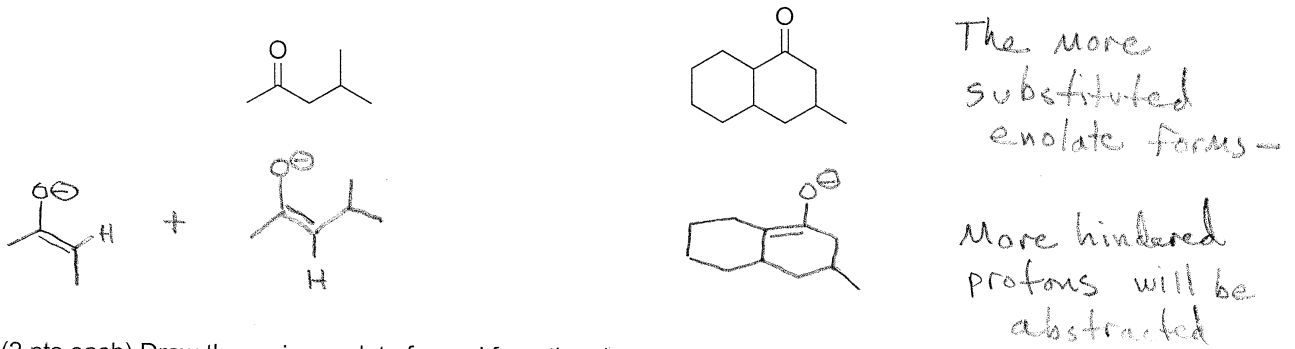
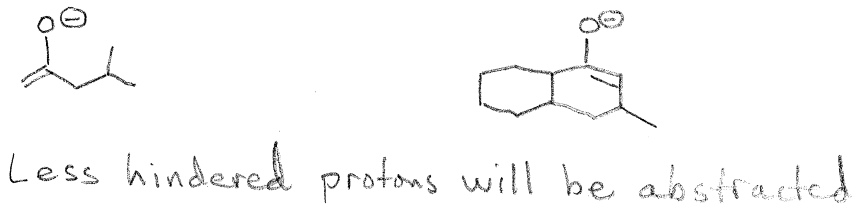


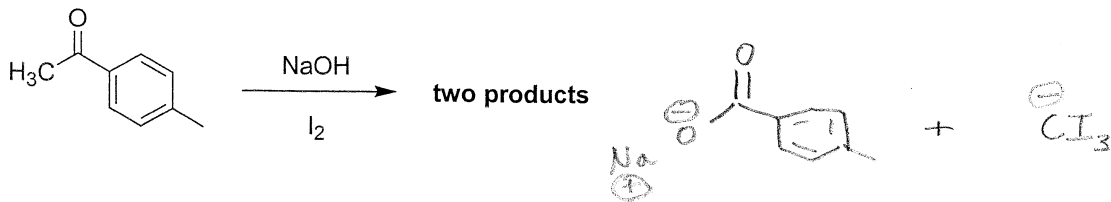
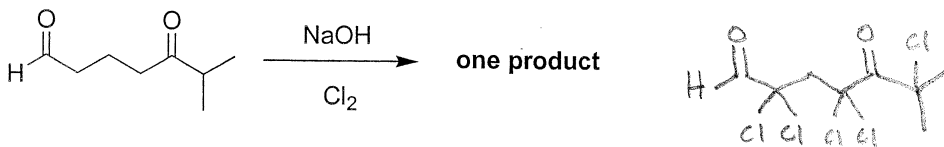
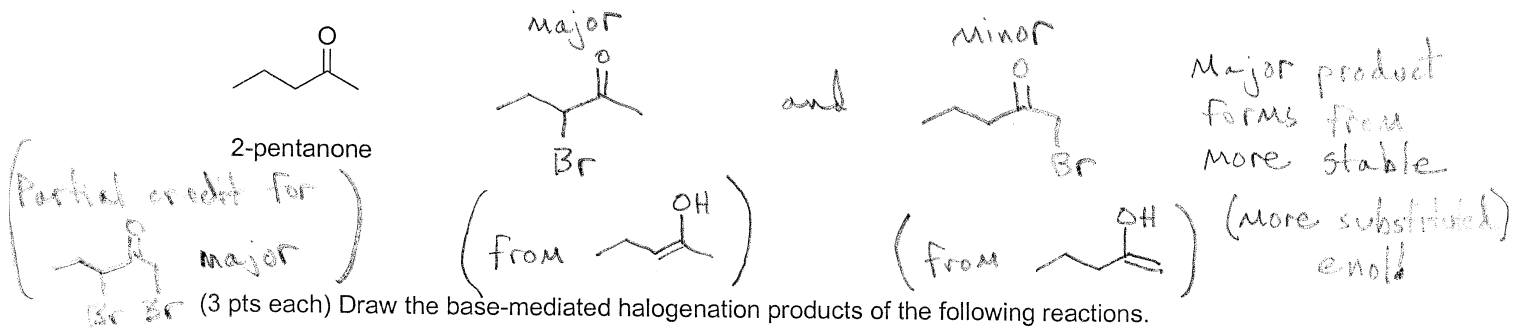
(2 pts each) Draw the major enolate(s) formed from the following compounds using base at higher temperature (25°C)



