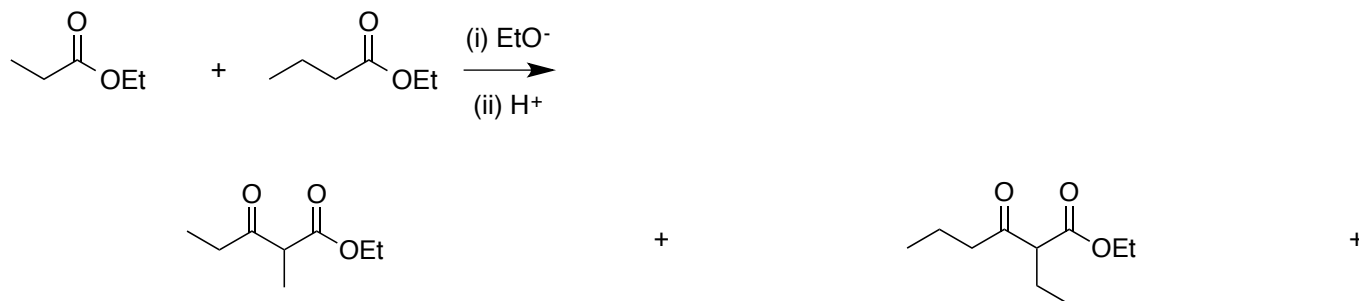
transesterification.



1,3-dicarbonyl

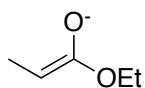
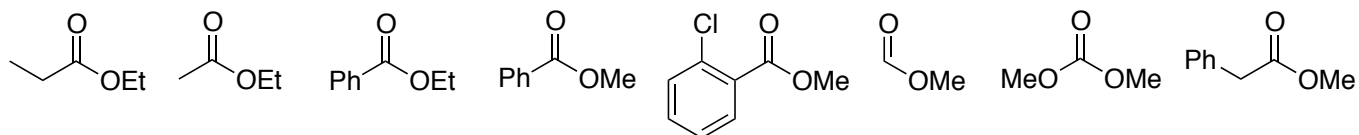


Uncontrolled Cross-Claisen Condensations

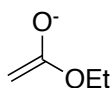


constitutional isomers

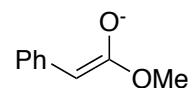
Controlled Cross-Claisen Condensations



enolate 1

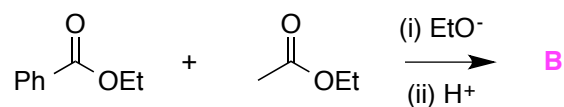
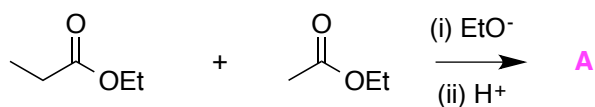


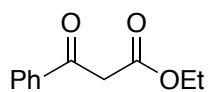
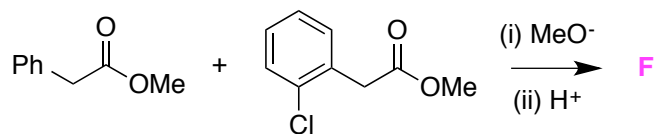
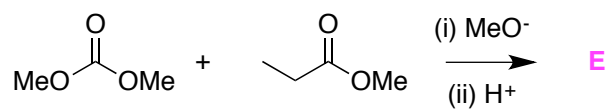
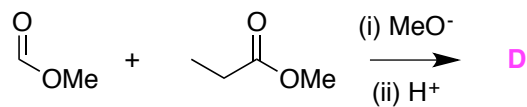
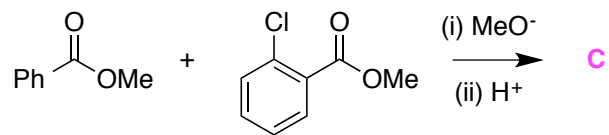
enolate 2



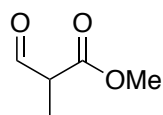
enolate 3

only one

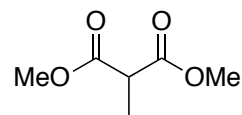




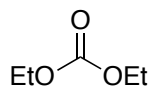
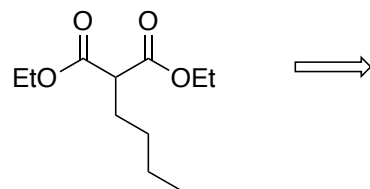
letter B



