

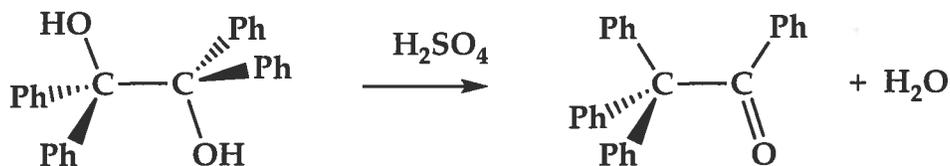
Chemistry 3331-100

Organic Chemistry / Dr. Barney Ellison

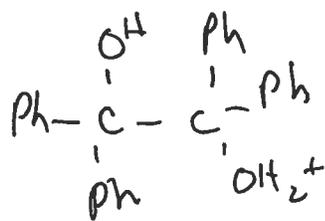
Thursday: October 23st @ 7:00pm → 9:00 / 2nd Exam / Hale Science 270

Name: Key (please print)

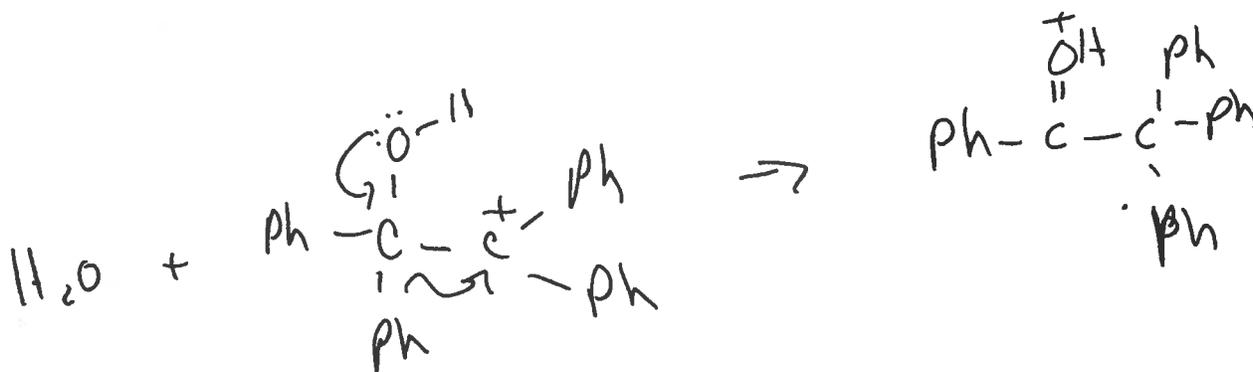
1. (10 pts) What is the mechanism for the following rearrangement?



↓ H⁺



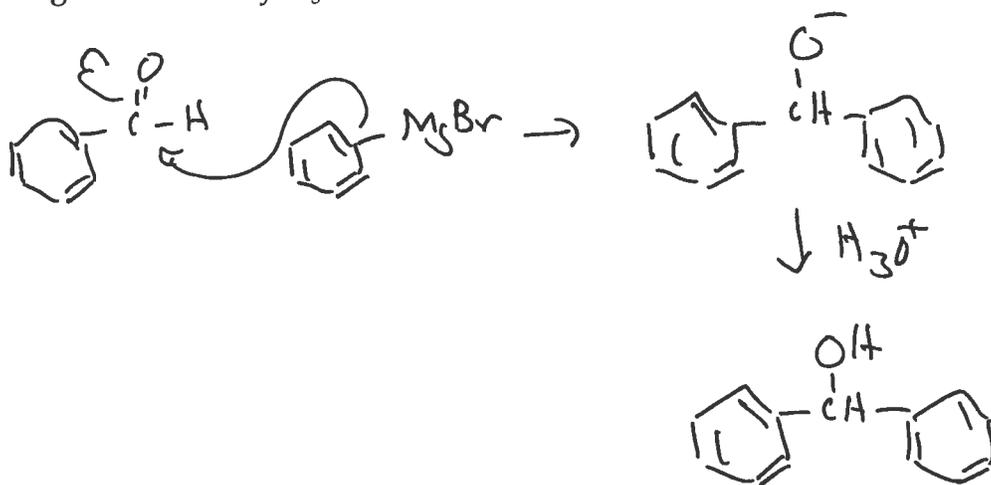
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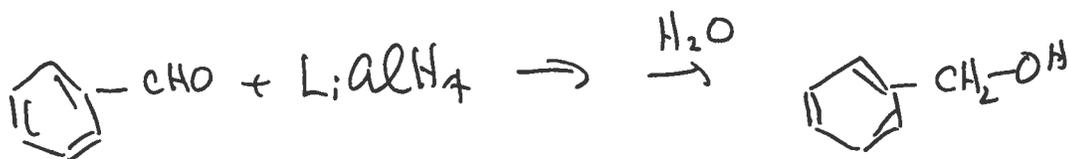
↑ H⁺

2. (15 pts) Give the expected products when benzaldehyde (C_6H_5CHO) reacts with the following:

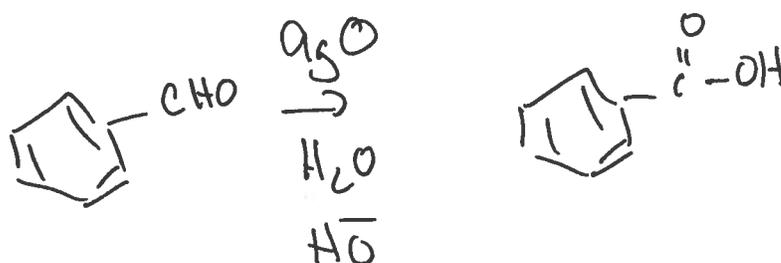
a) $PhMgBr$ followed by H_3O^+



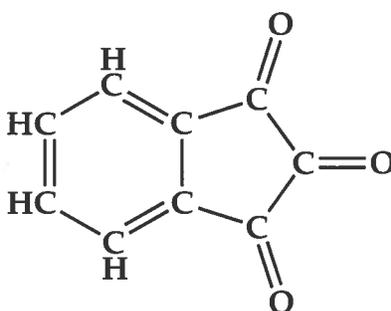
b) $LiAlH_4$ followed by H_3O^+



c) $Ag_2O/NaOH/H_2O$

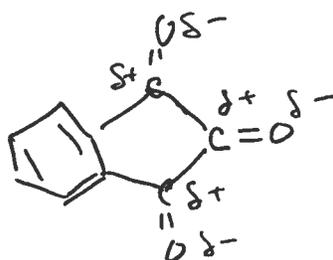


3. (10 pts) The compound ninhydrin exists as a hydrate. Why is a tri-carbonyl compound so unstable? Which carbonyl group will be hydrated? What is the structure of the hydrate?

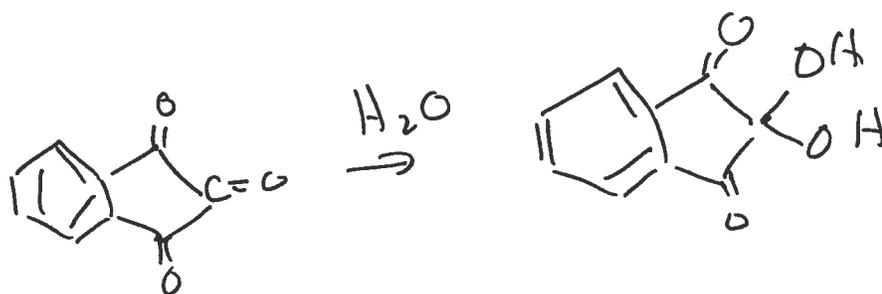


ninhydrin

a) Each carbonyl group is strong dipole & they all repel each other

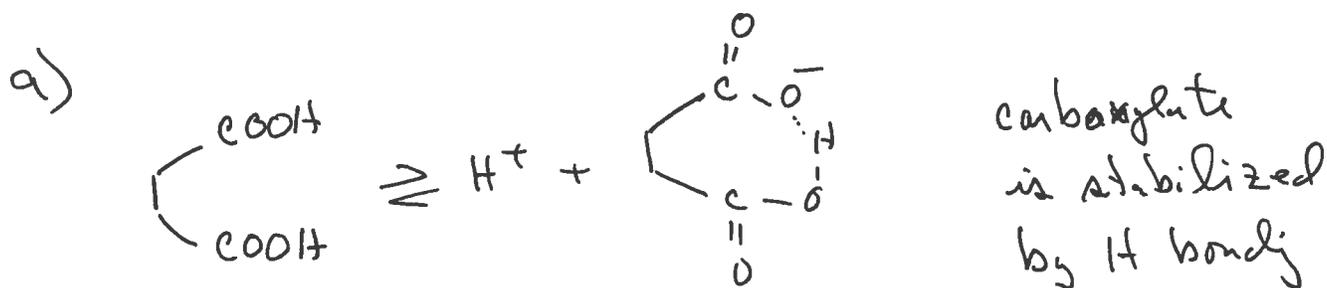


b)

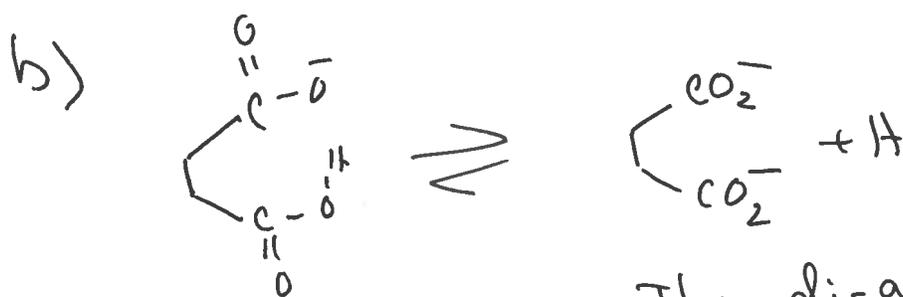


4. (10 pts) The $pK_a(\text{CH}_3\text{COOH})$ is 4.76. Succinic acid, $\text{HOOC-CH}_2\text{CH}_2\text{-COOH}$, is a diacid. It is measured that the 1st $pK_a(\text{succinic acid})$ is 4.21 and the 2nd $pK_a(\text{succinic acid})$ is 5.64.

Why is the 1st $pK_a(\text{succinic acid}) < pK_a(\text{CH}_3\text{COOH})$ and the 2nd $pK_a(\text{succinic acid}) > pK_a(\text{CH}_3\text{COOH})$?



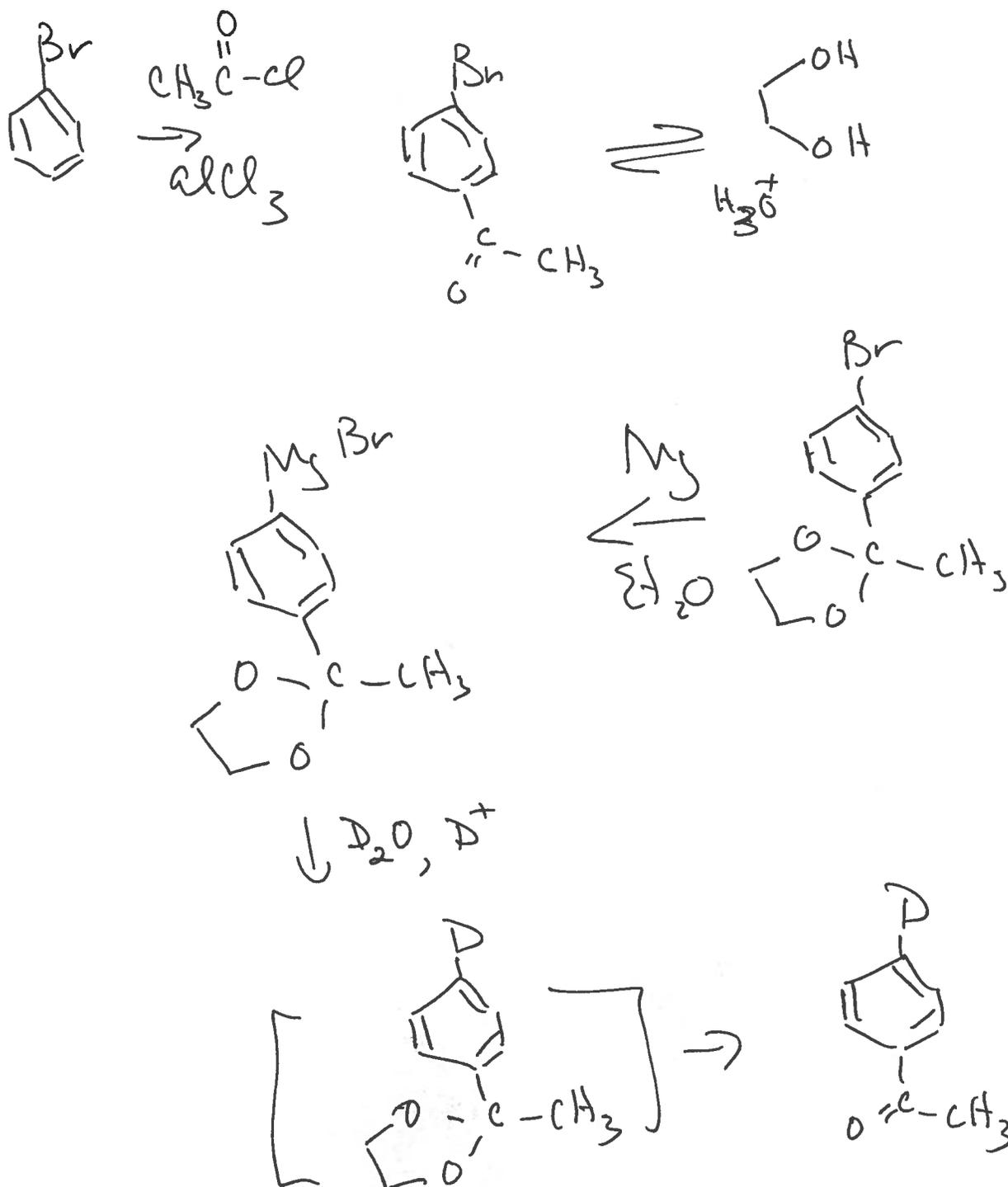
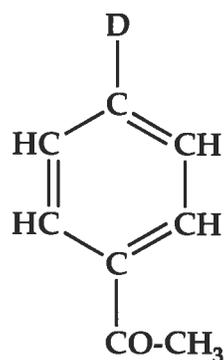
~~stabilization~~ Stabilization of the anion makes the diacid a stronger acid than CH_3COOH
 pK_a is less than 4.76



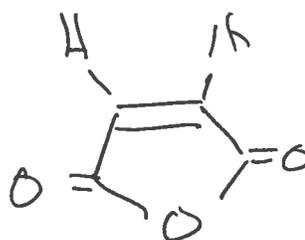
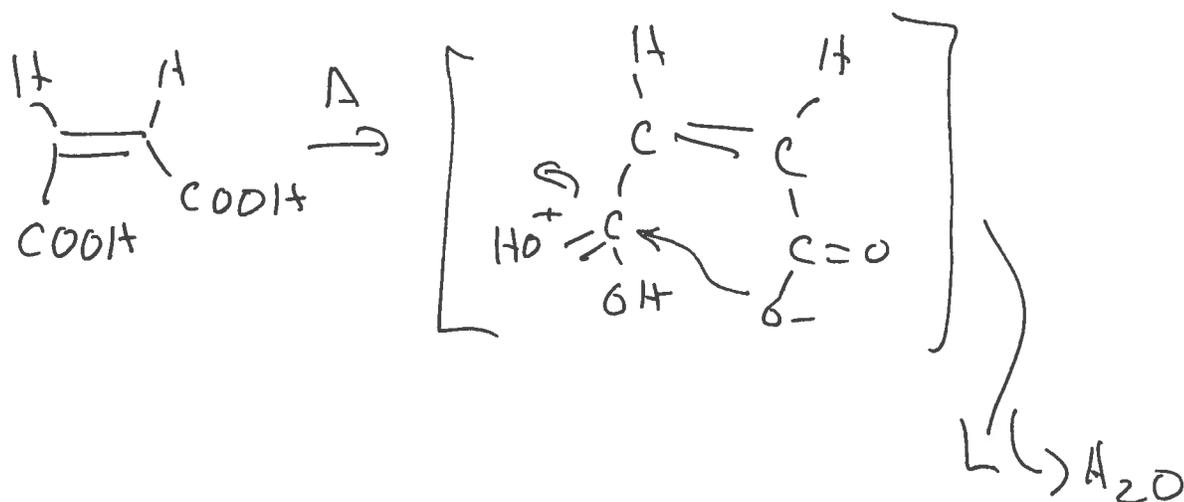
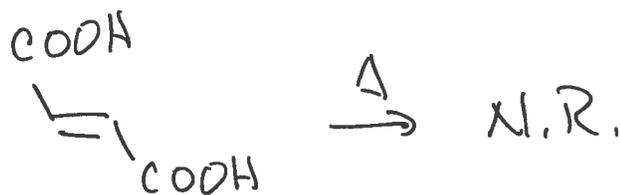
The di-anion is destabilized by 2 charges. So this is a weaker acid than CH_3COOH

$pK_a > 4.76$

5. (10 pts) Outline a synthesis of the deuterated ketone starting with bromobenzene.

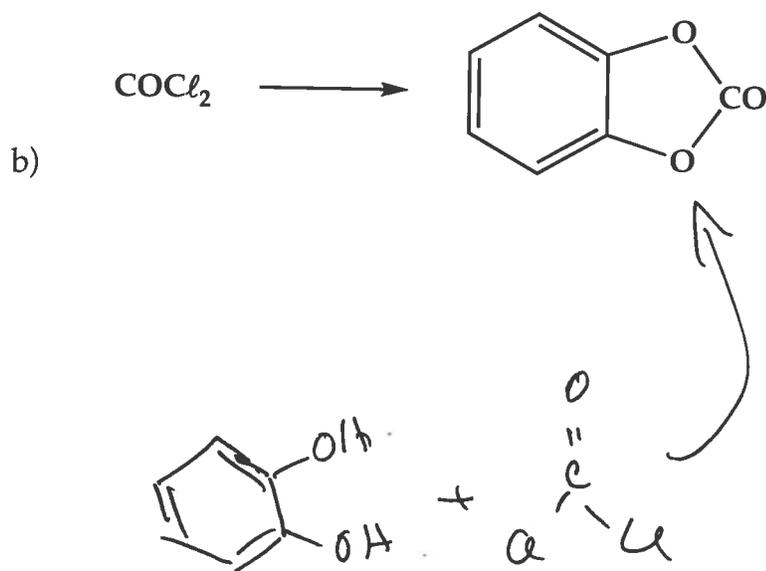
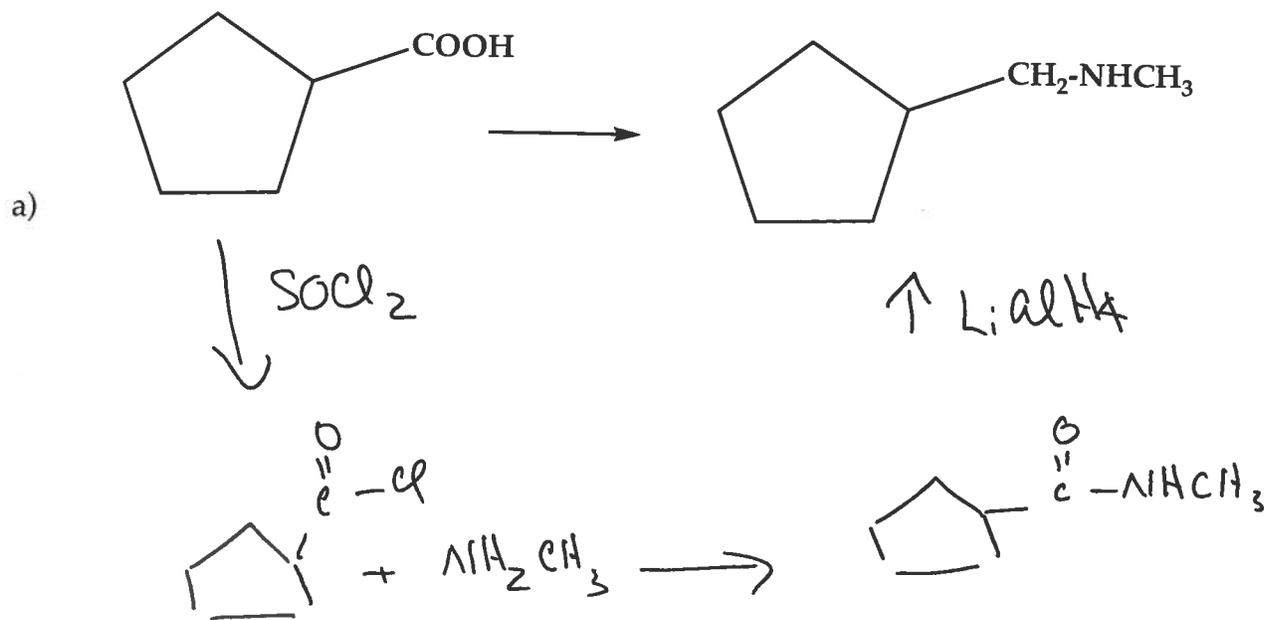


6. (10 pts) Fumaric acid, *trans*-HOOC-CH=CH-COOH, and maleic acid, *cis*-HOOC-CH=CH-COOH, are E, Z isomers. One forms a cyclic anhydride upon heating and the other does not. Which one forms the cyclic anhydride? Why?

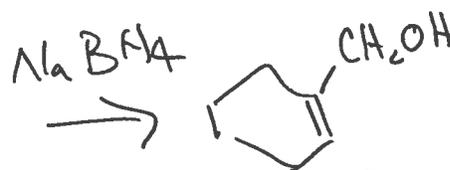
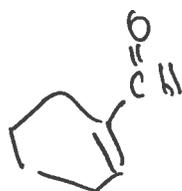
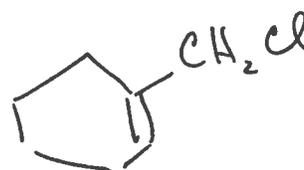
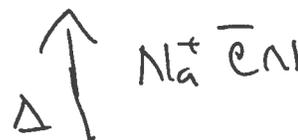
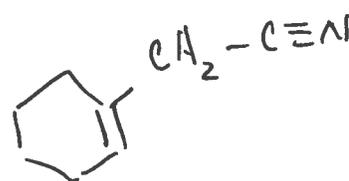
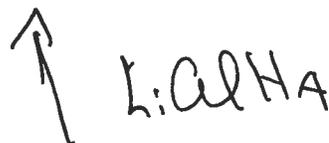
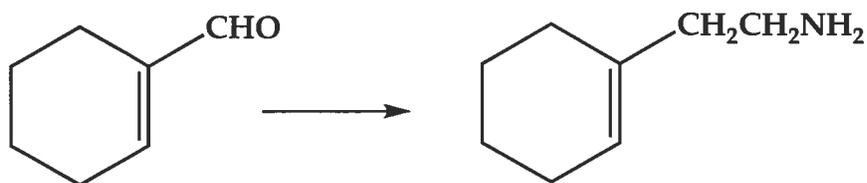


maleic anhydride

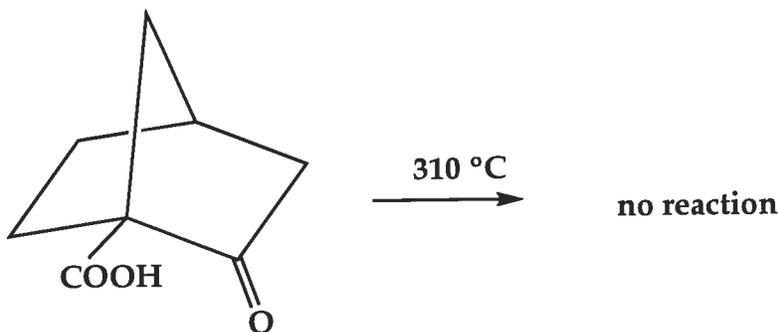
7. (10 pts) Starting with the indicated reagent, outline a synthesis of each of the following compounds



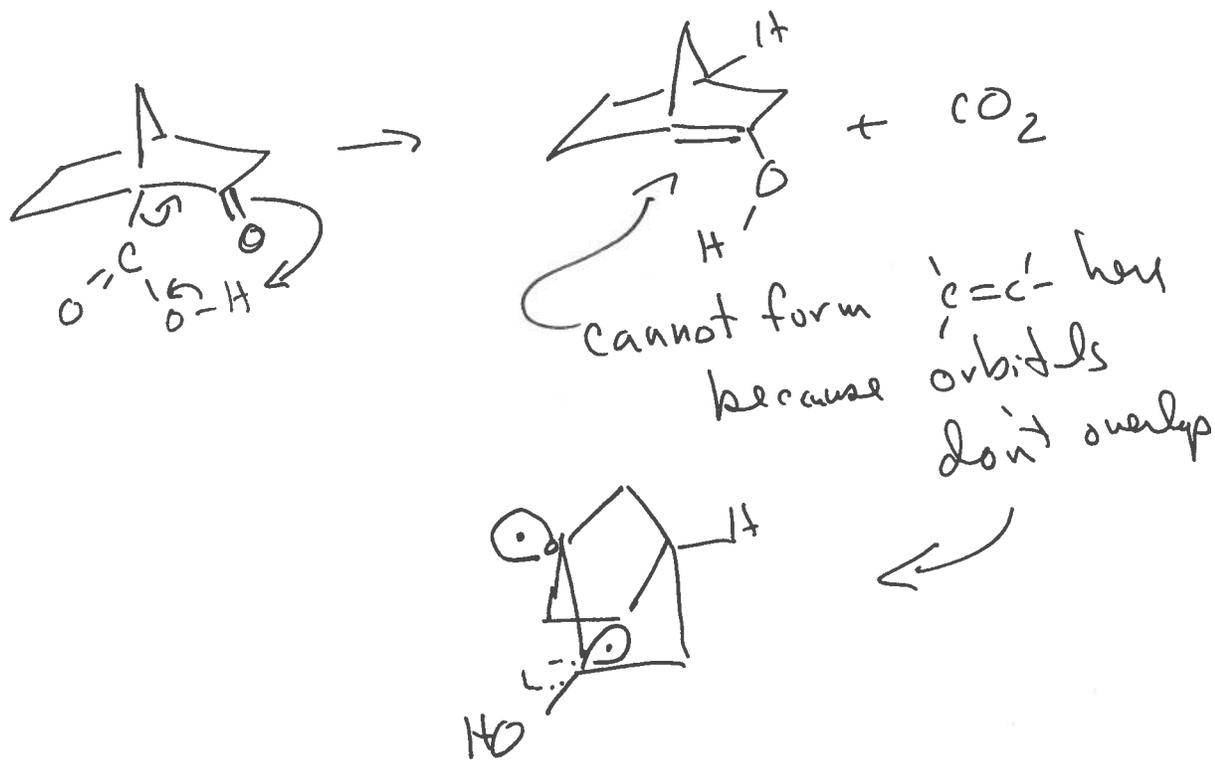
8. (10 pts) Suggest a route to carry out the following synthesis.



9. (10 pts) The following keto-acid is unusual because it cannot be decarboxylated by heating. Why is this bicyclic ketone resistant to decarboxylation?



Decarboxylation of β keto acids goes through enols.



10. (5 pts) What are the two products that result from the following reaction?