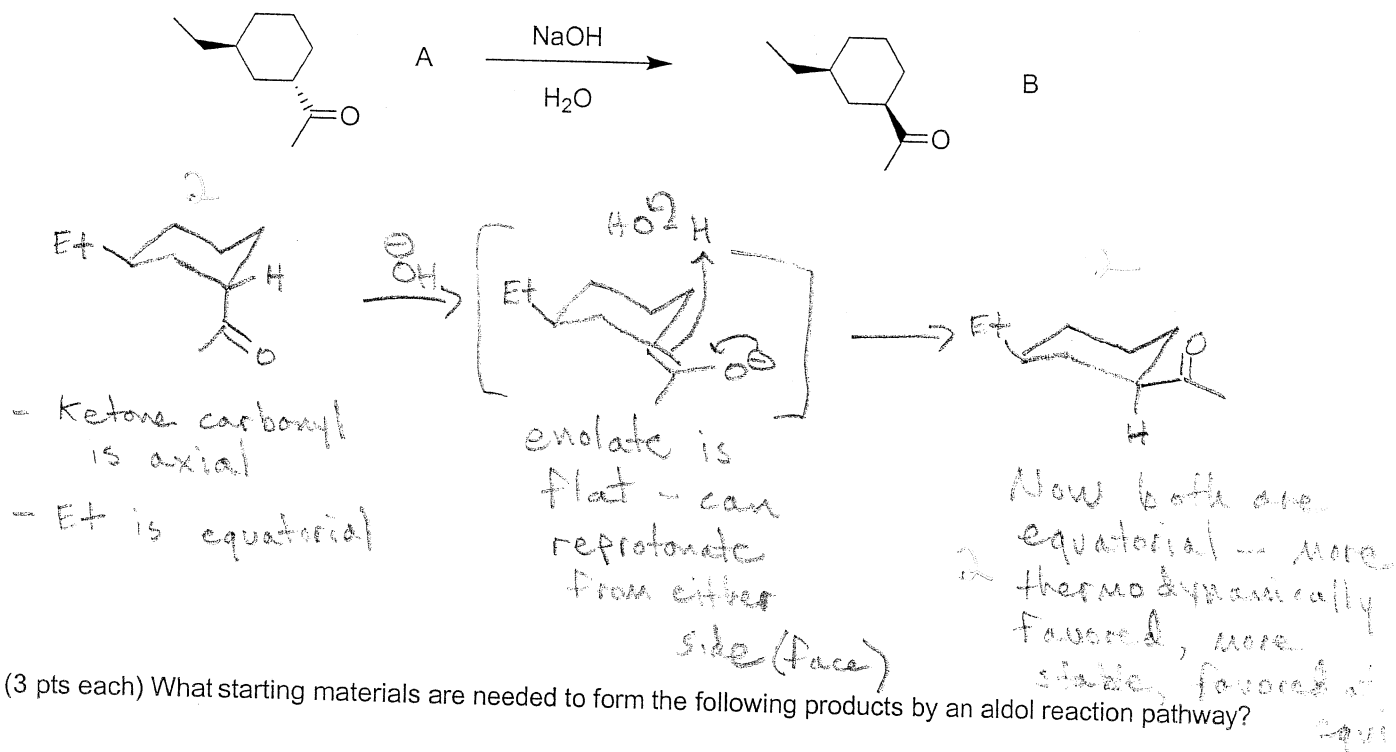
(2 pts each) Draw the major enolate formed from the above compounds using LDA at low temperature (-78°C)



