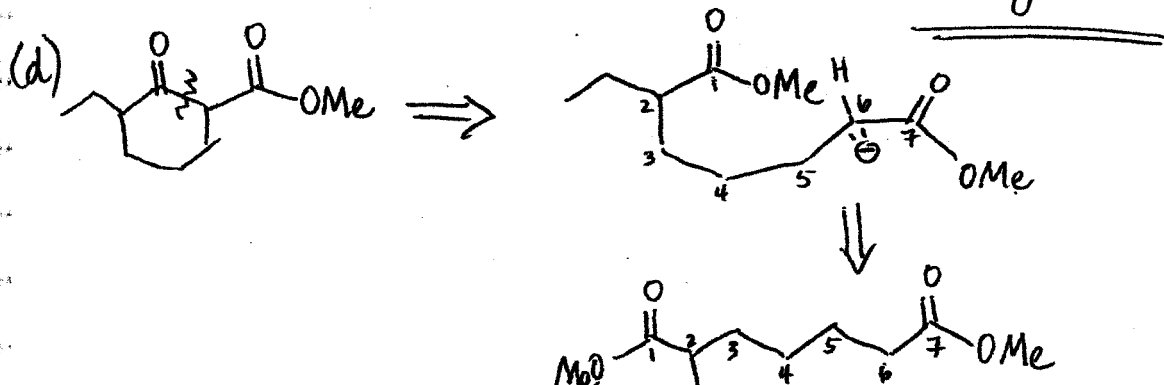
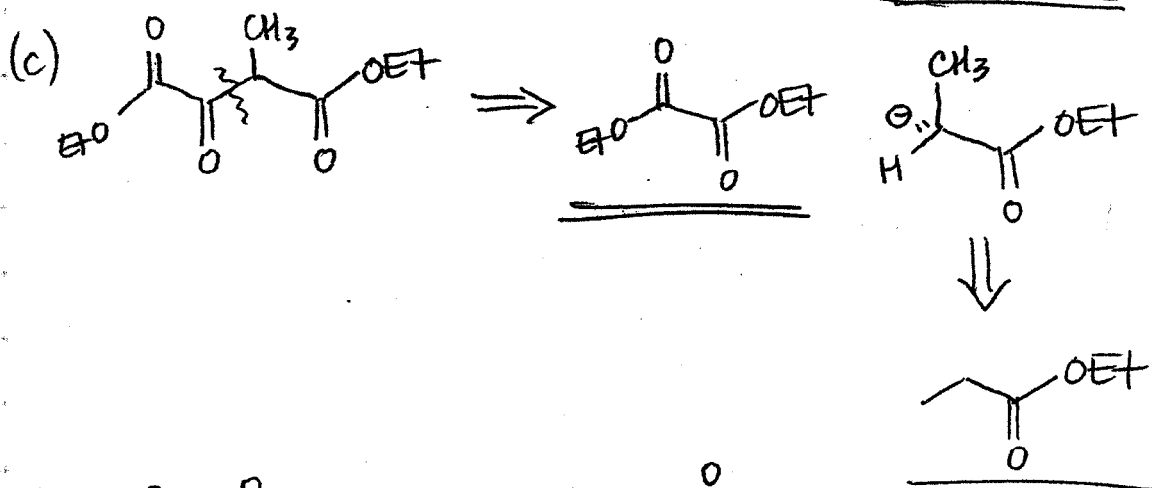
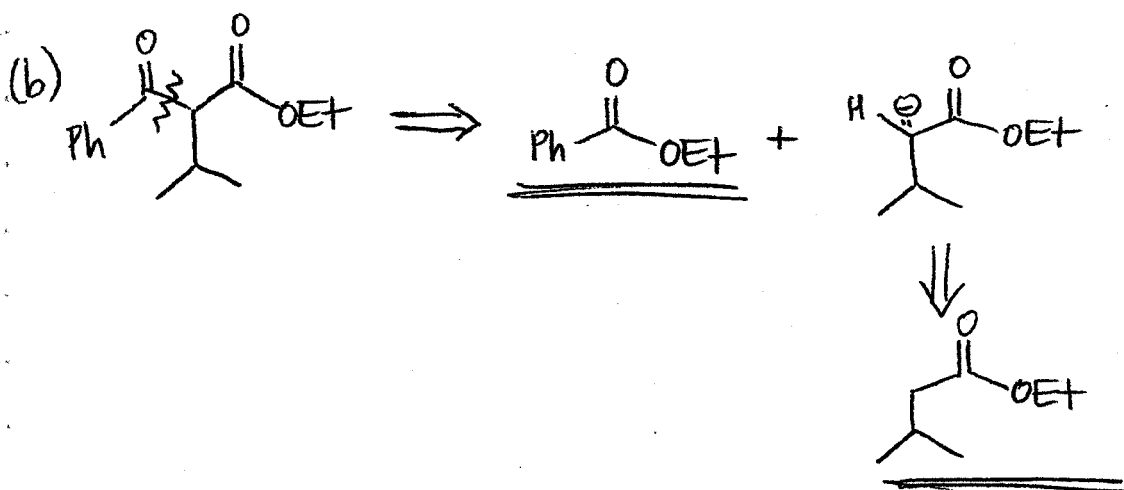
