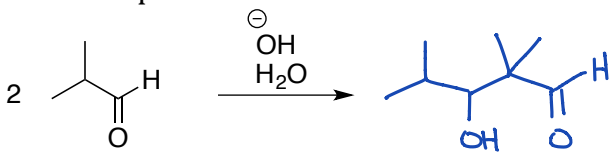
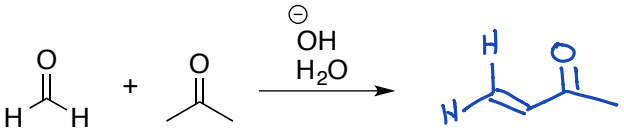
Chemistry 234
Chapter 23 Problem Set

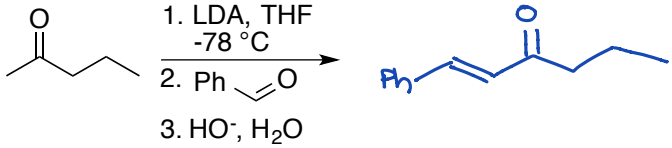
Carbonyl Condensation Chemistry

1) Draw the product formed from each of the aldol reactions/condensations below.

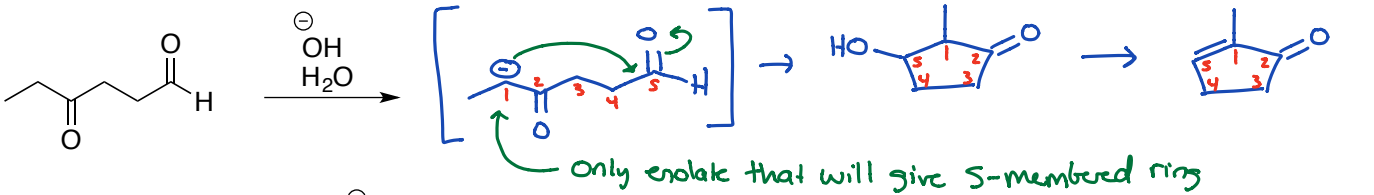


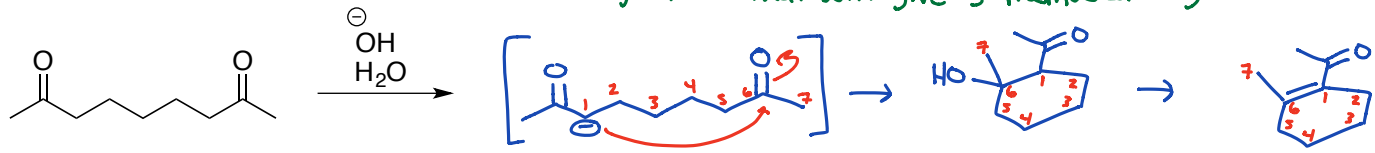
No β-H for elimination (dehydration) step.

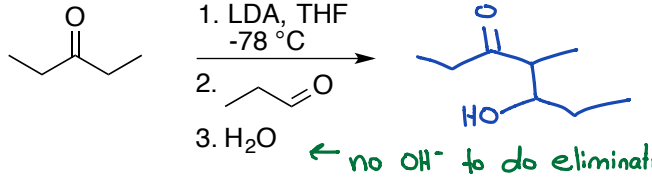




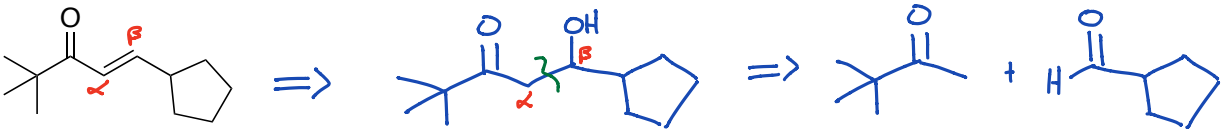
Intramolecular Aldol can only be used to set 5 or 6 membered rings