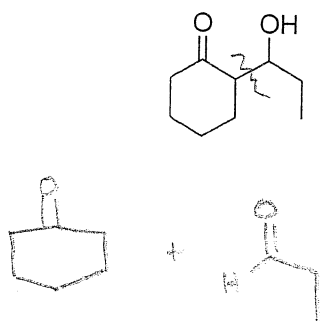
(5 pts) **Acid-mediated** bromination at room temperature of 2-pentanone forms two products, one major and one minor. Draw the products and indicate which is major/minor. Explain why the major product is major.



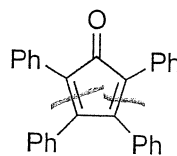
(6 pts) The *trans*-ketone A isomerizes to the *cis*-ketone B in aqueous base. Explain why structure B is favored at equilibrium **by drawing appropriate diagrams**.



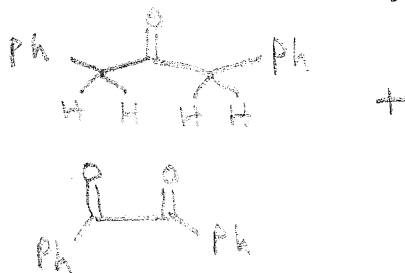
(3 pts each) What starting materials are needed to form the following products by an aldol reaction pathway?