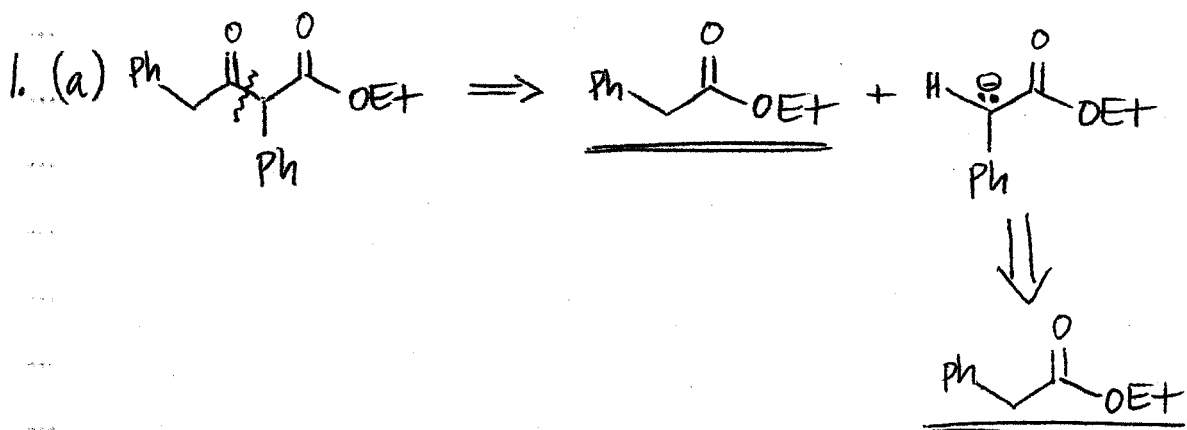
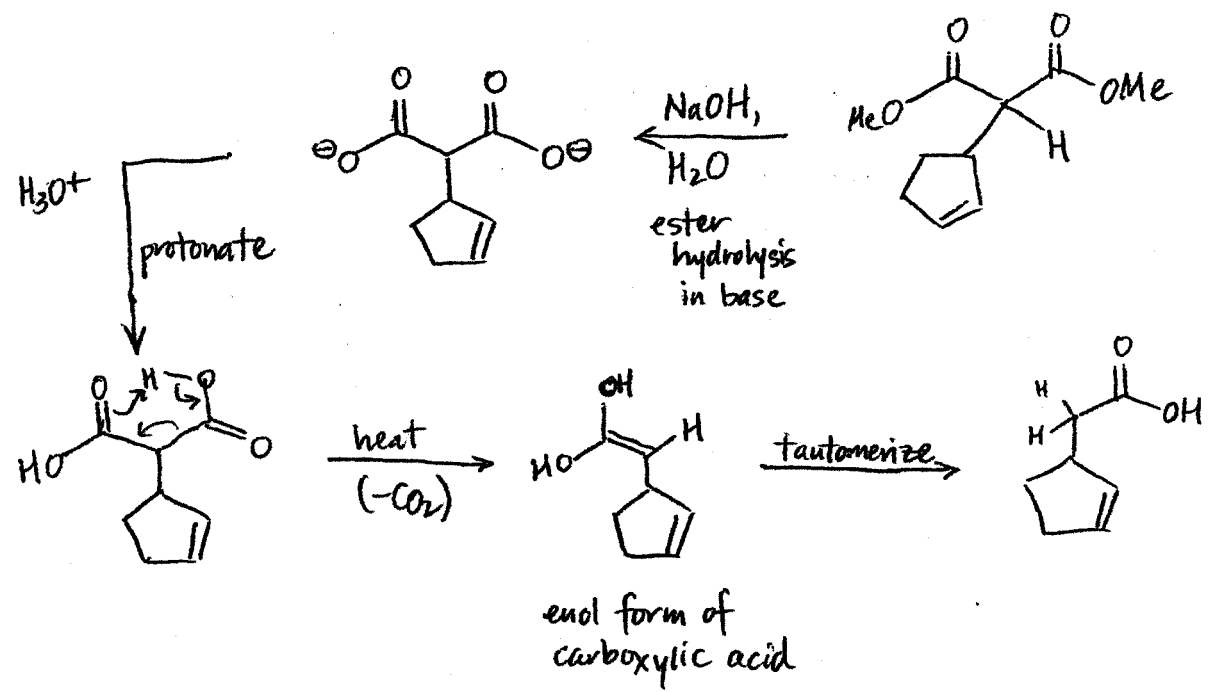