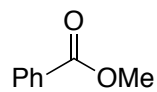
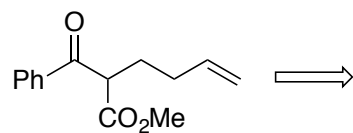
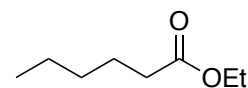
letter D



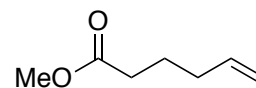
letter E



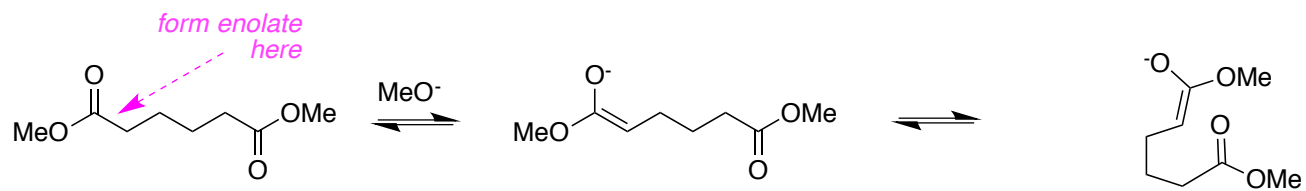
+



+



Intramolecular Reactions Of Ester Enolates With Esters (Dieckmann Reactions)

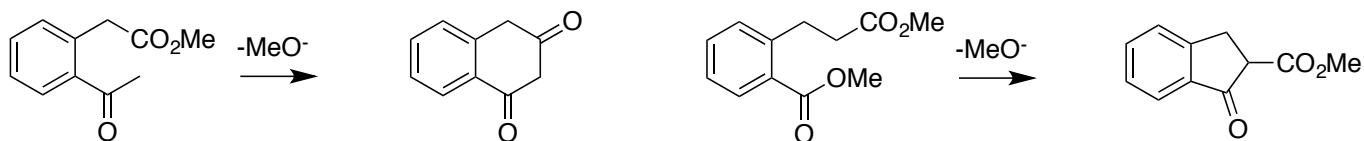


enolate

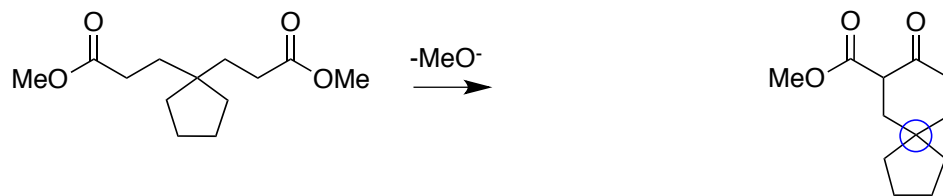
enolate in conformation for cyclization



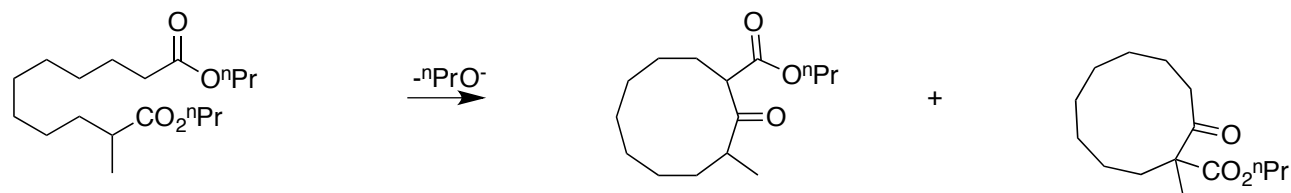
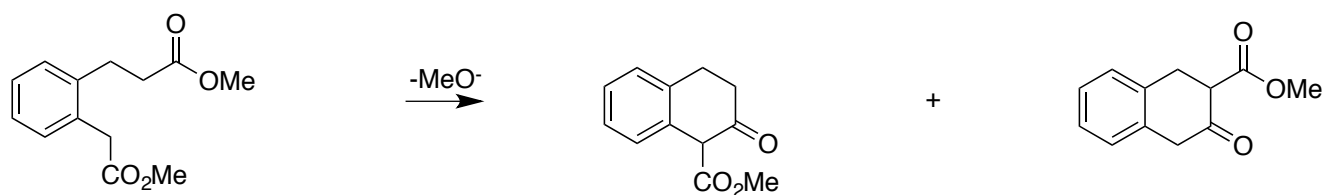
a cyclopentanone

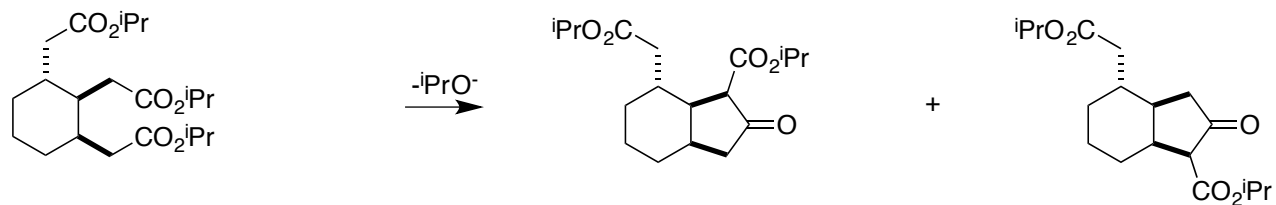


form a single point of contact between two rings.