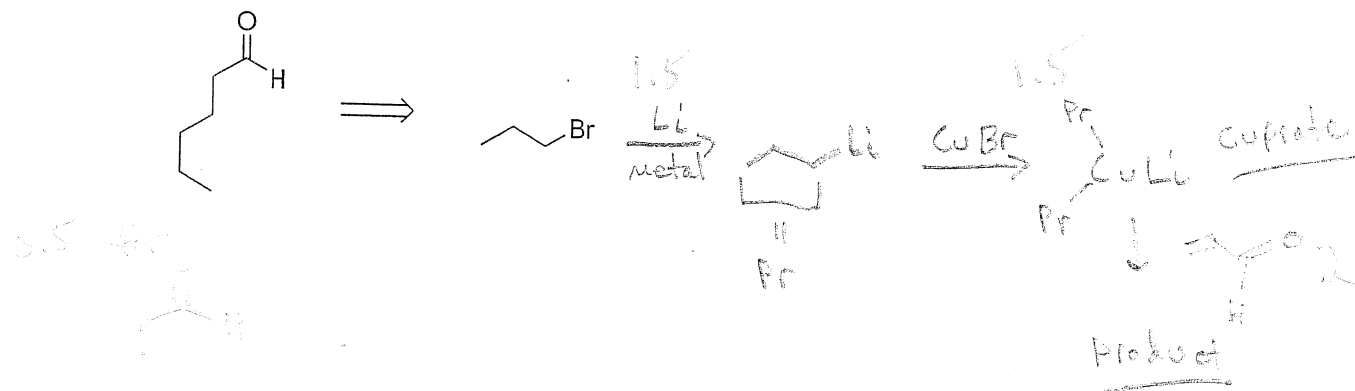
0.5 each  
0.5 each



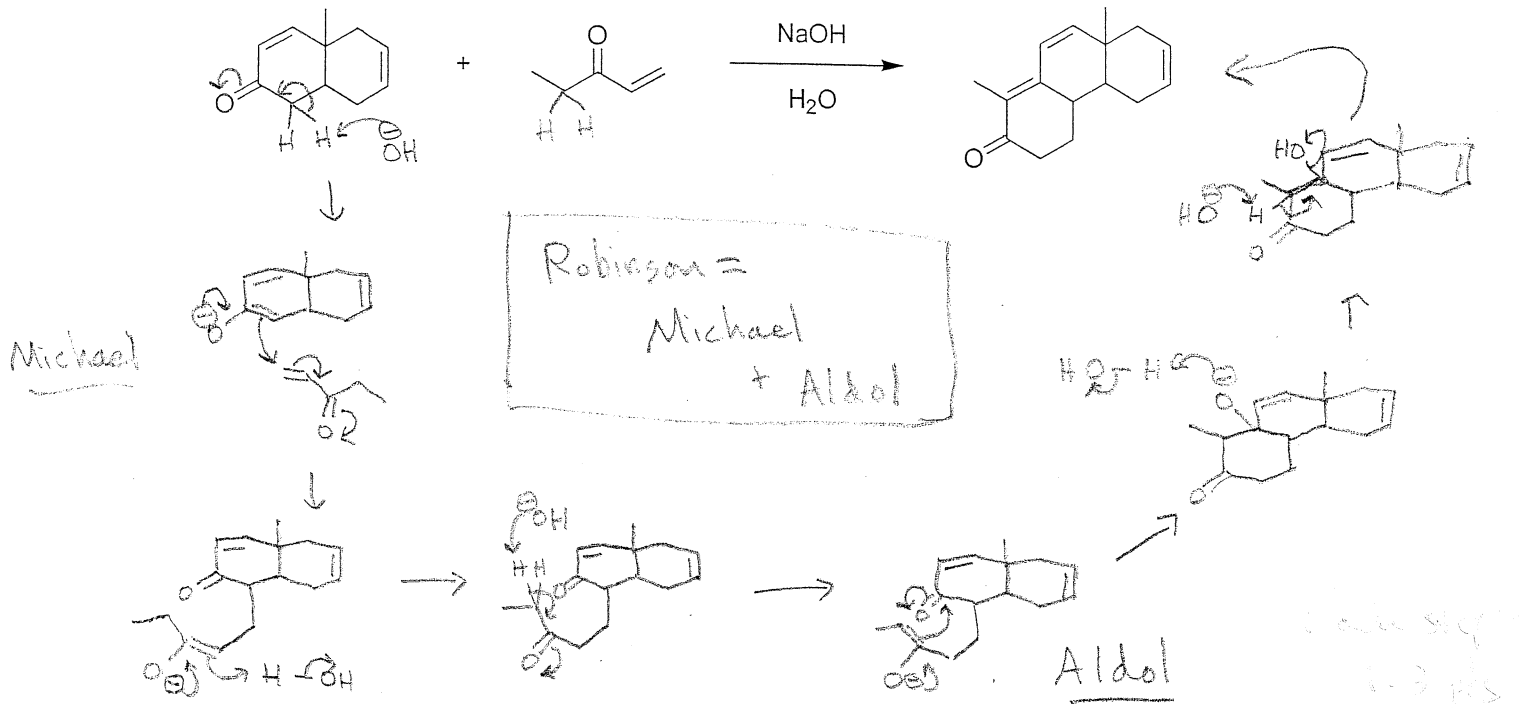
This compound forms beautiful purple microcrystals!



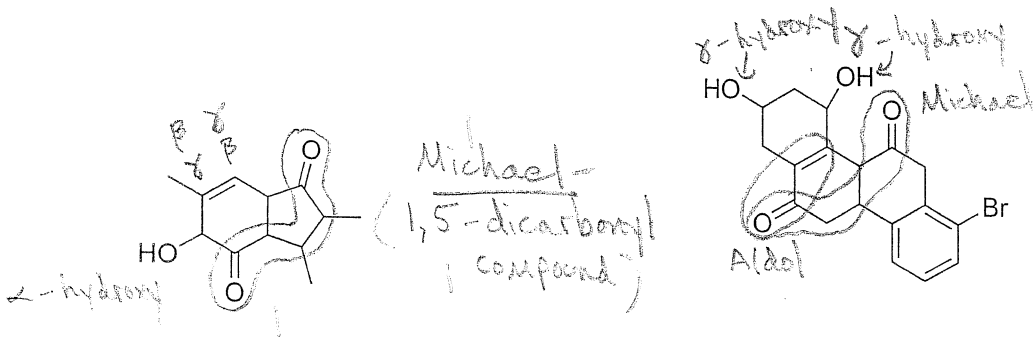
(5 pts) Synthesize the following compound from the indicated alkyl halide and an appropriate three-carbon aldehyde. It is not necessary to show mechanism, although mechanism may help you solve the problem. Hint: consider organometallic routes!