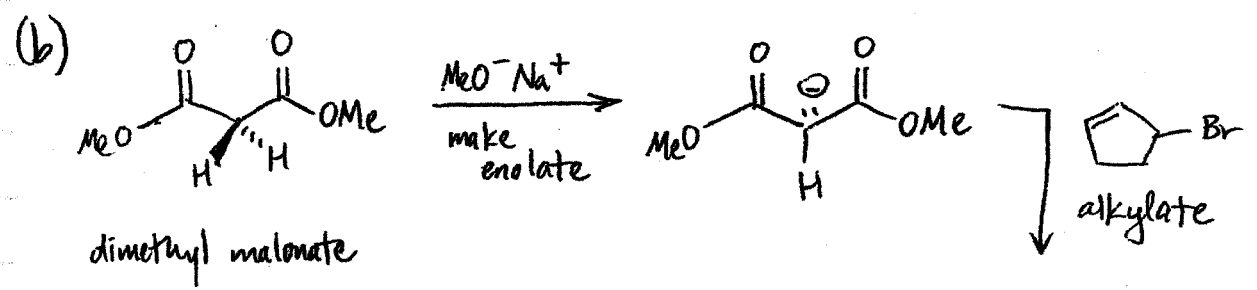
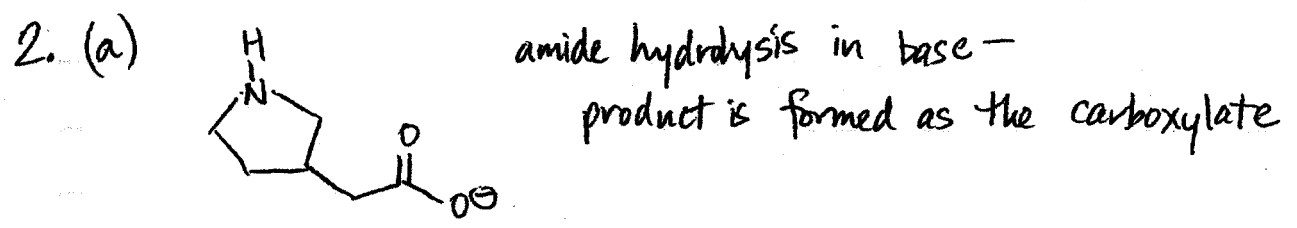
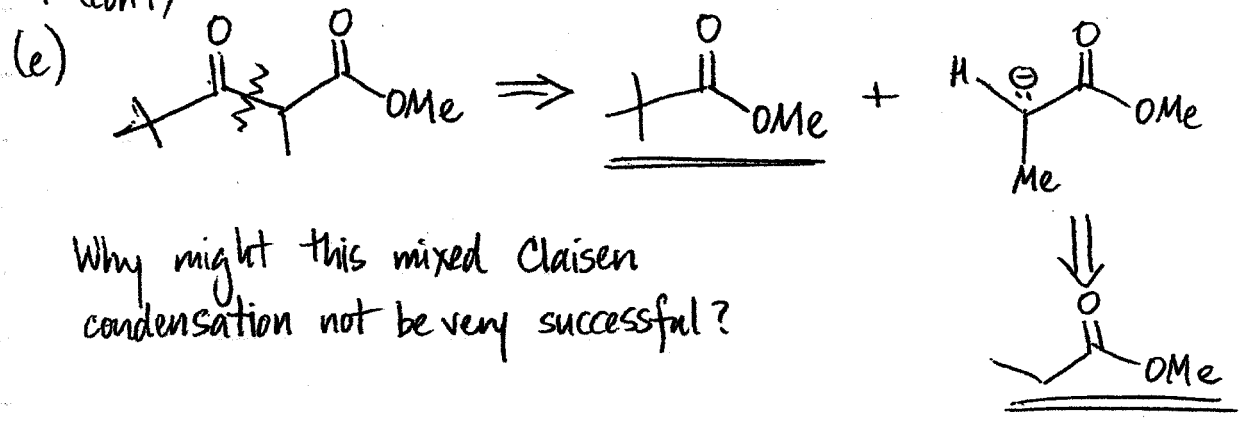


PROBLEM SET 13 SOLUTIONS

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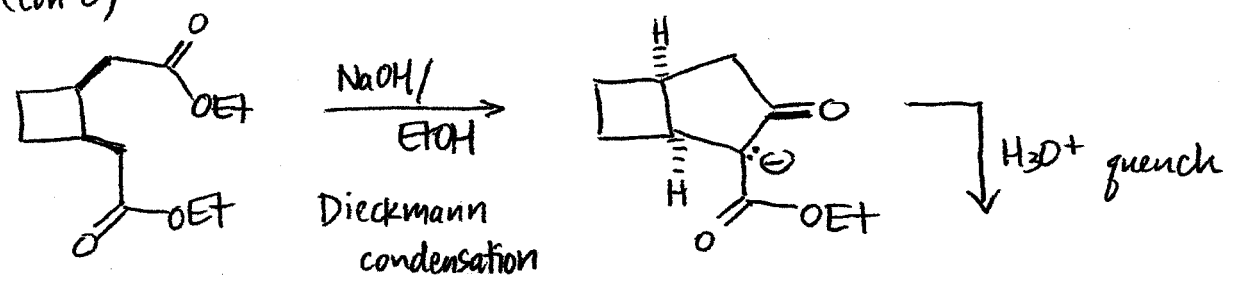
#1 (cont)



⊗ This is an example of the malonic ester synthesis.

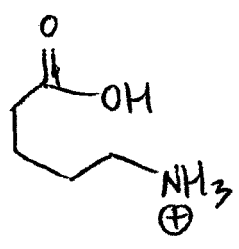
#2 (cont)

(c)



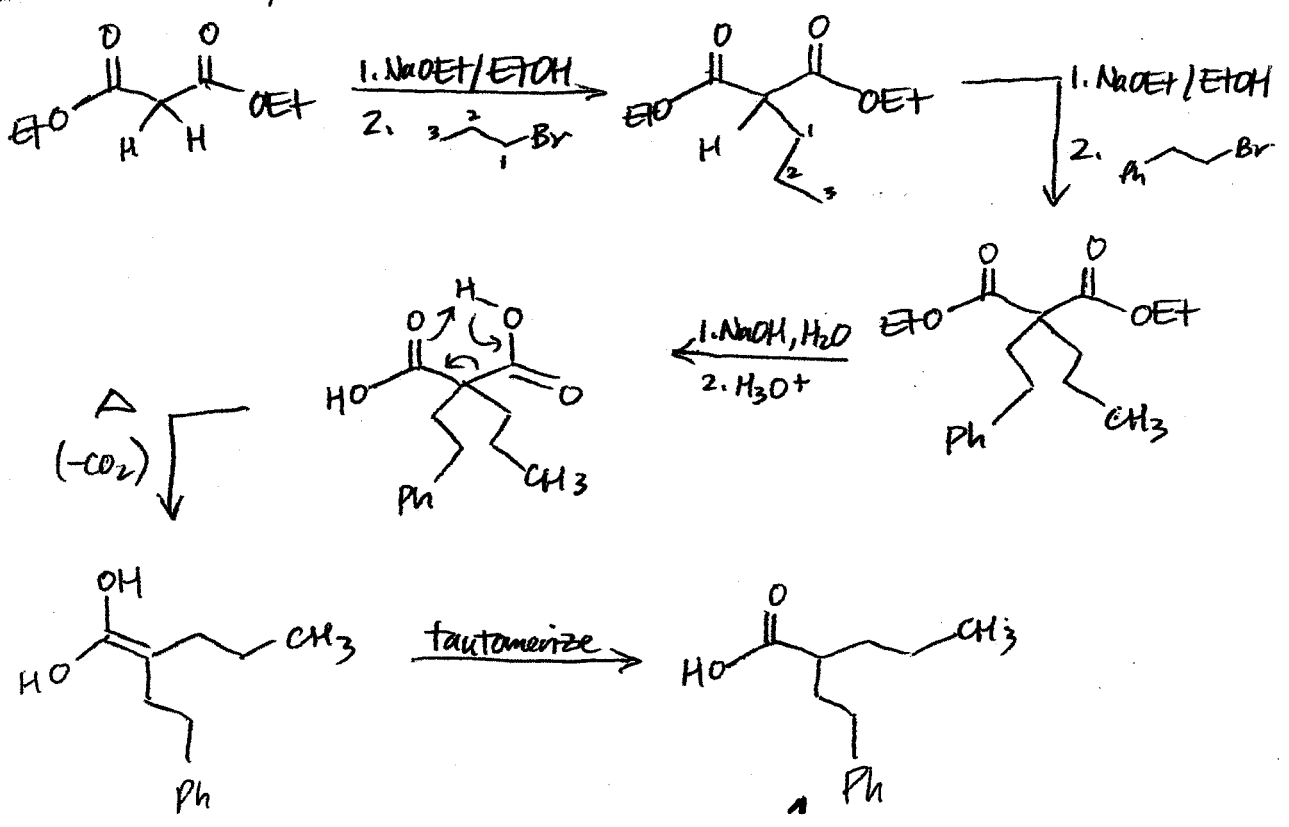
β -keto ester

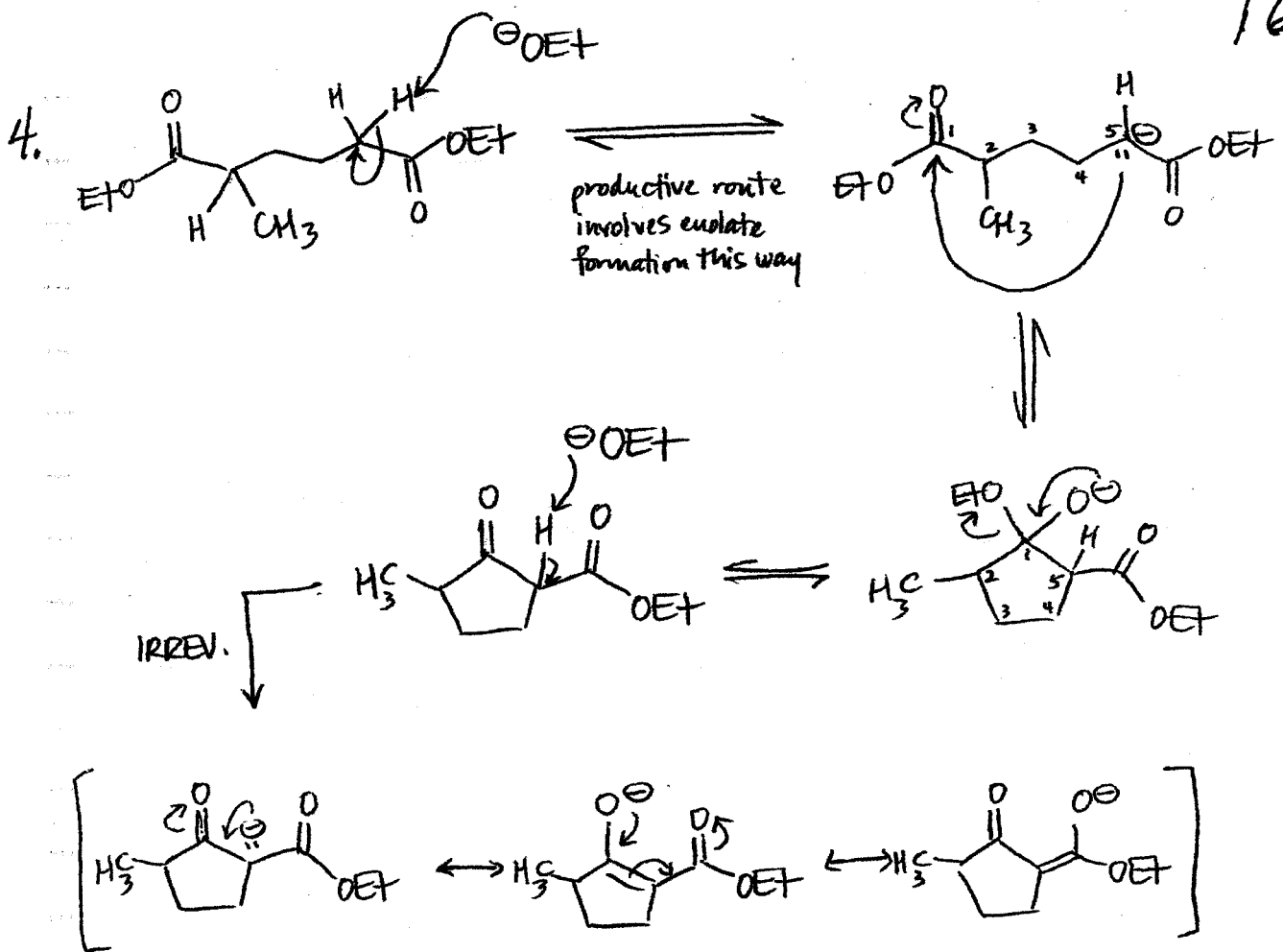
(d)



