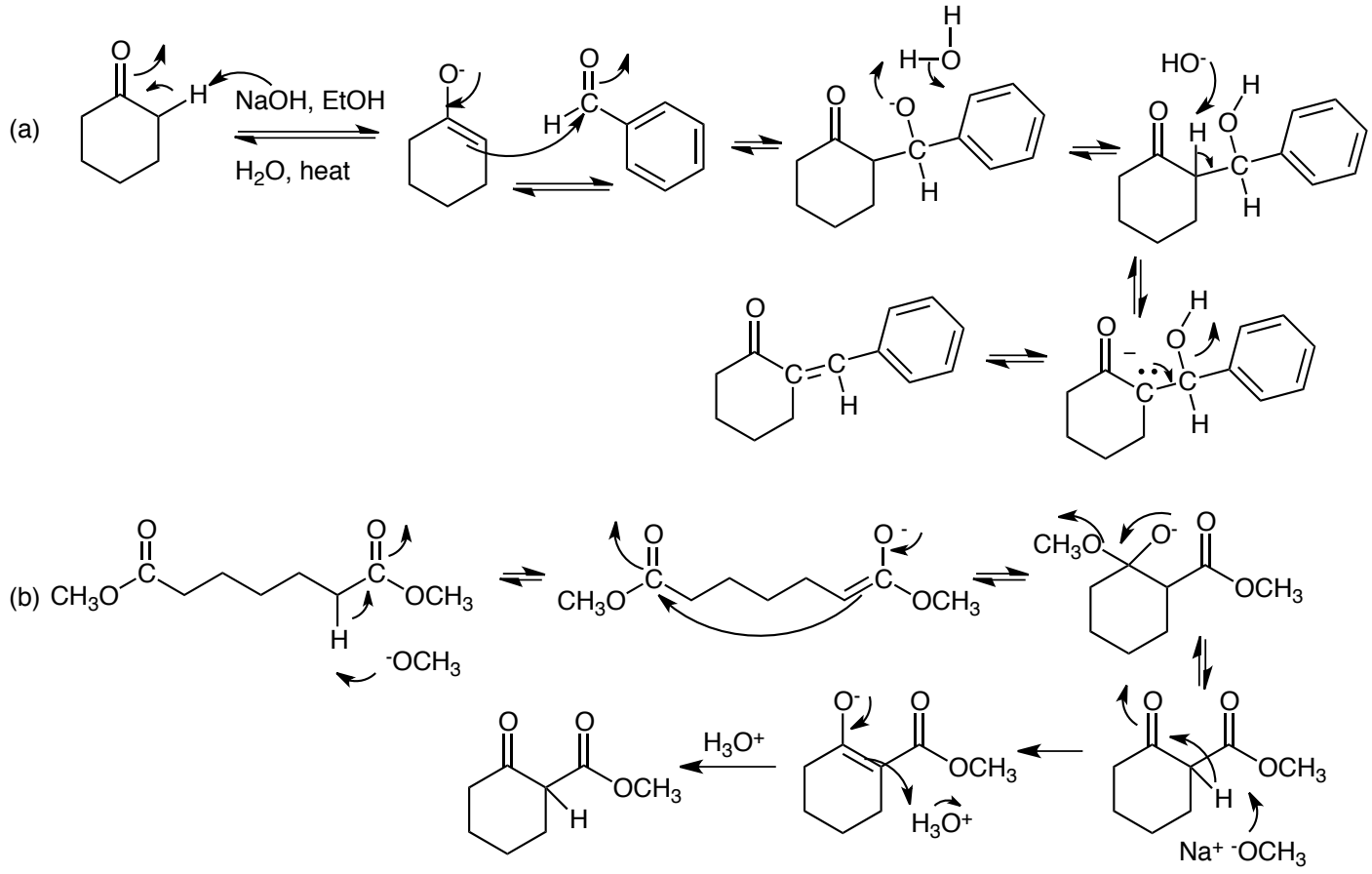
Name .....

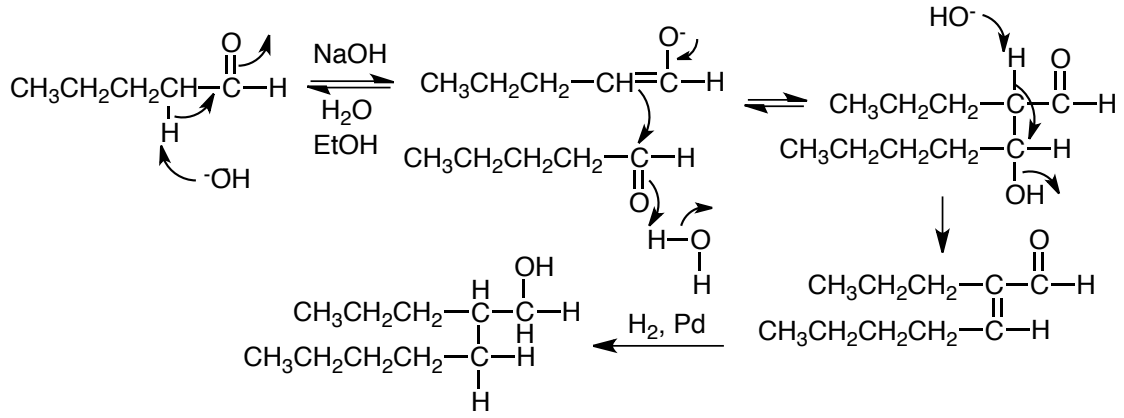
L.I.U.

Chem. 122, Sect 008, Quiz 4, 50 pts, Spring, 2011

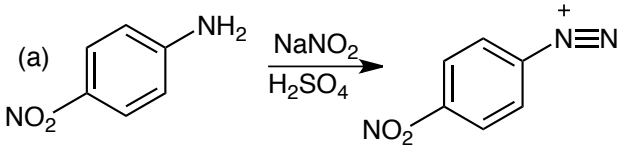
1. Give the product of the following reactions and show the complete reaction mechanism in each case. (20 pts)



2. Synthesize 3-propyl-1-heptanol using an aldol reaction. (10 pts)



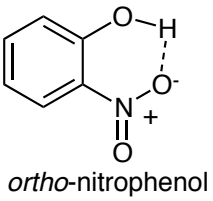
3. In the preparation of *p*-iodonitrobenzene, first we prepared Solution A by mixing ice, water, sulfuric acid and sodium nitrite with *p*-nitroaniline. (a) Show the reaction that occurred when these reagents were mixed. You do not need to show a mechanism. (b) Why is it necessary to keep Solution A cold at all times? (c) When solution A was added to solution B (KI in H_2O), we saw a lot of foaming. What was the cause of this? (10 pts)



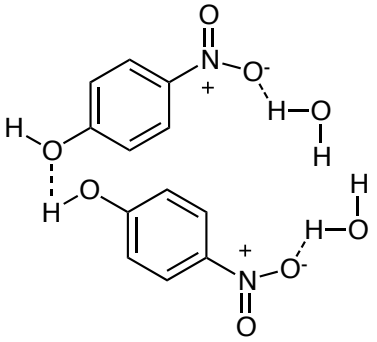
(b) The diazonium salt is unstable above about 5°C.
(c) The foaming was caused by the release of N_2 gas.

4. In the preparation of *p*-nitrophenol from phenol and nitric acid (a) which compound came over first during the steam distillation? Explain the structural and physical basis for this. (b) Why was it important to keep the cooling water in the condenser off most of the time? (c) A certain amount of black tar was also produced in this reaction. What was the origin of this material and would its production affect the yield of the reaction? (10 pts)

(a) The *ortho*-nitrophenol came over first due to the intramolecular H-bonding, which lowers its b. p. (less intermolecular H-bonding) and decreases its solubility in water (less H-bonding with water).



ortho-nitrophenol



(b) The cooling water must be kept off since the *ortho*-nitrophenol has a melting/freezing point of 44-45°C and can solidify in the condensing column and plug the tubing, particularly at the small opening of the vacuum adapter, thereby creating a closed system. Heating a closed system is very dangerous and can lead to explosions.

(c) The black tar is created by oxidation of the very electron rich phenol.