(8 pts) Draw a stepwise mechanism for the following Robinson annulation. This reaction was a key step in the synthesis of cortisone by R. B. Woodward and coworkers in 1951. Make your structures unambiguous!



(3 pts each) Do not write out explicit syntheses of the following molecules. Instead, for each one, indicate in words whether you would use an aldol, an aldol followed by dehydration, a Michael, or a Robinson annulation to synthesize them. Describe the "signature" that indicates the reaction type (i.e.  $\alpha,\beta$ -unsaturated, etc.) and circle it in the structure.

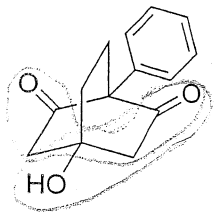


Michael-  
(1,5-dicarbonyl  
compound)

Robinson  
Annulation =

Michael  
+  
(1,5-dicarbonyl  
compound)  
Aldol  
( $\alpha,\beta$ -unsaturated  
carbonyl)

1 for each  
compound

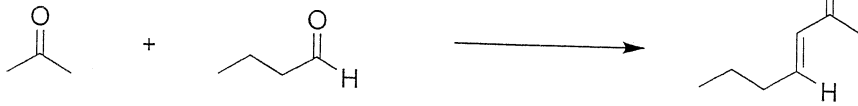


Aldol  
( $\beta$ -hydroxy carbonyl compound)

or  
Michael  
(1,5-dicarbonyl compound)

# Extra Credit (4 pts)

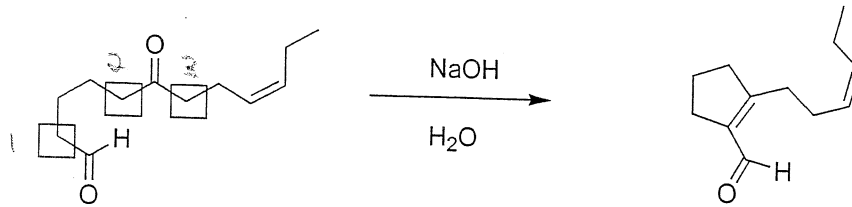
(4 pts) Describe (in words) a method to achieve the following mixed aldol condensation **without forming any additional products**:



Take acetone in an inert solvent and fully deprotonate it with a strong base (LDA or LHMDS) to form the enolate (low temperature also helps.) Next, add butyraldehyde to generate the aldolate product. Upon workup, treat the aldolate product with aqueous base (NaOH) and possibly heat to dehydrate to the  $\alpha, \beta$ -unsaturated product.

## EXTRA CREDIT (5 pts)

In forming certain perfume components (jasmine-like perfumes), the following process produces only one product. There are three acidic sites (boxed), yet only one reacts. **Draw a mechanism and use it to explain why** only a single product forms.

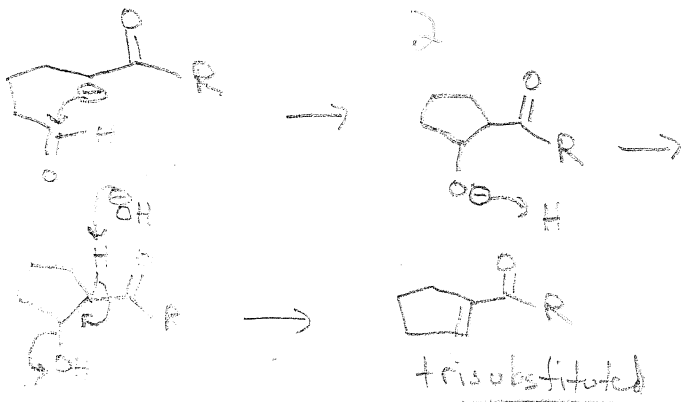


Product inventory time!

- ① - 5-membered ring forms
- ② - 5-membered ring forms
- ③ - 7-membered ring forms - less stable, unlikely

Reaction occurs at ① because the resulting product is more stable (i.e. it is a more substituted double bond)

Reaction at ②:



Reaction at ①:

