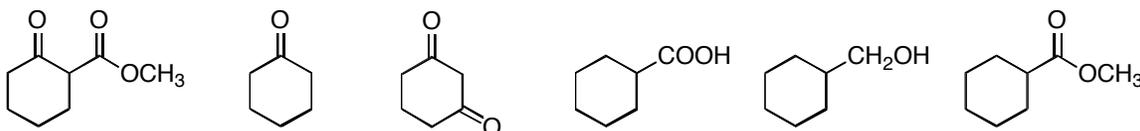


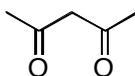
Problem Set #7

Due: November 22, 2006, 12:00 PM

1. For the following compounds circle or draw in the most acidic proton. Rank the following compounds in order of increasing acidity. Circle the molecules that would be more than 99% deprotonated by a solution of sodium ethoxide in ethanol.



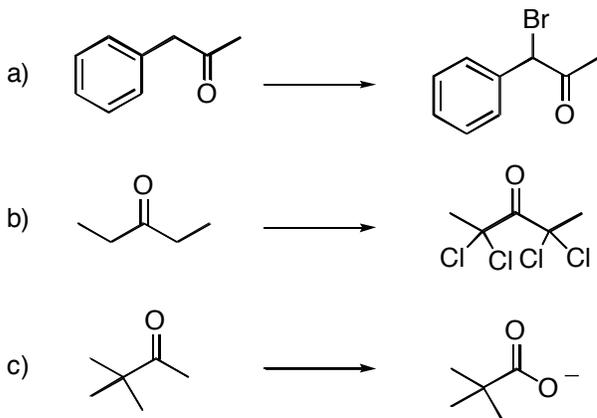
2. Pentane-2,4-dione exists as a tautomeric mixture of 8% keto and 92% enol forms. Draw the stable tautomer and explain its unusual stability.



3. Show that the two following compounds have the same conjugate base. Which compound is more acidic? Explain your reasoning using an argument regarding the relative free energies of the two compounds.

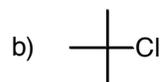


4. Provide the most appropriate reagents to form the given products.

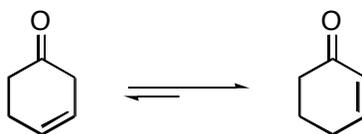


5. Account for the fact that treatment of 1,3-diphenyl-1,3-propanedione with I_2 and NaOH gives a precipitate of iodoform even though it is not a methyl ketone (show the mechanism). Note that besides iodoform, the other product of the reaction (after acidification) is two equivalents of benzoic acid.

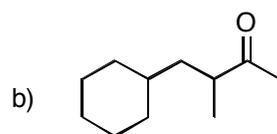
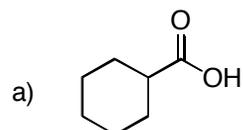
6. Give the product(s) that would be expected on reaction of 3-pentanone with 1 equivalent of LDA, followed by 1 equivalent of:



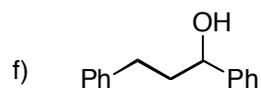
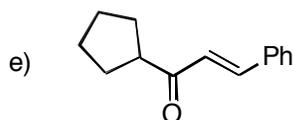
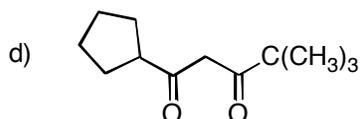
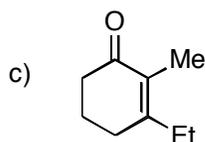
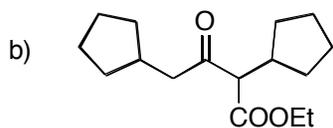
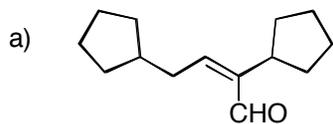
7. In either acid or base, 3-cyclohexenone comes to equilibrium with 2-cyclohexenone. a) Explain why the equilibrium favors the α,β -unsaturated ketone over the β,γ -unsaturated isomer. b) Provide a mechanism for this reaction in aqueous NaOH. c) Provide a mechanism for this reaction in dilute aqueous H_2SO_4 .



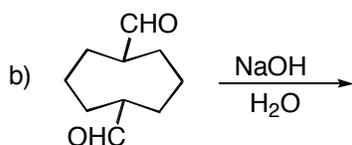
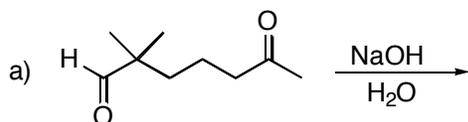
8. Show a synthesis for the following molecules that DOES NOT involve LDA. Use malonic or acetoacetic esters.



