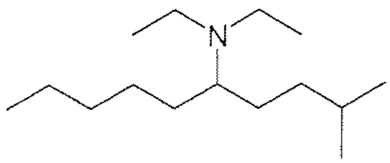
→ Although in the beginning of the rxn the kinetic enolate is formed faster + in higher yield because of sterics, the # of protons available to pick off (2 vs 1) + the activation barrier being lower (see diagram below). Using a weak base + high temps are conditions which allow thermal equilibrium to be established so the product ratio shifts to favor the more stable pdt.

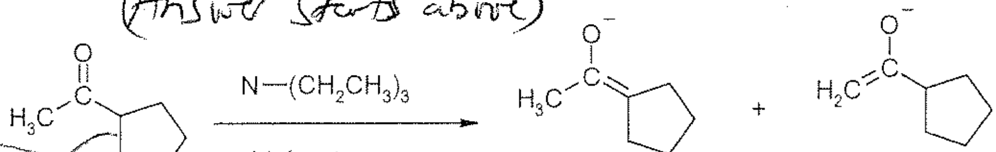
CHEM 2062 - Spring 2009 - **Exam #4** Name KEY

1. (3 pts) Give the **IUPAC** name of the following compound.



N,N-diethyl-2-methyl-5-decanamine

2. (7 pts) Explain why triethylamine and higher temperatures favor the formation of the major enolate shown below. (Answer starts above)



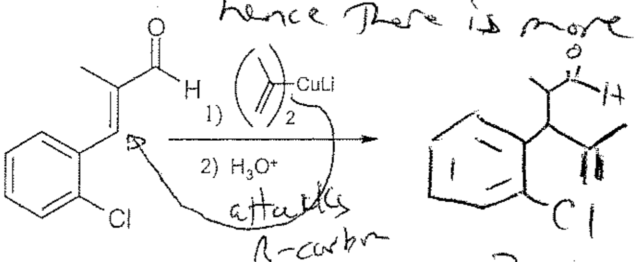
major enolate minor enolate

→ A weak base like triethylamine + higher temps favor the formation of a larger amount of the thermodynamic enolate because (a) the conj. acid of triethylamine is a strong enough acid to allow reprotonation of the enolates to occur so they can go back to the ketone starting material + (b) the higher temps allow enough energy for both enolates to go back over the activation barrier + reform SM. Both of these factors allow equilibrium to be attained so that the ratio of enolates is governed by their stabilities not how fast they are formed.

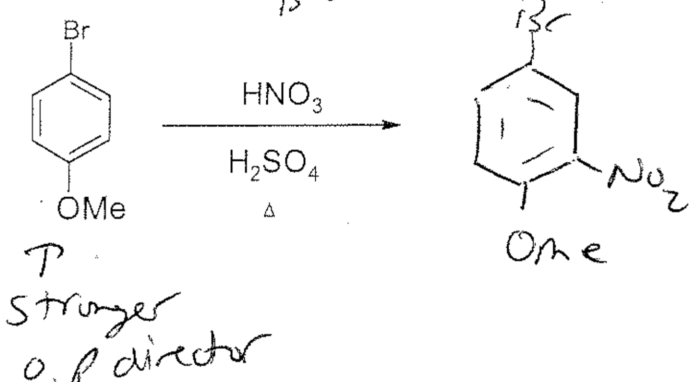
→ The more substituted enolate is more stable + hence there is more of it under these conditions where thermodynamic equilibrium is established.

3. (48 pts, 4 each) ~~Give the **major product(s)** or the~~ **reagents needed** or **starting material** for the ~~following transformations.~~ Be sure and indicate stereochemistry where necessary.

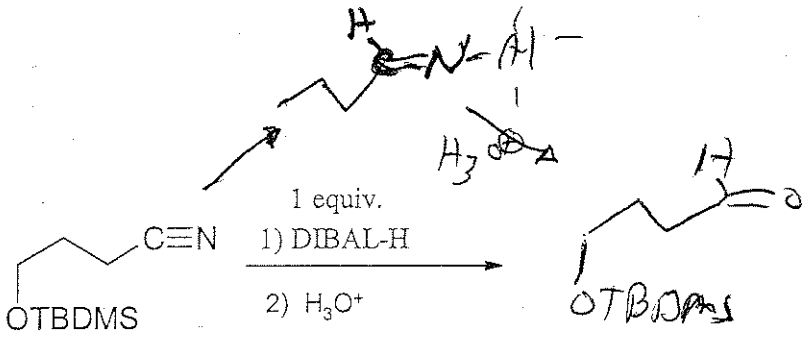
a)



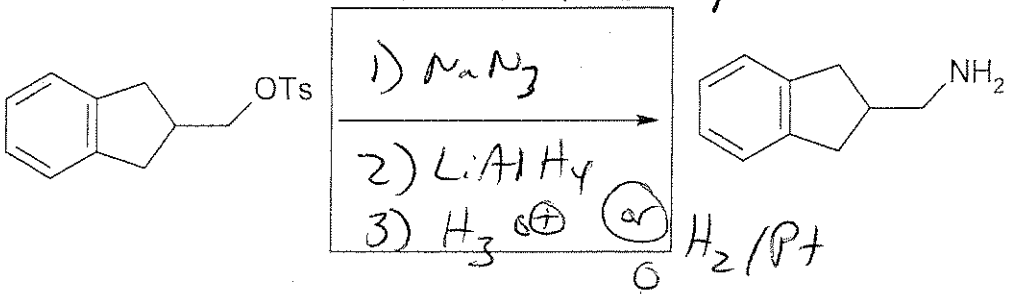
b)



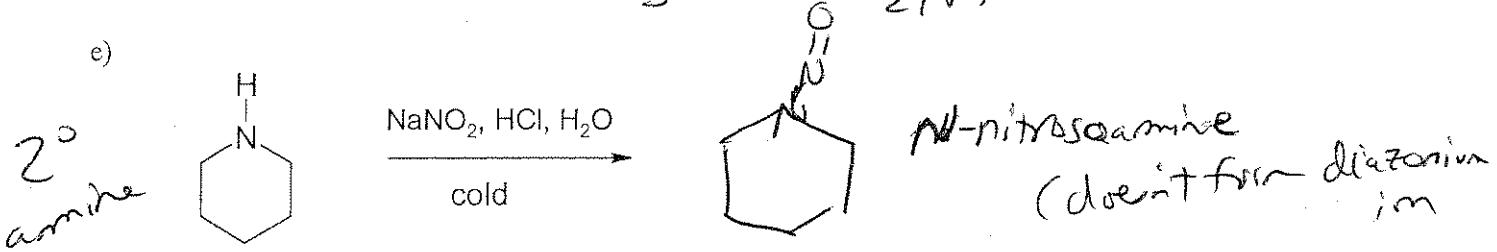
c)



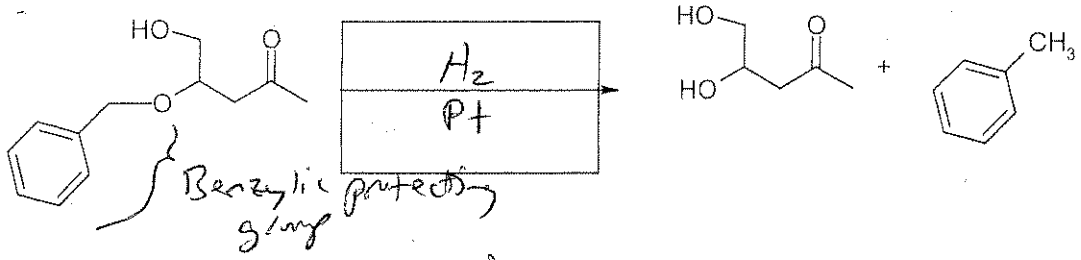
d)



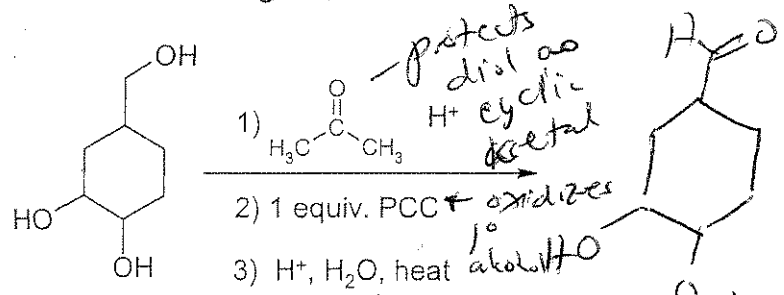
e)



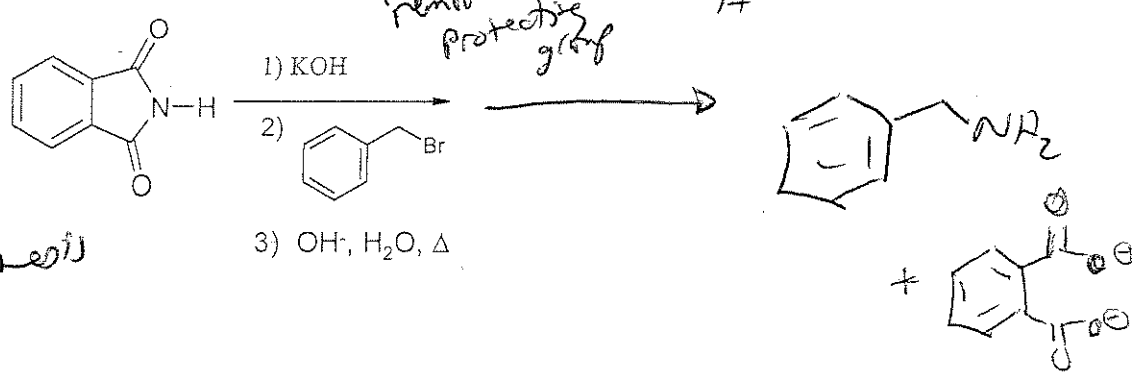
f)



g)

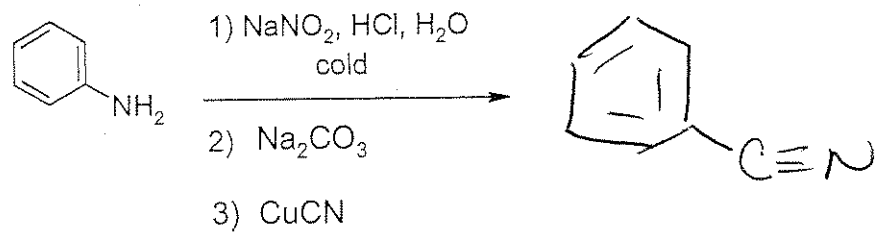


h)

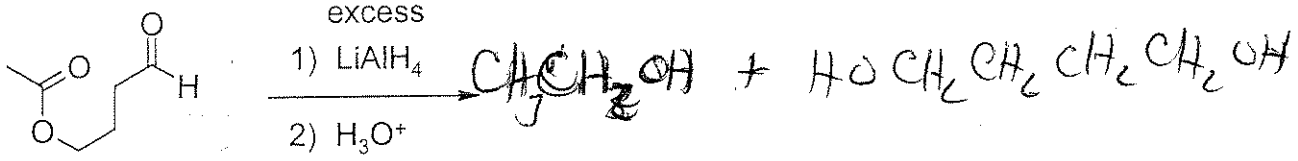


Gabriel Synthesis

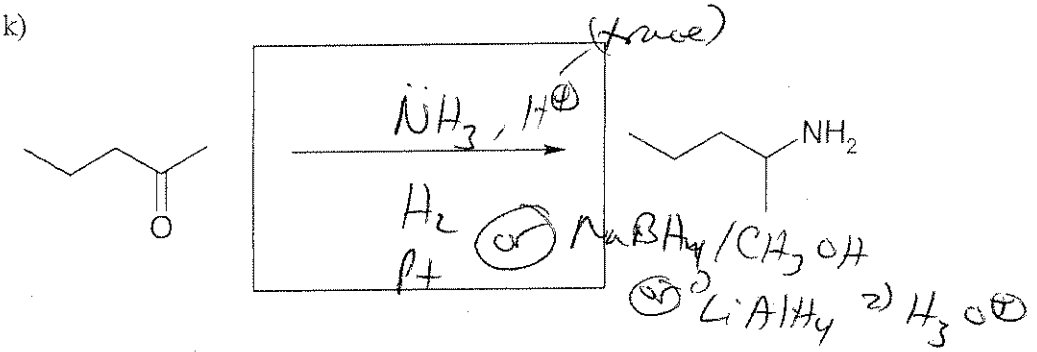
i)



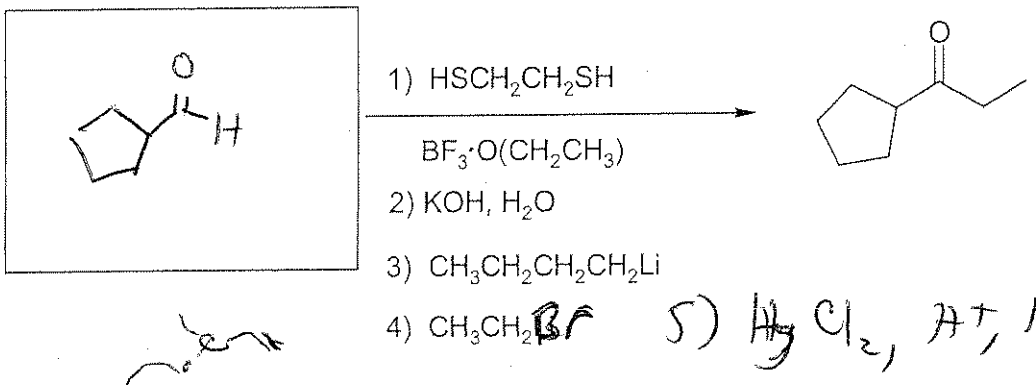
j)



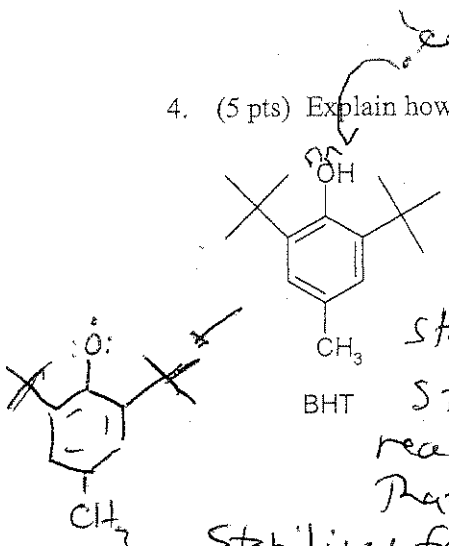
k)



l)



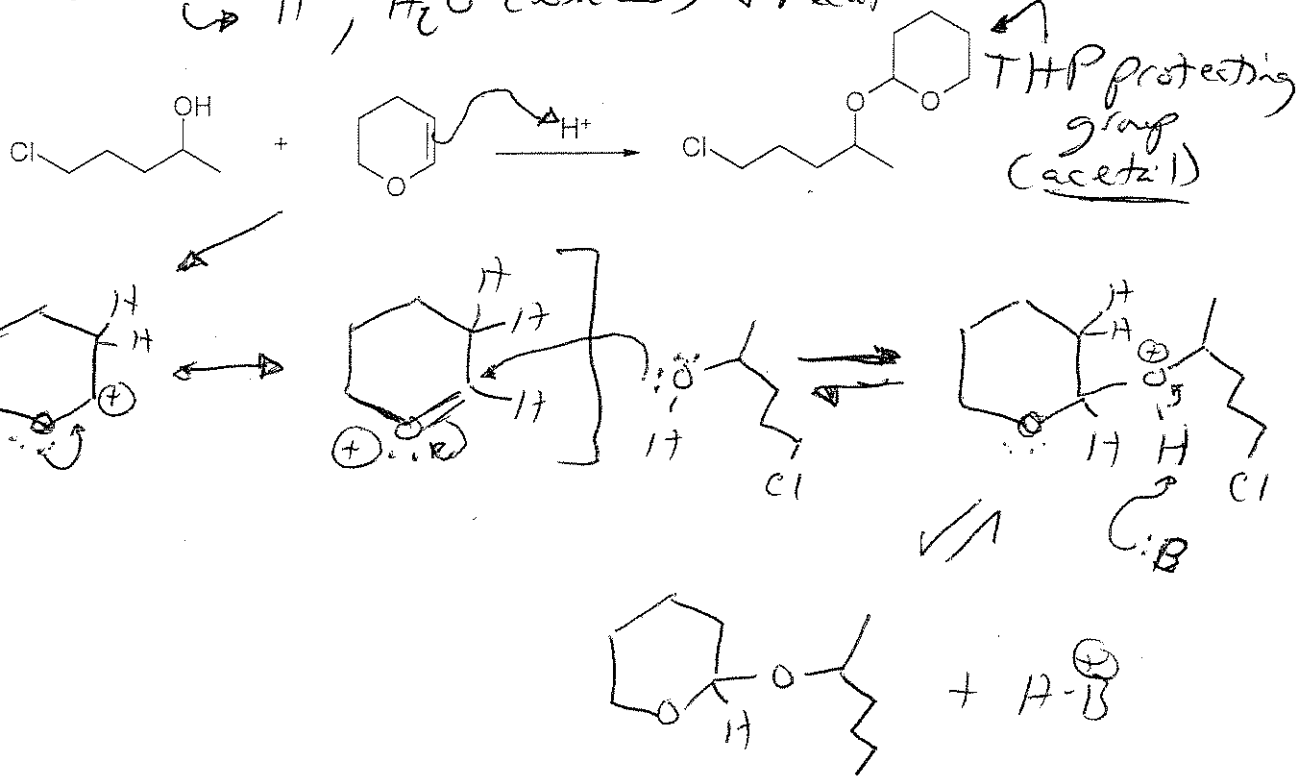
4. (5 pts) Explain how BHT acts as an inhibitor to autooxidation in foods.



BHT is a free radical scavenger. The phenolic hydrogen is easily abstracted by free-radicals formed in foods because the resulting phenoxy radical is stabilized by resonance delocalization. Once formed, the stabilized phenoxy radical is further hindered from reacting by the presence of the bulky t-butyl groups that are nearby. Consequently, once this hindered, stabilized free radical is formed it is unreactive & helps to terminate free-radical chain rxns that take place in food & cause spoilage.

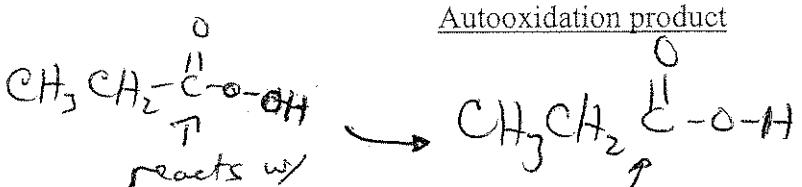
5. (8 pts) a) Give the complete mechanism for the following reaction.

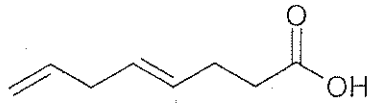
b) What conditions are used to remove this protecting group in the product to go back to the original alcohol? H^+, H_2O (excess) + heat

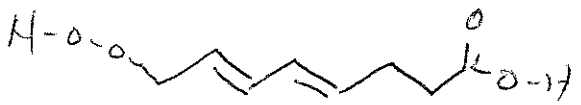


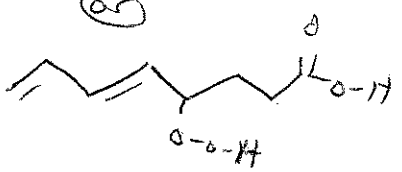
6. (4 pts, 2 each) Give the autooxidation products of:

Autooxidation product

a) CH_3CH_2CHO → 

b) 



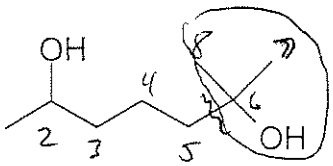


7. (6 pts) Show how you could make the 1-propanamine from bromoethane.

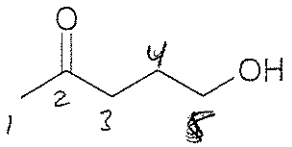
(Harder problem)

8. (11 pts) Prepare

need to add new group / new C-C bond



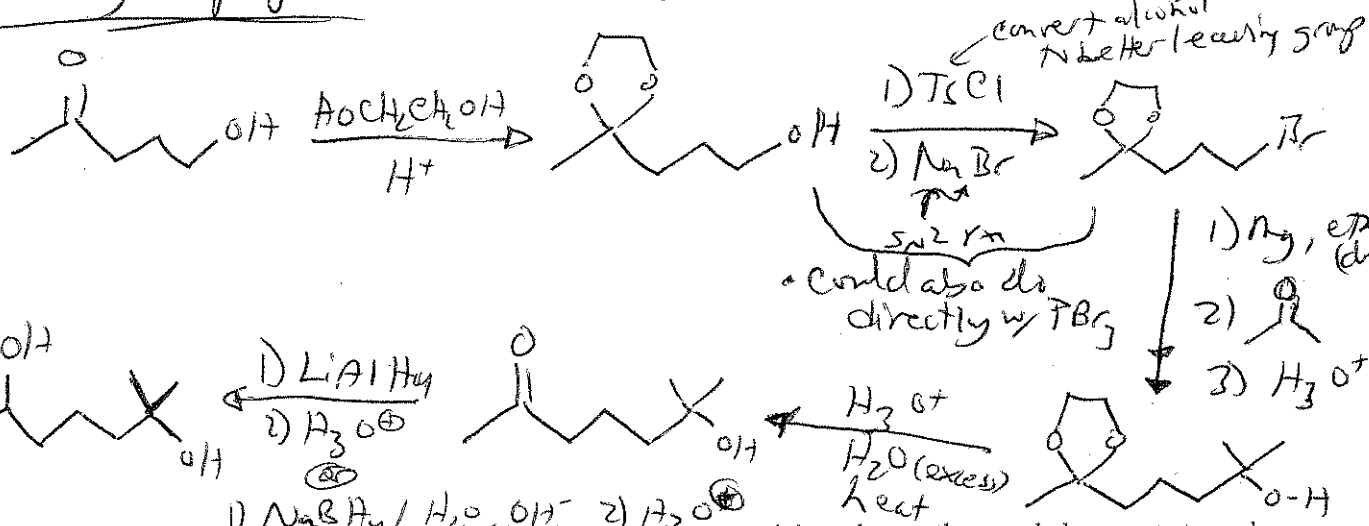
from



Show all reagents and the structure of the product after each step.