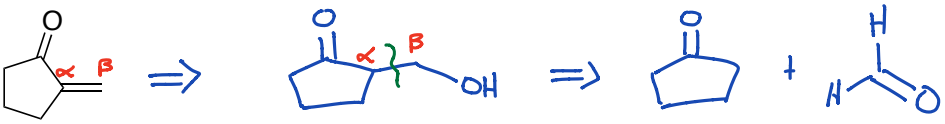


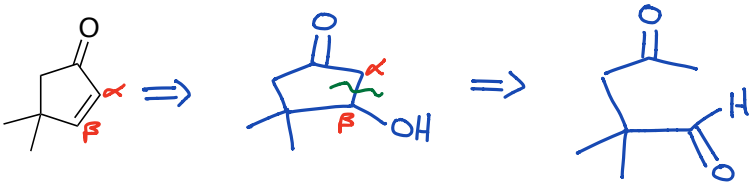




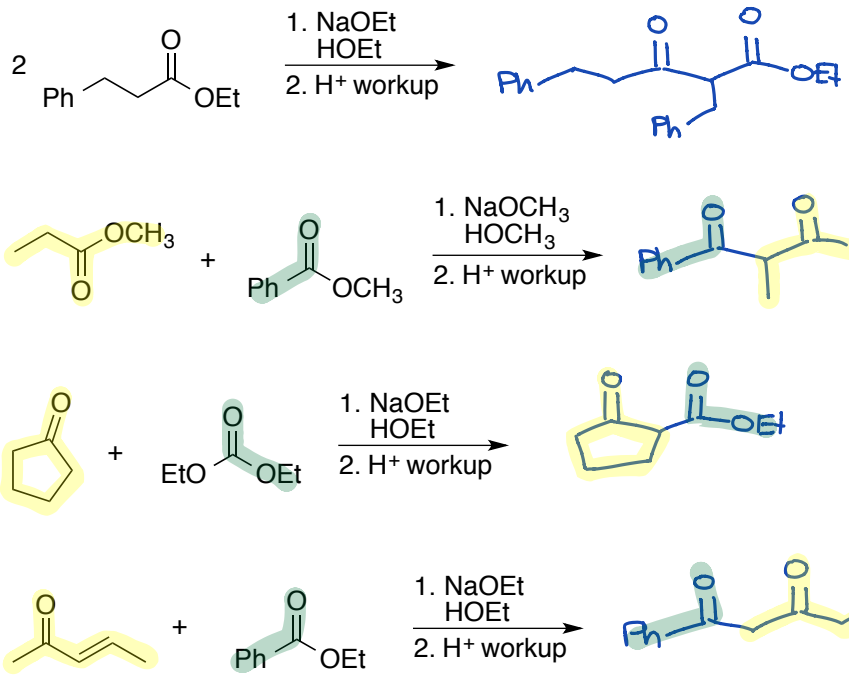
2) What starting material(s) is/are needed to prepare each compound below via an aldol reaction?



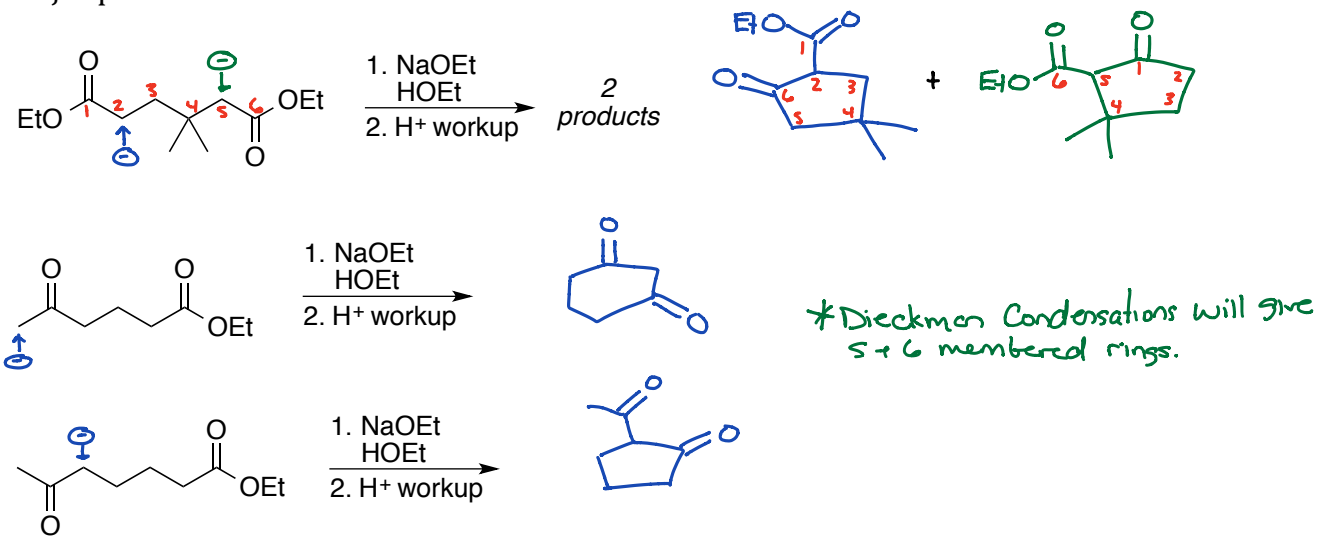




3) Predict the major organic product formed from each of the Claisen Condensation Reactions.



