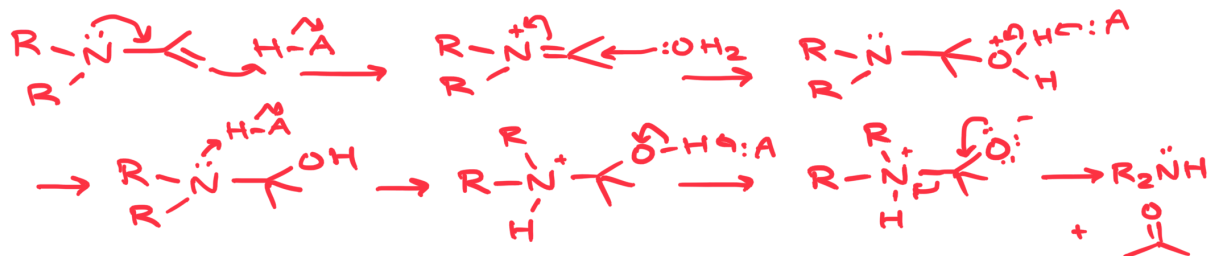


## Midterm 2 Review Packet Key

Please fill out evaluation form at the bottom so I can get your feedback on what to change for the remaining review sessions

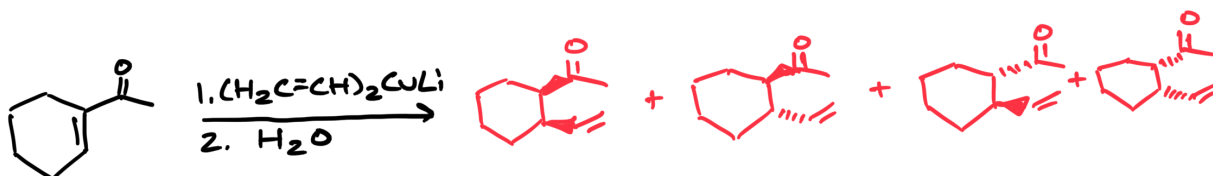
1. Draw the mechanism for Enamine Hydrolysis



Hydrolysis of Enamine follows three steps:

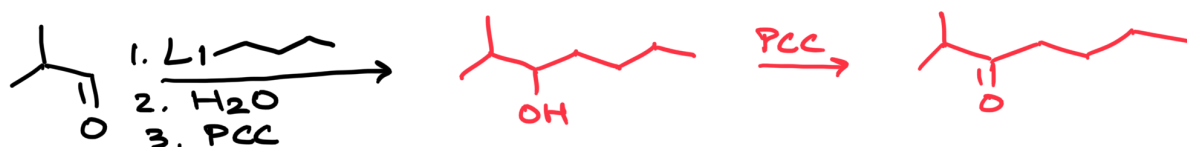
1. Protonation of the enamine to form an iminium ion (resonance stabilized)
  2. Nucleophilic attack of H<sub>2</sub>O, followed by deprotonation
  3. Proton transfer and loss of secondary amine from the carbonyl group
2. Draw the product or starting material for the following reactions

A.



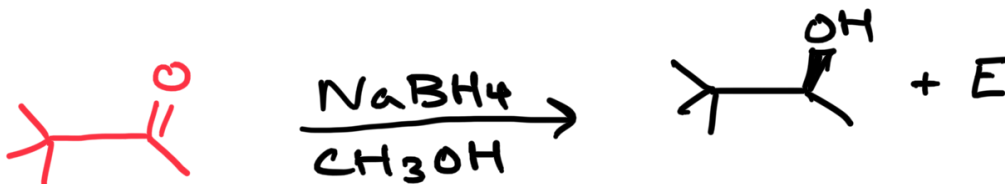
Organocuprate reagents form 1,4-addition products (start numbering from the oxygen atom). Because you are forming two stereogenic centers when the double bond gets removed (C3 & C4), you are going to form diastereomers rather than just enantiomers. You must draw all of them out.

B.



Organolithium and grignard reagents form 1,2-addition products. Like other reactions in chapter 17, it will add to the carbonyl group and then produce an alcohol (due to water workup). PCC oxidizes the alcohol group and produces a ketone.

C.

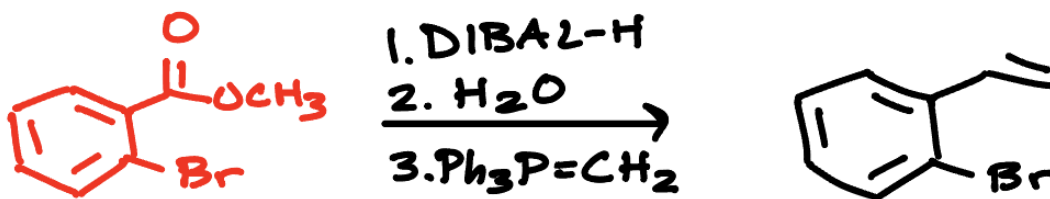


NaBH<sub>4</sub> is used for the reduction of aldehydes and ketones into alcohols. Since you are creating a stereogenic center, you have to indicate stereochemistry and write +E for the enantiomer.

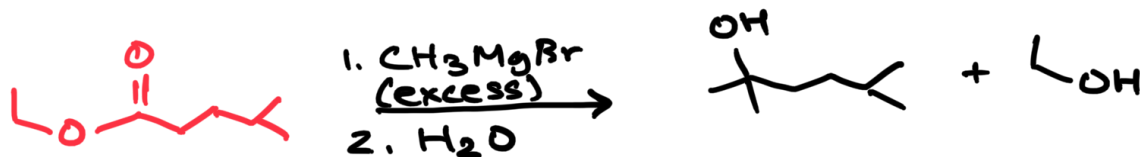
Steps:

1. Nucleophile donates H<sup>-</sup> to the carbonyl group breaking the pi bond
2. Protonation of O<sup>-</sup> by CH<sub>3</sub>OH to form new O-H bond

D.



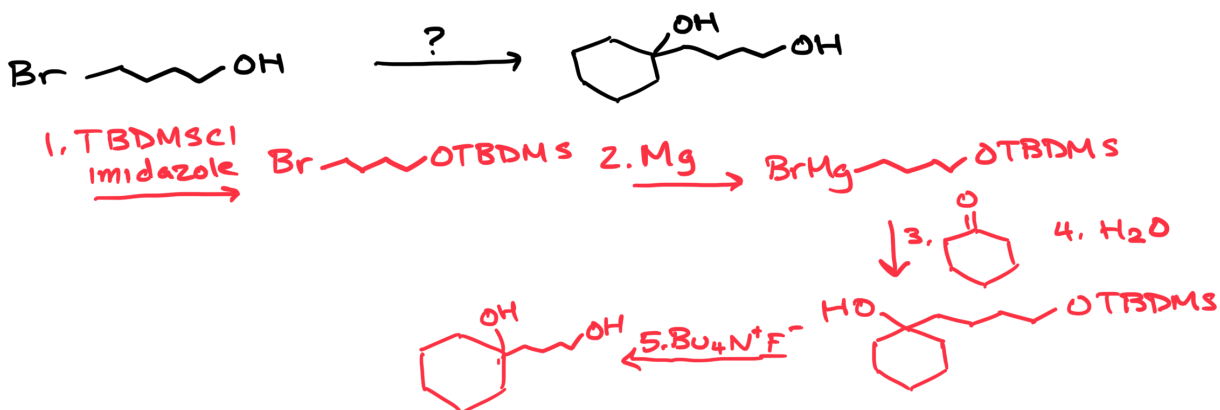
E.



Addition of grignard reagent. You need two equivalents (indicated by excess) when adding them to esters. You must show the second product that forms when the OR<sup>-</sup> group leaves (you will be marked off on exams if you miss this)

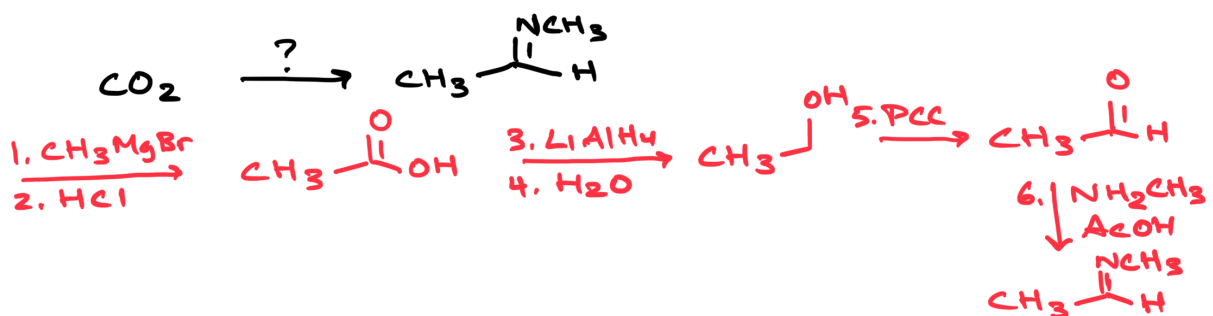
3. Provide the necessary reagents to produce the products from the starting material. Draw all intermediates.

A.

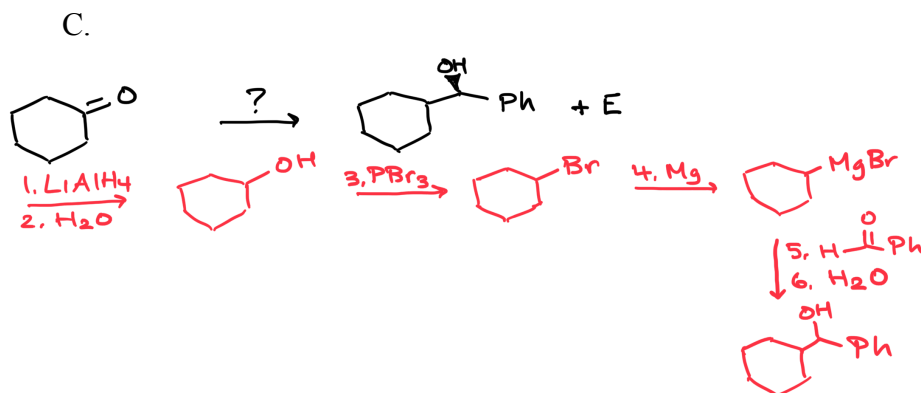


First step is to create the starting material into a grignard reagent but before doing this, you have to add a protecting group first. Why? N-H and O-H bonds undergo acid-base reactions with organometallic reagents so you would not get the product you were looking for. After protecting the OH group using TBDMS with imidazole, you can add in Mg to produce the grignard reagent. The final product indicates a tertiary alcohol so therefore, you have to add in a ketone, followed by a water workup. Finally, we remove the protecting group by adding  $\text{Bu}_4\text{N}^+\text{F}^-$ .

B.



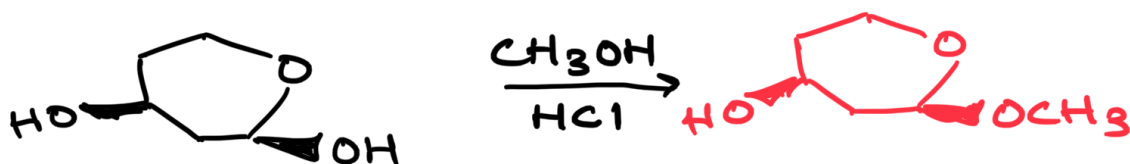
$\text{CO}_2$  reacts with grignard reagents to produce a carboxylic acid. Final product is an imine so you once again need an aldehyde starting material. Reducing the carboxylic acid and then using PCC will form the aldehyde. Final step is to add in a primary amine in acetic acid.



Reducing the ketone to produce an alcohol group and then using  $\text{PBr}_3$  to convert it into an alkyl bromide so that you can turn it into a grignard reagent. Since the product indicates a secondary alcohol, you have to add in an aldehyde followed by a water workup.

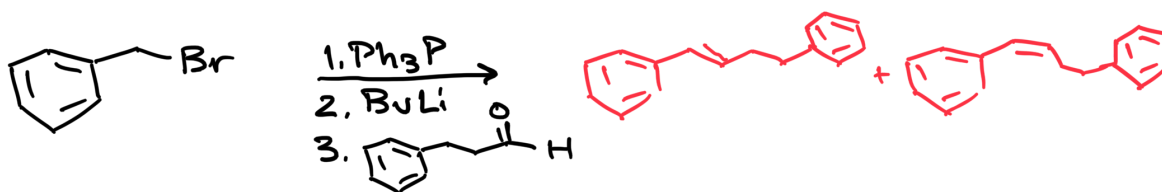
4. Draw the product or starting material for the following reactions

A.

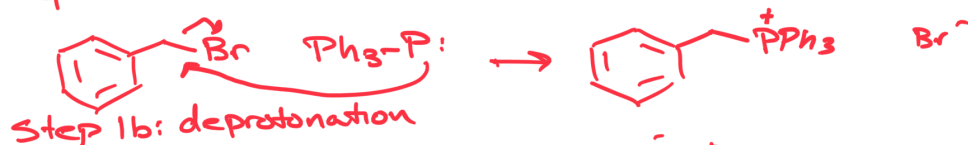


Cyclic Hemiacetal to a cyclic acetal is essentially replacing the OH group with an OR group. This substitution readily occurs because of carbocation stability (resonance stabilized). This makes the OH group of the hemiacetal different from the hydroxy group (the group on the left of the ring) in other alcohols and therefore when a compound that has an alcohol group and a hemiacetal OH group is treated with an alcohol and acid, only the hemiacetal OH group reacts.

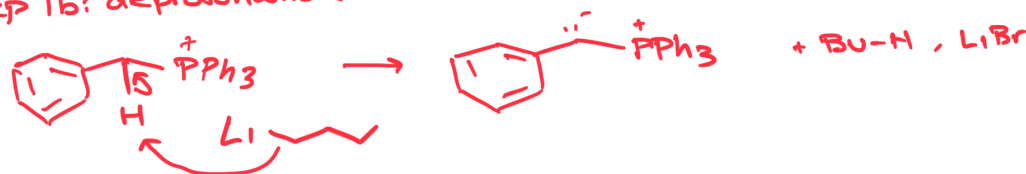
B.



Step 1a: Formation of Wittig Reagent ( $\text{S}_\text{N}2$ )



Step 1b: deprotonation



Step 2: Wittig Rxn

Wittig reactions are essentially replacing the  $\text{C=O}$  bond with a  $\text{C=C}$  bond. In cases like these where there's a long chain and it gets confusing as to how to orient the bonds correctly, I recommend just writing "R" and then drawing in the chain afterwards. You have to draw both products: E and Z isomers (E is different side; Z is same side)

C.



Formation of cyclic acetal by reacting the carbonyl group with a diol. Starting material needs to contain the carbonyl (just remember, ch.18 is all about aldehyde and ketone starting material) Acetals are used as protecting groups for aldehydes and ketones from basic, nucleophilic reagents.

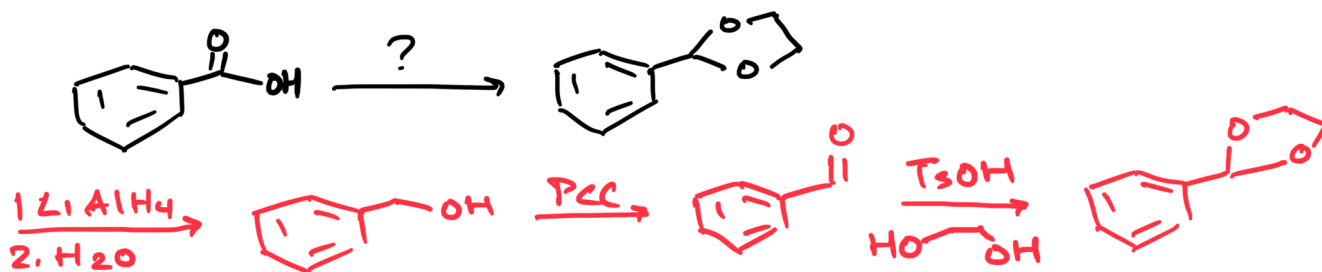
D.



Product is an enamine (double bond is adjacent and not directly on the nitrogen atom) Therefore the starting material needs a carbonyl group (aldehyde or ketone) and a secondary amine.

5. Provide the necessary reagents to produce the products from the starting material. Draw all intermediates.

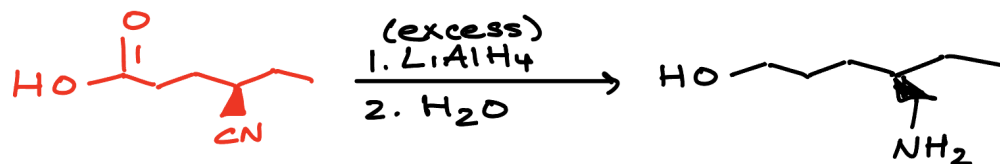
A.



Forming acetal so therefore you need an aldehyde or ketone starting material. Reducing the carboxylic acid into an alcohol then using PCC to create the aldehyde. Then simply add in the diol with TsOH to form the cyclic product.

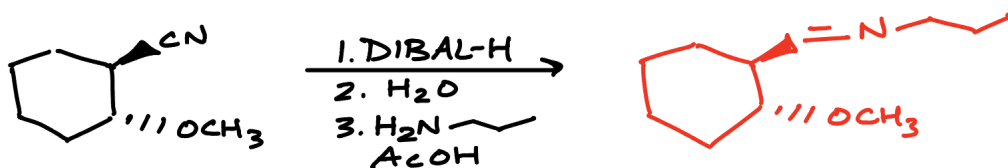
6. Draw the product, starting material, or reagents for the following reactions

A.



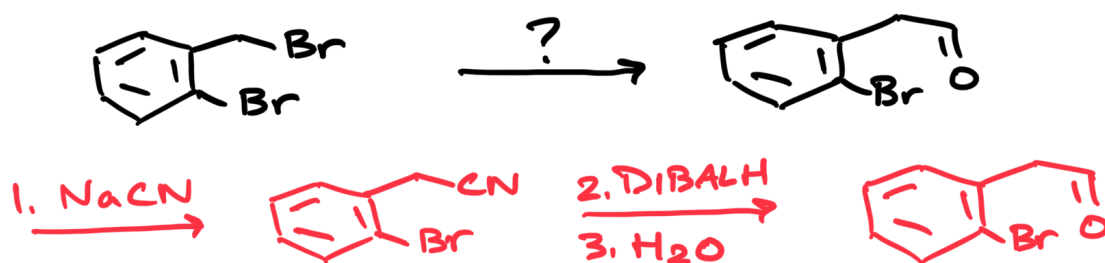
Excess indicates that there are two groups that reacted with  $\text{LiAlH}_4$ . In order to make the primary alcohol in the starting material you would need a carboxylic acid or aldehyde. You would also need a nitrile which reacts to form the primary amine.

B.



DIBAL-H is used to convert nitriles into aldehydes and with that aldehyde you are able to react with the primary amine to form an imine.

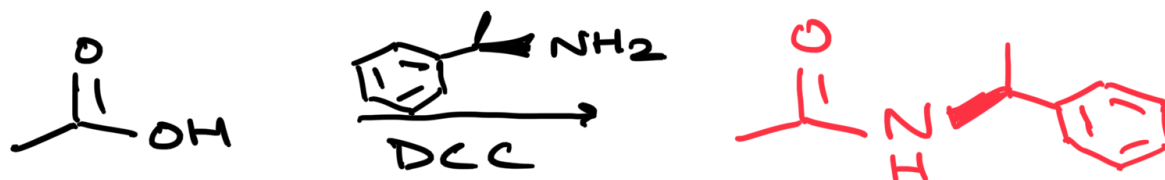
C.



S<sub>N</sub>2 mechanism of replacing BR with CN and then using DIBAL-H to produce the aldehyde product.

7. Draw the product or starting material for the following reactions

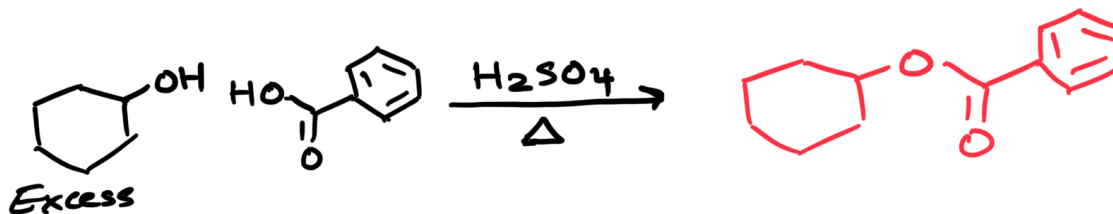
A.



Converting carboxylic acid to amide (DCC is an easy way to recognize this reaction).

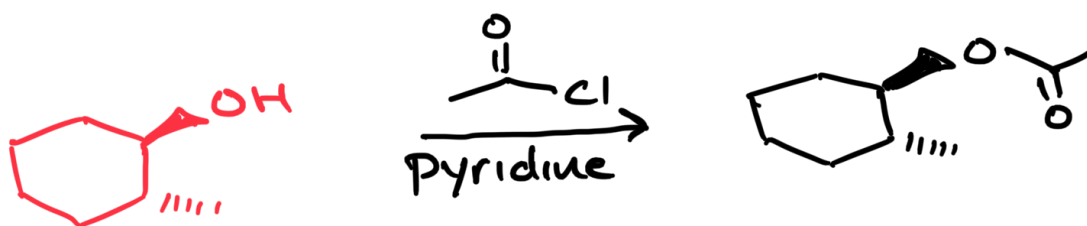
Importance of DCC: Without DCC, the amine deprotonates the carboxylic acid instead of nucleophilic attack on C=O. It has two functions: getting rid of the acidic proton & converting the oxygen into a good leaving group.

B.



Example of Fischer Esterification. Some things to remember: need excess alcohol, show heat, and need a strong acid such as HCl or  $\text{H}_2\text{SO}_4$ .

C.

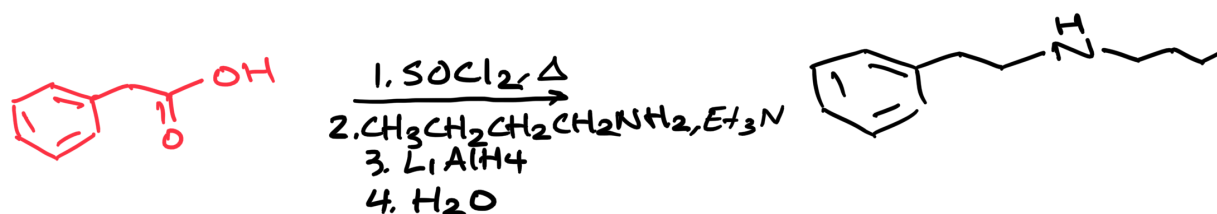


Reacting alcohol with acyl chloride to produce an ester.

Steps:

1. The nucleophile attacks the carbonyl group
2. Loss of proton and elimination of leaving group ( $\text{Cl}^-$ ) form the ester.

D.



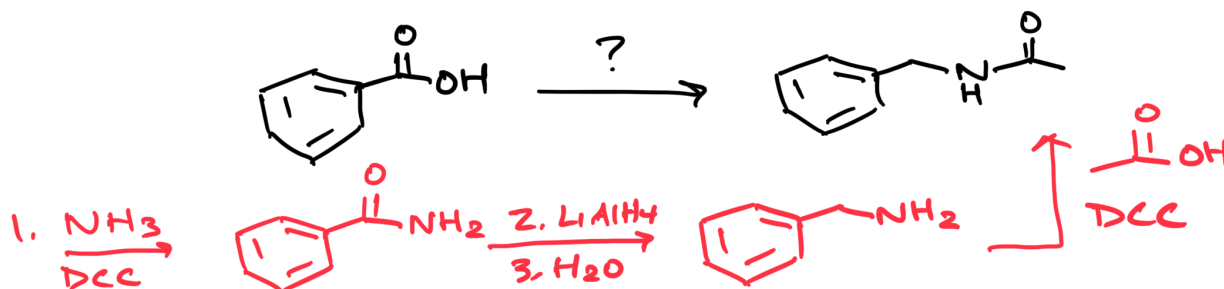
Short method if you know your reagents: See that you're adding  $\text{SOCl}_2$  and therefore need a carboxylic acid starting material

Longer method: Step 3 and 4 indicates the reduction of a carbonyl group which suggests that you have an amide after step 2. In order to form the amide, step 1 would need to have a chloride leaving group. In order to have a chloride group by addition of  $\text{SOCl}_2$ , you need a carboxylic acid starting material.



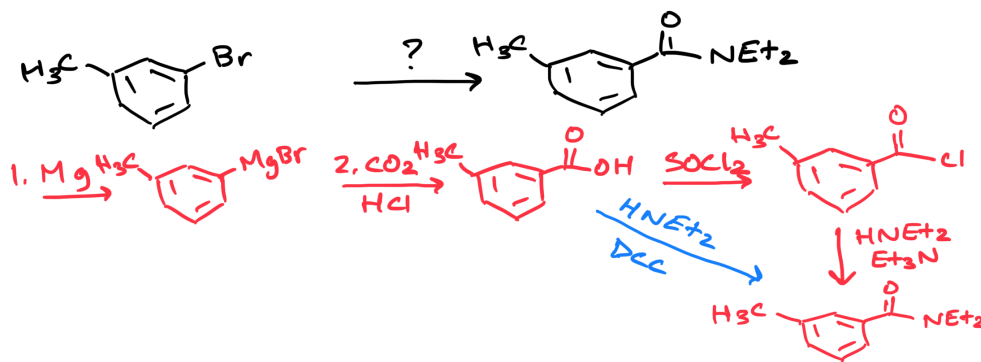
8. Provide the necessary reagents to produce the products from the starting material. Draw all intermediates.