(See back of Exam for retrosynthetic analysis)

One way to prepare (there may be other methods as well)



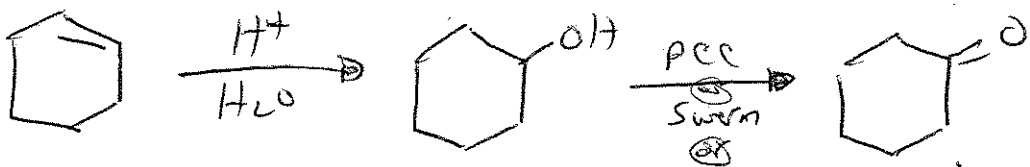
9. (8 pts) Design a synthesis using the given starting materials and any other needed reagents to make the compound shown below. Show all reagents and the structure of the product after each step.

and CH_3CH_2Br

Wittig rxn

See back of Exam for retrosynthetic analysis for

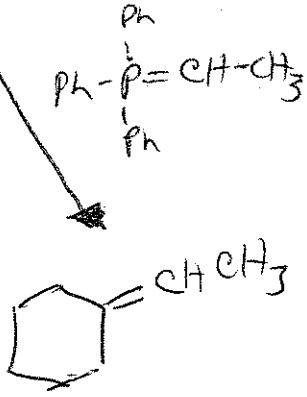
One way to prepare: (3 steps)