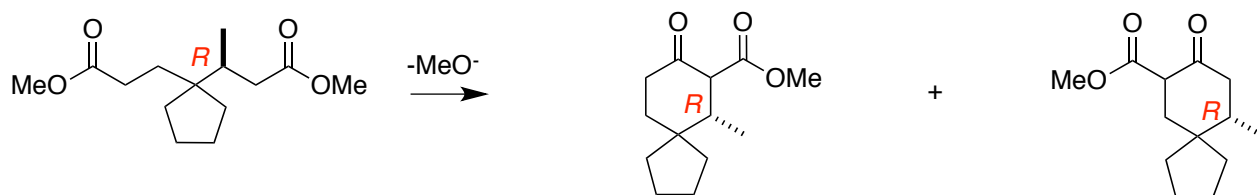


more than one
less
diminished in



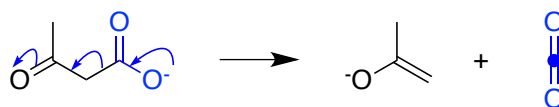


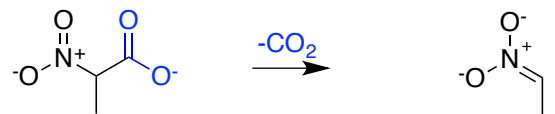
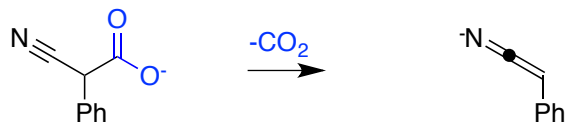
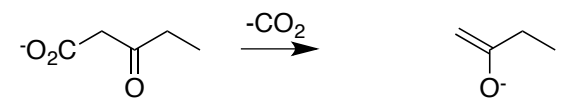
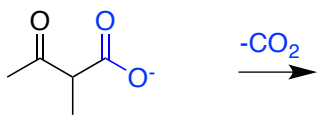
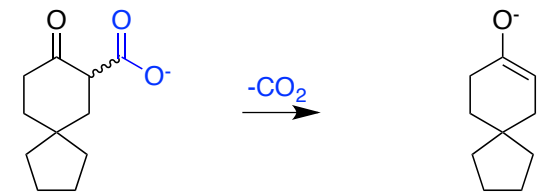
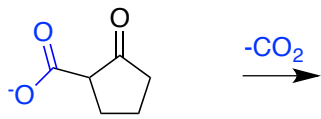
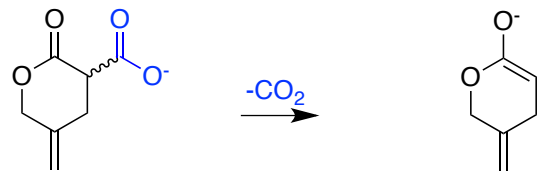
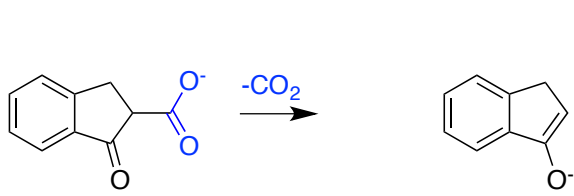
assume trans-fused 6,5-rings are not formed since they are less stable



the same configurations.