amide hydrolysis in acid —
product is an ammonium ion

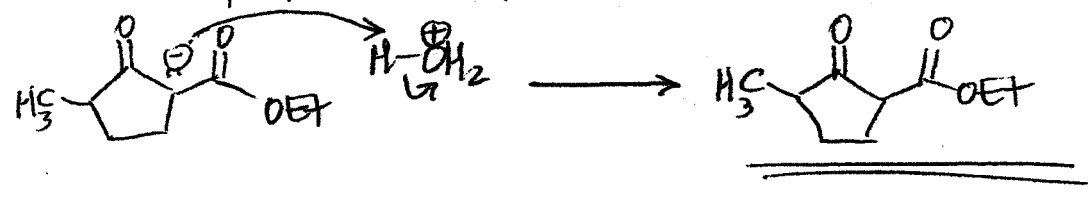
3. This synthesis is carried out via sequential enolate alkylation, followed by ester hydrolysis and decarboxylation. It's the malonic ester synthesis:



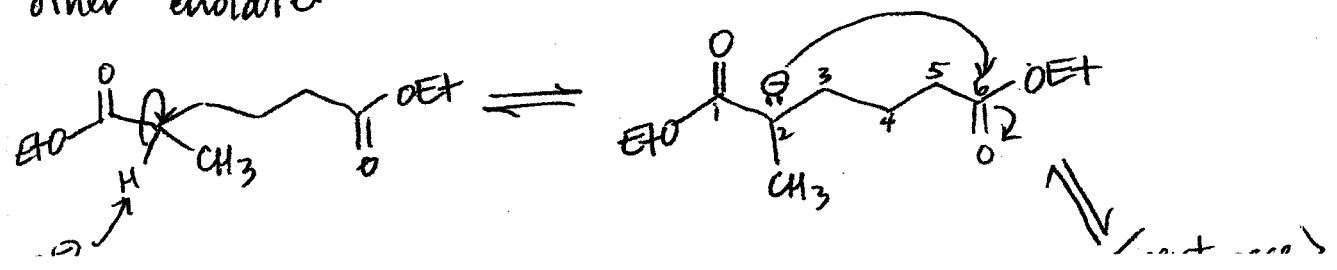


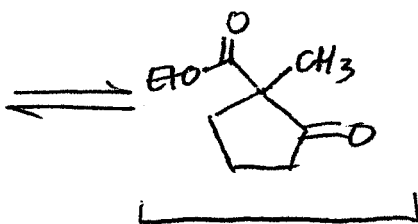
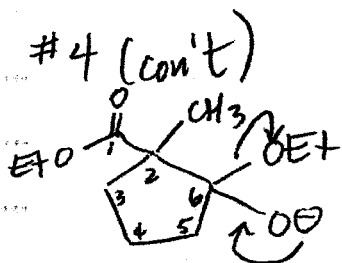
Dieckmann cyclization route shown here allows for irreversible deprotonation of the final β -ketoester product.

