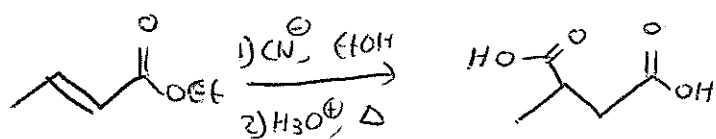


Chemistry 3331-100  
Organic Chemistry / Dr. Barney Ellison  
Thursday: Nov. 18<sup>th</sup> @ 7:00pm → 9:00 / 3<sup>rd</sup> Exam / Hale Science 230-270)

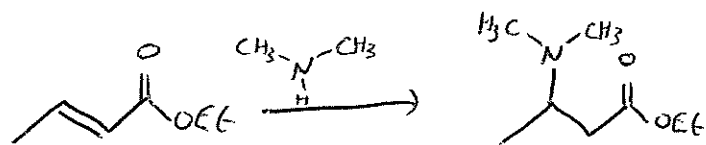
Name: KEY (please print)

1. (20 pts) What are the products formed when ethyl *trans*-butenoate (ethyl crotonate) reacts with:

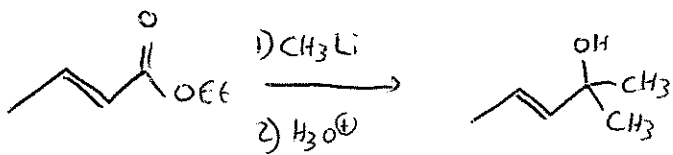
a)  $\text{CN}^-$  in EtOH followed by  $\text{H}_2\text{O}/\text{H}_3\text{O}^+ + \Delta$



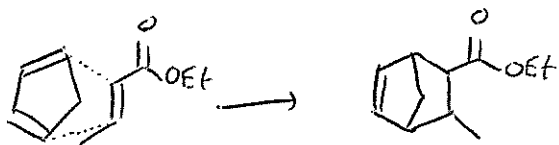
b)  $(\text{CH}_3)_2\text{NH}$  at room temperature



c)  $\text{CH}_3\text{Li}$  (excess) followed by  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$



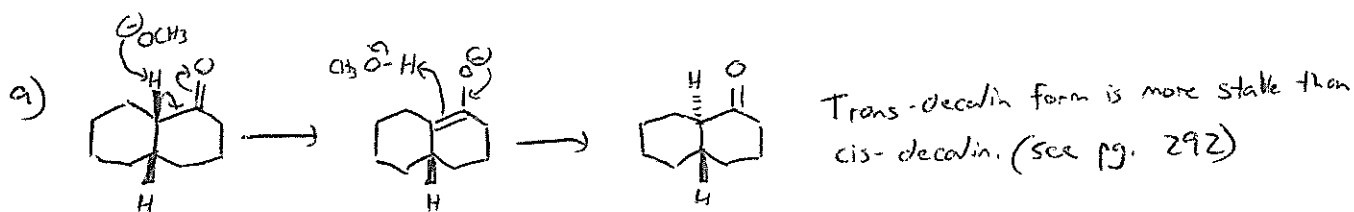
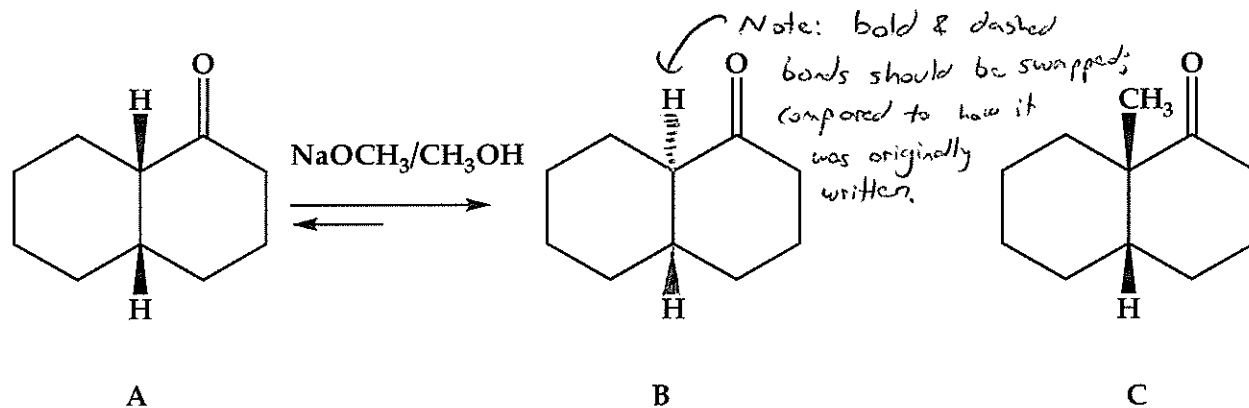
d) 1,3 cyclopentadiene



2. (10 pts) When compound A is treated with  $\text{CH}_3\text{OH}/\text{CH}_3\text{ONa}$ , isomerization to compound B follows.

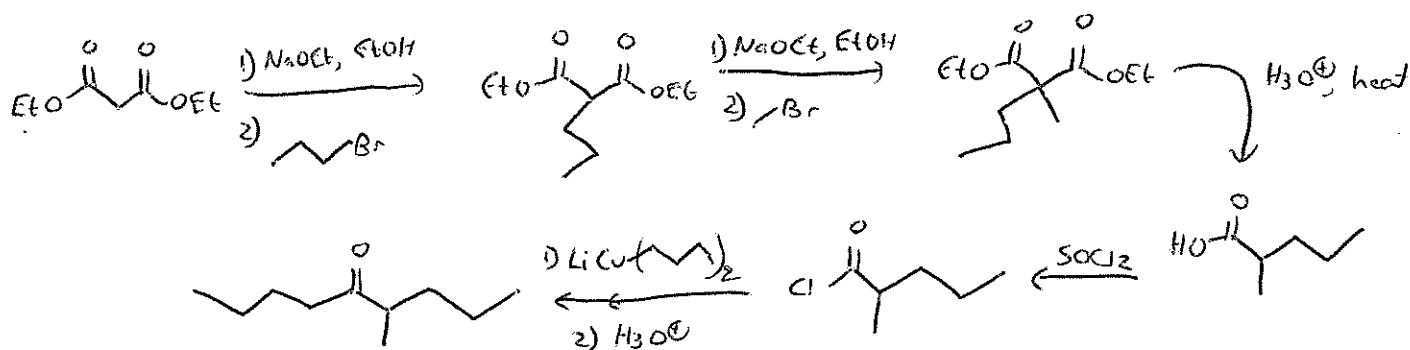
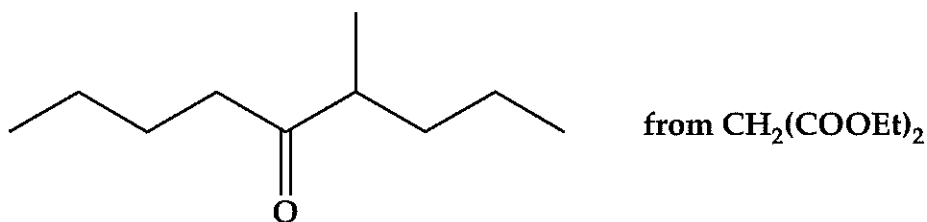
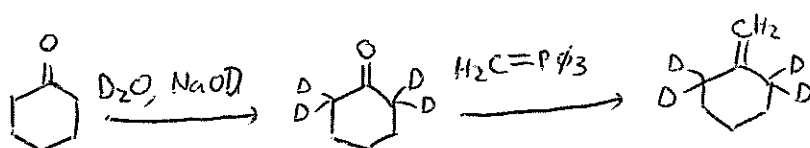
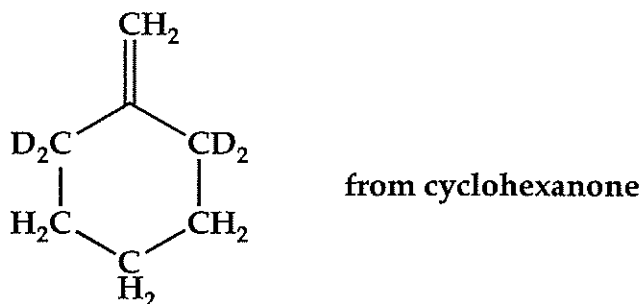
a) What is the mechanism for the reaction? Why does the equilibrium favor B?

b) If ketone C is subjected to the same conditions, no reaction occurs. Why?

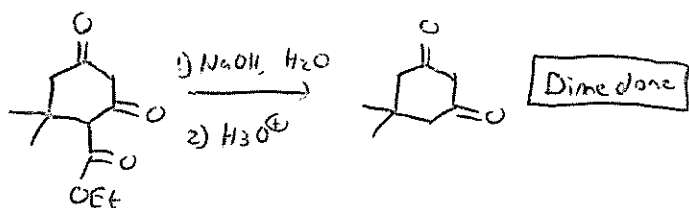
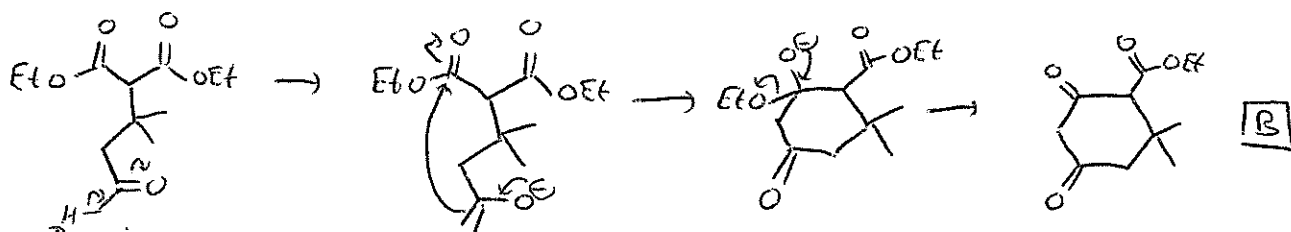
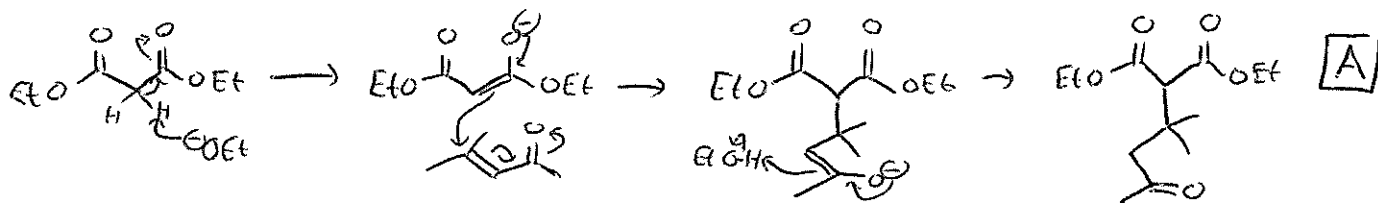
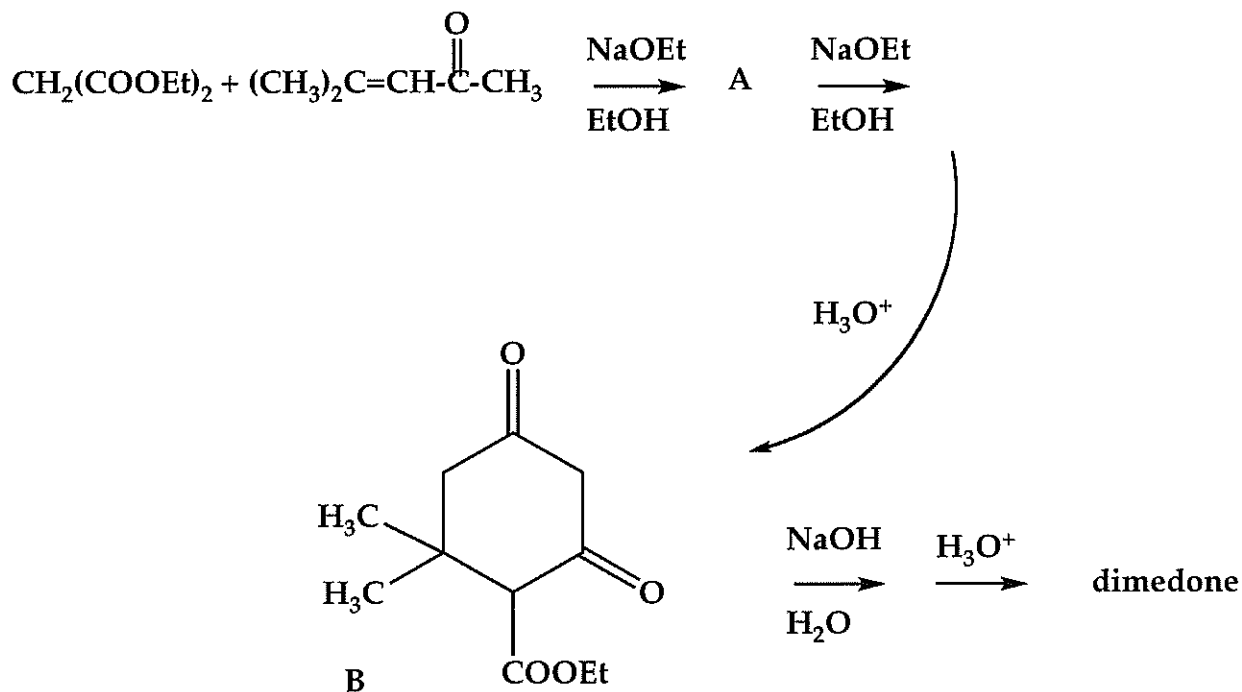


b) There is no  $\alpha$ -H to remove, so equilibration cannot occur.

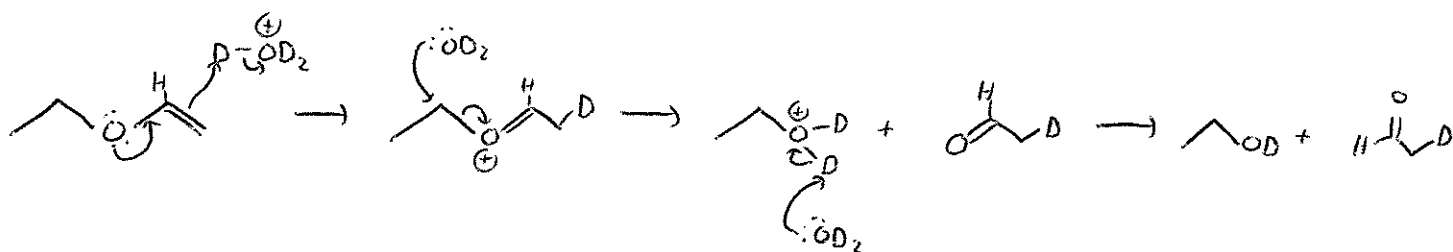
3. (10 pts) Devise a synthesis of the following targets. Use the indicated starting material and any other reagents you require.



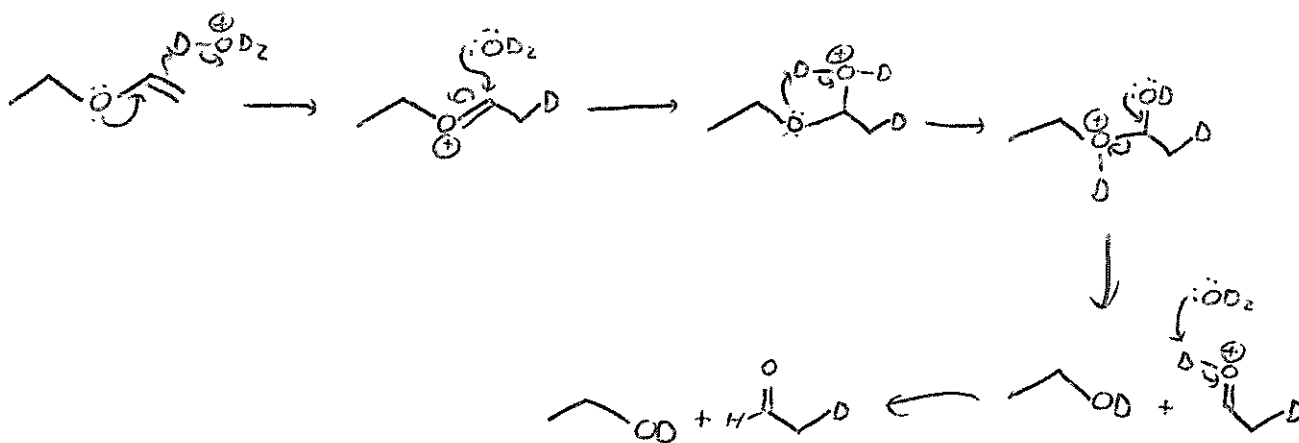
4. (10 pts) Dimedone can be prepared by the following route. What is the structure of A (a Michael-addition product) and dimedone? Provide a mechanism for each step up to compound B.



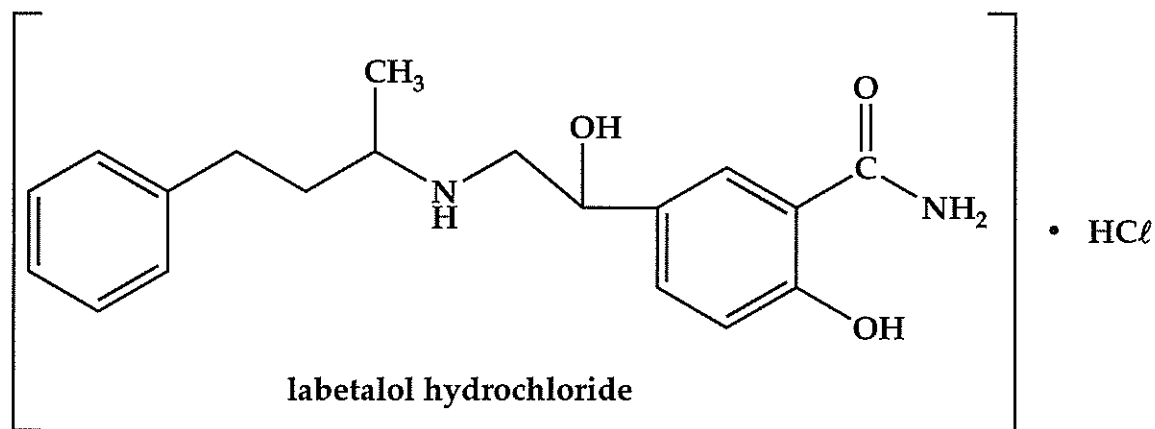
5. (10 pts) Ethyl vinyl ether,  $\text{EtO-CH=CH}_2$ , hydrolyzes in weakly acidic water to  $\text{CH}_3\text{CHO} + \text{EtOH}$ . Under the same conditions,  $\text{Et-O-Et}$  does not react. It appears that  $\text{CH}_3\text{CH}_2\text{-O-CH=CH}_2$  reacts  $10^{13}$  times as fast as  $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$ . This suggests that  $\text{EtO-CH=CH}_2$  reacts by an unusual mechanism. When the hydrolysis is carried out in  $\text{D}_2\text{O/D}_3\text{O}^+$ , one of the reaction products is  $\text{CDH}_2\text{CHO}$ . What is the mechanism of hydrolysis of  $\text{CH}_3\text{CH}_2\text{-O-CH=CH}_2$ ?



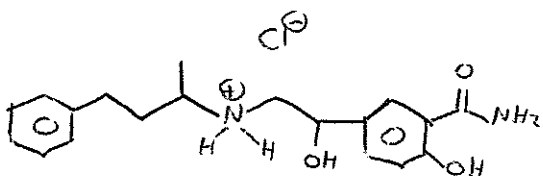
OR



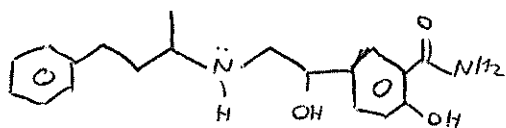
6. (10 pts) A pharmaceutical called labetalol is used to control blood pressure. It is sold as a chloride salt with the following structure.



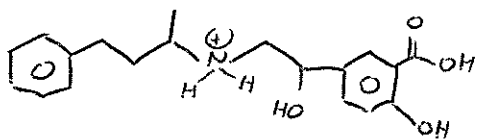
a) What is the exact structure of the chloride salt?



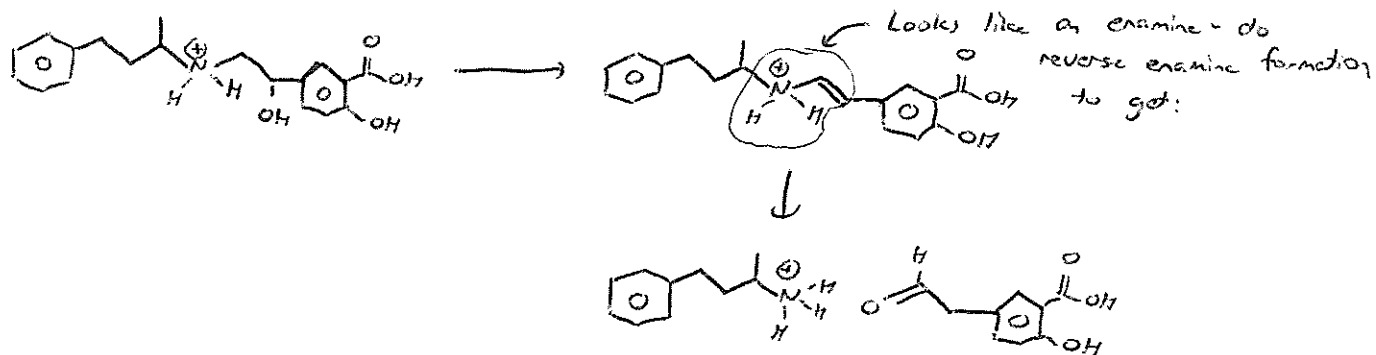
b) What happens to labetalol•HCl when it treated with 1 equivalent of NaOH at room temperature?



c) What are the products formed when labetalol is treated with 6 M aqueous HCl and heated?



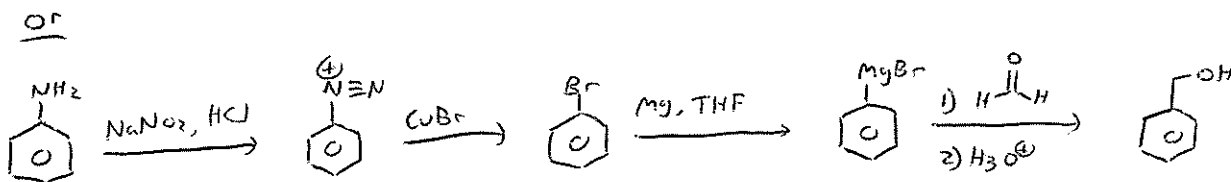
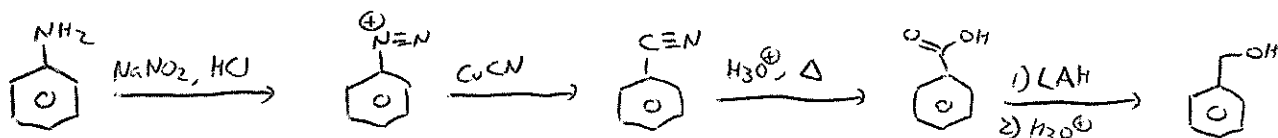
(Depending on conditions, can also show further rxns; not required though.)



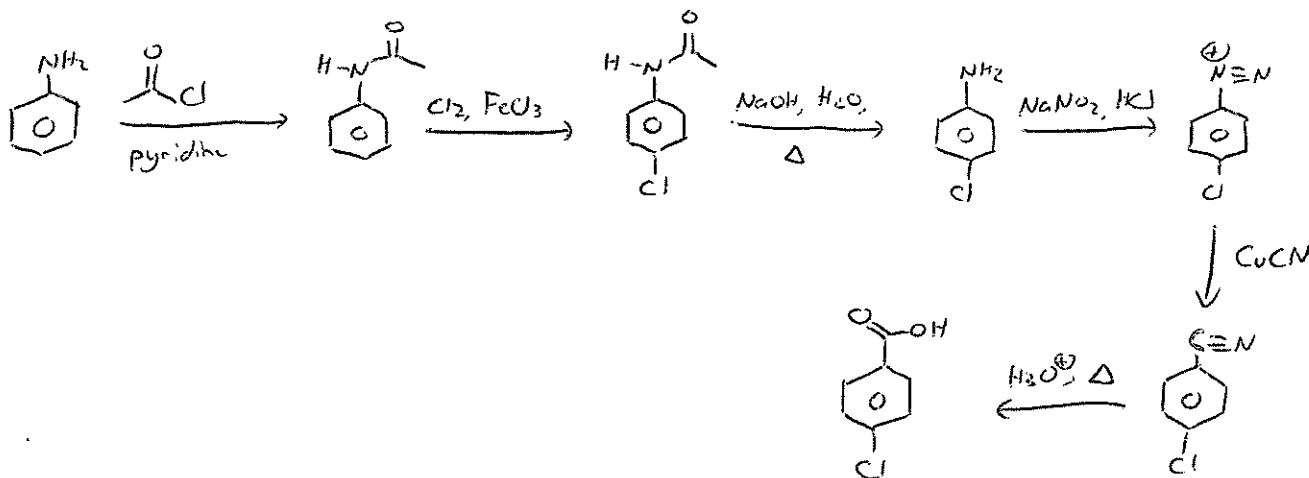


7. (10 pts) Outline a sequence of reactions that will convert aniline ( $C_6H_5NH_2$ ) to:

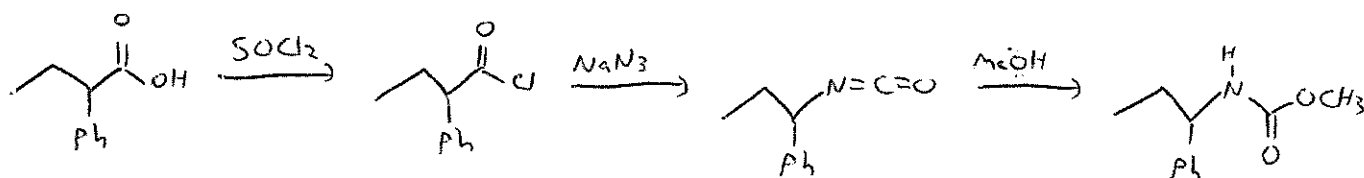
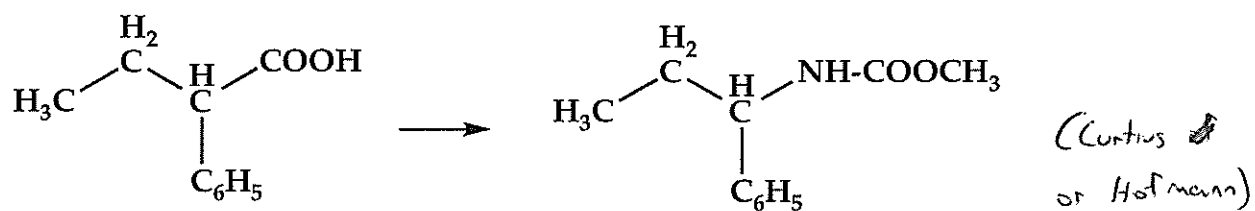
a)  $C_6H_5CH_2OH$

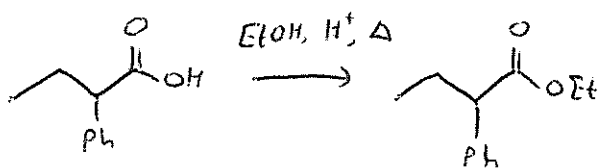
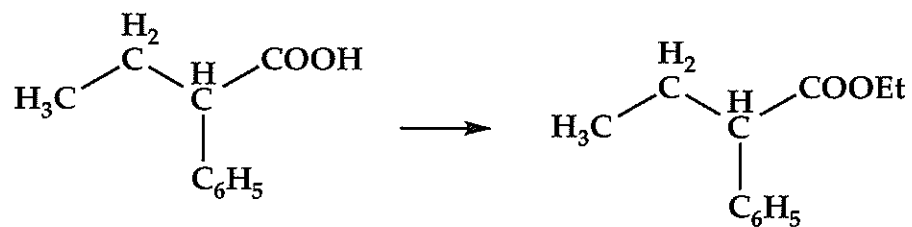


b) *para*-Cl- $C_6H_4$ -COOH *Cont* halogens without protecting  $NH_2$  - multiple Cl's will add.



8. (10 pts) Carry out the following transformations.





9. (10 pts) What is the mechanism for this reaction? This is tricky; the amine adds to the ester to start the reaction.