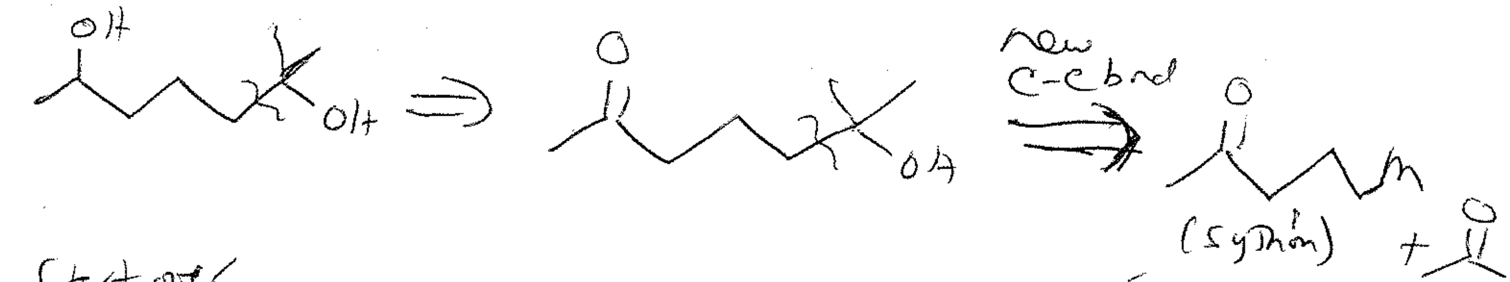
1) make Wittig reagent

$PPh_3 + CH_3CH_2Br \rightarrow Ph_3P^{\oplus}-CH_2CH_3$

$Ph_3P^{\oplus}-CH_2CH_3 \xrightarrow{CH_3CH_2CH_2CH_2Li} Ph_3P=CHCH_3$

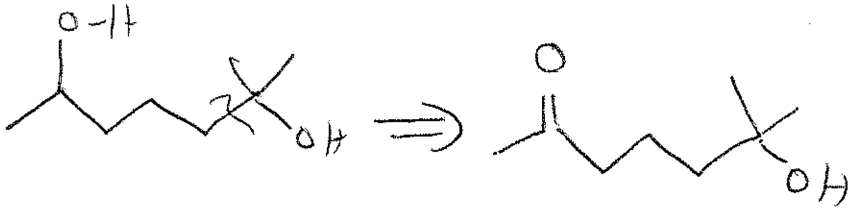


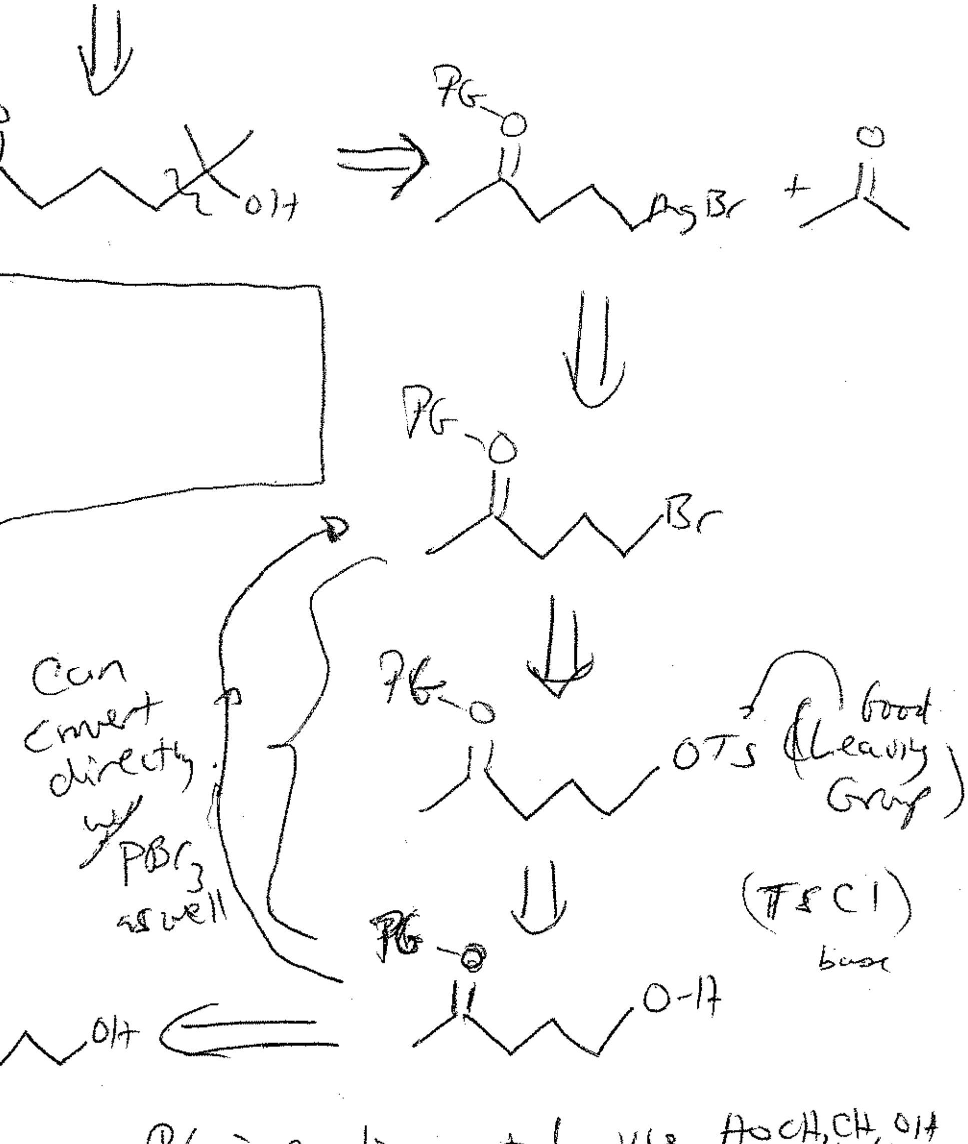
#8 Retrosynthetic Analysis:



Start over

(Grignard or organolithium but then can't have [C=O] so need PG for carbonyl)





PG = cyclic acetal use $HOCH_2CH_2OH$, H^+

#9 Retrosynthetic Analysis of