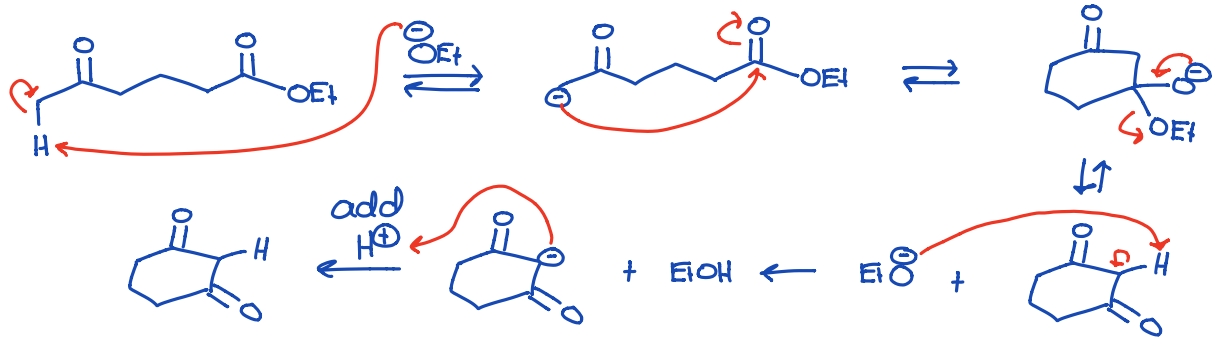
4) Each compound below undergoes a Dieckmann Condensation (Intramolecular Claisen). Predict the major products for each.



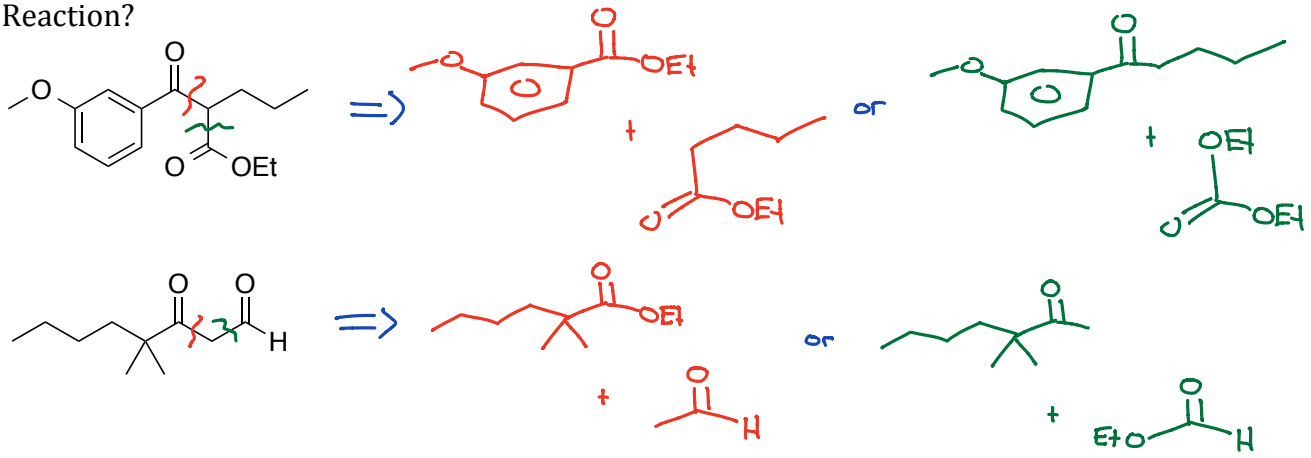
• Ketone α-H are more acidic than ester α-H.

*Dieckmon Condensations will give 5+6 membered rings.

5) Draw the complete electron pushing mechanism for the second reaction in question 4.

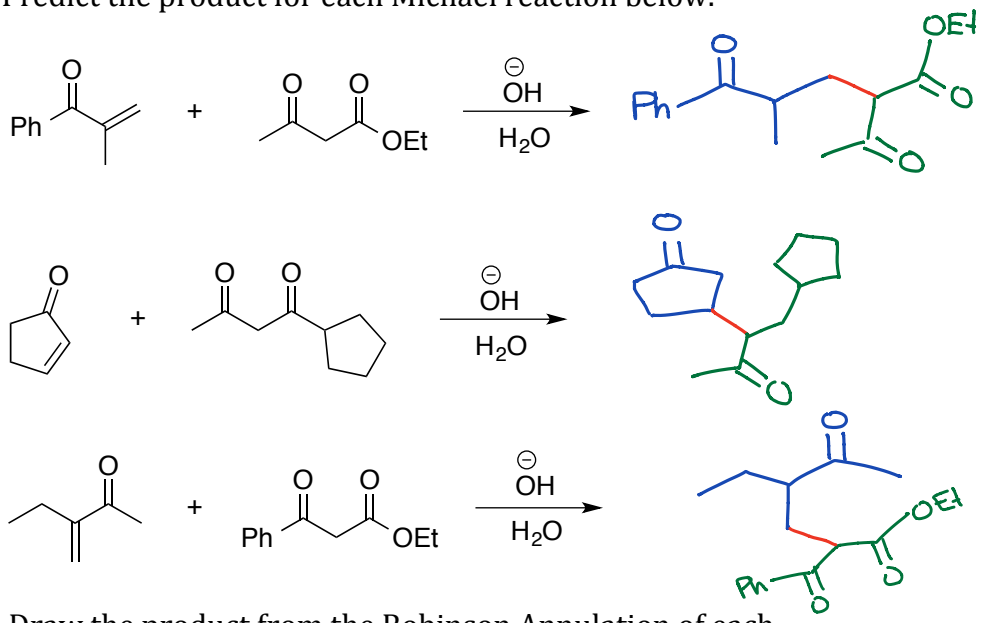


6) What starting materials are needed to synthesize each compound below by a Crossed Claisen Reaction?