Protic workup provides the product:



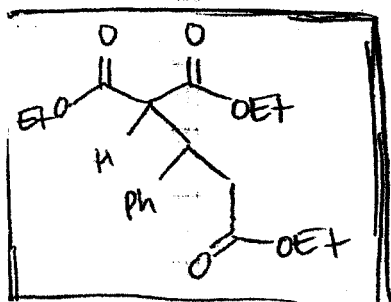
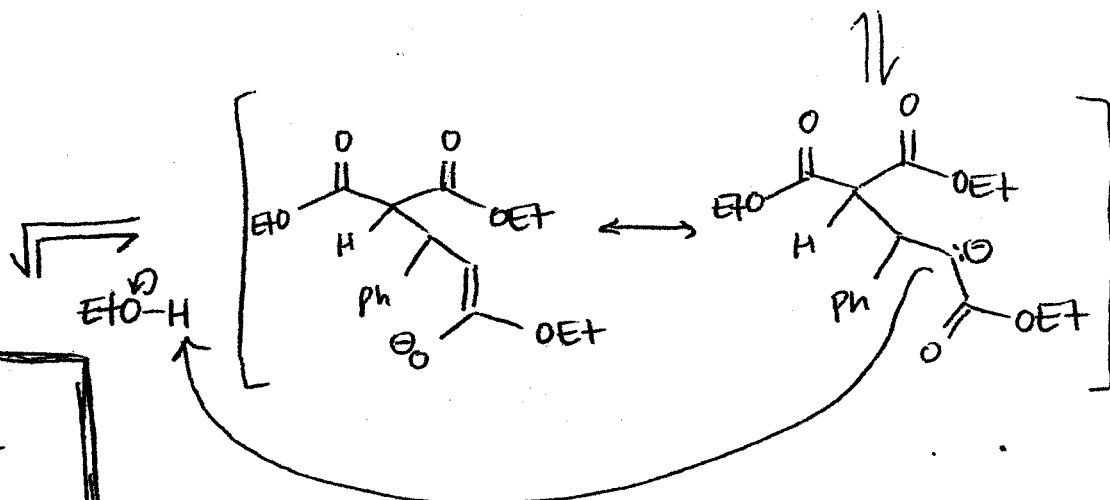
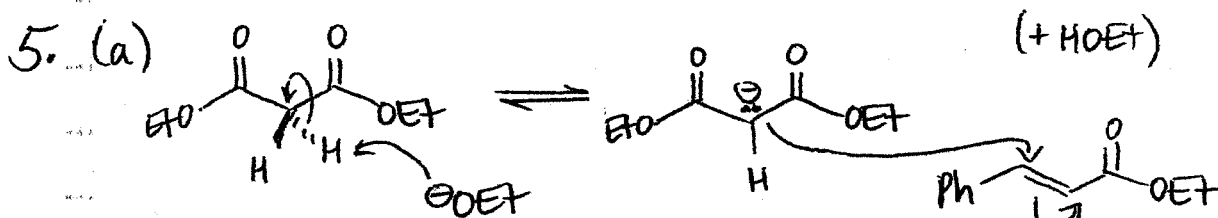
The other possible Dieckmann route involves formation of the other enolate:





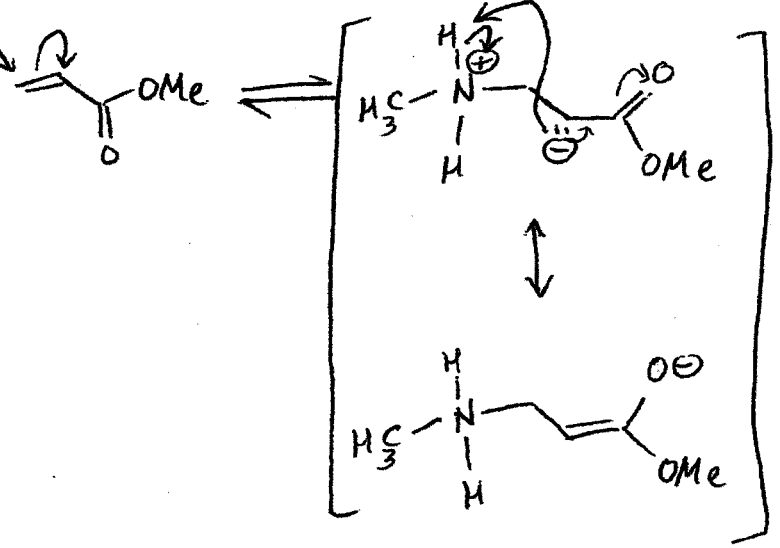
There is no α -H between the carbonyls of the β -keto ester product. So: there cannot be a final irreversible deprotonation to drive the equilibrium, and any β -keto ester that does form can revert to starting material.

