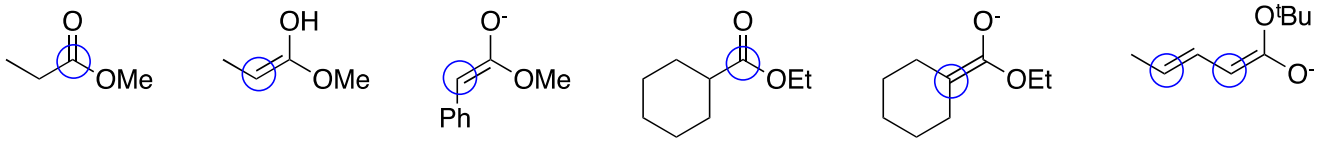
Reactions Of Ester Enolates With Esters

from chapter(s) _____ in the recommended text

A. Introduction

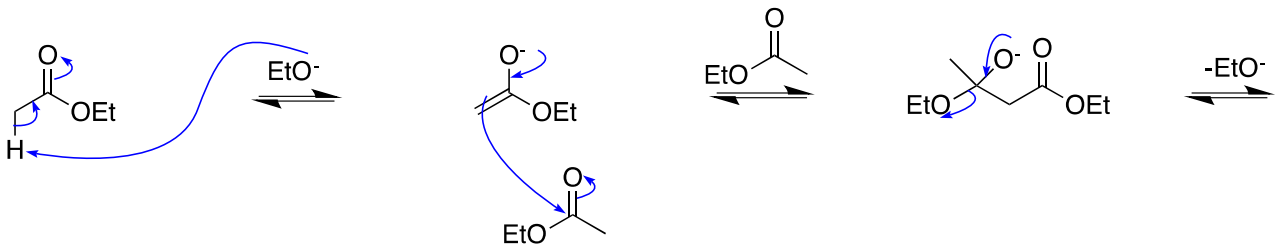
B. Enolates With Ester Electrophiles (Claisen Condensations)

Homocoupling Of Esters

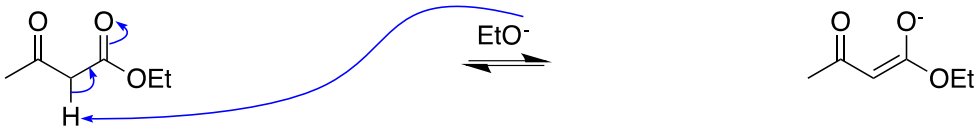


electrophile *nucleophile* *nucleophile* *electrophile* *nucleophile* *nucleophile*

enolates with esters.



ethyl acetate *enolate* *tetrahedral intermediate*



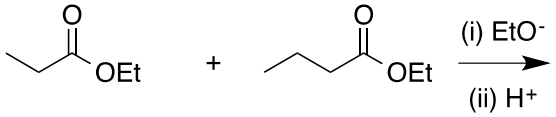
1,3-dicarbonyl *enolate*

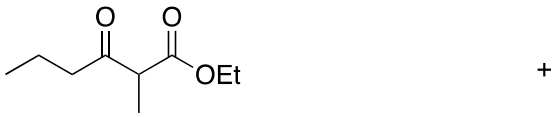
more stiochiometric.

transesterification.

1,3-dicarbonyl

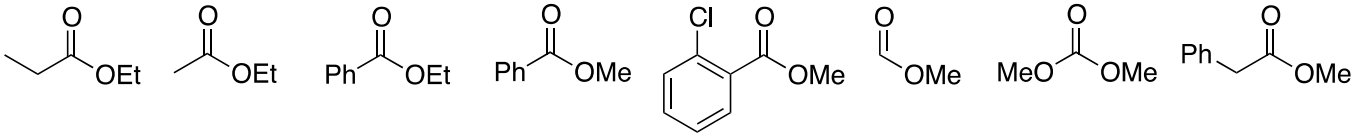
Uncontrolled Cross-Claisen Condensations