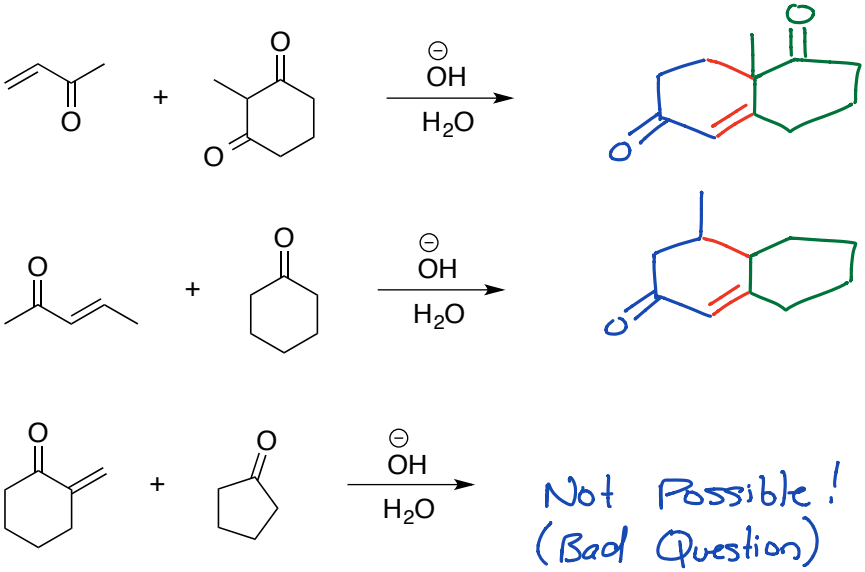


Conjugate Addition

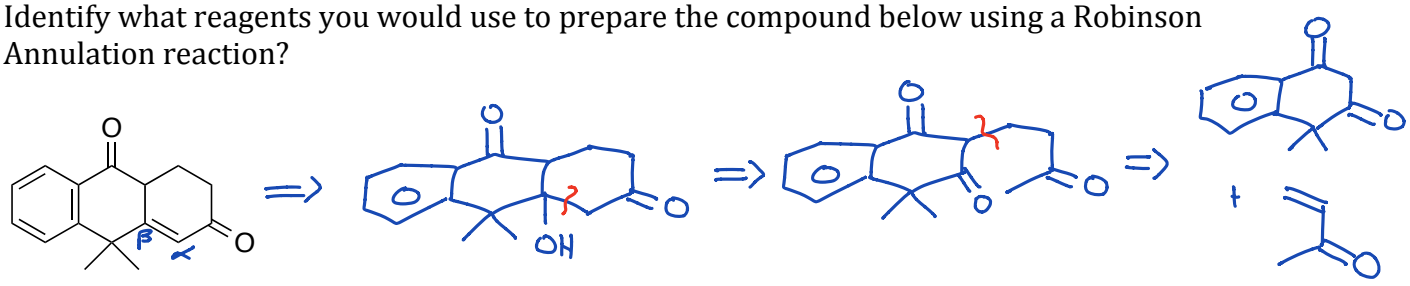
7) Predict the product for each Michael reaction below.



8) Draw the product from the Robinson Annulation of each.

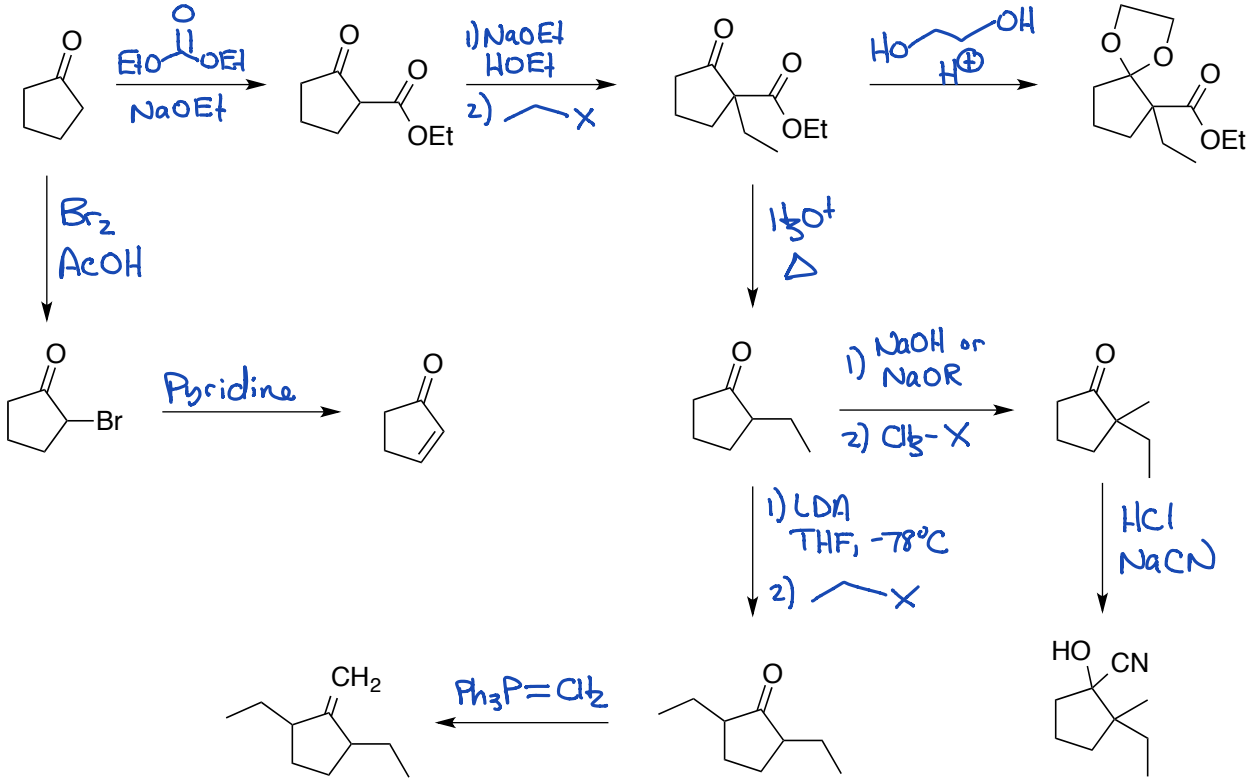


9) Identify what reagents you would use to prepare the compound below using a Robinson Annulation reaction?