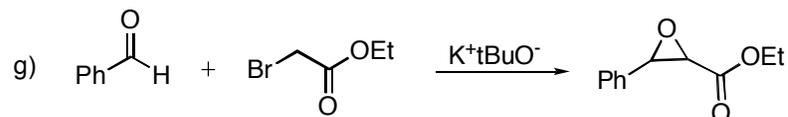
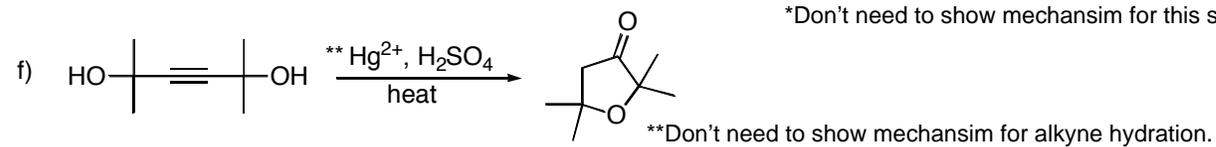
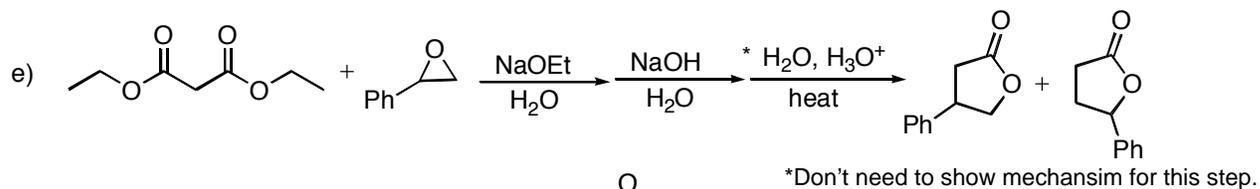
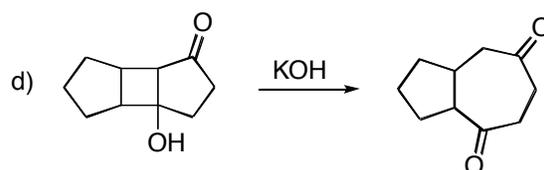
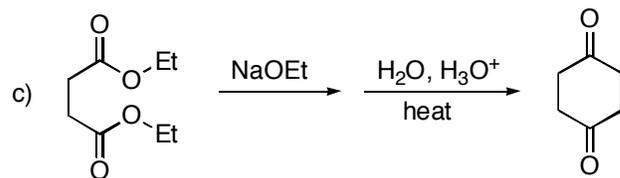
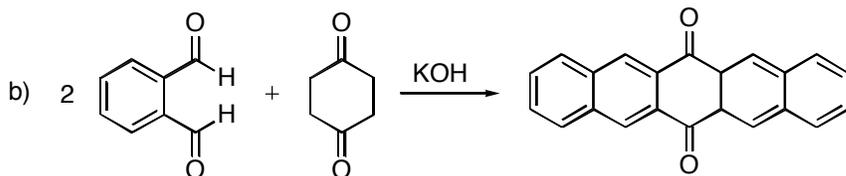
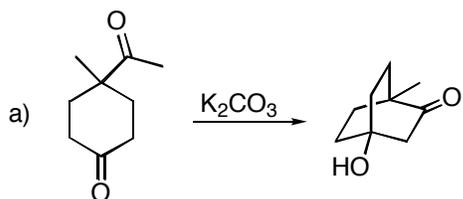
9. Provide a retrosynthetic analysis of how the following compounds could be made via an aldol, Claisen, or other type of condensation. Clearly indicate the starting materials that you would use.



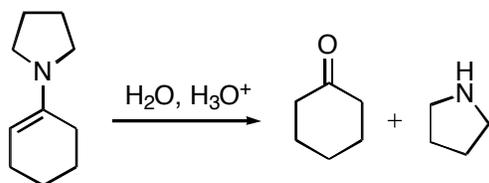
10. Provide products for the following reactions.



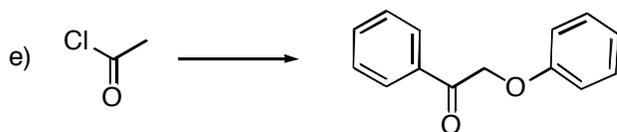
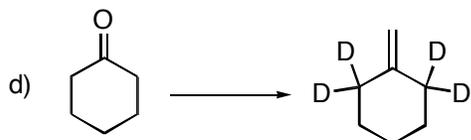
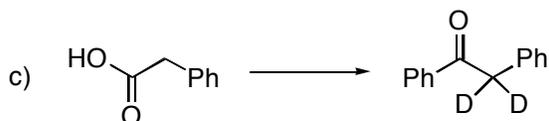
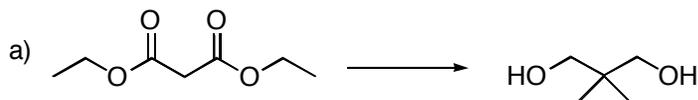
11. Provide a reasonable mechanism for each of the following transformations.



12. Provide a reasonable mechanism for the following transformation.



13. Propose a synthesis for each of the following compounds from the given starting materials.



14. Al Kylation, a graduate student in his tenth year of study, has suggested each of the below synthetic procedures. Explain why each one cannot be expected to work.