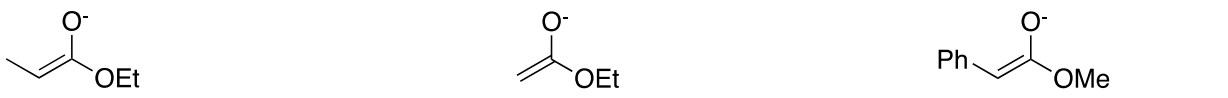




constitutional isomers

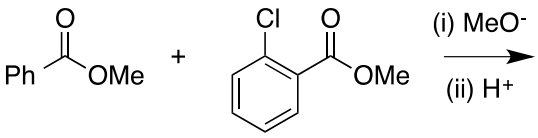
Controlled Cross-Claisen Condensations



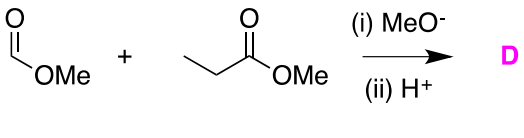


enolate 1 *enolate 2* *enolate 3*

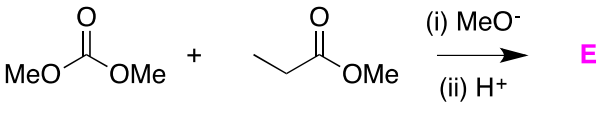
only one



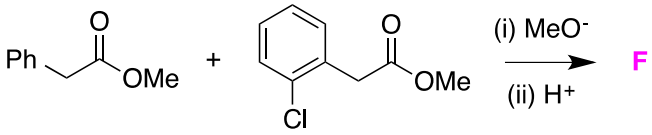
C



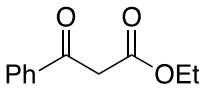
D



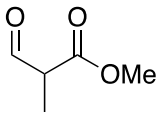
E



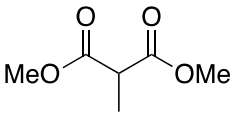
F



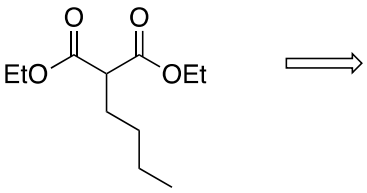
letter **B**



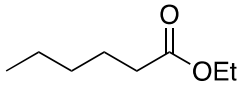
letter **D**

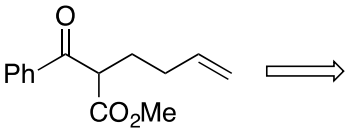


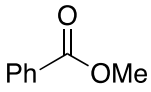
letter **E**



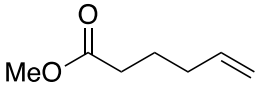
+



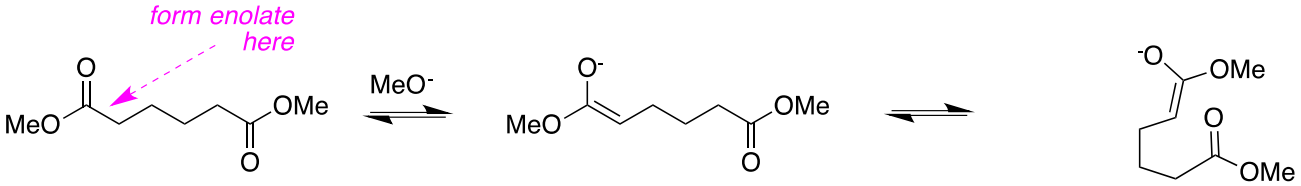




+



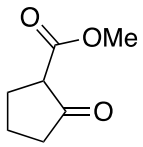
Intramolecular Reactions Of Ester Enolates With Esters (Dieckmann Reactions)



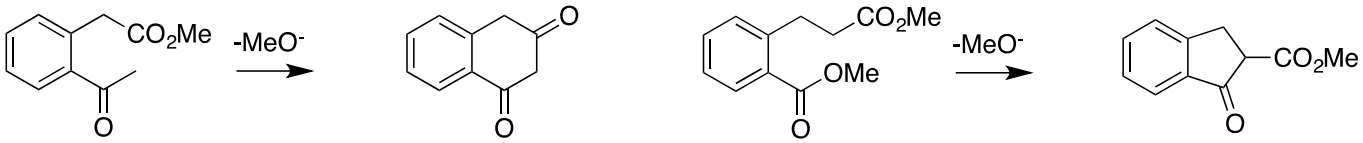
enolate

enolate in conformation for cyclization

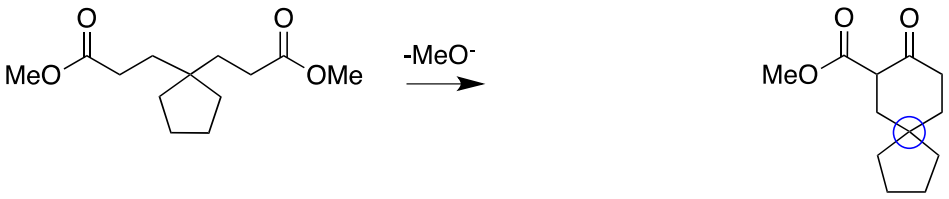
-MeO-



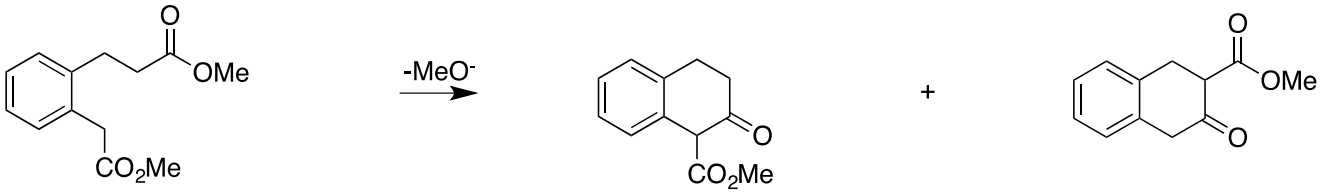
a cyclopentanone

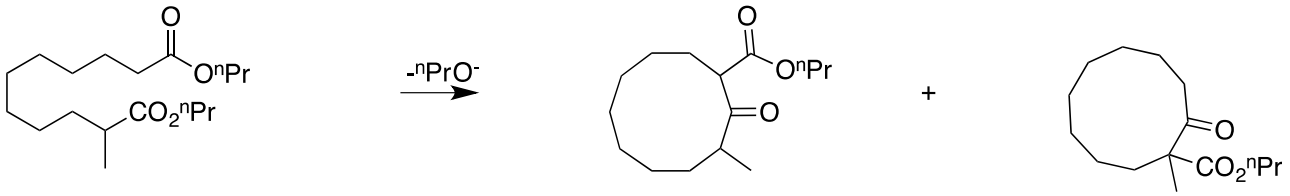


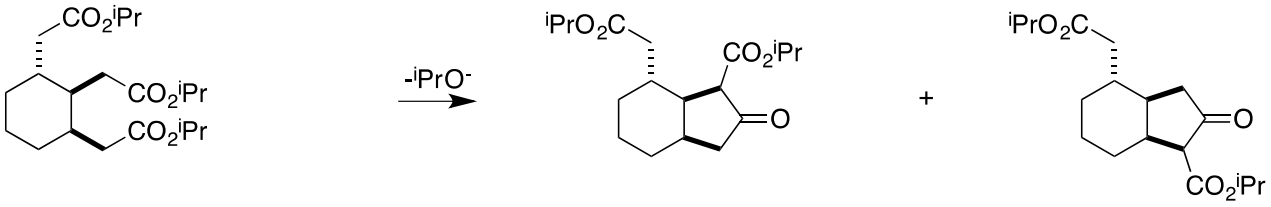
form a single point of contact between two rings.



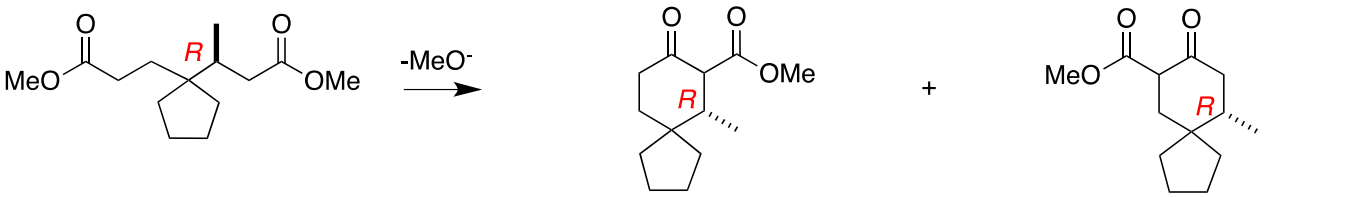
more than one
less
diminished in







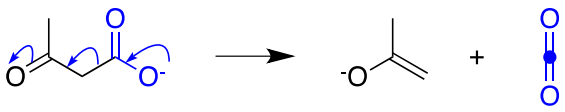
assume trans-fused 6,5-rings are not formed since they are less stable

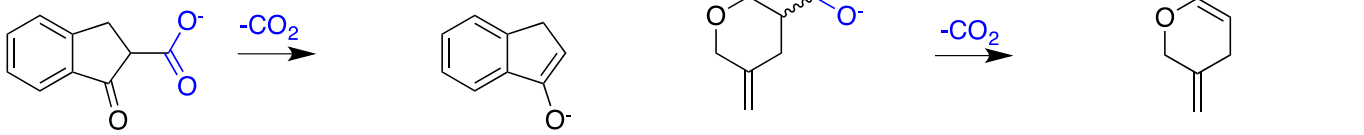


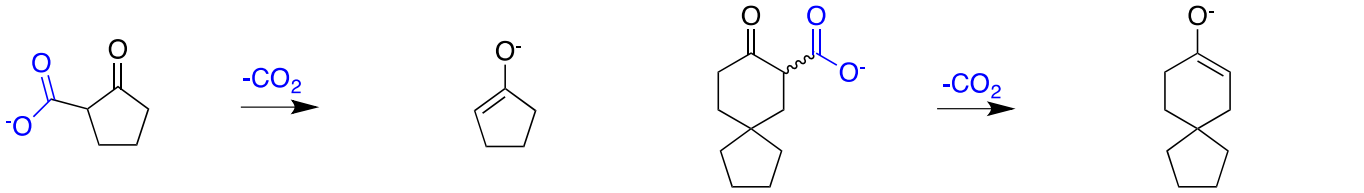
the same configurations.

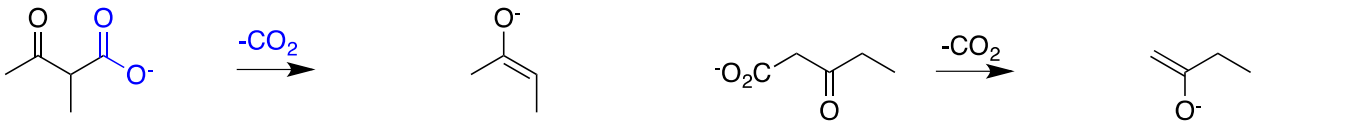
C. Decarboxylation Of 3-Oxocarboxylic Acids

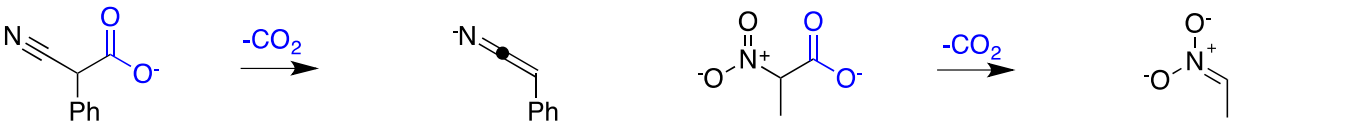
From Carboxylates




-CO2
-CO2


-CO2
-CO2

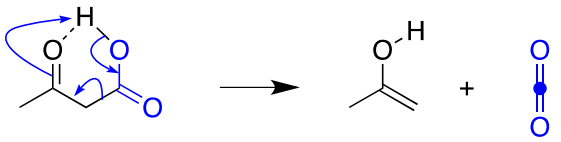

-CO2
-CO2

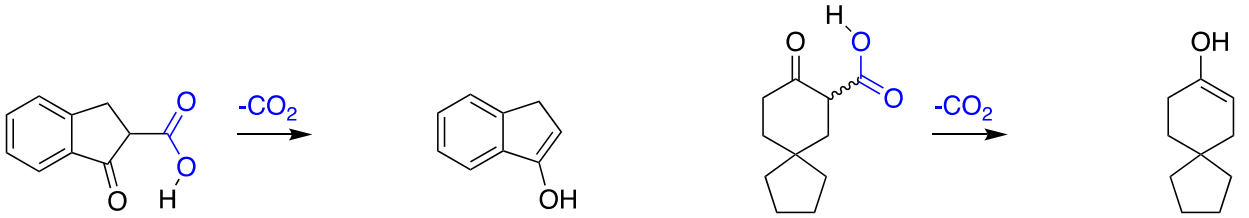

-CO2
-CO2

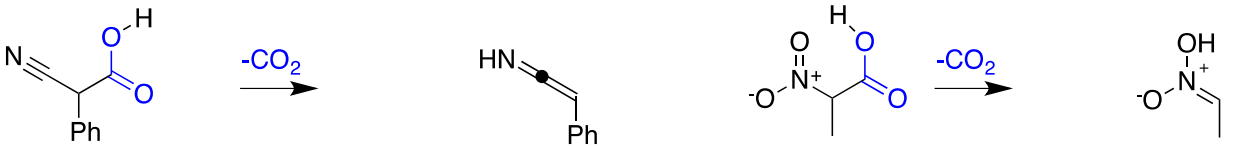
From Carboxylic Acids

carboxylates and *carboxylic acids*

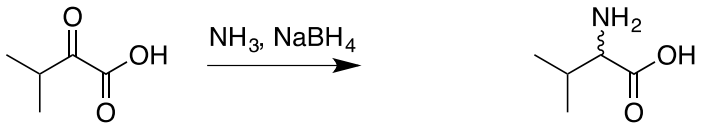
enols (whereas *carboxylates* produced *enolates*).



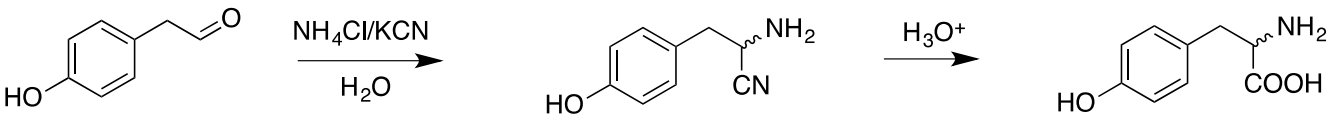




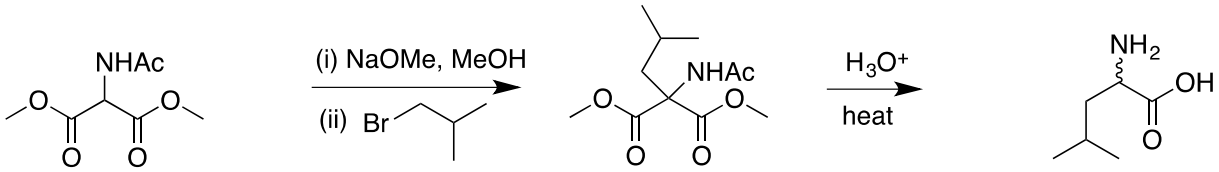
D. Classical Syntheses Of Amino Acids



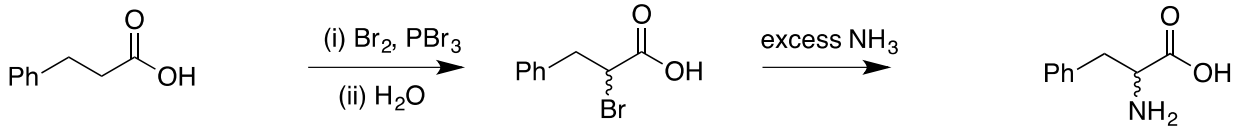
amino acid ____valine_____



amino acid tyrosine

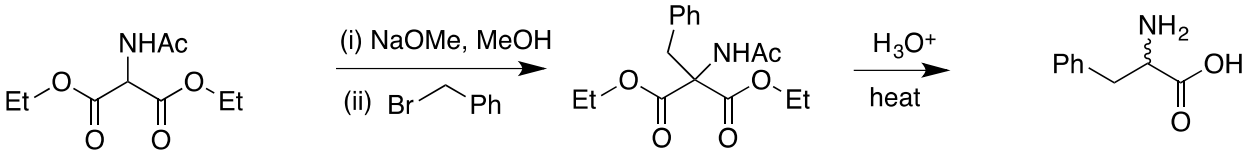


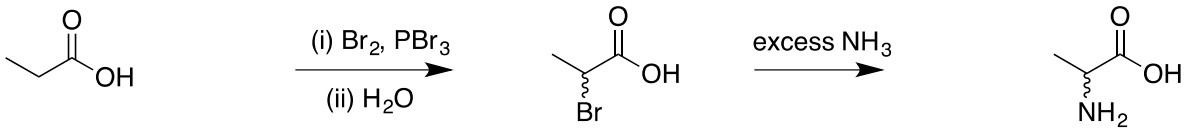
amino acid leucine

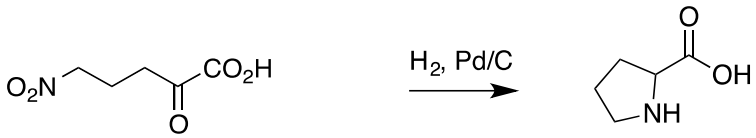


amino acid phenylalanine

racemates.

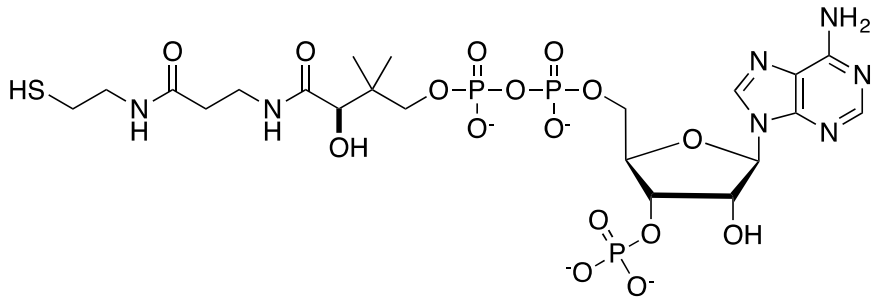

NHAc
Et
O
O
O
Et
O
O
(i) NaOMe, MeOH
(ii) Br
Ph
Ph
NHAc
Et
O
O
O
Et
O
O
H_3O^+
heat
NH_2
Ph
OH
O


O
OH
(i) Br_2, PBr_3
(ii) H_2O
O
OH
Br
excess NH_3
O
OH
NH_2

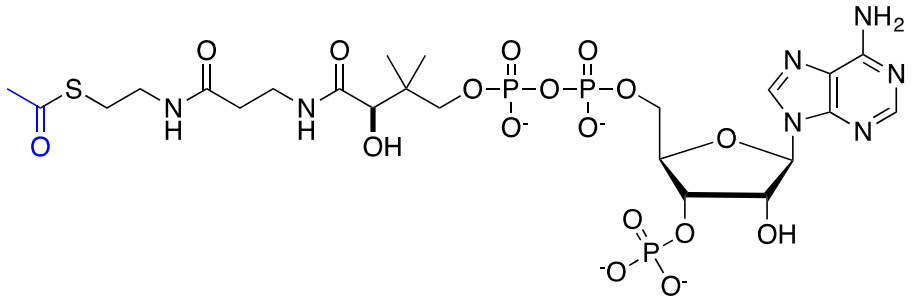

O_2N
CO_2H
O
H_2, Pd/C
O
OH
NH

E. Thioesters Are More Reactive Than Esters

stronger
better
milder



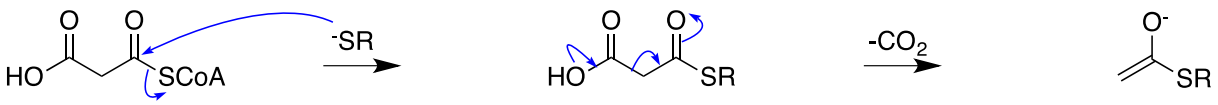
coenzyme A or CoASH



acyl coenzyme A or acyl-CoA

huge
better

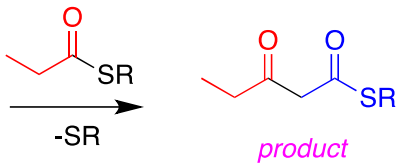
Nature's Equivalent To Claisen Condensations

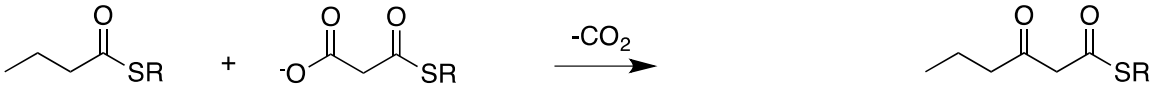


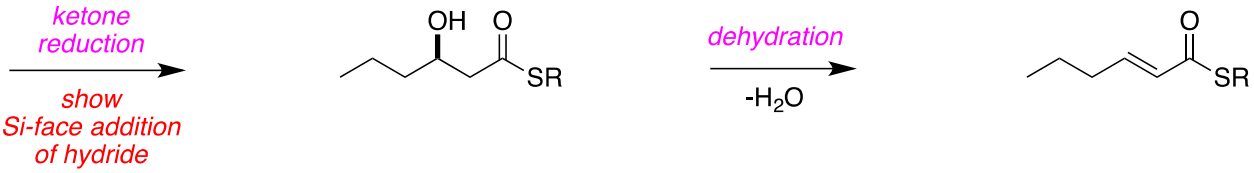
malonyl-CoA

transthioesterification product

enolate of thioester


O
SR
-SR
O
O
SR
product


O
SR
+
O
O
-O
SR
-CO2
O
O
SR


ketone
reduction
show
Si-face addition
of hydride
OH
O
SR
dehydration
-H2O
O
SR


hydrogenation
+H2
O
SR