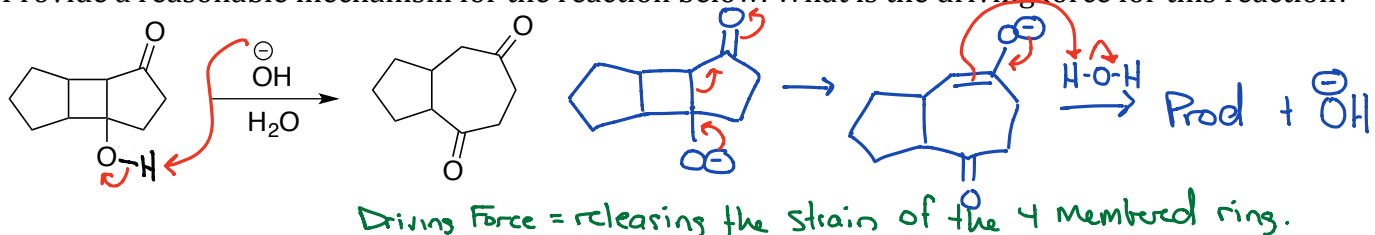


Part 5: Application to Synthesis

10) Fill in the missing reagents in the synthetic sequence below.

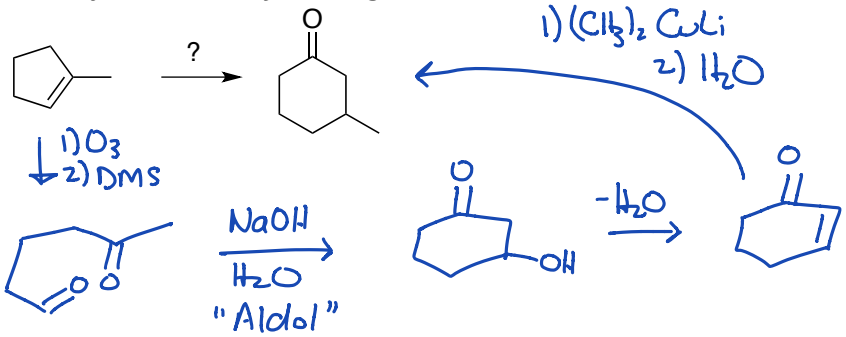


11) Provide a reasonable mechanism for the reaction below. What is the driving force for this reaction?

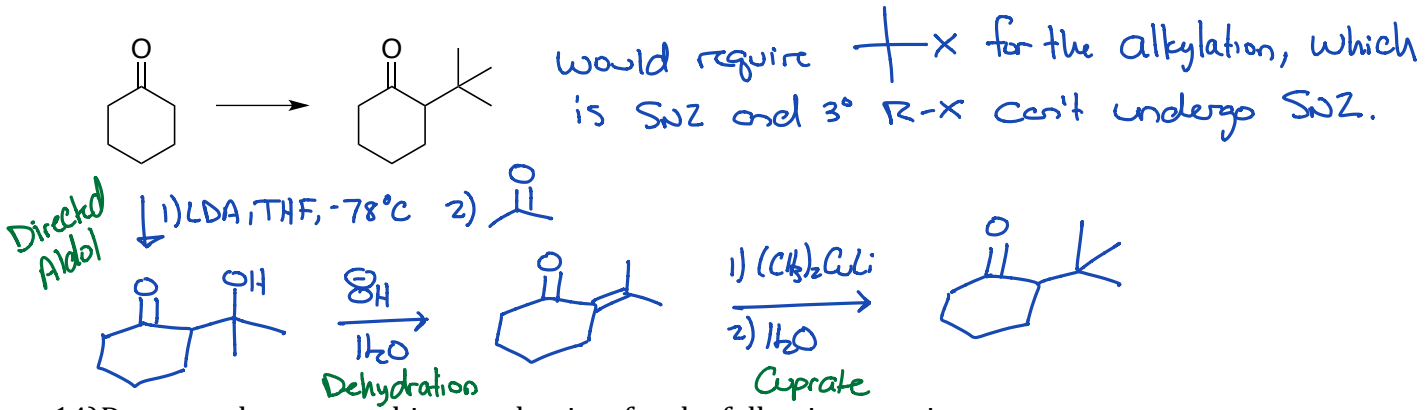


Driving Force = releasing the strain of the 4 membered ring.