A.



Starting material of carboxylic acid into amide. First step is to convert the starting material into an amide using  $\text{NH}_3$  & DCC followed by reduction to form an amine. This amine can now be used to create another amide with a carboxylic acid.

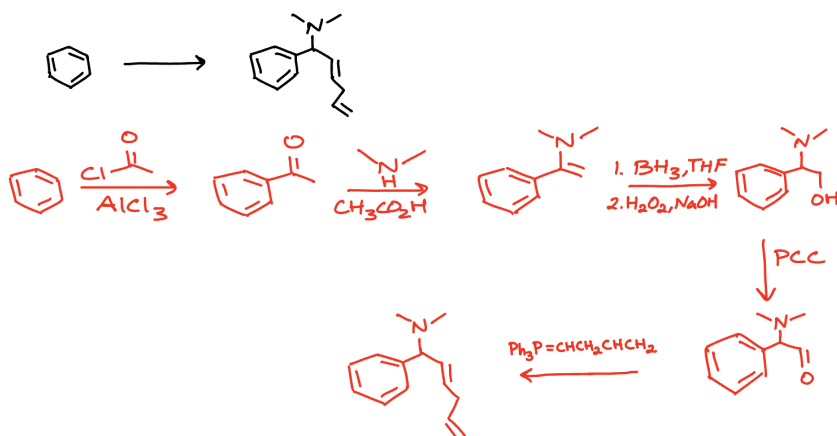
B.



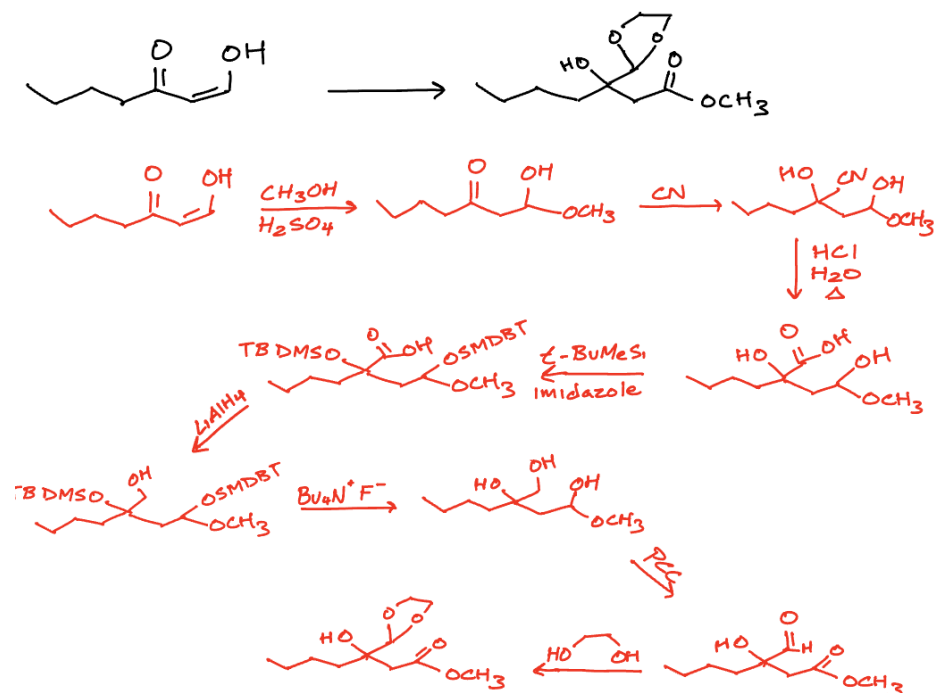
First step is to turn the starting material into a grignard reagent then using  $\text{CO}_2/\text{HCl}$  to convert it into a carboxylic acid and then converting to an amide. If you forget how to go from a carboxylic acid to amide, you can first turn it into an acyl chloride.

Challenge problems: Determine the reagents needed for the follow reactions (much harder than what you would see on exams so don't worry if you cannot solve these)

A.



B.



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