Here, the starting diester will be thermodynamically favored over the product β -keto ester \therefore this rxn is doomed!

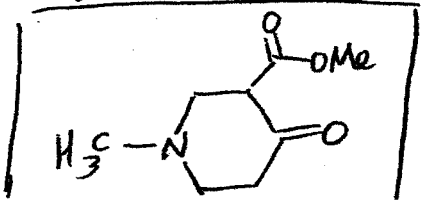
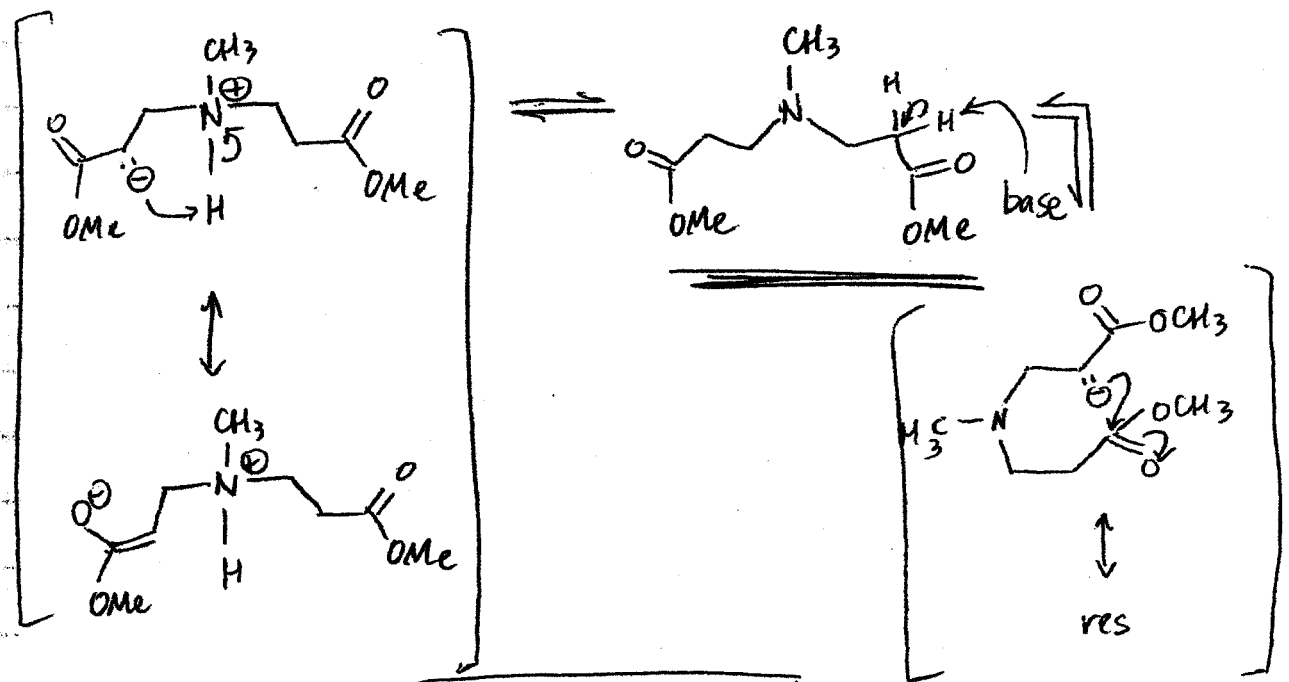
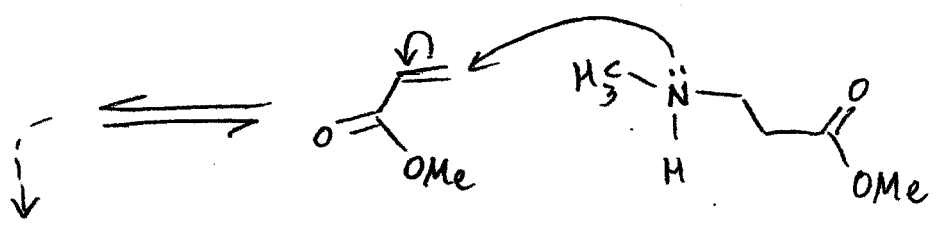


#5 (cont)

(b) $\text{H}_3\text{C}-\ddot{\text{N}}\text{H}_2$



\rightleftharpoons H^+ transfer



Dieckmann Condensation (several steps)