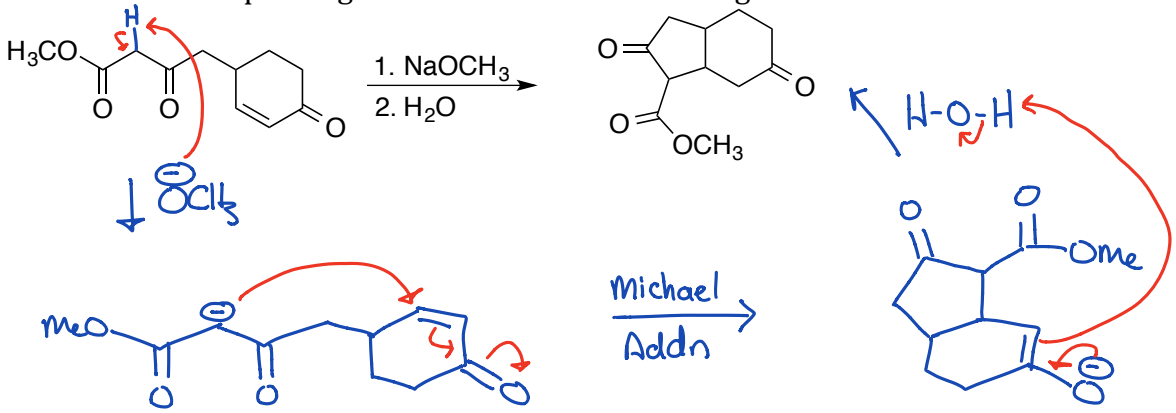
12) Propose an efficient synthesis for the following transformation. *Hint: You will need to use the ozonolysis reaction from organic I.*



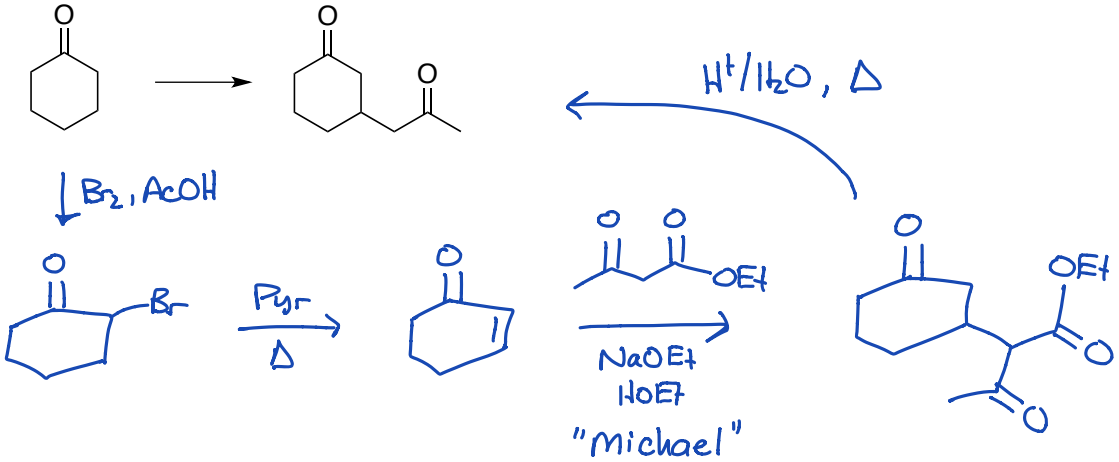
13) **Challenge:** The compound below cannot be prepared by direct alkylation of cyclohexanone. Explain why not and provide an alternative route to carry out the transformation. *Hint: at some stage, methyl cuprate might be useful.*



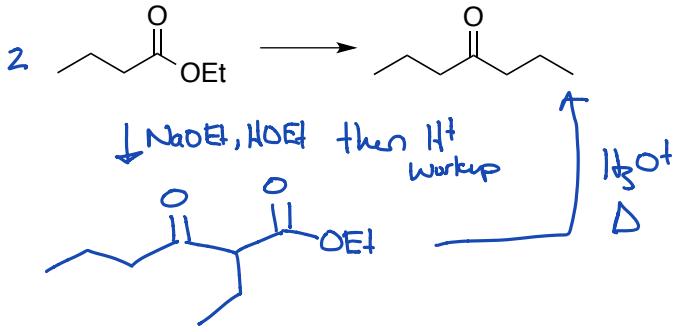
14) Draw an electron pushing mechanism for the following reaction.



