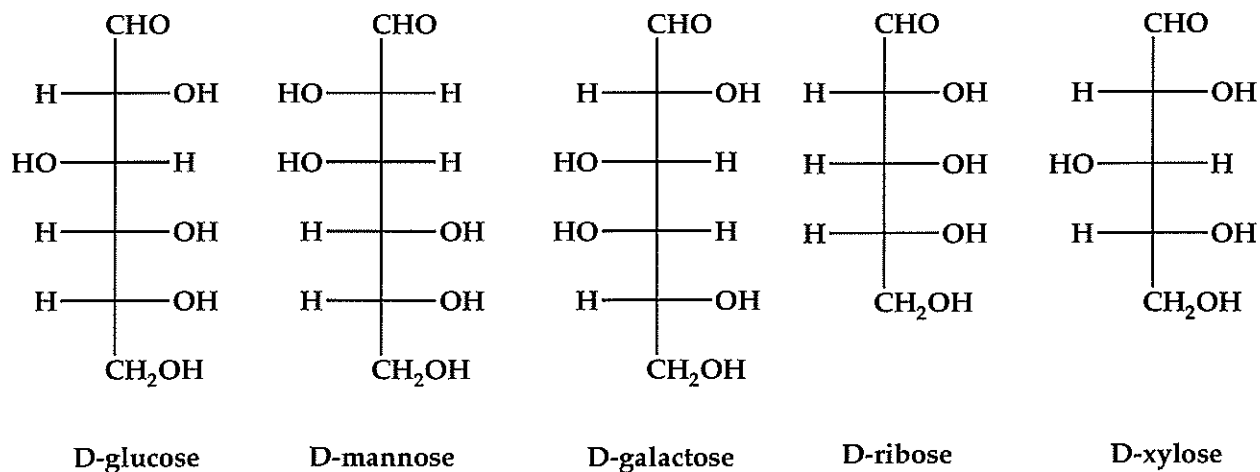


Chemistry 3331-100
Organic Chemistry/Dr. Barney Ellison

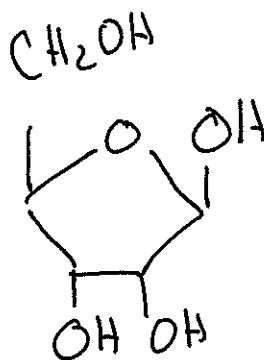
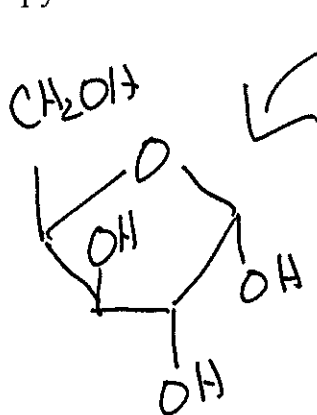
Saturday: May, 2nd @ 07:30 am → 10:00/Final Exam/Chemistry Humanities 1B50

Name: ky (please print)

1. (25 pts) Consider the following sugars.

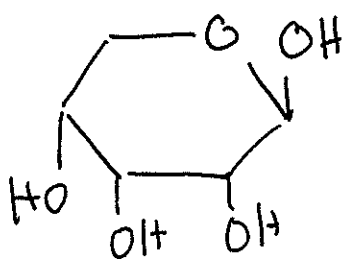


a) Write Haworth formulae for: α -D-xylofuranose, β -D-ribofuranose, β -L-ribofuranose

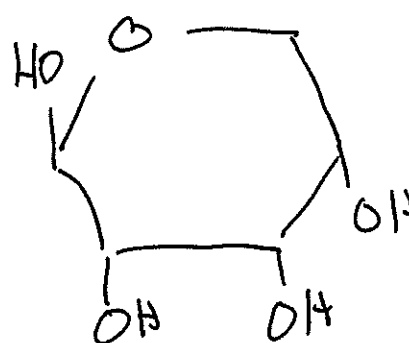


Muonon

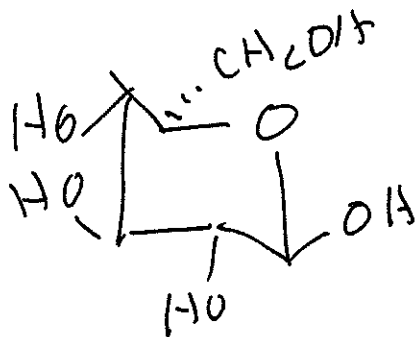
β -L-~~ribo~~ribofuranose



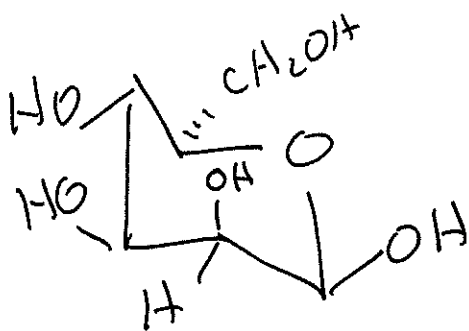
β -D-ribofuranose



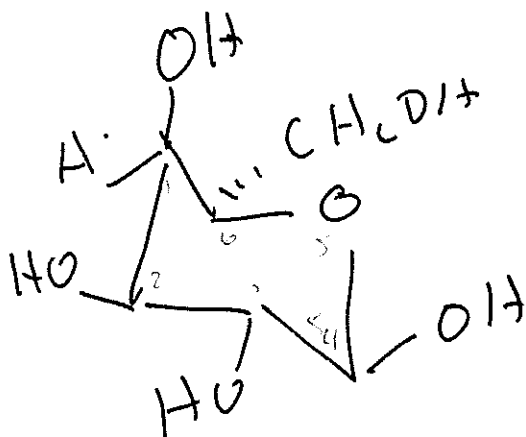
b) Write the chair form for: β -D-mannopyranose, β -L-galactopyranose



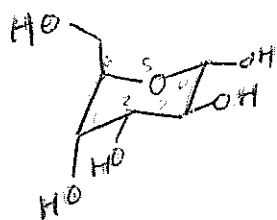
β -D-glucopyranose



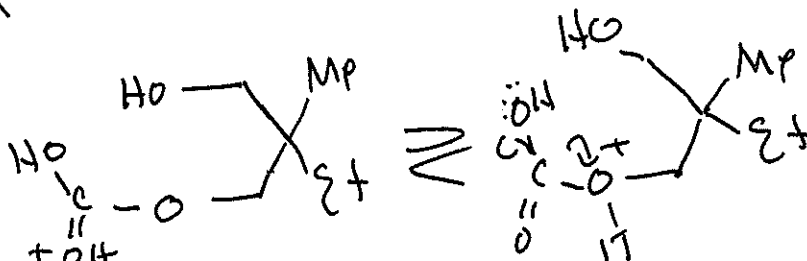
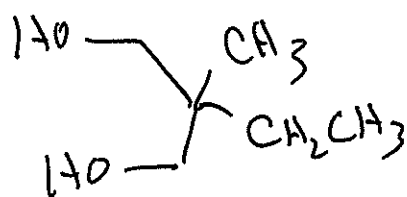
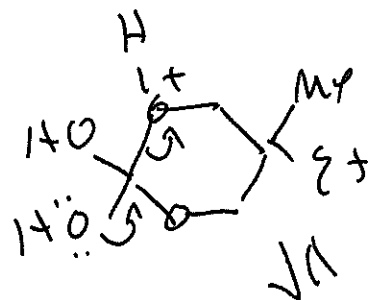
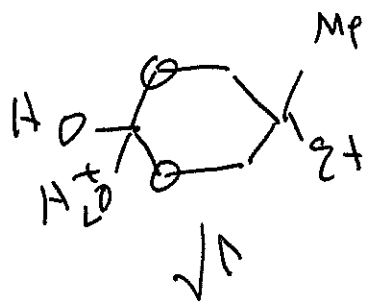
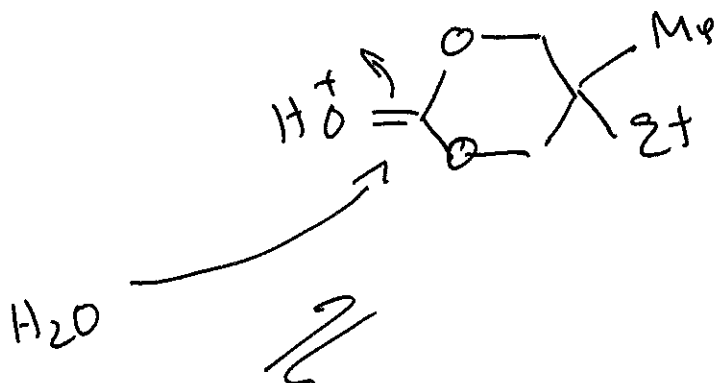
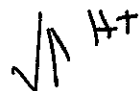
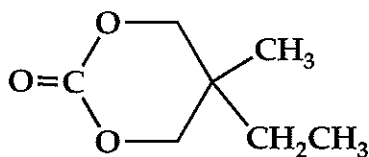
β -D-mannopyranose



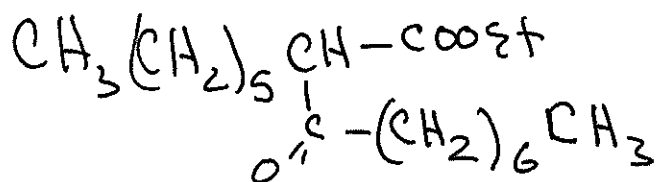
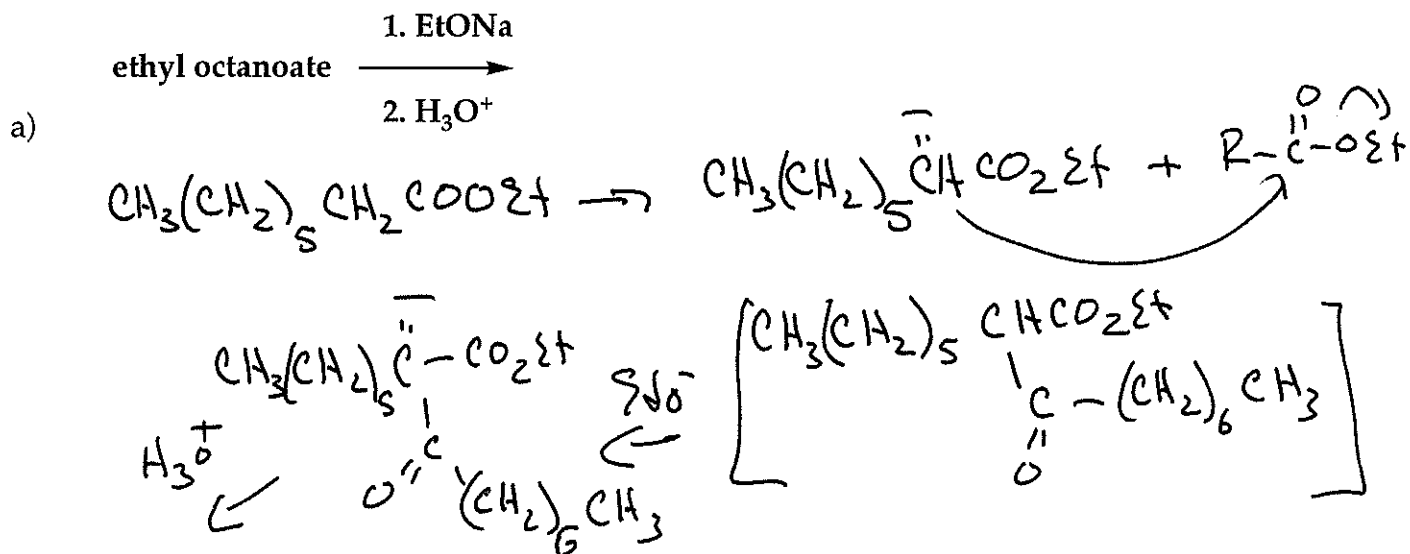
β -D-galactopyranose



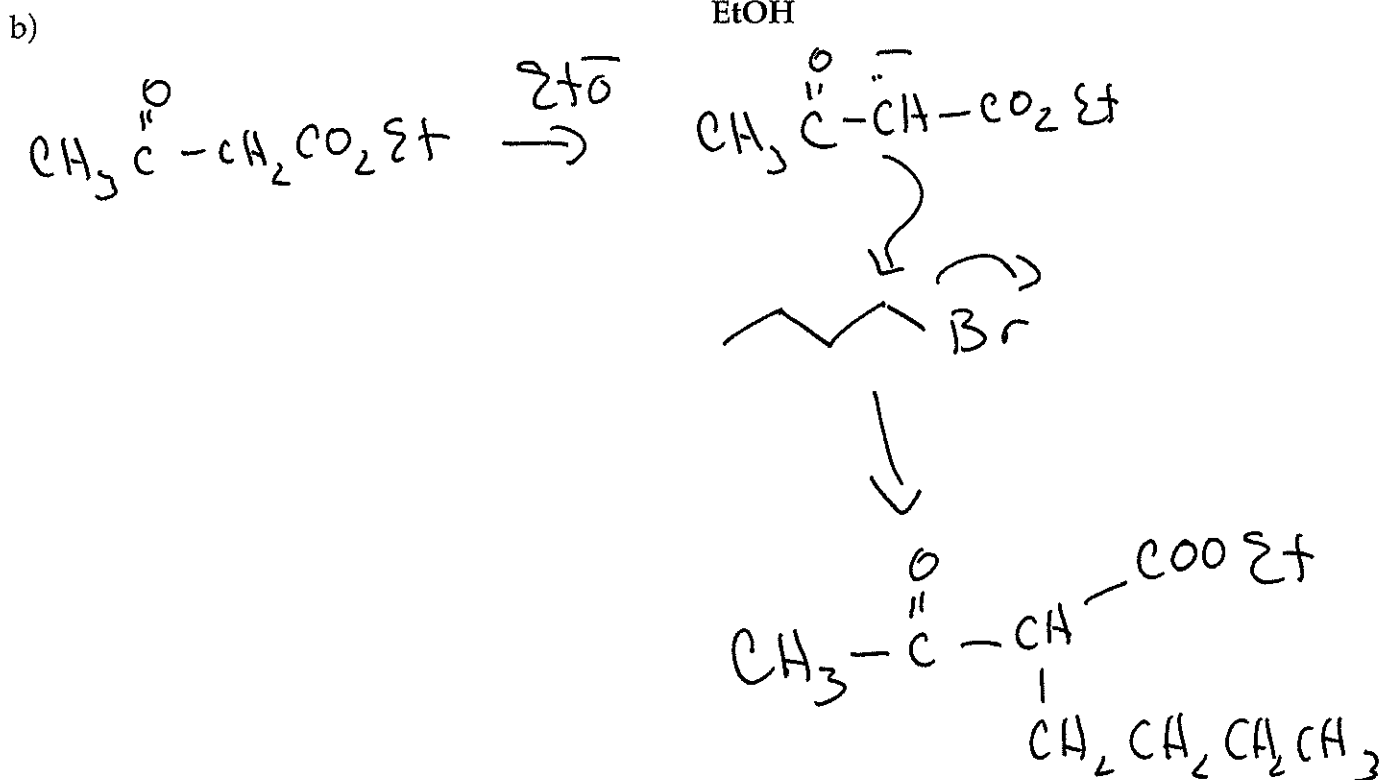
2. (10 pts) On being heated with a dilute solution of H_2SO_4 in water, the following compound decomposes to produce CO_2 . Show a mechanism?

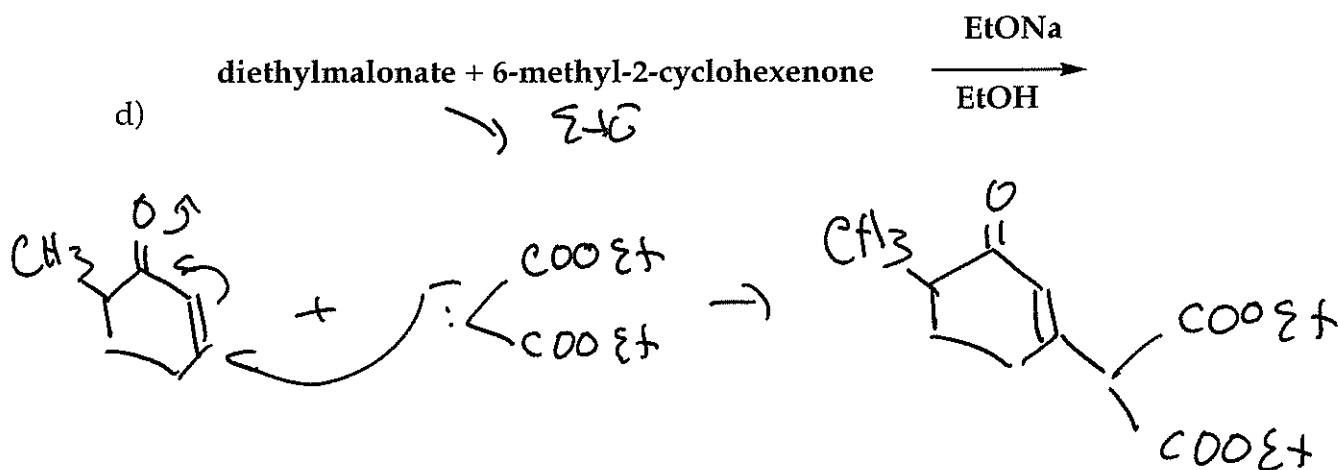
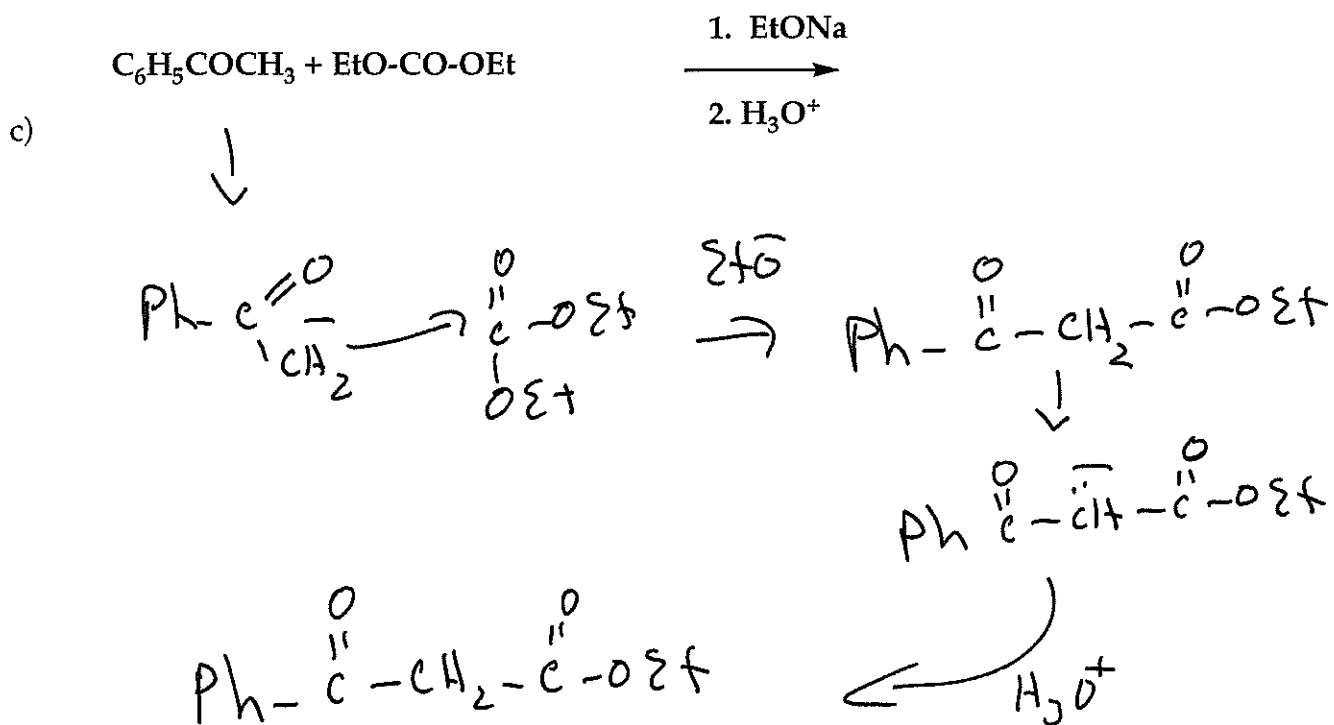


3. (20 pts) Give the structure of the principal organic product in each reaction.



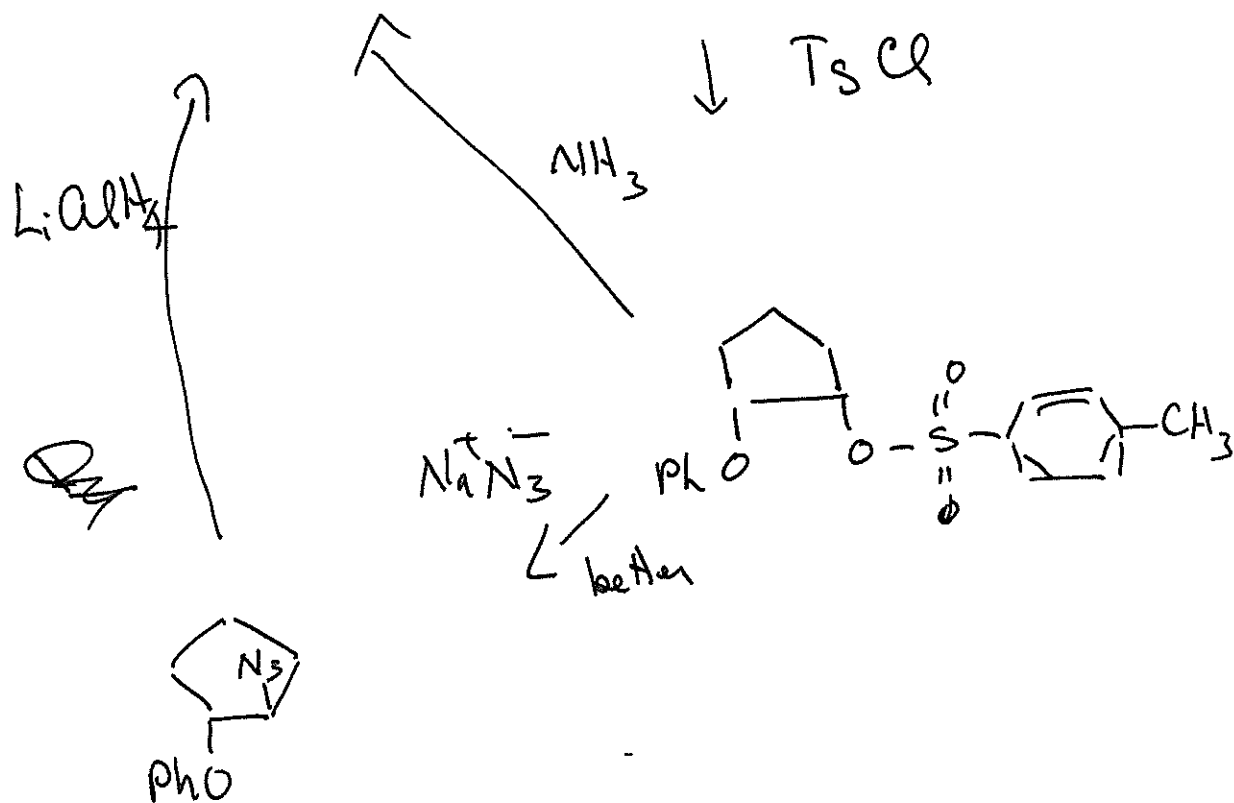
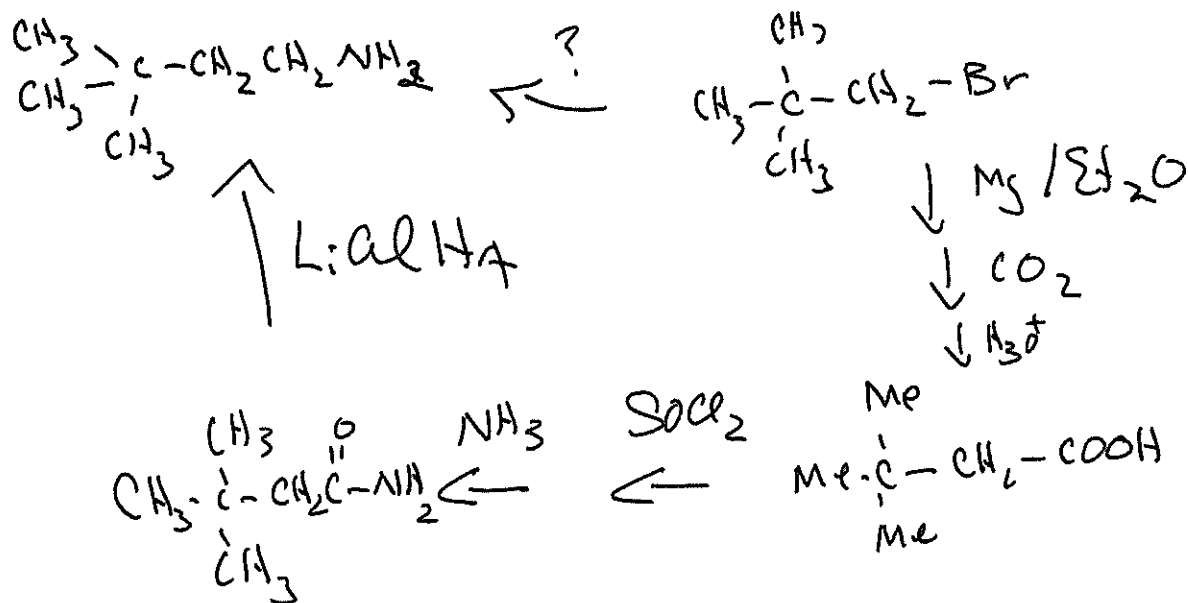
ethyl acetoacetate + 1-bromobutane



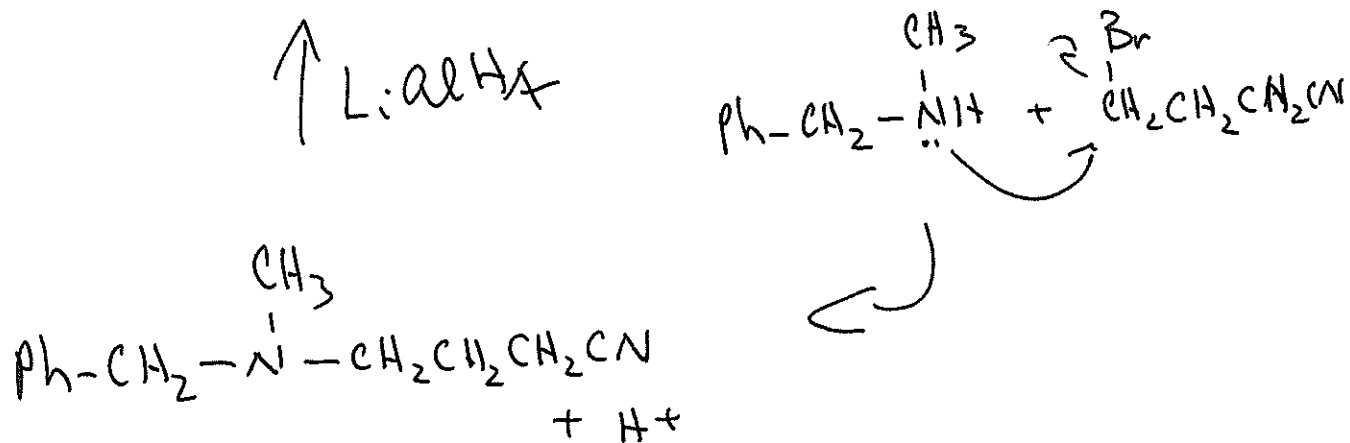


4. (20 pts) Devise efficient syntheses of each of the following targets.

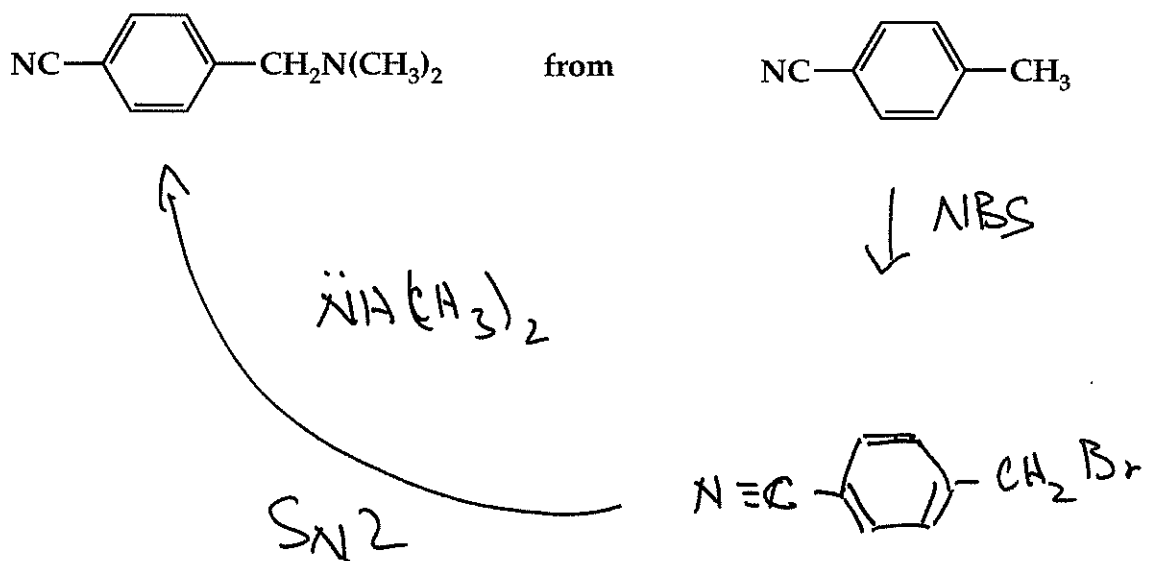
a) 3,3-dimethyl-1-butanamine from 1-bromo-2,2-dimethylpropane



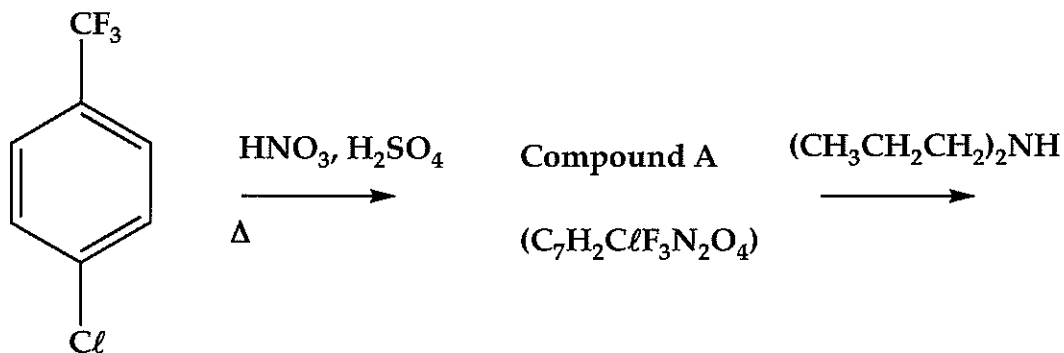
c) $\text{PhCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ from $\text{PhCH}_2\text{NHCH}_3$ and $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CN}$



d)

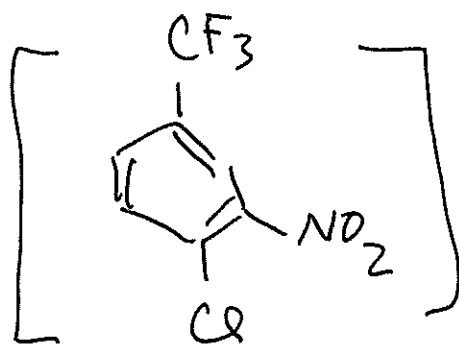


5. (10 pts) The herbicide *trifluralin* is prepared by the following sequence of reactions. What is compound A and give the structure of trifluralin.



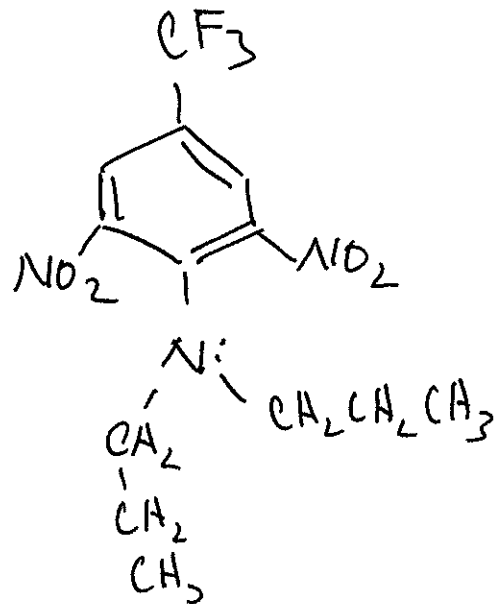
↓ HNO₃

-3 for ortho to CF₃

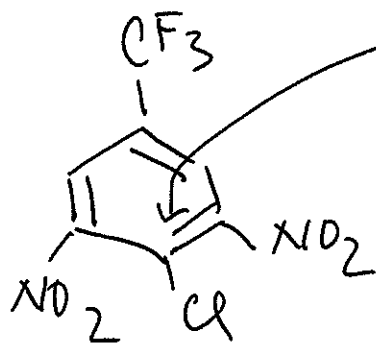


↓ HNO₃

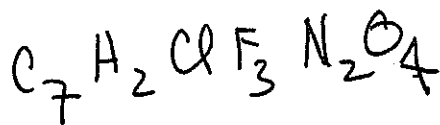
(Ph)₂NH



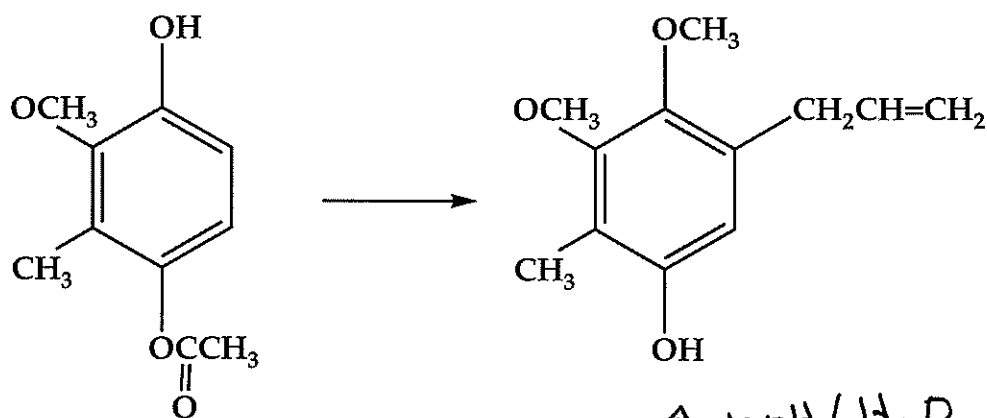
(A)



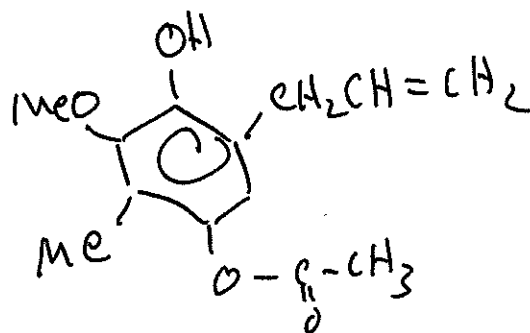
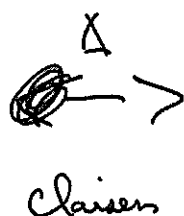
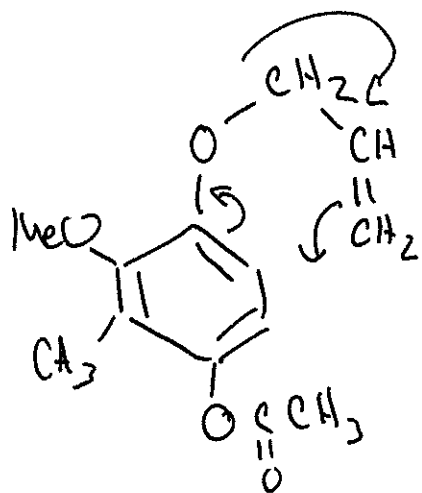
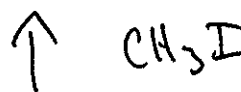
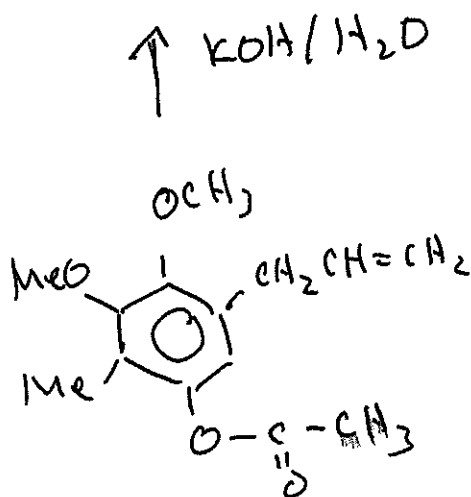
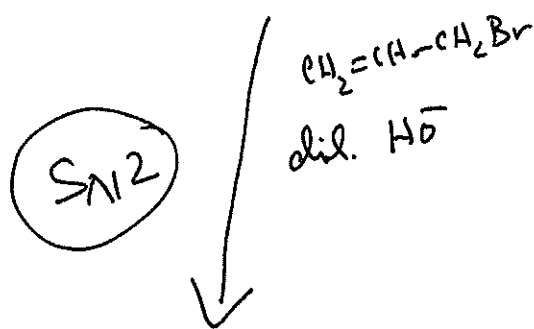
trifluralin



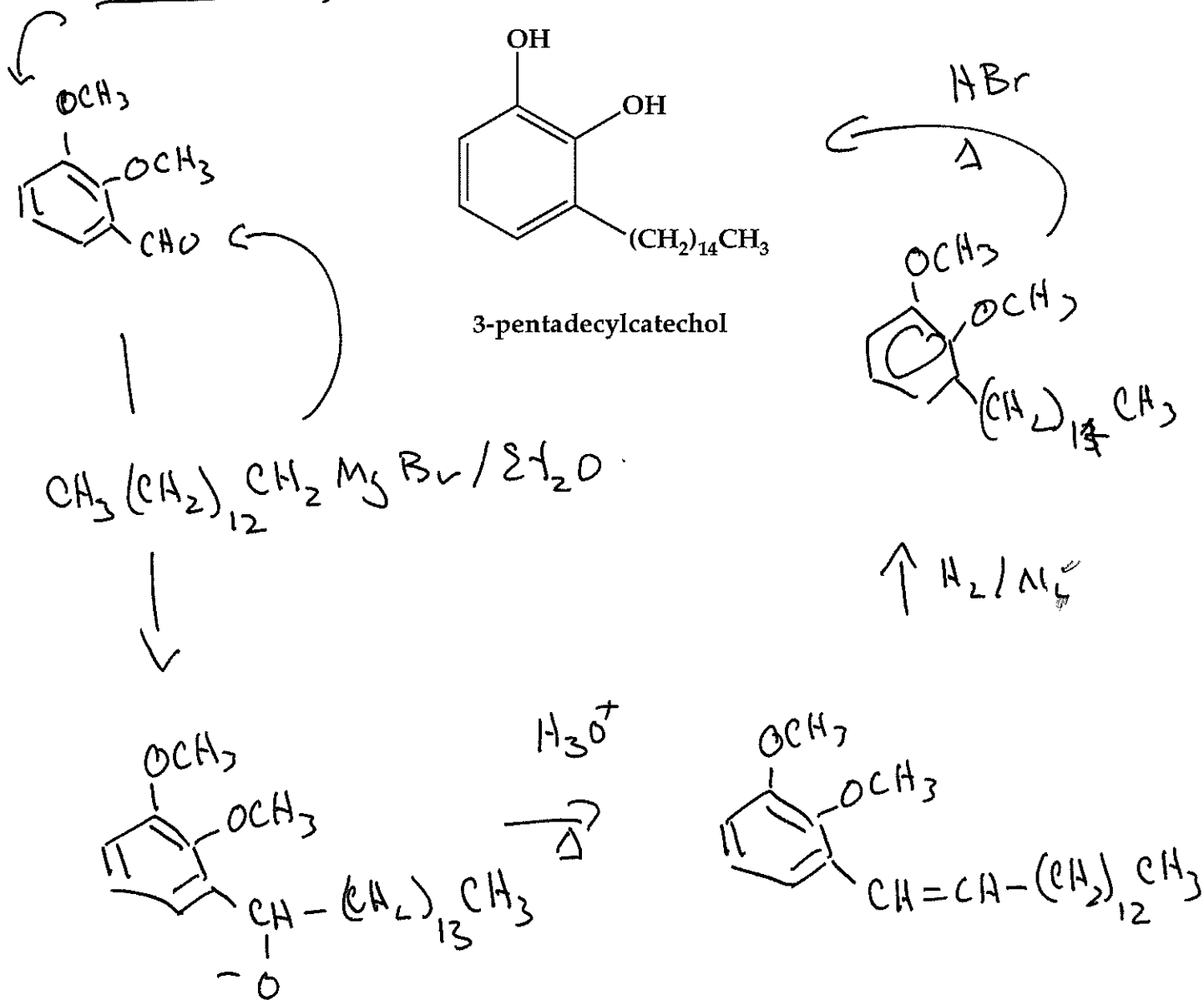
6. (10 pts) Describe a scheme for carrying out the following synthesis. Don't forget about the Claisen rearrangement.



work backwards



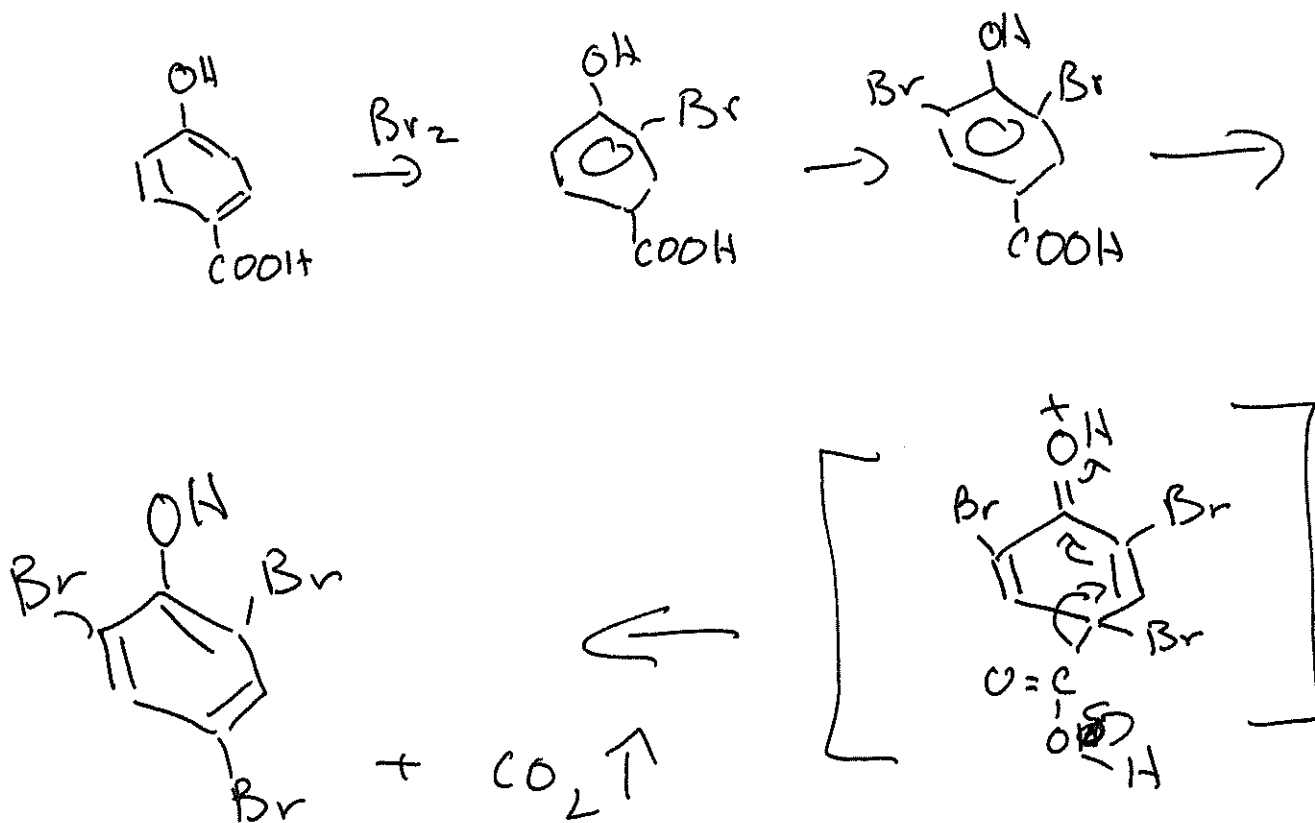
7. (15 pts) Outline a reasonable synthesis of 3-pentadecylcatechol from 2,3-dimethoxybenzaldehyde and any other necessary reagents.



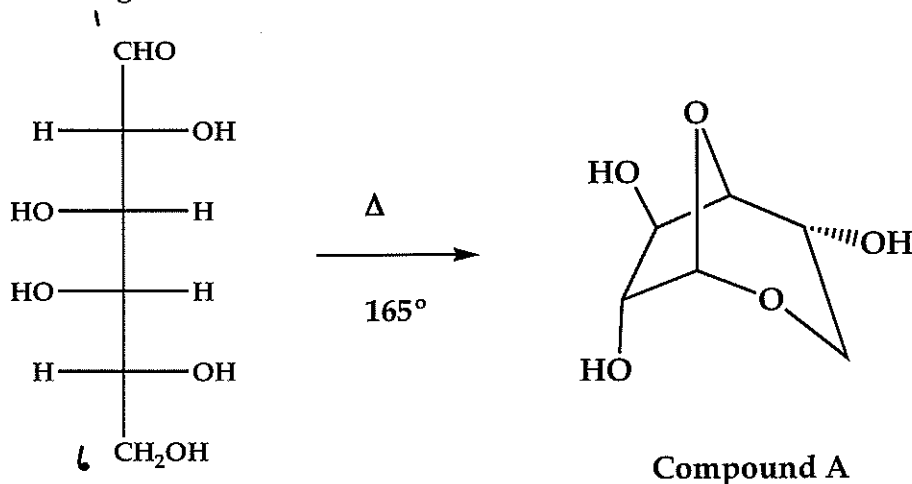
phenol is very activated

- 11 -

8. (10 pts) Treatment of *p*-hydroxybenzoic acid with $\text{Br}_2/\text{H}_2\text{O}$ leads to the evolution of CO_2 and the formation of 2,4,6-tribromophenol. Explain.



9. (10 pts) When D-galactose is heated to 165°, a small amount of A was isolated.



D-galactose

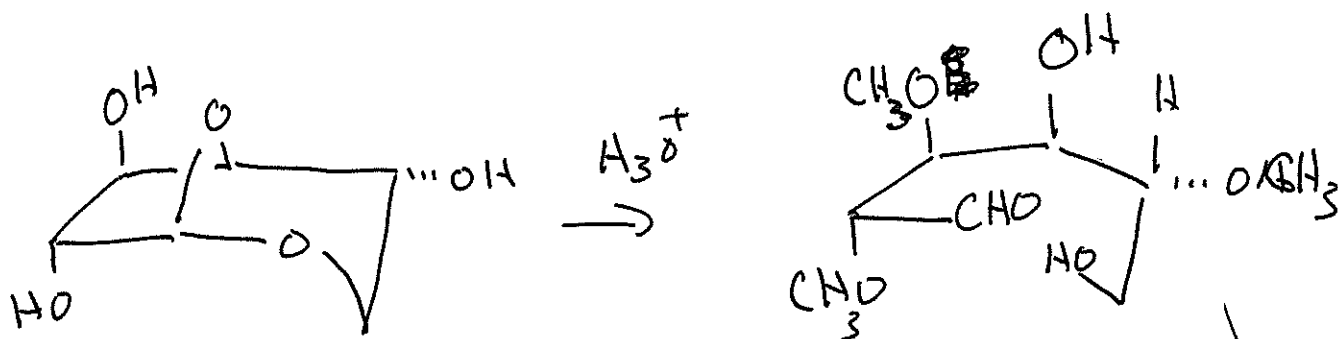
Compound A

Compound A was methylated by $\text{CH}_3\text{I}/\text{AgO}$ and then hydrolyzed to give a trimethyl ether of galactose.

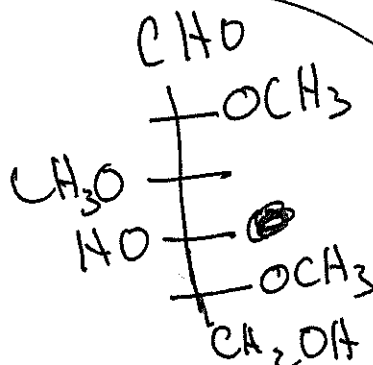
a) How many different trimethyl ethers can be formed from galactose?

(154), (653), (652), (643), (642), (543), (542), (432),
 (532),
 (632)
 10 total

b) Which trimethyl ether is compound A converted to?

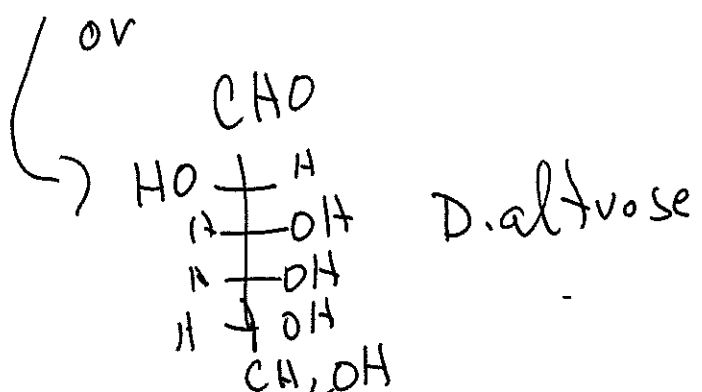
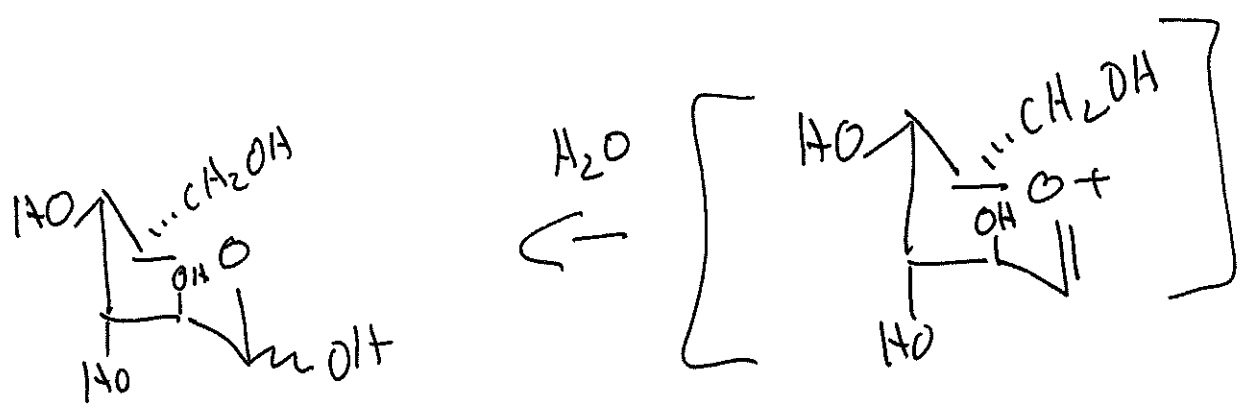
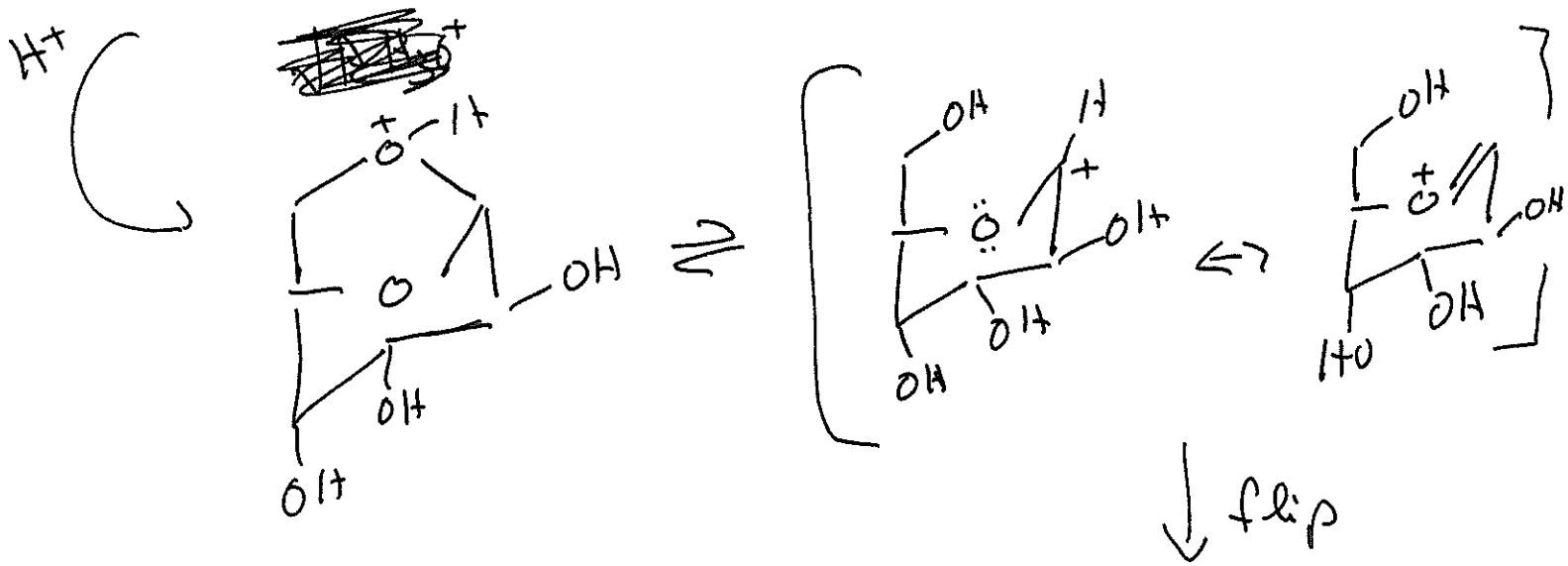
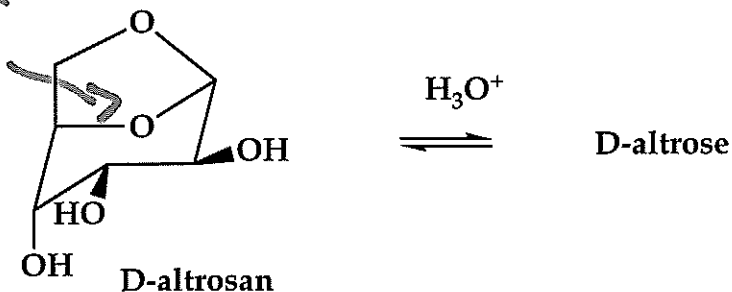


2,3,5 trimethyl galactose

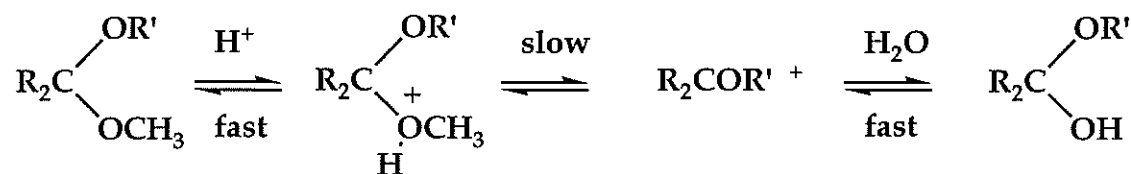


10. (10 pts) D-Altrosan is converted to D-altrose by dilute aqueous acid. Suggest a reasonable mechanism.

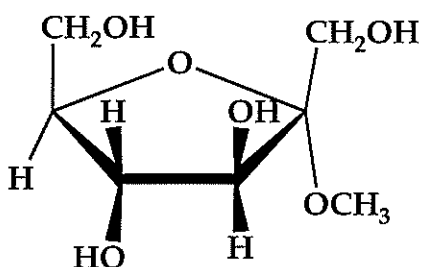
original typo



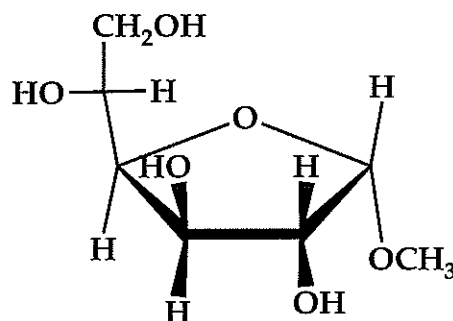
11. (10 pts) Recall the mechanism for acid-catalyzed acetal hydrolysis.



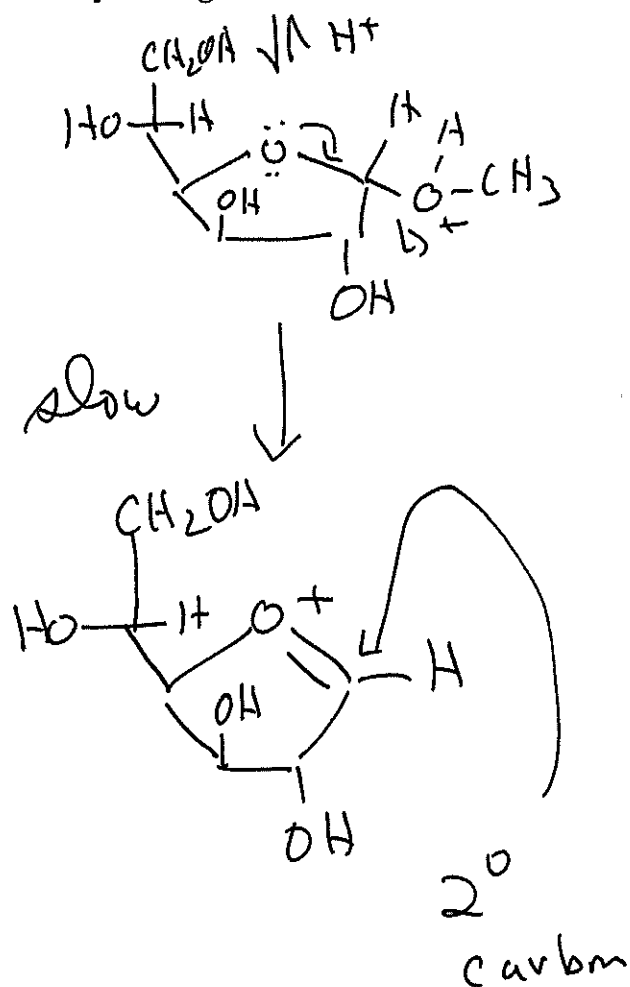
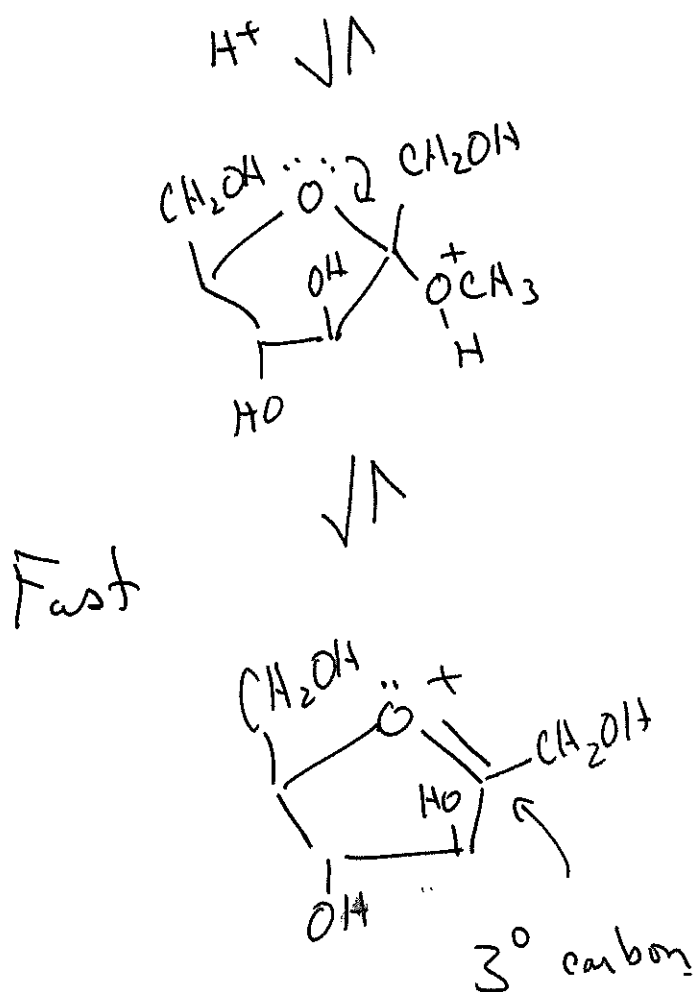
a) Methyl α -D-fructofuranoside undergoes acid-catalyzed hydrolysis 10^5 faster than methyl α -D-glucufuranoside. Why?



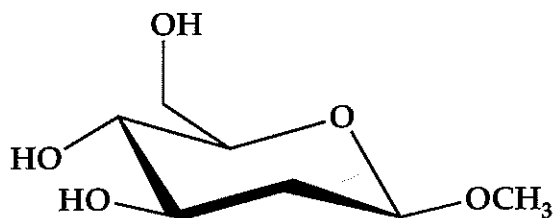
methyl α -D-fructofuranoside



methyl α -D-glucufuranoside



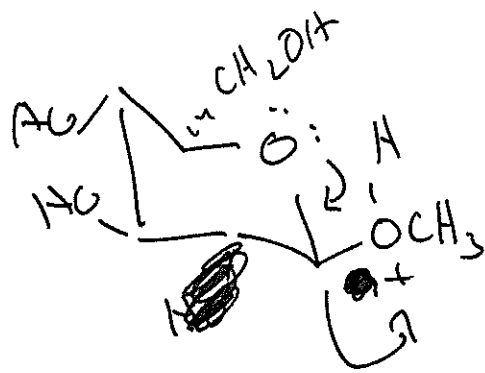
b) The β -methyl glucopyranoside of 2-deoxy-D-glucose undergoes hydrolysis thousands of times faster than that of the β -methyl glucopyranoside of glucose itself. Why?



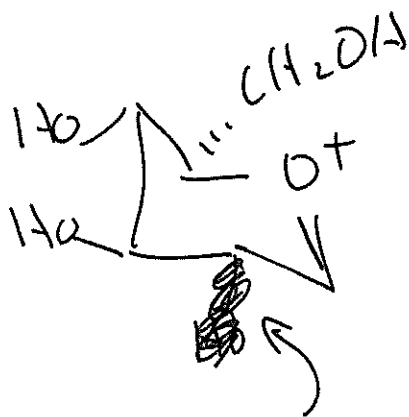
methyl β -D-2-deoxyglucopyranoside

faster

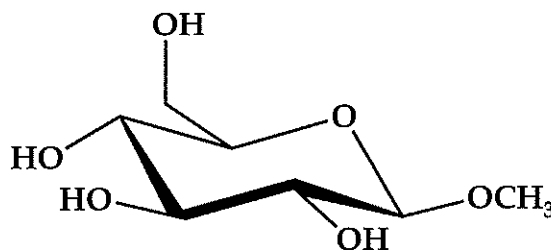
\checkmark H^+



\downarrow



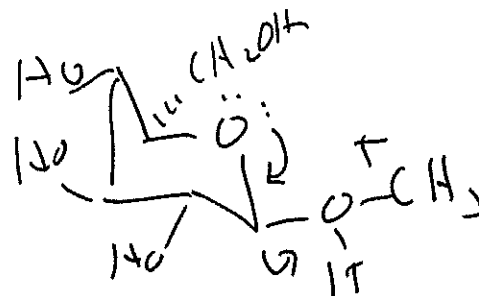
no electron withdrawing -OH group



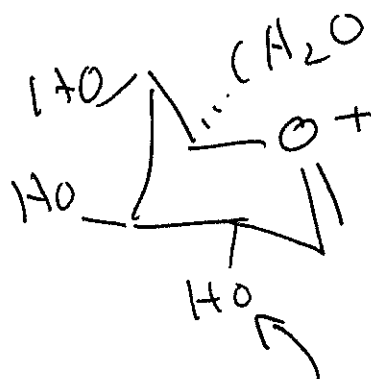
methyl β -D-glucopyranoside

\downarrow

slower



\downarrow



electron withdrawing group destabilizes cation