C. Decarboxylation Of 3-Oxocarboxylic Acids From Carboxylates

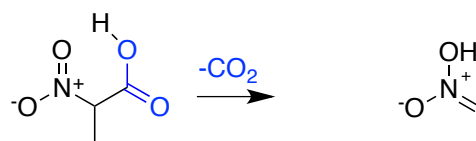
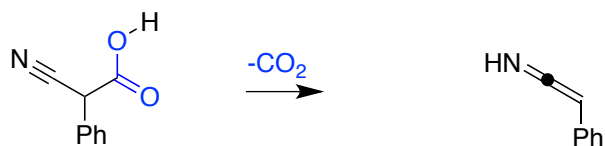
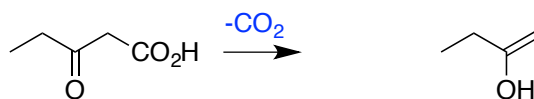
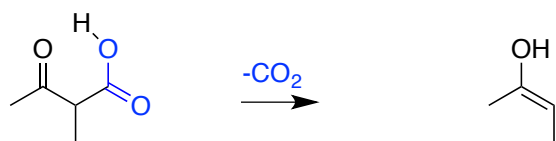
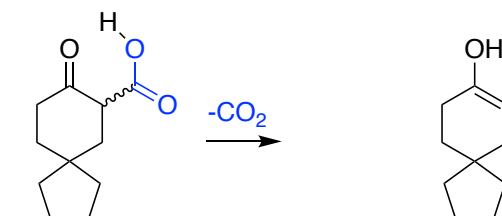
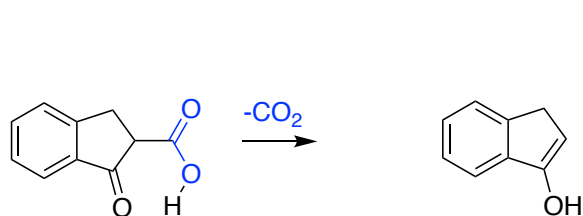
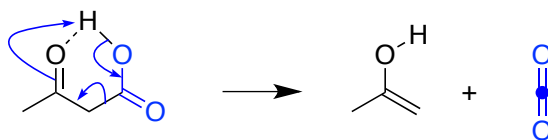




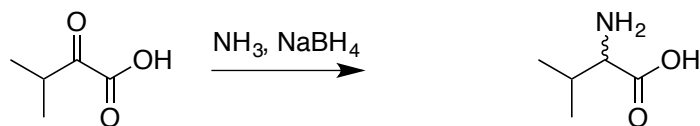
From Carboxylic Acids

carboxylates and *carboxylic acids*

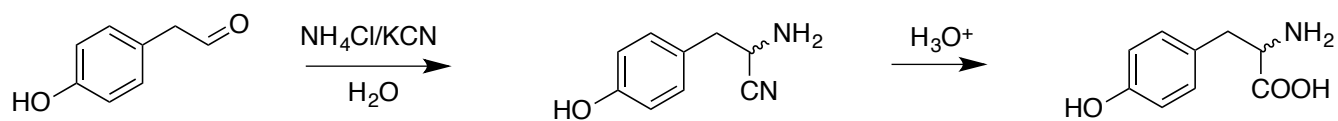
enols (whereas *carboxylates* produced *enolates*).



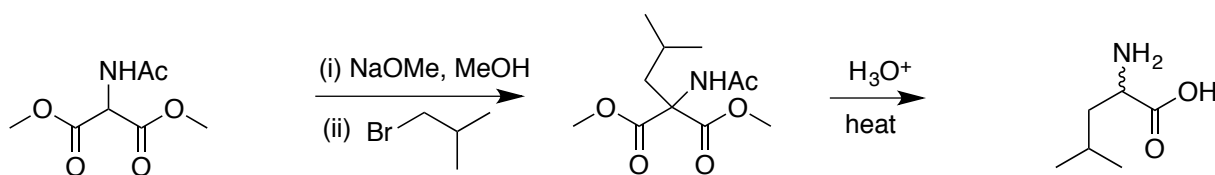
D. Classical Syntheses Of Amino Acids



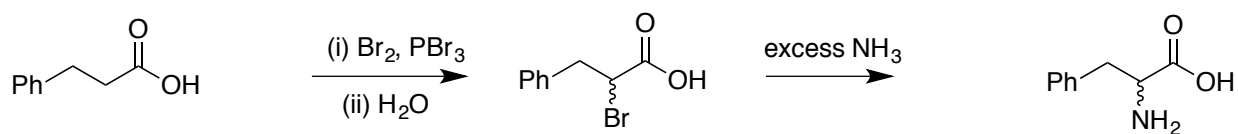
amino acid valine



amino acid tyrosine

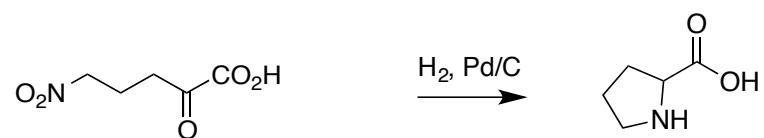
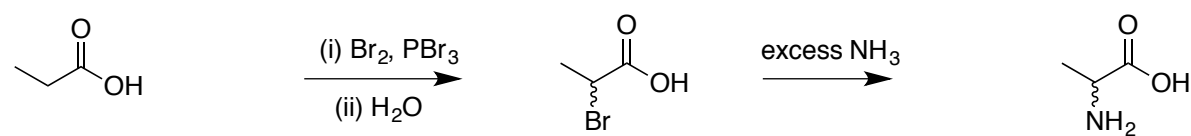
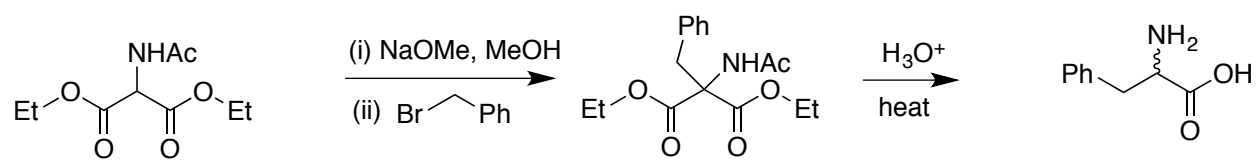


amino acid leucine



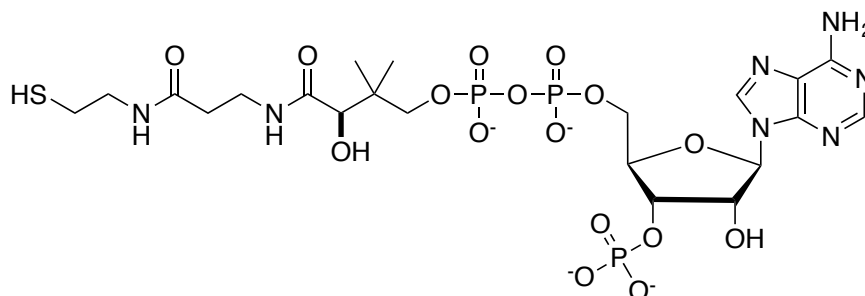
amino acid phenylalanine

racemates.

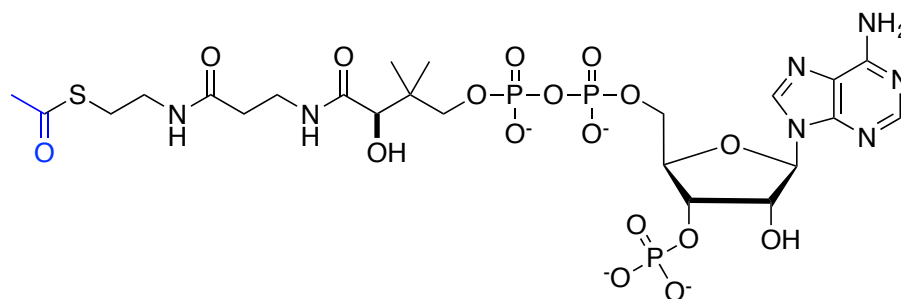


E. Thioesters Are More Reactive Than Esters

stronger
better
milder



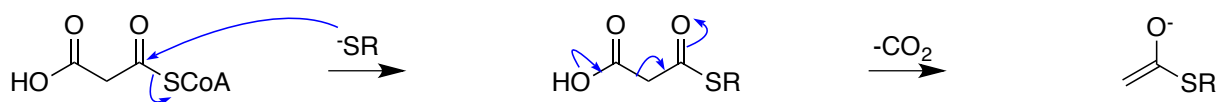
coenzyme A or CoASH



acyl coenzyme A or acyl-CoA

huge
better

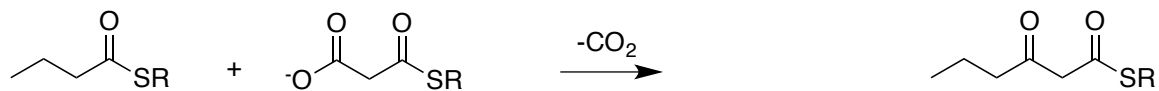
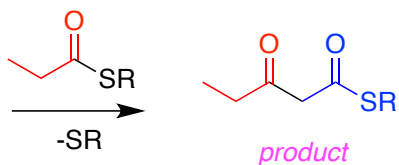
Nature's Equivalent To Claisen Condensations



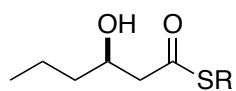
malonyl-CoA

transthioesterification product

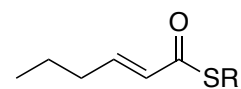
enolate of thioester



*ketone
reduction*
→
*show
Si-face addition
of hydride*



dehydration
→
-H₂O



hydrogenation
→
+H₂