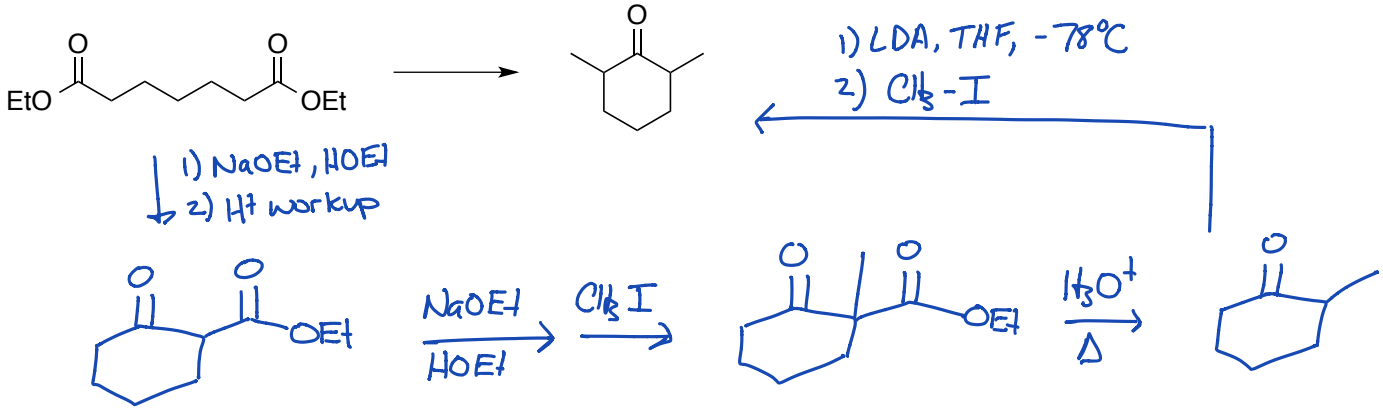
15) Devise a synthesis for the compound below starting with cycloheaxnone.



16) Devise a synthesis of the ketone below using the ester starting material provided. Your synthesis must involve the use of a Claisen condensation.



17) Devise an efficient synthesis for the following transformation.



18) **Reaction Combo**: Draw the organic products formed when butanal is treated with each reagent.

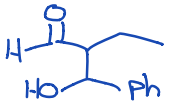
a) HO^-, $H_2C{=}O$, H_2O
b) 1. LDA, THF, -78 °C; 2. PhCHO; 3. H_2O
c) diethyl malonate, NaOEt, HOEt
d) CH_3-Li then H^+
e) $NaBH_4$, CH_3OH
f) $HOCH_2CH_2CH_2OH$, H^+
g) H_3C-NH_2, trace acid
h) $(CH_3)_2NH$, trace acid
i) H_2CrO_4
j) Br_2, AcOH
k) $Ph_3P{=}CH$-CH_3
l) 1. LDA, THF, -78 °C; 2. H_3C-I
m) HO^-, H_2O (rxn between two molecules of aldehyde)

See next page

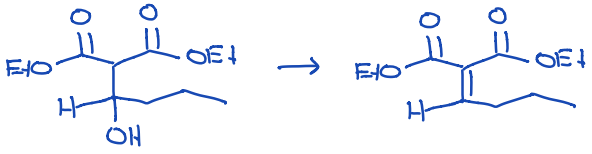
Q18

a) Crossed Aldol

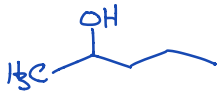
b) directed aldol



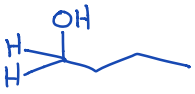
c)



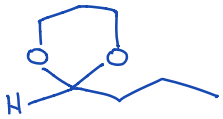
d)



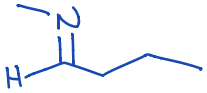
e)



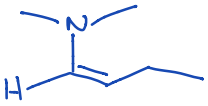
f)



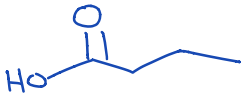
g)



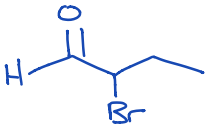
h)



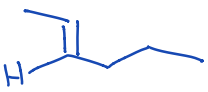
i)



j)

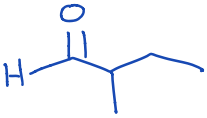


k)



+ Z isomer

l)



m) aldol b/t two molecules